MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

BIOGEOCHEMICAL STUDIES OF SELECTED POLLUTANTS IN THE OPEN WATERS OF THE MEDITERRANEAN (MED POL VIII)

ETUDES BIOGEOCHIMIQUES DE CERTAINS POLLUANTS AU LARGE DE LA MEDITERRANEE (MED POL VIII)

ADDENDUM

GREEK OCEANOGRAPHIC CRUISE 1980

CROISIERE OCEANOGRAPHIQUE DE LA GRECE 1980

MAP Technical Report Series No. 8, Addendum

UNEP
Athens, 1986

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PNUE: Etudes biogéochimiques de certains polluants au large de la Méditerranée (MED POL VIII). Addendum, Croisière Océanographique de la Grèce 1980. MAP Technical Reports Series No. 8, Addendum. UNEP, Athens 1986.

This issue is the addendum to the eighth volume of the Mediterranean Action Plan Technical Reports Series.

This Series will collect and disseminate selected scientific reports obtained through the implementation of the various MAP components: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

Cette édition constitue l'addendum du volume No. 8 de la série des Rapports techniques du Plan d'action pour la Méditerranée.

Cette série permettra de rassembler et de diffuser certains des rapports scientifiques établis dans le cadre de la mise en oeuvre des diverses composantes du PAM: Programme de surveillance continue et de recherche en matière de pollution (MED POL), Plan Bleu, Programme d'actions prioritaires, Aires spécialement protégées et Centre régional de lutte contre la pollution par les hydrocarbures.

INTRODUCTION

The United Nations Environment Programme (UNEP), in co-operation with the relevant specialized United Nations Agencies (FAO, WHO, WMO, IOC) , presented to the Intergovernmental Meeting of Mediterranean countries (Barcelona, 1975) a proposal for a Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL).

MED POL was approved and UNEP was requested to implement the Programme, consisting of seven pilot projects, in close collaboration with the relevant specialized United Nations Agencies.

Its pilot phase (MED POL-Phase I) was designed as the precursor of a long-term programme for pollution monitoring and research in the Mediterranean (MED POL-Phase II) to be carried out according to the provisions of the legal component of the Mediterranean Action Plan.

The pilot projects approved at the 1975 Barcelona Meeting as parts of MED POL-Phase I were:

MED POL I: Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters

MED POL II: Baseline Studies and Monitoring of Metals, particularly Mercury and Cadmium, in Marine Organisms

MED POL III: Baseline Studies and Monitoring of DDT, PCBs and Other Chlorinated Hydrocarbons in Marine Organisms

MED POL IV: Research on the Effects of Pollutants on Marine Organisms and their Populations

MED POL V: Research on the Effects of Pollutants on Marine Communities and Ecosystems

MED POL VI: Problems of Coastal Transport of Pollutants

MED POL VII: Coastal Water Quality Control

Subsequent to the 1975 Barcelona Meeting, several other projects were added or considered as collaterals to MED POL to broaden the scope of the programme and to provide the necessary support to it. They were:

MED POL VIII: Biogeochemical Studies of Selected Pollutants in the Open Waters of the Mediterranean

MED POL IX: Role of Sedimentation in the Pollution of the Mediterranean Sea

MED POL X: Pollutants from Land-Based Sources in the Mediterranean

MED POL XI: Intercalibration of Analytical Techniques and Common Maintenance Services

MED POL XII: Input of Pollutants into the Mediterranean Sea through the Atmosphere

MED POL XIII: Modelling of Marine Systems

Participants in the pilot projects were national research centres designated by the States participating in the Mediterranean Action Plan.

The co-ordination of the MED POL-Phase I (1975-1981) was carried out by UNEP as a part of the Mediterranean Action Plan (MAP).

The following United Nations Co-operating Agencies were responsible for the technical implementation of various pilot projects :

- The Food and Agriculture Organization of the United Nations (FAO) through the General Fisheries Council for the Mediterranean (GFCM) (MED POL II, III, IV and V),
- The United Nations Educational, Scientific and Cultural Organization (UNESCO) (MED POL IX and XIII),
- The World Health Organization (WHO) (MED POL VII and X),
- The World Meteorological Organization (WMO) (MED POL XII),
- The International Atomic Energy Agency (IAEA) (MED POL VIII and XI) and
- The Intergovernmental Oceanographic Commission (IOC) of UNESCO (MED POL I and VI)

This volume is the report of the Greek Oceanographic Cruise 1980. It appears as the addendum to the MAP Technical Reports Series No. 8 which is the collection of final reports of the Principal investigators who participated in the pilot project : "Biogeochemical Studies of Selected Pollutants in the Open Waters of the Mediterranean (MED POL VIII)".

INTRODUCTION

Le Programme des Nations Unies pour l'environnement (PNUE), en coopération avec les organismes spécialisés compétents des Nations Unies (FAO, OMS, OMM, COI), a présenté à la Réunion intergouvernementale des pays méditerranéens (Barcelone, 1975), une proposition de Programme coordonné de surveillance continue et de recherche en matière de pollution dans la Méditerranée (MED POL).

Le MED POL a été approuvé, et il a été demandé au PNUE de mettre en oeuvre le programme qui se compose de sept projets pilotes, en étroite collaboration avec les organismes spécialisés compétents des Nations Unies.

Sa phase pilote (MED POL - Phase I) a été conçue comme le prélude d'un programme à long terme de surveillance continue et de recherche en matière de pollution dans la Méditerranée (MED POL - Phase II) à mettre en oeuvre conformément aux dispositions de l'élément juridique du Plan d'action pour la Méditerranée.

Les projets pilotes approuvés à la Réunion intergouvernementale de Barcelone, en 1975, dans le cadre de la Phase I du MED POL, comprenaient:

MED POL I: Etudes de base et surveillance continue du pétrole et des hydrocarbures contenus dans les eaux de la mer

MED POL II: Etudes de base et surveillance continue des métaux, notamment du mercure et du cadmium, dans les organismes marins

MED POL III: Etudes de base et surveillance continue du DDT, des PCB et des autres hydrocarbures chlorés contenus dans les organismes marins

MED POL IV: Recherche sur les effets des polluants sur les organismes marins et leurs peuplements

MED POL V: Recherche sur les effets des polluants sur les communautés et écosystèmes marins

MED POL VI: Problèmes du transfert des polluants le long des côtes

MED POL VII: Contrôle de la qualité des eaux côtières

A la suite de la Réunion de Barcelone de 1975, plusieurs autres projets ont été adjoints ou considérés comme subsidiaires au MED POL en vue d'étendre la portée du programme et de lui assurer l'appui indispensable. Ce sont:

MED POL VIII: Etudes biogéochimiques de certains polluants au large de la Méditerranée

MED POL IX: Rôle de la sédimentation dans la pollution de la mer Méditerranée

MED POL X: Polluants d'origine tellurique dans la Méditerranée

MED POL XI: Inter-étalonnage des techniques d'analyse et services communs d'entretien

MED POL XII: Polluants d'origine tellurique dans la Méditerranée

MED POL XIII: Modélisation des systèmes marins

Les participants aux projets pilotes étaient des centres nationaux de recherche désignés par les Etats prenant part au Plan d'action pour la Méditerranée.

La coordination de MED POL - Phase I (1975-1981) a été assumée par le PNUE dans le cadre du Plan d'action pour la Méditerranée.

Les organismes coopérants des Nations Unies qui étaient chargés de l'exécution technique des divers projets pilotes sont les suivants:

- Organisation des Nations Unies pour l'alimentation et l'agriculture (FAO) par l'entremise du Conseil général des pêches pour la Méditerranée (CGPM) (MED POL II, III, IV et V).
- Organisation des Nations Unies pour l'éducation, la science et la culture (UNESCO) (MED POL IX et XIII).
- Organisation mondiale de la santé (OMS) (MED POL VII et X).
- Organisation météorologique mondiale (OMM) (MED POL XII).
- Agence internationale de l'énergie atomique (AIEA) (MED POL VIII et XI), et
- Commission océanographique intergouvernementale (COI) de l'UNESCO (MED POL I et VI).

Ce volume constitue le rapport de la Croisière Océanographique de la Grèce 1980. Il représente l'addendum de la série No. 8 des Rapports techniques du PAM qui rassemble les rapports finaux des chercheurs responsables participant au projet pilote intitulé: "Etudes biogéochimiques de certains polluants au large de la Méditerranée (MED POL VIII)".

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GREEK OCEANOGRAPHIC CRUISE 1980

CROISIERE OCEANOGRAPHIQUE DE LA GRECE 1980

In the framework of the national oceanographic programmes for the exploitation and research of the seas in order to assess the pollution problems, the first oceanographic cruise was carried out in March, 1980, in the Aegean Sea. In this, several national research institutes participated.

The intention of the programme was to provide an important supplement to that proposed by UNEP and its objectives.

This endeavour proved the high level of collaboration of joint scientific research by the national institutes with respect to the planning and performance of research programmes for the monitoring of pollution.

The ascertainment of such abilities quarantees the continuation of the efforts in the future. The results of the basic parameters obtained during the cruise are presented in this report.

The selection of the stations was made in such manner as to obtain a clear picture of the condition of the Aegean Sea (Figure A). In Table A are given the coordinates of the stations and the schedule of the cruise. The sampling and analytical techniques were those used in MED POL - PHASE I. All the analyses were performed with the available instrumentation of the research institutes which participated.

Cruise Coordination and Report Preparation

by

APOSTOLOS KATSAOUNIS
Chem. Oceanographer

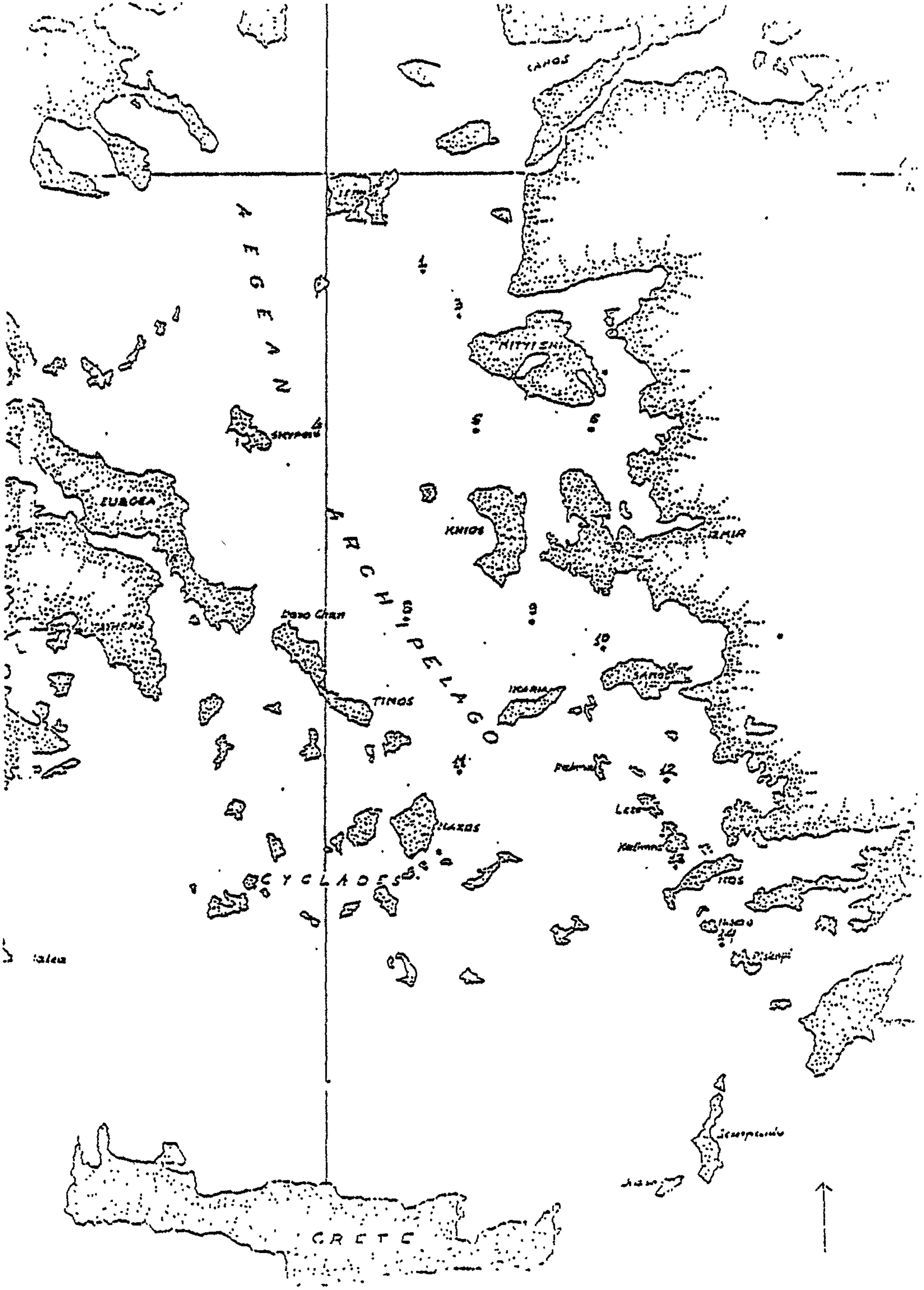

Fig. A. Sampling stations

TABLE A

Station No	Data	Time	Coordinates	
1	24/3	16:00	39° 35' N	25° 34' E
3	24/3	19:20	39° 23.5' N	25° 47' E
4	24/3	09:30	38° 50' N	24° 58' E
5	25/3	00:10	38° 52' N	25° 53' E
6	25/3	05:00	38° 52' N	26° 31.5' E
8	26/3	09:15	38° 00' N	25° 27' E
9	26/3	13:45	38° 00' N	26° 12' E
10	26/3	17:45	37° 52.5' N	26° 36' E
11	29/3	03:15	37° 20' N	25° 46' E
12	26/3	11:45	38° 18' N	26° 57' E
13	27/3	13:00	36° 54' N	27° 02' E
14	28/3	17:20	36° 37' N	27° 17' E

Participating Research Center:	Hydrographic Service/Oceanographic Department
Principal Investigator:	Alexandros Laskaratos

INTRODUCTION

In this paper are presented general data and are described the prevailing conditions during the cruise, of temperature, salinity and density in the Aegean Sea.

AREA STUDIED

The area studied, as well as the sampling stations, are shown in Figure A. In Table A are presented the analytical information for each station and the relative performed observations.

PREVIOUS INVESTIGATIONS

From the oceanographic point of view, the Aegean Sea shows a special interest, and for this reason it has been widely investigated by many Greeek and other research institutes. In spite of that, it is true that the available information is very limited (it is therefore impossible to compare the data obtained with those given by other investigators).

METHODS AND MATERIALS

Seawater sampling and in situ temperature measurements were performed using Nansen type bottles, with two protected reversing thermometers. For depths greater than 100 meters, the bottles were equipped with two protected and one unprotected reversing thermometer for the thermometric calculation of the depth.

After the foreseen treatment and correction of all temperature readings, the calculation of the thermometric depth sampling and the interpolation of the measurements to the accepted depths with the standard methods was done.

The salinity was measured with a Beckman conductive salinometer. The determination of dissolved oxygen was conducted on board ship using the Winkler (1888) method as was modified and improved by Jacobsen J.P., Robinson R.T., and Thompson T.G. (1950).

RESULTS AND DISCUSSIONS

The vertical distribution of the tested parameters at each station is shown in Figures 1 and 1a.

From the examination of these diagrams it is concluded that at the greater number of stations the characteristic conditions at the end of the winter season in the Aegean, that is the homogeneity of the water column in relation to temperature and salinity are observed.

This homogeneity is due to the vertical mixing of the water masses and is the consequence of the density increase of the surface waters due to their gradual cooling and to the salinity increase during the fall season and until the end of winter.

The intensity of these vertical movements determines the depth of their intrusion; the final measurement of temperature and salinity of the homogenous layer at the end of winter being dependent upon the intensity of the atmospheric phenomena during the winter period as well as upon the hydrological conditions which prevailed at the end of the previous summer, as supported by Lacombe et al. (1958).

The greatest intrusion depth of the convective processes (250m) is observed at station 4 while a greater stability of temperature (± 0.01°C) and salinity (±0.01°/oo) is observed at station 2 to a depth of 100m. On the contrary the formation of a seasonal thermocline is observed at the rest of the stations. It appears extremely weak at stations 5 and 13, somewhat stronger at stations 1 and 8, and, finally, stronger still and deeper, therefore "older" at stations 3, 6, 12, and 9. At this last station the homogenous layer of winter barely revels itself at 150m.

At station 12, due to the small depth, the thermocline has intruded to the bottom.

In Figures 2-2c, 3-3c, and 4-4c are illustrated the distribution of temperature salinity and density respectively at chosen cross sections along the stations. From these sections it can be concluded that there is a continuous change of temperature from station 14 to station 1. That is moving from south to north along the Eastern Aegean one meets the largest isotherm at the surface of station 14 and the smallest at the botton of station 1. The same is observed from the southernmost (11) to the northernmost (4).

A continuous temperature gradient with the eastern stations (6 and 10) being the warmer of the two cross sections and the western (4 and 8) the coolers, is also observed at the two sections with E-W orientation.

A notable temperature gradient from south to north is observed with such consistency that there is no isotherm which intersects all nine stations of the cross section in Figure 2b.

From Figures 3b and 3c it is concluded that there is also a salinity gradient from south to north, though not as continuous as in the case of temperature. Consequently the maximum salinity appears at stations 13, 14 and 9 to 200m depth.

From Figures 3 and 3a it is concluded that there is a salinity gradient also in E-W direction, the eastern stations the more saline of these cross sections. As for the density (Fig. 4-4c) there is an apparent increase from south to north, the waters of station 14 being the lightest while the waters of station 1 are the most dense, mainly due to the temperature gradient. The same is apparent in the cross section of stations 4, 8 and 11. In the cross section of stations 8, 9 and 10 an increase in density from East to West can be observed. However in the cross section of stations 4, 5 and 6, station 5 is denser than the other two (dome structure).

From the study of the T-S diagrams (Fig. 5) it is concluded that the stations can be separated into three groups in relation to their characteristics. The first group includes stations 3, 4, 5 and 8, the second the stations 6, 9, 10 and 11, and the third the stations 13 and 14. Station 12 is a totally separate case.

Among the stations in the first group, station 4 has the lowest temperatures and salinities in the layer of the top 50 meters.

It must be considered that these waters originate in the Agion Oros basin, which receives the cold fresh waters of the rivers of Northern Greece, as well as those of lower salinity and temperature of the Dardanelles.

These waters can be observed also at the surface layer of station 8, where, however, they have been considerably warmed and become more saline.

Station 5 is obviously affected by the waters of the second group (stations 6, 9, 10, and 11) which have higher temperature and salinity.

Station 3 appears to be much less affected by the waters of the second group than station 5.

Finally, station 1 has waters at its surface (0 meters) which are much more saline as well as much warmer than at all its other depths. These waters have an obvious origin, the second group, being lighter than those directly below them and "sitting" upon them.

All stations of this group terminate at their bottom and at approximately same point (Water type) with temperature of 14,25° ± 0,1°C and salinity of 38,80 ± 0.02°/oo. Only station 1 differs with respect to bottom temperature which is lower (13.83°C) possibly due to a more direct influence from the cold waters of the Dardanelles.

Among the stations of the second group, station 11 has the highest surface salinities and mean temperatures, while station 6, the lowest surface temperatures and salinities. Stations 9 and 11 appear to have a lamination in relation to their salinities, a more saline layer down to 200m and one less saline below that. It is unknown as to whether station 10 appears to have a lower salinity below 300 meters, because, due to the larger wire angle, no samples were obtained below that depth.

The two stations in the third group (13 and 14) differ from the others because of their high temperature and salinity.

Finally, station 12 is characterized by very high surface salinities which sharply decrease at the first depths in an isothermal manner and, subsequently by a temperature decrease with a stable salinity. It also shows an instability with respect to density which is the evidence that this phase is probably accompanied by convective processes.

Currents:

The limited number of stations obtained and the distance between them, their relative position, as well as the differences of their depths do not allow the application of dynamic calculations in order to draw conclusions for the prevailing currents. It is possible, however, to draw some qualitative conclusions for the possible movements from which, however we cannot have a concise picture. Therefore, from the profile of stations 4, 5 and 6 and the dome structure, it can be estimated that between stations 5 and 6 there is a vector towards the north while between stations 4 and 5 there is a vector towards the south. The first (towards the north) is larger than the second. This opinion concurs, generally, with what is already known from the bibliography; the previously mentioned in the analysis of water masses for stations 4 and 8 advocate the opinion that there is a surface water movement from station 4 to station 8. Also the fact that the waters of station 6 moving towards the north, lighter than those of station 5, have a tendency to "stick" to the right, being restricted, though, from the western shores of Asia Minor, as opposed with those incoming from station 4 which are found in the open sea advocate the opinion that the movement between station 5 and station 6 must be more intense than that between station 4 and station 5.

Also, the ot profile of stations 8, 9 and 10 shows that there must exist a northern current vector, around the stations 9 and 10. The existence of such a vector does not necessarily mean that the waters move in that direction. In this way, during the occupation of station 9, while a northwest wind of only 3-4 B intensity was prevailing, the vessel was displaced southwesterly 7/10 of a mile in one hour. This is evidence as to the fact that there prevailed currents in the area which had a strong westerly vector. It is, therefore, possible that the compound current at station 9 may be in a northwestern direction. It is of course impossible from the available data to draw conclusions about the relative significance of the northern and western vectors of the current. Of course, one such cyclonic current in the area south of the island of Chios concur with what is already known from the bibliography while on the map of the area it is noted that such significant enough currents often exist.

From the ot profiles of stations 4, 8 and 11 it is concluded that there possibly exists a current vector perpendicular to the cross-section 8-11. The previously mentioned cyclonic motion south of Chios as well as the relative structure of stations 9 and 11 (see T-S diagram) advocates in favour of this.

PUBLICATIONS

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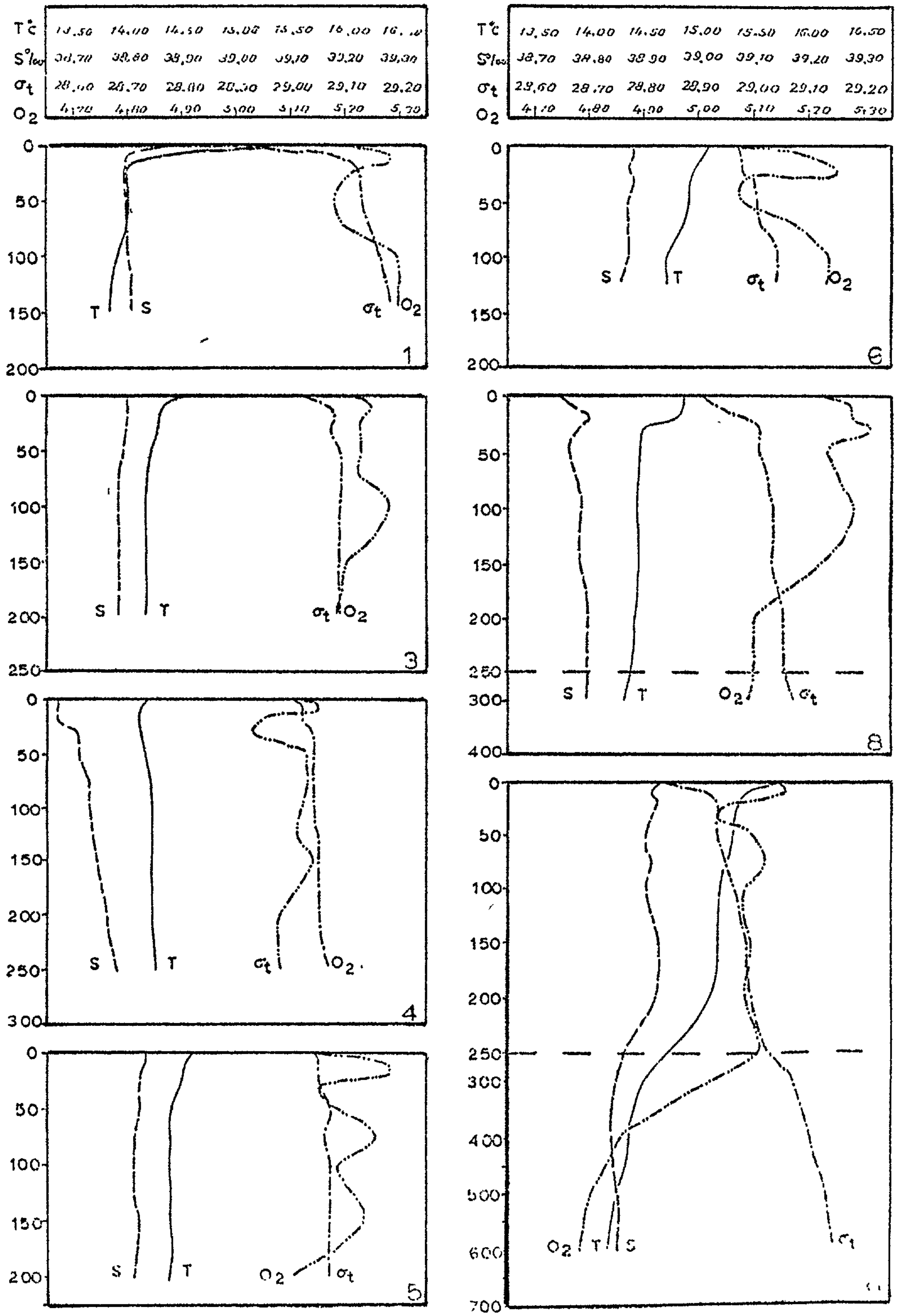

Fig. 1. Vertical distribution of temperature (T°C), salinity (S°/oo), density (σt), and dissolved oxygen (O_2 ml/l), at stations 1, 3, 4, 5, 6, 8 and 9

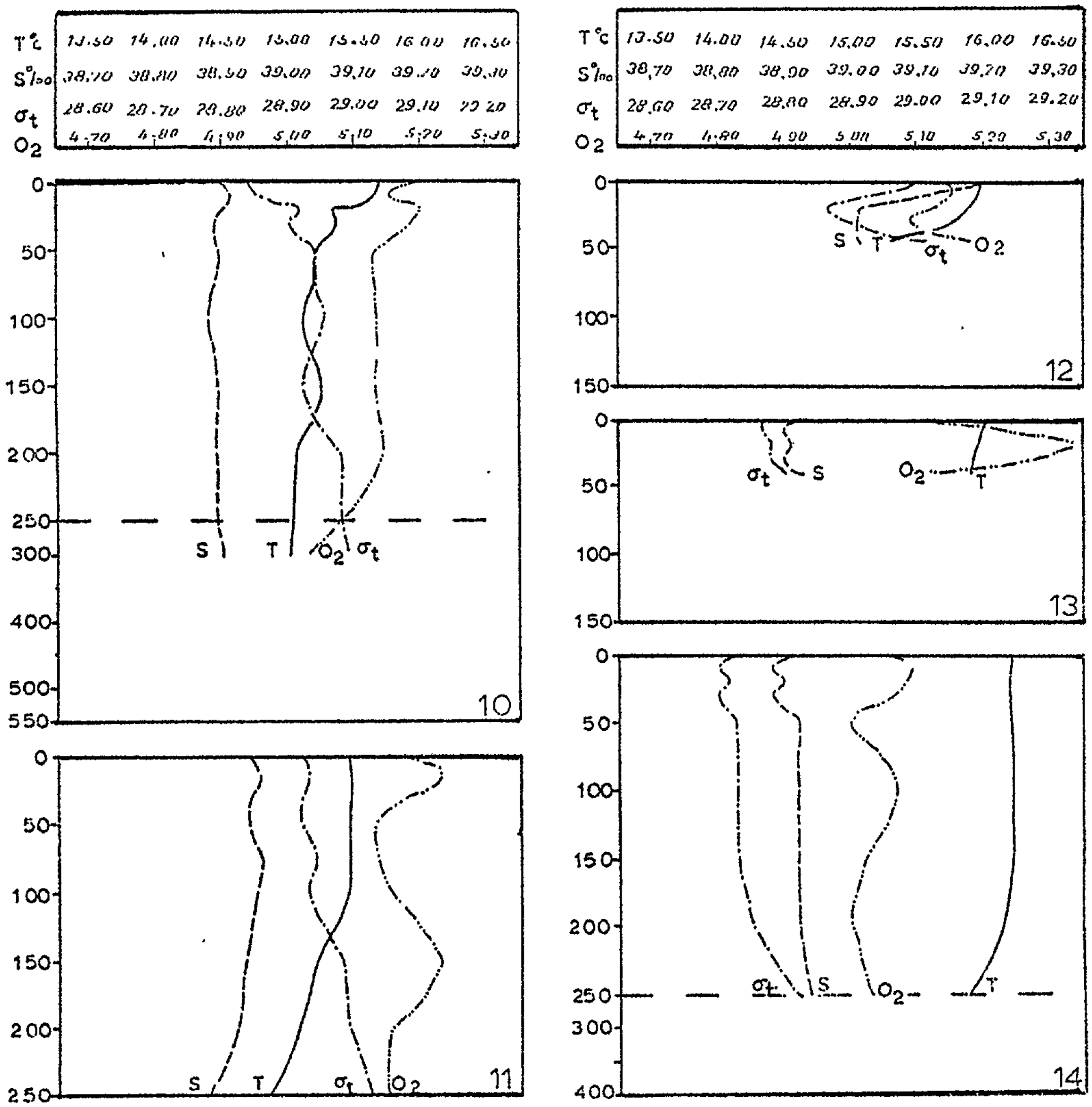

Fig. 1a. Vertical distribution of temperature (T°C), salinity (S°/₀₀), density (σt), and dissolved oxygen (O_2 ml/l), at stations 10, 11, 12, 13 and 14

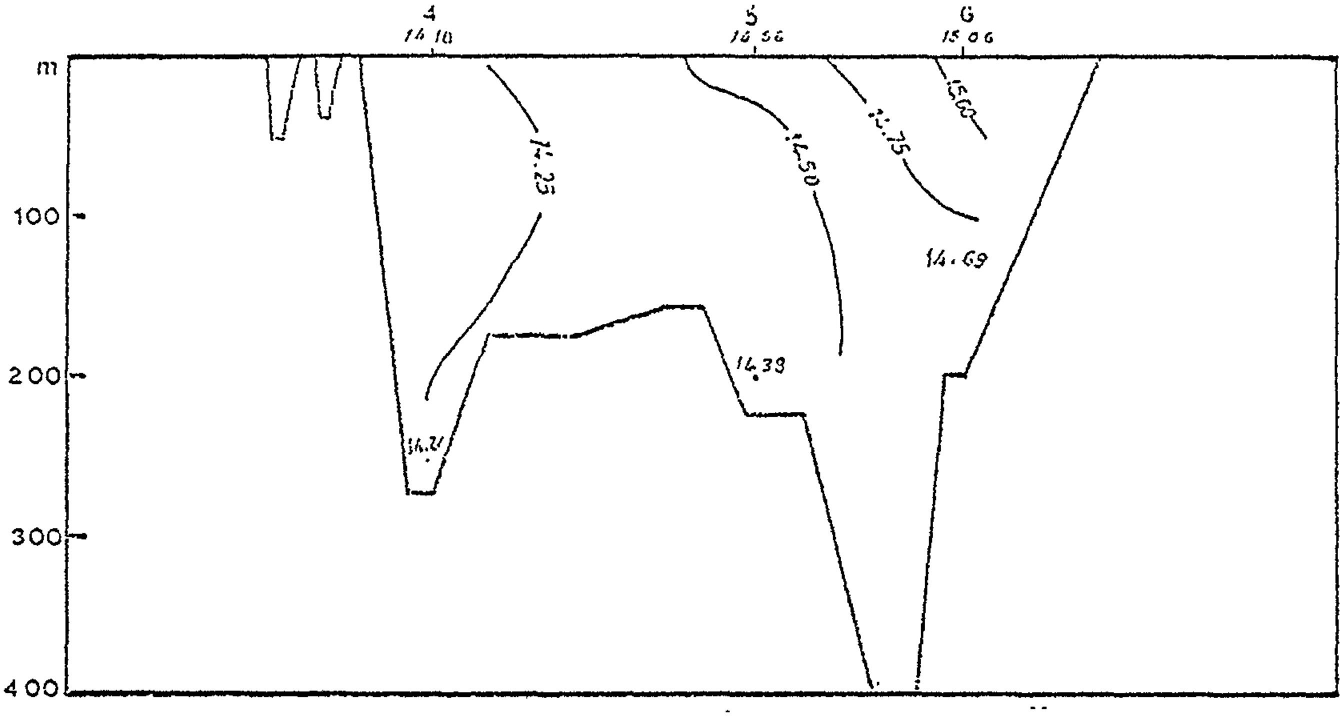

Fig. 2. Cross section of the vertical distribution of temperature at stations 4, 5 and 6

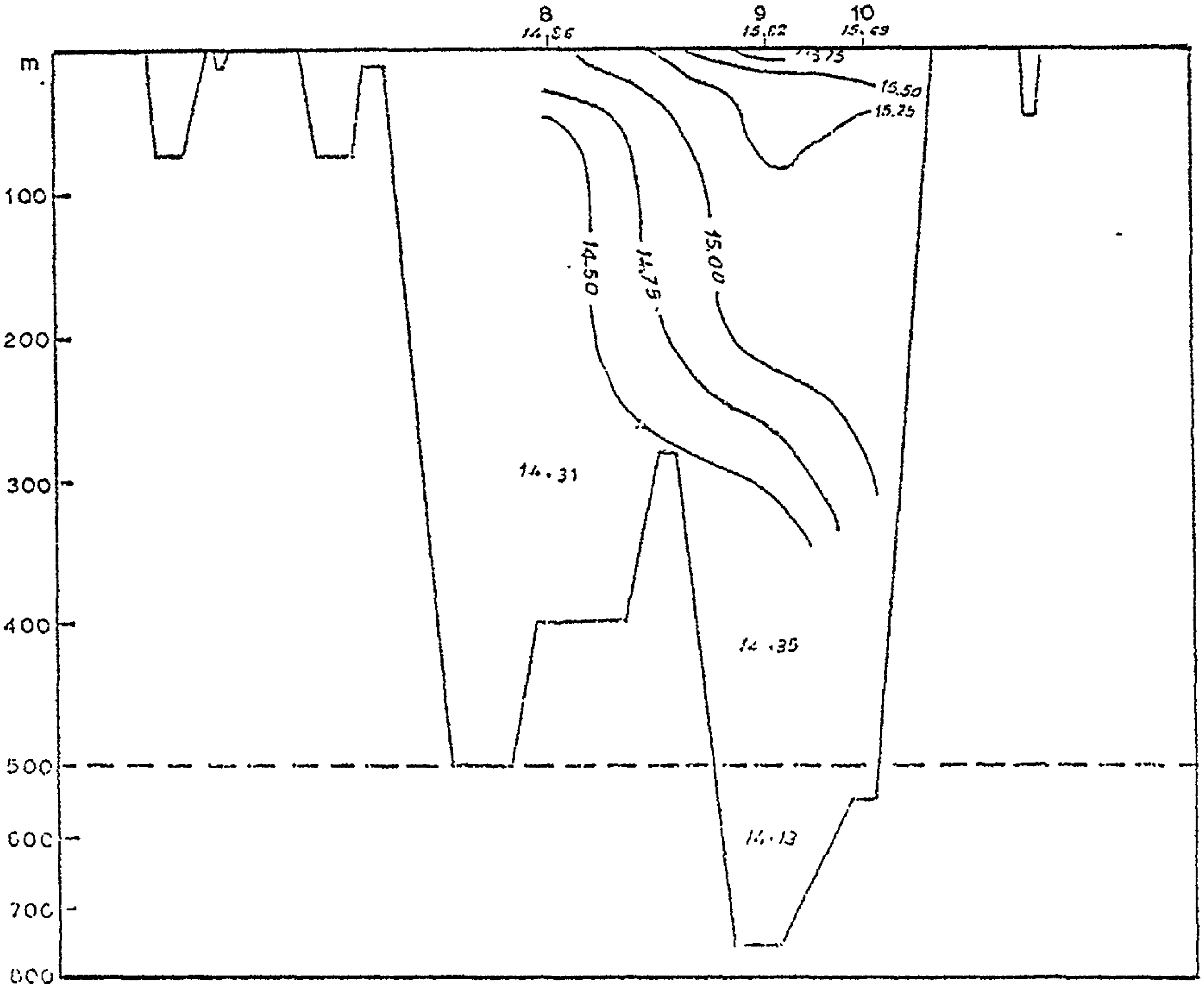

Fig. 2a. Cross section of the vertical distribution of temperature at stations 8, 9 and 10

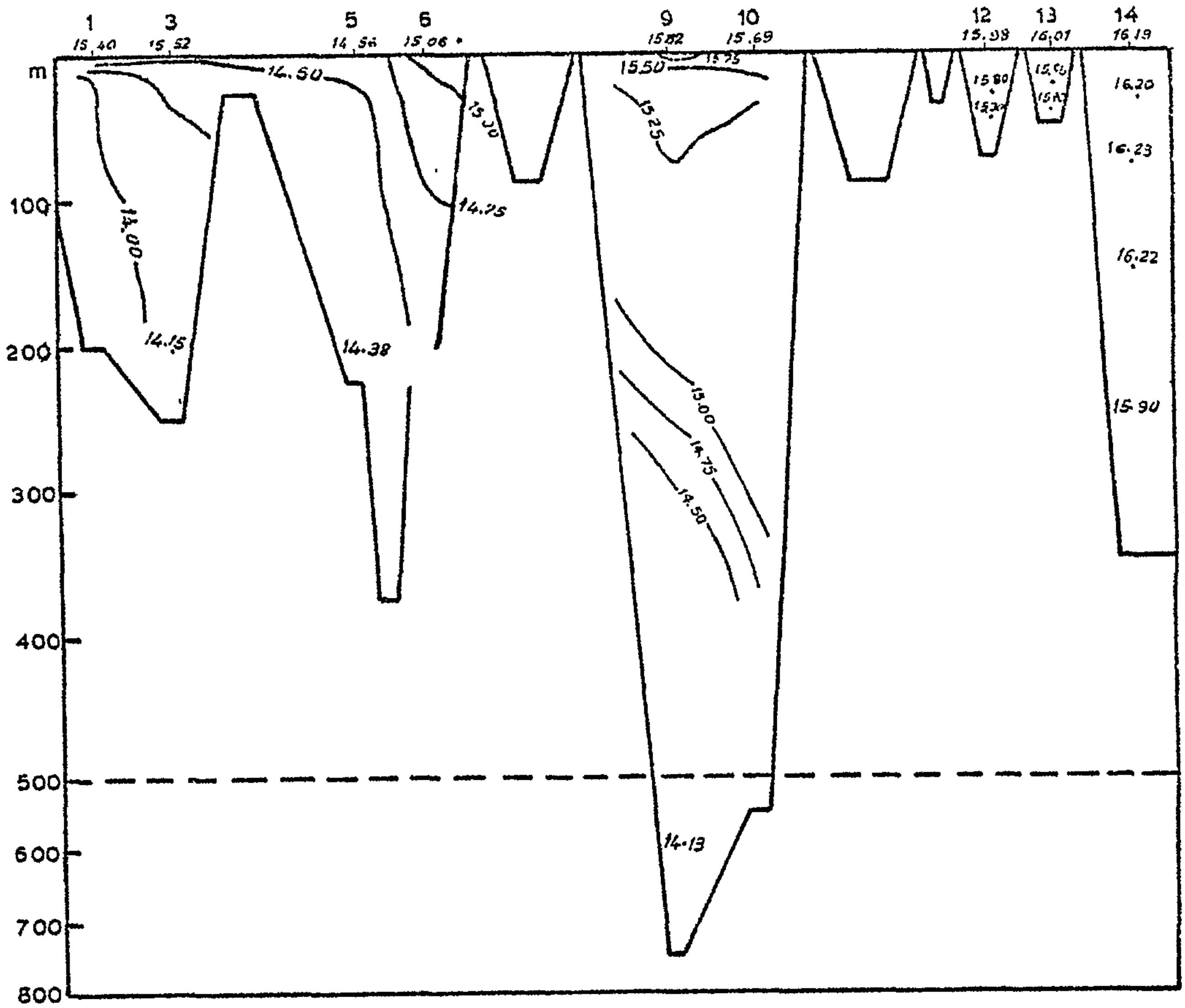

Fig. 2b. Cross section of the vertical distribution of temperature at stations 1, 3, 5, 6, 9, 10, 12, 13 and 14

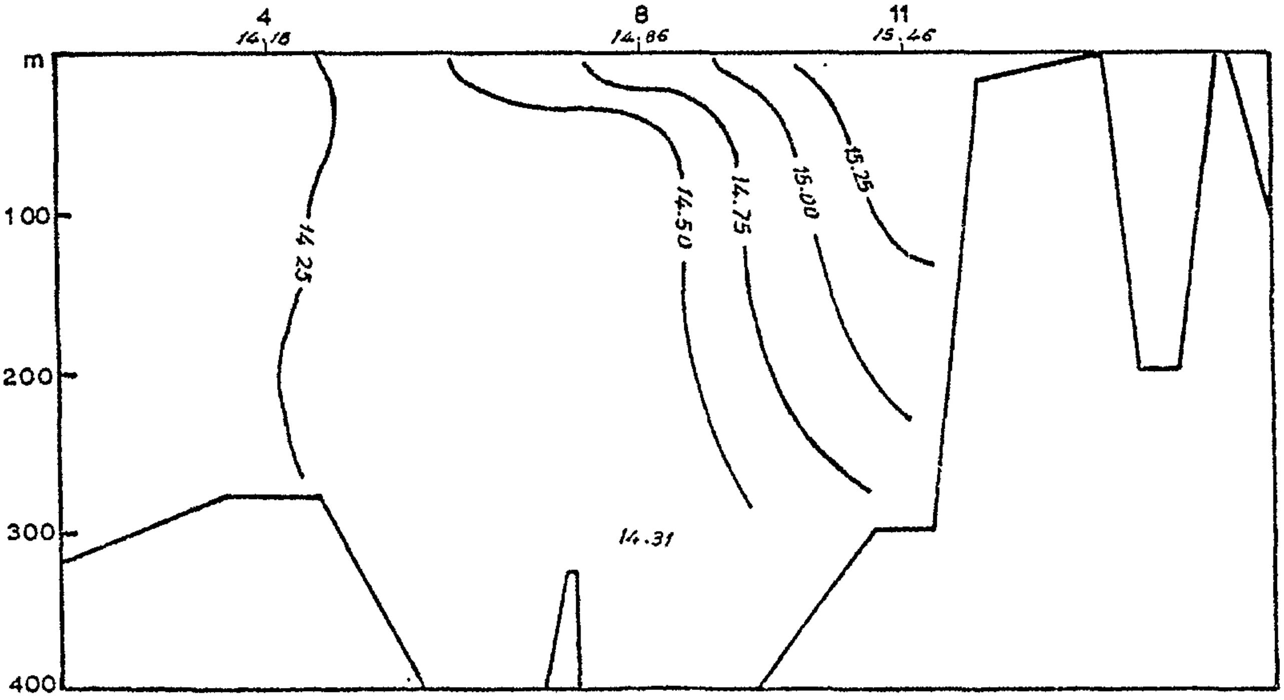

Fig. 2c. Cross section of the vertical distribution of temperature at stations 4, 8 and 11

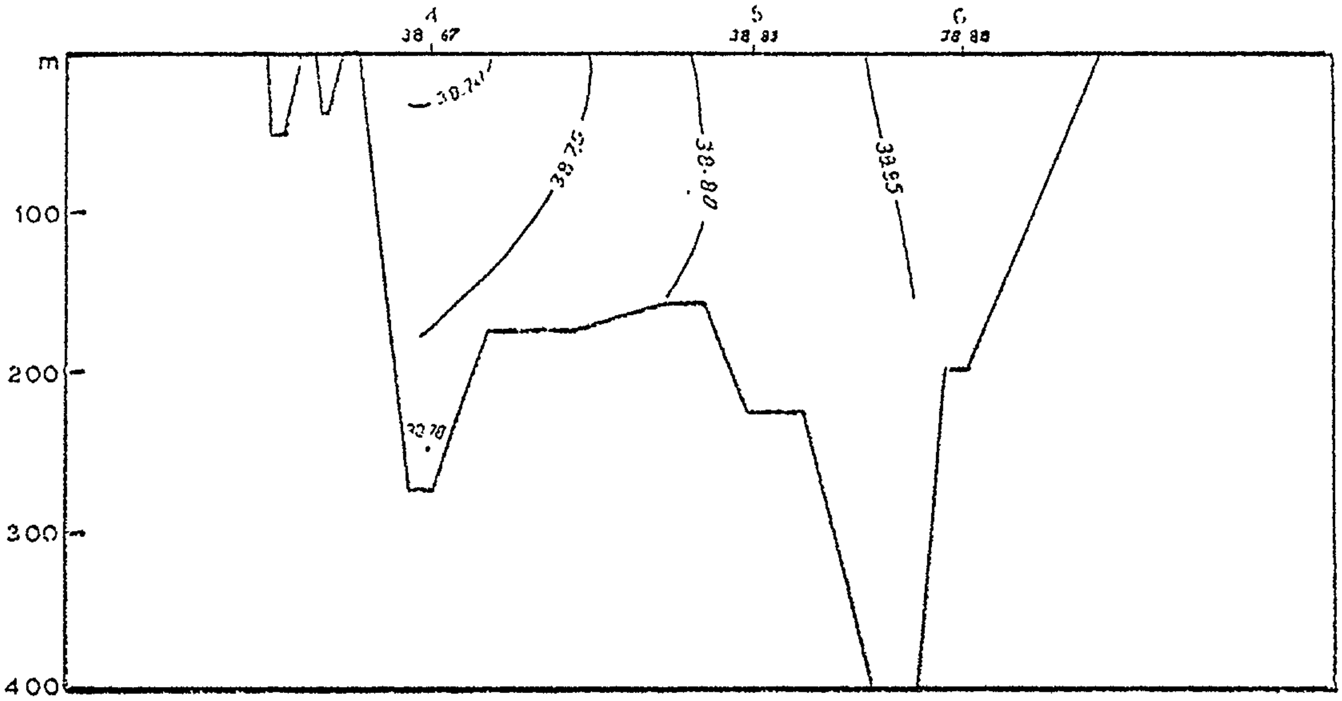

Fig. 3. Cross section of the vertical distribution of salinity at stations 4, 5 and 6

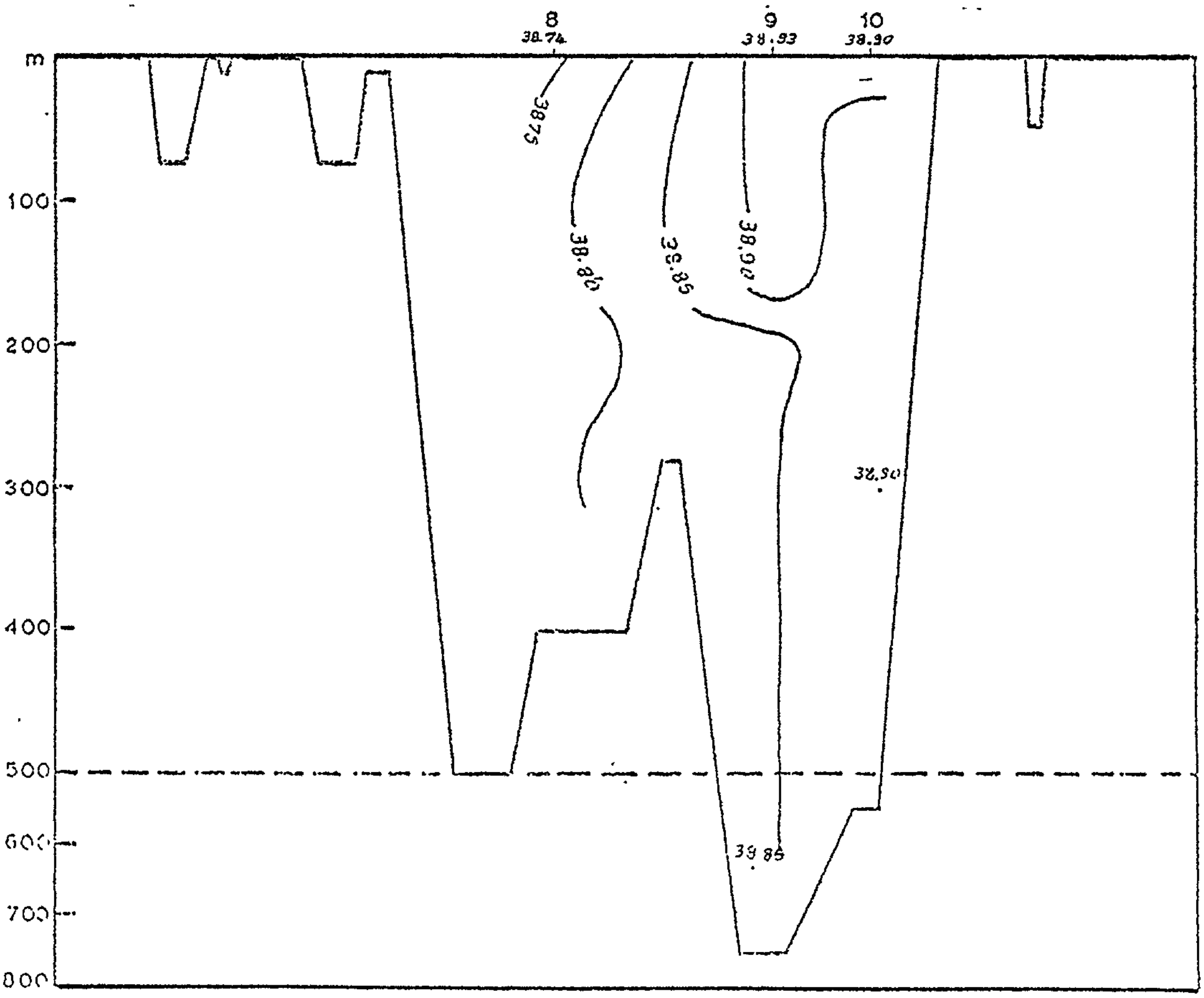

Fig. 3a. Cross section of the vertical distribution of salinity at stations 8, 9 and 10

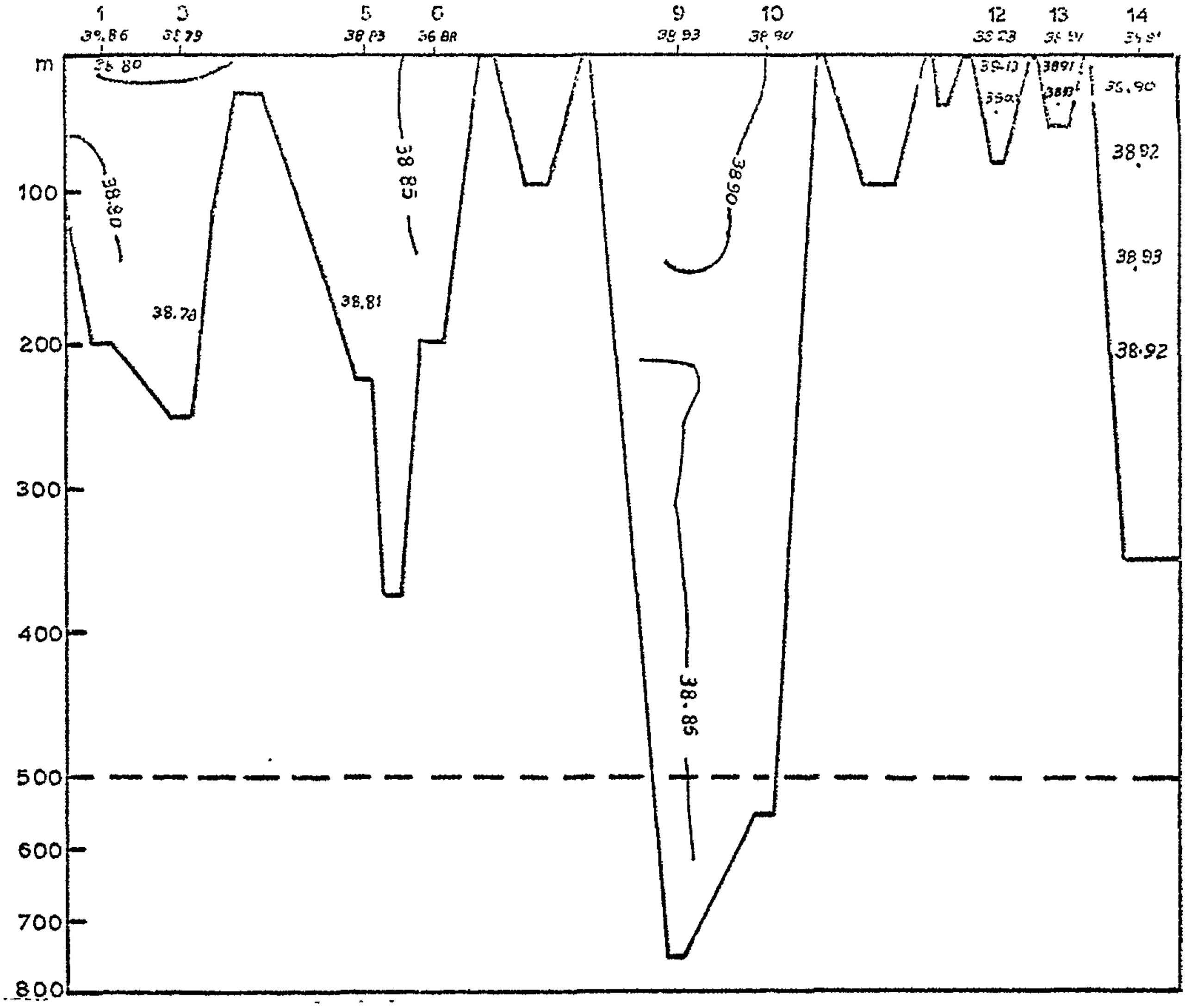

Fig. 3b. Cross section of the vertical distribution of salinity at stations 1, 3, 5, 6, 9, 10, 12, 13 and 14

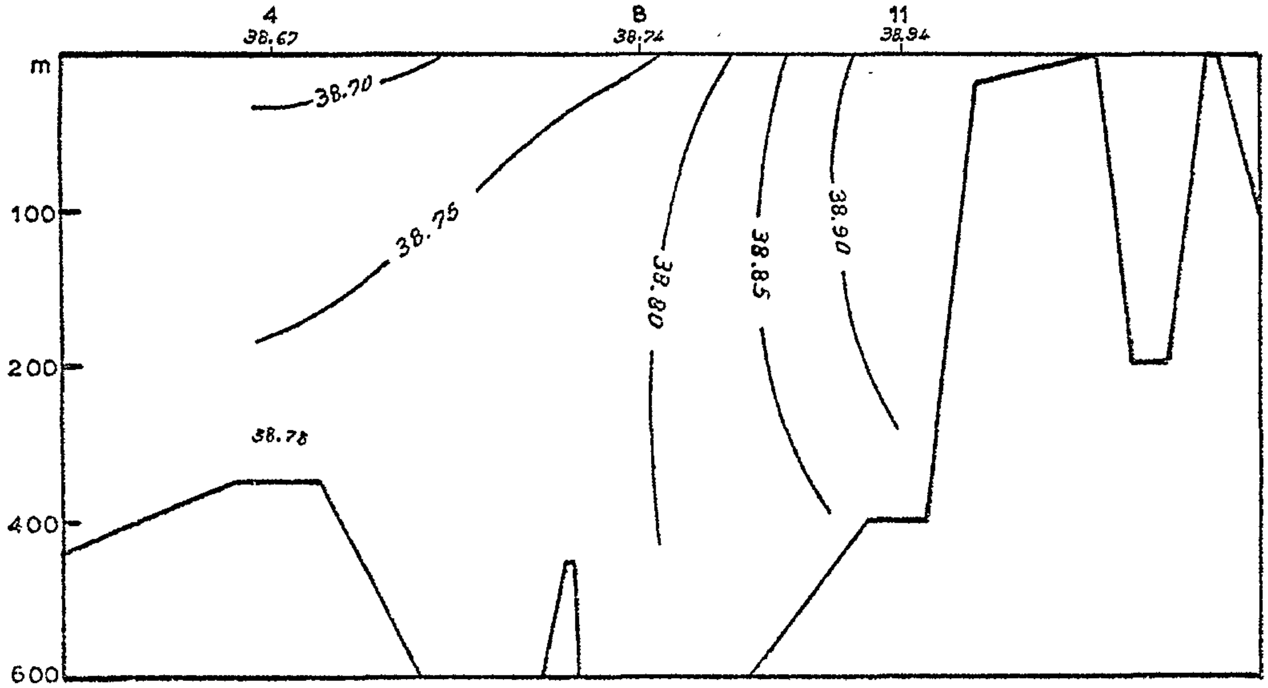

Fig. 3c. Cross section of the vertical distribution of salinity at stations 4, 8 and 11

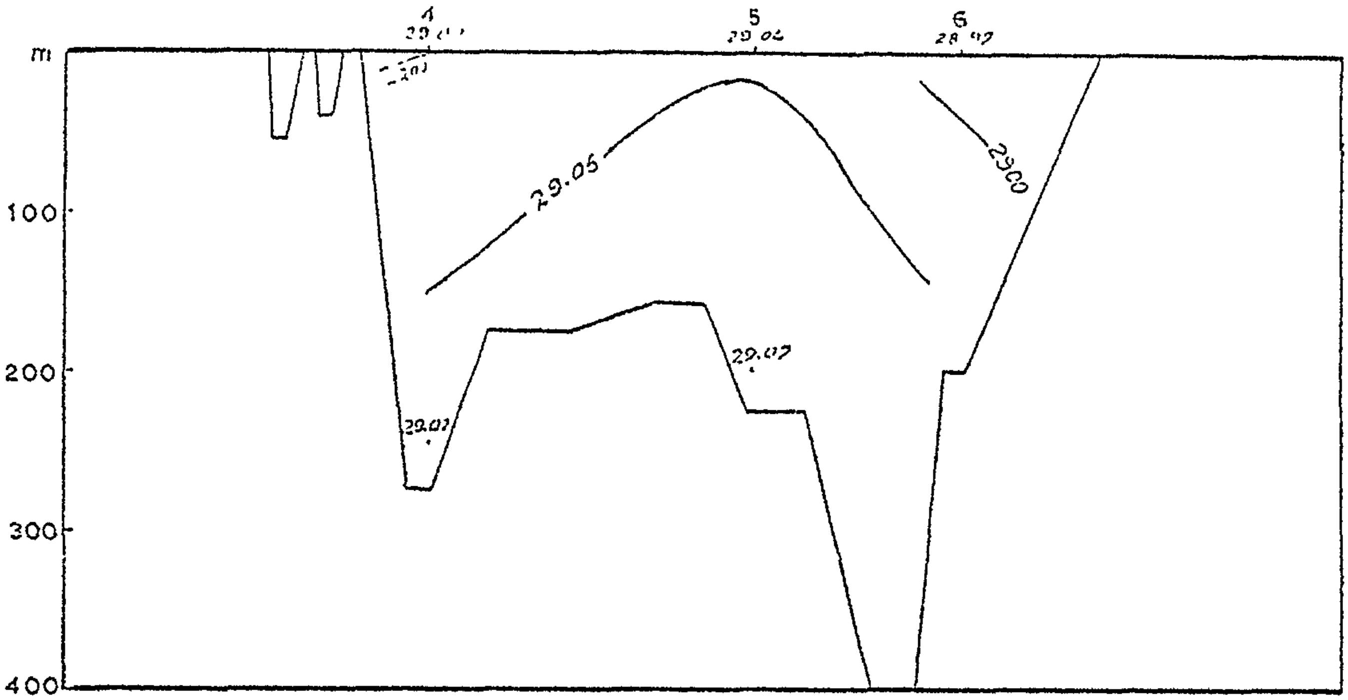

Fig. 4. Cross section of the vertical distribution of density at stations 4, 5 and 6

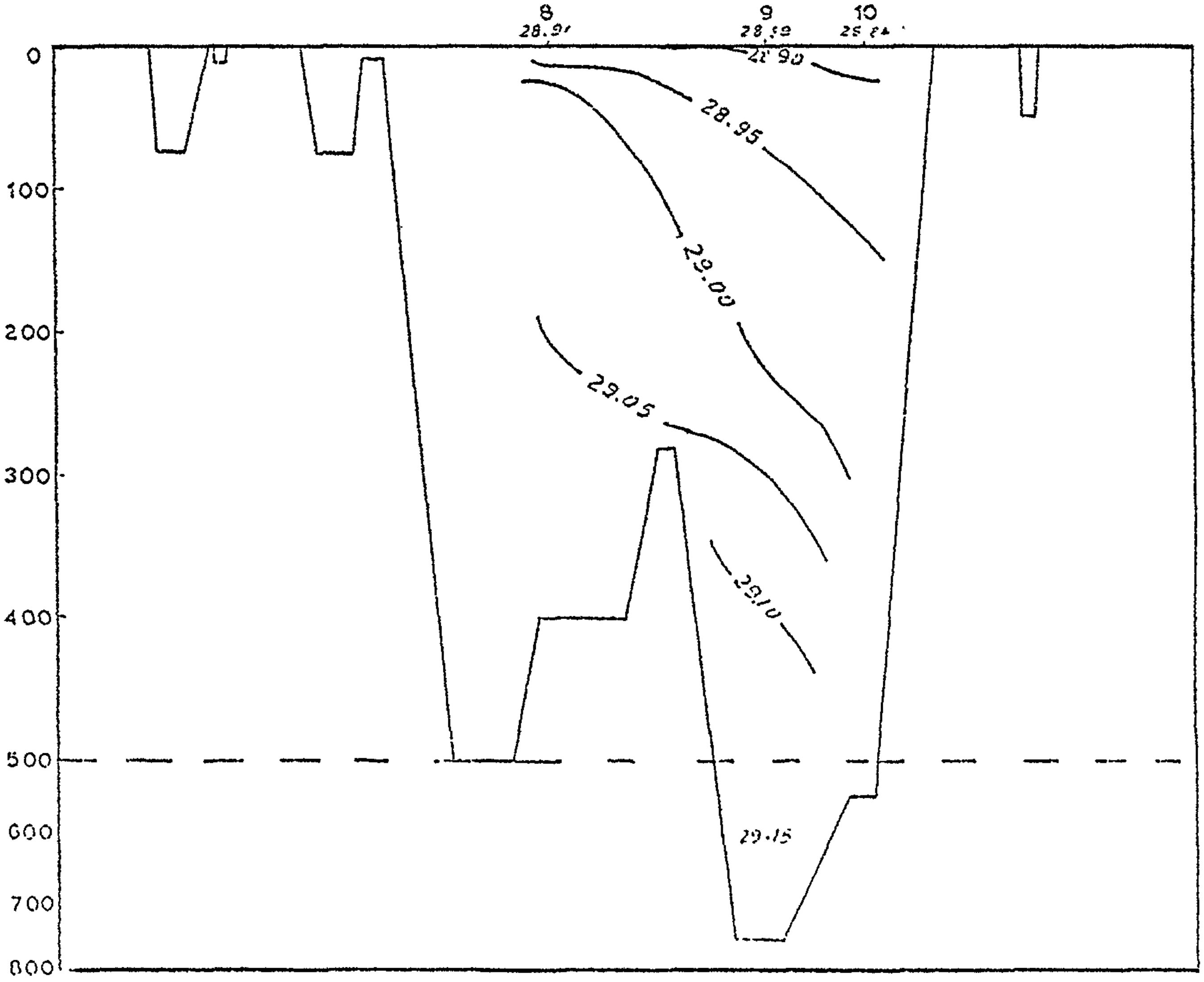

Fig. 4a. Cross section of the vertical distribution of density at stations 8, 9 and 10

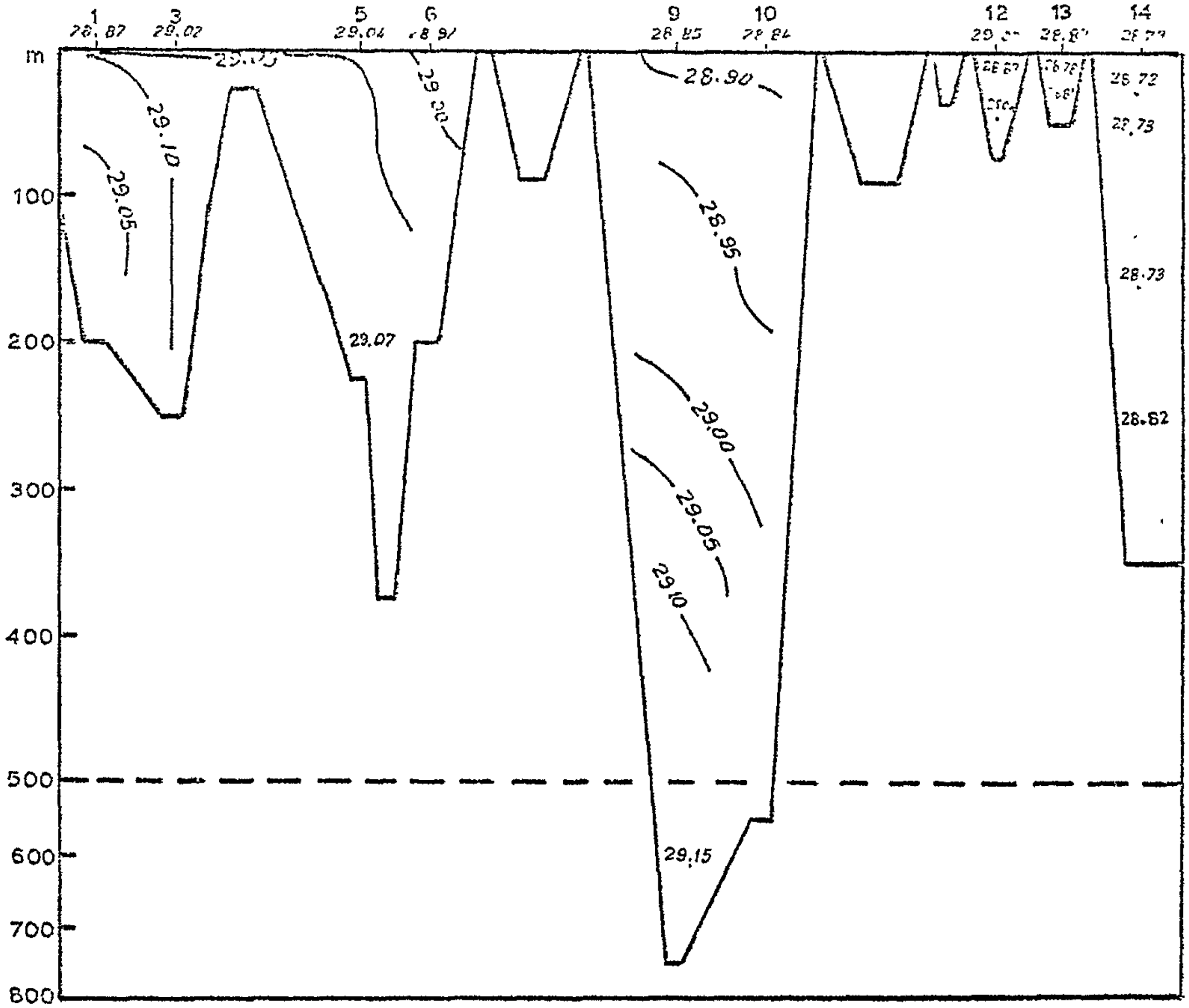

Fig. 4b. Cross section of the vertical distribution of density at stations 1, 3, 5, 6, 9, 10, 12, 13 and 14

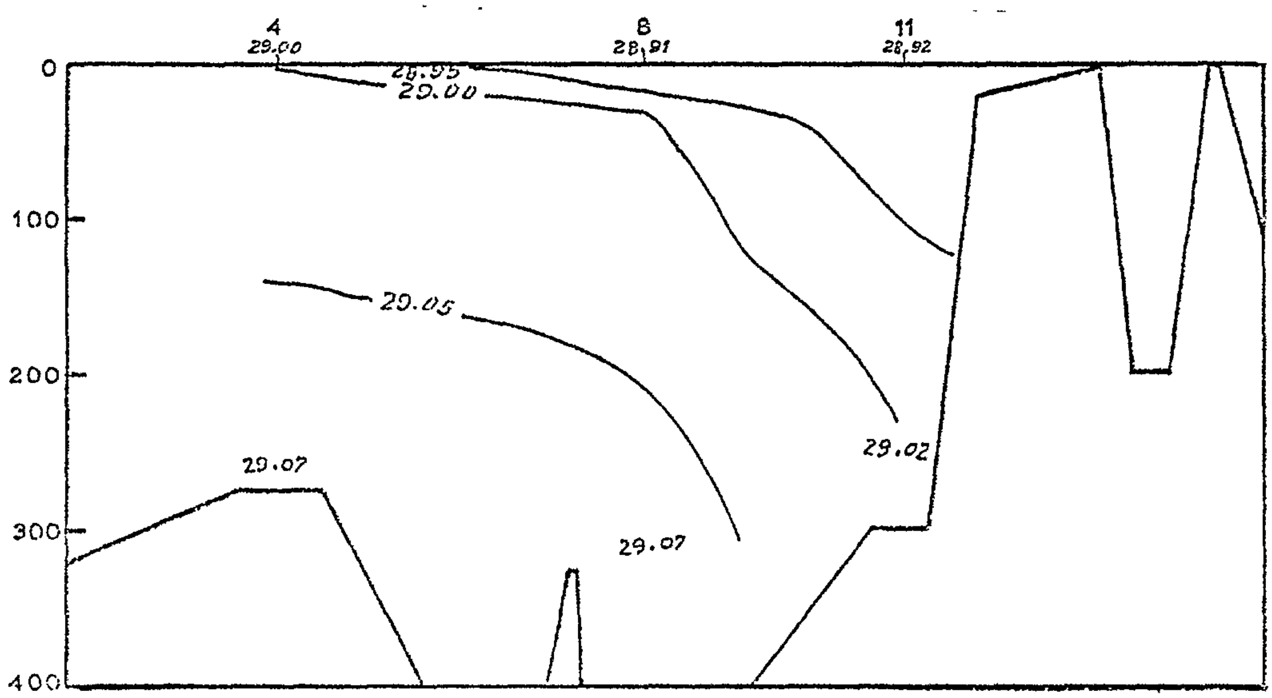

Fig. 4c. Cross section of the vertical distribution of density at stations 4, 8 and 11

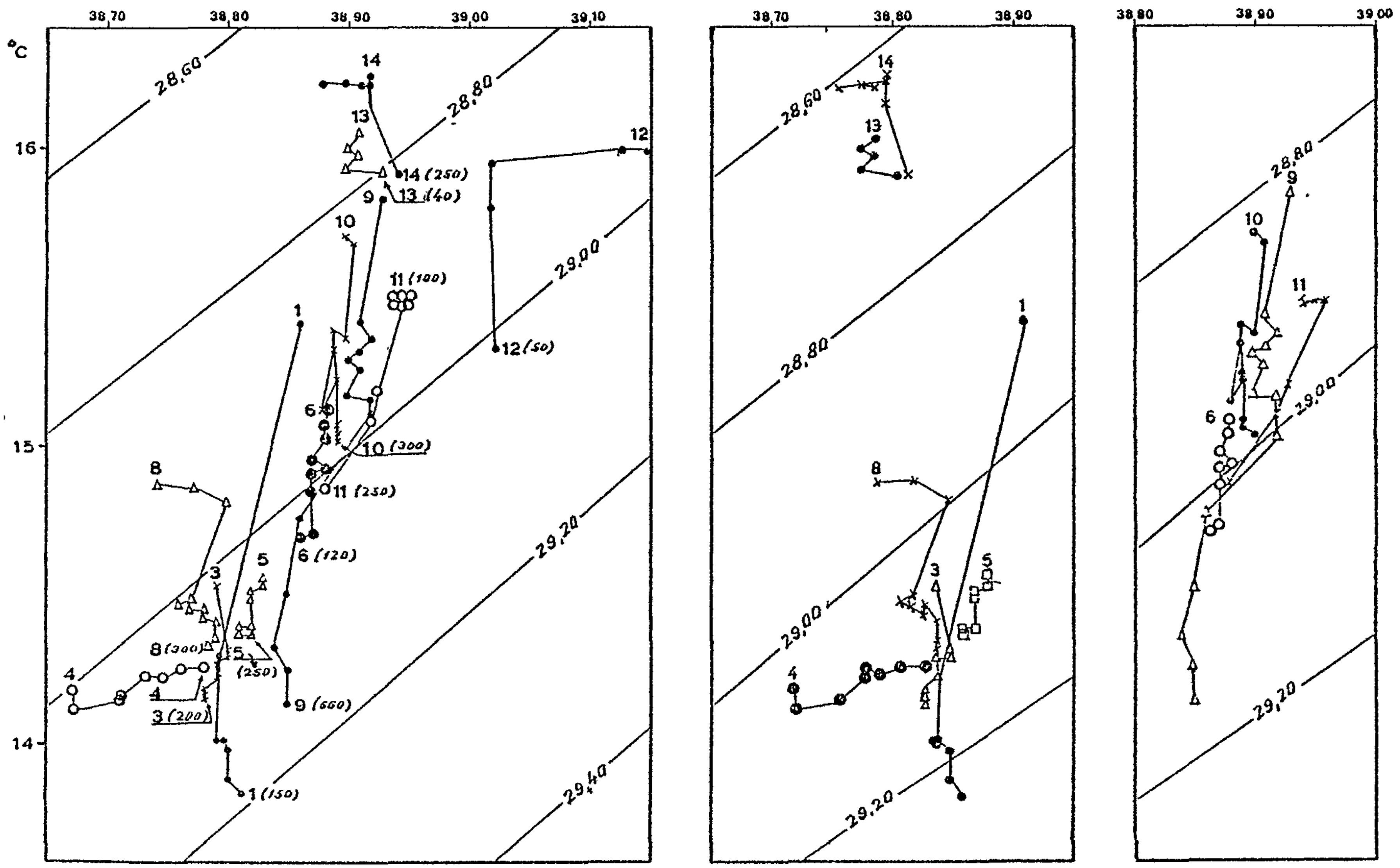

Fig. 5. T-S diagrams of stations in the Aegean Sea

COBALT, CHROMIUM, IRON, ANTIMONY, AND ZINC IN SEDIMENTS

Participating Research Centre: Radioanalytical Laboratory
Department of Chemistry
Nuclear Research Center
"Demokritos"
ATHENS
Greece

Principal Investigator: Michael Angelidis

INTRODUCTION

Trace elements when discharged to the marine environment will be transported by prevailing currents and removed by either physical, chemical or biological processes. Either through absorption, ion exchange, complexing of chelation, trace elements are picked up by particulate or organic matter and settle on the bottom. So, the bottom sediments are continually accumulating trace elements and they are a record of the long term input, dispersal and settling process in the overlying waters.

In this work five trace elements (Co, Cr, Fe, Sb, Zn) considered as "pollutants" have been analyzed by Instrumental Neutron Activation Analysis, from 11 stations in the Aegean Sea.

AREA STUDIED:

The area studied as well as the sampling stations are shown in Figure A.

MATERIALS AND METHODS:

Sediment samples were collected with a Diedz-Lafond grab during a cruise from 11 stations in the open waters of the Aegean Sea. The grab was covened with epoxy paint to eliminate contamination. Samples were placed in plastic containers and stored at -4°C until ready for analysis.

Sediment samples were air dried at 20-25°C for 3-4 days. Collected sediments had a wide variety of particle sizes. In order to make a viable inter-sediment comparison the trace element analysis was carried out on the $<55\ \mu m$ fraction, which was separated by wet sieving through a nylon sieve. The separates were freeze dried and a subsample was taken for trace element analysis.

Instrumental Neutron Activation Analysis (Grimanis et al 1977) was used for the determination of Co, Cr, Fe, Sb and Zn. Approximately, 0.3 gr of dried sample were placed in polyethylene tubes beat-scaled and irradiated at the "Demokritos" swimming pool reactor using the rotation system (thermal neutron flux $2.2 \times 10^{13}\ n.cm^{-2}s^{-1}$). Samples were counted on a GE (Li) detector connected with a Multichannel Analyzer.

RESULTS AND DISCUSSION

The distribution of 5 trace elements (Co, Cr, Fe, Sb and Zn) in the silt fraction of sediments and the percent silt values in sediments from 11 stations of the Aegean Sea are given in Table 1.

Ranges for these trace elements expressed as µg/g dry sediment varied as follows :

Co 10.3-21.2; Cr 57.5-148; Fe 17.3-30.8 (mg/g);
Sb 0.43-1.5; Zn 41.1-66.3

There is a difference between stations 4, 8 and 11 which are in the middle of the Aegean Sea and stations 1, 3, 5, 6, 9, 10, 12 and 14 which are closer to the continent. For the stations 4, 8 and 11 the average values of trace elements in the <55µm fraction of sediment, expressed as µg/g dry weight are: Co 16.6, Cr 73.8; Fe 20.5 (mg/g); Sb 0.66; Zn 45.1.

For the stations 1, 3, 5, 6, 9, 10, 12 and 14 which are closer to the continent, the average values of trace elements in the < 55 µm fraction of sediment, expressed as mg/g dry weight, are: Co 17.2; Cr 101.7; FE 26.1; (mg/g); Sb 1.0; Zn 52.5.

So, we observe a slight increase in the concentrations of trace elements in the near shore sediments. This slight increase may be attributed to difference in the sediment size. We noted that the sediments from the open Aegean Sea are coarsier than the near shore sediments.

CONCLUSIONS

Only a few sediment samples from the Aegean Sea were collected and analysed and it is not possible to arrive to concrete conclusions. However, the concentrations of the 5 trace elements analysed (Co, Cr, Fe, Sb, Zn) in the 55<µm fraction of sediment are similar compared with other unpolluted marine areas and lower compared with polluted areas (Chester and Stoner, 1975; Papakostidis et al 1975; Grimanis et al 1977; Satsmadjis and Voutsirou 1980; Angelidis et al 1980).

It seems that the sediments from the stations close to the continent have higher concentrations of all these 5 trace elements, than the sedments collected from the middle of the Aegean Sea. This trend may be attributed to the differences in the distribution of the particle sizes of the sediments. There is no evidence of any increased concentrations that could be a result of anthropogenic activity.

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Table 1. Percent silt values and trace element concentrations (µg/g dry weight) in the < 55 µm fraction of Aegean Sea sediments

Station	% silt (< 55 µm)	Cr	Co	Fe (mg/g)	Sb	Zn
1	76.4	69.3	12.5	26.4	0.7	48.0
S.D.		± 10.7	± 0.9	± 1.4	± 0.4	± 7.0
3	92.6	73.5	14.2	28.6	1.3	66.5
S.D.		± 13.6	± 2.6	± 0.8	± 0.08	± 4.3
4	25.7	74.4	18.1	21.8	0.9	43.7
S.D.		± 18.4	± 1.0	± 1.2	± 0.3	± 6.8
5	61.8	95.4	18.4	27.1	1.5	54.0
S.D.		± 27.2	± 1.1	± 1.6	± 0.6	± 12.8
6	30.4	85.8	10.3	24.0	1.0	52.7
S.D.		± 18.8	± 0.9	± 0.8	± 0.4	± 4.1
8	58.2	89.4	18.7	22.7	0.5	47.7
S.D.		± 23.1	± 1.2	± 1.2	± 0.2	± 4.9
9	94.8	97.4	21.2	28.3	0.8	53.4
S.D.		± 17.0	± 1.3	± 0.4	± 0.4	± 6.2
10	94.2	110	21.0	30.8	1.3	51.9
S.D.		± 22.8	± 0.9	± 2.3	± 0.1	± 7.1
11	60.0	57.5	13.0	17.3	0.43	44.2
S.D.		± 14.3	± 0.5	± 1.4	± 0.01	± 4.9
12	57.4	148	-	18.6	0.63	41.1
S.D.		± 25		± 0.4	± 0.03	± 2.1
14	88.9	132	19.5	24.5	0.74	52.1
S.D.		± 42.7	± 1.0	± 1.3	± 0.01	± 17.5

S.D. = Standard Deviation

Table 2. Concentration range of trace elements in sediments from various marine areas µg/g dry sediment

Area	Co	Cr	Fe (mg/g)	Zn
Present work < 55 µm	10.3- 20.1	57- 148	17.3- 30.8	41.1- 66.3
Saronikos Gulf Polluted[a]	5- 140	80- 1100	10- 400	50- 2500
Pagassitikos Gulf Average[b]	26.7	110	34.1	122
Evoikos Gulf urban[c]	15.1 29.6		24- 42	52- 147
World average near shore sediments unpolluted[d]		100		95

[a] Grimanis *et al.*, 1977

[b] Satsmadjis and Voutsinou, 1980

[c] Angelidis *et al.*, 1980

[d] Chester and Stoner, 1976

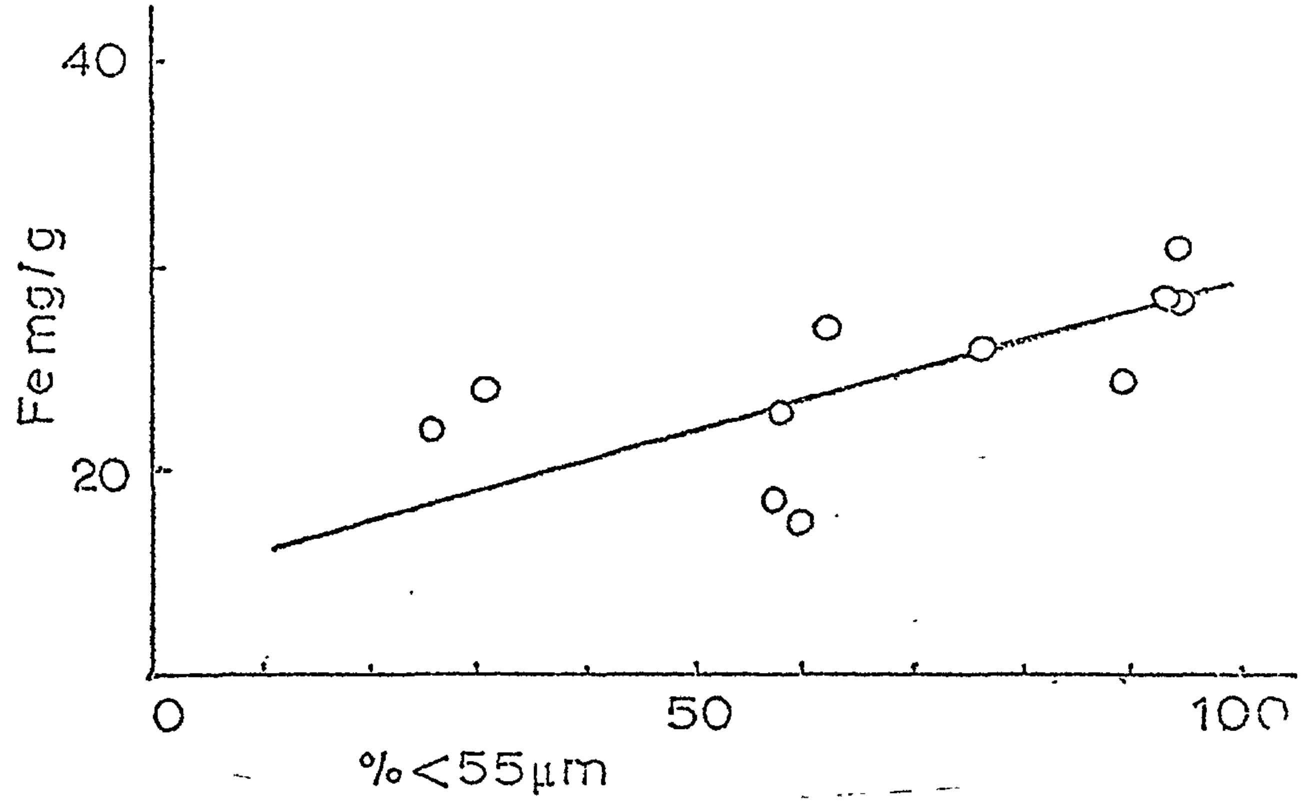

Fig. 1. Correlation between Fe concentration and particle size distribution

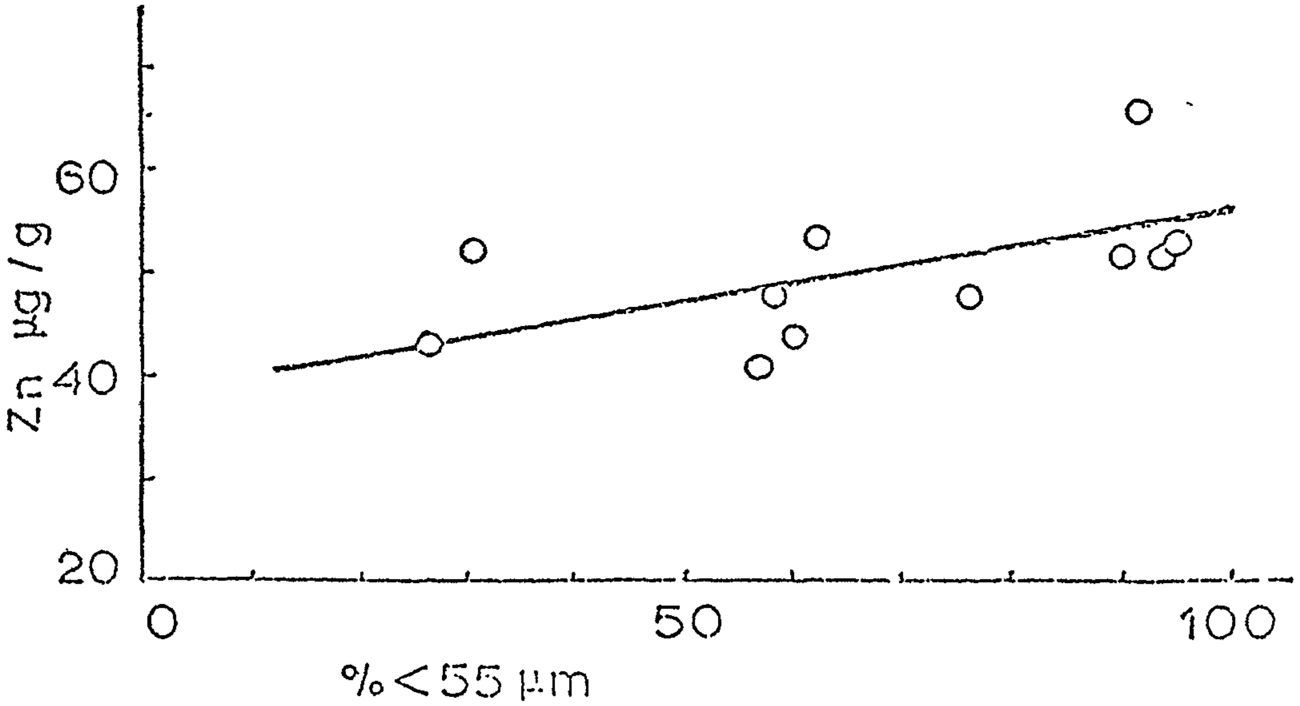

Fig. 2. Correlation between Zn concentration and particle size distribution

DISTRIBUTION OF NUTRITION SALTS

Participating Research Center:	Institute of Oceanographic and Fisheries Research ATHENS Greece
Principal Investigator:	Nicolaos Friligos

INTRODUCTION

In this part the nutrient content and the nutrient rations over a wide area of the Aegean Sea are examined.

AREA STUDIED

The area studied, as well as the sampling stations, are shown in Figure A.

PREVIOUS INVESTIGATIONS

Literature on the distribution and seasonal variation of nutrients in the southern Aegean Sea is limited to a few series of observations made by Mc Gill (1965) and Ignatiades (1973).

MATERIALS AND METHODS

The water samples were collected at standard depths covering all the water column.

Water samples for the analysis of nutrients were collected in 100 ml polyethylene bottles and kept under deep freeze, after the addition of mercuric chloride (0.04 M) until analysis. In the laboratory they were thawed, filtered through millipore membrane filters (HA, 0.45 µ) and analysed with a Technicon CSM_6 autoanalyser. The methods used were for nitrites, nitrates and silicates that of Armstrong et al (1967), for phosphate that of Murphy and Riley (1962), as automated by Hager et al (1968) and for ammonia that of Koroleff (1970) as automated by Slawyk and Mc Issac (1972).

RESULTS AND DISCUSSION

The integrated mean values and the depth at each station are summarized in Table 1.

Stations 1, 3, 4 which are located in the northern part of the Aegean Sea presented the highest values of nutrients in contrast to the stations 12, 13, 14 in southern Aegean, which presented the lowest values. This richness in nutrients in the northern Aegean Sea might be due to the water originating from the Black Sea (Lacombe et al., 1958). The higher values which were recorded at station 9 are in agreement with the results reported by Ignatiades (1965).

Variations in nutrient concentration between the surface and 200 m were not important, except at about 50m just beneath the thermocline, where high values of nutrients expecially nitrites were observed. Enrichment of nitrate, phosphate and silicate values were observed below 200m. These high values of nutrients coincide with low values of oxygen. It should be noted that in the Ionian and Western Mediterranean Sea, this enrichment occurs below 100m (Mc Gill, 1965). This is due to increased stratification in the Aegean Sea than in other areas (Miller, 1963).

Bumpus (1948) concluded that enrichment of the surface from the deep water in the Aegean Sea does not take place, because he found that the rate of vertical transfer for phosphorous was unusually low. However, Bumpus obtained a good correlation between turbulence and the change in nutrient concentration in the Ionian Sea and the Western Mediterranean.

Many authors including Cooper (1938) and Richards (1958) are of the opinion, that it is useful to look upon the N:Si:P ratios in various parts of the ocean, and that only certain values of the ratios are favourable for the bioproductivity. The best ratio for healthy diatoms is about 15:15:1.

The range, the mean, the ratios and the correlation coefficient of nutrients for all stations and depths are summarised in Table 2. The variations in nutrient concentrations generally agree with the nutrient results of the central Aegean Sea presented by Mc Gill (1965).

From the fifth column in Table 2, we see that ΣNI:Si:P ratios are close to the normal ones. The ΔSi:ΔP ratio were close to normal, while ΔNi: ΔP ratio approached the rather high value of 46.5.

The values found for the ratios ΣNi:P, Si:P and their correlation did not agree with those found by other authors (McGill, 1965: Ignatiades, 1973). It should be noted that there is also a disagreement in the ratio ΣNi:P found recently in Adriatic Sea (Scaccini-Cicatelli, 1972: Buljan et al., 1975) and the old ones (Mc Gill, 1965). It is argued, that some of the reported earlier low N:P and Si:P ratios and their poor correlation in the Aegean Sea have arisen, because the nutrient analysis methods were not so sensitive and especially in the case of N:P ratio they have taken into consideration only the nitrate form of nitrogent in the sea.

CONCLUSIONS

The mean values of nutrient for all stations and depths were the following: ammonia (0.33 µg-at/l), nitrites (0.26 µg-at/l), nitrates (0.57 µg-at/l), phosphates (0.075 µg-at/l). The values found for the rations N:P and Si:P did not agree with those found by other authors. Those reported earlier low nutrient ratios and poor correlation may be due either to low sensitivity nutrient analysis methods or in the case of N:P ratio they have considered only the nitrate form of nitrogen in the sea.

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Table 1. The integrated mean values of nutrients in µg-at/l and the maximum depth at each station

Station	NH_4-N	NO_2-N	NO_3-N	ΣNi	PO_4-P	SiO_4-Si	Depth
1	0.54	0.47	0.91	1.92	0.08	1.13	180
3	0.46	0.50	0.99	1.90	0.08	1.18	250
4	0.46	0.49	1.02	1.97	0.09	1.11	270
5	0.29	0.28	0.63	1.20	0.07	1.08	220
6	0.54	0.27	0.78	1.58	0.08	0.95	130
8	0.21	0.15	0.59	0.96	0.07	1.11	400
9	0.35	0.17	1.30	1.82	0.08	1.59	730
10	0.22	0.21	0.29	0.71	0.07	0.97	550
11	0.23	0.22	0.30	0.74	0.07	0.94	280
12	0.19	0.08	0.12	0.39	0.07	0.83	75
13	0.29	0.11	0.34	0.74	0.07	0.88	50
14	0.21	0.21	0.26	0.68	0.07	0.90	250

Table 2. Statistical analysis

Component	Number of observastions	Minimum and maximum values	Mean concentration (µg -at/1)	Mean concentration ration (by atoms)	Ratio of change	Correlation coefficient
PO_4-P	111	0.07-0.11	0.075±0.01			
NH_4-N	111	0.65-1.35	0.33±0.20			
NO_2-N	111	0.05-1.59	0.26±0.23			
NO_3-N	111	0.09-2.28	0.57±0.44			
ΣNi	111	0.27-3.92	1.17±0.77	ΣNi:P=15.6	ΔNi:ΔP=46.5	0.69
Si	111	0.75-3.27	1.05±0.30	Si:P=14.0	ΔSi:ΔP=10.2	0.39

Participating Research Centre: Institute of Oceanographic and Fisheries Research
ATHENS
Greece

Principal Investigator: Gabriel P. Gabrielides/E. Hadjigeorgiou

INTRODUCTION

In the framework of the oceanographic cruise, water samples were collected from a depth of 1 m in order to determine the concentration of dispersed/dissolved hydrocarbons.

AREA STUDIED

The area studied as well as the sampling stations are shown in Figure A.

PREVIOUS INVESTIGATIONS

The results of previous investigations are mentioned under section "Results and Discussion" and compared to the present study.

MATERIALS AND METHODS

a) Sampling. Gordon and Keizer (1974), after a big number of experiments, have concluded that any sampling device that is lowered open, through the surface film and water column, is not suitable for collecting water samples for hydrocarbon analysis. They suggest the use of a sampling device which can be lowered closed and opened only at the collection depth.

In the present cruise it was decied to use a sampler designed at the University of Goteborg, Department of Analytical Chemistry. A one litre wide-necked brown glass bottle was sealed with a clean teflon foil screwed with a cap having a hole in the centre. The bottle, already checked for its cleanliness in the laboratory, was attached to the sampler and lowered to the desired depth (1 m in our case). The teflon foil was punched by a mechanism triggered by the messenger. A few drops of concentrated mercuric chloride was added to the bottle as a preservative.

b) Solvent extraction. Many analytical methods in use, suffer from risk of contamination (especially when many transfer stages are involved) and loss of the fluorescing material, usually from evaporation steps. Keizer and Gordon (1973) found that when carbon tetrachloride was used as an extraction solvent, much of the fluorescing material in raw and spiked seawater was lost, most probably during the evaporation step.

Ahnoff and Eklund (1977) have utilised a method to minimise contamination and losses and to increase simplicity. The method, which was also used here, is as follows: A teflon coated magnetic stirring bar was added to the sampling bottle plus 10 ml of n-hexane. The water was extracted by stirring for about an hour. The phases were allowed to separate and the organic phase on top, was removed by a pasteur pipette and transferred into a clean screw capped test tube with teflon liner. Thus the same bottle was used for sampling and extraction and the same solvent for extraction and analysis. Also, since the concentration of petroleum hydrocarbons was measured directly in the untreated extract, it was not necessary to collect all the hexane.

c) Analysis. The analytical method used was that of fluorescence spetroscopy which is generally recognised as the best method yet developed for monitoring oil in seawater, due to its sensitivity and simplicity. The major drawbacks of the method are a) the uncertainty of what to use as a standard, b) the possible presence of biogenic material and c) the possibility that fluorescence characteristics of oils in seawater change during weathering.

The intensities of hexane extracts were measured in one cm quartz cells using a Perkin Elmer MPF-44A fluorescence spetrophotometer. An emission spectrum was obtained using a constant excitation wavelength of 310 nm. Also a synchronous excitation/emission spectrum was obtained for each sample using a wavelength difference of 200 nm. The SEF technique was first developed by Lloyd (1971) who also demonstrated that the wavelength of maximum emission is a function of ring number. Kuwait crude oil was used for calibration purposes.

RESULTS AND DISCUSSIONS

The results of the cruise are presented in Table 1 in µg/l and units of Kuwait crude oil equivalents. Comparing them with results obtained by other workers in other parts of the world, they appear high. One reason is probably the fact that no differentiation of hydrocarbons of biogenic origin is made. It must be noted however, that their contribution is not yet definitely confirmed. Gordon Jr. et al. (1978) working in Bedford Basin, Nova Scotia, concluded that biosynthesis does not appear to be an important source of hydrocarbons since the concentration of only one hydrocarbon, probably a polyunsaturated olefin, increased during the spring phytoplankton bloom. It is also argued that since biosynthesis is not an important hydrocarbon source in Bedford Basin, it could be unimportant for the ocean as a whole. On the other hand, there are no definite reports of aromatic hydrocarbons being synthesized by marine organisms (NAS 1975) and fluorescence is believed to measure only aromatic hydrocarbons.

The high concentrations rather indicate that the Mediterranean is badly polluted with petroleum hydrocarbons (Morris, 1974). Zsolnay et al. (1978) refer to some measurements they made in the Mediterranean during the winter of 1974-75 and conclude that the concentrations of aromatic hydrocarbons at a depth of 1 m were five times greater than those found in the N.W. Atlantic by Zsolnay (1977).

In another cruise Zsolnay (1979) reports that petroleum hydrocarbons in the Mediterranean averaged 6.9 to 25.8 ug/l with the Alboran Sea and the area off Libya having the highest concentrations.

Samples were also collected by Balkas (1980) at a depth of 1 m and a distance of 5 km from the coast of Asia Minor between Mersin and Akkuyu. The average oil concentrations found varied from 8.24 to 39.14 µg/l in Turkish crude oil equivalents with very high values occuring occasionally. Results on the concentrations of dissolved/dispersed hydrocarbons in the Levant Basin are reported by Oren (1980). His values vary from 0.3 to higher than 40 ug/l. The values of Mimikos (1980) for the areas around Lesvos and Rhodes islands do not exceed 5 ug/l, are comparatively low but they are in chrysene units.

All the above are not surprising if we take into consideration the large amounts of petroleum hydrocarbons which enter the Mediterranean Sea. Le Lourd (1977) estimates these amounts to be 0.5 to 1.0 million tons per year. The Aegean Sea is polluted by the traffic to and from the Black Sea and the natural seepage near Thasos island. As far as the absolute numbers found are concerned, it is difficult to make any comparisons due to the various methods and especially the different materials used for calibration purposes. Only if the polluting material was known and a sample of it was available for calibration, reliably accurate data of petroleum hydrocarbon concentrations in seawater could be obtained.

On the other hand, aromatic hydrocarbons have widely varying fluorescence characteristics depending upon their structure. Lloyd (1971) has demonstrated that the wavelength of maximum emission is a function of their ring number. This can be shown with a synchronous excitation emission spectrum. The one-ring compounds like benzene emit most strongly in the 280-290 nm region, the two-ring compounds like naphthalenes at about 310-330 nm and the 3 and 4-ring compounds between 340-380 nm. In most of the procedures used, the sample is excited at 310 nm and the emission is measured at about 360-380 nm. This means that the flourescence measured is only due to 3 and 4-ring compounds like anthracene, phenanthrene, chrysene etc. Another problem is the choice of the calibration standard and its content of 3 and 4-ring compounds which varies greatly from one petroleum product to the other. Gordon and Keizer (1974) examined various oils and found that the emission response at 374 nm (for the same weight of oil dissolved in hexane) varied by a factor of at least 30. Bunker oil had a big emission response and no.2 fuel oil a very low one. The reason is that even though no.2 fuel oil is 40% aromatic, its content in 3 and 4-ring compounds is low. Most of its aromatics are naphthalenic (2-ring compounds) and do not fluoresce at 374 nm.

The SEF spectra of our samples show that they do not contain large amounts of 3 and 4-ring compounds. Strong emission response appears in the 2-ring region (sample nos 3, 4, 5, 11, 13 and 14) and for many of them in the 1-ring region (sample nos 8, 9 10 and 12) (Fig. 1 and 2). This indicates that much of the pollution is probably due to light fuel oil. It can also be observed that stations away from tanker routes showed lower values.

Table 1: Concentrations of dissolved/dispersed hydrocarbons in Kuwait crude oil equivalents

Station No.	1	3	4	5	6	8	9	10	11	12	13	14
Cons µg/l	11,03	10.27	14.81	9.02	-	12.17	11.70	5.11	5.64	3.99	8.54	6.62

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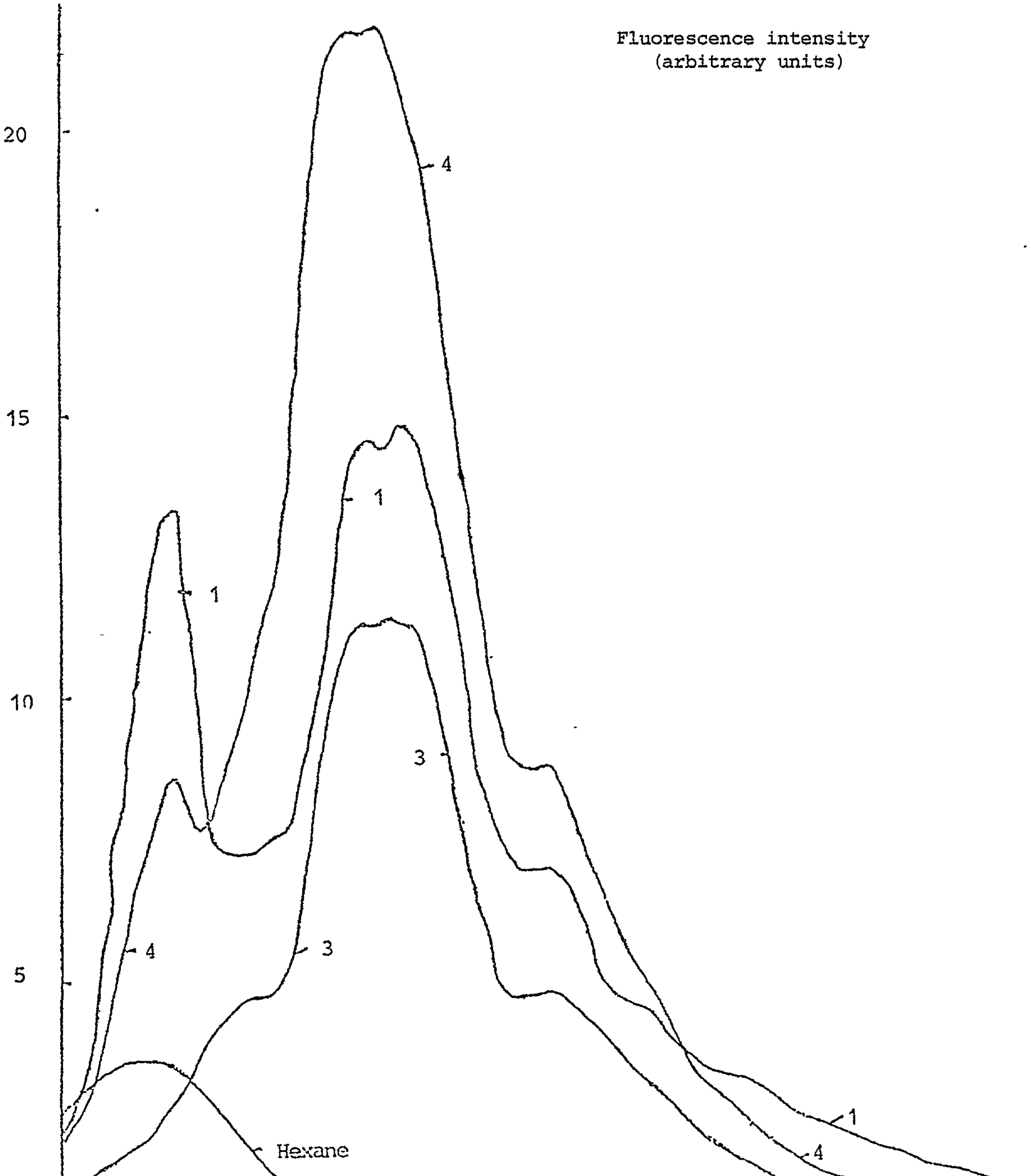

Fig. 1. Synchronous excitation emission spectra of sample Nos 1, 3 and 4 (Δ λ = 20 mn)

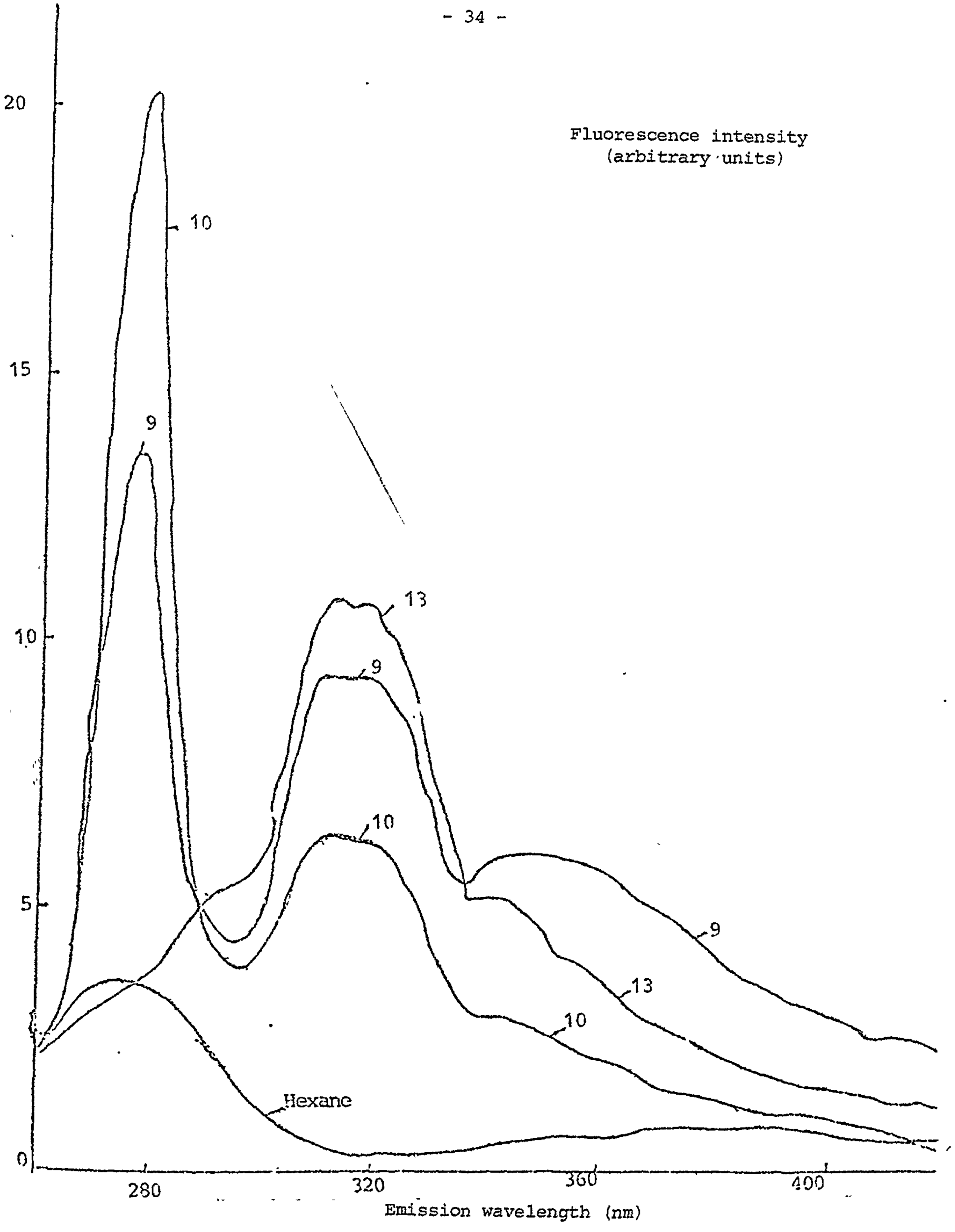

Fig. 2. Synchronous excitation emission spectra of sample Nos 9, 10, 13 ($\Delta\lambda$= 20 mn)

DETERMINATION OF POLYAROMATIC HYDROCARBONS (PAH) IN SEAWATER, PARTICULATE MATTER AND THE SEDIMENTS

Participating Research Centre: Analytical Laboratory
Department of Chemistry
Nuclear Research Centre
"Demokritos"
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Principal Investigator: Nicolas Mimicos

INTRODUCTION

Samples of seawater, particulate matter and sediments were analyzed for the presence of aromatic petroleum hydrocarbons. The concentrations ranged from 1.9-8.9 µg/l in seawater, 0.8-1.7 µg/l in particulate matter, and 105-335 µg/g dw in the sediments.

AREA STUDIED

The area studied, as well as the sampling stations, are shown in Figure A.

PREVIOUS INVESTIGATIONS

A monitoring of oil and petroleum hydrocarbons in coastal waters of several Greek islands and harbours was undertaken in our laboratory for a three year period (1977-1980), in the framework of UNEP MED-1.

MATERIAL AND METHODS

a) PAH in seawater. The sampling of seawater, which constitutes a major problem in the determination of petroleum hydrocarbons, was performed according to UNEP recommendations (IOC). A dark bottle of 2,8 lit. containing 50 ml of CCl_4-fluorescence quality attached to the sampler was lowered at 1 m depth for sampling the seawater column. After vigorous shaking of the bottle for several times the CCl_4 phase was drawn into a pipette and a new quantity of 50 ml of CCl_4 was added for a second extraction. The two aliquots were combined, evaporated in a few ml of aromatic free n-hexane and applied to a chromatographic column of partially deactivated Alumina for removal of non-petroleum material that fluoresces under the experimental conditions (Keizer and Gordon, 1973). The collected n-hexane eluate was concentrated by evaporation and its fluorescence was measured in the vicinity of 360 nm, after excitation at 310 nm, using a P.E. Fluorometer Model 203.

Using bottles without CCl_4, water samples were taken simultaneously following the same procedure at a depth of 1m and 10m. The samples were extracted in site with aromatic free n-hexane (2 times x 15 ml). The combined extracts were stored in the dark at appromately 0°C and were cleaned and analysed at the laboratory as previously described.

b) Particulate matter. Since particulate matter provides a means for hydrocarbons transport and of their incorporation into the food chain we have included them in our study. A quantity of 2.8 lit. of seawater was filtered under pressure using a 0.45 um filter which was previously washed in a soxhlet apparatus in order to avoid interference of the organic material. The retained particulates were, in turn, extracted for 8h with n-hexane. The cleaning and fluorometric determination procedures were the same as for the water samples.

c) Sediments. The sediments act as sink for unoxidised petroleum hydrocarbons, thus the degree of oil contamination in any given area may be better assessed by examining the oil concentrations in sediments than the overlying water. Sediments were collected using a grab type sampling device and were stored in dark at approximately 0^oC. After draining on n-hexane rinsed whatman no.1 filter paper over vacuum to remove excess of water, an amount of 1g wet sediment was extracted for 6 hours in a soxhlet apparatus with aromatic free n-hexane (Hargrave, and Phillips, 1975). The cleaning and the fluorometric determination procedures were the same as for the water samples.

RESULTS AND DISCUSSION

1. PAH in seawater. The complete data are presented in Table 1. South Lousianna crude oil was used for the calibration of our fluorometer. No significant difference between the CCl_4 and n-hexane values was noted. This was also true for the estimated values of water samples taken at 1m and 10m depths respectively. Nevertheless, the n-hexane values are generally lower than those of CCl_4.

   The observed values are lower than those reported by other workers in other regions concerning mainly coastal water of the Mediterranean Sea (Zsolany 19179, Balkas 1980, Mimicos 1980), but not of the same magnitude as we would expect in the case of open sea waters (NBS). This fact might be attributed to two main reasons:

a) The sampling stations are, in their majority situated in the routes of considerable shipping activity and it is therefore not surprising the observed large concentrations of hydrocarbons. This is more true for the Mediterranean which is considered as one polluted closed sea.

b) The second reason could be a possible contamination of the collected samples, despite the taken precautions, due to shipborne pollution (Keizer, and Gordon, 1973). Also, the use of an unchecked hydrographic wire could probably be a serious source for sampling error (NBS).

2. PAH in particulate matter. The data are presented in Table 1. The fact that the values for particulate matter are lower than those for seawater suggests that a large portion of the total oil, present in seawater, is in a sufficiently finely divided form, so that it is not retained by the filter. At this point it should be stressed on, that these finely divided particles might be of greater ecological importance than the larger ones.

3. PAH in sediments. Fluorescence spectroscopy has been suggested as an analytical method for estimating oil in various environmental samples. Though, several sources of error arise from the assumption that fluorescence intensity in samples is quantitatively related to the standard oil used for the calibration of the instrument. Fluorescence analysis detects only aromatic compounds which varies in different oils and these compositional variations change during weathering and degradation processes which, in turn, should be more accentuated for the sediments. . For the above reasons and pending further continuation of the project it is preferred to refrain from drawing any final conclusions at the present.

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Table 1. Results of data

Sampling Stations	Date of sampling	Time of sampling	Sediments µg/g dry weight a	Particulates µg/L	Sea Water µg/L CCl$_4$ 1m	n-Hexane 1m c	n-Hexane 10m c
4	24.3.80	09.15	225	b	8,7	8,6	8,6
1	24.3.80	16.20	200	0,9	2,6	2,7	2,7
3	24.3.80	17.25	335	b	2,6	1,7	1,7
5	24.3.80	24.00	105	b	5,6	3,4	1,7
6	25.3.80	04.45	145	b	8,9	2,7	b
8	26.3.80	09.15	150	1,0	3,7	3,4	3,5
9	26.3.80	13.50	170	0,8	3,7	b	2,2
10	26.3.80	17.50	147	0,8	2,6	6,5	1,7
12	26.3.80	23.25	162	0,8	3,7	1,7	3,4
13	28.3.80	12.55	b	5,2 d	1,9	1,7	3,4
14	28.3.80	17.30	140	1,7	3,7	1,7	1,7
11	29.3.80	03.10	170	1,0	1,9	3,4	1,7

a. average of duplicate determinations

b. no sampling

c. average of duplicate determinations

d. very high value in comparison to the values of sea water suggesting a contamination of the sample

ARSENIC, COPPER AND MERCURY IN PLANKTON

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INTRODUCTION

Phytoplankton and zooplankton play an important role in the fate of toxic elements in the marine environment for several reasons.

1. They are the basis of the pelagic food chains that include important commercial fish and thus transport toxic elements through the food chain.
2. They transport toxic elements in deeper waters by sedimentation of dead organisms and their particulate products (faeces, exoskeleton, etc.).

AREA STUDIED

The area studied as well as the sampling stations are shown in Figure A.

MATERIAL AND METHODS

a. Sampling methods. Plankton samples were collected during a cruise from 9 stations in the open waters of the Aegean Sea. Two different plankton nets were used: a 60 u mesh size net that collects mixed phytoplankton and zooplankton samples and a 250 u mesh size net that collects mainly zooplankton. Nets were equipped with PVC cod ends to avoid contamination of samples. Samples were collected by oblique 15-30 min near surface tours and stored in polyethylene containers in deep freeze (-18^{o}C).

Each sample was inspected under a stereoscope and foreign particles were removed using an eyedropper and by successive filtration through nets of 800 m mesh size. Samples were lyophilized and subsequently homogenized by grinding.

b. Analytical methods. Neutron activation analysis combined with radiochemical separations was used for the determination of As, Cu and Hg. Approximately 0.2 g of dried sample and solutions of appropriate standards were placed in polyethylene or quarts tubes heat-sealed and irradiated at the "Demokritos" swimming pool reactor using the rotation system (thermal neutron flux 2.2 x 10^{12n} $cm^{-2}s^{-1}$). Samples were counted on a 37 cm germaniumlithium drifted detector connected with a multichannel analyzer.

RESULTS AND DISCUSSION

Results are presented in Tables 1 and 2. Hg concentrations (only 6 samples analyzed) are about the same in both mixed plankton and zooplankton samples. As concentrations are higher in zooplankton samples whereas Cu concentrations are higher in mixed plankton samples.

There is a considerable variability of concentrations of all three trace elements from station to station. Station 11 and 14 mixed plankton samples show increased concentrations of As and Cu. In contrast for zooplankton samples station 1 shows the highest concentration of As and station 13 the highest concentration of Cu.

A relatively high Hg concentration appears in zooplankton from station 3. Thus, although variations do exist there is no specific pattern.

It should be mentioned that the concentrations of trace elements depend not only from the area but mainly from species composition.

In Table 3 a comparision is made with other data from the Aegean Sea. Cu and Hg compare reasonably well whereas As concentrations are higher. As, Hg and Cu concentrations compare reasonably well with concentrations reported in the literature (Boh, 1975; Leatherland et al, 1973; Martin and Knawer, 1973; Nicholl et al, 1959).

CONCLUSIONS

In view of the fact that only a few samples were collected and analysed, it is not possible to arrive to concrete conclusions. Nevertheless, there is no evidence of any increased concentrations that could be a result of anthropogenic activity

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Table 1. As, Cu and Hg in mixed plankton samples (60 µm mesh size net) µg/g dry weight

Station	As	Cu	Hg
1	2.7	15	*
3	2.2	44	0.14
4	2.8	-	*
5	4.7	57	0.15
6	4.4	34	*
9	8.3	42	*
11	10.5	64	*
13	-	53	*
14	6.2	77	*
Mean	5.2±3	48±19	0.15±0.01

* Analysis not completed

Table 2. As, Cu and Hg in 200 plankton samples (250 µm mesh size net) µg/g dry weight

Station	As	Cu	Hg
1	28.5	18	0.16
3	17.7	25	0.25
4	12.6	15	0.10
5	11.9	25	*
6	27.0	25	*
9	7.4	53	0.15
11	4.5	14	*
13	2.5	67	*
14	4.2	*	*
Mean	13±9	30±19	0.17±0.06

* Analysis not completed

Table 3. As, Cu and Hg in plankton (ug/g dry weight)

Area	As	Cu	Hg	Reference
Aegean Sea				
Euphasia Kronii	5.4	-	-	(a)
Mixed plankton	18	-	-	(a)
Zooplankton	18	-	-	(a)
Saronikos Gulf				
Acartia clausi	3.0	55	0.29	(b)
open oceanic waters				
mixed plankton and zooplankton	6-15	9-90	0.04-0.50	(c), (d) (e), (f)
Aegean Sea (present work				
Mixed plankton	5.2	48	0.15	
Zooplankton	13	30	0.17	

a. Zafiropoulos and Grimanis, 1977

b. Papadopoulou *et al.*, 1978

c. Bohn, 1975

d. Leatherland *et al.*, 1973

e. Martin and Knauer, 1973

f. Nicholl, Cure and Bouen, 1959

DISSSOLVED AND PARTICULATE ZINC, COPPER AND LEAD IN SURFACE WATERS

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Introduction - Previous Investigations

Although an international concern has been expressed the last years on the pollution of the Mediterranean Sea and a number of initiatives for the monitoring of pollution have been undertaken on international and national levels, very little, practically nothing, is known about the distribution of trace metals in the seawater of the Mediterranean and in particular of its eastern section. The only available data are those reported by Fukai and Hynh-Ngoc (1976) concerning the distribution of dissolved Cu, Hg, Zn and Cd on surface seawater samples collected from off-shore waters of the eastern Mediterranean. Unfortunately only two of these samples were taken from the Aegean Sea (39° 38'N, 25° 39' E; 38° 16' N, 24° 57' E.) and a third one from the Cretan Sea (36° 09' N, 25° 53'E).

The scarcity of systematic data on dissolved trace metal distribution and the non-existence at present, to the best of our knowledge, of any particulate trace metal determination in the same area, made the present survey necessary, not only for the establishment of the level of trace metals in the area, but also for the assessment and a more valid comparison of the results yielded from our previous studies on polluted coastal greek waters (Scoullos, 1979, 1980).

The area studied

The area studied was the Aegean Sea or Aegean Archipelago (see Figure 3) which is the northeastern part of the eastern Mediterranean. It is surrounded from W,N, and E, by the coasts of Greece and Turkey, which form a horseshoe shape. Its southern part is opened to the Cretan Sea and its northern part is connected, through a narrow channel to the Marmara Sea, which in turn is joined with the Black Sea.

Three major cities are located on it; Athens and Thessaloniki in Greece and Smyrna in Asia Minor, Turkey. These cities can influence the trace metal levels through their sewarage outfalls and the trade, industrial etc. activities related with them. However, the rivers discharged along the northern and eastern coasts and the water from the Marmara sea which inflows the Aegean sea from the N.E. (and quite often, has properties distinctly different from those of the Aegean) may play an important role in the trace metal distributions.

The sampled grid of stations, most of which were located in the central and eastern Aegean Sea is given in figures 3 - 8. Most of the stations sampled represent offshore, deep (up to 730 m) waters, however an effort was made to include in the sampled stations few representative localities from relatively shallow (50-75 m) in-shore waters (e.g. st. 12-13).

Methods and Materials

Sampling and storage.

Surface water samples (6-9 l) were collected from all stations (except st. 1) by using a polyethylene bucket with a nylon rope. The sampe of st. 1 was collected from 80 cm depth by using a non-metallic Niskin bottle.

After collection, the samples were transferred in 10 l polyethylene containers which had previously been aged consecutively with 0.1 N HNO_3 and 0.1 N HCL and then washed with seawater and rinsed with sample. On arrival back to the laboratory and within approximately two weeks the containers were thoroughly shaken and their volumes were carefully measured.

The differenciation between dissolved and particulate species of metal in seawater was made arbitrarily by filtration through prewashed 0.45 um membrane Nuflow-Oxoid filters

After filtration the samples were returned to their containers and stored in a dark cool place until the preconcentration process was commenced.

The filters were washed free of absorbed salts, dried at 60°C, and stored in plastic petri dishes until required for the determination of the acid-soluble particulate metal content.

Sample treatment and analysis

All water used in the metal preconcentration and analysis processes was metal-free, bi-distilled of excellent quality. All reagents, e.g. nitric acid 70% w/w, hydrochloric acid 50% and ammonia were metal free and redistilled. Chelex-100 resin was used for the preconcentration of the metals. Only specially designed P.T.E.E. (Teflon) beakers were used for the digestion of the filters. Borosilicate resin columns similar to those described by Riley and Taylor (1968) were used. The treatment of the columns, the regeneration of the Chelex-100 resin, the preconcentration of the dissolved metals on them and the elution were made following the method described by Riley and Taylor (op.cit.). The water was passed at a slower rate also collected and analysed in order to determine the efficiency of the columns.

The suspended solids on the membrane filters were placed in P.T.E.E. beakers and leached (refluxed) at ca 90° with 24ml and 2M redistilled nitric acid overnight. Addition of few drops of concentrated nitric acid and repeated (3-4 times) leaching, dissolved completely the solids and therefore the samples were not centrifuged, but were evaporated almost to dryness on a hot plate.

The residue was then dissolved in 0.1 M redistilled HNO_3, made up to 50ml and stored in polyethylene bottles ready for AAS. Blanks were prepared for both the dissolved and particulate metal determinations following the same process.

For the determination of zinc an air-acetylene flame was used at 213.9nm and a Perkin-Elmer 306 Atomic Absorption Spectrophotometer was employed.

For the determination of copper and lead flameless Atomic Absorption Spectroscopy was used employing the above mentioned instrument with the addition of H G A 2000 Controller and Ramp. The experimental conditions used in the flameless AAS are summarized in Table 1.

Table 1

Metal	Wavelength (n.m)	Drying		Charring		Atomising		Volume μ 1
		t sec	TC°	t sec	TC°	t sec	TC°	
Cu	324.7	60	120	36	700	7.5	2.300	15
Pb	235.5	35	100	50	525	9	2.000	75

All measurements were done in triplicate or in duplicate only when they were identical. However, the precision/reproducibility, in terms of standard deviation $\sigma = \sqrt{\frac{\Sigma(x_i - x)^2}{n-1}}$ (where n = number of measurements and x mean) was not more than 5 and the coefficient of variation cv = $\frac{\sigma \cdot 100}{\bar{x}}$ ranged between 5 and 10.

Results and Discussion

The results of the determination of zinc, copper and lead in their dissolved and particulate phases are given in Tables 2, 3 and 4. Figures 1 and 2 show the fluctuation of dissolved and particulate metals (in µg/l) from station to station, in correlation with the salinity. Figures 1 and 2 show the surface distribution of the aforementioned metals expressed as µg/l.

Fukai and Ngoc (1967) postulated that there is a possible correlation between salinity and dissolved zinc. The results yielded from the present work do not support in a conclusive way this hypothesis since no clear correlation has been found between salinity and any of the metals, in particular in the dissolved phase. It must be noted however, that in general, higher salinities are paralleled by higher particulate metal concentrations, with one distinct exception at st. 12 (Fig. 2). In the case of the dissolved metals (Fig. 1) a reverse correlation (apart st. 12) were also found at st. 2 and 11.

A distinct characteristic of all metal distributions is the considerably higher concentrations found at st. 1, which is located at the very northern part of the area sampled. A more detailed description, on the basis of the surface distributions of each metal is given below.

Zinc: The highest concentration of dissolved zinc (9.5 µg/l) was found at station 1 in the northern part of the Aegean Sea. This value is considerably higher than those found in the central and southern parts which range around 4 µg/l.

As was already stated previously, there is no clear correlation between dissolved zinc and salinity; most of the southern stations, for example, having lower dissolved zinc concentrations had higher salinities too. This leads to the conclusion that there is a geographical rather than any other differentiation among the stations. Station 13 of the southern part, being close to the port of Calymnos Island had an elevated zinc content, due probably to transport and trade activities taking place there.

Particulate zinc had an untypically high (3 µg/l) maximum value again at st.1.

High (1.0-1.6) concentrations were also observed at both sides of Lesbos island along the coast of Turkey, down to the northern coast of Samos island, whereas the central and south Aegean (st. 8, 11, and 14) had concentrations below 0.5 µg/l (0.3-0.5 µg/l). The rest of the stations have values ranging between 0.5-1 µg/l.

This total zinc (dissolved and particulate) (Table 2) ranged between 4.5 and 10 µg/l) or 12.5 µg/l if station 1 is to be included) with an a real average of 6.5 µg/l). The mean percentage contribution of particulate zinc to the total zinc content is approximately 12%.

Copper: Both dissolved and particulate copper had fairly stable concentrations throughout the studied area. Apart from station 10, having a very high value (2.3 µg/l) indicating probably a direct influence from a land-based source, the highest concentration was found at station 1 (1.5 µg/l). The rest of the area had concentrations ranging between 0.5 and 1 ug/l. It is noteworthy that the dissolved copper content at the southern stations, (namely 11, 12, 13 and 14) was in the range 0.5-0.7 µg/l, whereas that of the northern stations (except st. 6) varied between 0.7-1.0 µg/l.

A distribution similar to that of dissolved copper has been shown also by the particulate one. Station 1 (with 0.8 µg/l) and stations 9, 10 and 13 (with 0.5-0.6 µg/l) influenced by several sources, eg: coastal waters, runoff and probably anthropogenic inputs, give an idea of the higher limits of particulate copper in the area.

The rest of the studied part of the Aegean Sea has markedly uniformed, very low concentrations ranging between 0.2-0.3 µg/l.

The averaged, over the entire area, total copper content (dissolved and particulate, in µg/l) is slightly higher than 1 µg/l (Table 4) and the percentage contribution of particulate copper in this value, although fluctuating widely from station to station, is approximately 30%, twice as much as that of zinc.

Lead: The surface distribution of lead resemble closely those of zinc. Dissolved lead had a maximum concentration of 2.6 µg/l at st. 1.

The central and southern sections of the Aegean have concentrations ranging between 0.7-0.9 µg/l, with the exception of st. 4 having 1.1 µg/l. However there is a clear tendency of the dissolved lead concentrations to be increased towards the northern part of the area studied.

Particulate lead had its maximum value (0.9 µg/l) at st. 6. Stations 1, 9 and 10 had concentrations of 0.6-0.7 µg/l, whereas those of the central and southern sections (namely st. 4, 8, 11, 12 and 14) ranged between 0.2-0.3 µg/l. Stations 3, 4 and 13 had intermediate values (0.3-0.4 µg/l).

The total (dissolved and particulate) lead concentrations of the Aegean ranges between 1-2.5 µg/l (Table 4) which seems rather high. The percentage contribution of particulate lead to the total is similar to that of copper varying widely between 20 and 40% and regulated, in large, by the distance of each station from the coast and the seawater circulation.

Comparisons and conclusions

The determination of the concentrations of zinc, copper and lead in both their dissolved and particulate phases in seawater from the Aegean sea provided useful information about the levels and the surface distribution of these metals, taking into account that this is the first time that a systematic study on the trace metals is undertaken in this region.

The ranges and the averaged trace metal concentrations of the Aegean Sea are given in Table 5 together with those reported by previous workers for the same and the other seas. From Table 5 it is immediately apparent that the concentrations found in the Aegean Sea are within the range reported for other Mediterranean regions. However, the averaged values are higher that those reported for other Mediterranean areas. Zinc in particular (5.6 µg/l) being in very good agreement with that reported by previous workers (5.3 µg/l), in spite of the different analytical techniques used, is more than double than the average for the Mediterranean.

Copper concentrations, although was found higher than that reported previously and that of the whole Mediterranean, is still very low when compared with regions outside the Mediterranean. Finally the dissolved lead concentrations are very high (1.2 µg/l) but unfortunately there are no available data for comparison other than a value reported by Chow and Patterson (1966) which seems to be very low, six times lower than the average found in the Aegean. Although the comparisons provide, in general the necessary background information for the understanding of the status of the trace metal levels and metal pollution in a sea, they may not be strictly scientifically valid since it is known that each sea consists of subregions having often distinctly different characteristics. The studied area for example can be broadly divided into three subregions:

a) The northeastern part, which seems to be influenced partly from the north, possibly from the sea of Marmara water (st. 1) and partly from the discharges and other anthropogenic imputs from land-based sources. The role of the frequent passage of ships in this area must also be taken into account. The elevated concentrations of nearly all metals, in both their dissolved and particulate phases (Fig. 1 and 2) at certain stations (e.g. St. 6, 9 and 10) may indicate some of the sources. Station 6, for example, located outside the Gulf of Smyrna is probably influenced by the discharges from the city and the area of Smyrna and the runoff from the coasts of Asia Minor.

b) The southern (except st. 13) and central Aegean Sea section (including mainly st. 8, 11, 12 and 14), which is also the most "open" seems to be unaffected by pollution and has the lowest trace metal concentrations throughout.

c) The north-central part (including st. 3, 4 and 5), being in an intermediate location between the two previous sections, has also intermediate concentrations for nearly all metals.

In conclusion, the Aegean Sea has rather low copper concentrations but elevated lead and zinc ones in comparison with non Mediterranean offshore waters. Compared with the average for the Mediterranean all metal concentrations were found higher, influenced probably by the water of the Marmara (and Black) Seas, the extremely high salinities and the land-locked character of this sea. Thus, the higher trace metal levels tend to appear at the stations located closer to the coastline and the Marmara Sea.

In order to better understand the described distributions, and extension of the present project will be necessary, in order to include a study of more metals from a denser grid of stations and all standard depths.

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Table II. Dissolved and particulate zinc in surface waters of the Aegean sea

STATION No	Zn dissolved	Zn particulate	Zn total	% contribution of Zn part/Zn tot.
	← in µg/l →			
1	9.5	3.0	12.5	24.0
3	5.1	1.0	6.1	16.4
4	5.4	0.7	6.1	11.5
5	6.0	0.8	6.8	11.8
6	8.9	1.0	9.9	10.1
8	6.5	0.5	7.0	7.1
9	4.5	1.2	5.7	21.0
10	6.9	1.6	8.5	18.8
11	4.2	0.3	4.5	6.7
12	4.7	0.6	5.3	11.3
13	6.2	0.9	7.1	12.7
14	4.0	0.4	4.4	9.1
Range	4 - 9.5	0.3 - 3	4.4 - 12.5	6.7 - 24.0
Mean areal	6.0	1.0	7.0	14.3
Range*	4 - 8.9	0.3 - 1.6	4.4 - 9.9	6.7 - 21.0
Mean areal*	5.6	0.8	6.5	12.3

* (Excluding St. 1)

Table III. Dissolved and particulate copper in surface waters in the Aegean sea

STATION No	Cu dissolved	Cu particulate	Cu total	% contribution made by Cu part. to Cu tot.
	←	in µg/l	→	
1	1.5	0.8	2.3	34.7
3	0.7	0.3	1.0	30.0
4	1.0	0.3	1.3	23.0
5	0.9	0.2	1.1	18.0
6	0.5	0.3	0.8	37.5
8	0.9	0.3	1.2	25.0
9	0.8	0.6	1.4	42.8
10	2.3	0.5	2.8	17.8
11	0.5	0.2	0.7	28.6
12	0.5	0.3	0.8	37.5
13	0.7	0.5	1.2	41.7
14	0.6	0.2	0.8	16.0
Range	0.5-2.3	0.2-0.8	0.7-2.8	16 - 43
Mean areal	0.9	0.4	1.3	29.4
Range*	0.5-1.0	0.2-0.6	0.7-1.4	
Mean areal*	0.7	0.35	1.05	

* (Excluding St. 1 and 10)

Table IV. Dissolved and particulate lead in surface waters in the Aegean sea

STATION No	Pb dissolved	Pb particulate	Pb total	% contribution made by the Pb part. to Pb total
	←	in µg/l	→	
1	2.6	0.6	3.2	18.7
3	1.0	0.4	1.4	28.5
4	0.9	0.3	1.2	36
5	1.8	0.4	2.2	18.2
6	1.5	0.9	2.4	37.5
8	1.3	0.3	1.6	8.7
9	1.0	0.7	1.7	41.1
10	1.5	0.6	2.1	28.5
11	0.9	0.2	1.1	18.2
12	0.7	0.3	1.0	30
13	0.9	0.5	1.4	35.7
14	1.1	0.3	1.4	21.5
Range	0.9-2.6	0.2-0.9	1.0-3.2	18.2-41
Mean areal	1.3	0.45	1.75	25.7
Range*	0.9-1.8	0.2-0.9	1.0-8.4	18.2-41.1
Mean areal*	1.2	0.44	1.64	26.8

* (Excluding St. 1)

Table V. A comparison of the concentrations of dissolved zinc, copper and lead found in the Aegean sea with concentrations reported in the same and other seas (in g/1)

AREA STUDIED	Year of sampling	DEPTH	Z I N G		C O P P E R		L E A D		REFERNCES
			RANGE	MEAN	RANGE	MEAN	RANGE	MEAN	
N.W.ATLANTIC	1962-65	0.200		4.3		1.2		0.02	7,8
N.E.PACIFIC	1971	5	0.8-3.4	2.0	0.4-1.2	0.8		0.35	9, 10
BLACK SEA	1969	1-2150	0.21-42.4	1.9	0.04-66.3	1.8			11
N.W.MEDOTERRA-NEAN	1974	Surface	0.1-9.9	2.3	0.03-21.6	0.8			12
MEDITERRANEAN	1973-75	"	0.1-7.9	2.3	0.06-4.9	0.4		0.2	1, 10
AEGEAN SEA	1975	"	4.7-5.8	5.3	0.25-0.64	0.45			1
AEGEAN SEA	1980	Surface	4.0-8.9	5.6	0.5-1.0	0.75	0.9-1.8	1.2	Present Work

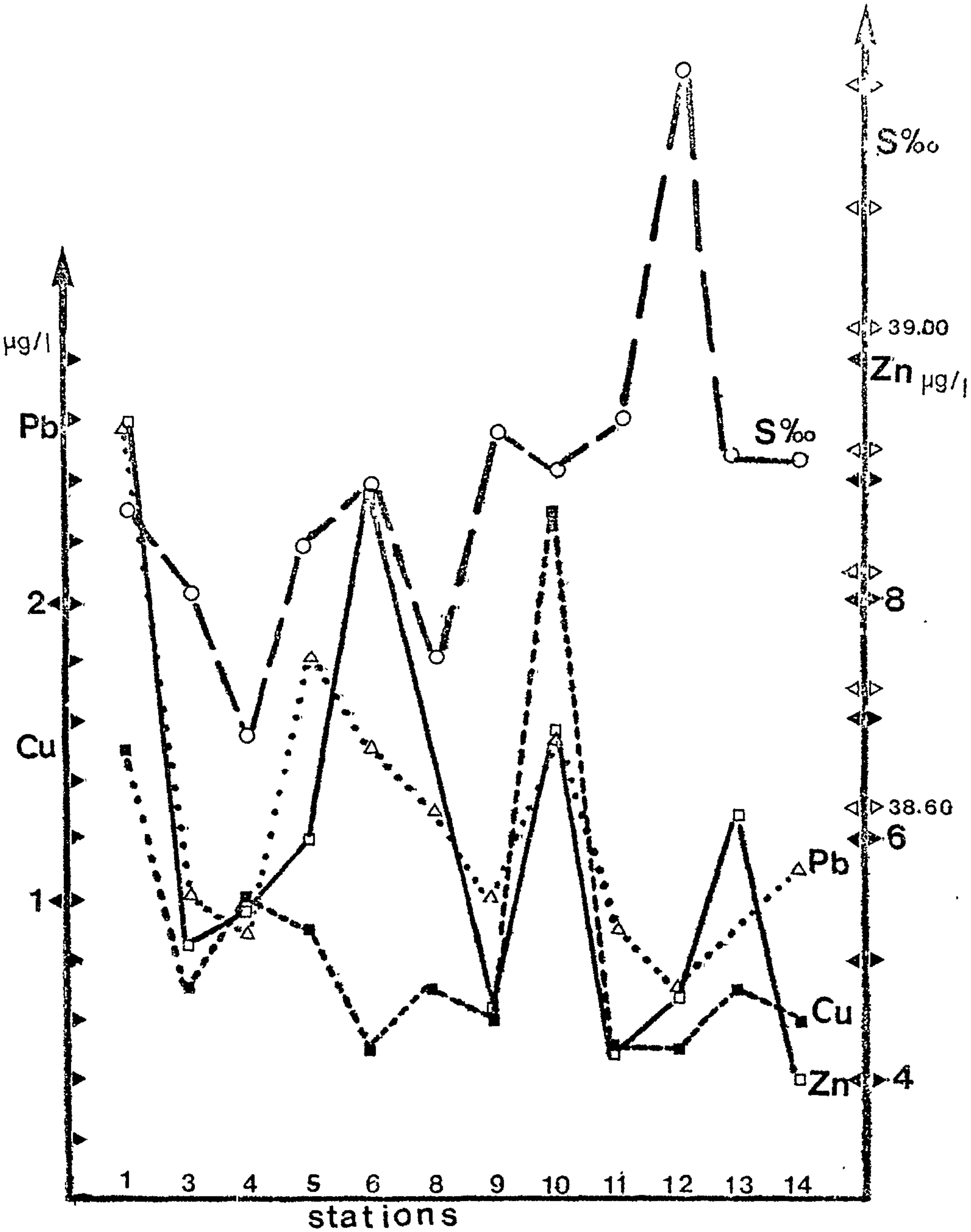

Fig. 1. The station to station variation of the dissolved zinc, copper and lead concentrations in comparison with the salinity

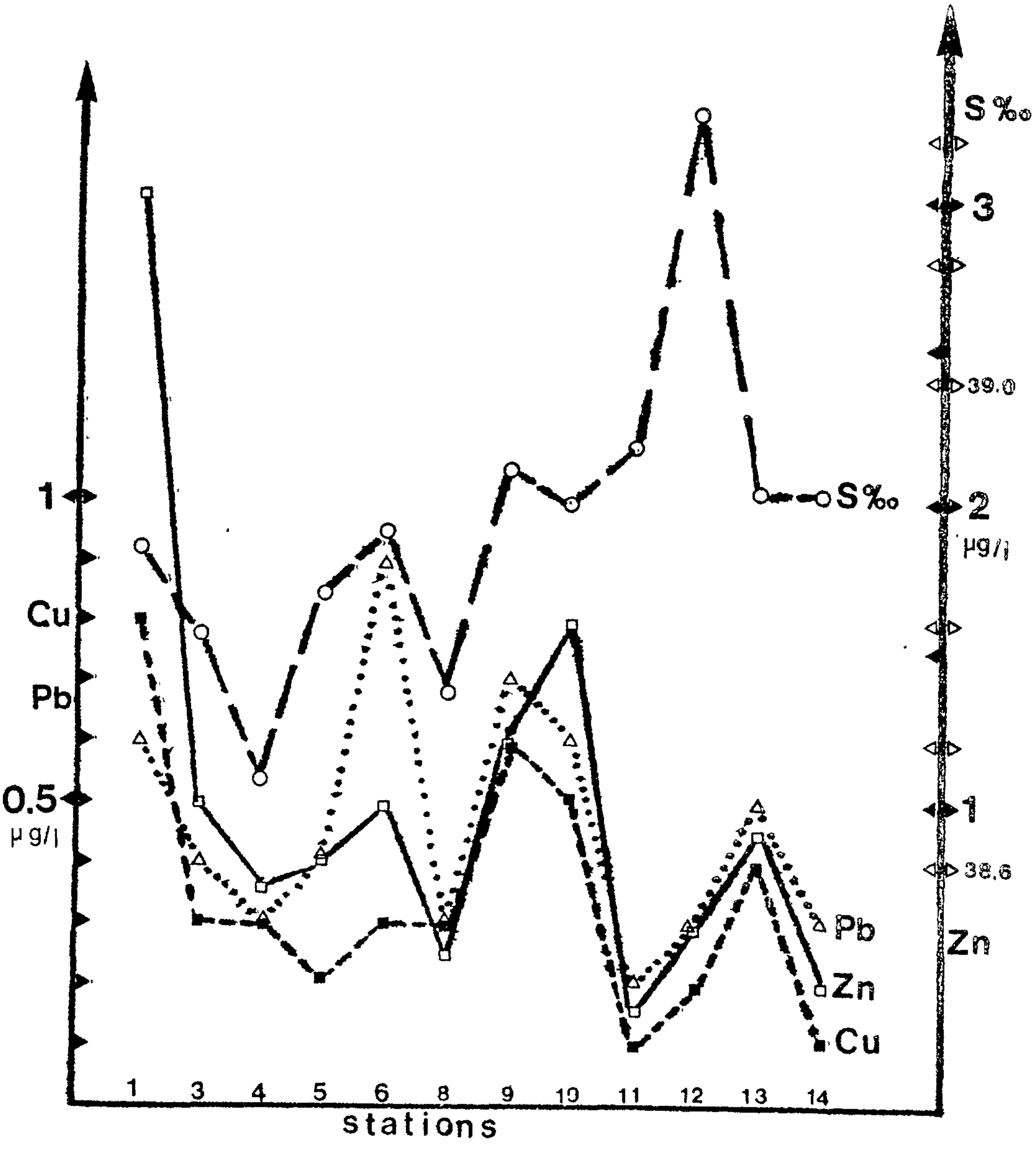

Fig. 2. The station to station variation of the particulate zinc, copper and lead concentrations in comparison with the salinity

Fig. 3. Spatial distribution of dissolved zinc in surface waters of the Aegean sea

Fig. 4. Spatial distribution of particulate zinc in surface waters of the Aegean sea

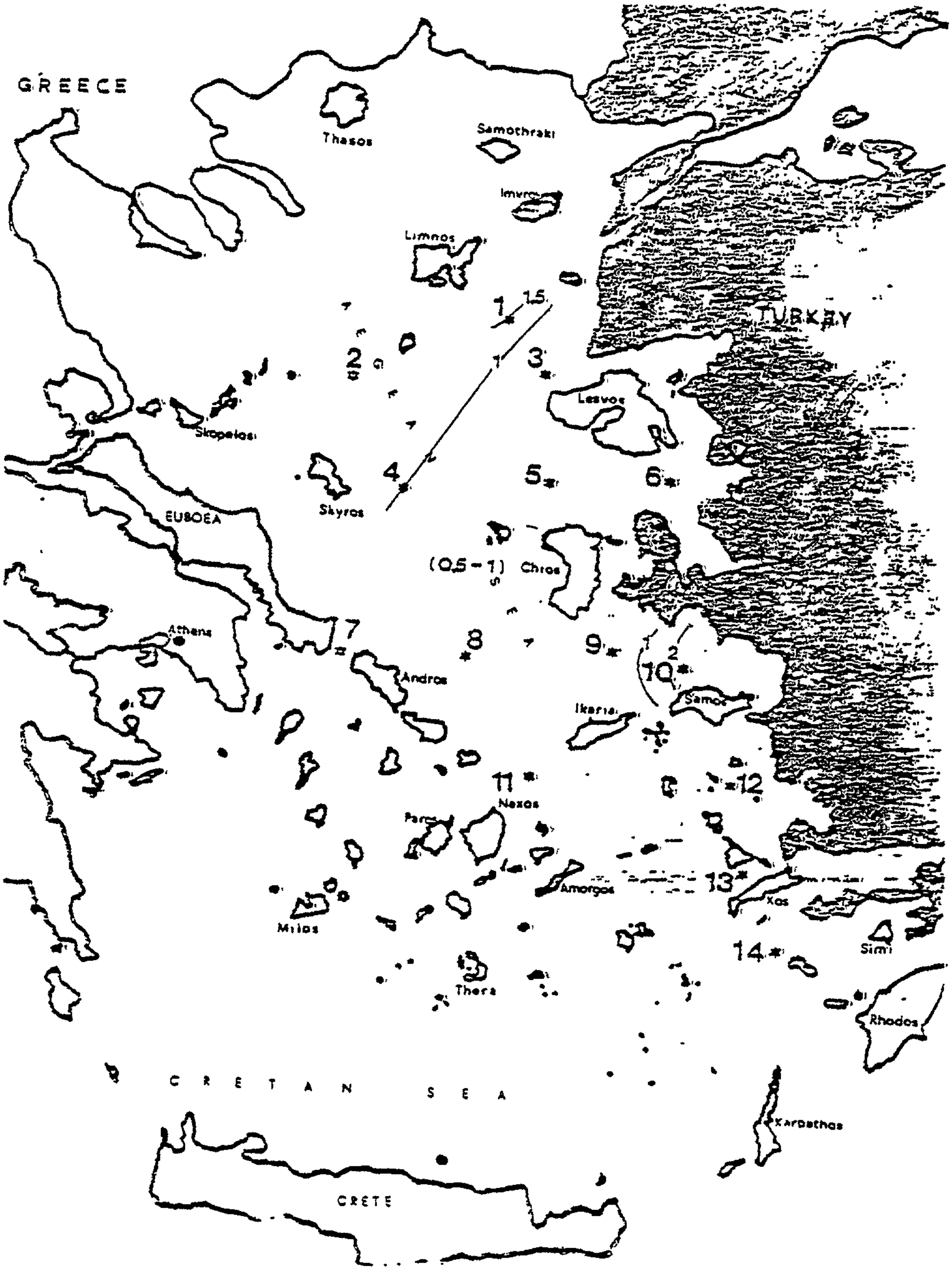

Fig. 5. Spatial distribution of dissolved copper in surface waters of the Aegean sea

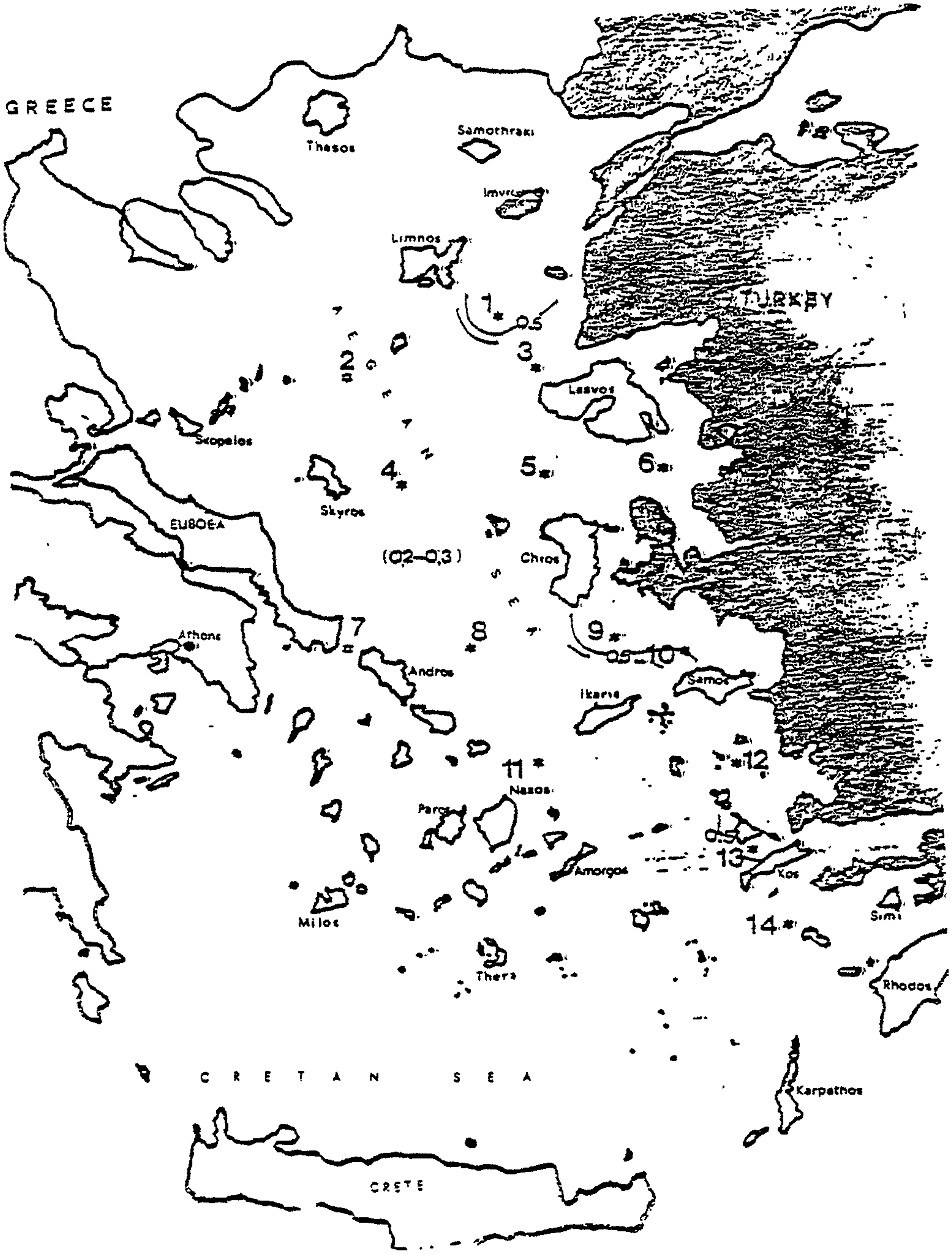

Fig. 6. Spatial distribution of particulate copper in surface waters of the Aegean sea

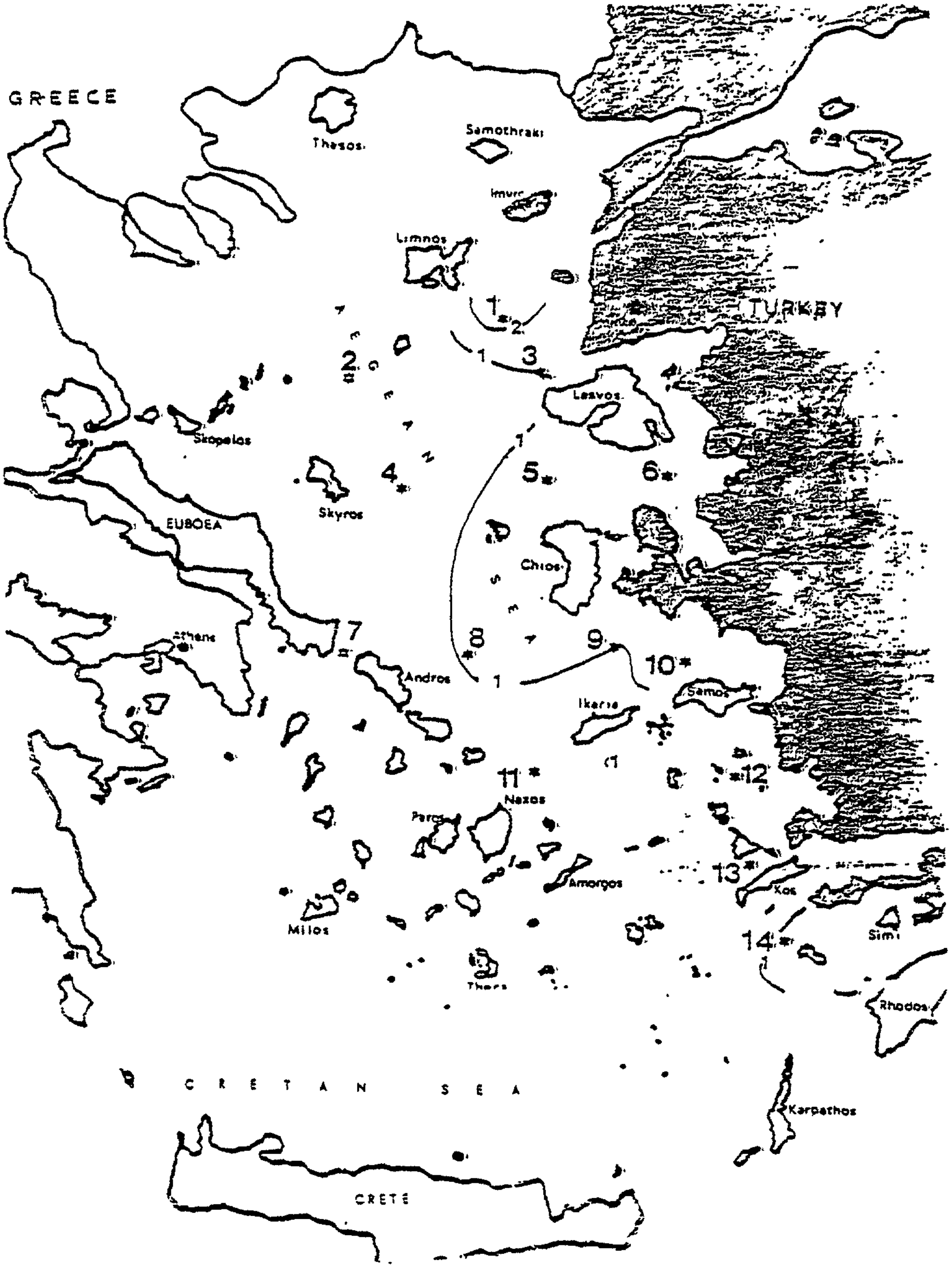

Fig. 7. Spatial distribution of dissolved lead in surface waters of the Aegean sea

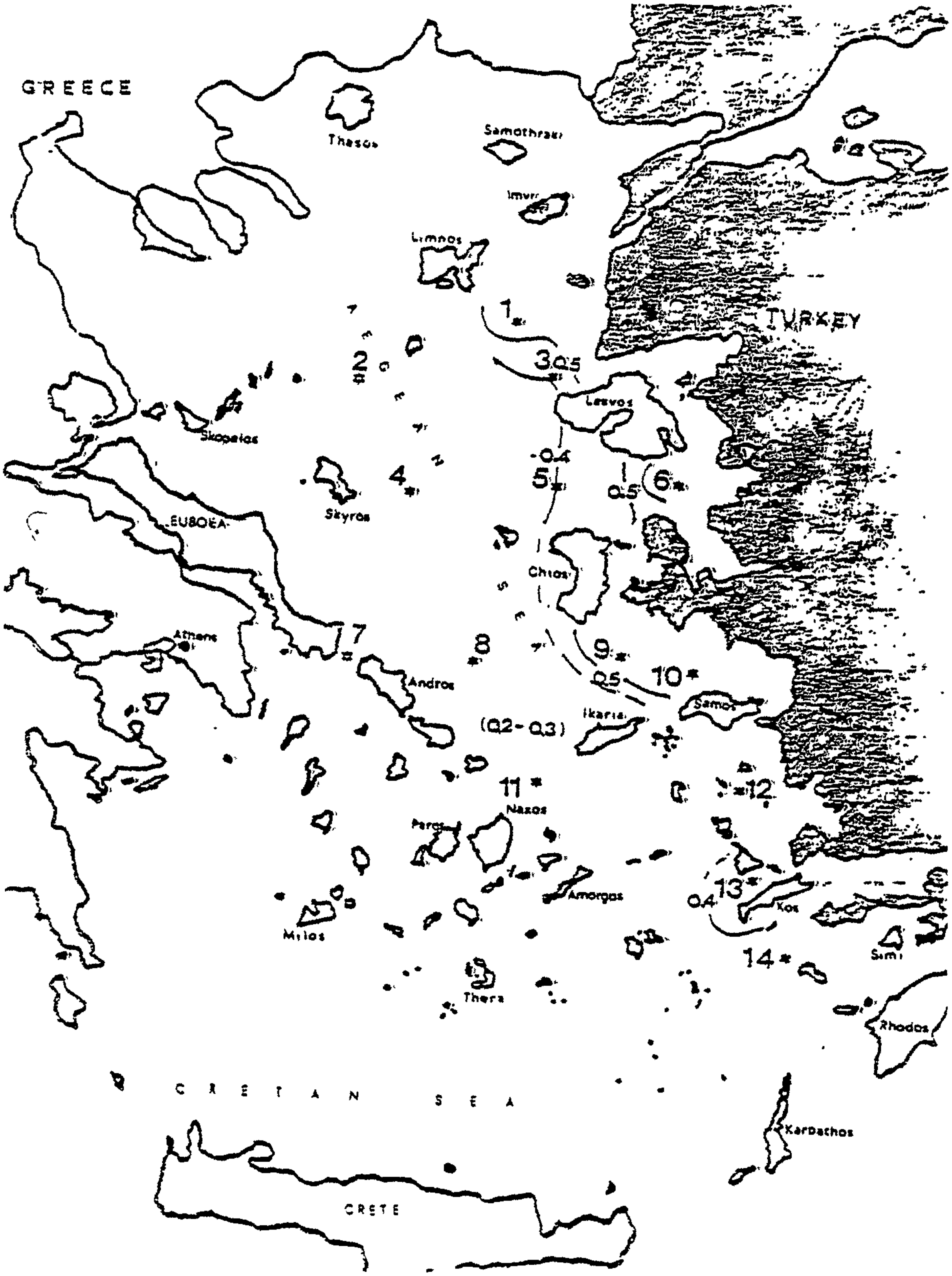

Fig. 8. Spatial distribution of particulate lead in surface waters of the Aegean sea

ZOOPLANKTON

Participating Research Centre: Zoological Laboratory
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ATHENS
Greece

Principal Investigator: M. Moraitou-Apostolopoulou

INTRODUCTION

Zooplankton samples were collected for quantitative and qualitative analysis at stations 1, 3, 4, 5, 6, 9, 11, 13 and 14.

AREA STUDIED

The area studied as well as the sampling stations are shown in Figure A.

MATERIALS AND METHOD

The net used had a 250 u mesh apperture size. The haulings lasted 30 min. Subsamples (1/2 to 1/16) were obtained by a Folsom plankton splitter. Copepods the most important zooplankton group were identified down to the species level, while the other groups were enumerated as such.

RESULTS AND DISCUSSION

The examination of plankton samples revealed a quantitative poorness, 876 (station 5) to 11.009 (station 6) zooplanktonic individuals were counted at each sample. The mean number of individuals per sample was 3.064. These numbers must be considered as low for the season of sampling (March). In Saronicos Gulf a mean number of 41.554 indiv/sample were found during March (Moraitou-Apostolopoulou, 1974).

Nocturnal samples were usually the most rich due to the diurnal vertical migration.

Copepods constituted the main zooplankton group forming the 70,01% of the total zooplankton numbers. 41 copepod species were identified. Clausocalanus paululus (3881) and Clausocalanus pergens (3116) were the most abundant, followed by Calanus minor (2.730), Lucicutia flavicornis (1554) and Oithona plumifera (968). Very abundant were also the different Copepodids of Calanidae (4.425).

Temora stylifera the leading form of the Aegean was rare (68). This scarceness must be attributed mainly to the thermophilic character of the species. Acartia clausi the form that is found in very dense concentrations in Saronicos Gulf was also scarce (168 ind. counted). This must be due not only to the small size of this species (not sufficiently retained by the net apperture size), but also to the high salinities and the usually pelagic character of the area. Acartia becomes very abundant in neretic areas with reduced salinities during the cold period and is found in swarms in polluted areas.

The absence of Cladocerans must also be attributed to the same reasons. In addition most Cladocerans are thermophilic.

Among the other zooplanktonic groups Appendicularian (2.614), Salps (1.151) and Chaetognaths (1.076) were the most abundant.

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