MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

INTERNATIONAL ATOMIC ENERGY AGENCY

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)

FINAL REPORTS OF PRINCIPAL INVESTIGATORS
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This volume is the eighth issue 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.

Ce volume constitue le huitième numéro 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 of the MAP Technical Reports Series 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 de la série des Rapports techniques du PAM rassemble les rapports finaux des chercheurs responsables qui ont participé au projet pilote intitulé: "Etudes biogéochimiques de certains polluants au large de la Méditerranée (MED POL VIII)".

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Centre de Recherche participant:	Centre des Faibles Radioactivités Laboratoire mixte CNRS-CEA GIF-SUR-YVETTE France
Chercheur principal:	R. CHESSELET

Introduction

Les études ici présentées sur le contenu en métaux des aérosols et des particules en suspension ont été entreprises pour déterminer le rôle de la matière particulaire dans le transport des métaux vers les océans et à l'intérieur de ces eaux. Ces études sont complémentaires au travail exécuté par le Laboratoire AIEA à Monaco, dont le compte rendu se trouve dans une autre partie de ce rapport.

Zones étudiées

A. Zone comprise entre Nice (France) et Calvi - Carte des stations pour l'étude des particules marines - (carte 1).

Methodologie *

Etude des particules marines.

L'eau de mer, prélevée à differentes profondeurs à l'aide de bouteilles Niskin (PVC) (30 l) est filtrée sur des membranes nuclépores de porosité 0,4 um, qui collectent plus de 95% de la matière en suspension. Al, Fe, Cu, Pb, Zn, Cd, As, sont dosés par spectrométrie d'absorption atomique sans flammes par voie électro-thermique.

Méthodologie analytique

Le dosage des métaux (Cu, Pb, Zn, Fe, Al, Cd, As) nécessite une solubilisation préalable des particules recueillies sur filtre par une attaque dite "à la bombe". Ensuite les métaux, en raison de leur très faible concentration sont dosés par une méthode de très haute sensibilité et qui autorise le micro-échantillonage: il s'agit de la spectrométrie d'absorption atomique par voie électro-thermique. Au tableau 1 sont présentées des caractéristiques essentielles de cette méthode analytique appliquée au dosage du Cu, Pb, Cd, As,Zn, Fe, Al, dans les particules en suspension dans l'ocean.

Afin de s'assurer de la fiabilité de nos dosages, de nombreux contrôles de la justesse ont été effectués à l'aide de standards de référence du N.B.S., de la méthode des ajouts dosés et par une autre méthode lorsque cela était possible (activation neutronique pour Al, Fe, Zn, As, dilution isotopique pour Pb, méthode des hydrures pour As).

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* Les méthodes de prélèvement et d'analyse sont les mêmes que celles utilisées dans l'Atlantique, en prenant des précautions extremes contre les contaminations accidentelles.

Resultats et interpretation

Chimie des particules marines

Les concentrations des éléments Al, Fe, Cn, Pb, Zn, Cd, As sont données aux tableaux 2-3-4.

Discussion

Les concentrations de Matière Totale Particulaire collectée sont d'environ 10 µg/l. Elles sont très voisines des concentrations de matière totale en suspension que nous observons dans l'Atlantique et le Pacifique.

Les concentrations de Al, élément qui peut être considéré comme indicateur des concentrations des alumino-silicates (1-2-3-4-6) sont du méme ordre de grandeur quelle que soit la station (Al = 100 ng/l). Cette concentration est très proche de la concentration d'Al mesurée sur l'ensemble des prélèvements GEOSECS dans l'Atlantique et le Pacifique. Il a été montré que pour ces deux océans les concentrations en Al sont en partie gouvernées par un flux atmosphérique d'origine continentale.

Bien que l'on observe un certain gradient des concentrations moyennes pour les métaux trace étudiés entre la station proche de la côte du Sud de la France (Station 1) et la Station 3, les valeurs moyennes des concentrations de ces éléments sont trés voisines des concentrations moyennes de ces éléments à l'échelle de l'Atlantique et du Pacifique.

Un certain nombre d'échantillons ont été pris à des profondeurs quiasiment identiques et d'autre part certains filtres proviennent d'échantillons provenant d'une même bouteille. Cette étude a été faite dans le but d'étudier la variablilité des concentrations.

La variabilité que nous constatons ici (tableaux 2-3-4) est d'un facteur 2.4 en moyenne: variabilité qui est exactement semblable à celle observée sur 500 échantillons dans le programme C.F.R.-GE.OSECS.

Cette variabilité ne peut pas être prise comme une indication d'une contamination accidentelle ou d'une erreur d'analyse.

Quand on considère les moyennes observées pour chaque station et pour chacun des élements (Al-Fe-Cu-Pb-Zn-Cd) on observe une diminution de la côte vers le large (de la station 1 vers la station 3).

Ce gradient suggère l'existence d'un effet lié à la proximité du talus continental. Cet effet se superposerait à l'apport atmosphérique et les résultats seront discutés dans la section suivante.

Les figures 1,2,3,4 donnent les concentrations en fonction de la profondeur. On constate que la variabilité dont nous avons fait état au paragraphe 3 se retrouve à toutes les prfondeurs et aux trois stations. D'autre part, on n'observe aucun accroissement ou diminution marqué avec la profondeur, ce qui suggère que nous nous trouvons en présence de particules marines appartenant au "bruit de fond" particulaire de l'ocean. Cette donnée est en accord avec celle qui a été établie à l'échelle de l'ocean au cours du programme GEOSECS. Il semble que pour le PB; on observe à la station 1 dans les eaux de surface, une très grande concentration qui pourrait avoir pour origine l'influence de la pollution locale.

Discussion des Facteurs d'Enrichissement

Il est d'usage afin de permettre des comparaisons d'exprimer les concentrations en éléments-traces dans la matière particulaire, que ce soit sous forme de particules marines ou d'aérosols, sous forme de Facteurs d'Enrichissement.

Nous avons adopté ici le mode de calcul généralement admis:

Nous comparons les abondances relatives de ces élements à leur abondance relative moyenne de la croûte terrestre, en prenant l'aluminium comme élément de référence. On obtient ainsi pour chaque élément un Facteur d'Enrichissement:

$$F/_{\text{Ecroûte}} = \frac{(\ X/\mathrm{Al})\ \ \text{particule}}{(\ X/\mathrm{Al})\ \ \text{croûte}}$$

Les Facteurs d'Enrichissement en Fe, Cu, Pb, Cd, Zn ainsi calculés sont donnés dans les figures 5-6.

On constate que les $^{F}/E$ ainsi calculés sont trop élevés ($>$10) pour que les concentrations des métaux en traces (Cu, Pb, As, Cd, Zn) puissent être expliquées par leurs abondances moyennes dans les particules d'origine détritique continentale.

Dans les figures 5-6 on a fait figurer les valeurs moyennes de l'enrichissement dans les particules de l'Atlantique Nord (4-2).

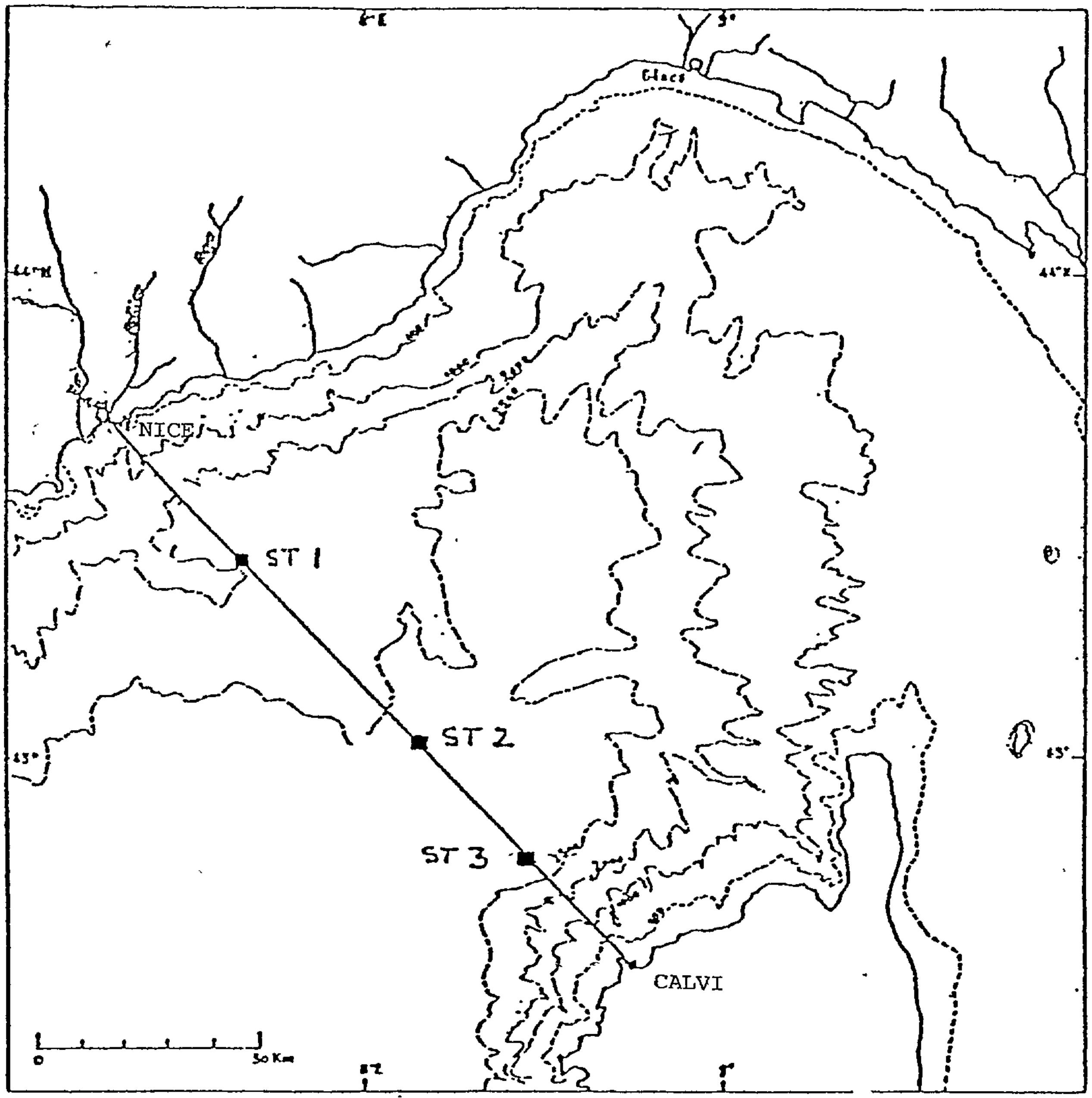
La comparaison qui est alors possible montre que les $^{F}/E$ sont très proches de ceux observés pour l'Atlantique (7). Pour des raisons de commodité sur les figures 5-6 n'ont pas été figurées les fourchettes des $^{F}/E$ observés dans l'Atlantique. Il n'en demeure pas moins que pour le Fe, le Cu et le Pb ces Enrichissements ont tendance à être supérieurs en Méditerranée dans la région étudiée, à ceux observés dans l'Atlantique.

Discussion de l'origine de l'enrichissement.

Etant admis qu'il a été démontré à l'échelle de l'Atlantique que l'apport atmosphérique exerce un certain contrôle sur la chimie des particules marines, on peut tenter de calculer de la même façon que l'on a opéré dans l'Atlantique le flux des particules en suspension dans l'étude présentée ici et comparer les valeurs de ces flux à ceux qui ont été présentés pour l'Atlantique Nord. Cette comparison figure au tableau 5. Pour calculer ces flux on a utilisé une vitesse de chute des particules de 80 m/an, fondée sur la distribution des tailles des particules observées dans l'Atlantique, à partir de comparaisons de mesures effectuées au Coulter-Counter entre la Méditerranée et l'Atlantique. Il semble qu'il n'y ait pas de différence dans les distributions de taille entre les particules du Méditerranée et d'Atlantique. On peut donc considérer cette vitesse de chute comme valable pour le site de la Méditerranée. Il nous parait significatif à l'examen du tableau 5 que les flux calculés en Méditerranée au cours de cette étude soient 2-3 fois supérieurs à ceux de l'Atlantique Nord alors que le flux d'Al est pratiquement identique.

Cette valeur du flux des éléments-traces comprenant la famille des métaux lourds en Méditerranée peut être considérée comme une première indication de l'influence de la pollution sur la chimie des particules marines. Il faut cependant rappeler ici que nous avons pu montrer que les flux d'origine volcanique pouvaient entrer en compétition avec les flux anthropogéniques (5). La deuxième partie de l'étude portant sur la chimie de l'aérosol marin devrait permettre de répondre à la question soulevée dans la première partie de cette étude.

Une étude limitée de la chimie des particules en Méditerranée démontre l'existence d'anomalies (enrichissements) dans la chimie des métaux Cu, Pb, Cd, Zn et peut-être Fe, associés à la matière particulaire en suspension. Cependant les concentrations et les Enrichissements observées sont du même ordre de grandeur que ceux qui ont été observés à grande échelle dans l'Atlantique et le Pacifique, il semble donc que la chimie des métaux en traces dans la Méditerranée obéisse à des lois identiques à celles qui régissent leur chimie à l'échelle de l'océan global



Carte 1. Carte des stations pour l'étude des particules marines

Tableau 1. Caractéristiques essentielles de la méthode analytique appliquée

	Al	Fe	Cu	Pb	Zn	Cd	As
Detection limit	$5\ 10^{-10}$ g	$5\ 10^{-11}$ g	$5\ 10^{-11}$ g	10^{-11} g	$5\ 10^{-12}$ g	10^{-11} g	10^{-10} g
Sensibility $\Delta c / \Delta A$	$3\ 10^{-10}$	$2\ 10^{-11}$	$2\ 10^{-11}$	$0{,}5\ 10^{-11}$	$2\ 10^{-12}$	$0{,}4\ 10^{-11}$	$0{,}5\ 10^{-10}$
Precision	10 %	10%	10 %	5 ÷ 10 %	10 %	10 %	10 - 15 %

Tableau 2. Variabilité des concentrations - Station 1

Sample	DEPTH (m)	T.S.M. µg/l	Al ng/l	Fe ng/l	Cu ng/l	Pb ng/l	Zn ng/l	Cd ng/l
Ko 005	250	13,9	242	1097	<0,1	155,4	26,8	3,2
Ko 105	250	33,2	375	2125	8	106,8	27,4	1,3
Ko 003	300	6,4	103	262	<0,1	14,1	16,3	1,7
Ko 002	350	12,9	128	977	14,8	11,1	4,0	2,7
Ko 104	350	19,6	242	2011	63,4	31,7	23,4	1,6
Ko 008	910	20,9	275	1217	29,1	64,8	15,1	1,4
Ko 009	1660	5,4	70	337	8,2	10,8	13,1	1,3
Ko 010	1670	8,9	98	942	28,2	17,2	17,7	1,1
Ko 001	1680	18	54	2640	34,2	69,0	4,0	4,0
Ko 006	1680	9,5	43	1097	15,4	35,4	15,4	4
Geometric Mean		14,8	128	1029	20	34,5	13,7	2

Tableau 3. Variabilité des concentrations - Station 3

Sample	DEPTH (m)	T.S.M. µg/l	Al ng/l	Fe ng/l	Cu ng/l	Pb ng/l
Ko 208	50	49	113	108	17,6	17,4
Ko 209	290	24,5	344	710	44,8	34,5
Ko 210	300	10,5	82	630	24,8	13,7
Ko 306	500	12,7	80	161	1,7	7,3
Ko 307	510	6,8	103	278	55,7	70,3
Ko 305	790	9,8	171	470	13	14,6
Ko 401	1080	5,5	80	170	1,7	4,6
Ko 308	1090	3	51	398	0,3	10,3
Ko 309	1100	9,6	57	478	22,3	8,2
Ko 310	1490	5	59	450	61	11,2
Ko 303	1500	7,1	74	158	3,4	7,5
Ko 302	1880	2,3	40	347	1,4	6,2
Ko 301	1890		26	172	13,4	3,5
Geometric Mean		12,1	79	248	8,4	11,2

Tableau 4. Variabilité des concentrations - Station 2

Sample	DEPTH (m)	T.S.M. µg/1	Al ng/1	Fe ng/1	Cu ng/1	Pb ng/1	Zn ng/1	Cd ng/1
Ko 109	50	46,5	86	172	<0,1	17,5		0,9
Ko 103	490	11,6	124	520	12,2	6,5	12,2	0,6
Ko 106	500	7,3	78	662	10,5	12,5	13,1	1,1
Ko 110	700	≤5	97	348	39	24,8		0,9
Ko 202	700	5	161	1020	40	48,5		0,9
Ko 102	880	10,9	150	348	0,9	16,1	15,1	0,3
Ko 101	980	9,3	107	148	12,2	5,1	13,1	0,6
Ko 108	1500	4,1	93	588	22,8	36,2	18,8	
Ko 207	2000	7,9	140	93	7,4	3,9		0,5
Ko 205	2370	≤3	120	498	26	30,5		0,7
Ko 204	2380	6,8	143	421	14	9,8		0,4
Ko 203	2390	3,9	54	441	15	11,9		0,6
Geometric Mean		11,2	107	364	13,1	14,2		0,6

Tableau 5. Comparaison des valeurs de flux

Φ 10^{-4} g/m²/an	Al	Fe	Cu	Pb	Cd
MEDITERRANEAN this study	86	2.91	10	11	0,5
NORTH ATLANTIC (c.f.r. cnrs 1977)	90	160	2,4	7	0,1

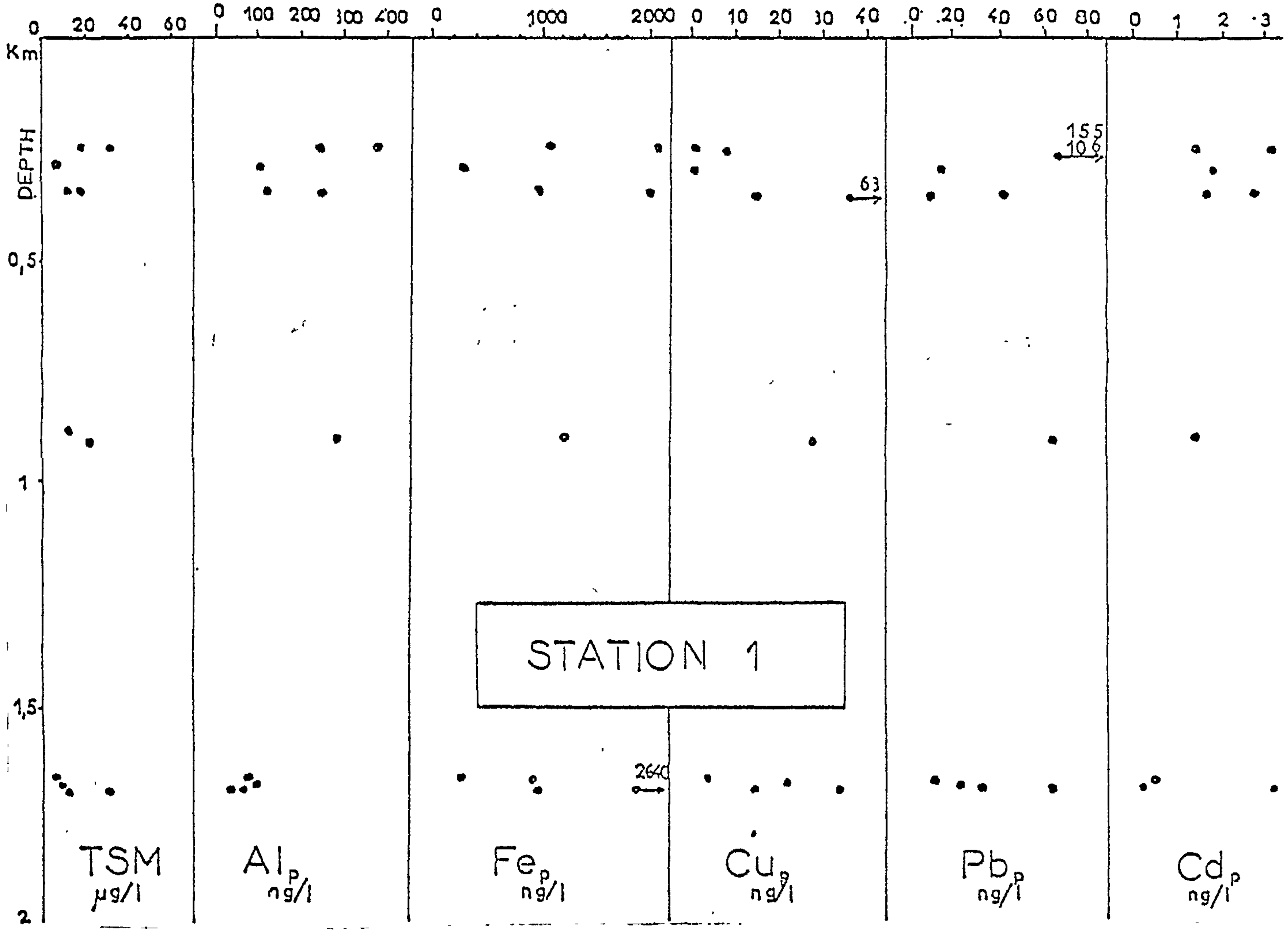


Fig. 1. Concentrations en fonction de la profondeur

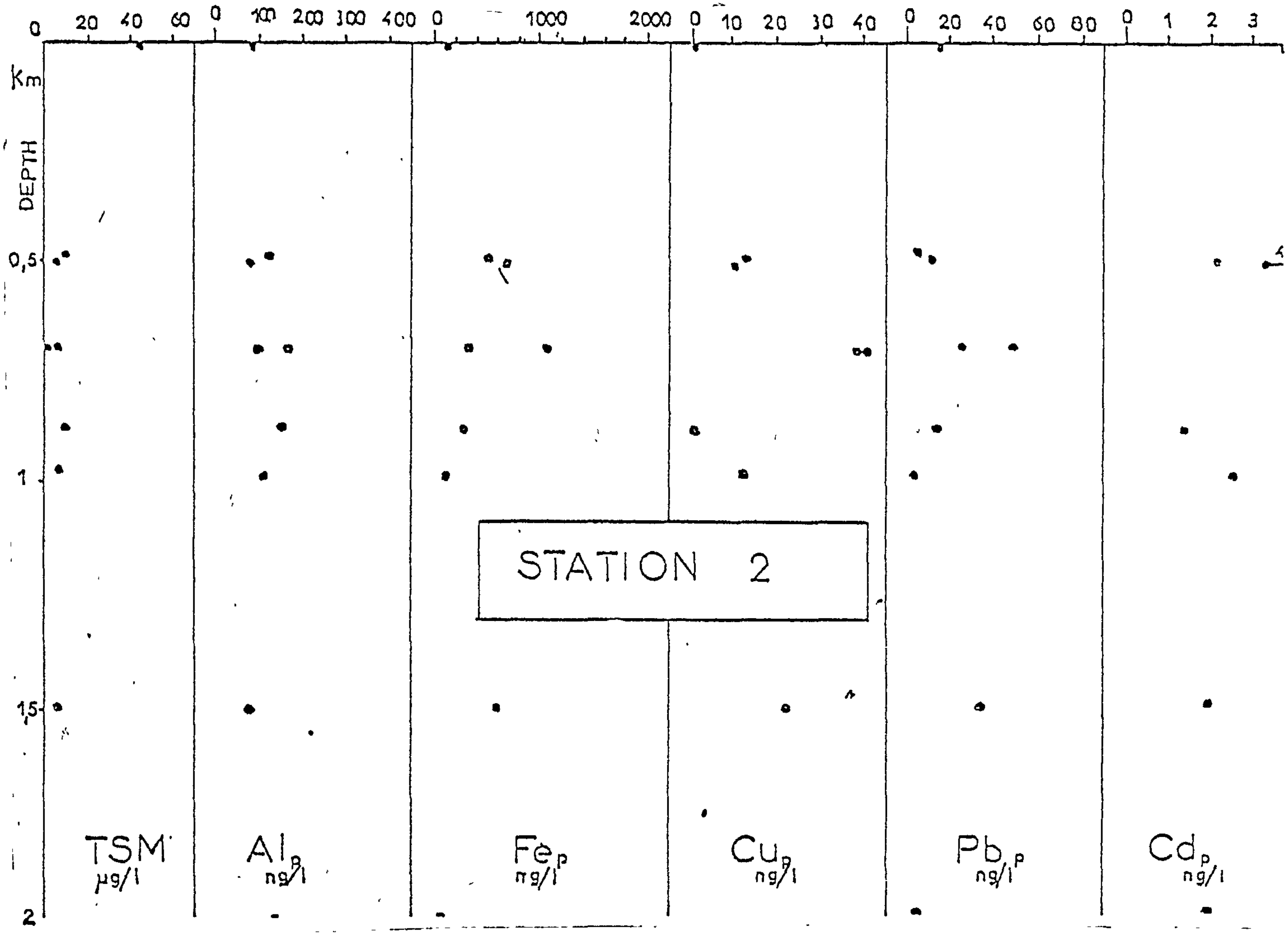


Fig. 2. Concentrations en fonction de la profondeur

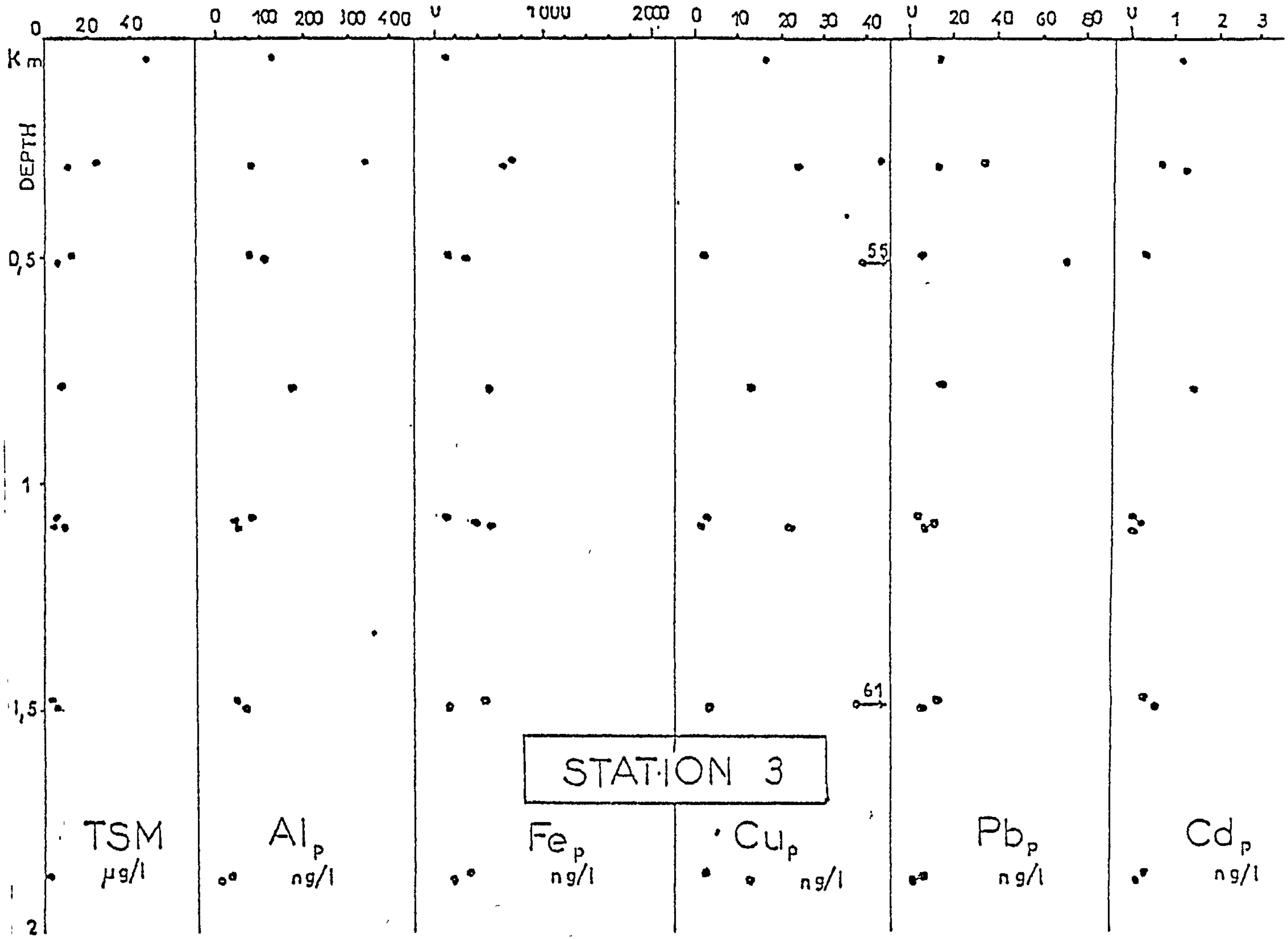


Fig. 3. Concentrations en fonction de la profondeur

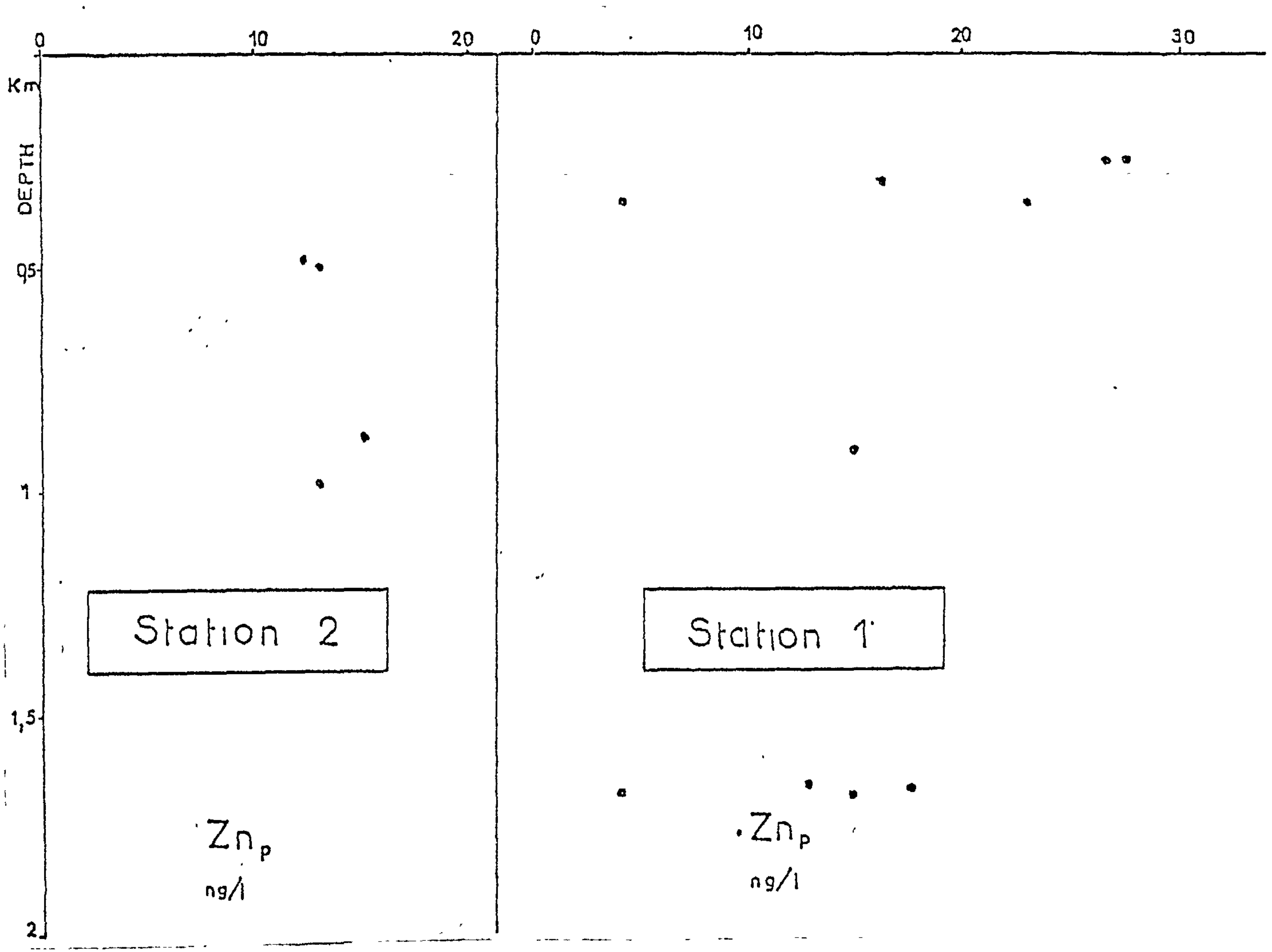


Fig. 4. Concentrations en fonction de la profondeur

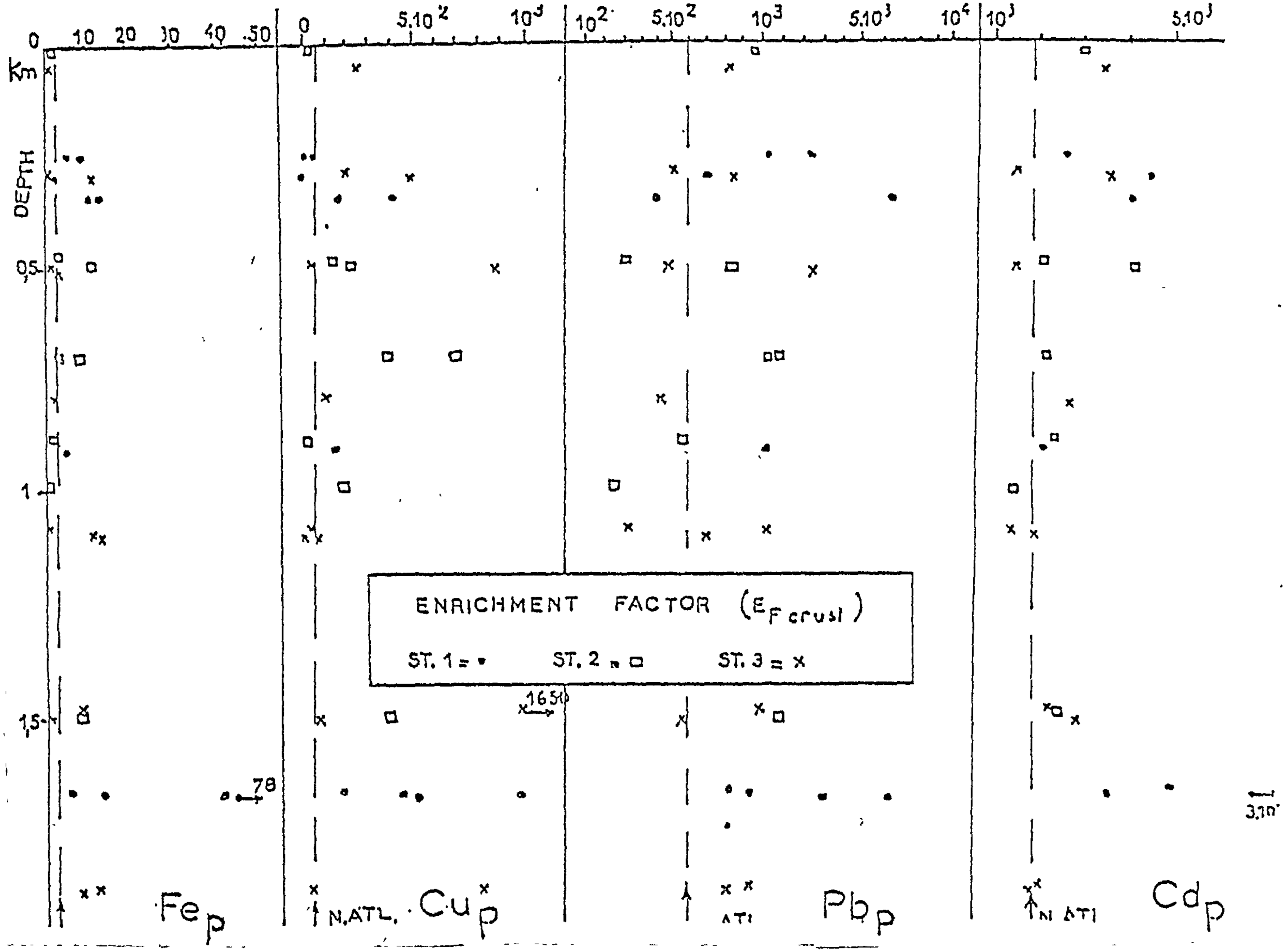


Fig. 5. Facteurs d'enrichissement

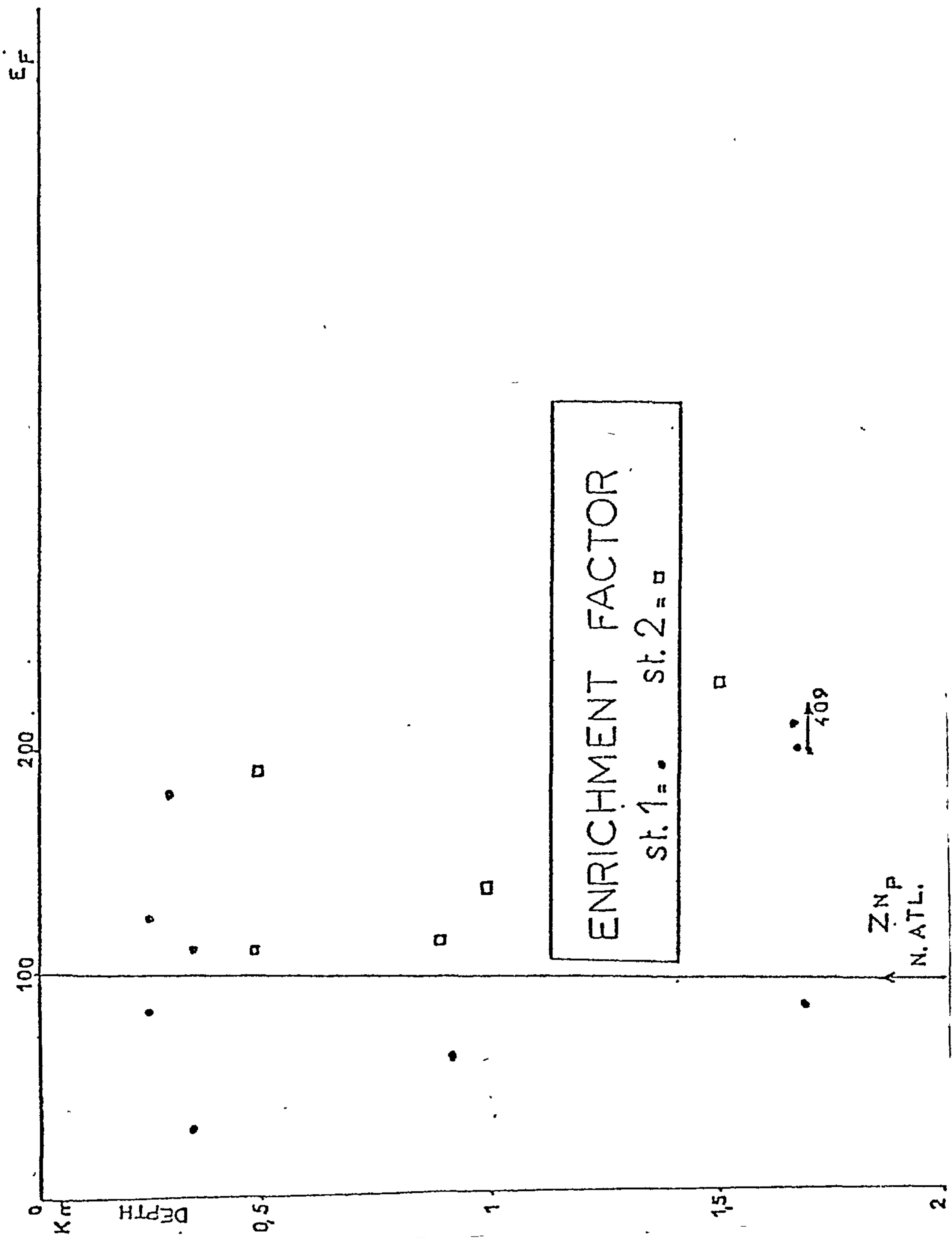


Fig. 6. Facteurs d'enrichissement

Participating Research Centres

Nuclear Research Center "Demokritos"
Department of Chemistry
Nuclear and Radiochemical Analysis
Laboratory
ATHENS
Greece

Principal Investigator: C. PAPADOPOULOU

Introduction:

In our laboratory studies of trace elements in the marine environment have been initiated in 1963. Since then 20 papers have been published on this subject.

The project "Biogeochemical studies of selected pollutants in the open waters of the Mediterranean" had two aims:

(a) The determination of Vanadium, Arsenic and other trace elements which are potential pollutants in organisms of well defined foodchains in order to acquire information on present levels of these elements and their possible biomagnification through foodchains.

(b) The determination of trace elements in particulate products of zooplankton in order to estimate the role of pelagic organisms in vertical transport of these elements.

Area(s) studied:

Scomber japonicus colias specimens were collected from the area South of Andros island on 30 August 1977. Specimens of Trachurus mediterraneus were collected South of Karystos, Evia Island, on 22 August 1977 and Skiathos Island on 28 September 1977. Plankton samples were also collected from Skiathos Island simultaneously with the Trachurus m. specimens (see attached map).

All three areas are typically oligotrophic areas of the Aegean Sea with salinities ranging from about 37.4 / to 39.2 and temperatures from about 14.2°C to 25.6°C.

In order to compare the levels of trace elements in marine organisms, sampling was performed in two areas: the Aegean Sea, a relatively unproductive region of the Mediterranean and the more productive western Mediterranean.

Our laboratory has collaborated in this project with the International Laboratory of Marine Radioactivity in:

(a) Analyzing samples from the western Mediterranean. The following determinations have been performed: for Zn, Co, Cs, Se, Rb, 38 samples; for As 28; for V 44; for Ag 20; for Sc and Sb 11; for Cr 4 and for Fe 3. Dr. C. Papadopoulou and D. Zafiropoulos have also participated in the "Hayes" cruise from Piraeus to Corsica (June 1977).

(b) Sampling and analyzing plankton and fish fron the Aegean Sea. The pelagic foodchain: plankton collected with nets of different mesh size, and the pelagic fish Trachurus mediterraneus as well as Scomber japonicus colias were sampled and determination of As, V, Se, Co, Cs, Zn and Rb was performed.

Material and methods:

Neutron Activation Analysis was used for the determination of all trace elements studied.

Results and their interpretation:

Arsenic and Vanadium concentrations in the flesh and liver of Trachurus m. are shown in table 1. Arsenic values in the flesh of Trachurus m. ranged from 3.9 to 9.2 µg/g whereas a composite liver sample was found to have 14.1 µg/g. There is a considerable variation (standard deviation 30 per cent) of As concentrations due to individual differences between specimens. Arsenic concentrations are higher in fish collected from Skiathos Island (74 µg/g) than in fish collected from Karystos (3.5 µg/g).

Vanadium concentrations in the flesh of Trachurus m. ranged from 0.071 to 0.15 µg/g. Individual variation is also considerable (28 per cent S.D.). Concentrations of As and V in the flesh and liver of Scomber j.c. are shown in table 2. Mean As values are 8 and 15 ug/g in the flesh and liver of Scomber j.c. respectively. Individual variation is somewhat lower (25 per cent S.D.).

Vanadium mean values are 0.014 and 0.024 µg/g in the flesh and liver of Scomber j.c. respectively. Individual variation is quite high (47 per cent S.D.). Concentrations of Zinc, Co, Se, Cs and Rb in the flesh and liver of Trachurus m. are shown in table 3. Mean values for the flesh of Skiathos specimens are: Zn 19 µg/g, Co 0.030 µg/g, Se 2.9 µg/g, Cs 0.067 µg/g and Rb 0.032 µg/g. For Karystos specimens mean values are : Zn 29 µg/g, Co 0.027 ug/g, Se 2.1 µg/g, Cs 0.027 µg/g and Rb 0.024 µg/g.

Zn and Co concentrations show a quite high individual variation (50 per cent S.D.) whereas Se, Cs and Rb show somewhat lower individual variation (25 per cent, 20 per cent and 16 per cent respectively).

Specimens caught from Karystos have similar concentrations of Co and Se, slightly higher concentrations of Zn and lower concentrations of Cs and Rb.

Table 4 shows concentrations of Zn, Co, Se, Cs and Rb in the flesh of Scomber j.c. Mean values are: Zn 24 µg/g, Co 0.027 µg/g, Se 3.0 µg/g, Cs 0.041 µg/g and Rb 0.23 µg/g. Individual variation for Zn and Co is 25 per cent S.D. for Se 27 per cent, Cs 12 per cent and Rb 35 per cent S.D.

Concentrations of As, Zn, Co, Se, Cs and Rb in the flesh of Scomber j.c. compare very well with those in Trachurus m. whereas V values for Trachurus m. are one order of magnitude higher than those of Scomber j.c.

Se and Cs concentrations in the liver of Scomber j.c. are comparable to those found in the liver of Trachurus m. whereas Zn and Co values are two times higher in Trachurus m. (table 5).

Rb values are higher for the liver of Trachurus m. than for liver of Scomber j.c. (mean of 3 specimens 0.19 µg/g).

As, Zn, Co and Se accumulates preferable in the liver of both fish species. Cs and Rb concentrations are about the same in flesh and liver.

Concentrations of As, Zn, Co, Se, Cs, Rb and V in plankton and Trachurus m. are shown in table 6.

Assuming that the plankton samples of different sizes and Trachurus m. represent different levels of a foodchain, no trend of "foodchain magnification" can be observed.

As, Zn, Cs and V concentrations decrease in higher food level, whereas Se concentrations are constant and Co shows no trend at all.

Conclusions:

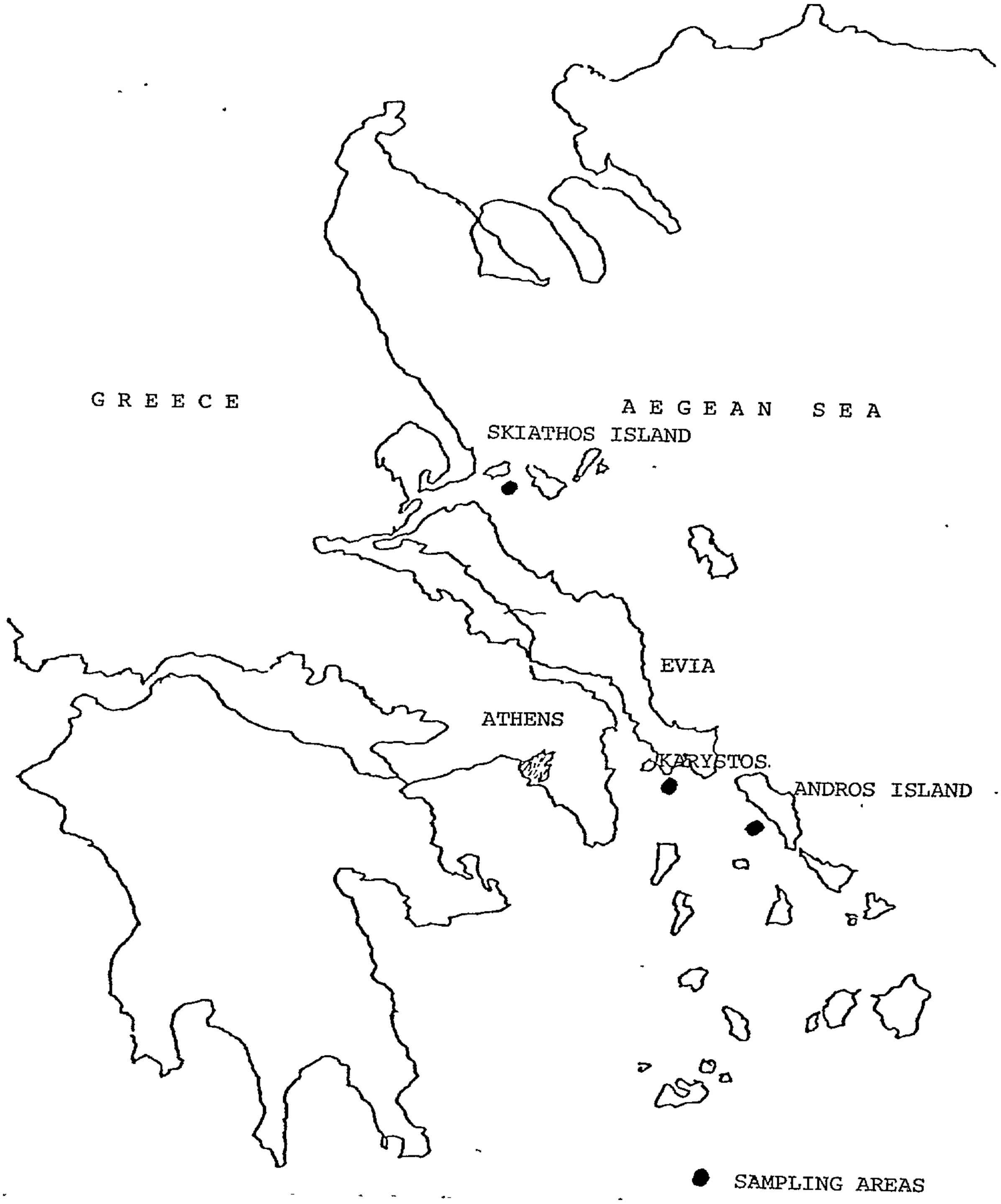
Arsenic concentrations found in Scomber j.c., and Trachurus m. are in relatively good agreement with those reported in Pagellus Erythrinus, Gobius niger and Sargus annularis from both polluted and non-polluted waters of the Aegean Sea.

Zn, Co, Se and Cs concentrations in the flesh and liver of the two fish studied are also in good agreement. Comparing values found in this study with values obtained from previous work of our Laboratory for Pagellus erythrinus, Sargus annularis, Gobius niger and Mullus barbatus, and taking into consideration the differences in ecology and feeding habits we can observe that differences in concentrations are relatively small.

Single specimen analysis is indispensable in trace element analysis of fish for a statistical treatment of results. Variations between specimens of the same species from the same station were found to range from 8 up to 50 per cent (standard deviation of the mean).

The absence of "foodchain magnification" is not surprising. In fact Zn shows a decrease of one order to magnitude and V an increase of two orders of magnitude with increasing food level. The hypothesis of foodchain magnification is based on the theory of foodchain. It is clear that defining a pelagic foodchain is very complex and difficult. Stomach analysis of the Trachurus m. specimens caught from Skiathos Island showed that their food consisted of gastripod, decapod and ostracod larvae and copepods. The presence of fish scales also indicated that Trachurus m. were also feeding on small clupeids.

To the best of our knowledge data concerning V concentrations in fish from the Aegean Sea were non-existent up to now. There is a need of a more extensive study of V levels in various fish species, and from different sea areas



Map. Sampling areas

TABLE 1

Arsenic and Vanadium concentrations in *Trachurus mediterraneus* (μg/g, dry)

SAMPLE	As(1)	V(2)
Skiathos Island (flesh)		
1	4.0	0.11 ±0.01
2	8.7	0.083±0.008
3	6.0	0.15 ±0.01
4	9.2	0.071±0.009
5	9.2	0.069±0.008
7	5.0	0.074±0.007
10	7.3	0.120±0.009
13	6.7	0.089±0.008
14	8.1	0.086±0.007
Mean	7±2	0.095±0.027
Liver	14.1(3)	-
Karystos		
1	3.9	-
2	3.1	-
3	3.6	-
Mean	3.5±0.4	-

(1) Analytical standard deviations for As are up to 10 per cent
(2) ± Overall standard error of the counting technique
(3) Composite from 14 specimens

TABLE 2

Arsenic and Vanadium concentrations in *Scomber japonicus colias* from Andros island (μg/g dry)

	As(1)		V(2)	
SAMPLE	Flesh	Liver	Flesh	Liver
5	4.4	15.1	-	-
6	6.4	14.3	<0.01	-
7	11.4	25.5	<0.007	-
8	6.8	14.3	0.014±0.006	-
9	-	-	0.011±0.006	-
24	9.2	15.0	0.018±0.005	0.020±0.002
26	-	-	0.013±0.005	-
27	9.6	13.5	-	-
28	8.8	13.6	<0.007	-
29	7.3	9.7	<0.008	-
30	9.7	13.2	-	0.028±0.008
Mean	8±2	15.±4	0.014±0.003	0.024

(1) Analytical standard deviations for As are up to 10 per cent

(2) ± Overall standard error of the counting technique

TABLE 3

Trace element concentrations in *Trachurus mediterraneus* (µg/g dry± standard deviation)

SAMPLE	Zn	Co	Se	Cs	Rb
Skiathos (flesh)					
1	20±0.8	0.030±0.003	1.8±0.1	0.066±0.066	0.35±0.07
2	25±0.9	0.026±0.002	4.2±0.2	0.077±0.005	0.28±0.05
3	27±1.0	0.042±0.003	2.2±0.1	0.019±0.005	0.34±0.06
4	42±1.5	0.037±0.003	3.8±0.2	0.073±0.006	0.25±0.06
5	22±0.8	0.019±0.002	2.8±0.1	0.081±0.005	0.29±0.04
6	23±0.9	0.020±0.002	3.5±0.2	0.086±0.006	0.37±0.05
7	20±0.7	0.022±0.002	2.6±0.1	0.066±0.004	0.33±0.04
8	9±1.5	0.024±0.002	2.7±0.1	0.060±0.004	0.26±0.03
9	5±1.4	0.031±0.002	3.1±0.1	0.069±0.004	0.38±0.04
10	10±1.7	0.028±0.002	2.5±0.1	0.071±0.004	0.26±0.03
11	11±2.0	0.024±0.002	2.0±0.1	0.057±0.004	0.32±0.04
12	14±2.1	0.056±0.003	2.5±0.1	0.066±0.004	0.40±0.05
13	20±2.1	0.069±0.003	3.3±0.1	0.061±0.004	0.35±0.04
14	16±2.0	0.040±0.002	2.4±0.1	0.042±0.003	0.35±0.03
Mean	19±9	0.030±0.014	2.9±0.7	0.067±0.012	0.39±0.05
Liver	154±5.0	0.75±0.03	35±1.3	0.048±0.003	0.38±0.08
Karystos (flesh)					
2	22±1.6	0.030±0.009	2.7±0.1	0.035±0.003	-
3	31±1.0	0.020±0.001	1.5±0.1	0.021±0.001	0.19±0.02
4	34±1.2	0.030±0.002	2.1±0.1	0.024±0.002	0.28±0.02
Mean	29±6	0.027±0.006	2.1±0.6	0.027±0.007	0.94±0.06

TABLE 4

Trace elements in the flesh of *Scober japonicus colias* from Andros (μg/g, dry± standard deviation)

SAMPLE	Zn	Co	Se	Cs	Rb
5	11±0.6	0.014±0.002	2.2±0.1	0.037±0.003	0.25±0.04
6	28±1.2	0.024±0.003	2.8±0.1	0.045±0.004	0.18±0.05
7	23±1.0	0.024±0.002	2.5±0.1	0.051±0.003	0.28±0.04
8	25±1.0	0.034±0.003	2.4±0.1	0.046±0.003	0.26±0.04
9	21±1.0	0.027±0.003	2.3±0.1	0.035±0.003	0.26±0.05
10	20±0.9	0.032±0.003	3.1±0.1	0.041±0.004	0.26±0.05
24	39±1.6	0.022±0.003	2.1±0.1	0.036±0.004	0.25±0.05
26	22±1.1	0.035±0.004	4.2±1.0	0.036±0.003	-
27	20±1.0	0.034±0.004	4.3±1.0	0.039±0.003	0.16±0.06
28	26±1.3	0.018±0.003	3.1±0.7	0.039±0.003	0.10±0.05
29	25±1.2	0.027±0.003	3.7±0.9	0.046±0.003	0.22±0.06
30	26±1.3	0.027±0.003	3.8±0.9	0.041±0.002	0.31±0.06
Mean	24±6	0.027±0.007	3.0±0.8	0.041±0.005	0.23±0.08

TABLE 5

Trace element concentrations in the liver of *Scober japonicus colias* from Andros (µg/g, dry± standard deviation)

SAMPLE	Zn	Co	Se	Cs
5	66±2	0.17±0.01	30±1.1	0.020±0.004
6	77±3	0.26±0.01	32±1.2	0.026±0.004
7	97±3	0.28±0.01	36±1.3	0.038±0.004
8	86±3	0.40±0.02	33±1.2	0.020±0.008
9	85±3	0.34±0.02	25±1.0	0.032±0.004
10	91±3	0.29±0.02	45±2.0	0.024±0.005
24	98±3	0.36±0.02	33±2.1	0.031±0.004
25	97±6	0.61±0.07	56±2.7	0.070±0.010
26	89±6	0.42±0.05	43±2.0	0.047±0.008
27	87±6	0.46±0.05	45±2.2	0.058±0.009
28	84±6	0.23±0.04	31±1.5	0.055±0.009
29	103±6	0.58±0.06	50±2.5	0.060±0.010
30	91±6	0.49±0.05	46±2.3	0.040±0.005
Mean	89±9.7	0.38±0.12	39±9	0.040±0.017

TABLE 6

Trace element concentrations in plankton and *Trachurus mediterraneus*
(μg/g, dry± standard deviation)

SAMPLE	As(2)	Zn	Co	Se	Cs	Rb	V(3)
60u net sample	18	-	-	-	-	-	-
250u net sample	18	162±5	0.060±0.002	2.0±0.3	0.99±0.035	0.32±0.08	11.1±0.4
600u net sample	7.7	119±4	0.36±0.014	2.2±0.3	0.37±0.013	-	4.6±0.2
Euphasia kronii	5.4	77±3	0.17±0.07	1.8±0.3	0.55±0.020	0.17±0.05	1.62±0.03
Trachurus m. (flesh)(1)	7±2	19±9	0.030±0.014	2.9±0.7	0.067±0.012	0.32±0.05	0.095±0.02

(1) For Zn, Co, Se, Cs and Rb mean of 14 specimens analyzed, for As and V mean of 9 specimens

(2) Analytical standard deviations for As are up to 10 per cent

(3) Overall standard error of the counting technique

Participating Research Centre:

Department of Physiology and
Biochemistry
The Old University
MSIDA
Malta

Principal Investigator:

J.V. BANNISTER

Area(s) studied:

Mullets of the species (Mugil cephalus) were obtained from the coast around Malta.

Material and methods:

Species of about 120 mm length were caught live by means of nets and were acclimated for two months in a large tank filled with continuously running sea water. The fish were fed pelleted food containing 80 per cent protein.

After the acclimation period species were placed in tanks contaminated with 0,5 ppb or 1.0 ppb chlorinated hydrocarbons. The contaminants used were DDT, Aldrin and PCB. The chlorinated hydrocarbons were obtained from Analabs Inc. Species were contaminated with either of these chlorinated hydrocarbons.

At the end of the contamination period, the contaminated mullets were disected and pooled samples of brain, kidney, eyes, heart, liver, gills, skin, stomach, red and white muscle were obtained. The deposition of chlorinated hydrocarbons in these tissues was estimated according to the following procedure.

The combined organs were weighed and homogenised in a 10 per cent mixture of petroleum ether with a Kolbe homogeniser. The petroleum ether solution was concentrated to 20 ml by rotary evaporation. This solution was extracted thrice with 10 ml acetonitrille previously saturated with hexane. The three fractions of acetonitrile extracts were combined and diluted with 250 ml of 10 per cent sodium chloride solution previously depleted of any contaminants with hexane. The aqueous acetonitrile solution was extracted thrice with 50 ml of n-hexane. The three fractions were combined and concentrated by rotary evaporation (temperature 50°C) up to 5-10 ml and Na_2SD_4 solid added. The solution was now ready for Florisil treatment. The purification for elusion was done on a small column, filled with dried Florisil activated at 130°C overnight (Dimensions of the column = internal diameter 8 mm filled up to 5-7 cm, elutant n-hexane 20-25 ml). The solution was concentrated to 2-3 ml.

The separation of PCB from other chlorinated hydrocarbons was carried out put on silica gel. The silica gel is heated to 200°C overnight. The internal column diameter is 10 mm, and the column was filled up to 20 cm. After having introduced the concentrated solution, the PCB is first eluted with 40-50 ml of n-hexane. DDT and the other hydrocarbons were afterwards collected with 40-50 ml of benzene. The hexane and benzene solutions were concentrated to a constant volume (2-5 ml) for analysis.

Results and their interpretation.

Pesticide levels are to be measured by an instrument which detects both changed and unchanged pesticides. Yet since this apparatus was out of order during the period of analysis, samples are to be analyzed as soon as this instrument is serviced.

Currently under investigation is the clearance rate of chlorinated hydrocarbons by mullets. Preparations are also in hand so that similar experiments to those being carried out on mullets can be started on the mussels (*Mytilus galloprovincialis*).

Participating Research Centre:	International Laboratory of Marine Radioactivity - IAEA MONACO VILLE Monaco
Principle Investigators:	D. ELDER - S.W. FOWLER - R. FUKAI

Introduction

The overall philosophy of MED VIII has been twofold. First, to gather as much information as possible on inputs, levels and fluxes of pollutants in all major components of the open Mediterranean in order that a general model of the biogeochemical cycles of these substances can be elaborated. Second, these data are intended to supplement and enhance those presently being gathered on levels in selected marine species in the coastal areas.

The marine biogeochemical cycle of a given pollutant can be conceptualized as outlined diagramatically in figure 1.

The approach used in MED VIII has been to measure a suite of heavy metals and organochlorine compounds in the prime components shown in figure 1.

Baseline measurements were made on samples collected during five oceanographic cruises during the period 1977-1979. In addition, determination of trace elements in marine aerosols and particulate matter in sea water were carried out by the Centre des Faibles Radioactivités, CNRS, France.

The biokinetic behaviour of arsenic, vanadium, nickel and PCBs in various marine organisms was examined in order to gain information on the fluxes of these substances once they enter biological cycles.

Vertical flux studies of pollutants were undertaken by utilizing both in situ measurements and analyses of freshly-produced biogenic particulates which account for a large fraction of the particulates trapped at depth using sediment traps.

Heavy metals in sea water and sediments

The results of the measurements of heavy metals on open Mediterranean surface waters are summarized in table 1.

Since far more than half of the samples were below the detection limit for Cu measurements and approximately half of those were below the detection limit for Cd measurements, the average values for these metals represent only the upper limits of the average concentrations. In these cases comparisons between different zones in the Mediterranean are less meaningful. However, the grand averages for the Mediterranean of these metals, < 0.33 µg/l for Cu and < 0.13 µg/l for Cd, appear to be similar to the values given for oceanic waters by other investigators in this field. There was no correlation between the appearance of high Cu values and high Cd values.

The average concentration of Zn tends to differ from one zone to another; values are higher in the northwestern Mediterranean and Aegean basins and lower in the Tyrrhenian and south Levantine basins, despite the large associated uncertainties. The grand average for the Mediterranean of Zn tends to be lower than the values given in the reference cited above.

The zonal differences in the distribution of Hg are not clear from the average concentrations presented in table 1 due to large associated uncertainties. It appears, however, that average concentrations are lower in the southwestern Mediterranean and south Levantine basins. The grand average of Hg is lower than the values given in some references for the Atlantic and Pacific by various investigators, but similar to or slightly higher than those given by others. Our values are definitely higher than those reported for the western Pacific by investigators in Japan.

The vertical distribution of selected trace metals in off-shore sediments was studied in two core samples taken in 1978 from 500 m and 1000 m depth off Villefranche. Selected trace metals such as Mn, Cu, Zn, Pb, etc. were measured in several vertical sections of each core. For the Pb measurements various pretreatment procedures were applied to differentiate between the different chemical forms of Pb so that total organic Pb, alkyl Pb, etc. could be distinguished. The vertical distribution of these different chemical forms of Pb within the cores indicates that Pb in the upper parts of the sediment cores is introduced anthropologically (the Pb concentration decreases from the surface of the sediments to 6-8 cm depths for both sediment cores and the concentration of Pb at the surface in the 500 m core is higher than that in the upper 1000 m core. Considering the sedimentation rate in the area of study and the vertical distribution of Pb within the sediments there appears to be a downward migration of certain forms of Pb in the sediments.

Trace elements in biota

During the period 1975-1977 pelagic organisms ranging in size from plankton to tuna were sampled throughout the Mediterranean and analyzed for selected heavy metals. Large zooplankton and small nekton from both western and eastern basins were sorted according to individual species thus allowing realistic comparisons to be made between levels in similar species inhabiting different areas. One example is given in table 2 which shows the levels of several metals in euphausiid zooplankton from four regions of the Mediterranean. In general, although occasional high concentrations were noted, the levels encountered in the majority of the organisms were not too unlike those reported for pelagic species from other oceanic regions.

Chlorinated hydrocarbons in biota

Pelagic species from the central and western basins of the Mediterranean Sea were surveyed for PCBs and DDT. Residue levels in mixed microplankton from two cruises, which traversed the same general region of the eastern Mediterranean, show some clear differences. PCBs were significantly higher in samples from St. 3a and 6a taken aboard the Atlantis II (table 3). A careful examination of possible sources of contamination suggested that the observed differences may be real.

The ranges of residue concentrations in euphausiids (9.8 to 110 ppb dry for PCB and 2.5 to 115 ppb for DDT) were similar to those measured in mixed plankton. Euphausiids from the eastern basin had higher DDT/PCB ratios than those of the central region. This is due to a greater relative decrease in DDT levels compared to PCB concentrations in going from the central to the eastern region. A pelagic tunicate, P. atlanticum, sampled at one station in the Ionian Sea contained far less PCB and DDT than similar sized individuals from the Levantine basin. Different sized mesopelagic fish, M. glaciale, sampled from a single population, displayed a trend towards increasing DDT/PCB and DDE/PCB ratios with increasing size of fish. Finally, the relatively high levels of chlorinated hydrocarbons (PCB = 660 ppb; DDT = 127 PPB) found in the amphipod Anchylomera blossevillei, may be typical for this group of organisms.

Tuna muscle contained concentrations of PCB and DDT ranging from 8 to 90 ng/g dry and 2.4 to 50 ng/g dry, respectively. Gut contents, which were primarily composed of euphausiids, contained levels (PCB = 67 - 383 ng/g; DDT = 57 - 198 ng/g) which corresponded to those in tuna muscle.

Levels of organochlorine compounds in selected macrozooplankton and nekton as well as mixed microzooplankton have been compared with those in similar species from other oceanic areas. Although the data are sparse, PCBs in macrozooplankton and nekton do not appear to differ significantly from concentrations in similar species measured elsewhere. In the case of microzooplankton there was a trend towards slightly lower values in these organisms.

Vertical flux of trace metals and chlorinated hydrocarbons

Samples of sedimenting particles were collected off the coast by means of sediment traps. Examination of the material showed that zooplankton faecal pellets comprised a relatively large fraction of the total sample. Fluxes of these particulates ranged from 0.40 to 0.77 g $m^{-2}d^{-1}$ over a four-month period. Levels of heavy metals (cd, Cu, Zn, Fe and Mn) in biogenic particulates were high and compared favourably with concentrations of the same elements in freshly-produced biogenic detritus collected immediately over the traps. Clearly, sinking biogenic debris will be instrumental in effecting the downward vertical transport of these metals in certain areas of the Mediterranean.

The same samples discussed above were analysed for chlorinated hydrocarbons. Table 4 shows that PCB levels were relatively high in the sinking particulates with flux averaging about 100 ug PCB $m^{-2}y^{-1}$ in this area. These measurements compare very well with independent estimates of the same order made by measuring PCBs in sections of sediment cores taken from the same region. These studies underscore the importance of sinking biogenic particulate matter in removing PCBs from the upper layers of the water column and transporting them to depth.

Biokinetic studies

The behavious and fate of arsenic and vanadium in Mediterranean species was examined in controlled laboratory experiments utilizing radiotracers and stable element techniques. Over a concentration range from approximately 2 to 100 g/l arsenic uptake in the Mediterranean mussel (Mytilus galloprovincialis) and shrimp (Lysmata seticaudata) was dependent upon the arsenic concetration in sea water. Most of the arsenic accumulated was in muscle tissue, and it was taken up by mussels more rapidly at higher temperatures. The increased rate of molting at higher temperature made a temperature effect study difficult. Arsenic uptake was inversely related to salinity in both species and As concentrations on a whole-body weight were higher in smaller than in larger individuals.

Preliminary studies with phytoplankton show that arsenate is rapidly metabolized to a lipid extractable form. Using Dunaliella as the primary producer in a three component food chain it was shown that this lipid soluble arsenic is transferred efficiently to a herbivore (Artemia salina), and subsequently to a carnivorous shrimp. It also appears that Artemia and *shrimp cannot mobilize inorganic arsenic into the lipid fraction;* arsenate absorbed directly from sea water by these organisms is converted largely to arsenite.

Vanadium-48 and stable vanadium were used to study the uptake from water and elimination of vanadium in four benthic invertebrates - mussels, shrimp and crabs. The highest concentration factor (=30) was noted in mussels after three weeks' exposure. Over a concetration range from approximately 2 to 100 µg V/l, uptake in mussels and shrimp was dependent upon the vanadium concentration in sea water. Uptake in mussels and shrimp appeared to be independent of temperature over a range of 13°C to 24°C but was slightly increased at low salinity ($19^{o}/oo$). Vanadium behaves differently from arsenic in that the majority of vanadium ($>$90%) becomes fixed to shells of mussels and crustaceans suggesting that surface absorption plays a strong role in the bioaccumulation of this element. Both radiotracer experiments and stable element data showed that byssus threads of mussels rapidly accumulated vanadium to high levels. Because of the remarkable ability of byssal threads to take up this element, some consideration might be given to using this tissue as a biological monitor for measuring changes in vanadium levels in the natural environment.

Chlorinated hydrocarbon biocycling

Several different experiments were designed to assess the bioaccummulation potential, tissue distribution and depuration of PCB available from water, food and sediments. In order to test the bioavailability of sediment-bound PCB, comparisons were made of the accumulation of a mixture from sediments and from water by benthic worms. Uptake from sediments was dose-dependent, attaining equilibrium concentration factors of approximately 3 to 4 after two months. Susequent PCB elimination rates were concentration-dependent, with higher initial loss rates evident in the worms containing higher levers of PCBs. Accummulation of PCBs from water was much more rapid; concentration factors reached approximately 800 after only two weeks. Estimates were made of the relative importance of sediments and water as a source of PCBs to worms exposed to these contaminants in the natural environment. Calculations based on experimentally derived PCB concentration factors and ambient PCB levels in sediments and water suggest that compared to water, sediments contribute the bulk of these compounds to the worms.

The influence of uptake pathway on PCB accumulation and tissue distribution was examined by allowing shrimp to accumulate DP-5 from either food or sea water and analysing their tissues during a period of one month. Regardless of the uptake pathway the relative tissue distribution was similar. The viscera which includes the hepatopancreas reached the highest levels. Concentrations of PCB in viscera were over an order of magnitude higher than those in exoskeleton and muscle suggesting that surface sorption plays a minor role in the accumulation of PCB from water by shrimp. Despite the fact that PCBs were rapidly absorbed into internal tissues, molted exoskeletons contained significant amounts of these compounds. Concentration factors in molts as high as 10^3 to 10^4 clearly illustrate the importance of crustacean molting as a process for redistributing PCBs in the marine environment. These experiments demonstrate the ease with which PCBs are transferred from the environment to benthic shrimp.

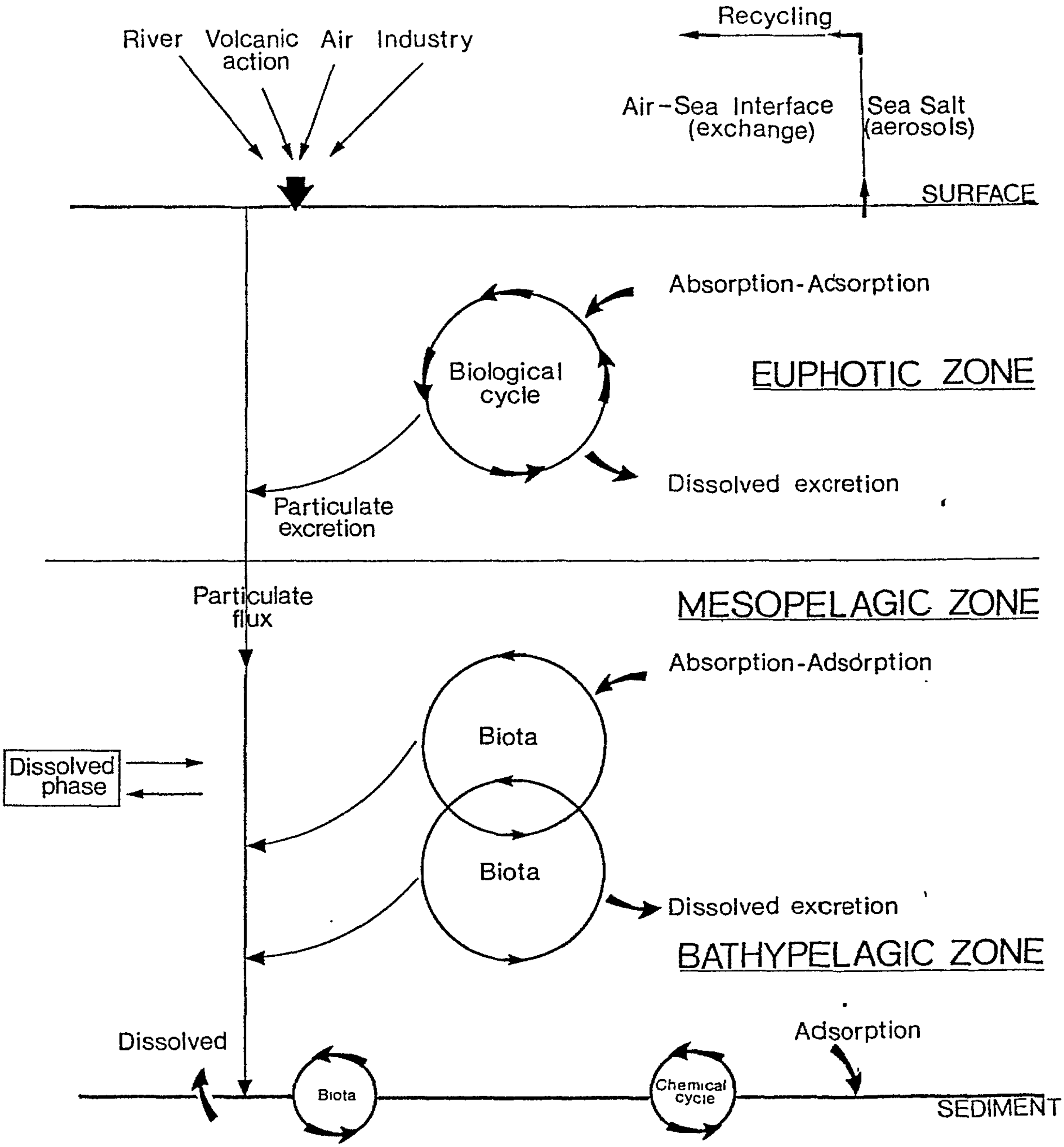


Fig. 1. Conceptual scheme of the marine biogeochemical cycle of a given pollutant

Table 1. Average concentrations of copper, zinc, cadmium and mercury in various zones of the Mediterranean sea

	Zone	n*	Cu µg/l**	n*	Zn µg/l**	n*	Cd µg/l**	n*	Hg ng/l**
II	N.W. Med.	34	<0.4±0.2 (<0.04-5.8)	34	2.7±0.4 (0.02-10)	33	<0.15±0.03 (<0.02-0.70)	7	20± 3 (8-32)
III	S.W. Med.	13	<0.10±0.04 (<0.04-0.60)	13	1.2±0.5 (0.02-6.0)	13	<0.11±0.04 (<0.02-0.51)	14	14±2 (5 - 30)
IV	Tyrrhenian	9	<0.18±0.08 (<0.04-0.62)	9	0.9±0.3 (0.02-2.3)	9	<0.11±0.04 (<0.02-0.33)	10	26±4 (10 - 40)
VI-VII	Ionian-Central	6	< 0.7±0.4 (<0.04-2.5)	6	1.8±0.9 (0.02-5.7)	6	<0.15±0.09 (<0.02-0.57)	6	30±10 (5 - 80).
VIII	Aegean	4	<0.3±0.1 (<0.04-0.64)	4	3 ± 1 (0.9-5.8)	4	<0.07±0.02 (<0.02-0.12)	3	40±20 (15-80)
X	S.Levantin	4	<0.04±0.01 (<0.04)	4	0.9±0.2 (0.3-1.3)	4	<0.04±0.03 (<0.02-0.11)	4	16 + 2 (12-20)
	Grand average	70	<0.33±0.09 (<0.04-5.8)	70	2.0±0.2 (0.02-10)	69	<0.13±0.02 (<0.02-0.70)	44	22±3 (5-80)

*n = No. of samples measured

** = Uncertainties are expressed in terms of standard errors. Ranges are given in brackets

<u>Table 2.</u> Trace metals in euphausiids (*Euphausia* sp.) from the open Mediterranean Sea. Values in parentheses represent samples of *Meganyctiphanes norvegica*.

Region	Station	Range of size (cm)	µg/g dry As	V	Zn	Co	Cs	Ag	Se	Sb	Rb	Sc	Fe	Hg*
Eastern	A-3a		49.9	<0.06	58	0.29	0.18	2.7	7.2	0.050	0.11	0.005	150	
	A-6a		33.8	0.24	107	0.24	0.23		4.6		0.31			
	S-2		38.7		100	0.15	0.60		4.0		0.25			
	S-3		38.4		123	0.15	0.43		4.2		0.65			
	S-4		47.2	0.84	140	0.26	0.16	0.92	2.3	0.046	0.08	0.040	80	0.028
Ionian Sea	H-4(≈1)			0.37										
	H-4(1.5-2)													0.148
	H-14(≈ 1)		56.9		84	0.15	0.12		3.6		0.32			0.100
	H-14(1.5-2)													0.192
	H-14			(<0.07)	(39)	(0.06)	(0.06)	(0.16)	(2.9)		(0.27)			(0.092)
Tyrrhenian Sea	H-23(≈1)		20.0	0.48	120	0.23	0.29	2.3	2.9	0.031	0.17	0.038	191	0.076
	H-23(1.5-2)													0.178
	H-37(>2)		34.9	1.24	57	0.19	0.26	1.7	3.5	0.040	0.11	0.013		0.239
	H-37			(1.10)	(144)	(0.25)	(0.08)		(3.3)		(0.38)			
Northwestern	CS-46		29.6	0.23	39	0.23	0.33	1.2	3.4	0.050	0.11	0.070		0.189

* analyzed by AAS

Table 3. Chlorinated hydrocarbon residues in microplankton collected in the eastern Mediterranean during two cruises in 1977

		μg/Kg dry*				
Cruise	Station†	PCB (DP-5)	pp'DDT	pp'DDD	pp'DDE	$\frac{\Sigma DDT}{PCB}$
Atlantis II (4/77)	1	30	7.1	2.4	2.7	0.40
	3a	100	8.7	1.1	3.6	0.13
	6a	230	20	3.1	8.9	0.14
Shikmona (7/77)	1	35	6.9	12	13.6	0.92
	2	19	17	58	9.9	4.57
	3	22	9.4	2.7	2.5	0.66
	4	15	6.2	6.2	6.8	1.25

\+ Stations refer to those in Fig. 1

* Dry weight averaged 11% of wet weight

Table 4. Estimates of PCB flux in the Ligurian sea

Date	Particulate PCB μg/Kg dry	Mass Flux $g\ m^{-2}d^{-1}$	PCB Flux $\mu g\ m^{-2}y^{-1}$
6/78	650	0.77	183
7/78	300	0.64	70
8/78	710	0.40	104
10/78	200	0.77	56
		$\bar{X}$ =	103

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Scientific results

The aim of the present project was the establishment of the biokinetical uptake of V and Ni by marine organisms.

Preliminary considerations resulted in the selection of Pseudomonas sp. as representative for typical marine bacteria, *Dunaliella* sp. for phytoplankton, *Mytilus edulis* for invertebrates, *Penaeus kerathurus* for crustacea and *Solea solea* for fish.

The primary sources of V and Ni for *Pseudomonas* and *Dunaliella* were appropriate culture mediums enriched with solutions of one or both elements.

An outstanding and most interesting part of the experiment was the reproduction of a natural trophic chain:

bacteria mussels fish
crustaces

The transfer of V and Ni from bacteria to mussels was performed by means of previously contaminated bacteria and phytoplankton. The resulting concentration factors for a 15 days- cultrue-time were the following:

Pseudomonas	*Dunaliella*
cf V = 0.5	cf V = 2.9
cf Ni= 6.0	cf Ni = 12.5

Pseudomonas were able to develop in cultures containing very high concentrations of V (50 ppm) and Ni (10 ppm) whereas inhibitory effects were detected for *Dunaliella* at 50 ppm of V and 2.5 ppm of Ni.

The concentration factor in the secondary trophic transfer (*Pseudomonas* to *Mytillus edulis*) was very low for a feeding time of 1 day; namely:

cf V = 0.08
cf Ni = 0.21

The concentration factor in the terciary trophic transfer (*Mytilus edulis* to *Penaeus Kerathurus* and *Solea solea*) was even lower than the secondary one for a feeding time of 19 days:

Mytilus edulis to *Solea solea*

cf V muscular tissues = 0.001
cf V liver = 0.012

Mytilus edulis to *Penaeus Kerathurus*

cf V mixed soft tissues = 0.004

More interesting results were gathered by direct V and Ni contamination of mussels; i.e. using POLIKARPOV'S terminology, " direct absorption" from the water. In fact, the concentration factors resulting from severe experimental conditions were very high (table 1).

TABLE 1

V Enriched sea water (ppm)	Time (days)	Mean V content of mussels (ppm)	Cf
10	1	8	0.8
10	2	20	2.0
50	1	9	0.2
50	2	24	0.5
100	1	269	2.7
100	2	357	3.6

The results shown in table 1 seem to demonstrate the existence of a critical concentration in the enriched sea water culture between 50 and 100 ppm of V.

The sudden increase from 0.20 - 0.47 (at 50 ppm) to 2.69 - 3.57 (at 100 ppm) allows us to introduce the above mentioned hypothesis. In order to gain further knowledge on the "critical concentration" and its determination, a new series of experiments were conducted. Their results are shown in table 2.

TABLE 2

V Enriched sea water (ppm)	Time (days)	Mean V content of mussels (ppm)	Cf
50	1	16	0.3
60	1	23	0.4
70	2	142	1.0
80	1	76	0.9
90	1	250	2.8
100	1	650	6.5

Direct absorption of Ni

A series of observations in mussel cultures (*Mytilus edulis*) containing 1,2,5,10 and 100 ppm of Ni were conducted in a similar way as for the determination of V direct absorption pathway. After 4 days the level of incorporated Ni was that shown in table 3.

TABLE 3

Ni concentration in enriched s/w culture (ppm)	Time (days)	Ni concentration in soft tissues of mussels (w/w)	Cf
1	4	6	6
2	4	9	9
5	4	14	3
10	4	34	3
100	4	52	1

Somewhat contrary to the observations made in the V experiment, the Cf of a culture containing 150 ppm of Ni (0.5) is of the order of one tenth lower than in cultures containing 0 to 1 ppm Ni (mean value of 4.3)

The meaning of this difference is not clear yet, nevertheless some physiological implications must be assumed; namely that the V cultures are more toxic at a 100 ppm level (excretion mechanisms excluded). In order to know the V concentration in natural systems, two species of sea fish (Mullus barbatus and Pagellus erythrinus) and sediments were collected and analyzed. Analytical values and cf's are shown in table 5.

TABLE 5

V in organism	V in sea water (g/l)	V in dorsal muscle	Cf
Mullus barbatus	0.7×10^{-6}	0.02 ppm	30
Pagellus erythrinus	0.7×10^{-6}	0.05 ppm	70
Sediments	0.7×10^{-6}	28.00 ppm	3.8×10^{4}

We want to point out that the V content of Mullus barbatus is conspicuous, a benthic organism feeding in high V contaming sediments is lower than in Pagellus erythrinus.

Though we agree that this experiment is not absolutely complete (effects of the variability under experimental conditions were not considered), the results seem to be consistent since the mean cf/day for 50 ppm V in the first experimental series was 0.33 and 0.32 in the second one; between 60 and 70 ppm V results in a cf increase by a factor of three (0.32 to 1.0); at 80 and 90 ppm V the cf increases abruptly (0.95 to 2.80) and; between 90 and 100 ppm V the cf increases further (2.80 to 6.50).

Up to now we lack evidence about how physiological changes (including deteriorated excretion mechanisms) can affect the equilibrium factors of organism absorption and V culture content - when V concentrations exceed certain levels.

Ni uptake from Ni enriched sea water by bacteria and microalgae

As for Vanadium, we checked the biokinetics of Ni uptake through trophic and direct absorption pathways.

Experiments were performed using Ni enriched sea water and selected organisms. Pseudomonas sp and Dunaliella sp were chosen as representive of bacterial and phytoplanktonic populations respectively.

Preliminary experiments showed that the minimum inhibitory levels of Ni for both organisms were: 100 ppm for Pseudomonas and 2.5 ppm for Dunaliella. The concentration factors for a feeding time of 20 days were 6 and 12.5 respectibility. Table 4 summarizes experimental conditions and results.

TABLE 4

Organism	Ni concentration s/n enriched culture (ppm)	Time (days)	Ni concentration in organisms	Cf (20 days)
Pseudomonas ps	5	20	30	6
Dunaliella	1	20	12	12

Discussion

Our results are in agreement with Polikarpov's statement that the majority of marine organisms concentrate more radionuclides (and that includes trace metals) by direct absorption from the water rather than by feeding. In consequence our results suggest that food chain transfer may be disregarded - in general - as the main factor in bioaccumulation and transfer of vanadium.

The rapid enrichment of vanadium observed in mussel shells over soft parts may be explained by invoking two different pathways in the incorporation of vanadium: 1) by biochemical mechanisms for soft tissues; 2) by physiochemical processes involving, perhaps, calcium carbonate as the prime matrix for concentration.

The analysis of two species of marine fishes show only moderate levels of vanadium in their tissues even though they live in sediments containing high levels of vanadium. This is to be expected if - as stated before - food chain transfer of vanadium is negligible in marine organisms.

Finally, it is noteworthy that the results from this preliminary study have encouraged us to continue both systematic environmental sampling and laboratory experiments which should help clarify the mechanisms involved in the direct absorption of Vanadium and Nickel from water.

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