MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

WORLD METEOROLOGICAL ORGANIZATION

AIRBORNE POLLUTION OF THE MEDITERRANEAN SEA.

REPORT AND PROCEEDINGS OF A WMO/UNEP WORKSHOP

POLLUTION PAR VOIE ATMOSPHERIQUE DE LA MER MEDITERRANEE.

RAPPORT ET ACTES DES JOURNEES D'ETUDE OMM/PNUE

MAP Technical Reports Series No 31

UNEP
Athens, 1989

For bibliographic purposes this volume may be cited as:

UNEP/WMO: Airborne Pollution of the Mediterranean Sea. Report and Proceedings of a WMO/UNEP Workshop. MAP Technical Reports Series No. 31. UNEP, Athens, 1989.

Pour des fins bibliographiques, citer le présent volume comme suit:

PNUE/OMM: Pollution par voie atmosphérique de la mer Méditerranée. Rapport et actes des Journées d'étude OMM/PNUE. MAP Technical Reports Series No. 31. UNEP, Athens, 1989.

This volume is the thirty-first issue of the Mediterranean Action Plan Technical Report Series.

This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Oil Combating Centre.

Ce volume constitue le trente et unième numéro de la série des Rapports techniques du Plan d'action pour la Méditerranée.

Cette série comprend certains rapports élaborés au cours de diverses activités menées dans le cadre des composantes du Plan d'action pour la Méditerranée: 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.

GENERAL INTRODUCTION

The United Nations Environment Programme (UNEP) convened an Intergovernmental Meeting on the Protection of the Mediterranean (Barcelona), 28 January - 4 February 1975), which was attended by representatives of 16 States bordering on the Mediterranean Sea. The meeting discussed the various measures necessary for the prevention and control of pollution of the Mediterranean Sea, and concluded by adopting an Action Plan consisting of three substantive components:

- Integrated planning of the development and management of the resources of the Mediterranean Basin (management component);
- Co-ordinated programme for research, monitoring and exchange of information and assessment of the state of pollution and of protection measures (assessment component);
- Framework convention and related protocols with their technical annexes for the protection of the Mediterranean environment (legal component).

All components of the Action Plan are interdependent and provide a framework for comprehensive action to promote both the protection and the continued development of the Mediterranean ecoregion. No component is an end in itself. The Action Plan is intended to assist the Mediterranean Governments in formulating their national policies related to the continuous development and protection of the Mediterranean area and to improve their ability to identify various options for alternative patterns of development and to make choices and appropriate allocations of resources.

MED POL - Phase I (1976-1980)

The Co-ordinated Mediterranean Research and Monitoring Programme (MED POL) was approved as the assessment (scientific/technical component of the Action Plan.

The general objectives of its pilot phase (MED POL - Phase I), which evolved through a series of expert and intergovernmental meetings, were:

- to formulate and carry out a co-ordinated pollution monitoring and research programme taking into account the goals of the Mediterranean Action Plan and the capabilities of the Mediterranean research centres to participate in it;
- to assist national research centres in developing their capabilities to participate in the programme;
- to analyse the sources, amounts, levels, pathways, trends and effects of pollutants relevant to the Mediterranean Sea;

- to provide the scientific/technical information needed by the Governments of the Mediterranean States and the EEC for the negotiation and implementation of the Convention for the Protection of the Mediterranean Sea against Pollution and its related protocols;
- to build up consistent time-series of data on the sources, pathways, levels and effects of pollutants in the Mediterranean Sea and thus to contribute to the scientific knowledge of the Mediterranean Sea.

MED POL - Phase I was implemented in the period from 1975 to 1980. The large number of national research centres designated by their Governments to participate in MED POL (83 research centres) from 15 Mediterranean States and the EEC), the diversity of the programme and its geographic coverage, the impressive number of Mediterranean scientists and technicians (about 200) and the number of co-operating agencies and supporting organizations involved in it, qualifies MED POL as certainly one of the largest and most complex co-operative scientific programmes with a specific and well-defined aim ever undertaken in the Mediterranean Basin.

MED POL - Phase II (1981-1990)

The Intergovernmental Review Meeting of Mediterranean Coastal States and First Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution, and its related protocols (Geneva, 5-10 February 1989), having examined the status of MED POL - Phase I, recommended that during the 1979/80 biennium a Long-term pollution monitoring and research programme should be formulated.

Based on the recommendations made at various expert and intergovernmental meetings, a draft Long-term (1981-1990) Programme for pollution monitoring and Research in the Mediterranean (MED POL-Phase II) was formulated by the Secretariat of the Barcelona Convention (UNEP), in co-operation with the United Nations Agencies which were responsible for the technical implementation of MED POL-Phase I, and it was formally approved by the Second Meeting of the Contracting Parties of the Mediterranean Sea against pollution and its related protocols and Intergovernmental Review Meeting of Mediterranean Coastal States of the Action Plan held in Cannes, 2-7 March 1981.

The general long-term objectives of MED POL-Phase II were to further the goals of the Barcelona Convention by assisting the Parties to prevent, abate and combat pollution of the Mediterranean Sea area and to protect and enhance the marine environment of the area. The specific objectives were designed to provide, on a continuous basis, the Parties to the Barcelona Convention and its related protocols with:

- information required for the implementation of the Convention and the protocols;

- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;

- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;

- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis;

- periodic assessment of the state of pollution of the Mediterranean Sea.

The monitoring of, and research on, pollutants affecting the Mediterranean marine environment reflects primarily the immediate and long-term requirements of the Barcelona Convention and its protocols, but also takes into account factors needed for the understanding of the relationship between the socio-economic development of the region and the pollution of the Mediterranean Sea.

As in MED POL-Phase I, the overall co-ordination and guidance for MED POL-Phase II is provided by UNEP as the secretariat of the Mediterranean Action Plan (MAP). Co-operating specialized United Nations Agencies (FAO, UNESCO, WHO, WMO, IAEA, IOC) are responsible for the technical implementation and day-to-day co-ordination of the work of national centres participating in monitoring and research.

The first eight volumes of the MAP Technical Reports Series present the collection of final reports of the principal Investigators who participated in the relevant pilot projects (MED POL I - MED POL VIII). The ninth volume of the MAP Technical Reports Series is the final report on the implementation of MED POL-Phase I, prepared, primarily, on the basis of individual final reports of the principal investigators with the co-operation of relevant United Nations Agencies (FAO, UNESCO, WHO, WMO, IAEA, IOC).

From the tenth volume onwards, the MAP Technical Report Series contains final reports on research projects, assessment documents, and other reports on activities performed within the framework of MED POL-Phase II, as well as documentation originating from other components of the Mediterranean Action Plan.

This thirty-first volume of the MAP Technical Reports Series contains the report and proceedings of the WMO/UNEP Workshop on Airborne Pollution of the Mediterranean Sea (Belgrade, Yugoslavia, 10-13 November 1987).

INTRODUCTION GENERALE

Le Programme des Nations Unies pour l'environnement (PNUE) a convoqué une réunion intergouvernementale sur la protection de la Méditerranée (Barcelone, 28 janvier - 4 février 1975) à laquelle ont pris part des représentants de 16 Etats riverains de la mer Méditerranée. La réunion a examiné les diverses mesures nécessaires à la prévention et à la lutte antipollution en mer Méditerranée, et elle s'est conclue sur l'adoption d'un Plan d'action comportant trois éléments fondamentaux:

- Planification intégrée du développement et de la gestion des ressources du bassin méditerranéen (élément "gestion");

- Programme coordonné de surveillance continue, de recherche, d'échange de renseignements et d'évaluation de l'état de la pollution et des mesures de protection (élément "évaluation");

- Convention cadre et protocoles y relatifs avec leurs annexes techniques pour la protection du milieu méditerranéen (élément juridique).

Tous les éléments du Plan d'action étaient interdépendants et fournissaient le cadre d'une action d'ensemble en vue de promouvoir, tant la protection que le développement continus de l'écorégion méditerranéenne. Aucun élément ne constituait une fin à lui seul. Le Plan d'action était destiné à aider les gouvernements méditerranéens à formuler leurs politiques nationales en matière de développement continu et de protection de zone de la Méditerranée et à accroître leur faculté d'identifier les diverses options s'offrant pour les schémas de développement, d'arrêter leurs choix et d'y affecter les ressources appropriées.

MED POL - Phase I (1976-1980)

Le programme coordonné de sruveillance continue et de recherche en matière de pollution de la Méditerranée (MED POL) a été approuvé au titre de l'élément "évaluation" (scientifique/technique) du Plan d'action.

Sa phase pilote (MED POL-Phase I) avait les objectifs généraux ci-dessous, élaborés au cours d'une série de réunions d'experts et de réunions intergouvernementales:

- formuler et exécuter un programme coordonné de surveillance continue et de recherche en matière de pollution en tenant compte des buts du Plan d'action pour la Méditerranée et de l'aptitude des centres de recherche méditerranéens à y participer;

- aider les centres de recherche nationaux à se rendre plus aptes à cette participation;

- étudier les sources, l'étendue, le degré, les parcours, les tendances et les effets des polluants affectant la mer Méditerranée;

- fournir l'information scientifique et technique nécessaire aux gouvernements des pays méditerranéens et à la Communauté économique européenne pour négocier et mettre en oeuvre la Convention pour la protection de la mer Méditerranée contre la pollution et les protocoles y relatifs;
- constituer des séries chronologiques cohérentes de données sur les sources, les cheminements, les degrés et les effets des polluants de la mer Méditerranée et contribuer par là à la connaissance scientifique de cette mer.

La Phase I du MED POL a été mise en oeuvre au cours de la période 1975-1980. Le grand nombre de centres de recherche nationaux désignés par leurs gouvernements pour participer au MED POL (83 centres de recherche de 15 Etats méditerranéens et de la CEE), la diversité du programme et sa couverture géographique, l'effectif impressionnant de scientifiques et techniciens méditerranéens (environ 200) ainsi que la quantité d'organismes coopérants et d'organisations d'appui qui y étaient engagés permettent sans conteste de caractériser le MED POL comme l'un des programmes de coopération scientifique les plus vastes et les plus complexes, comportant un objectif spécifique et bien défini, qui ait jamais été entrepris dans le bassin méditerranéen.

MED POL-Phase II (1981-1990)

La réunion intergouvernementale des Etats riverains de la Méditerranée chargés d'évaluer l'état d'avancement du Plan d'action et première réunion des Parties contractantes à la Convention pour la protection de la mer Méditerranée contre la pollution et aux protocoles y relatifs (Genève, 5-10 février 1979), ayant examiné la situation de la Phase I du MED POL, a recommandé que, durant la période biennale 1979-80, soit formulé un programme à long terme de surveillance continue et de recherche en matière de pollution.

Sur la base des recommandations énoncées lors des diverses réunions d'experts et réunions intergouvernementales, un projet de programme à long terme (1981-1990) de surveillance continue et de recherche en matière de pollution (MED POL - Phase II) a été formulé par le secrétariat de la Convention de Barcelone (PNUE), en coopération avec les organismes des Nations Unies chargés de l'exécution technique de MED POL - Phase I, et il a été officiellement approuvé lors de la deuxième réunion des Parties contractantes à la Convention pour la protection de la mer Méditerranée contre la pollution et aux protocoles y relatifs et réunion intergouvernementale des Etats riverains de la mer Méditerranée chargée d'évaluer l'état d'avancement du Plan d'action, qui s'est tenue à Cannes du 2 au 7 mars 1981.

L'objectif général à long terme de la Phase II du MED POL était de concourir à la réalisation des objectifs de la Convention de Barcelone en aidant les parties contractantes à prévenir, réduire et combattre la pollution dans la zone de la mer Méditerranée ainsi qu'à protéger et améliorer le milieu marin dans cette zone. Les objectifs particuliers étaient de fournir constamment aux Parties contractantes à la Convention de Barcelone et aux Protocoles y relatifs:

- les renseignements dont elles avaient besoin pour appliquer la Convention et les protocoles;

- des indications et une évaluation de l'efficacité des mesures prises pour prévenir la pollution en application de la Convention et des protocoles;

- des renseignements scientifiques qui pourraient servir à réviser et modifier les dispositions pertinentes de la Convention et des protocoles et à rédiger des protocoles additionnels;

- des informations qui pourraient servir à formuler sur les plans national, bilatéral et multilatéral, les décisions de gestion, respectueuses de l'environnement, qui seraient indispensables à la poursuite du développement socio-économique de la région méditerranéenne;

- une évaluation périodique de l'état de pollution de la mer Méditerranée.

La surveillance continue des polluants affectant le milieu marin de la Méditerranée ainsi que la recherche menée à leur sujet répondent en premier lieu aux prescriptions immédiates et à long terme de la Convention de Barcelone et des protocoles y relatifs, mais elles tiennent également compte des facteurs requis pour la compréhension des relations existant entre le développement socio-économique de la région et la pollution de la mer Méditerranée.

Comme lors de la Phase I du MED POL, la coordination et la direction générales de la Phase II étaient assurées par le PNUE, par l'intermédiaire du secrétariat du Plan d'action pour la Méditerranée (PAM). Les organismes spécialisés coopérants des Nations Unies (FAO, UNESCO, OMS, OMM, AIEA, COI) étaient chargés de l'exécution technique et de la coordination quotidienne des travaux des centres de recherche nationaux participant au programme de surveillance continue et de recherche.

Les huit premiers volumes de la Série des rapports techniques du PAM rassemblent les rapports finaux de chercheurs responsables qui ont participé aux projets pilotes correspondants (MED POL I - MED POL VIII). Le neuvième volume de cette même Série se compose du rapport final sur la mise en oeuvre de la Phase I du programme MED POL, établi essentiellement sur la base des rapports finaux individuels des chercheurs responsables avec la coopération des organismes compétents des Nations Unies (FAO, UNESCO, OMS, OMM, AIEA, COI).

A partir du dixième volume, la Série des rapports techniques du PAM, comprends des rapports finaux sur les projets de "recherche", des documents d'évaluation et d'autres rapports d'activités effectués dans le cadre de MED POL-Phase II, ainsi que de la documentation prise dans d'autres domaines du Plan d'action pour la Méditerranée.

Ce trente-et-unième volume de la Série des rapports techniques du PAM comprends le rapport et les actes des Journées d'étude OMM/PNUE sur la pollution par voie atmosphérique de la mer Méditerranée (Belgrade, Yougoslavie, 10-13 novembre 1987).

AIRBORNE POLLUTION OF THE MEDITERRANEAN SEA

Report and Proceedings of a WMO/UNEP Workshop

Belgrade, Yugoslavia, 10-13 November 1987

Sponsored by: WMO, UNEP and
the Hydrometeorological Institute of Yugoslavia

POLLUTION PAR VOIE ATMOSPHERIQUE DE LA MER MEDITERRANEE

Rapport et actes des Journées d'étude OMM/PNUE

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Organisé sour l'égide de: OMM, PNUE et
Institut hydrométéorologique de Yougoslavie

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ABSTRACT

A WMO/UNEP Workshop on Airborne Pollution of the Mediterranean Sea was convened from 10 to 13 November 1987 to discuss preliminary results of a pilot project on studying air pollutant deposition and pollutant concentrations in air in the Mediterranean launched in 1986 and relevant research activities conducted within the UNEP's MED POL Research Activity "L" on pollutant-transfer processes at air/sea interface co-ordinated by the World Meteorological Organization. The workshop also agreed on detailed proposals for an airborne pollution monitoring and modelling programme to be implemented within the framework of national monitoring agreements. A summary report of the workshop including the programme proposals, appears as Part I of this document.

Scientific papers presented at the workshop are included in Part II of this document. This part is preceded by an overview of airborne pollution over the Mediterranean prepared after the workshop especially for the present publication to summarize the present knowledge and to review ongoing activities in the region.

RESUME

Des Journées d'étude OMM/PNUE sur la pollution par voie atmosphérique de la mer Méditerranée ont été organisées du 10 au 13 novembre 1987 afin d'examiner les résultats préliminaires d'un projet pilote portant sur l'étude du dépôt des polluants atmosphériques et des concentrations de polluants dans l'air en Méditerranée; ce projet a été lancé en 1986 et les activités ont été menées dans le cadre de l'activité de recherche "L" du programme MED POL du PNUE, activité consacrée aux processus de transfert des polluants à l'interface air/mer et coordonnée par l'Organisation météorologique mondiale. Les participants à ces Journées d'étude sont également convenus de propositions détaillées en vue d'un programme de surveillance continue et de modélisation de la pollution par voie atmosphérique à mettre en oeuvre dans le cadre d'accords nationaux de surveillance continue. Un rapport succint des Journées d'étude comportant les propositions de programme figure à l'annexe I du présent document.

Les communications scientifiques présentées à ces Journées d'étude sont reproduites dans la partie II du présent document. Cette partie est précédée d'une vue d'ensemble de la pollution par voie atmosphérique en Méditerranée qui a été spécialement rédigée pour la présente publication afin de récapituler les connaissances actuelles et de passer en revue les activités en cours dans la région.

FOREWORD

During the past ten to fifteen years there has been an increased emphasis on studies of the atmospheric transport of pollutants from land into the marine environment. Many of these studies showed that large quantities of natural or anthropogenic substances could enter the seas through the atmosphere both from seaside and even distant land-based sources. This is especially true for semi-enclosed seas. Thus preliminary flux estimates for some elements such as Hg, Cd, Pb, Cr and transuranic elements indicated that the atmospheric transport of these pollutants is at least comparable in magnitude to riverine inputs into the Mediterranean.

It should also be kept in mind that airborne pollutants undergo complex horizontal and vertical mixing and chemical transformation in the atmosphere and for quantitative estimates of their input to the marine environment it is not enough to organize pollutant deposition measurements at a number of sea-shore monitoring sites. Such estimates for the whole sea could be made only by applying air pollutant transport models based on good knowledge of the governing meteorological processes.

The WMO/UNEP workshop in Belgrade considered some results of activities carried out in the Mediterranean on studying air pollutant transport and deposition, developing new measurement techniques and atmospheric transport models and collecting relevant meteorological and climatological data.

The detailed monitoring and modelling programme prepared during the workshop was submitted to the First Meeting of the Scientific and Technical Committee of the Barcelona Convention (Athens, May 1988) which agreed that this programme "should be initiated within the framework of national monitoring agreements in as many countries as possible on a voluntary basis".

AVANT-PROPOS

Au cours des dix à quinze dernières années, une place croissante a été accordée aux études concernant le transfert atmosphérique des polluants du milieu terrestre au milieu marin. Bon nombre de ces études ont montré que d'importantes quantités de substances naturelles ou anthropogènes pouvaient pénétrer dans la mer par voie atmosphérique, aussi bien à partir du littoral que de sources terrestres éloignées. Cette notion est tout spécialement valable pour les mers semi-fermées. Ainsi, des estimations préliminaires des flux pour certains éléments tels que Hg, Cd, Pb, Cr et les éléments transuraniens ont indiqué que le transfert atmosphérique de ces polluants était d'une ampleur au moins comparable à celle des apports des cours d'eau dans la Méditerranée.

Il convient de garder à l'esprit que les polluants véhiculés par voie atmosphérique sont soumis à des processus complexes de brassage horizontal et vertical et de transformation chimique dans l'atmosphère, et pour procéder à des estimations quantitatives de leur apport, il ne suffit pas d'effectuer des mesures du dépôt de polluants à un certain nombre de sites de surveillance le long du littoral. Pour l'ensemble de la mer, ces estimations ne pouvaient être établies qu'en appliquant des modèles de transfert des polluants atmosphériques reposant sur de bonnes connaissances des processus météorologiques en jeu.

Lors des Journées d'étude de Belgrade, les participants ont examiné plusieurs résultats des activités menées en Méditerranée afin d'étudier le transfert et le dépôt des polluants atmosphériques, de mettre au point de nouvelles techniques de mesure et des modèles de transfert atmosphérique, et de recueillir des données meteorologiques et climatologiques pertinentes.

Le programme détaillé de sruveillance continue et de modélisation préparé au cours des Journées d'étude a été soumis à la première réunion du Comité scientifique et technique de la Convention de Barcelone (Athènes, mai 1988) qui est convenu que ce programme "devrait être amorcé dans le cadre d'accords nationaux de surveillance continue dans autant de pays que possible sur une base volontaire".

PART I:

REPORT OF THE WMO/UNEP WORKSHOP ON AIRBORNE POLLUTION OF THE MEDITERRANEAN SEA

(Belgrade, 10-13 November 1987)

BACKGROUND

It is now recognized that a substantial fraction of the contamination entering the ocean and especially semi-enclosed seas derives from sources located on land via atmospheric inputs. Contaminants of major concern are heavy metals and metalloids, petroleum hydrocarbons, chlorinated hydrocarbons and pathogenic micro-organisms. In 1985 the GESAMP* Working Group No. 14 on the Interchange of Pollutants between the Atmosphere and the Oceans reviewed the information available for the Mediterranean Sea and concluded that for some elements such as Hg, Cd, Pb, Cr and transuranic elements, the atmospheric transport of contaminants is at least comparable in magnitude to riverine inputs into the Mediterranean.

Since 1983 a number of research projects dealing with airborne pollution had been implemented in national institutions of the Mediterranean countries within a research component of the Long-Term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL-Phase II). Furthermore, the Fourth Ordinary Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution and its Related Protocols recommended that a pilot project on studying air pollutant deposition into the region and pollutant concentrations in air should be initiated in 1986 in as many countries as possible. According to the recommendation of the GESAMP Working Group No. 14 cadmium was selected as a pilot contaminant for the project and some WMO Background Air Pollution Monitoring Network (BAPMON) stations were mentioned as possible sites for sampling.

To discuss preliminary results of the pilot project and relevant research and monitoring activities and to elaborate detailed programme proposals and recommendations for future research and monitoring, a Workshop on Airborne Pollution of the Mediterranean Sea was proposed. The following topics were included in the scientific programme of the Workshop:

- atmospheric concentrations and deposition of pollutants in the Mediterranean: research and monitoring;
- modelling of air pollutant transport and deposition;
- development and testing of methods for sampling and analysis;
- assessment of airborne pollution load of the Mediterranean Sea and its coastal regions;
- methodologies for assessing emissions of important pollutants into the atmosphere from various types and groups of sources.

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* GESAMP = IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution

The Workshop took place in Belgrade, Yugoslavia, from 10 to 13 November 1987 at the kind invitation of the Federal Hydrometeorological Institute of Yugoslavia. It was attended by 32 participants from 10 Mediterranean countries. The representatives of WMO, UNEP (MAP) and IAEA were also present. A list of participants is given in Annex I.

1. OPENING OF THE WORKSHOP

Mr. I. Delijanic, Assistant Director of the Federal Hydrometeorological Institute of the Socialist Federal Republic of Yugoslavia and Chairman of the Local Organizing Committee chaired the opening session of the Workshop.

The Workshop was opened by Mr. A. Soudine, Scientific Officer WMO, who welcomed the participants on behalf of the Secretary-General of WMO, noted the activities of WMO in studying marine environment pollution through the atmosphere and briefly outlined the events leading to the meeting and the importance of the airborne pollution problem in assessing and controlling marine pollution in the Mediterranean region. On behalf of the participants he also expressed thanks to the Federal Hydrometeorological Institute of Yugoslavia for hosting the Workshop, for providing good facilities for the fruitful work and for the hospitality.

Mr L. Jeftic, Senior Marine Scientist, Mediterranean Co-ordinating Unit, UNEP, welcomed all participants on behalf of the Executive Director of UNEP and stressed the importance of the assessment of the airborne pollution of the Mediterranean Sea. Monitoring of the pollution which reaches the Mediterranean Sea through the atmosphere is the fourth and last component of the pollution monitoring programme of the Mediterranean Sea to be developed since the monitoring of sources of pollution, coastal waters and open waters is already established.

Mr Joze Roskar, Director of the Federal Hydrometeorological Institute, welcomed the Workshop participants and pointed out the historical importance of the Mediterranean region as the cradle of our civilization and the danger of the pollution of the Mediterranean Sea which is a shallow sea with only one opening in the Gibraltar Strait and its water renews only every hundred years. The problem is even greater taking into consideration the rapidly increasing number of inhabitants in the region and the threat to human health that this problem poses. After the UN Conference on the Environment in 1972 and Barcelona meeting in 1975 when the Action Plan for the Mediterranean protection was accepted, greater attention has been paid to this problem. UNEP and other specialized agencies of UN have prepared a master plan already applied in 83 laboratories in 16 countries which is known as the Long-Term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL). The periods of 1975 to 1980 and 1981 to 1990 have been marked by the First Phase of MED POL and Second Phase of MED POL respectively. He noted that Yugoslavia has played an active role in all the activities in the Region devoted to avoiding environment degradation as well as improvement of air and water quality. In accordance with this principle of preventing the adverse anthropogenic pollution impact on the Mediterranean Sea, the Federal

Hydrometeorological Institute of Yugoslavia accepted the role of hosting this Workshop organized by WMO and UNEP with the conviction that it would offer the basis for future work in the form of its conclusions and proposals for further monitoring and research activities on the airborne pollution of the Mediterranean Sea.

Mr Patrick Buat-Ménard, Chairman of the Workshop committee, presented scientific topics to be addressed by the speakers. He stressed that the workshop was being held at a critical time for the future since the specific recommendations related to the pilot project on the transport of atmospheric contaminants to the Mediterranean Sea should be the major output of the meeting. Both coastal and basin-wide pollution should be considered, keeping in mind the need to combine modelling approaches and field experiments. He insisted on the need for the assessment of pollutant fluxes on a regional basis within the Mediterranean Basin and the need for long term time series measurements of high quality to take into account the expected spatial and temporal variabilities. He finally outlined that the pilot project should be realistic or in other words feasible with the available expertise, manpower and potential funding for the participants in the MED POL programme.

Mr A. Soudine informed the meeting of the fortieth anniversary of the Meteorological Service of Yugoslavia which was established in 1947 and on behalf of the participants congratulated Dr J. Riskar and his staff on this occasion and wished them all the best and every success.

Mr M. Slavnic from the Federal Hydrometeorological Institute of Yugoslavia provided more detailed information on the programme of the Workshop and other organizational matters.

2. NOMINATION OF OFFICERS AND ORGANIZATION OF WORK

The meeting agreed that Mr P. Buat-Ménard, Chairman of the Workshop Committee, would chair the meeting and Mr A. Palumbo and Mr Z. Janjic as members of the Workshop Committee would assist him in chairing sub-sessions. Mr A. Soudine acted as Technical Secretary and Mr U. Dayan was invited to be Rapporteur.

The Chairman explained the programme of work, the order and the time allocated for each presentation.

3. PRESENTATION OF PAPERS

A total of 14 papers were presented and discussed at the four sessions of the meeting. A list of the papers presented, and of their authors, is given in Annex II.

At the first session chaired by Mr P. Buat-Ménard, the papers were discussed which dealt with field measurements of contaminants. The following results were presented:

1. On average amounts of dustloading in the Western and Eastern Mediterranean and Southern Adriatic, on concentrations of some trace metals and their average fluxes in the above regions.

2. On temporal variability and seasonal patterns of concentrations for elements of continental origin (both natural and anthropogenic), on relationship between concentrations and the frequency and amount of rainfall, on relationship between the mean ratio of high and low concentration periods and mass median diameter of the elements and on application of three-dimensional air-mass trajectories for identifying origin areas of the elements.

3. On geochemical study of atmospheric deposition in the North Western Mediterranean and influence of air mass origin on concentration of major ions and some heavy metals in precipitation.

4. On precipitation chemistry and contaminant concentrations in air for some monitoring stations along the Adriatic coast and in Italy.

The second session chaired by Mr A. Palumbo was devoted to the development and application of laser techniques for the determination of air pollutant properties, and both short range (coastal) and long range (open sea) distribution of air pollutant concentrations all over the Mediterranean area with a fine vertical resolution, to the possibility to use lichens as bioindicators for assessing air pollution by chlorinated hydrocarbons.

Meteorological aspects and modelling of atmospheric transport of pollutants were discussed at the third session chaired by Mr Z. Janjic. Results were presented on the collection and calculation of meteorological and climatological data required for modelling of air pollutant transport, on evaluating pollutant dispersion by land and sea breezes, and the use of a limited area model with step-like mountains for calculating 3-D and 2-D air-pollutant trajectories and on the development of a three-dimensional model for calculating and predicting pollutant concentration fields using a PBL (planetary boundary layer) formulation based on higher order closure assumptions.

At a short final session chaired by Mr P. Buat-Ménard, two matters were discussed: the influence of mass-particle size distribution on the dry deposition and the results of ozone monitoring in the Adriatic and Aegean coastal regions. It was shown that large particles composing a small quantitative part of the total aerosol, determine to a large extent the dry deposition of sea-salt and mineral particles. For ozone, results were presented on high level ozone production in urban and industrial areas and its transport to and high concentrations in the air at remote sites.

4. SUMMARY OF THE SCIENTIFIC DISCUSSIONS RAISED DURING THE WORKSHOP

4.1. Field measurements of contaminants in the Mediterranean Sea

1. The Meeting agreed that although the most practical way to analyze the potential influence of air mass origin on concentration of major ions and some heavy metals in precipitation is by using air parcel trajectories calculation, this technique should be applied with care due to the necessity for a precise conjunction of these data with meteorological conditions mainly with the time of storm occurrences.

2. Due to great concern for the quality of coastal and open Mediterranean waters and also to human life on coastlines, Workshop participants mentioned the necessity to investigate the transfer of contaminants from the sea to the atmosphere as well.

3. The Meeting stressed difficulties in applying typical values of the Mediterranean Basin by airborne contaminants due to high variability of concentrations exerted both in time and in space.

4. The Meeting, furthermore, discussed the evidence of presence of gypsum in Saharan sediments as detected in the Western Mediterranean region but not in the Eastern part and emphasized the lack of sufficient knowledge on the mechanism of the volcanic contribution to pollution loading in the Mediterranean.

5. The use of bioindicators such as lichens for distinction of atmospheric pollution was accepted to be very economically attractive but was questioned by some scientists due to incapability of their application during short pollution episodes.

6. The Meeting discussed the possible efficacy to implement new techniques and approaches for determination of air pollutant properties such as light scattering and others and stressed that such sophisticated techniques should be evaluated along their real potential for future application in the MED POL programme.

7. Complexity involved in flux calculation from the atmosphere to the sea was discussed by some participants in view of previously mentioned uncertainties in the rates of dry deposition. Therefore, it was agreed that results received recently on particle size distribution which are believed to be of great concern to dry deposition rates, should be used to reevaluate dry deposition fluxes especially for some inorganic contaminants which affect marine fauna and flora in the Mediterranean Basin.

8. The Meeting stressed the necessity to measure wet and dry deposition separately in order to avoid contamination of wet samples mostly by alkaline materials during hazy weather conditions.

9. The Meeting also mentioned the important role of ozone to air quality deterioration and recommended a continuous monitoring of this contaminant which may also serve as a tracer, especially during the summer season.

10. The participants agreed unanimously that cruises provide very important information and, therefore, should be encouraged.

4.2. Meteorological aspects and modelling of atmospheric transport of contaminants

1. The Meeting discussed the appropriate parameters needed for modelling and concluded that differing data sets are needed depending on the scales of the processes considered and on complexity of the model used.

2. Concerning the horizontal scales, the participants have identified two main areas of interest:

   - local scales (in the order of 100 km) for simulation of coastal atmospheric conditions and,

   - regional scales (in the order of 1000 km) for simulation of long-range transport (LRT) phenomena in the open sea.

3. Regarding a possible way to overcome the problem of scarcity of meteorological data above the Mediterranean Basin, the Meeting discussed two possible ways to obtain the data: one by using all existing meteorological records and the other by using comprehensive synoptic scale fine-mesh atmospheric models as 4-dimensional interpolation tools.

4. The most practical way to merge LRT model for the open sea with a sequential Eulerian model for coastal zones and estuaries was stressed by one of the participants who suggested that the best available routine observational data should be used to prepare adequate input data sets for an LRT model to predict the flow configuration on each point grid of a fine mesh. The calculated results after validation could serve as higher resolution input values to sequential dispersion models for simulation of local scale effects such as recirculation of contaminants, weak frontal effects, etc.

5. The Meeting suggested that a sequential Eulerian model should be used for simulation of selected worst cases of contaminant dispersion and transport over the Mediterranean Basin versus a climatological model that might be used on a seasonal scale.

6. The common opinion was to adopt as a beginning the most widely used approach in similar studies elsewhere in which simple single-layer Lagrangean models are applied.

7. Regarding the question raised about the most appropriate isobaric level for construction of the trajectories, a point was made by one of the participants explaining the rationale behind choosing the 850 hPa level. This level is believed to represent the intermediate level between surface winds and the geostrophic (frictionless) wind drift layer.

5. PROPOSAL FOR A MONITORING PROGRAMME ON AIRBORNE POLLUTION OF THE MEDITERRANEAN SEA

The Meeting recognized the importance of atmospheric transport of contaminants from diverse land-based sources to the Mediterranean region. Previous measurements have shown evidence that such a contamination may be of concern for the quality of coastal and open Mediterranean waters, marine life and human life on coastlines. The common opinion was expressed that over the last years research and monitoring activities on airborne pollution had essentially increased and were steadily developing The Meeting agreed that a monitoring and modelling programme on pollutant transport to the Mediterranean Sea through the atmosphere should start as soon as possible.

The major goals of this programme should be the following:

- to evaluate the importance of the atmospheric transport and deposition of land-based contaminants to coastal and open Mediterranean waters;
- to assess the airborne contamination level of trace substances which can affect the quality of human life on coastlines:
- to identify sources and source regions for these atmospheric contaminants;
- to develop predictive models of the airborne contamination of the Mediterranean environment to provide the basis for future action.

The Meeting agreed that for an assessment of airborne pollution two horizontal scales have to be considered:

- local scale for impact studies close to "hot spots", i.e. large seaside cities and industrial sources;
- large scale for an evaluation of the level of contamination of open Mediterranean waters. This would require the implementation of selected permanent reference stations distant enough from local pollution sources. Such stations should be exposed most of the time to maritime air and could be located at remote coastal sites, on Mediterranean islands, and also on existing offshore platforms. Complementary information could be obtained during cruises on board research vessels.

Because of the expected temporal variability of atmospheric concentrations and fluxes of contaminants, any monitoring programme should be run continuously for several years. Furthermore, since the ultimate goal is to predict atmospheric contaminant inputs, a simultaneous effort should be undertaken to model the atmospheric transport and deposition of these contaminants at the different spatial scales considered. The models would be progressively calibrated using the data gathered from the field measurements.

5.1. Monitoring programme

The Meeting discussed the chemical parameters to be measured as well as physical parameters necessary for the interruption of the data. The list of these parameters is given in Annex III and consists of:

a) inorganic, organic and radioactive contaminants of concern for marine waters, marine life and human life along coastlines;

b) tracers of natural and anthropogenic sources;

c) meteorological parameters.

The following recommendations deal with standardized sampling and analytical procedures which should be adopted for the acquisition of high quality data for the monitoring programme.

5.1.1. Sampling procedures

- Sampling frequency

On the basis of the experience of previous monitoring programmes either on land or over other regional seas, the Meeting recommended that the sampling duration both for air and rain concentration determinations should not generally exceed one week. When feasible, higher sampling frequency, on a daily basis or even shorter, would be desirable for selected contaminants. This would allow the use of field data for model calibration exercises.

- Aerosols

In order to minimize sample and analytical contamination problems, the use of high volume aerosol filter samplers (as for the BAPMoN network) is recommended. The meeting recognized, however, that specific collection substrates have to be used to sample inorganic and organic contaminants. Based on presently available expertise and analytical difficulties, it is recommended that in the first phase of the monitoring programme, priority should be given to the sampling of inorganic contaminants, including radionuclides. The following chemical parameters should be analysed:

- heavy metals: Cd, Pb first priority
  Cu, Zn second priority
- other inorganic elements indicators of natural and anthropogenic contributions: Na, Al, SO_4^{2-}
- radionuclides: Cs, transuranic elements. Because of the very low levels of these contaminants, the analysis may require the use of composite filter samples integrating up to a month of sampling.
- organic species: PCBs, DDTs, HCHs (hexachlorocyclohexanes), PAHs and other particulate hydrocarbons.

When feasible, other possible parameters to be studied would be:

- elemental carbon, fluorides;
- heavy metals such as Hg, Sn, As, Se.

Furthermore, useful information on the particle size distributions of the atmospheric contaminants could be obtained through the use of high-volume cascade impactor samplers. This would allow to improve model calculations of dry deposition fluxes.

- Gas phase

Due to its importance in air quality and atmospheric chemistry, the meeting recommends the implementation of continuous ozone monitoring during the summer season and, if necessary (e.g. at some impact or "hot spot" sites), throughout the year. This is particularly relevant for impact stations where expected high ozone levels may generate photochemical smog and influence the transformation of some organic compounds such as hydrocarbons.

- Atmospheric deposition

Owing to sampling difficulties, direct measurements of dry deposition for atmospheric contaminants cannot be considered as feasible at the present stage in a continuous monitoring programme. The Meeting recommended to estimate dry deposition fluxes using aerosol concentration data and relevant deposition models to the sea surface.

Wet deposition (rain) should ideally be collected on an event basis. Owing to recent developments in instrumentation, it is recommended that a fully automatic device be employed, similar to that used in the BAPMoN network. The Meeting recognized, however, that rain collections on an event basis may not be feasible at all stations. It is therefore recommended that precipitation be collected on a weekly basis. When considering the various chemical parameters (see section on aerosols) to be measured, the Meeting recognized that for contaminants such as heavy metals and organic species the sampling protocols have to be different from the standard procedures used for major ions.

It is therefore recommended that 3 rain collectors be implemented at each station:

- one for pH, acidity, alkalinity, conductivity and major ions: the standard BAPMoN procedure is recommended;

- one for heavy metals and radionuclides: rain-collecting bottles should be preacidified;

- one for organic species: the collection surface should be made of stainless steel. The rain sample processing should meet the procedures adopted in MED POL for organic species in seawater.

The Meeting recommends that first priority should be given to the implementation of two rain collectors, one for major ions and one for heavy metals and radionuclides.

- Meteorological parameters during the sampling periods

The Meeting recommended that the sampling sites should be located as close as possible, or within a major meteorological station such as a surface synoptic station or a main meteorological station.

The sampling records should be accompanied by the records on the chronology of precipitation events that occurred during the sampling period. These records should include the beginning and ending times of the precipitation event as well as the information on intensity on preferably hourly basis.

In addition to this, the sampling records should be accompanied at least by the data on the wind speed and direction, air and sea temperature and humidity and other weather phenomena.

If these data are not available or representative from the nearby major meteorological station, they should be measured at the sampling site during the sampling period.

5.1.2. Analytical procedures

The Meeting recommends the use of the best available techniques either in individual laboratories or in central laboratories nominated by participating countries for conducting analyses within the programme. Such techniques can be found in WMO or UNEP reference handbooks which should be provided to the participating laboratories.

The Meeting recommended that intercomparisons and intercalibrations of analytical methods be carried out. These exercises could be coordinated by various host countries or international organizations.

5.1.3. Data reporting and exchange of information

The Meeting recommended that monitoring data from background stations should be reported on weekly-averaged basis for precipitation chemistry and on daily basis for pollutant concentrations in air (particles). The corresponding formats, based on the existing WMO BAPMoN formats, are given as Annexes IV and V. The annual national data reports should be sent to the Co-ordinating Unit for the Mediterranean Action Plan (MED Unit) not later than 1 march of the following year. Copies of all national reports would be sent then to WMO co-ordinating these activities within MED POL. At the beginning of the monitoring programme implementation the WMO BAPMoN Data Centre (National Climatic Centre, Asheville, N.C., USA) could be used for preliminary treatment and storage of the data. Other wise a regional data centre should be nominated for this purpose.

National reports from impact stations containing generalised results should also be sent to the MED Unit annually by 1 March of the following year.

It was recognized that review reports on national activities relevant to the study of airborne pollution of the Mediterranean Sea (including information on national projects and programme, laboratories and their potentialities and needs, scientists involved in studies, cruises, meetings, etc.) could be very useful for further planning and co-ordination of the programme. This information should be collected as soon as possible by the MED Unit and WMO through the National Co-ordinators for MED POL and then up-dated annually.

The Meeting recommended that countries who joined the programme should nominate one or several monitoring stations for the programme and report information on the stations to the MED Unit using the format given in Annex VI.

5.1.4. Assistance and training

The Meeting recommended that mutual bilateral and multilateral assistance in programme implementation should be encouraged through consultant services, joint cruises, on-job training, etc.

Furthermore, the Meeting was of the opinion that sampling equipment and analytical instruments available in national institutions willing to participate in the monitoring programme could be insufficient for the implementation of the programme to the needed extent. In this connexion it was emphasized that assistance should be provided to the participating institutions to get necessary sampling equipment using funds available for the monitoring component of MED POL.

It was also recommended that the WMO training courses on background air pollution measurements held every year in English or in French should be used for training as fully as possible. WMO was invited to provide information on the courses regularly and well in advance.

5.1.5. Emission inventories

The Meeting expressed the view that gathering and compilation of emission data for selected pollutants are the important prerequisite of reliable model calculations. The collection of emission data should be initiated as soon as possible using common methodologies which should be prepared by a consultant in line with the LBS Protocol.

5.2. Proposal for a modelling programme

5.2.1. General

Concerning the horizontal scales, two main areas of interest were identified. These are:

- local scales (in the order of 100 km); and
- regional scales (in the order of 1000 km and more).

Both of these areas require international cooperation, coordination and data exchange.

On both scales, two separate problems should be addressed. These are:

- emission, horizontal and vertical diffusion, transformation, dry and wet deposition rates, and

- meteorological driving parameters.

5.2.2. Pollution emission, transport, diffusion, transformation and deposition

The common approach to similar studies elsewhere is the use of simple single-layer Lagrangean models. The Meeting noted with satisfaction, however, that primarily due to improved computational resources, and better understanding of the processes involved, more sophisticated and potentially more powerful Eulerian models including those based on higher order closure hypotheses and more appropriate treatment or orography are becoming available in the scientific community and in the weather services in the region. The Meeting recommended that further research using both approaches be encouraged.

The Meeting recognized that in order to apply and verify such models, the observed data on pollution, concentration and deposition should be available on various spatial and temporal scales. The Meeting also agreed that high quality information on concentration fields is necessary. This information can be obtained by direct measurements and as output from forecasting models fed with data on pollution sources. In this connection, it is essential that an inventory of the pollution sources be made, preferably by an independent contractor or by national authorities using common methodologies.

5.2.3. Meteorological driving parameters

Meteorological parameters are needed on various spatial and temporal scales depending on the scales of the processes considered, and on the complexity of the model for simulating the transport, diffusion, transformation and deposition of the pollutants.

The Workshop stressed the need for appropriate treatment of specificities of PBL over the sea. Possible sources of observational data are the ALPEX and the Med Alpex data sets and the WMO sponsored compilation of meteorological data above the Mediterranean region by Dayan and Miller (in press). In this connection, it is important to improve our knowledge of the processes at the sea-air interface by means of theoretical as well as more detailed observational studies. Two possible ways to obtain the relevant meteorological data have emerged. One is to use the existing meteorological records in order to identify predominant weather patterns in the region, or in the local areas, and to estimate the pollution transport and deposition on the basis of the data obtained in this way. The other possibility is to use comprehensive synoptic scale fine-mesh atmospheric models as 4-dimensional interpolation tools. Both approaches have advantages and disadvantages and require further research.

The main advantage of the models based on climatological data is their simplicity and relatively low computational cost so that they can be used to obtain qualitative answers relatively quickly.

On the other hand, having in mind the lack and/or scarcity of observed meteorological data particularly over the sea, the approach based on model synthesized data may provide better insight into the relevant processes. The data produced by the model can be used to study the pollution propagation in the atmosphere on various scales either by coupling a model used for 4-dimensional interpolation, or to drive finer mesh models on local scales. This approach is particularly interesting because it can form a basis for developing a forecasting capability.

Having all this in mind, the Meeting recommended:

- that information on available data and models be collected;
- that all available means be used to specify the meteorological data needed without further delay;

- that, in the longer run, research should be supported aimed at 4-dimensional model interpolation with the possibility of coupling the sophisticated pollution transport, diffusion, transformation and deposition models with the ultimate goal of developing a forecasting capability for the Mediterranean region.

- that a meteorological institute in the region should be nominated to co-ordinate modelling activities, to collect relevant data and to make (in future) model calculations of air pollutant transport and deposition for the whole region.

5.3. Co-ordination and programme implementation monitoring

For better co-ordination and monitoring of implementation of the proposed programme the Workshop recommended that an Ad Hoc Expert Group on Airborne Pollution of the Mediterranean Sea be established and National Co-ordinators for MED POL were invited to inform the MED Unit and WMO about the names of the designated experts. It was assumed that the Ad Hoc Expert Group would work by correspondence, at least until the next workshop. Mr P. Buat-Ménard, Chairman of the Workshop Committee, was proposed as the Chairman of the Group.

It was also recommended that the Second Workshop on Airborne Pollution of the Mediterranean Sea should be held at the end of 1989 to consider first results of the monitoring and modelling programme on transport of pollutants to the Mediterranean region through the atmosphere and implementation of the recommended research activities, and to clarify monitoring programme requirements.

6. ADOPTION OF THE REPORT AND CLOSURE OF THE WORKSHOP

A draft report of the Workshop was unanimously adopted and the WMO representative was requested to finalize it, taking into account comments made by the participants as soon as possible after the meeting.

All the participants thanked the Federal Hydrometeorological Institute of Yugoslavia for hosting the Workshop and providing excellent facilities for fruitful work, as well as for the warm hospitality extended.

The Workshop was closed at 12.30 on the 13th of November 1987.

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ANNEX II

List of papers presented

1. F. Dulac, P. Buat-Ménard, U. Ezat, S. Melki, G. Bergametti. Influence of mass-particle size distributions ont he dry deposition rates of atmospheric trace elements over the western Mediterranean sea.

2. S. Guerzoni, R. Lenaz, G. Quarantotto. Trace metals characterization of airborne particles from different Mediterranean areas.

3. V. Djuricic. Some characteristics of air and precipitation chemistry of selected stations along the Adriatic coast.

4. L. Cruciani. Review of chemical data by the Italian Meteorological Service.

5. J. Morelli. Time variability of the atmospheric input in the north-western Mediterranean basin.

6. G. Bergametti, E. Remoudaki, A. Dutot, P. Buat-Ménard. Factors influencing the seasonal variability of the elemental composition of atmospheric aerosol particles over the north-western Mediterranean.

7. T. Cvitas, L. Klasinc. Tropospheric ozone production and transport in the Mediterranean.

8. U. Dayan, J.M. Miller. Meteorological and climatological data for the assessment of atmospheric transport of pollutants in the Mediterranean basin.

9. Z. Janjic, F. Mesinger, S. Nickovic, B. Rajkovic. Synoptic-scale transport of passive substances and its model simulation over European region.

10. M. Ivanovic. Mathematical model of unsteady diffusion of pollutants over complex terrain.

11. E. Wakshal, I. Mahrer. Assessment of atmospheric pollution sources of the eastern Mediterranean Sea and its coastal area of Israel.

12. A. Nejjar. Application of light scattering techniques to the determination of air pollutants properties.

13. J.P. Villeneuve. Use of lichens as bioindicator for atmospheric pollution by chlorinated hydrocarbons.

14. G. Cali, A. Palumbo. Remote sensing of airborne pollution over the Mediterranean Sea.

ANNEX III

List of recommended parameters

Precipitation	Routine programme	Extended programme
pH	+	+
Conductivity	+	+
Acidity	+	+
Alkalinity	+	+
SO_4^{-2}-S	+	+
NH_4	+	+
NO_3-N	+	+
Na	+	+
K	+	+
Mg	+	+
Ca	+	+
Cl	+	+
Cd	+	+
Pb	+	+
Cu	+	+
Zn	+	+
Radionuclides	-	+
Organic compounds	-	+
Precipitation amount	+	+
Particles		
SO_4^{-2}-S	-	+
Na	-	+
Al	-	+
Cd	+	+
Pb	+	+
Cu	-	+
Zn	-	+
Radionuclides	-	+
Organic compounds	-	+
Total SPM	+	+
Air volume	+	+
Gas		
O_3 *)	+	+
Meteorological parameters		
Wind speed	+	+
Wind direction	+	+
Air temperature	+	+
Sea surface temperature **)	+	+
Dew point	+	+
Relative humidity	+	+
Barometric pressure	+	+

*) at impact stations
**) when applicable

ANNEX IV

Weekly Precipitation Data Form

MAIL TO:

Country		Area				Site		
☐	☐	☐	☐	☐	☐	☐	☐	☐
2	3	4	5	6	7	8	9	10

2 ____________________
1 Agency

____
Station name

____
Site Address

Agency	Project		Time
0	0	☐	☐
11	12	13	14

Sample start day ——————→

Year		Month		Day	
☐	☐	☐	☐	☐	☐
15	16	17	18	19	20

Have siting criteria changed? Yes ☐ No ☐

Parameter Name	Method	Units		Parameter Code					Method		Units		DP		Value			
*Precip (NG)	Volumetric	mm	(23-32)	6	5	3	0	1	7	1	2	9	0	(33-36)				
Precip (SG)	Volumetric	mm	(37-46)	6	5	3	0	1	8	1	2	9	0	(47-50)				
pH	Glass Electrode	pH	(51-60)	6	5	3	0	2	8	1	6	1		(61-64)				
Conductivity	Cond. Cell	µS/cm	(65-74)	6	5	3	0	3	8	1	6	9		(75-78)				

Parameter Name	Method	Units		Parameter Code					Method		Units		DP		Value			
Na		mg/l	(23-32)	6	5	3	1	1			6	2		(33-36)				
K		mg/l	(37-46)	6	5	3	1	2			6	2		(47-50)				
Mg		mg/l	(51-60)	6	5	3	1	3			6	2		(61-64)				
Ca		mg/l	(65-74)	6	5	3	1	4			6	2		(75-78)				

Parameter Name	Method	Units		Parameter Code					Method		Units		DP		Value			
Cl		mg/l	(23-32)	6	5	3	1	6			6	2		(33-36)				
NH_4-(N)		mg/l	(37-46)	6	5	3	1	8			6	2		(47-50)				
NO_3-(N)		mg/l	(51-60)	6	5	3	2	1			6	2		(61-64)				
SO_4-(S)		mg/l	(65-74)	6	5	3	2	2			6	2		(75-78)				

Parameter Name	Method	Units		Parameter Code					Method		Units		DP		Value			
Acidity	Alkaline Tit.	µeq/l	(23-32)	6	5	3	3	0	8	1	6	7		(33-36)				
Alkalinity	Alkaline Tit.	µeq/l	(37-46)	6	5	3	3	1	8	1	6	7		(47-50)				
			(51-60)											(61-64)				
			(65-74)											(75-78)				

Parameter Name	Method	Units		Parameter Code					Method		Units		DP		Value			
Cd		µg/1	(23-32)	6	5	3	3	2			6	3		(33-36)				
Pb		µg/1	(37-46)	6	5	3	3	7			6	3		(47-50)				
Cu		µg/1	(51-60)	6	5	3	3	3			6	3		(61-64)				
Zn		µg/1	(65-74)	6	5	3	3	8			6	3		(75-78)				

*(NG) Denotes National Gauge
(SG) Denotes Sampling Gauge

ANNEX V

DAILY DATA FORM

MAIL TO:

24-hour or greater sampling interval

2

Agency

Station name

Site Address

Time Interval

Area						Site			
					.				
2	3	4	5	6	7	8	9	10	

Agency	Project		Time	Year		Month		
Q	0							
11	12	13	14	15	16	17	18	

	PARAMETER	PARAMETER	PARAMETER	PARAMETER
NAME	SPM	Cd	Pb	
PARAMETER CODE	1 1 1 0 1			
	23 24 25 26 27	37 38 39 40 41	51 52 53 54 55	65 66 67 68 69
Method	7 5			
	28 29	42 43	56 57	70 71
Units	0 1			
	30 31	44 45	58 59	72 73
DP				
	32	46	60	74

Day 19 20	St 21	Hr 22	33	34	35	36	47	48	49	50	61	62	63	64	75	76	77	78
0 1																		
0 2																		
0 3																		
0 4																		
0 5																		
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2 8																		
2 9																		
3 0																		
3 1																		
	DP →		4 3	2	1	0	4 3	2	1	0	4 3	2	1	0	4 3	2	1	0

Enter Local Standard Time, 24 hour clock

Background information about each station

Name of the station: ______________________

Responsible national institute: ______________________

Full address: ______________________

____

Country: ______________ Tel. No.: ______________

Latitude: ______________ Longitude: ______________

Elevation: ______________

Distance from the nearest meteorological station: ______________

Surrounding area (agricultural land, forest, important sources, etc., if possible. If the monitoring station is within a monitoring network, this should be indicated: ______________________

____

____

____

____

____

Monitored parameters: a) at present ______________________

____

b) being planned ______________________

____

____

Available equipment: a) for sampling ______________________

____

b) for analysis ______________________

____

For selection of a background monitoring site, the following criteria should be met:

(a) Absence of local contamination sources (industrial plants, mining activities, automobile traffic, major shipping lanes),

(b) Full exposure to maritime air most of the time,

(c) Availability of power sources,

(d) Proximity of weather stations providing basic meteorological data,

(e) The number of locations of sites should conform with the requirements of the transport models used.

PART II

SCIENTIFIC PAPERS

AN OVERVIEW OF AIRBORNE POLLUTION OVER THE MEDITERRANEAN

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INTRODUCTION

It is now well recognized that a significant part of the contaminants entering the Mediterranean Sea are transported via the atmosphere. In 1985, the GESAMP* Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans concluded, on the basis of the available information, that for some elements the atmospheric inputs of pollutants are at least comparable in magnitude to riverine inputs into the Mediterranean Sea. Both local sources in the vicinity of the basin and source-areas up to thousands of kilometres away contribute to the contamination of the atmosphere and the sea. Identified contaminants of major concern are heavy metals and metalloïds, petroleum hydrocarbons, chlorinated hydrocarbons and pathogenic microorganisms. At certain times natural materials such as Saharan dusts or volcanic emissions can be important sources for some trace substances entering the Mediterranean environment.

Over the last decade, significant progress has been made in understanding the atmospheric transport and removal processes of such materials. However, although the importance of this transport path can now be inferred, the data base available is too limited to allow quantitative estimates of atmospheric fluxes to the whole Mediterranean region. Thus one of the major unresolved issues is to define the spatial and temporal variability of atmospheric concentrations and fluxes and to assess the connections with changes in weather, climate and human activity.

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* GESAMP - IMO/FAO/Unesco/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution

The factors controlling the fluctuations of concentrations and fluxes in time and space are of four types:

i) heterogeneity in geographical locations of emissions and possible changes in emission strengths on diurnal, seasonal or annual time scale;

ii) physical and chemical transformations of atmospheric trace constituents which can be homogeneous (gas phase chemistry) or heterogeneous (gas to particle conversion, gas-liquid and solid-liquid reactions);

iii) changes in mesoscale meteorological conditions which can modify the transport patterns by generating various wind-directions, diffusion and scavenging en route;

iv) variations in the efficiency of deposition processes controlled by local meteorological conditions, with both dry and wet deposition processes and rates having to be assessed (it must be emphasised that dry deposition is essentially a continuous process whereas precipitation is sporadic, particularly during summer).

In this paper, we review the current position and ongoing programmes in the Mediterranean area. The need for continuing research and monitoring efforts will be emphasized as underlined during the UNEP/WMO workshop on airborne pollution of the Mediterranean Sea held in Belgrade (Yugoslavia) from 10 to 13 November 1987.

LEVELS OF ATMOSPHERIC CONTAMINANTS OVER THE MEDITERRANEAN

Atmospheric concentrations in "hot spot" areas

All around the Mediterranean Sea there are large seaside cities and industrial sources which are strong emitters of contaminants into the atmosphere. Moreover, each of these "hot spots" must be considered as a particular case because industrial and urban activities, local topography and the micrometeorology can be completely different from one situation to another.

Relatively few studies have investigated the concentrations of contaminants and their deposition in the vicinity of these area sources. For example Gomes et al., (1988a), by using both measured concentrations and a Caussian plume model estimated the emissions of some heavy metals from the large industrial area of Fos/Berre near Marseille (France). They point out that this single area represents about 5 to 10% of the total French emissions of heavy metals as Zn, Cu, Cd. In another paper (Gomes et al., 1988b), these authors point out that the northern coast of the western Mediterranean is the main receptor area for these heavy metals, especially during northerly wind conditions (Mistral).

During the Belgrade meeting, Cvitas and Klasinc (in this issue) presented a study of the photochemical smog (with particular emphasis on ozone) in the urban area of Athens (Greece) and in the Saronikos Bay. These authors concluded that primary pollutants sometimes get carried into the Saronikos bay region where secondary pollutants can be generated under the influence of solar radiation. Moreover, such photochemical pollution can subsequently be blown back into the city by sea-breeze effects. This work which documents the occurrence of intense air pollution episodes in Athens complements previous studies on the same subject by Lalas et al., (1983) and Cvitas et al., (1985).

Obviously, it is in the vicinity of the "hot spots" that the higher levels of contaminants are observed. These two examples illustrate the importance of studying such coastal industrial or urban sources which can have direct influence on the local environment and human health. At present, new techniques are being developed to monitor some atmospheric contaminants emitted from "hot spot" areas. At the Workshop in Belgrade Cali and Palumbo (in this issue) and Nejjar (in this issue) presented remote-sensing techniques on airborne pollution studies. For example DIAL (Differential Absorption Lidar) with an emission in the UV-visible range allows measurements of atmospheric distribution and concentrations of aerosols and gases as SO_2, NO_2, I_2, H_2O as well as some meteorological parameters. With an IR emission hydrocarbons HCl, $H2_s$, NH_3 could be measured.

Atmospheric concentrations and deposition in open sea areas

The level of atmospheric contaminants over the open sea is determined by the transport of these substances from land-based emission sources. Obviously, these concentrations are significantly lower than those observed in "hot spot" areas but their impact, especially on seawater composition, is potentially significant for many trace substances such as heavy metals and synthetic organics.

In the beginning of the 1980's the PHYCEMED programme (a joint research programme organized by IFREMER* /France/ in collaboration with CNRS** and French universities) was launched in order to understand the physical, chemical and biological processes which control the air-sea exchange of contaminants and their transfer in the water column and to the sediments of the Mediterranean Sea. During two cruises mainly conducted in the western part of the Mediterranean Basin, atmospheric contaminants (Pb, Cd, As, Hg, Cu, Zn, organic compounds) were measured. Arnold (1985) and Dulac et al., (1987) concluded that drastic changes (up to one order of magnitude) can be observed in the atmospheric concentrations of contaminants in less than 48 hours. Accordingly, these authors put forward a strong case for the introduction of a long-term series of measurements which could identify the meteorological parameters and the source terms controlling such high concentrations situations.

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* IFREMER - Institut français de recherches et d'exploitation de la mer

** CNRS - Centre national de recherches scientifiques

Based on mean atmospheric concentrations and assuming certain dry and wet deposition removal rates, a first attempt to estimate the deposition of heavy metals in the western Mediterranean was made by Arnold et al., (1982), Arnold (1985) and Dulac et al., (1988). The calculations suggest that the atmospheric inputs of metals such as Pb and Cd are significantly greater than riverine inputs and other coastal effluent discharges in this part of the Mediterranean Basin.

It was however concluded that more accurate assessments of dry and wet deposition fluxes were needed in order to confirm such a diagnostic. For example, the paper presented by Dulac et al., (in this issue) assessed the contribution of the dry deposition only over the open sea by fitting size distributions of particulate contaminants obtained from cascade impactor samplings with the use of a dry deposition model (Slinn, 1983). These authors show that the dry deposition of Al, Pb and Cd in the western Mediterranean was 320, 0.52, and 0.023 mg/m2/yr respectively. By comparing with total atmospheric deposition measured in Corsica (Bergametti et al., this issue), it appears that approximately one third of the total aluminium deposition comes from dry removal process. A large part of the dry deposition of Al is controlled by the gravitational settling of large particles, especially during Saharan dust transport events.

The Italian project called EOLO (Eolian contribution to the marine sedimentation) has a similar goal but the investigated area is larger since it covers the whole basin including the Adriatic Sea. In this issue, Guerzoni et al., present the results obtained from the EOLO I and II cruises. They observe strong differences in total dust loadings between the western Mediterranean, the southern Adriatic and the eastern Mediterranean (35; 19; 51 /f/g/m3 respectively). For heavy metals, the highest concentrations are always found in the western Mediterranean while low values are observed in the eastern basin for lead and in the southern Adriatic for Zn and Cd. These concentration data are the first available for the eastern part of the basin since the work of Chester et al., (1984).

These two examples of open sea studies underline again the problem of the variability in space and time of atmospheric concentrations and deposition fluxes. More recently, long-term series measurements made in various coastal areas of the Mediterranean Sea were undertaken to provide more representative data which would be reliable from a climatological point of view.

Long-term series measurements at land based stations

As mentioned above, land-based stations are the most appropriate to assess the temporal variability of atmospheric concentrations of contaminants.

The existing WMO's BAPMON (Background Air Pollution Monitoring Network) includes stations which are of potential high interest for the understanding of the pollution of the Mediterranean region. As an example, the work presented during the workshop by Crucciani (in this issue) reports data on precipitation samples collected on a monthly basis at five Italian BAPMON stations and on a weekly basis at Messina (a station of the MEDPOL programme) and at Vigna di Valle. The procedures used allow collection of wet deposition only by using an open/close collector. Moreover, suspended particulate matter was also monitored with high volume samplers. Special attention was paid in this study to the pH of precipitations which is significantly lower than that which can be inferred from the $CO_2/HCO_3^-/CO_3^{2-}$ equilibrium. This shift is interpreted as due to temporal and spatial fluctuations of both natural and contaminant substances in rain. When available, the data on aerosol composition will enable these observations to be better understood.

A similar approach was adopted at the Hydrometeorological Institute of Croatia (Yugoslavia) through an extensive study of the chemistry of precipitation from three stations included in EMEP* and MEDPOL networks. Major ions are monitored on a daily or weekly basis using standard analytical methods. The major conclusion from data gathered over a 5-year period is that precipitation chemistry at these stations is little affected by anthropogenic emissions. This conclusion is supported by climatological considerations (wind roses patterns) which demonstrate the major influence of marine emissions and sea-spray on rain composition.

The work presented during the workshop by Morelli (in this issue) is based on measurements of bulk deposition at the Bavella Pass (South Corsica) (Löye-Pilot et al., 1986, 1987). By combining data on pH calcium enrichment in rain and red dust content with air mass trajectory analyses, these authors demonstrate the influence of Saharan dust on the acidity of rain. When there is no input of Saharan dust, pH ranges between 4.1-5.6. These low values of pH are attributed to the influence of anthropogenic European emissions of S and N compounds. The pH increases in values up to 6 or 7 during Saharan dust events is interpreted as due to the neutralization of acidic species by calcium carbonates. Another conclusion is that this atmospheric input of red dust into the western Mediterranean Sea is of the same order of magnitude as the average downstream flow of solids in the Rhone River (4.3* 106 tonnes). Consequently, they confirm the important role played by Aerolian dust in the geochemistry and sedimentology of this marine area.

The work presented by Bergametti et al. (in this issue) provides further information on the temporal variability of atmospheric concentrations and deposition of natural and anthropogenic aerosols. Over a one-year period (April 1985 - April 1986) daily aerosol samples and two-week deposition measurements were taken at a coastal station located in northwestern Corsica (Capo Cavallo). Local meteorological parameters and 3D air mass trajectories were also available. These authors showed that the atmospheric concentrations of long-range transported aerosols were subject to a seasonal cycle mainly controlled by precipitation (Bergametti et al., 1988). The atmospheric concentrations of elements such as Al, Pb, Cu and Mn are 3 to 5 times higher during summer than during winter because there is little rainfall at this time of year to scavenge the aerosol. Air mass trajectories allowed the identification of the type of transport associated with the highest concentrations.

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* EMEP: ECE/WMO/UNEP Co-operative Programme for the Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe.

Higher concentrations of atmospheric pollutants were observed during cases of transport from north to north-east, i.e. from north European countries (France, Federal Republic of Germany, Benelux, northern part of Italy), while lower concentrations were observed for episodes of transport from Africa. For crustal material (Al, Si, Fe), concentrations ten times higher were measured during Saharan dust events. As previously mentioned by Löye-Pilot et al., (1986), these events control the atmospheric fluxes of these elements into the western Mediterranean Sea.

Deposition measurements of such pollutants as lead or copper confirm a considerable influence of atmospheric input on seawater contamination in this region.

Information on the temporal and spatial deposition patterns of contaminants can also be retrieved from bio-indicators of atmospheric pollution. An example is shown of lichens, slow growing plants which absorb pollutants from the atmosphere. During the Belgrade workshop, Villeneuve et al., (in this issue), presented preliminary results concerning the chlorinated hydrocarbon concentrations deduced from lichens sampled near Monaco (France). These results showed that the concentration of chlorinated hydrocarbons in lichens collected in southern France are of the same order of magnitude as in industrial areas in Italy and Norway. The accumulation factors, calculated from lichens and atmospheric concentrations of PCB's are in the same range in south France and in Antarctica. Lichens appear to be a useful bio-indicator in studying pollution of the atmosphere both by chlorinated hydrocarbons and by radionuclides and heavy metals.

CLIMATOLOGY OF ATMOSPHERIC TRANSPORT

Evaluating the pathways of contaminants to the Mediterranean region requires a comprehensive understanding of the climatology and the meteorology of the region.

During the workshop, Dayan and Miller (in this issue) presented a summary of meteorological and climatological data necessary for the comprehensive and quantitative assessment of airborne pollution in the Mediterranean. Meteorological basic data are integrated in model calculations such as trajectories to provide more sophisticated and more usable meteorological information for geochemists and modellers. Another interesting result shown by these authors was the rainfall charts for typical months (January and July). This kind of information is essential to understand spatial and temporal variability of atmospheric wet deposition in the Mediterranean region.

Mesinger et al. (in this issue) presented a model to calculate backward air mass trajectories in order to simulate the atmospheric transport of passive substances over Europe. By comparing 3-D and 2-D trajectories, these authors pointed out significant differences between the two types. These differences depend on the vertical and horizontal shear and changes from case to case and within a case show regional variability.

Another important consideration for understanding the concentrations of contaminants in coastal areas is the micrometeorological conditions, particularly the land-sea breeze effects. Wakshal and Mahrer (in this issue) used a three-dimensional numerical model for studying the sea and land breeze circulation over the coastal area of Israel. They showed the important influence of sea and land breezes and the local topography on the transport of pollutants.

MODELLING THE TRANSPORT AND DEPOSITION PROCESSES

As underlined by GESAMP (1985) and Buat-Ménard (1986) the modelling of atmospheric transport and deposition is critical to an understanding of and thus the prediction of atmospheric pollution. Various modelling approaches are necessary to take into account the various time and space scales.

In the off-shore transport mode, it may be assumed that a considerable fraction of pollutant deposition will occur on areas relatively close to the major coastal sources. In this mode, the transport of pollutant air parcels takes place in the turbulent, relatively shallow boundary layer which is well mixed in the vertical plane. The flow is essentially two-dimensional in the horizontal plane. On such a scale, the well-known Gaussian plume model is of the most practical application since assumptions that the windfield is uniform and that the turbulence is homogeneous are approximatively valid within the boundary layer and therefore lead to a considerable simplification in the prediction of pollutant dispersion. The work by Gomes <u>et</u> <u>al</u>. (1988) is an example of such an application to a local area source located on the Mediterranean coast.

In contrast to offshore transport, long-range transport involves mechanisms that incorporate materials into the upper troposphere. The polluted air parcel eventually undergoes subsequent large-scale descent and again becomes incorporated into the boundary layer. During ascent, interactions with hydrometers can physically alter, effectively remove and vertically displace some of the trace constituents.

During the Belgrade meeting, Ivanovic (in this issue) presented a three-dimensional mathematical model of Eulerian type. The model is intended to be as general as possible to include unsteady change of concentration due to both diffusion and advection processes as well as temporal and spatial variations of the strength of the pollution sources.

Because the long-range transport of air pollutants from Europe to the Mediterranean appears potentially important, such transport models are also necessary. Nevertheless, whatever the quality of the model used, the reliability of output data will depend to a large extent on the quality of the required input data. This underlines the need to continue research efforts simultaneously in all the aspects of studying the airborne pollution of the Mediterranean Sea including measurements and modelling.

CONCLUSION

From this brief overview, it can be seen that significant progress in understanding the atmospheric pollution over the Mediterranean Sea has been made over the last few years. However, as recommended by the GESAMP working group and as emphasized during the Belgrade workshop, considerable future research and monitoring efforts are required in order to develop a comprehensive assessment of atmospheric pollution over the entire Mediterranean Basin. The detailed recommendations of the Belgrade workshop on an airborne pollution monitoring and modelling programme emphasize the need both for extensive field measurements and modelling approaches. It is essential that such an assessment of airborne pollution considers two horizontal scales: (1) local scale and (2) large scale. Also, the success of the proposed monitoring programme will require that the sampling and analytical methods among the different countries should be intercompared and if possible standardized. Finally, a central data base should be implemented by MED-POL with easy access, especially for modelling purposes. These combined efforts should allow in the near future the development of a predictive capability which would permit a better control of air quality over the Mediterranean Basin and consequently a reduction of the contamination of coastal and open sea Mediterranean waters.

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INFLUENCE DE LA GRANULOMETRIE SUR LE DEPOT SEC DES ELEMENTS TRACE DE L'AEROSOL EN MEDITERRANEE OCCIDENTALE

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RESUME

Les distributions granulométriques des éléments dans l'aérosol atmosphérique ont été déterminées pour Na, Al, Cd et Pb à partir de 17 échantillons, collectés à l'aide d'un impacteur à cascade à grand débit en Méditerranée occidentale, entre 1980 et 1983. Pour la plupart des échantillons les distributions granulométriques des particules portant ces quatre éléments sont lognormales. Le diamètre médian en masse (DMM) du Na, caractéristique des particules de sels marins, est le plus fort, avec une valeur médiane de 5,9 um. La valeur médiane pour le DMM de l'Al, caractéristique des aérosols d'origine crustale, est de 2,8 um. Les plus petits DMM sont ceux du Cd and Pb, d'origine de pollution : 0,7 um. Des vitesses de dépôt sec sont calculées à l'aide du modèle de dépôt de Slinn et Slinn (1980), en utilisant trois approches de la granulométrie des éléments : (1) en réduisant les distributions à leur seul DMM ; (2) en considérant les distributions directement fournies par l'impacteur à cascade ; (3) en discrétisant en 100 intervalles successifs les distributions ajustées à des lognormales. La première approche sous-estime les vitesses de dépôt sec. Les deux autres donnent des résultats similaires pour Cd et Pb, de l'ordre de 0,05 cm/s. Toutefois pour les quatre éléments étudiés, plus d'un cinquième du flux total de dépôt sec est dû à des particules de plus de 7,2 um de diamètre (collectées par le premier étage de l'impacteur). Pour Na et Al, la troisième méthode donne des résultats au moins un ordre de grandeur supérieur à ceux obtenus par les deux autres méthodes. Les vitesses de dépôt sec de l'Al calculées par la troisième méthode sont les plus proches des valeurs mesurées en 1985-1986 sur un site côtier au Nord-Ouest de la Corse (moyennes calculée et mesurée : 1,8 et 3,0 cm/s respectivement). Ceci met en évidence que les flux de retombées sèches des aérosols de sels marins et des aérosols d'origine crustale sont contrôlés par les plus grosses particules.

Avertissement : Cet article est une version française abrégée de Dulac et al., (1988).

INTRODUCTION

Dans un précédent article, nous avons étudié les facteurs qui influencent la variabilité des concentrations atmosphériques en Méditerranée occidentale, en combinant les informations géochimiques sur des éléments traceurs des sources naturelles et anthropiques d'aérosols (Al, Na, Br, Mn, V, Pb et Cd), et les trajectoires tridimensionnelles des masses d'air échantillonnées (Dulac et al., 1987). La connaissance des flux biogéochimiques de ces éléments dans la mer requiert une estimation quantitative de leurs apports par voie atmosphérique, et la connaissance de la variabilité temporelle de ces apports. Ceci implique de connaître les facteurs influençant les vitesses de transfert depuis l'atmosphère par voie sèche et humide. La contribution du dépôt par voie humide au flux total de retombées est généralement prépondérante pour les éléments en trace de l'atmosphère des régions océaniques (Arimoto et al., 1985; Uematsu et al., 1985; Dedeurwaerder et al., 1986). En Méditerranée occidentale aussi, le dépôt atmosphérique total des particules minérales d'origine crustale apparaît contrôlé par des évènements sporadiques, pluies rouges et brumes sèches (Loye-Pilot et al., 1986; Bergametti, 1987; Bergametti et al., 1988). Cependant, le dépôt par voie sèche est un phénomène quasi continu qui doit aussi être connu pour mesurer l'impact des apports atmosphériques sur le système marin méditerranéen, car le climat de cette région est caractérisé par de longues périodes sans précipitation (GESAMP, 1985). De plus, les temps de résidence dans les eaux de surface de certains éléments réactifs peuvent être suffisamment courts (quelques jours ou semaines; Coale and Bruland, 1985) pour que le dépôt sec contrôle leurs cycles biogéochimiques dans les eaux superficielles. Enfin la proximité des sources d'aérosol africaines doit induire des vitesses de dépôt sec plus fortes qu'au-dessus des régions de plein océan, par suite de la présence d'une fraction plus importante de grosses particules dans l'aérosol d'origine crustale.

Les flux de dépôt des éléments sont généralement calculés à partir de leurs concentrations atmosphériques, à cause de la difficulté à réaliser des mesures directes en mer (Hicks et al., 1980). Bien qu'il existe déjà des modèles du dépôt sec des particules à la surface de l'eau, la connaissance des processus mis en jeu est encore imparfaite (Slinn, 1983). Dans cet article, nous présentons des résultats de calcul et quelques mesures des flux et des vitesses dépôt sec d'éléments en traces de l'atmosphère en Méditerranée occidentale, dans le but de montrer la sensibilité des résultats aux distributions granulométriques des éléments dans l'aérosol. Les flux de dépôt sec d'Al, Cd, Na et Pb ont été calculés à partir du modèle de dépôt sec de Slinn and Slinn (1980), appliqué à nos données sur les concentrations atmosphériques des éléments en fonction de la taille des particules (Dulac, 1986; Dulac et al., 1987).

ECHANTILLONNAGE ET METHODES D'ANALYSE

Dix-sept échantillons de l'aérosol séparé en classes de tailles ont été collectés dans toute la Méditerranée occidentale, à l'occasion de 4 campagnes entre septembre 1980 et octobre 1983. La localisation des différents échantillons est reportée sur la Figure 1. Les prélèvements ont duré entre 1 et 5 jours, et ont été effectués en haut d'une tour à l'avant du navire, sur des filtres WHATMAN ® 41, à l'aide d'un impacteur à cascade modèle SIERRA ® 235. Il s'agit d'un impacteur à fentes rectangulaires à 5 étages d'impaction, opérant à grand débit d'air. Au débit nominal de 68 m^3/h, les diamètres de coupure sont les suivants, de l'étage 1 à l'étage 5 : 7,2; 3; 1,5; 0,95; 0,49 um (Knuth, 1979). Le diamètre de coupure est considéré comme la limite inférieure de taille des particules recueillies sur un étage donné. Un filtre final collecte les plus petite particules. Les volumes d'air échantillonnés sont compris entre 1000 et 4000 m^3. Les concentrations élémentaires totales déterminées à partir de cet échantillonneur sont comparables aux concentrations déterminées à partir de filtres totaux effectués parallèlement (Dulac, 1986). Treize autres échantillons d'impacteur ont été collectés entre février 1985 et avril 1986, en haut d'une tour météorologique de 10m située au Cap Cavallo, sur la côte nord-ouest de la Corse (Fig. 1). Ce site d'échantillonnage est en vue directe de la mer, à 700m du rivage et à environ 300m d'altitude. Trente échantillons de 9 à 21 jours de dépôt atmosphérique total ont aussi été collectés sur ce site, à l'aide d'un collecteur de type C.R.A.P.A.L. (Lambert and Nezami, 1965; Bergametti, 1987). Il s'agit d'un collecteur hémisphérique en plexiglass de 0,1 m^2 de surface, avec un col de 10 cm de hauteur, recouvert par un filet de nylon de maille 1mm. La base du collecteur est reliée à un récipient en polyéthylène lavé à l'acide, contenant 0,5 l d'eau désionisée Milli-Q ®, acidifiée à pH 1 avec du HNO_3 suprapur. Le récipient est maintenu à l'obscurité durant la période d'échantillonnage, et changé tous les 10 jours environ. Avant le changement de récipient, le collecteur est soigneusement rincé avec 0,5 l supplémentaire de la solution de HNO_3. Les solutions ainsi recueillies sont filtrées au laboratoire en atmosphère contrôlée sur filtre NUCLEPORE ® de porosité 0,4 um, et un dosage de Al est effectué dans les fractions particulaire et dissoute. Cinq de ces échantillons de dépôt total ont été obtenus durant des périodes sans précipitation (en juillet et septembre 1985, et mars 1986).

Les échantillons obtenus en mer ont été analysés par spectrométrie d'absorption atomique à flamme et au four (Na, Al, Pb et Cd) et par activation neutronique instrumentale (Na et Al). Les procédures d'analyse ont déjà été décrites (Dulac, 1986; Delmas et al., 1987; Dulac et al., 1987). Le dosage d'Al dans les échantillons d'impacteur de Corse, et dans la fraction particulaire des échantillons de dépôt total a été effectué par fluorescence X (Elichegaray et al., 1982; Bergametti, 1987). La fraction d'Al dissous dans les échantillons de dépôt total a été dosée par spectrométrie d'absorption atomique au four. La précision des mesures est typiquement de ±10% en absorption atomique, et de ±5% en activation neutronique et en fluorescence X.

DISTRIBUTION GRANULOMETRIQUE DES ELEMENTS

Les flux de retombées sèches des éléments ont été souvent calculés dans le passé en utilisant uniquement la vitesse de dépôt des particules ayant pour taille le diamètre médian en masse (DMM) de leur distribution granulométrique, le DMM étant le diamètre tel que les deux fractions de particules plus petites et plus grosses portent chacunes 50% de la masse de l'élément. Il a été depuis reconnu essentiel de prendre en compte la dispersion de la granulométrie des particules qui portent les éléments, et de calculer leurs flux de dépôt comme la somme des flux partiels correspondants à différentes classes de taille des particules (McDonald et al., 1982; Meszaros, 1982; Dedeurwaerder et al., 1986; Arimoto et al., 1985; Arimoto and Duce, 1986). Les distributions granulométriques des éléments sont généralement tirées d'échantillons obtenus par des impacteurs à cascade, car leur mesure à partir d'échantillons réels de dépôt sec sur des surfaces artificielles n'est pas possible.

Nous avons utilisé trois méthodes différentes pour prendre en compte la granulométrie des éléments dans les calculs de flux de retombées sèches, et pour tester leur influence sur les résultats. La méthode la plus simple est de considérer la distribution discrète directement tirée de l'impacteur ("méthode à 6 intervalles") (McDonald et al., 1982; Dedeurwaerder et al., 1986). Les deux autres méthodes reposent sur l'ajustement de cette distribution discrète à une distribution continue par une méthode de régression. Une méthode simplifiée consiste à réduire la distribution à son seul DMM ("méthode à 1 intervalle"). Une méthode plus sophistiquée consiste à rediscrétiser cette distribution ajustée, mais en 100 intervalles de taille ("méthode à 100 intervalles"), chacun de ces intervalles portant 1% de la masse totale de l'élément, et étant caractérisé par le diamètre en son centre ($D_{0,5\%}$; $D_{1,5\%}$; ... $D_{99,5\%}$; Arimoto et al., 1985). Les distributions de la masse élémentaire des éléments en fonction de la taille des particules ont été ajustées à des lognormales monomodales. Ce type de distribution a déjà été validé pour les particules atmosphériques, de sels marins (Na, Cl) (Woodcock, 1953), d'origine crustale (Al) (Patterson and Gillette, 1977; Buat-Ménard et al., 1983), de sulfates (S) (Whitby, 1978) et de Pb-210 (Arimoto and Duce, 1986). L'ajustement fournit pour chaque distribution un DMM et un écart-type (sigma), qui suffisent à la caractériser. Le détail de la méthode d'ajustement a été publié ailleurs (Dulac, 1986; Dulac et al., 1988).

CALCUL DES FLUX DE DEPOT SEC

Le flux (F) de dépôt sec d'un élément peut s'exprimer comme le produit de la concentration atmosphérique (C) de l'élément par sa vitesse de dépôt (V): $F = C.V$. Quelques mesures de vitesses de dépôt sec ont été obtenues à partir d'expériences en soufflerie (Möller and Schumann, 1970; Sehmel and Sutter, 1974; Little and Wiffen, 1977) mais les mesures directes effectuées au-dessus des étendues d'eau naturelles sont assez controversées (Wesely and Williams, 1981; Sievering et al., 1982). C'est pourquoi ces vitesses sont généralement calculées à l'aide de modèles mathématiques (Slinn et al., 1978; Sehmel, 1980; Slinn and Slinn, 1980; Williams, 1982), bien que d'importantes incertitudes demeurent (Slinn, 1983; Sievering, 1984), en particulier pour les particules submicroniques (Arimoto and Duce, 1986).

Nous avons calculé les vitesses de dépôt sec des éléments en utilisant le modèle de Slinn et Slinn (1980) de dépôt des particules sur les surfaces d'eau naturelles. En résumé, ce modèle fait l'hypothèse de deux couches au-dessus de la surface de l'eau. Dans la couche supérieure (environ 10 m de haut), le flux des particules est gouverné par la sédimentation gravitationnelle et la turbulence. Le dépôt à l'interface air-mer se situe dans une couche visqueuse sous-jacente dans laquelle la turbulence est négligeable. Dans cette couche, les particules hygroscopiques peuvent croître par absorption d'humidité. Le modèle considère un état stationnaire (flux constant et croissance instantanée des particules hygroscopiques à leur taille d'équilibre lorsqu'elles pénètrent dans la couche inférieure) et suppose les particules sphériques. Il ne prend pas en compte la réémission des particules par la surface de la mer (Fairall and Larsen, 1984). Des corrections pour prendre en compte la capture des particules par les vagues qui se brisent et par la formation de gros aérosols de sels marins ont été déjà proposées (Williams, 1982) et discutées (Slinn, 1983). Elles n'ont pas été considérées ici, bien que les différences puissent être significatives pour les particules submicroniques (Arimoto and Duce, 1986). Le détail des équations utilisées a été publié ailleurs (Dulac, 1986; Dulac <u>et</u> <u>al</u>., 1988). La vitesse moyenne du vent pendant chaque échantillonnage a été considérée. Nous avons utilisé un coefficient de traînée constant de 0,0013, qui correspond à une atmosphère en état de stabilité neutre et à un vent stable à 10 m au-dessus de l'eau (Krauss, 1972). Le taux d'évaporation d'eau a été supposé nul, et la densité des particules hydrophobes (de taille constante) de 2,5. L'humidité relative dans les couches supérieure et inférieure du modèle a été supposée de 75 et 90% respectivement. Dans ces conditions, la densité des particules de NaCl est respectivement de 2,1 (état sec) et 1,1 (Eriksson, 1959). D'après Fitzgerald (1975) leur diamètre à l'équilibre (Dh) s'exprime en fonction de leur diamètre à l'état sec (Ds) par:

$$Dh = 2,3489 \, . \, Ds^{1,00638}$$

Les calculs ont été conduits pour Na, Al, Pb et Cd, en suposant Al porté par des particules minérales hydrophobes, et Na, Pb et Cd par des particules hygroscopiques de type NaCl.

A partir des vitesses de dépôt sec calculées (Vd) et des concentrations élémentaires (C) mesurées à partir des échantillons d'impacteurs collectés en mer, les flux de dépôt sec de Na, Al, Cd et Pb ont été calculés comme suit :

1) <u>méthode à 1 intervalle</u> : $F_1 = C \, . \, K(\mathrm{sigma}) \, . \, Vd(DMM)$

avec : $K(\mathrm{sigma}) = \mathrm{sigma}^{2 \, . \, \mathrm{Ln(sigma)}}$
K(sigma) est ≥ 1; le produit K(sigma) . Vd(DMM) est la vitesse de dépôt correspondant au flux moyen (Slinn, 1983).

2) <u>méthode à 6 intervalles</u> : $F_6 = \Sigma_{i=1 \text{ à } 6} \, C_i \, . \, Vd(D_i)$

avec : D_1 = 10 µm; D_2 = 5 µm; D_3 = 2,5 µm; D_4 = 1,25 µm; D_5 = 0,75 µm; et D_6 = 0,25 µm (respectivement étage 1 à 5 et filtre final de l'impacteur).

3) méthode à 100 intervalles : $F_{100}=(C / 100) . \Sigma_{i=0,5 \text{ à } 99,5} Vd(D_i)$

où D_i est le diamètre médian de l'intervalle de taille des particules portant le ième % de la masse cumulée de la distribution lognormale.

RESULTATS

Les concentrations par étage, de Al, Na, Cd et Pb, tirées des 17 échantillons d'impacteur collectés en mer ont été publiées dans Dulac (1986) et résumées dans Dulac et al. (1987). Les éléments étant présents sur tous les étages d'impacteur sont, compte tenu des courbes d'efficacité d'impaction (Knuth, 1979), portés par des particules présentant de larges distributions continues en diamètre. L'ajustement à une lognormale monomodale a un niveau de probabilité de 99% pour 40 des distributions granulométriques (8 de Na, 13 d'Al, 11 de Pb et 8 de Cd) sur les 47 disponibles. Les 7 autres distributions ont été écartées des calculs suivants. Un résumé des paramètres (DMM et sigma) de ces distributions ajustées de manière satisfaisante est donné au Tableau 1. Au Tableau 2 se trouvent les concentrations atmosphériques et les flux de dépôt sec moyens. Les profils moyens en fonction de la granulométrie, des distributions ajustées, et des flux de dépôt sec sont donnés à la Figure 2. La Figure 3 montre la comparaison des flux de dépôt sec calculés en utilisant les 3 méthodes décrites précédemment.

Les concentrations par étage d'Al, tirées des 13 échantillons d'impacteur collectés en Corse figurent dans Bergametti (1987). Ces 13 distributions granulométriques d'Al présentent aussi une probabilité d'ajustement de 99%. Le DMM moyen de ces distributions est de 2,3 ±0,4 µm. Dans le présent travail, les calculs de flux n'ont pas été appliqués à ces échantillons.

DISCUSSION

Diamètres médians en masse

La variabilité observée pour les DMM (Tab. 1) est la plus faible pour Na (facteur 2,3) et la plus forte pour Cd (facteur 4,2). Les DMM observés à Eniwetok (Tab. 1) semblent moins variables. De même les concentrations élémentaires sont plus stables au-dessus du plein océan Pacifique (Buat-Ménard et al., 1983; Arimoto et al., 1985) qu'au-dessus de la Méditerranée (Dulac et al., 1987).

La comparaison des DMM observés au-dessus de la Méditerranée et à Eniwetok montre aussi que le DMM de Na est plus grand dans le Pacifique. Ceci est imputable aux vitesses moyennes de vent importantes observées à Eniwetok, 9-10 m/s (Arimoto et al., 1985), comparées à environ 5 m/s pendant l'échantillonnage en méditerranée.

Au contraire, le DMM de l'Al est de 50% plus grand pour les échantillons méditerranéens que pour les échantillons du Pacifique. Ceci doit être dû à la proximité des sources continentales de particules en Méditerranée, qui influence aussi le niveau des concentrations atmosphériques élémentaires (Dulac et al., 1987). En effet les échantillons montrant un DMM de l'Al supérieur à 3,5 µm ont généralement été obtenus près des côtes africaines (échantillons) 5, 8, 9 et 12; Fig. 1), et correspondent aux plus fortes concentrations atmosphériques d'Al (≥ 500 ng/m^3). L'analyse des trajectoires de masses d'air (Dulac, 1986; Dulac et al., 1987) a montré que durant toutes les périodes d'échantillonnage correspondantes, et seulement durant celles-ci, des transports depuis l'Afrique ont eu lieu. Cependant, les DMM de l'Al observés en Corse durant deux tels épisodes d'apports de poussières sont de 2,0 et 2,3 µm, et par conséquent ne diffèrent pas des autres valeurs observées sur le même site (2,3 ±0,4 µm). Ceci suggère une décroissance du DMM durant le transport des aérosols depuis l'Afrique, probablement due à la sédimentation gravitationnelle en route de la fraction grossière des particules. D'ailleurs le DMM moyen de l'Al en Corse (2,3 µm), à environ 1000 km des côtes africaines, est à peine plus grand que le DMM observé à Eniwetok (2,0 µm), à environ 5000 km des sources continentales de particules. Ces observations sont en accord avec les calculs de Schütz (1979), qui prédisent que la fraction grossière de l'aérosol pendant des évènements de transport de poussières détritiques éoliennes en Atlantique tropical doit sédimenter durant les premiers 1500 km du transport, et qu'au delà la décroissance du DMM est tout à fait limitée.

Etant donné la proximité des sources continentales de particules, il peut sembler paradoxal que le DMM du Pb est plus faible en Méditerranée qu'à Eniwetok (Tab. 2). En fait ceci s'explique par le fait que la moitié des retombées sèches de Pb à Eniwetok est due à un recyclage de Pb à partir de la microcouche de surface de la mer, par des particules de sels marins de diamètre supérieur à 7,2 µm (Settle and Paterson, 1982; Arimoto et al., 1985), alors que cette composante est négligeable en Méditerranée occidentale (Dulac et al., 1987).

Flux de dépôt sec

La comparaison entre les flux de dépôt sec calculés par les 3 différentes approches montre que la méthode à 100 intervalles donne généralement les plus fortes valeurs, et la méthode à 1 intervalle les plus faibles (Fig. 3). De plus, les domaines de variations des résultats montrent que la méthode à 100 intervalles induit une variabilité des flux beaucoup plus grande que les deux autres méthodes, en particulier pour Na et Al qui présentent les plus fortes valeurs de flux de dépôt. La variabilité des flux des éléments de pollution Pb et Cd, qui sont portés par de plus petites particules, est beaucoups plus faible.

Les plus fortes valeurs obtenues en utilisant la méthode à 100 intervalles démontrent l'importance de la fraction des plus grosses particules sur le dépôt sec. En effet, le dernier % de la distribution en masse cumulée est en général composé de particules de plus de 10 µm de diamètre, et parfois de plus de 100 µm dans le cas de Al et Na (Tab. 3), dont les vitesses de chute par gravité sont très importantes

(> 10 cm/s). Ceci est illustré par les résultats concernant la contribution des plus grosses particules aux concentrations atmosphériques et aux flux de dépôt sec (calculés en utilisant la méthode à 100 intervalles) présentés au Tableau 3 et à la Figure 2. Les particules de plus de 7,2 µm représentent respectivement 10 à 40 et 20 à 60% de la charge atmosphérique de Al et Na, mais sont responsables d'environ 90% des flux de dépôt sec. Et, bien que ces grosses particules portent moins de 10% du Pb et du Cd atmosphériques, elles sont en moyenne responsables de plus de 20% du dépôt sec de Pb, et de 30% du dépôt sec de Cd (Fig. 2). Ces résultats sont en accord avec ceux obtenus sur l'atoll d'Eniwetok (Arimoto et al., 1985; Arimoto et Duce, 1986). Mais il apparaît de plus dans le Tableau 3 que les plus grosses particules portant le dernier % de la masse atmosphérique des éléments, sont responsables de 20 à 35% des flux de dépôt sec de tous les éléments considérés (Tab. 3). Il est donc clair que des calculs précis des flux de dépôt sec recquièrent une parfaite connaissance des distributions des masses élémentaires en fonction de la taille des particules.

Nous avons effectué des calculs comparatifs pour des conditions météorologiques et d'échantillonnage moyennes. Ils montrent que l'écart-type des distributions masse-taille, qui mesure leur étendue, est le paramètre le plus critique pour le calcul des flux. En effet, si le DMM de la distribution est multiplié par 2, toutes conditions égales par ailleurs, le flux résultant est multiplié par 4. Mais celui-ci augmente d'un facteur 50 si l'écart-type de la distribution passe de 1 à 2. Une telle sensibilité induit de grandes incertitudes sur les flux de dépôt calculés précédemment, d'autant plus que le nombre de points expérimentaux des distributions fournis par l'impacteur est plutôt limité. Dans la mesure où un seul étage échantillonne les particules de plus de 7,2 µm de diamètre, l'ajustement des distributions de Na et Al au-delà de cette taille est particulièrement problématique.

Cependant, pour ces deux éléments, Arimoto et al. (1985) ont vérifié que les flux de dépôt sec mesurés sur une surface de plastique sont comparables, à un facteur 3 près, aux flux calculés en utilisant la méthode à 100 intervalles, même dans le cas de DMM de plus de 10 µm. Un tel accord permet de valider la méthode de description de la granulométrie par les 100 intervalles. En ce qui concerne le présent travail, les mesures des retombées sèches d'Al effectuées en Corse à partir des 5 échantillons de dépôt total effectués en période sans précipitation, confirment également les résultats obtenus par la méthode à 100 intervalles (Tab. 4). De plus, l'examen en microscopie electronique à balayage d'échantillons atmosphériques corses a confirmé la présence de grandes particules minérales, de plusieurs dizaines de microns de diamètre dont la contribution au flux de dépôt sec doit être prédominante (Dulac et al., 1988). La présence de telles particules transportées depuis l'Afrique a déjà été observée aux Barbades (Prospero et al., 1970).

Ces considérations montrent que l'utilisation seule de la vitesse de dépôt sec correspondant au DMM des éléments (méthode à 1 intervalle) est assurément inadéquate pour des calculs réalistes de flux de dépôt sec, et que les distributions granulométriques doivent être considérées dans leur totalité. Pour les éléments de pollution tels que Pb et Cd, les flux de dépôt sec calculés en utilisant la méthode à 6 intervalles sont grossièrement comparables aux flux calculés à partir de la méthode à 100 intervalles. Compte tenu de toutes les incertitudes liées à ces calculs de flux, nous pouvons conclure que les valeurs simplement calculées à partir des distributions expérimentales non ajustées (méthode à 6 intervalles) fournissent l'ordre de grandeur des flux de retombées sèches de ces éléments.

Vitesses de dépôt sec

Au Tableau 5 sont résumés les résultats de calcul des vitesses de dépôt sec élémentaires apparentes (Vd*), déduites des calculs de flux par la relation:

$$Vd^* = F_{100} / C$$

La vitesse apparente de dépôt sec du Na varie entre 1 et 9 cm/s, à l'exception d'une valeur exceptionnellement forte d'environ 2 m/s, qui correspond à un DMM inhabituel de 10,8 µm. Un tel DMM n'est pas irréaliste, mais dans ce cas l'ajustement à une lognormale implique l'existence de particules atmosphériques de plus de 1mm de diamètre et peut être mis en doute : bien que la probabilité de l'ajustement est supérieure à 99,9%, il ne porte que sur une fraction faible de la distribution, puisque peut-être près de la moitié de la masse totale de Na de cet échantillon, constituée par des particules de diamètre > 10,8 µm, n'a pas été recueillie par l'impacteur.

La vitesse apparent de dépôt sec de l'Al est aussi de l'ordre du cm/s, et varie entre 0,2 et 10 cm/s. Outre ces grandes variations, il y a une séparation nette entre les périodes de fortes concentrations de poussières minérales et la situation de fond, la vitesse moyenne apparente étant respectivement de 3,9 et 0,87 cm/s. De telles variations sont probablement à relier aux fortes variations parallèles du DMM de l'Al: les moyennes correspondantes ± les écart-types sont de 4,5 ± 0,7 et 2,5 ± 0,5 µm respectivement. Une telle variabilité suggère que la forte influence des épisodes de transport de poussières africaines sur les concentrations atmosphériques d'Al est encore plus forte sur les flux de dépôt sec. Enfin cela montre à nouveau la nécessité d'appréhender correctement les distributions granulométriques d'Al et Na. Les vitesses de dépôt sec d'Al mesurées à partir des échantillons d'aérosols et de dépôt effectués en Corse sont aussi données au Tableau 5. Les valeurs observées varient entre 1,3 et 6,9 cm/s, et confirment donc les valeurs calculées.

Malgré la présence d'une fraction non négligeable de Pb et Cd sur la fraction grossière de l'aérosol (Fig. 2), les vitesses apparentes de dépôt sec calculées pour ces éléments sont d'un ordre de grandeur inférieures à celles de Al ou Na, généralement inférieures à 0,1 cm/s (Tab. 5). L'étendue des distributions granulométriques de Pb et Cd vers les plus grosses particules est inférieure à celle d'Al et Na (cf. $D_{95\%}$ et $D_{99\%}$, Tab. 3) et ceci se traduit clairement au niveau des vitesses de dépôt sec apparentes.

CONCLUSIONS

Trois méthodes différentes pour décrire la répartition de la masse des éléments en fonction de la taille des particules atmosphériques, ont été utilisées pour calculer les flux de dépôt sec des éléments en Méditerranée occidentale. La comparaison des résultats montre le rôle majeur joué par les grosses particules (D > 7,2 µm). Les vitesses de dépôt sec de l'Al calculées par la troisième méthode, qui consiste à calculer la somme des flux partiels dus aux particules issues de 100 intervalles de taille successifs de distributions lognormales, sont proches des valeurs mesurées en Corse. Les flux moyens journaliers de dépôt sec des éléments calculés par cette méthode (Tab. 1) permettent donc d'estimer les flux moyens à l'échelle de l'année. Sur la base de 360 jours de dépôt sec, les retombées annuelles par m^2 en Méditerranée occidentale seraient de 320 mg d'Al, 0,52 mg de Pb et 0,023 mg de Cd. La quantité totale d'Al recueillie durant un an de collecte du dépôt atmosphérique total en Corse est de 970 mg/m^2. Par comparaison, le dépôt sec serait responsable d'un tiers des retombées totales d'Al en Méditerrannée occidentale. Cette fraction est deux fois plus forte que celle déterminée en plein océan Pacifique (Arimoto et al., 1985), et ceci confirme l'influence de la proximité des sources africaines sur le dépôt sec de l'Al en Méditerranée occidentale.

REMERCIEMENTS

Nous tenons à remercier les équipages des N.O. Le Noroît, Le Suroît et Le Cornide de Savedra, ainsi que le personnel du sémaphore de Cap Cavallo pour leur aide durant les campagnes de prélèvements. Nous remercions également la Marine Nationale qui nous a accordé l'accès au sémaphore, et la Direction de la Météorologie Nationale, ministère des Transports, qui nous a permis d'utiliser la tour météorologique de Cap Cavallo. Nous sommes reconnaissants de l'assistance fournie par le Laboratoire Pierre Süe d'Analyse par Activation de Saclay. Ce travail a été financé par le Centre National de la Recherche Scientifique, le Commissariat à l'Energie Atomique et IFREMER.

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Tableau 1

Diamètres médians en masse (DMM) en Méditerranée et à Eniwetok.
Sigma est l'écart-type des distributions lognormales ajustées,
et N le nombre de valeurs

ELEMENT	MEDITERRANEEE OCCIDENTALE					ENIWETOK*	
	EXTREMES		N	DMM, Médiane (µm)	DMM, Moyenne géométrique (µm)		N
	DMM (µm)	Sigma					
Na	4,6-10,8	0,6-1,9	8	5,9	6,3	8,6*	4*
Al	1,9- 5,2	0,6-1,6	13	2,8	2,9	2,0*	4*
Cd	0,5- 2,1	0,5-1,6	8	0,68	0,82	-	-
Pb	0,4- 0,9	0,6-1,2	11	0,69	0,61	0,8*	4*

* *Pacifique nord tropical; Arimoto et al., (1985)*

Tableau 2

Concentrations atmosphériques et flux de dépôt sec moyens.

ELEMENT	CONCENTRATION MOYENNE° (ng m^{-3})	FLUX DE DEPOT SEC MOYEN* (µg m^{-2} j^{-1})	NOMBRE D'ECHANTILLONS
Na	1400	30000	8
Al	340	870	13
Pb	44	1,45	11
Cd	0,66	0,064	8

• moyenne des concentrations totales, sommes des 6 étages d'impacteur

* flux calculés à l'aide de la méthode à 100 intervalles de taille (cf. texte)

Tableau 3

Contributions (en %) des plus grosses particules à la charge atmosphérique totale et au flux de dépôt sec de Na, Al, Cd et Pb.

ELEMENT	DOMAINE DE TAILLE DES PARTICULES	CONTRIBUTION A LA CHARGE ATMOSPHERIQUE		CONTRIBUTION AU FLUX DE DEPOT SEC°	
		Extrêmes	Moyenne	Extrêmes	Moyenne
Na	* D> 7,2 µm	22-59	43	60-100	90
	** D> $D_{95\%}$ (68 µm)	-	5	23-92	57
	*** D> $D_{99\%}$ (273 µm)	-	1	7-65	31
Al	D> 7,2 µm	10-42	24	49-100	87
	D> $D_{95\%}$ (25 µm)	-	5	32-83	66
	D> $D_{99\%}$ (81 µm)	-	1	11-53	35
Cd	D> 7,2 µm	0- 8	3,5	0-84	32
	D> $D_{95\%}$ (5,7 µm)	-	5	19-76	48
	D> $D_{99\%}$ (16 µm)	-	1	6-53	23
Pb	D> 7,2 µm	0- 2	1	0-40	23
	D> $D_{95\%}$ (3,7 µm)	-	5	26-64	52
	D> $D_{99\%}$ (9,5 µm)	-	1	8-30	22

° flux calculés à l'aide de la méthode à 100 intervalles de taille (cf. texte)

* correspond aux particules collectées par l'étage 1 de l'impacteur à cascade

** particules formant les 5 derniers % de la distribution cumulée en masse ($D_{95,5\%}$ moyen)

*** particules formant le dernier % de la distribution cumulée en masse ($D_{99,5\%}$ moyen)

Tableau 4

Flux de dépôt sec des éléments en Méditerranée occidentale.

ELEMENT	UNITE	EXTREMES	MOYENNE	NOMBRE DE VALEURS
Na*	mg/m^2/j	0,4- 208	30	8
		0,4- 15^	4,6	7^
Al*	µg/m^2/j	17 -6550	870	13
Al°	µg/m^2/j	390 -2700	1090	5
Cd*	ng/m^2/j	0,2- 175	64	8
Pb*	ng/m^2/j	460 -2400	1450	11

* calculs à l'aide du modèle de dépôt sec de Slinn and Slinn (1980), appliqué à des distributions masse-taille lognormales discrétisées en 100 intervalles de taille

° mesures au site de Cap Cavallo, Corse

^ résultats de la ligne précédente, la valeur de 208 mg/m^2/j exceptée

Tableau 5

Vitesses apparentes de dépôt sec des éléments (cm/s)
en Méditerranée occidentale.

ELEMENT	EXTREMES	MEDIANE	MOYENNE PONDEREE+	ECART-TYPE	NOMBRE DE VALEURS
Na*	0,93-190	2,50	20,2	267 %	8
	0,93-8,7^	2,26	3,2	89 %	7^
Al*	0,18-9,7	0,69	1,8	140 %	13
Al≤ 260 ng/m^3	0,18-2,6	0,49	0,87	100 %	9
Al≥ 500 ng/m^3	1,07-9,7	3,1	3,9	91 %	4
Al°	1,3-6,9	3,8	3,0	59 %	5
Cd*	0,0074-0,33	0,053	0,13	100 %	8
Pb*	0,020-0,068	0,041	0,043	40 %	11

\+ par les durées d'échantillonnage

* calculs à l'aide du modèle de dépôt sec de Slinn and Slinn (1980), appliqué à des distributions masse-taille lognormales discrétisées en 100 intervalles de taille

° mesures au site de Cap Cavallo, Corse

^ résultats de la ligne précédente, la valeur de 190 cm/s exceptée

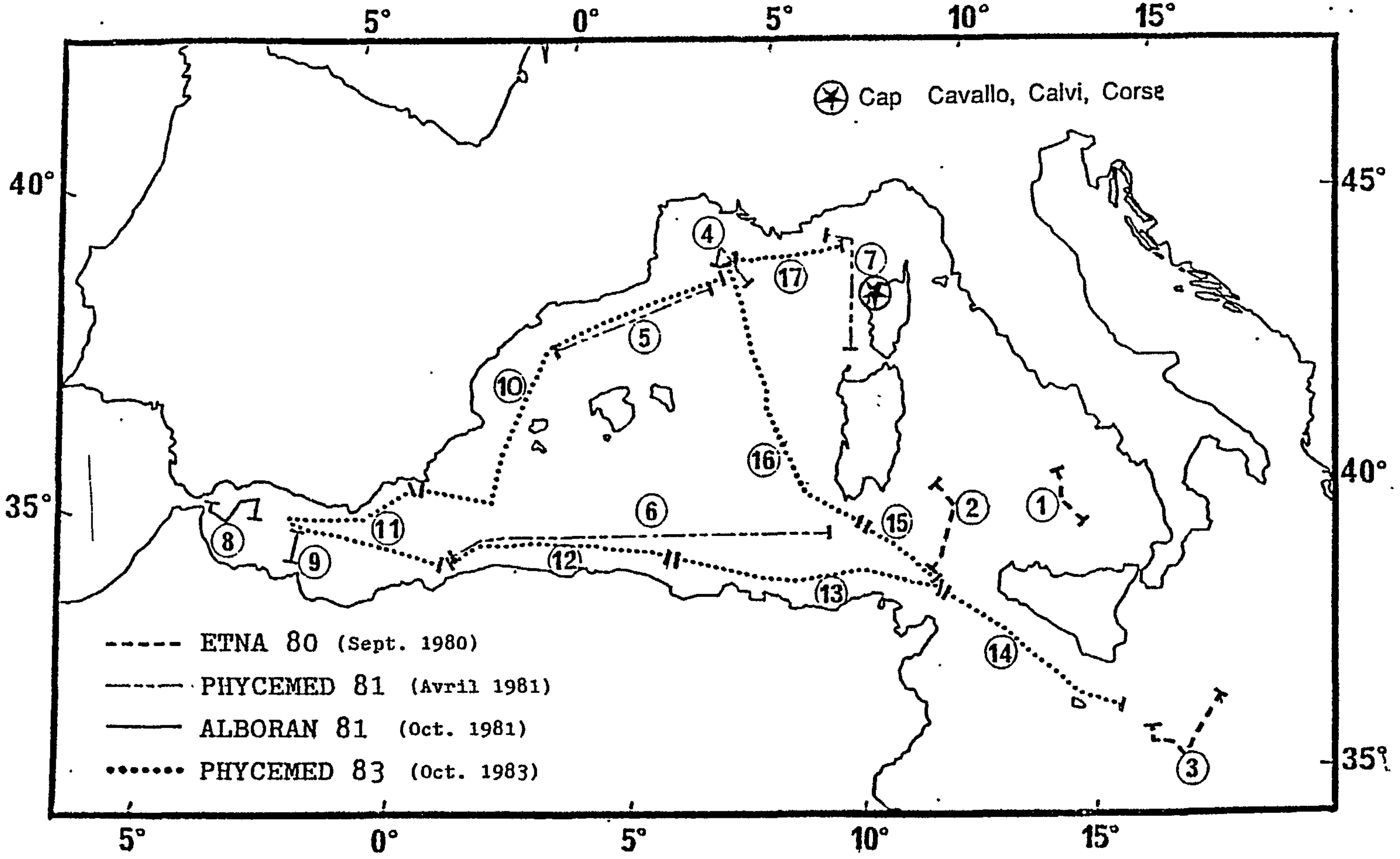
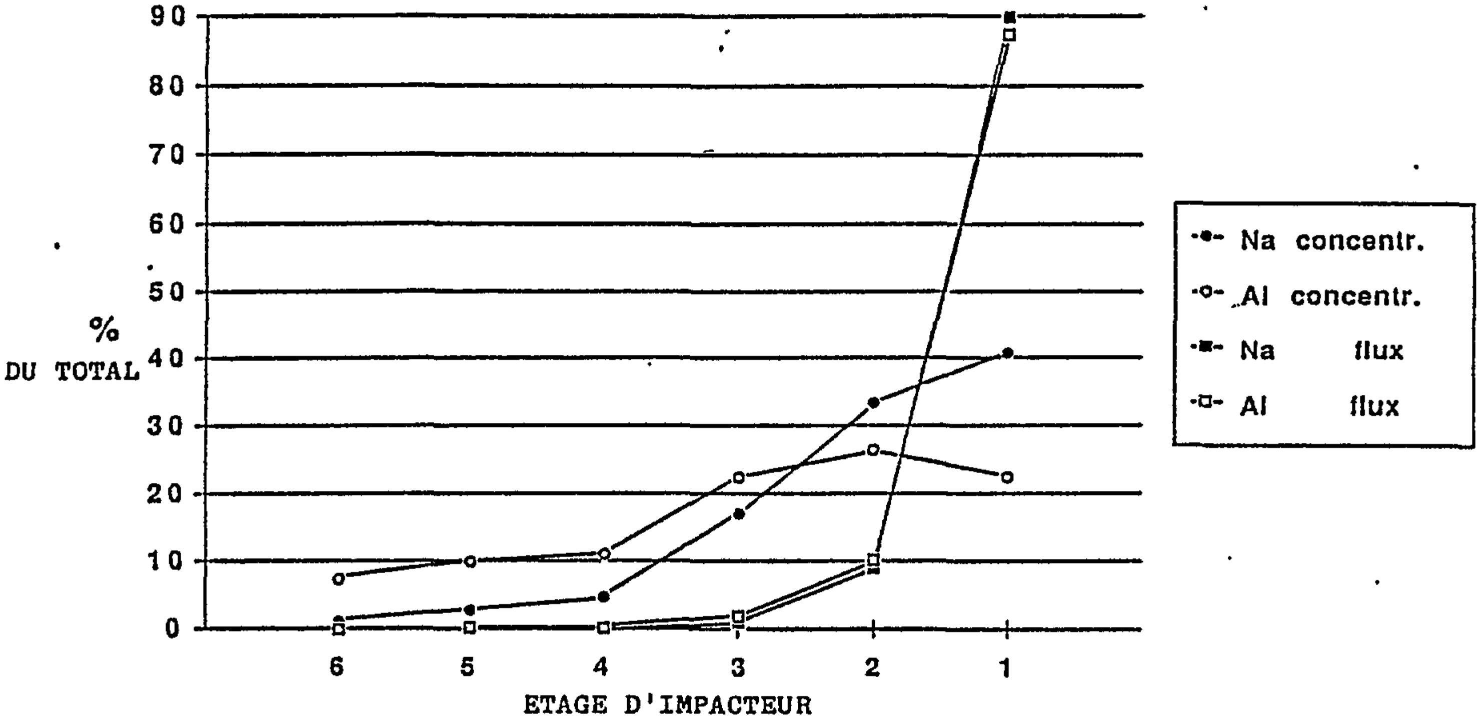


Fig. 1 - Localisation des échantillons en Méditerranée occidentale



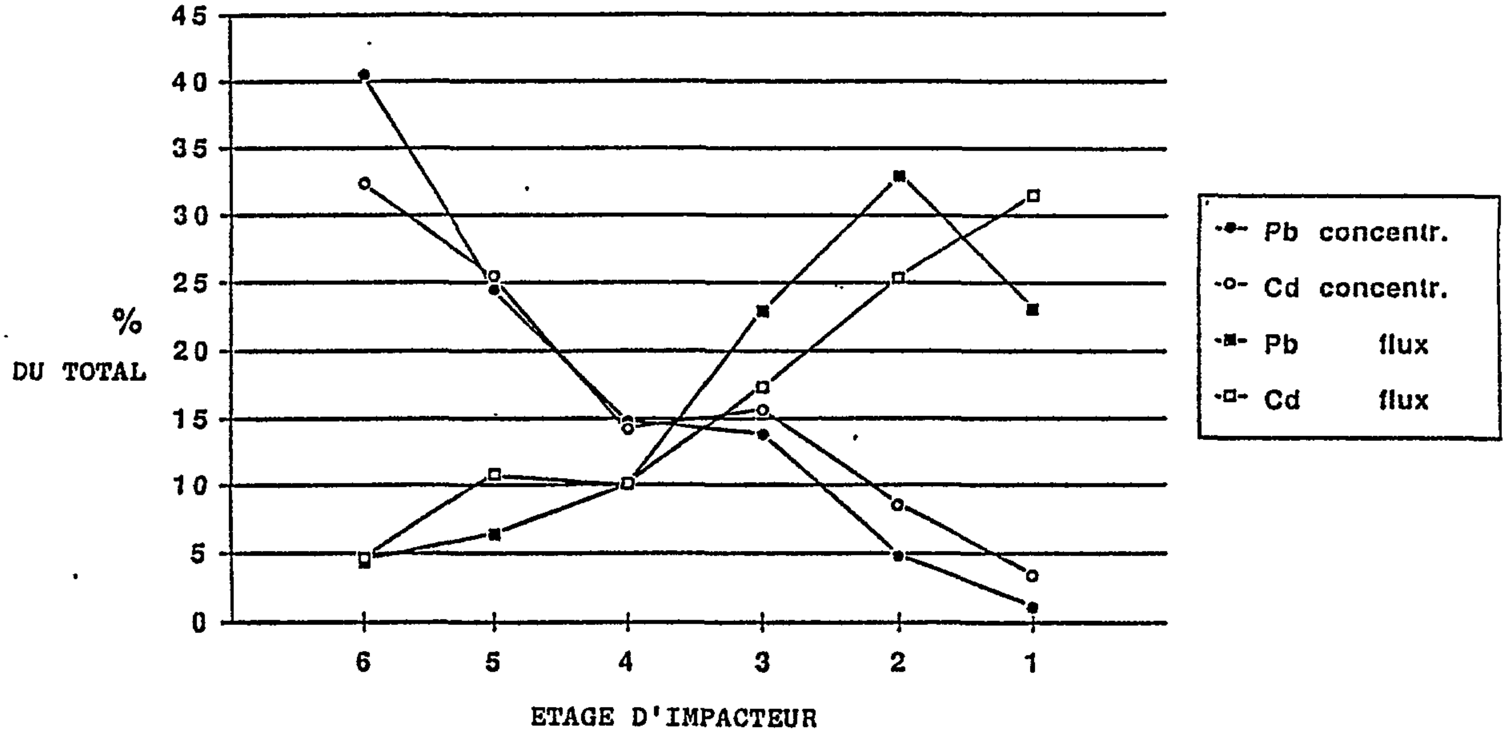


Fig. 2 - Influence des distributions masse-taille sur les concentrations atmosphériques, et les flux de dépôt sec calculés (voir valeurs moyennes en Tab. 1).
Classes de diamètre des particules, de l'étage 1 à 6:
7,2 µm; 3-7,2 µm; 1,5-3 µm; 0.95-1,5 µm; 0,49-0,95 µm; 0,49 µm

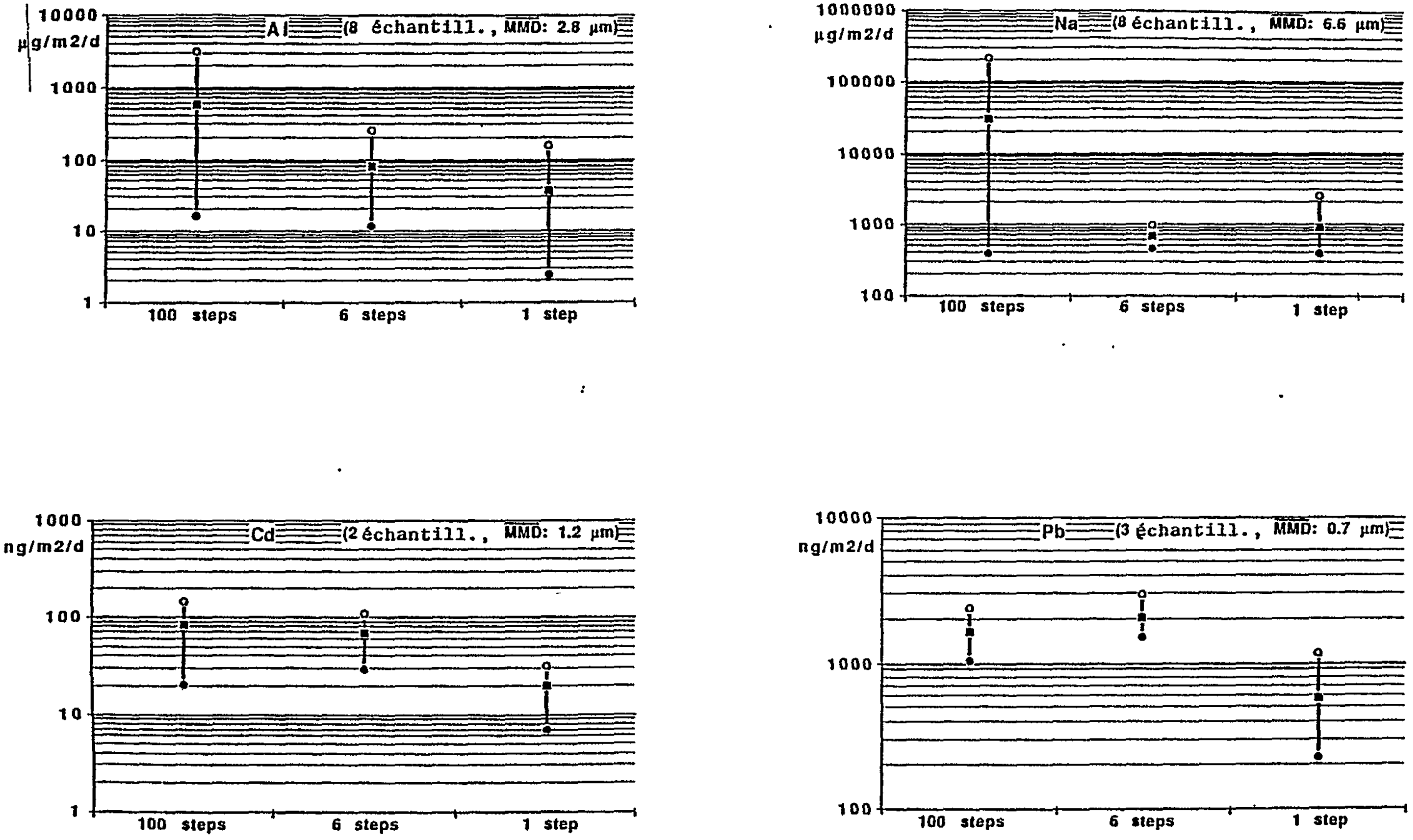


Fig. 3 - Comparaison des flux de dépôt sec calculés. Pour plusieurs échantillons d'impacteur, deux étages ont été regroupés pour les analyses: la méthode de calcul des flux à 6 intervalles n'a pas pu être appliquée à ces échantillons.

TRACE METALS CHARACTERIZATION OF AIRBORNE PARTICLES FROM DIFFERENT MEDITERRANEAN AREAS

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ABSTRACT

Dust samples were collected at the seawater-air interface in order to investigate the atmospheric input of particles and metals to the Mediterranean Sea. Data from three distinct areas, namely Western Mediterranean (WM), Southern Adriatic (SA) and Eastern Mediterranean (EM), were presented.

The samples were collected with the contemporary use of filtration and impingement catching systems. Trace metals analyses were carried out with AA fitted with graphite furnace, after complete dissolution of the sample in a teflon bomb.

Average amounts of total (soluble + insoluble) dust-loading were different in three areas, with values of 35, 19 and 51 $\mu g\ m^{-3}$ respectively.

Trace metals show values ranging from 2.1 to 30.6 $ng\ m^{-3}$ for Pb, 0.01 to 0.11 for Cd and 4.8 to 32.2 for Zn.

Average flux data are comparable with those of Arnold (1982), showing the following values: Pb = 66-963 $ng.cm^{-2}.y^{-1}$, Cd = 0.3-3.4, Zn = 126-1013.

Maxima for all the metals studied were found in the western Mediterranean while minima for lead were found in the Eastern Mediterranean and the southern Adriatic showed the lowest values of cadmium and zinc.

INTRODUCTION

In recent years there has been a great deal of concern at the introduction of pollutant trace metals into the oceans. The transport of atmospheric particulates can result in the introduction of such pollutants directly to open ocean areas.

There are a number of sources for the element in the marine aerosol. These include low temperature crustal weathering, sea-salt generation, volcanic activity, rock volatilization, release from plant surfaces, forest fires and a variety of anthropogenic activities such as high temperature emissions (Pacyna, 1984).

Crust-derived material is a ubiquitous component of the marine aerosol and the distribution of the elements in the oceanic atmosphere can often be related to the mixing of non-crustal material with the crustal "end-member" (Chester et al., 1986). Several aerosol characteristics such as elemental concentrations and size distributions change as the proportion of crustal and non-crustal components vary.

There are still relatively few data on the elemental composition of particulates from the lower marine troposphere, and those that are available are usually from the western part of the Mediterranean basin. The Mediterranean SE Trade (15% of mean yearly trajectories), with a reservoir of crustal material in North African deserts, and northerly winds (25%0 with a reservoir of pollutant material in northern Europe may therefore be regarded as two contrasting wind systems from the point of view of particulate supply mechanisms.

With no seasonal variation of northerly flow, pollutants can reach the western Mediterranean at all times of the year, while during the summer Saharan dust is transported to the sea (D'Almeida, 1986).

In the eastern Mediterranean 27% of the trajectories have W/NW origin (pollutant) and 16% of the trajectories (from S) represent the Saharan and North Africa contribution (WMO, 1985).

Dust transportation

Eolian transport of dusts over the Mediterranean basin occurs mainly in two separate ways:

(a) direct transportation of dusts released from land, and

(b) indirect transportation of particles already in suspension in the lower atmosphere.

The direct mode is due to the contemporary occurrence of vorticity of the same direction, both in the high and lower atmosphere. There are three conditions permitting this kind of transportation: (i) a minimum of pressure over Spain and Morocco (straight transport); (ii) an anticyclonic condition over the Balkan Region (cyclonic rotation), and (iii) a contemporary anticyclonic situation in Spain and Morocco (anticyclonic rotation). In all the three described conditions long-distance transportation of Saharan dust occurs, and in the last 10 years, 34 episodes have been recorded (Prodi and Fea, 1978). Another less meaningful diffusion is due to local winds, in the absence of strong dynamics on a larger scale.

The indirect way is the more frequent in the Mediterranean area. It generally occurs with extended uniform pressure on the ground and contemporary contrasting dynamics between the earth's surface and the lower atmosphere. Peculiar to this kind of transportation is some seasonal variability, a strong correlation with wind direction and a continuous dust load.

Over some regions of the Mediterranean Sea, therefore, crust-derived components can make a significant contribution to the total particulate trace metals (Cr, Pb, Zn, Ni) in the atmosphere. One such region is that underlying the SE Trades off the southern coast of Europe, where outbreaks of Saharan dust can result in the injection of crustal material into the atmosphere in amounts sufficient to mask elements supplied from other sources, including anthropogenic emissions.

MATERIALS AND METHODS

Study area

In order, therefore, to try first of all to obtain one sample representative of the marine aerosol crustal "end-member" and another from the "northern polluted belt", several mesh-collected atmospheric particulates from the collection at the Marine Geology Institute were selected for analysis.

Most of the sampling activity during the years 1980-87 was conducted during indirect transport conditions.

Because of its continuity and its fairly high average mass loading (20-40 µg m^{-3}), even when compared to the direct episodes (150-200 µg m^{-3}), it seems that indirect transportation accounts for more than half of the total load related to SE Trades (Lenaz et al., in press).

A total of nine mesh samples was chosen in three separate areas (Fig. 1): Western Mediterranean (WM), Southern Adriatic (SA) and Eastern Mediterranean (EM).

Sampling

Sampling cruises along the Mediterranean started in the 1980's, chiefly to determine the Eolian contribution to the present sedimentation (Fig. 2). The research project was carried out with continuous sampling (8012 hours) at the sea-air interface, following long tracks with the aim of understanding the differences in composition (mineralogy, grain size, chemicals, pollen etc.) of dusts in relation to wind vectors and seasonal variability. For this reason the sampling methodology followed that proposed by Prospero and co-workers (1981), i.e. the collection of dusts on nylon mesh-panels ($2m^2$) on the bow of the ship (Landuzzi et al., 1982); Tomadin et al., 1983; Tomadin et al., 1984).

In addition to the impingement catching system a high volume system was operated on board at the same time from 1983 in order to obtain more reliable data on dust loadings and the percentages of soluble and insoluble fractions.

During the ship cruises meteorological data were collected by means of an automatic portable meteo-station, together with "true wind" velocity and direction.

Mesh collection efficiency

The mesh collection technique samples mainly the soil-sized fraction of the marine aerosol and since it does not quantitatively retain the full spectrum of atmospheric particles, it cannot be used to describe the total elemental distributions in oceanic air. The major mass of aerosol elements having a predominantly crustal origin occurs in particles with radius > 1 micron (Duce et al., 1983) and it is this size class which is most effectively retained by the meshes (Chester and Stoner, 1974). Chester et al., (1986) show that under conditions in which the concentrations of crustal material in the atmosphere are relatively high, the meshes can retain a non-quantitative fraction of the small sized (industrial processes < ≈ 1 micron) aerosol material.

In addition to soil-sized crust-derived components the meshes also retain sea-salt particules. However, these were removed by washing the particles from the meshes in a distilled water rinse.

Aerosol sampling for mesh collection is carried out under rigorously controlled conditions in which winds impinge on the bows from restricted sectors.

Chemical analyses

Complete dissolution of the sample was obtained with teflon bomb digestion at 170 C, with a mixture of aqua-regia and HF. The analyses were conducted with an AA Spectophotometer equipped with a graphite furnace. Analytical precision and procedures are presented in detail elsewhere (Guerzoni et al., 1987).

RESULTS AND DISCUSSION

Mineralogy

Samples collected with the impingement catching system mainly consist of silty-clays or clayey-silts, with a modal class of 4-8 µm, and with a low sand content.

The results of mineralogical and sedimentological study are summarized in Fig. 3, where the principal trends are outlined. Even when the meteorological situation leads to an indirect event, with neither mobilisation of dust from land nor direct transport to the sampling site, the crustal contribution is generally as follows (Fig. 3):

(a) organized Illite, Chlorite, Serpentine and Hematite, Na/K >1, high levels of organic matter (>>2%), from S-SE (desert areas).

(b) Quartz, Plagioclase, K-Feldspar, Palygorskite, Calcite and Dolomite, Na/K <1, organic matter <2%, from S-SE (desert areas).

Those figures were fairly constant, with similar wind patterns, over the entire period of the study, and showed close relations (both in load and in composition) with wind direction (Lenaz et al., in press).

Chemical data

All the nine chosen samples of the three separate areas had soil-sized atmospheric Al concentrations of 500 ng m^{-3} of air; the maxima (1,600) were found in the EM samples and the overall average was 1,100 ng m^{-3}. These are among the highest recorded over the World Ocean and are an indication of the dominance of crustal components in the aerosols.

Average amounts of total dust-loading were 35 (25-50) µg m^{-3} for WM, 19 (15-26) µg m^{-3} for SA and 51 (46-55) µg m^{-3} for EM; the insoluble fraction accounted for approximately 40% of the total.

The results of trace metals analyses, together with the dust load of the insoluble fraction, are presented in Table 1.

Lead values range from 2.1 to 30.6 ng m^{-3} (average 8.8), with a strong decrease of values going eastward and the minimum in the sample #9, close to the island of Crete.

Zinc shows a different pattern: the maxima are still in the WM area (up to 32.2 ng m^{-3}) and the values decrease to the SA and EM, but minima are in the upper part of SA region (sample #4, 4.0 ng m^{-3}) and high values are encountered around southern Italy (samples #6, 7), probably related to local input from industrial areas.

Cadmium gives the maxima, once more, in the WM region (average 0.06 ng m^{-3}), the minima in the SA area (average 0.02) and significant values in the EM region (average 0.04 ng m^{-3}).

In Table 2 a comparison with other Mediterranean and southern California coastal data is presented. Zn and Al values are comparable with La Jolla data (similar sampling technique); Cd and Pb are lower than other published data, probably because of the previously-discussed low efficiency of meshes in collecting particles smaller than 2 microns. The high solubility (> 80%) also affects the low figures of cadmium found in our samples.

Flux data

Average flux data (dry deposition estimates, based on a deposition velocity of 1 cm sec^{-1}) are presented in Table 1, and Table 3 shows a comparison with other marine areas.

The flux data calculated in the present study are comparable to those of Arnold (1982), showing the following values: Pb=280 (66-963) ng $cm^{-2}.y^{-1}$, Cd=1.2 (0.3-3.4), Zn=354 (126-1013). Some recent studies (Buat-Ménard et al., present report) demonstrate that the deposition velocity might be different for the various metals, so the figures presented here are only rough indications.

Maxima for all the studied metals were found on the WM (Pb=963, Cd=3.4, Zn=1013 ng cm^{-2} y^{-1}), whilst minima for lead (66 ng cm^{-2} y^{-1}) were found in the EM and the SA showed the lowest values of cadmium (0.3 ng cm^{-2} y^{-1}) and zinc (126 ng cm^{-2} y^{-1}).

Baseline levels and enrichment factors (EF)

Al is commonly used as an indicator of the amount of crustal material present in the atmosphere, and in order to assess the enrichment of elements in an aerosol relative to the crustal source many authors have used an enrichment factor (EF) which is calculated according to the equation:

EF crust = (E/Al air)/(E/Al crust)

in which E/Al air and E/Al crust are the concentrations of an element E and of Al in the atmosphere and crustal material respectively. Because the composition of crustal material itself varies the EF (crust)-value is only a crude estimate of the magnitude of the crustal source strength, and in general EF (crust)- values between ≈1 and <10 are taken as an indication that an element has a mainly crustal source, and those >10 are considered to indicate that a substantial portion of the element has a non-crustal origin.

The EF(crust)-values for the elements analyzed in the nine mesh-collected samples are listed in Table 1 (see also Fig. 5), from which it can be seen that, on average, they are ≈50 (7-236) for Pb and ≈15 for Zn (5-62) and Cd (6-30). The same aerosols have concentrations of Fe, Ni, Mn and V similar to those of continental crust (Guerzoni et al., 1987).

Although the mesh collection technique samples mainly soil-sized particles, some small-sized material is retained resulting in the aerosols having EF (crust)-values >10 for some elements. The highest average EF(crust)-values for Pb, Zn and Cd in the soil-sized aerosols are found for samples collected from around the Spanish coast (average of samples #1 and 2; Pb-151, Zn=38, Cd=28). For the same marine area Dulac et al., (1987) presented much higher figures, 595 and 2680 on average for Pb and Cd respectively. Our figures are comparable with mesh-panels samples data published by Chester et al., (1986), with average values of 13 for Zn, 34 for Cd and 74 for Pb.

However, under those conditions in which crust-derived components dominate the aerosol, as seems to be the case for SA and EM samples, non-crustal material can be diluted, and for those samples EF(crust)-values for all elements should <10 in the total spectrum of atmospheric particulates. In fact, even the "natural" particulates of the Mediterranean SE trades resulted enriched in Cd, Zn and Pb (average of samples #7, 8, 9 are Pb=8, Zn=6 and Cd=10).

CONCLUSIONS

From the analyses of the insoluble fraction of the atmospheric particles (dry deposition) of nine mesh-panels samples, chosen from the Marine Geology Institute collection, we provide information on the differences among three separate Mediterranean areas.

The high contribution of the crustal material, especially in the southern Adriatic and eastern Mediterranean, with values of Al >1,000 ng m^{-3}, is partly due to the sampling methodology and is mainly related to SE Trades.

There are geographical variations in the distribution of Pb, Zn and Cd which may be related to anthropogenic sources. In particular, the concentration of these elements are highest in "coastal" atmospheric particulates adjacent to industrialized sources (with northern Trades, i.e. samples #1, 2 and 6; around Spain and southern Italy).

Cd values, even if lower in comparison with other published data, present enrichments correlated with SE Trades. The low figures are due to the sampling method and the high solubility of the element.

Wet deposition and small particles (< 2 microns) analyses deserve future effort, to get a clearer description of all the problems involved in estimating the trace metals contribution to the Mediterranean Sea from the atmosphere.

ACKNOWLEDGEMENTS

We are grateful to A. Cesari (sampling and meto data), V. Landuzzi (mineralogical analyses) and G. Rampazzo (chemical analyses) for their valuable help. The figures were drawn by G. Zini. Constructive criticisms by D. O. Suman are gratefully acknowledged.

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Table 1

Relevant data of the nine mesh-collected samples (WM: Western Mediterranean, samples # 1,2,3; Southern Adriatic, samples # 4,5,6; EM: Eastern Mediterranean, samples # 7,8,9; see Fig. 1 for locations)

Sample	Load ug/m^3	AL ng/m^3	PB ng/m^3	ng/cm^2/Y	EF	NZ ng/m^3	ng/cm^2/Y	EF	CD ng/m^3	ng/cm^2/Y	EF
PAN83/01 (1)	11.2	597	30.6	963	236	32.2	1013	62	0.04	1.4	30
02 (2)	20.8	1626	23.4	737	66	19.6	617	14	0.11	3.4	26
03 (3)	10.1	852	5.1	161	28	4.9	154	7	0.02	0.6	9
avg. WM	14.0	1025	19 7	620	110	18 9	595	28	0.06	1.8	22
EOL82/01 (4)	6.4	552	4.6	145	39	4.0	126	8	0.02	0.6	14
02 (5)	10.8	795	4.3	135	25	4.8	150	7	0.02	0.8	13
06 (6)	6.0	499	2.6	82	24	8.9	280	21	0.01	0.3	7
avg. SA	7 7	615	3.8	121	29	5 9	185	12	0.02	0.6	11
MR83/01 (7)	22.0	1806	3.6	113	9	11.8	372	7	0.06	2.0	15
02 (8)	21.4	1749	3.3	104	9	9.8	309	6	0.04	1.1	8
03 (9)	18.2	1400	2.1	66	7	5.6	176	5	0.02	0.7	6
avg EM	20.5	1652	3 0	94	8	9.1	286	6	0.04	1.3	10
overall avg.	**14.1**	**1098**	**8.8**	**278**	**49**	**11.3**	**355**	**15**	**0.04**	**1.2**	**14**

Table 2

Concentrations of metals in atmospheric particulates (ng m^{-3}); (a) Dulac et al., 1986; (b) Hodge et al., 1978; (c) Chester et al., 1984.

Element	Present work	Western Med.[a]	La Jolla & Ensenada[b]	Eastern Med. & Thyrrenian[c]
Cd	0.04	1.88	0.22	0.40
Pb	8.8	38.9	355	12.0
Zn	11.3	--	21.5	--
Al	1,098	324	2,140	--

Table 3

Estimated mean fluxes of trace metals from the atmosphere to the sea surface (ng cm^{-2} y^{-1}); (a), (b) as Tab. 2; (c) Cambray et al., 1975; (d) Arnold et al., 1982.

Element	Present work	Western Med.[a]	La Jolla & Ensenada[b]	North Sea[c]	N. York Bight[d]
Cd	1.2	13.0	5.9	43.0	30.0
Pb	280	1,050	1,685	2,650	3,900
Zn	354	1,080	993	8,950	1,400
Al	34,500	5,000	112,000	30,000	6,000

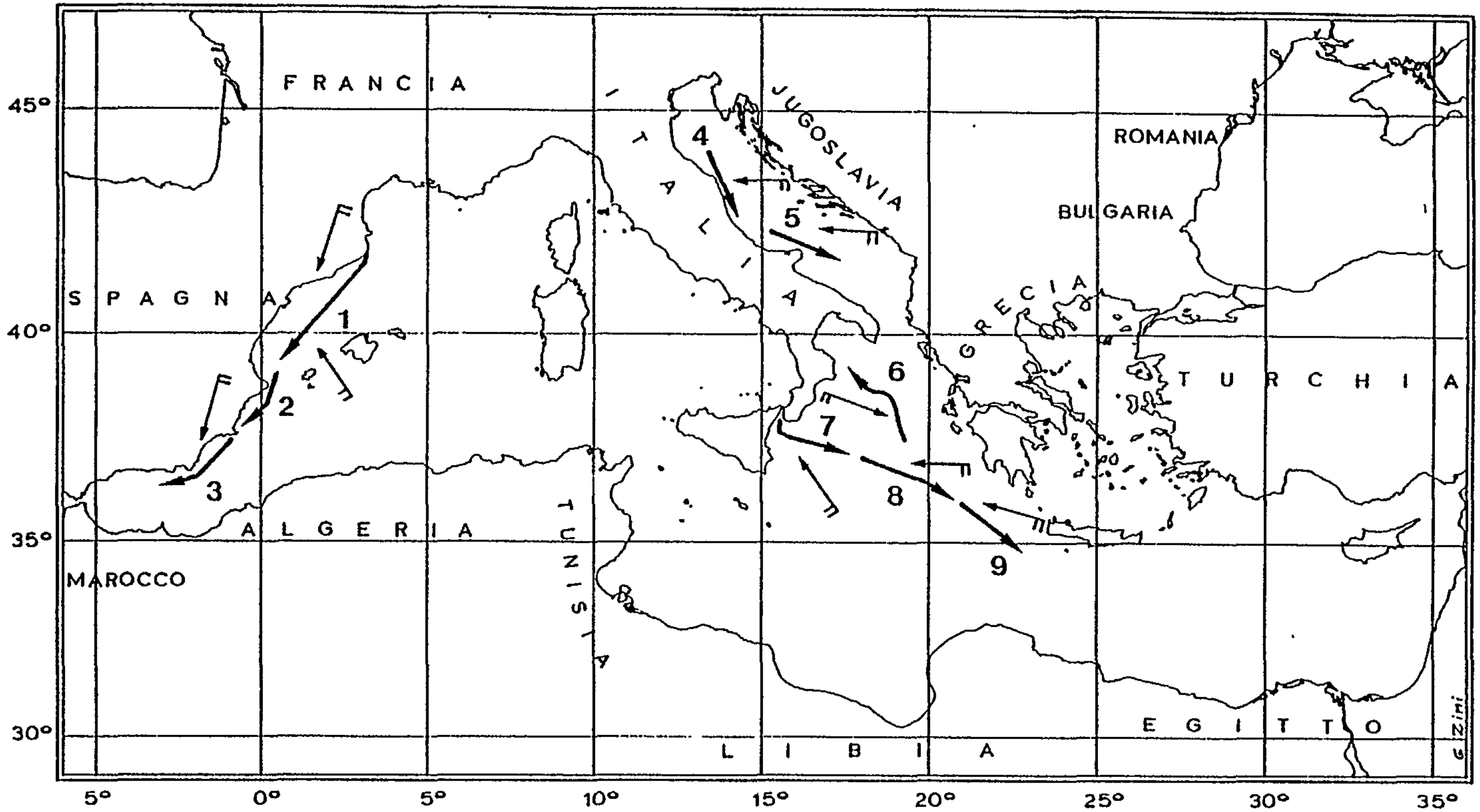

Fig. 1 - Station locations (samples 1 to 9) and prevailing winds (arrows) during sampling period (8-12 hours). Samples # 1,2,3 in text are reported as WM=Western Mediterranean; #4,5,6 as SA=Southern Adriatic; #7,8,9 as EM=Eastern Mediterranean.

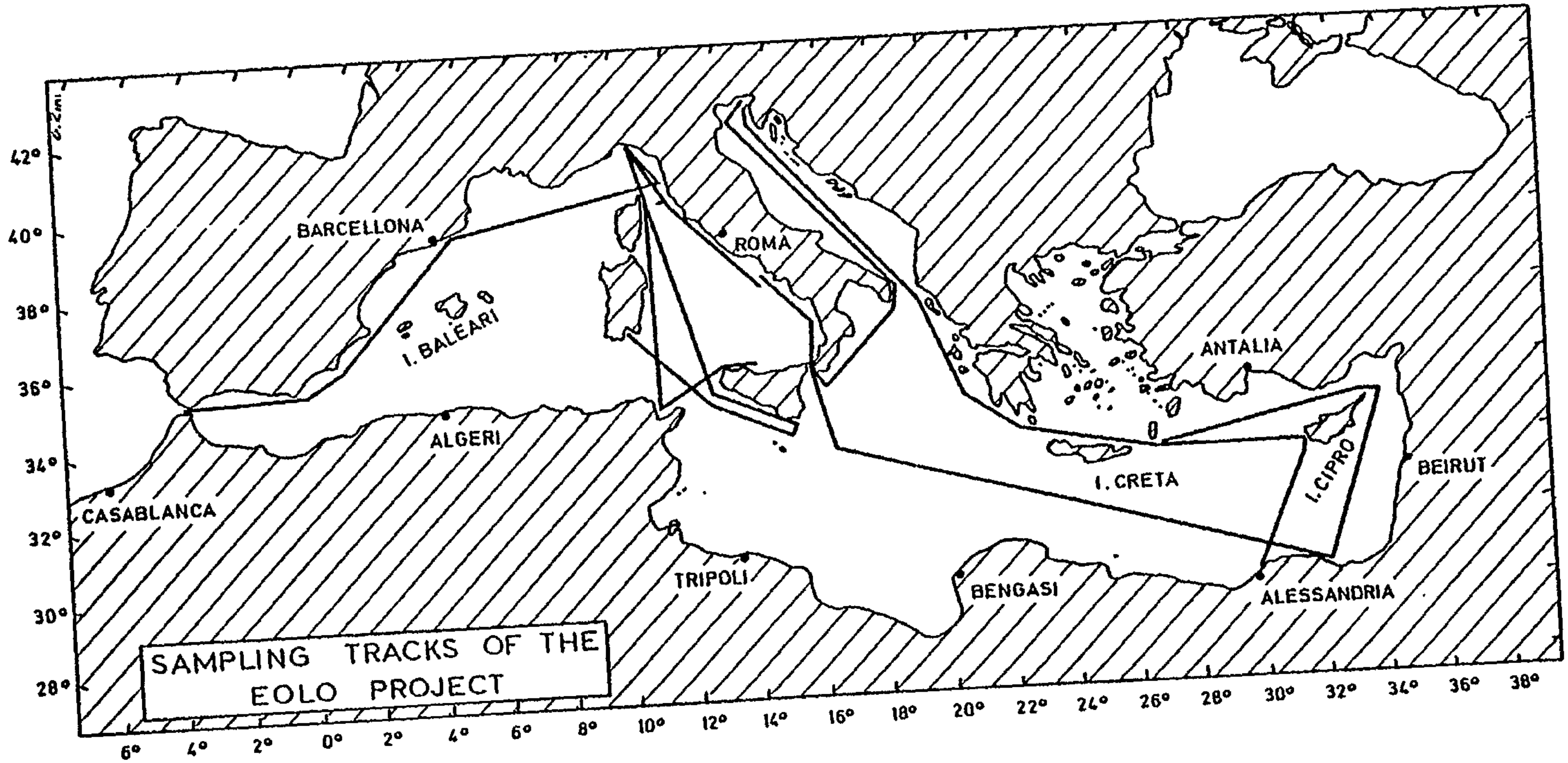

Fig. 2 - Sampling tracks followed during Marine Geology Institute cruises in the period 1980-1987.

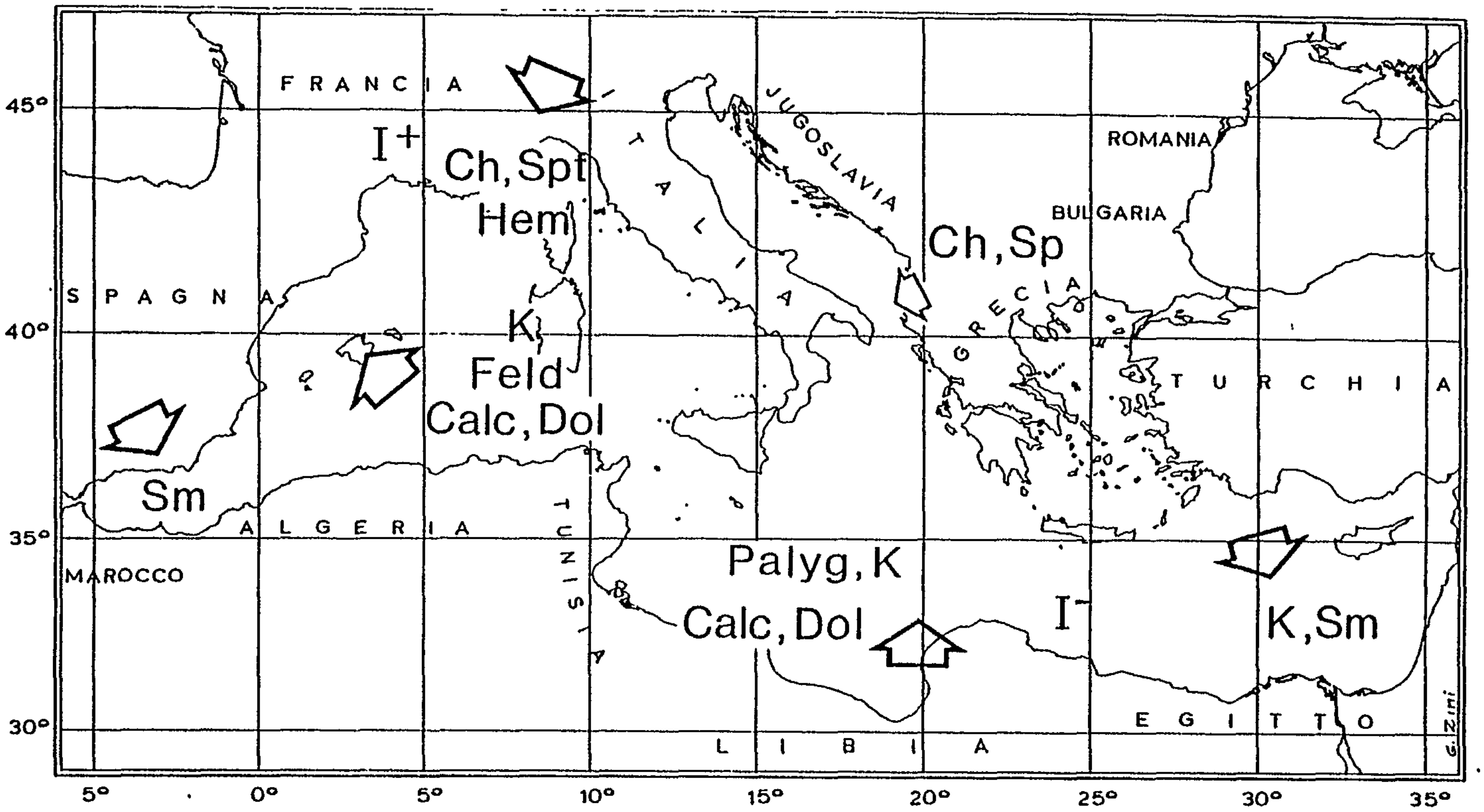

Fig. 3 - Synthesis of mineralogical results (from Lenaz *et al.*, in press): arrows represent direction and characteristic mineral input to the Mediterranean. Palyg.=Palygorskite; K-Kaolinite; Cal=Calcite; Dol=Dolomite; I=poorly crystalized Illite; Ch=Chlorite; Spt=Serpentyne; Hem=Hematite.

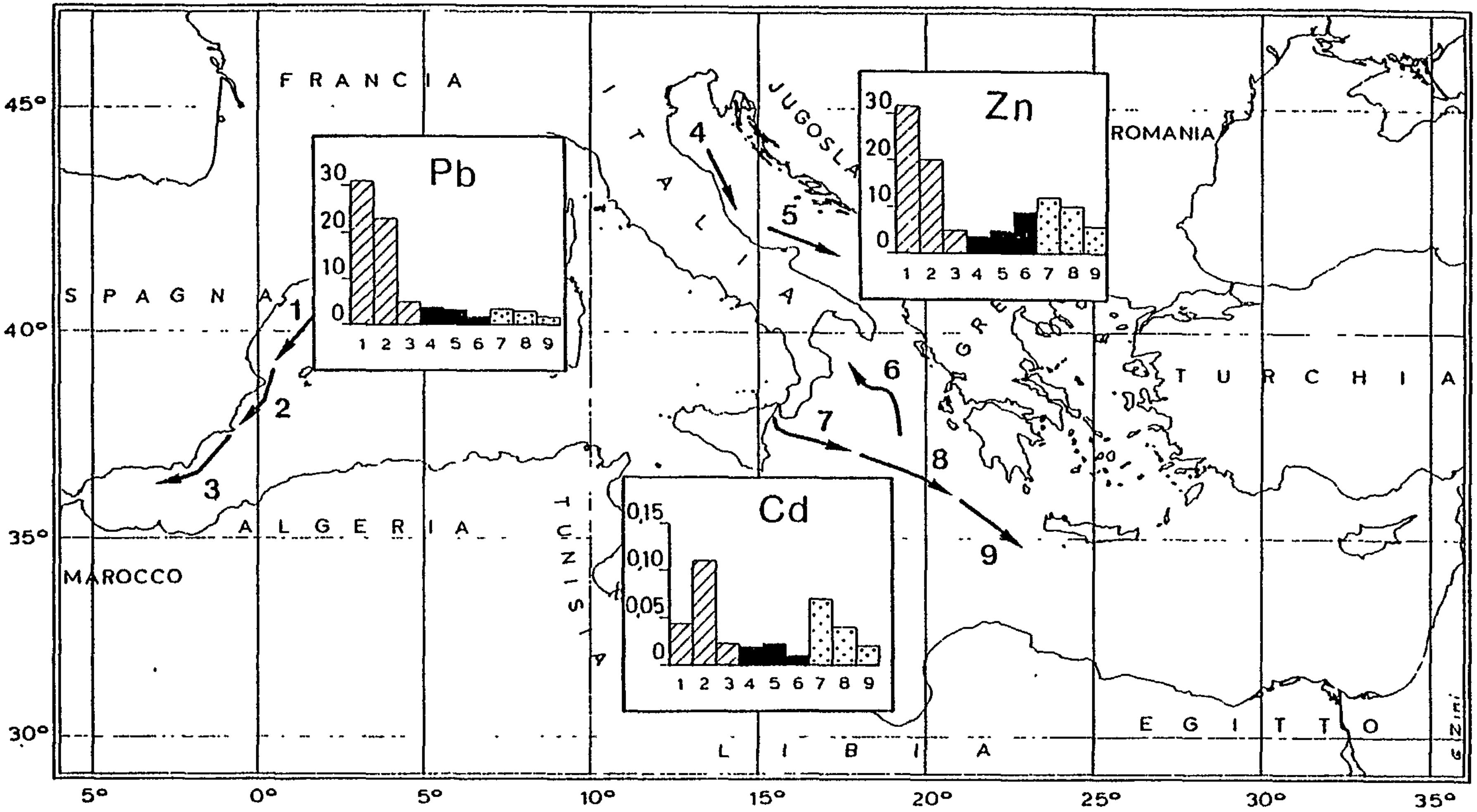

Fig. 4 - Concentration (ng m^{-3}) of Pb, Cd, Zn in dust samples; each histogram corresponds to one sample (#1-9); see Table 1 for data.

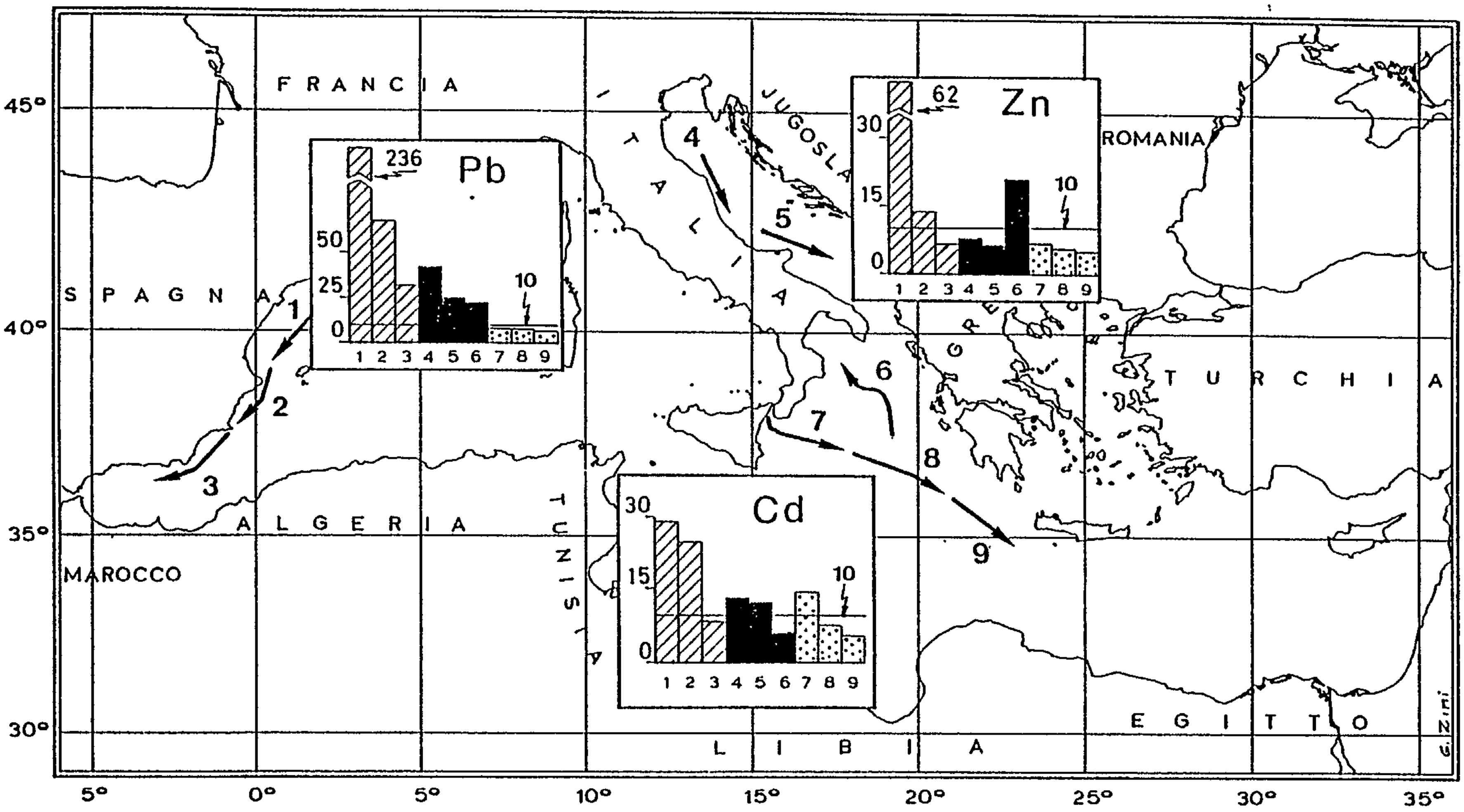

Fig. 5 - EF(crust)-values of Pb, Cd, Zn in dust samples; each histogram corresponds to one sample (#1-9); see Table 1 for data.

SOME PRECIPITATION CHEMISTRY CHARACTERISTICS OF SELECTED STATIONS ALONG THE ADRIATIC COAST

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INTRODUCTION

The concentration of major ions in atmospheric precipitation has been studied in Yugoslavia for many years and the results obtained show that long-distance and local sources as well as the sea through formation of sea-sprays and their atmospheric transport, can significantly influence the concentrations of H^+-ions (pH) and sulphates, nitrates, chlorides and calcium at various time scales from a few hours to seasons and years. Dust originated in the North Africa and transported over the Mediterranean Sea is another source of substances changing the acidity of precipitation in Yugoslavia. To evaluate the influence of pollutant source areas on precipitation chemistry, the annual variations of monthly means and the seasonal correlation coefficients between concentrations of major ions and pH values are considered on the basis of 1982-1986 data from three stations along the Adriactic coast.

MATERIALS AND METHODS

In the Socialist Republic of Croatia there is a rather dense network of stations for precipitation and air chemistry data measuring.

The concentration of SO_2, smoke, NO_x and chlorides in the air was measured and the following 12 compounds in precipitation were analysed: pH value, electric conductivity, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, F^-, Na^+, Ca^{2+}, K^+, Mg^{2+}. Samples were taken daily, and also on a weekly basis at certain stations. Chemical analyses were made in the Hydrometeorological Institute of Croatia in Zagreb, utilising standard methods from WMO (1978). Chemical analyses of samples from the regional stations included in EMEP and MEDPOL networks were made in the Federal Hydrometeorological Institute in Belgrade, also using standard WMO methods (WMO, 1978).

The results of precipitation chemistry of the following three stations are discussed in this paper: Pula - on the northern Adriatic coast; Zavizan on the summit of Velebit, which forms a natural boundary between the continent and the Adriatic coast; and Dubrovnik on the southern Adriatic coast (Fig. 1). The data presented were gathered over the five-year period: 1982-1986.

Though the stations at Pula and Dubrovnik are situated in the suburbs of the towns surveyed, they are nevertheless polluted by local sources.

Zavizan, the regional station, included in EMEP and MEDPOL networks, lies 1594 m above sea level and is mainly influenced by distant pollution sources through long-range transport.

It should be noted that at Zavizan 98%, at Dubrovnik 93% and at Pula only 67% of the total amounts of precipitation were chemically analyzed.

From the twelve compounds to be analyzed in precipitation, this paper deals with: pH value, SO_4^{2-}-S, NO_3^--N, Cl^- and Ca^{2+} ion concentration. For these compounds the annual variations of monthly means and the seasonal correlation coefficients between the given ion concentration and the pH values were calculated. For the purpose of air flow estimation at the three locations, the annual wind roses for the above mentioned five-year period were also made.

RESULTS

(a) Wind

The annual wind roses were made on the basis of meteorological data measured in climatological terms (7 a.m., 2 p.m. and 9 p.m. local time). Figs. 2 a-e, 3 a-e and 4 a-e show that they are very similar throughout the whole period of the study.

The prevailing winds at Pula are SE (jugo) and NE (bora) winds. Sea-breeze flow (NW) and calms occur fairly frequently. The highest wind velocities (9-14 m/s) are correlated to southwesterly and northeasterly winds.

In Dubrovnik the prevailing winds are from the North/northerly directions (bora-NNE, or sea breeze NNW) and southern (jugo SE) quadrants. Calm spells are very rare. The highest wind velocities (5-6 m/s) are correlated to northeast and southeast winds, especially in winter.

Taking the prevailing winds into account it is evident that Pula and Dubrovnik are influenced, to a high degree, by the sea.

The Zavisan station has a very characteristic wind rose showing the presence of strong channel effects. The prevailing winds are from the east and the west. Calm spells are rather frequent as at Pula. The highest wind velocities (7-15 m/s) are correlated to SSE, S or SSW winds.

(b) pH value

The annual variations of volume weighted pH monthly means over the five-year period 1982-1986 (Fig. 5) show that the values are often lower than 5.6 - the level for acid rain.

The daily samples show that pH values lie between 3.8 and 7.5 at Dubrovnik, 3.7 and 7.6 at Zavizan and 4.2 and 7.5 at Pula, and the monthly means are between 4.4 and 7.2.

The monthly pH values calculated at Zavizan are below 5.6 for 55% over the five-year time span. Dubrovnik with 38% and Pula with 30% of the time with pH values below 5.6 show a lower degree of precipitation pollution. At Dubrovnik these low pH values are distributed throughout the whole year, whilst at Pula these values occur mostly in winter.

The distribution of the volume weighted pH monthly means indicates the influence of local urban sources of pollution (especially in winter) at Dubrovnik and Pula, whereas the station of Zavizan, isolated from local sources, shows low pH values throughout the whole year.

Moreover, at the coastal stations (Dubrovnik and Pula) the high acidification might be regarded as occurring under the influence of the sea.

(c) Sulphates

The amount of sulphur from SO_4^{2-} ions in precipitation at Zavizan is considerably lower than at Dubrovnik and Pula (Figs. 6.a-c). This would indicate that sulphates in precipitation at coastal stations may originate not only from anthropogenic sources but also from sea-spray, which is brought to the coast by sea-breeze flows. Thereby a higher concentration of SO_4^{2-} ions occurs in the warm period of the year.

The influence of anthropogenic sources is stronger in the cold periods of the year because of unfavourable meteorological conditions. This also occurred at the other coastal stations (Poje and Bolanca, 1974).

The concentrations of SO_4^{2-}-S in the daily samples are from 0 to 40 or 55 mg/dm^3 at Pula and Dubrovnik, respectively, and from 0 to 13.7 mg/dm^3 at Zavizan.

The deviations from mean values are rather significant, especially at Zavizan. The annual means at Pula and Zavizan were highest in 1984 and in Dubrovnik in 1982 during a period in which the deviations at all three stations were also most noticeable.

(d) Nitrates

In precipitation, the concentration of nitrates, the second main pollutant next to sulphates is much higher at Pula and Dubrovnik than at Zavizan, and is also higher at Pula than at Dubrovnik (Figs. 7.a-c).

It is well known that the presence of nitrates in precipitation is a consequence of the presence of NO_x gases in the air, resulting from combustion of fossil fuels (such as sulphur) and also from vehicular traffic and both of these factors are more evident near Pula than Dubrovnik and Zavizan. The influence of vehicular traffic is especially high in summer, when the concentration of NO_3^--N ions is higher at Pula.

In the daily samples the concentration of NO_3^--N ions reaches 45.8 mg/dm^3 at Pula, 16.7 mg/dm^3 at Dubrovnik, and 14.7 mg/dm^3 at Zavizan, whereas the monthly means at Pula reached 16.7 mg/dm^3 and at Zavizan only 3.3 mg/dm^3.

The standard deviations are less than for SO_4^{2-}-S ions at Dubrovnik as well as at Pula, whilst at Zavizan they are quite significant, especially for 1985 and 1986.

The annual means and deviations show a negative trend in 1985 and 1986, whereas at Zavizan they were much higher over the same period. Depending on the prevailing winds, the cause for this is presumed to be long-range transport, probably from Italy or eastern Europe.

(e) Chlorides

The concentrations of Cl^- ions in precipitation also show the influence of the sea: at Dubrovnik they are two and at Pula one order of magnitude higher than at Zavizan (Figs. 8. a-c). Concentrations were highest at Dubrovnik: in the daily samples 0.41 to 3410 mg/dm^3 and the monthly mean reached 1393 mg/dm^3, reflecting the openness of the station to the sea. The deviations are also significant. At Pula the daily concentrations ranged from 0.98 to 158 mg/dm^3, and the monthly mean reached 55 mg/dm^3. At Zavizan, the deviations were less: the daily concentrations ranged from 0.1 to 15.3 mg/dm^3, and the monthly means only 4 mg/dm^3.

The annual deviations indicate the lowest Cl^- concentration occurred in summer, and the highest in autumn and winter. The concentration of Cl^- ions was never as low as zero over the whole period, indicating that all three stations were influenced by the sea.

The annual means show stagnation at Zavizan after 1983, an increase at Pula, whereas at Dubrovnik the means tend to vary considerably and show no regularity.

(f) Calcium

Calcium in precipitation causes a lower acidity level, i.e. a higher pH value and indicates that there is dust in the sample (Granat, 1982).

The concentration of Ca^{2+} ions is lower at Zavizan than at Pula and Dubrovnik; in the daily samples it reached 26.9 mg/dm³, whilst at Pula it ranged from 0.8 to 76.5 mg/dm³, and at Dubrovnik from 0.20 to 112.2 mg/dm³ (Figs. 9.a-c).

The monthly means increased to 12 mg/dm³ at Zavizan, and to 39 mg/dm³ at Pula and Dubrovnik.

The highest concentrations occurred in spring or summer when there is a higher level of dust in the air.

It is noted that there was a drastic drop in the level of Ca^{2+} concentration at Pula after 1983, whilst annual variations showed a drop in Ca^{2+} concentration at all three stations.

Low concentrations of Ca^{2+} ions at Zavizan also caused lower pH values at Zavizan, because the quantity of Ca^{2+} ions was not high enough to raise the pH value as was the case at the other two stations (Granat, 1982).

(g) Correlations

The seasonal correlation coefficients were considered in order to find the connection between pH and the four ion concentrations discussed in this paper.

At Pula the correlation coefficients were very much more that at the other two stations and were stronger (Figs. 10. a-c).

At Dubrovnik they were positive (except for sulphates) but not high, whilst at Pula and Zavizan they were both positive and negative.

At all three stations, especially at Zavizan, the strongest positive correlation coefficients are for pH and Ca^{2+}. This means that the higher the Ca^{2+} concentration, the higher the pH value, which would support the fact that positive Ca^{2+} ions neutralize acid precipitation, and increase its pH value.

The rather significant negative correlation coefficients between pH and $SO_4{}^{2-}$-S and $NO_3{}^{-}$-N concentrations for Zavizan and Pula would also support the surmise that these ions decrease the pH value.

A more precise conclusion could be reached if the concentrations (given by analytical methods) with ionic balance calculation were to be verified.

A more satisfactory method, perhaps, would be to use the correlation coefficient calculation between the ion discussed and the logarithm of H^+ ions. This will be done later.

CONCLUSIONS

The results from data gathered over a five-year period for the three stations discussed indicate that Pula and Dubrovnik are significantly influenced by the sea and there is even a mild sea influence at Zavizan, a station 1594 m above sea level.

There is a higher concentration level of all ions discussed at Pula and Dubrovnik than at Zavizan. This would also confirm that Zavizan is mainly under the influence of long-distance sources, whereas Pula and Dubrovnik are also influenced by local sources of pollution. But since they are not major industrial centres, anthropogenic sources have a weaker influence on the precipitation chemistry than does the sea. Only at Pula is the pollution from industry and vehicular traffic slightly heavier.

Because of the prevailing winds at these three stations, the transport of pollution to the Adriatic, and thereby to the Mediterranean, could be expected but it is still not significant.

ACKNOWLEDGEMENTS

The research was supported by Union for Scientific Research of Croatia. Particular thanks are due to the Chemical Laboratory of the Hydrometeorological Institute of Croatia for making the chemical analyses available. The author wishes to express her gratitude to Djurdja Belec who performed the computer calculations.

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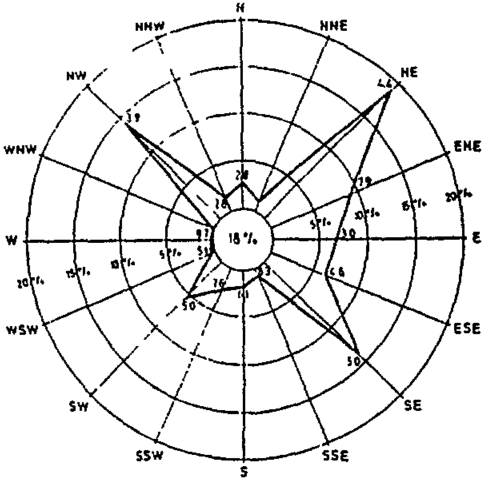
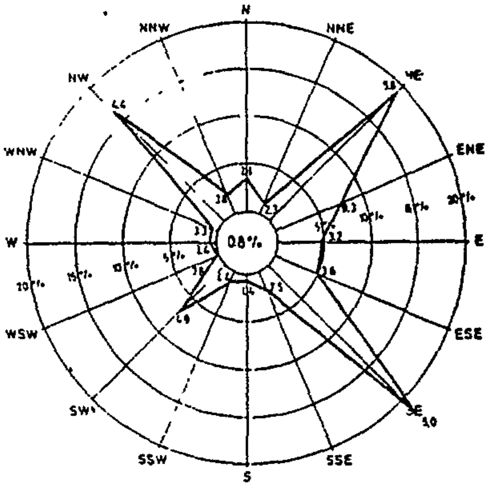
Fig. 1. Location of stations

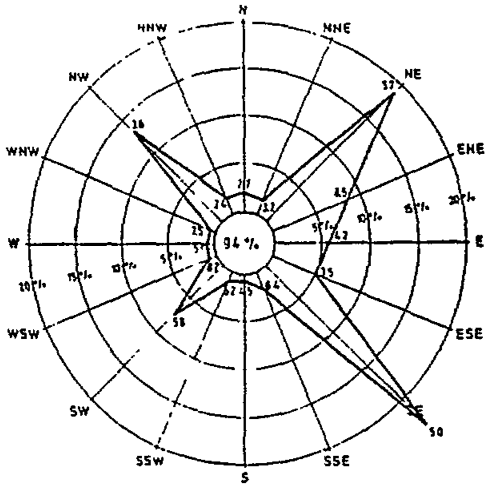
STATION PULA
YEAR 1982



STATION PULA
YEAR 1983



STATION PULA
YEAR 1984



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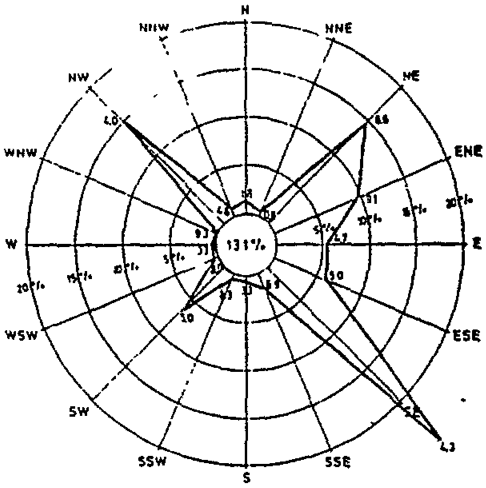
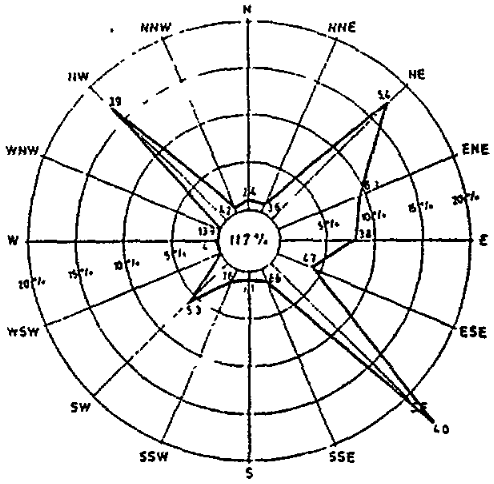
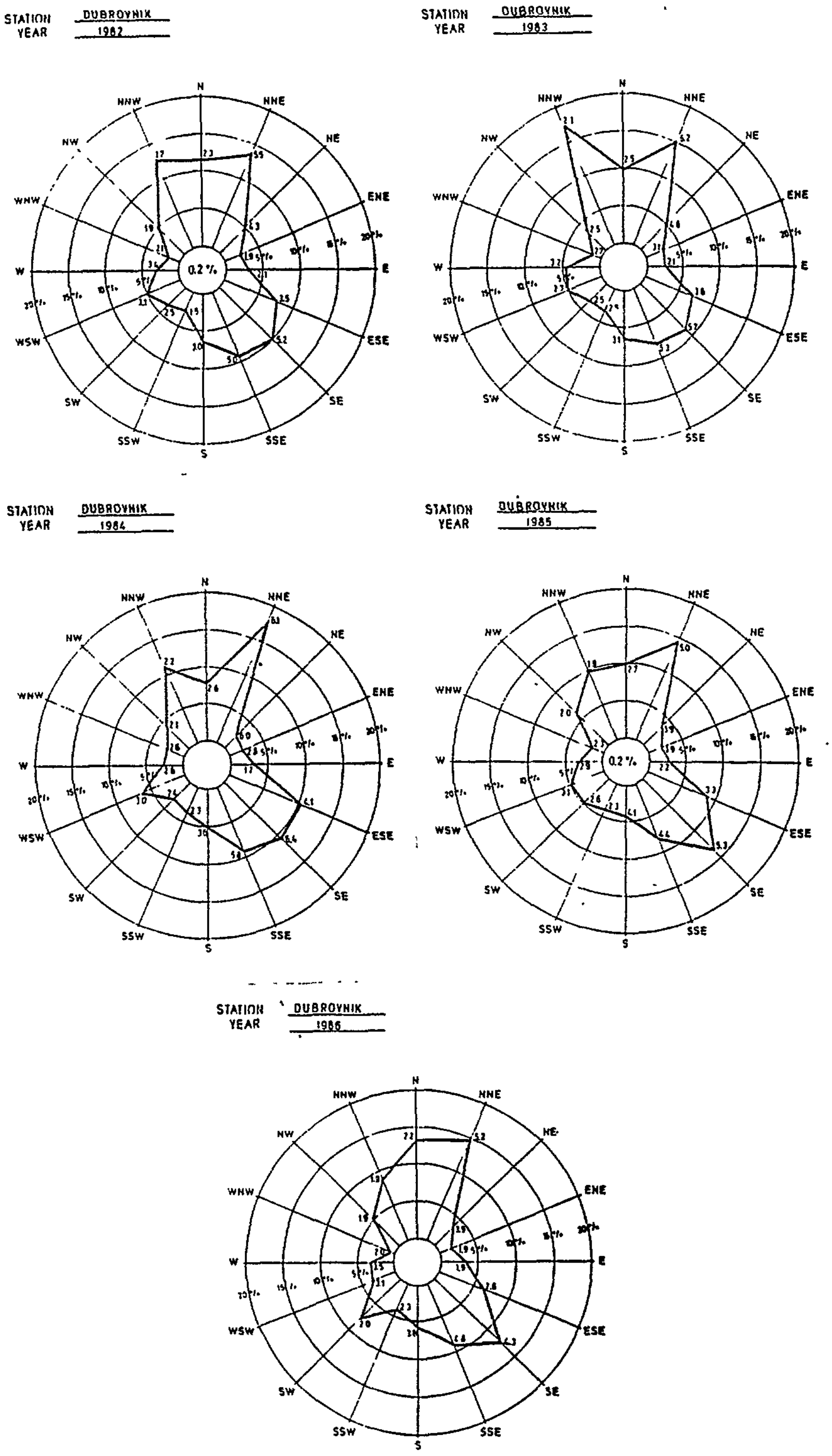
YEAR 1985



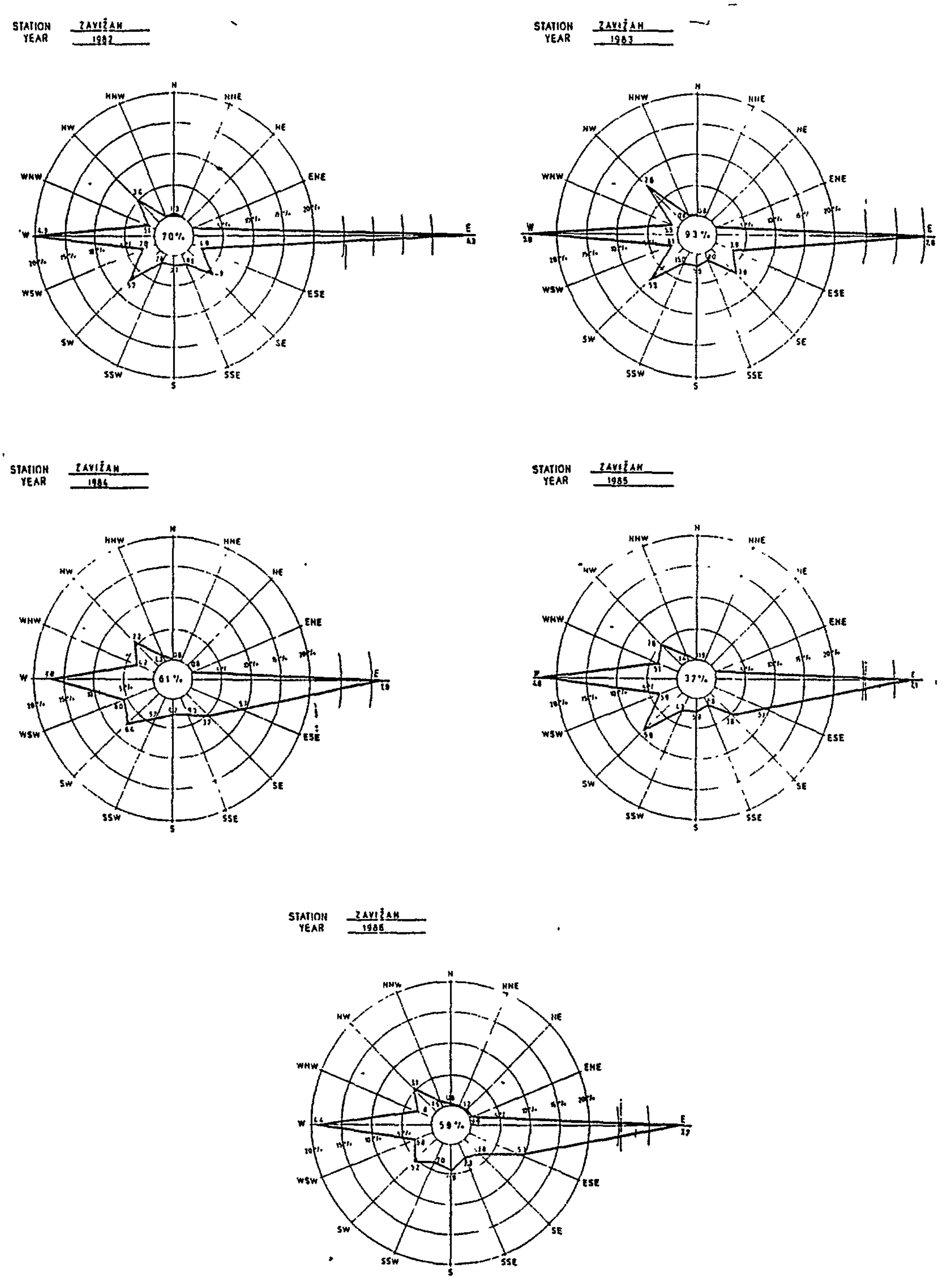
STATION PULA
YEAR 1986



Figs. 2.a-e. - Annual wind roses for station at Pula, 1982-1986



Figs. 3.a-e. - Annual wind roses for station at Dubrovnik, 1982-1986



Figs. 4.a-e. - Annual wind roses for station at Zavizan, 1982-1986

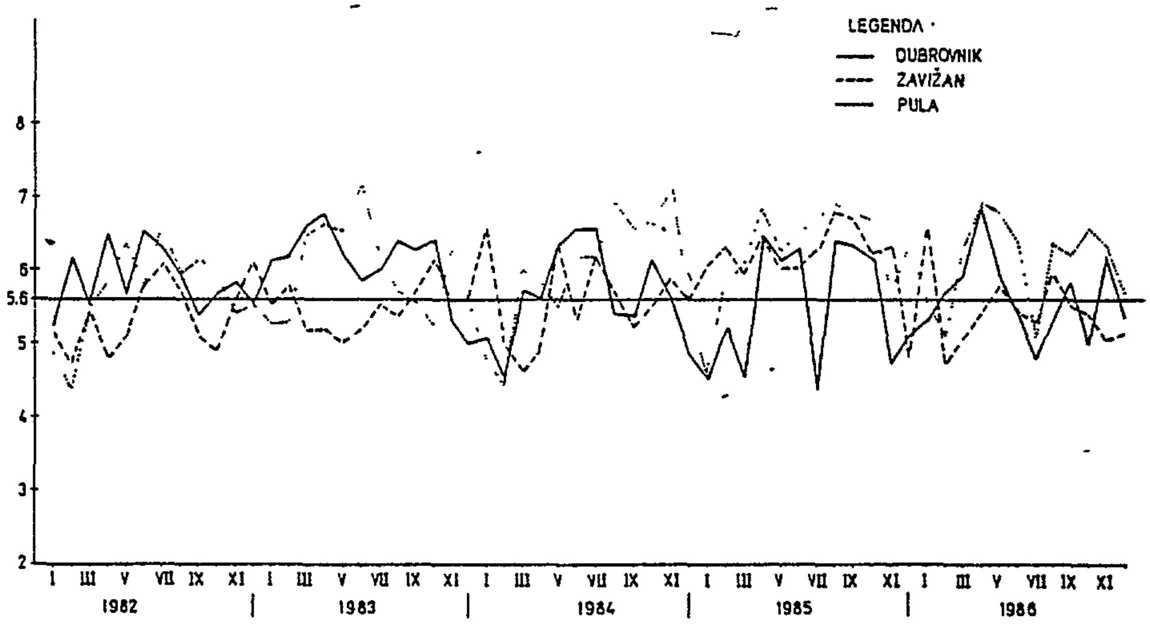


Fig. 5 - Volume weighted monthly means of pH value for Pula, Dubrovnik and Zavizan, 1982-1986

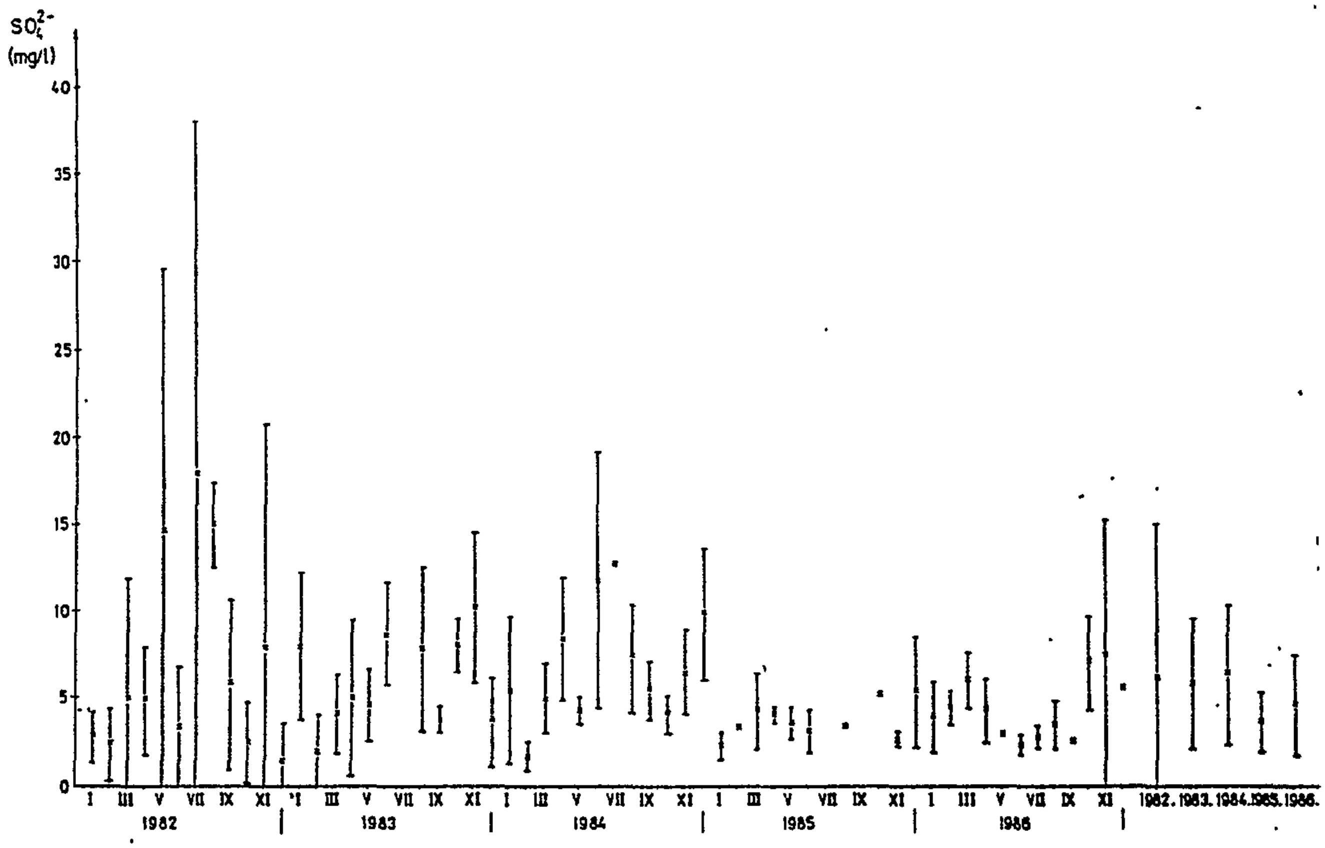


Fig. 6a. - Monthly means (x) and standard deviations of SO_4^{2-}-S ion concentration in precipitation, Pula, 1982-1986

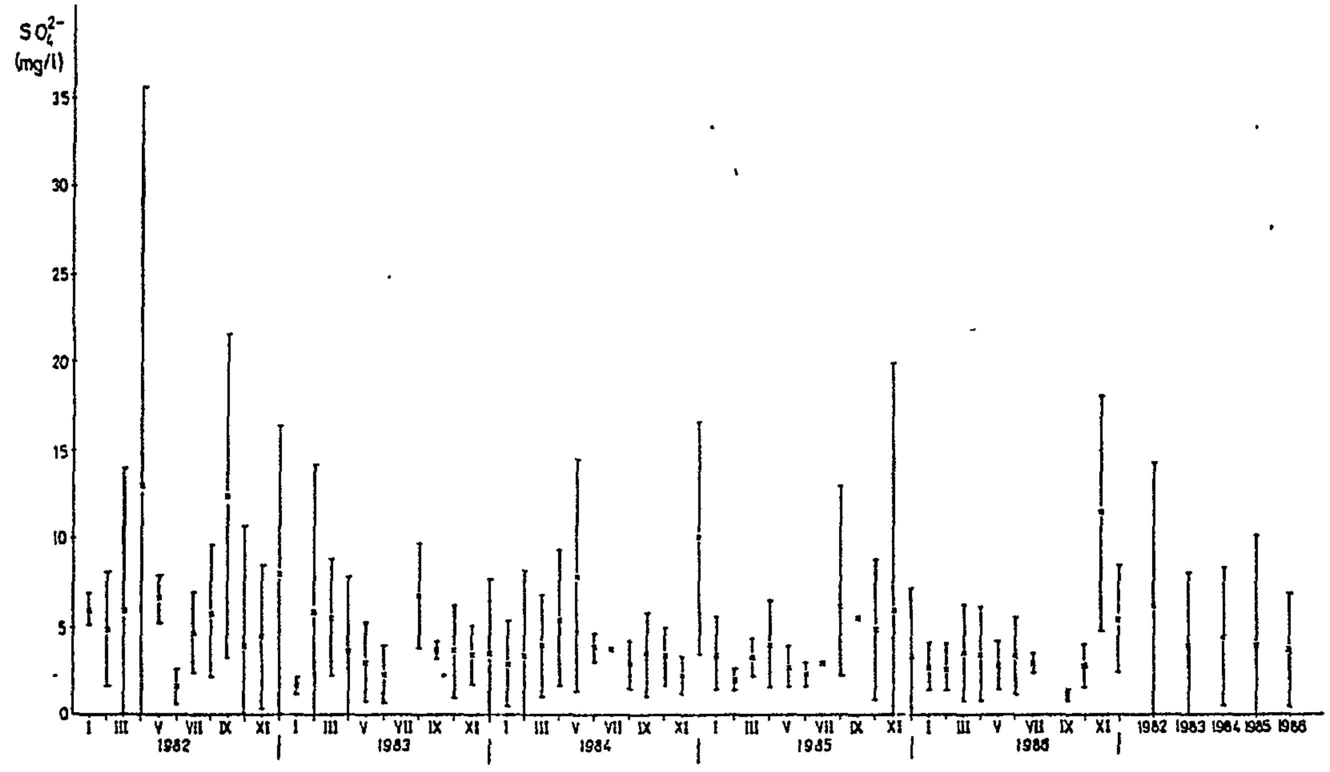


Fig. 6 b. - Monthly means (x) and standard deviations of SO$_4{}^{2-}$-S ion concentration in precipitation, Dubrovnik, 1982-1986

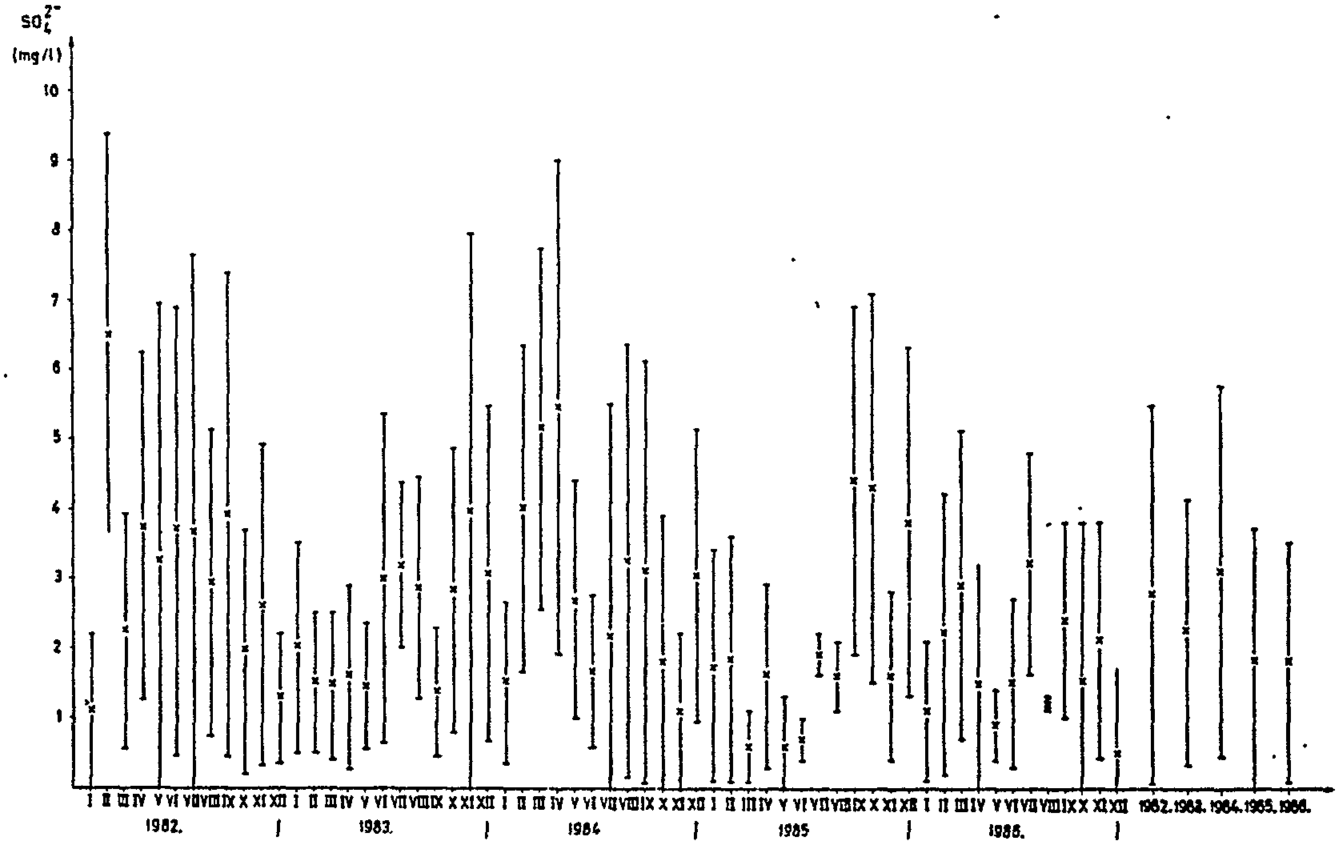


Fig. 6c. - Monthly means (x) and standard deviations of SO$_4{}^{2-}$-S ion concentration in precipitation, Zavizan, 1982-1986

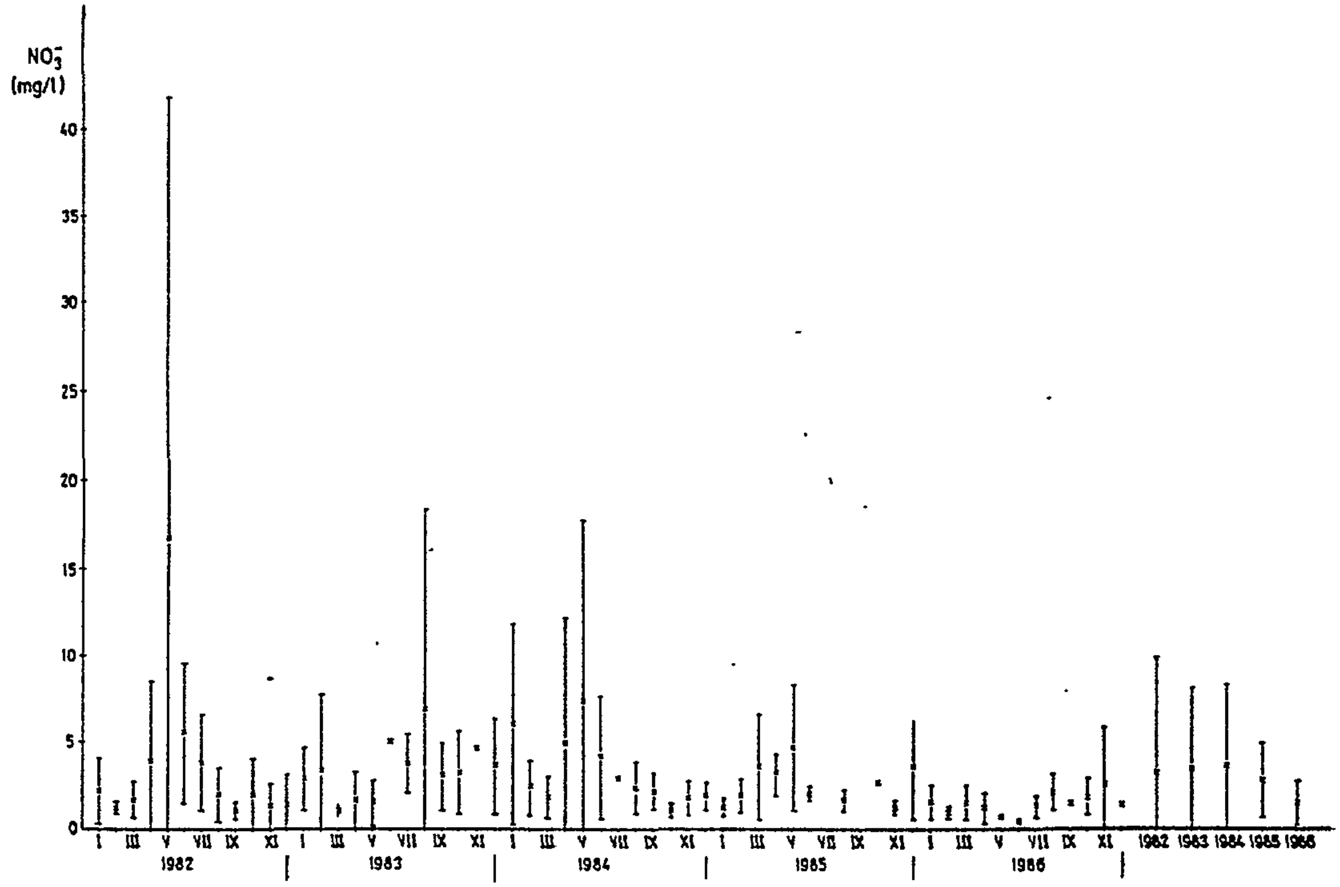


Fig. 7a. - Monthly means (x) and standard deviations of NO$_3^-$-N ion concentration in precipitation, Pula, 1982-1986

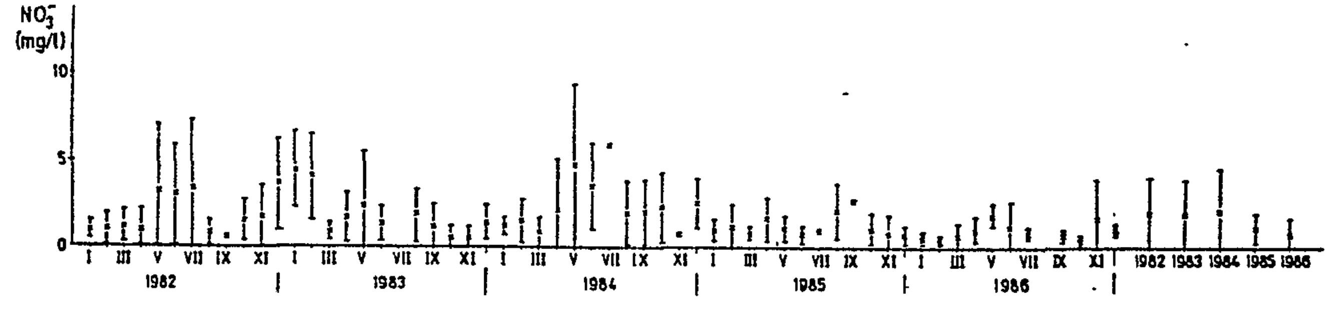


Fig. 7b. - Monthly means (x) and standard deviations of NO$_3^-$-N ion concentration in precipitation, Dubrovnik, 1982-1986

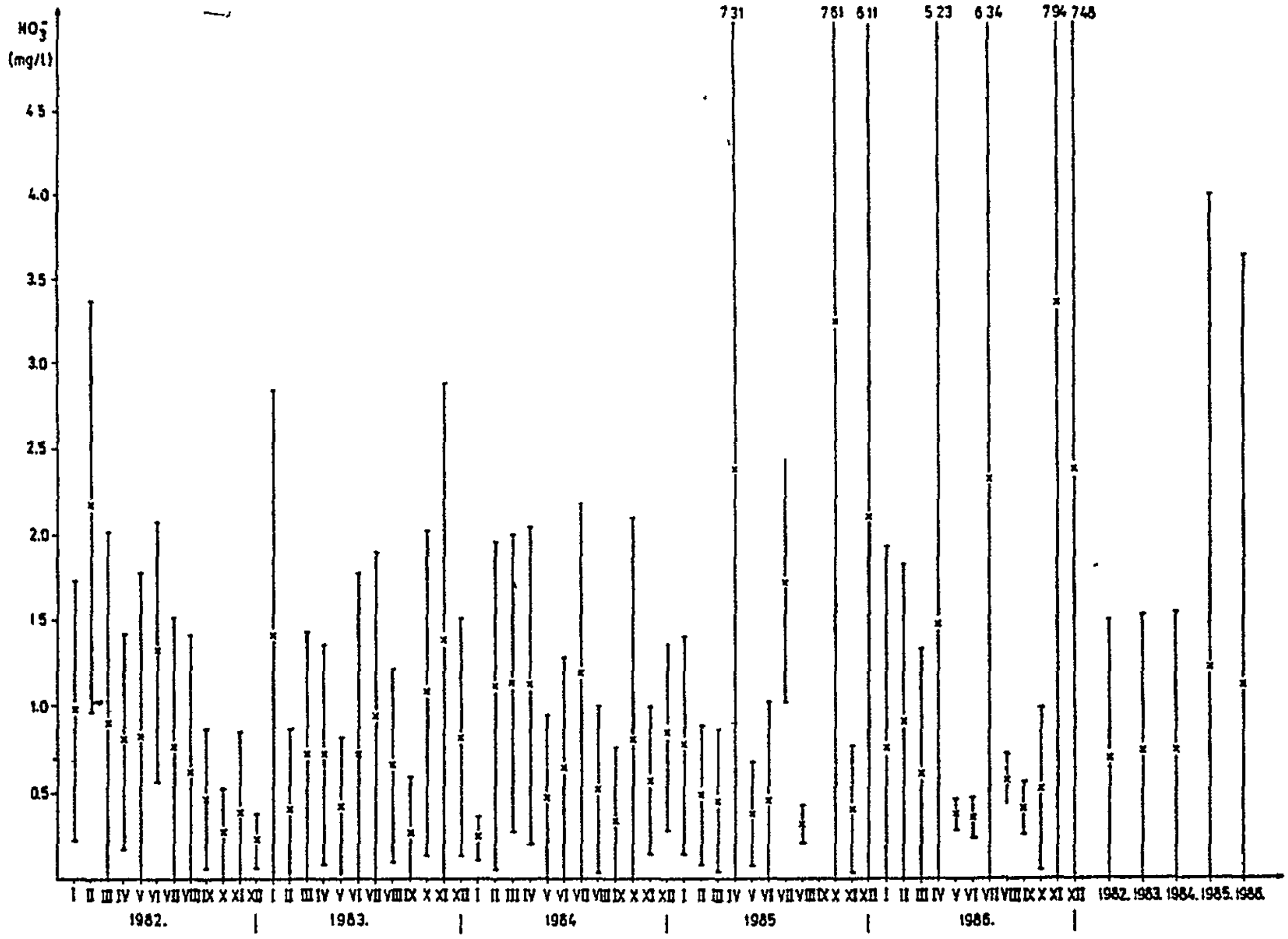


Fig. 7c. - Monthly means (x) and standard deviations of NO_3^--N ion concentration in precipitation, Zavizan, 1982-1986

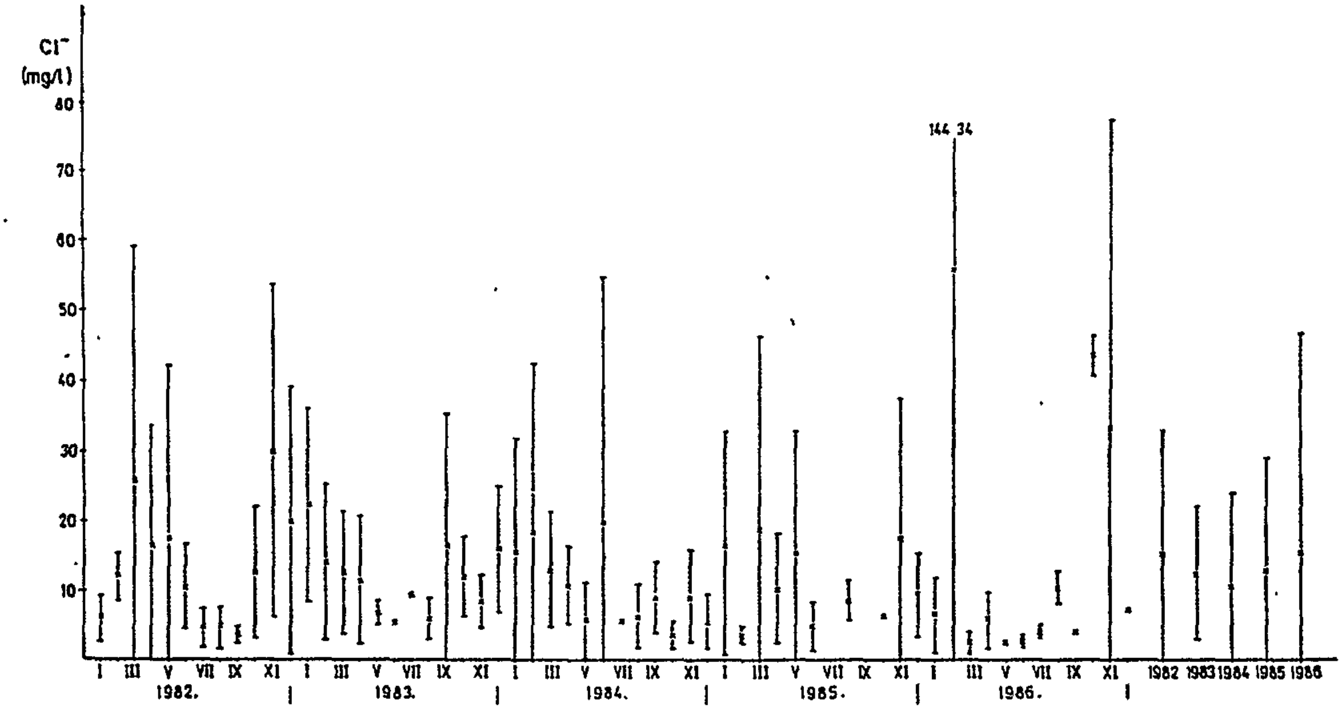


Fig. 8a. - Monthly means (x) and standard deviations of Cl^- ion concentrations in precipitation, Pula, 1982-1986.

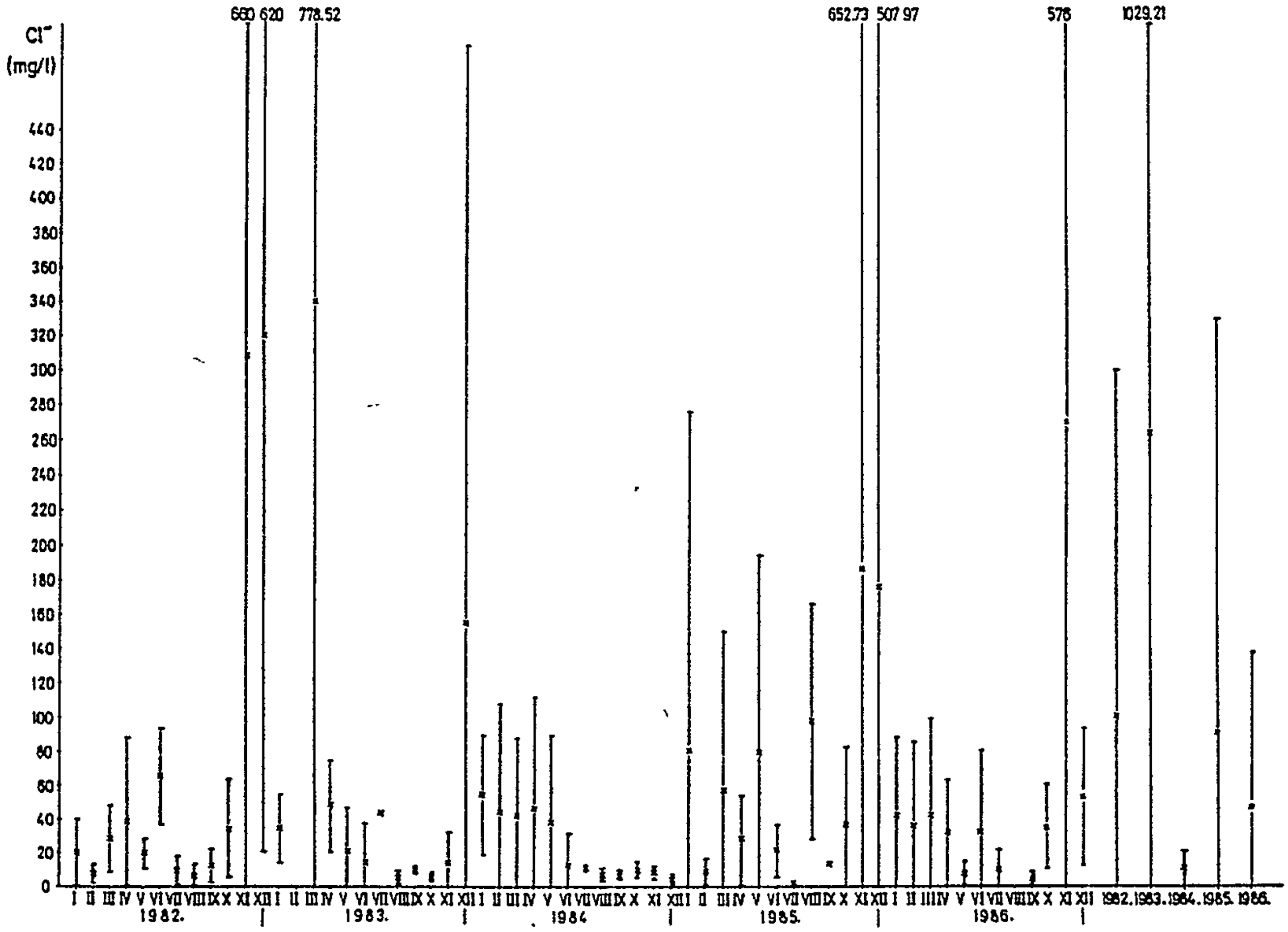


Fig. 8b. - Monthly means (x) and standard deviations of Cl⁻ ion concentrations in precipitation, Dubrovnik, 1982-1986.

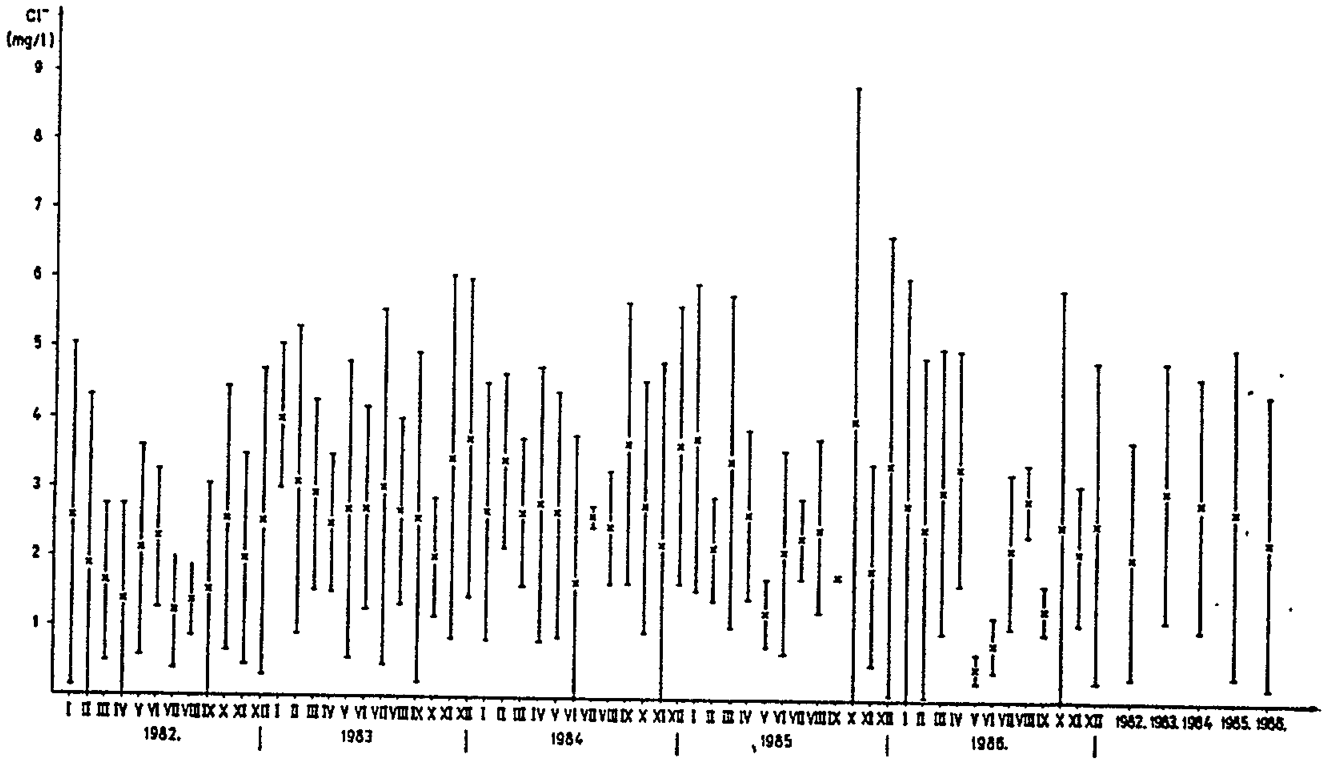


Fig. 8c. - Monthly means (x) and standard deviations of Cl⁻ ion concentrations in precipitation, Zavizan, 1982-1986.

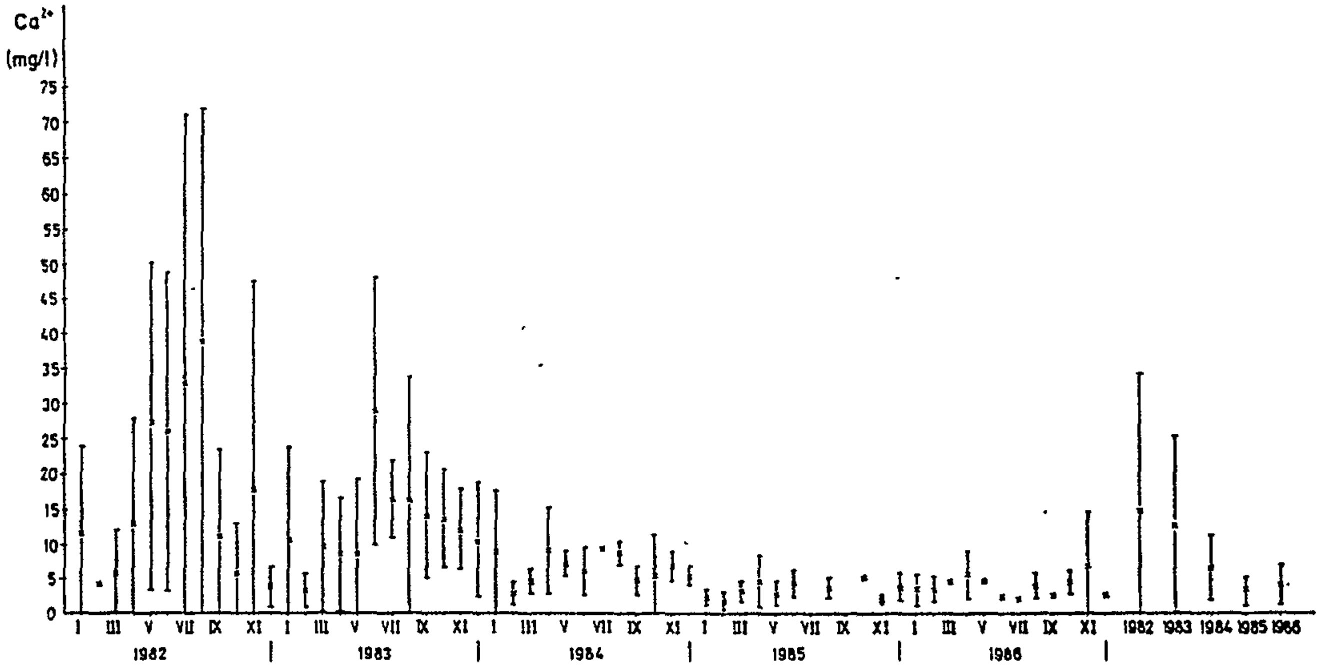


Fig. 9a. - Monthly means (x) and standard deviations of Ca^{2+} ion concentrations in precipitation, Pula, 1982-1986.

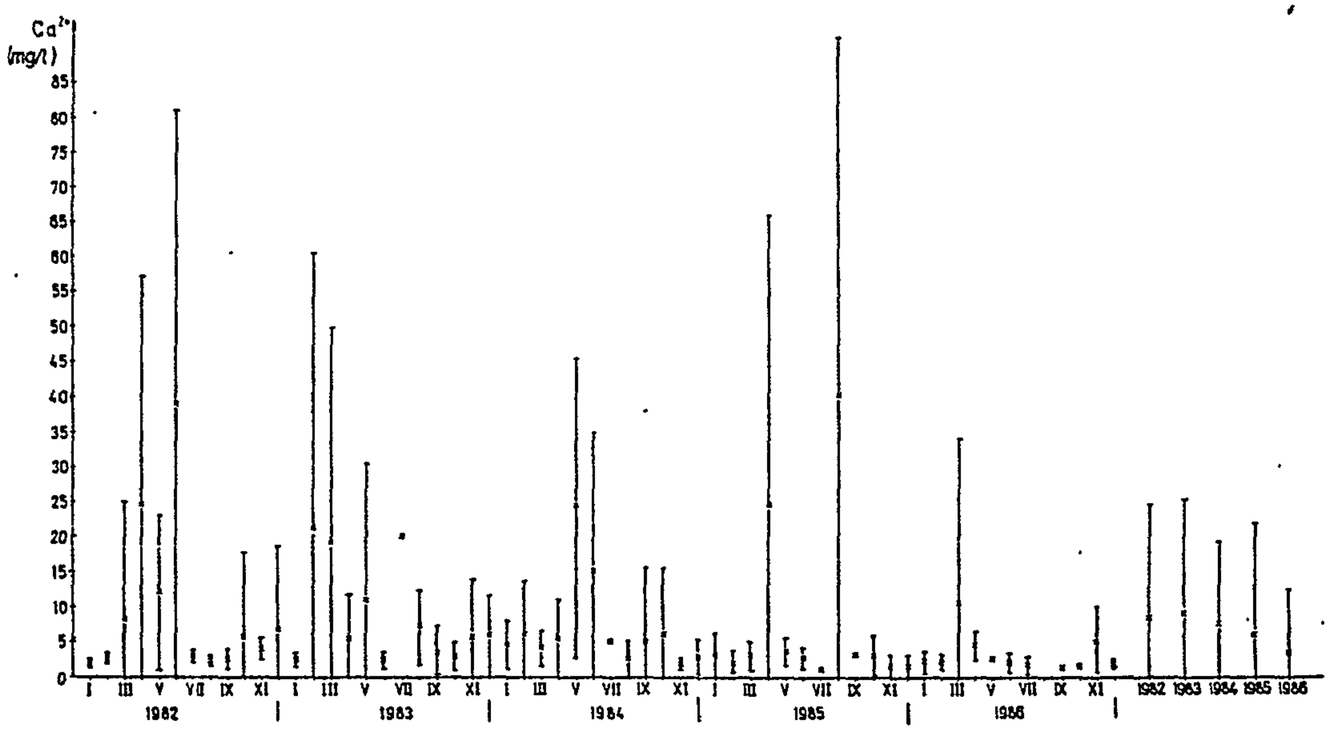


Fig. 9b. - Monthly means (x) and standard deviations of Ca^{2+} ion concentrations in precipitation, Dubrovnik, 1982-1986.

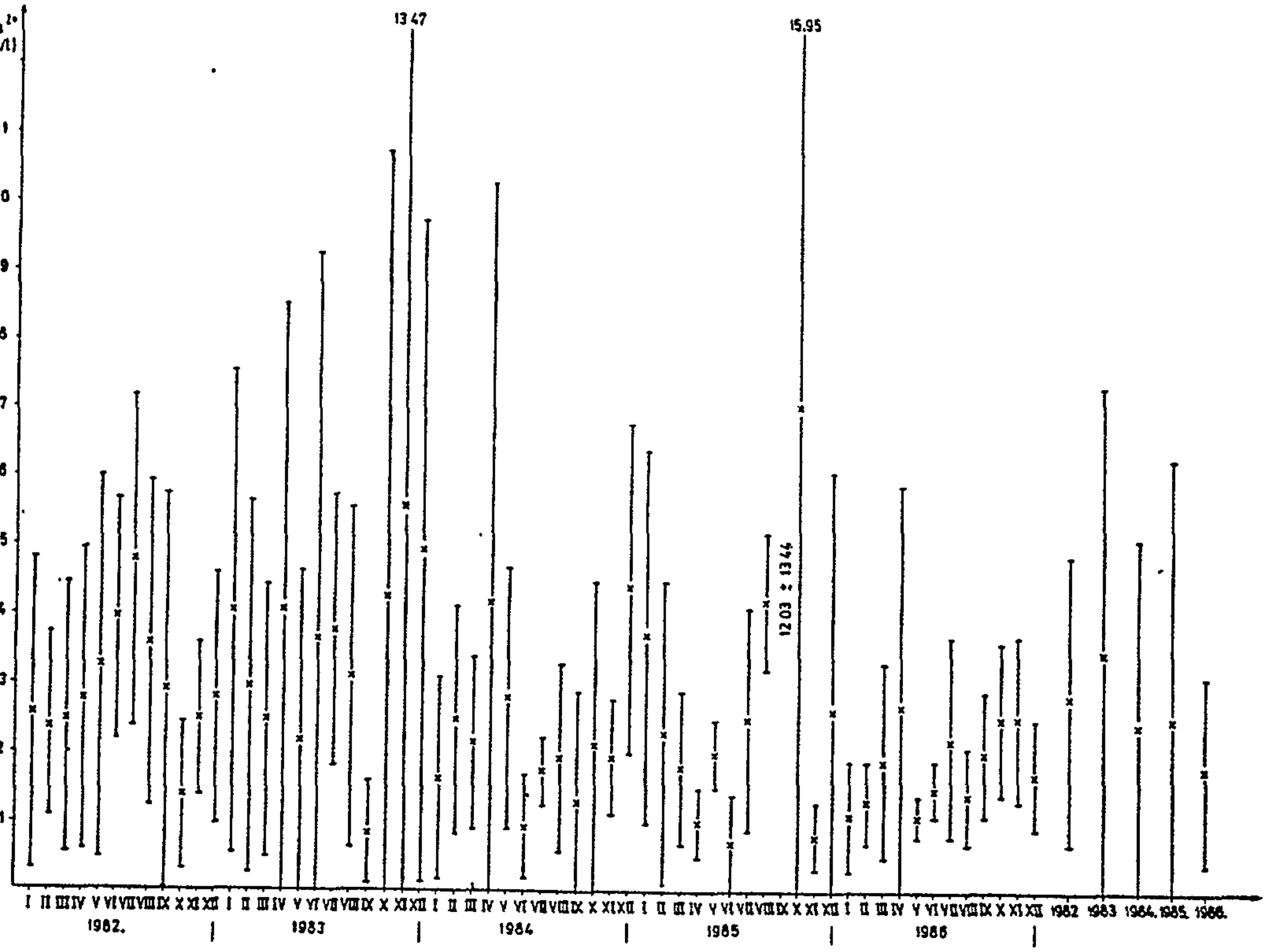


Fig. 9c. - Monthly means (x) and standard deviations of Ca²⁺ ion concentrations in precipitation, Zavizan, 1982-1986.

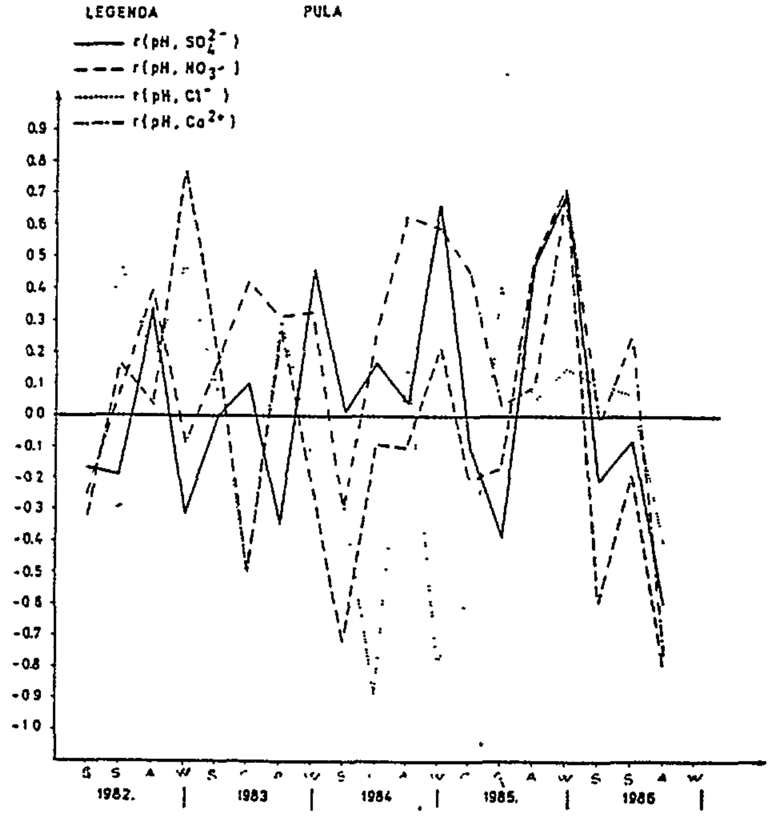


Fig. 10a. - Seasonal linear correlation coefficients discussing ion concentrations and pH values, Pula, 1982-1986.

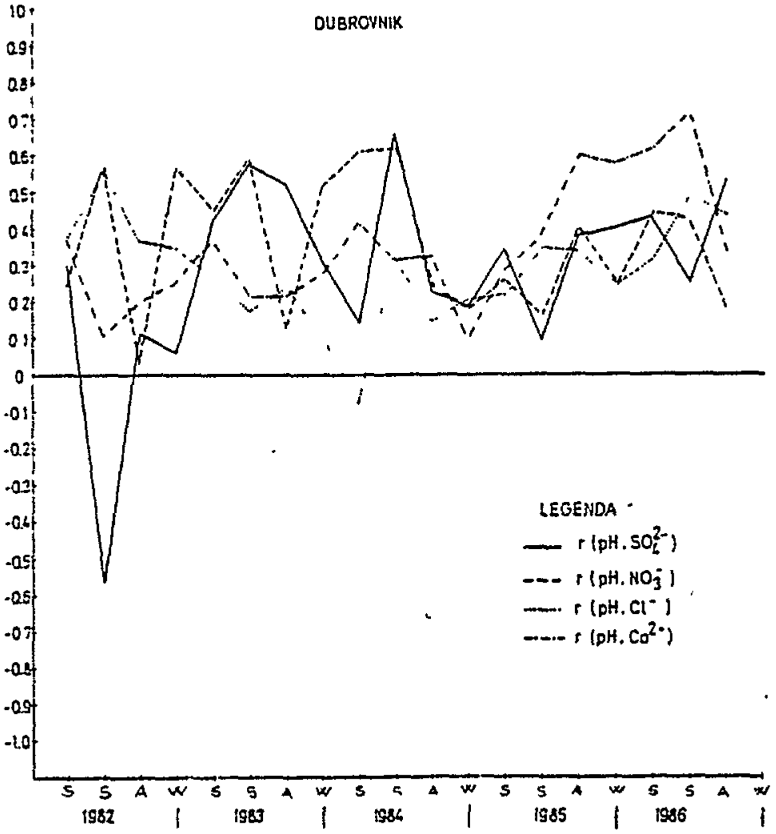


Fig. 10b. - Seasonal linear correlation coefficients discussing ion concentrations and pH values, Dubrovnik, 1982-1986.

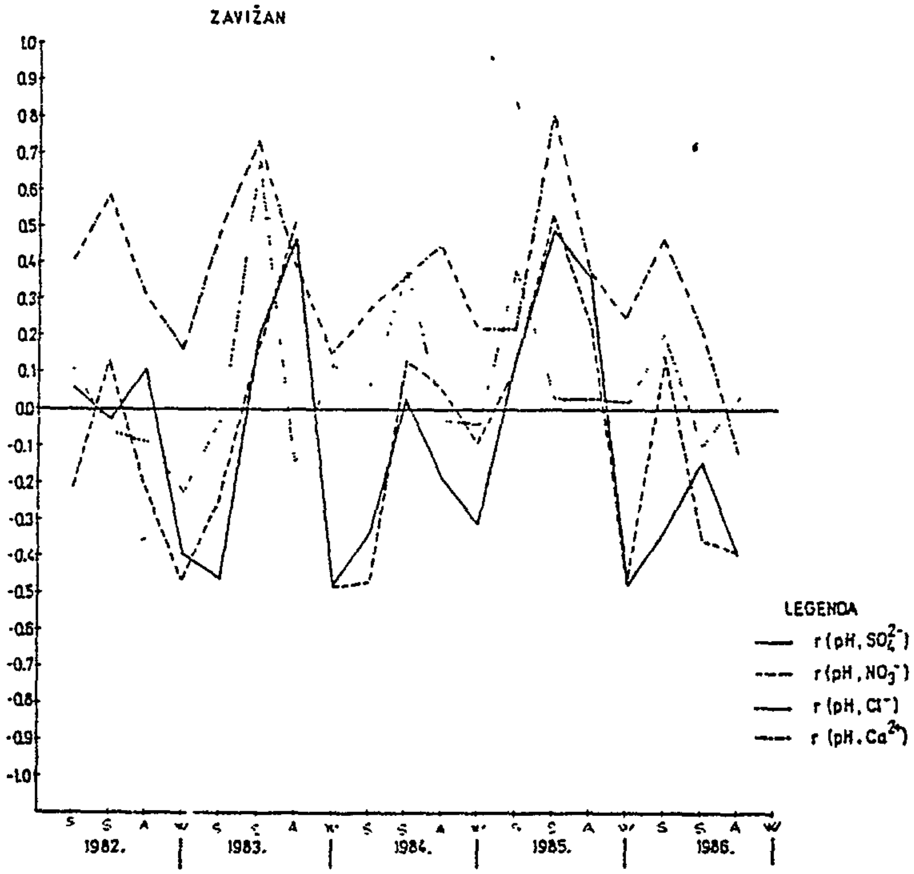


Fig. 10c. - Seasonal linear correlation coefficients discussing ion concentrations and pH values, Zavizan, 1982-1986.

REVIEW OF CHEMICAL DATA BY THE ITALIAN METEOROLOGICAL SERVICE

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INTRODUCTION

The Italian Meteorological Service has participated in the WMO-BAPMON (Background Air Pollution Monitoring Network) programme operation, since 1975, four regional stations (Verona, Viterbo, Santa Maria di Leuca and Trapani) and one baseline station, located at Monte Cimone (2165 ms 1, 1 at 44° 11' N, long 10° 42' E).

The aim of the WMO programme is "to obtain, on a global and regional basis, background concentration levels of atmospheric constituents, their variability and possible long-term changes from which the influence of human activities on the composition of the atmosphere can be judged". This should permit studies on:

- the possible effects on climate (Marenco, 1983; Butkovic et al., 1983; Callis and Natarajan, 1981);
- the transport and deposition of potentially harmful substances (Watts, 1980; Garland, 1978; Hales, 1989);
- the atmospheric part of biogeochemical cycles, including exchange rates (Pitts et al., 1978; WMO, 1982).

The Italian Meteorological Service is also involved in the MEDPOL programme and, in accordance with its aim to contribute to the pollutant sources inventory, the concentration monitoring, the study on the transport and effects of pollutants, operates a station at Messina and another one, not involved in this programme, at Vigna di Valle (about 40 km far from Rome), both from 1985 (see Fig. 1 - Map of stations location).

MATERIALS AND METHODS

Precipitation samples are collected monthly at the stations involved in the BAPMON programme, and weekly at Vigna di Valle and Messina, using an open/close rain collector which separates dry fall-out from wet samples.

In order to be representative on a regional basis, precipitation must exclude dry deposition. If deposition is avoided, rainout (removal process in the cloud) and washout (removal process below the cloud) are the mechanisms which control the composition of the sample. Both aerosols and some reactive gases are collected by precipitation. Proper sampling and analysis of precipitation provide a measure of the burden of trace substances in the lower troposphere and of the ability of the atmosphere to clean itself.

The whole set of measurements carried out and the instrumentations used are summarized in Table 1, while methods and techniques are mentioned in the WMO N.491 (international operations handbook for measurements of background atmospheric pollution).

Suspended particular matter is monitored with high-volume samplers (SARTORIUS DUST SAMPLER HV100 at Messina and GENERAL METAL WORK GMW2000 HV SAMPLER at Monte Cimone).

One of the most outstanding features of HiVol sampling is the possibility of carrying out many individual determinations, preserving a substantial portion of the filter for years, thus enabling retrospective surveys for new parameters to be undertaken.

RESULTS AND DISCUSSION

(a) pH

The pH of anatmospheric precipitation can be considered as the result of the effect of both meteorological variations and different factors related to natural components as well as anthropogenic activities.

In the precipitation field, the definition of acidity takes into account the contribution of the atmospheric carbon dioxide that, in the presence of water, behaves like a weak acid according to:

$$CO_2 + H_2O \Longleftrightarrow H_2CO_3 \Longleftrightarrow HCO_3^- + H^+$$

With a constant atmospheric carbon dioxide concentration of 320 ppm, for a precipitation constituted only by water and carbon dioxide, we have pH = 5.65.

Taking into account the CO_2 data measured continuously at Monte Cimone, classified "baseline station" according to the WMO requirements (9), it can be pointed out that the values are noticeably higher than 320ppm (present value = 350ppm) with a positive trend of 1.0 ÷ 1.5 ppm per year (Cundari and Colombo, 1984).

This situation cannot however justify the shift from pH ≈ 5.65 observed at Monte Cimone. In fact, this value has the maximum frequency in the range 4.0 ÷ 5.0 with a mean value over the period 1975 ÷ 1987 of 5.21 (see Fig. 2).

It should be interesting to evaluate how this shift is influenced by temporal and spatial fluctuations of the natural chemical constituents, in respect of pollutants' long-range transport.

A shift from pH ≈ 5.65 can also be observed for the other stations, according to their different locations, mainly in respect of environmental and human influences.

A clear example can be obtained from the Verona data, where the effects of the anthropogenic sources and the meteorological phenomenon of subsidence (which hampers the lower layers' atmospheric mixing), cause a pH shift towards acid values, with a maximum frequency in the range 4.0 ÷ 4.5, while for Viterbo, a station representative of a less industrialized area, we have the maximum in the range 4.5 ÷ 5.0 (see Figs. 3, 4).

The station of Santa Maria di Leuca, located on rocks 104 msl in a small village close to Gallipoli (Lecce), shows us a different pattern because of the lack of sizable pollutant anthropogenic sources and also because of the sea aerosol neutralizing effect (Wisniewski, 1983). As a consequence, pH values are more frequently in the range 4.5 ÷ 6.0 and the mean value is higher than the value we have for the baseline station (see Fig. 5).

A very different pattern emerges on the other hand at Trapani station, where pH values are more frequently in the range 6.0 ÷ 7.5 (see Fig.6). Apart from its location (since no important anthropogenic pollutant sources are present in the surroundings), this can be justified also by the neutralizing effect both of particulate matter coming from Africa and of the marine aerosol.

Such statistics have also been recorded at Messina station, involved in the MEDPOL programme, where the data used have been obtained from weekly samples (see Fig.7). This situation, very different from that of the Santa Maria di Leuca and Trapani stations, could be explained by taking into account that the station, located on a low hill, faces the sea close to the port, which acts as a pollutant source.

Rather different could be the explanation for the Vigna di Valle data. This station might be affected, in fact, by polluted air masses transport from the Rome area and, sometimes, by West-Northwest trajectories that could act as a vehicle of pollution from the Civitavecchia area, because of its port and its thermo-electric power plant (see Fig. 8).

(b) Ionic composition

According to R. M. Harrison and C. A. Pio (1983), an attempt to study correlations between different ions has been made. As rain samples, collected at the stations located near the sea, may be influenced in their ionic composition by salt sea spray, we used the following equations, respectively for sea (<1> and <2>) and rain (<3> and <4>) water, where ions are expressed on an equivalent basis:

<1> $Mg^{2+} = 0.23\ Na^{+}$
<2> $Na^{+} + Mg^{2+} = 1.05\ Cl^{-}$
<3> $Mg^{2+} = 0.22\ Na^{+} + 3$
<4> $Na^{+} + Mg^{2+} = 1.13\ Cl^{-} - 19$

Looking at the graphics obtained by equation <1>, we have a satisfactory linear regression coefficient only for Viterbo station.

There is no correlation at all for the Monte Cimone and Verona stations, while for Santa Maria di Leuca and Trapni, even if r is not satisfactory, the values are grouped along a straight line (see Figs. 9, 10, 11, 12, 13).

The situation is rather different, looking at the graphics obtained by equation <2> where, with the sole exception of Verona, all the r values are higher than 0.9 (see Figs. 14, 15, 16, 17, 18).

A better result is obviously obtained using equation <3> even if we have a satisfactory r for Viterbo only, indicating that, for such a station, Na^{+} and Mg^{2} are almost exclusively of salt sea spray origin (see Figs. 19, 20, 21, 22, 23).

In equation <4>, we have r similar to that for equation <2>, with similar patterns (see Figs. 24, 25, 26, 27, 28).

CONCLUSIONS

Concerning the pH values for the BAPMON stations, there has been a slight shift in respect of previous statistical elaborations (Cruciani and Olori, 1984) even if the overall patterns remain relatively unchanged.

For the Messina and Vigna di Valle stations, the pH values seem to be very interesting, so as to justify a further consideration in an attempt to correlate them with meteorological situations and parameters.

According to the studies carried out in ionic composition and correlation, we may conclude:

i) there is a good linear regression for most of the correlations tested;

ii) there is no direct correlation between Na^{+} and Mg^{2+} for any station except for Viterbo;

iii) Na^{+} and Mg^{2+} are mainly related to Cl^{-} as they are in the sea salt spray.

Regarding SPM, studies by X-RF are in progress to identify the chemical constituents captured by the filter with the aim of correlating them both with wet samples and possible meteorological parameters.

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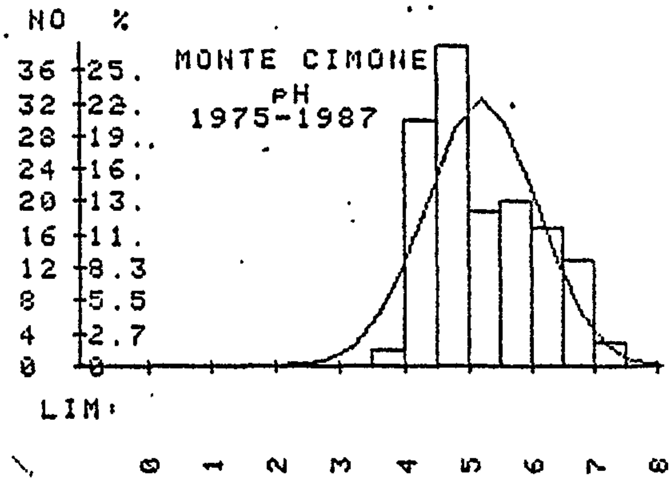
WMO n.491, 1982. International operations handbook for measurements of background atmospheric pollution.

Table 1

Measurements on precipitations samples

PROGRAMME	STATION	SAMPLING	PARAMETER TO BE DETERMINED	INSTRUMENTATION AT VIGNA DI VALLE LAB
BAPMON	M.CIMONE VERONA VITERBO S. MARIA LEUCA TRAPANI	MONTHLY	pH, Ac/Alc	PHILIPS PW9422 Phmeter
			Conductivity	" PW9527 Conductivimeter
			NO_3 -N SO_4 -S NH_3 -N Cl	PYE UNICAM SP8-150 Spectrophotometer UV/VIS
			Na, K, Mg, Ca	PYE UNICAM SP2900 spectrophotometer AA, recently equipped with a PU9090 (data graphic system), PU9095 (video furnace programmer) and a SP9 furnace power supply and auto-sampler, to analyze heavy metals.
MEDPOL	MESSINA	WEEKLY	AS IN THE BAPMON PROGRAMME INCLUDING ALSO SPM ONLY FOR MESSINA	AS FOR THE BAPMON PROGRAMME
EXPERI-MENTAL	VIGNA DI VALLE			NOTE 1) SPM is also monitored at M. CIMONE. 2) The VIGNA DI VALLE Laboratory has been recently equipped with a DIONEX 4000i Ionic chromatography with autosampler.

Fig. 1 - Map of stations location



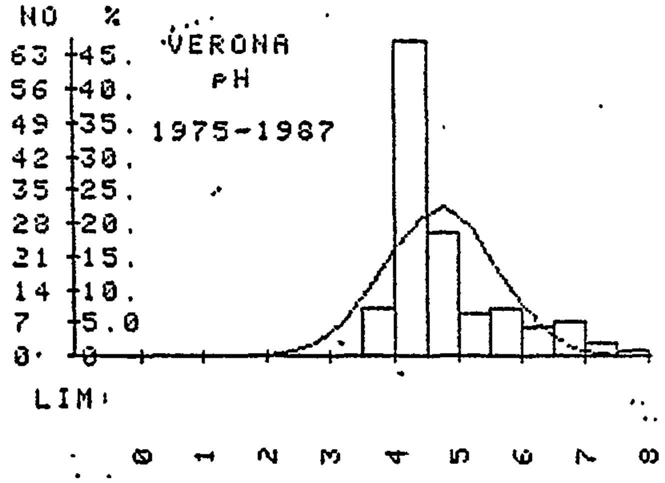
STATISTICA A CELLE

NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
8	3.50	2	1.40
9	4.00	30	20.98
10	4.50	39	27.27
11	5.00	19	13.29
12	5.50	20	13.99
13	6.00	17	11.89
14	6.50	13	9.09
15	7.00	3	2.10

MEDIA = 5.21

DEV. STANDARD = .88

FIG. 2



STATISTICA A CELLE

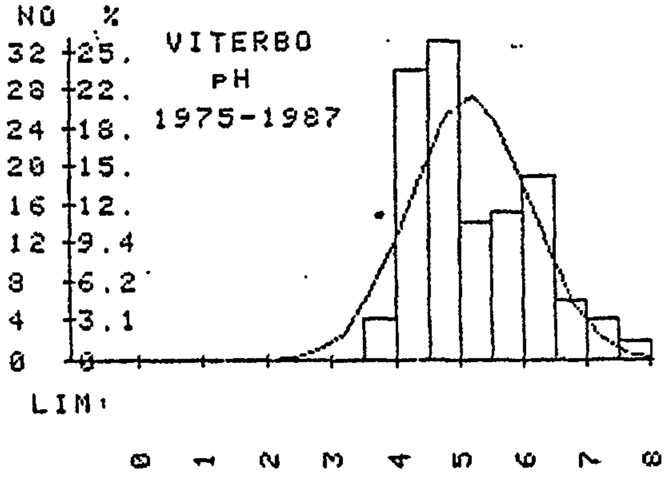
NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
8	3.50	10	7.25
9	4 00	66	47.83
10	4.50	26	18.84
11	5.00	9	6.52
12	5.50	10	7.25
13	6.00	6	4.35
14	6.50	7	5.07
15	7.00	3	2.17
16	7.50	1	.72

MEDIA = 4.72

DEV. STANDARD = .88

FIG. 3

Figs. 2 and 3 - Frequency histograms and cell statistics for pH values measured from: April 1975 to May 1987 for BAPMON stations;



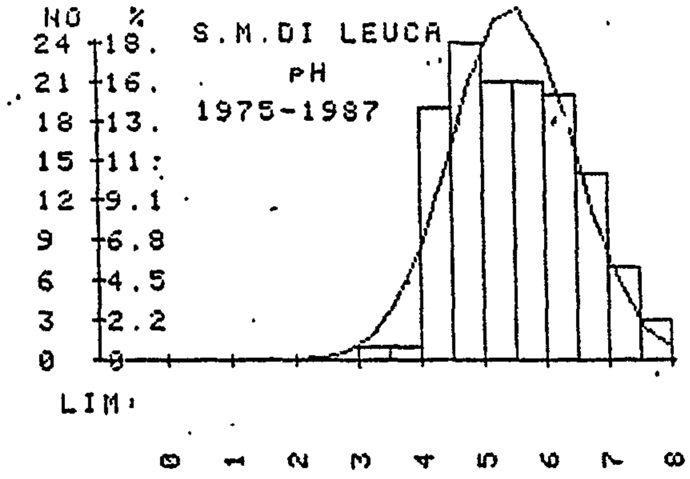
STATISTICA A CELLE

NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
8	3.50	4	3.15
9	4.00	30	23.62
10	4.50	33	25.98
11	5.00	14	11.02
12	5.50	15	11.81
13	6.00	19	14.96
14	6.50	6	4.72
15	7 00	4	3.15
16	7.50	2	1.57

MEDIA = 5.16

DEV. STANDARD =.93

FIG. 4



STATISTICA A CELLE

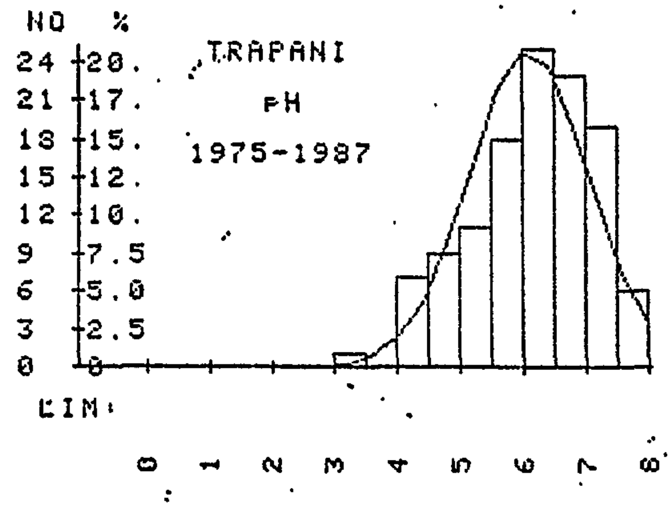
NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
7	3.00	1	.76
8	3.50	1	.76
9	4.00	19	14.50
10	4.50	24	18.32
11	5.00	21	16.03
12	5.50	21	16.03
13	6.00	20	15.27
14	6.50	14	10.69
15	7.00	7	5.34
16	7.50	3	2.29

MEDIA = 5.48

DEV. STANDARD = .97

FIG. 5

Figs. 4 and 5 - Frequency histograms and cell statistics for pH values measured from: April 1975 to May 1987 for BAPMON stations;



STATISTICA A CELLE

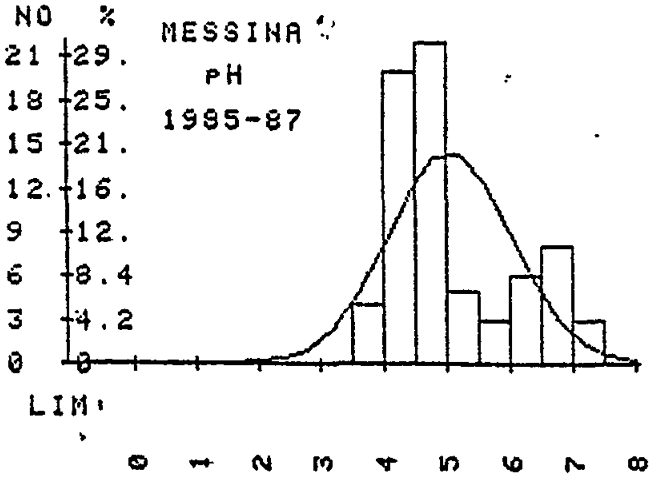
NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
7	3.00	1	.84
9	4.00	7	5.88
10	4.50	9	7.56
11	5.00	11	9.24
12	5.50	18	15.13
13	6.00	25	21.01
14	6.50	23	19.33
15	7.00	19	15.97
16	7.50	6	5.04

MEDIA = 6.10

DEV. STANDARD = .95

FIG. 6

Fig. 6 - Frequency histograms and cell statistics for pH values measured from: April 1975 to May 1987 for BAPMON stations;



STATISTICA A CELLE

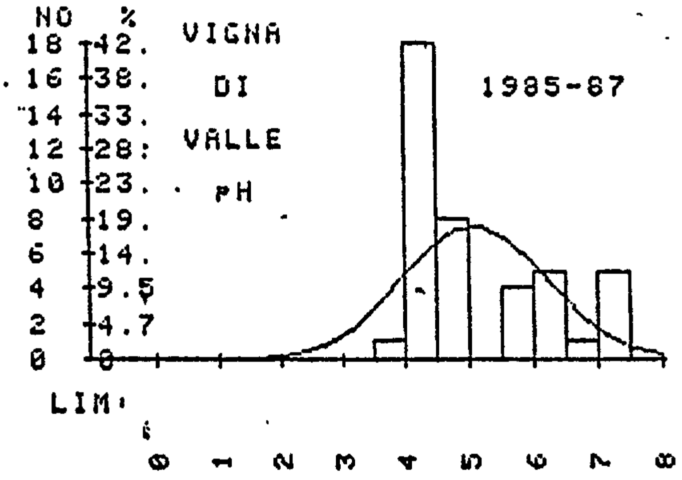
NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
8	3.50	4	5.63
9	4.00	20	28.17
10	4.50	22	30.99
11	5.00	5	7.04
12	5.50	3	4.23
13	6.00	6	8.45
14	6.50	8	11.27
15	7.00	3	4.23

MEDIA = 5.05

DEV. STANDARD = .97

FIG. 7

Fig. 7 - Frequency histograms and cell statistics for pH values measured from: June 1985 to June 1987 for Messina station



STATISTICA A CELLE

NUM. CELLA	LIMITE INFERI.	NUMERO DI OSS.	FREQUENZA %RELATIVA
8	3.50	1	2.38
9	4.00	18	42.86
10	4.50	8	19.05
12	5.50	4	9.52
13	6.00	5	11.90
14	6.50	1	2.38
15	7.00	5	11.90

MEDIA = 5.07

DEV. STANDARD = 1.10

FIG. 8

Fig. 8 - Frequency histograms and cell statistics for pH values measured from: January 1985 to January 1987 for Vigna di Valle station

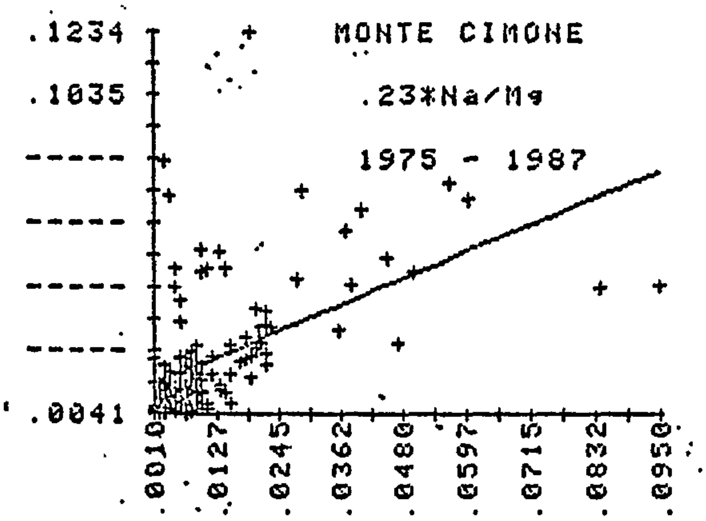


FIG. 9

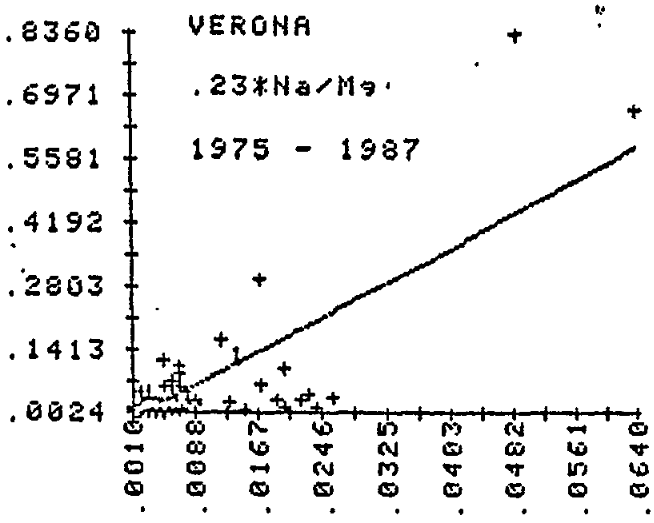
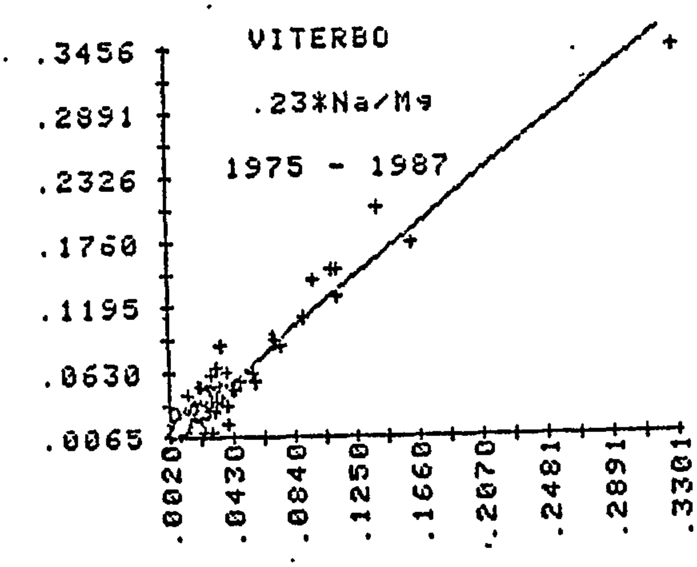


FIG. 10

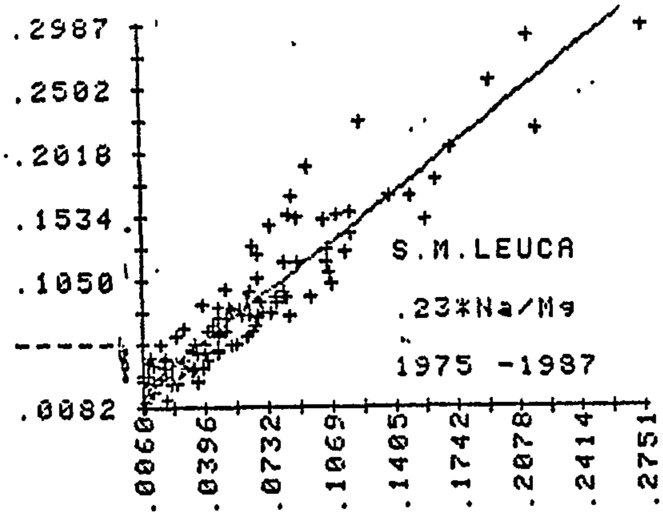
Figs. 9 and 10 - Correlations for all the stations using eq.<1>, valid for seawater



```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL108       0.2
REG     1      0.2       0.2 999.9
RESID107       0.0       0.0
R QUADRATO=          0.938

YHAT =      0.008 +       1.101 X
```

FIG. 11

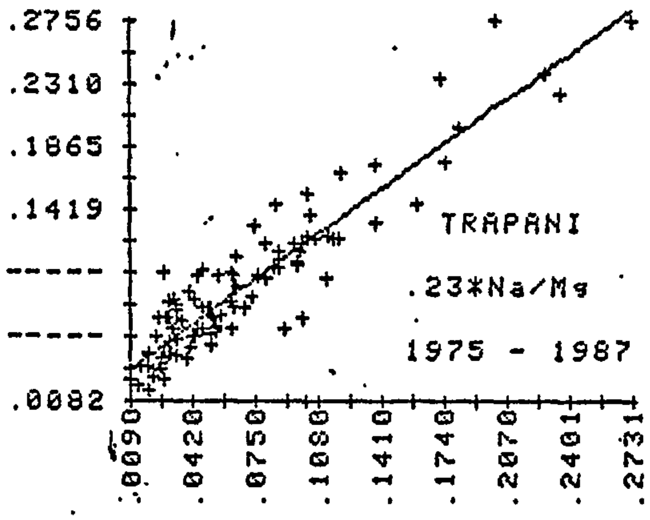


```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL113       0.4
REG     1      0.3       0.3 801.6
RESID112       0.0       0.0
R QUADRATO=          0.877

YHAT =      0.015 +       1.120 X
```

FIG. 12

Figs. 11 and 12 - Correlations for all the stations using eq.<1>, valid for seawater

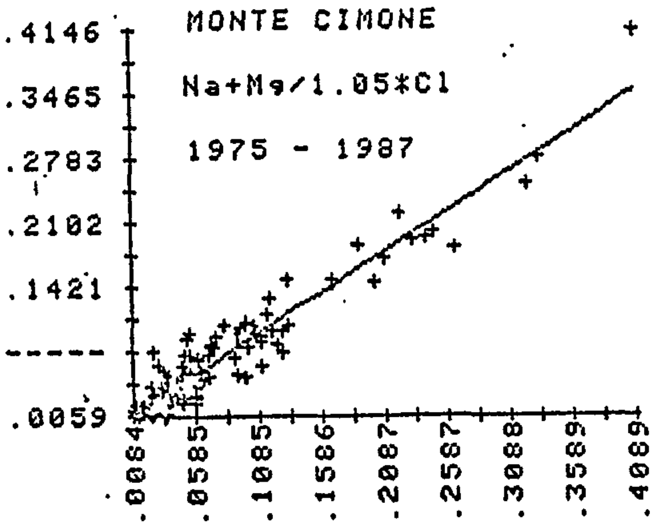


```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ      SM     .F
TOTAL102       0.3
REG     1      0.2      0.2 477.9
RESID101       0.1      0.0
R QUADRATO=        0.826

YHAT =     0.021 +      0.957 X
```

FIG. 13

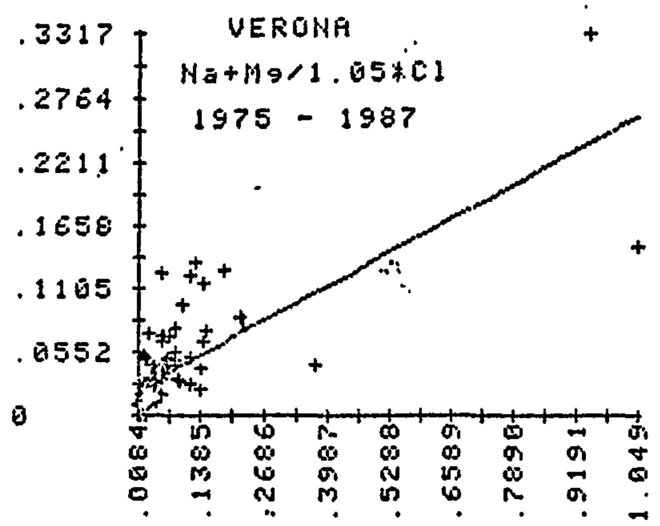
Fig. 13 - Correlations for all the stations using eq.<1>, valid for seawater



```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ      SM      F
TOTAL128       0.5
REG    1       0.4      0.4 999.9
RESID127       0.0      0.0
R QUADRATO=         0.916

YHAT =      0.001 +       0.857 X
```

FIG. 14

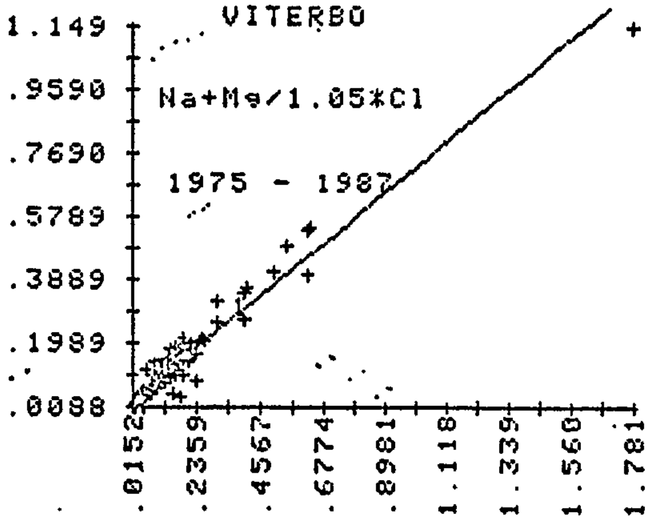


```
  ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ      SM      F
TOTAL132       0.2
REG    1       0.1      0.1 171.9
RESID131       0.1      0.0
R QUADRATO=         0.568

YHAT =      0.021 +       0.229 X
```

FIG. 15

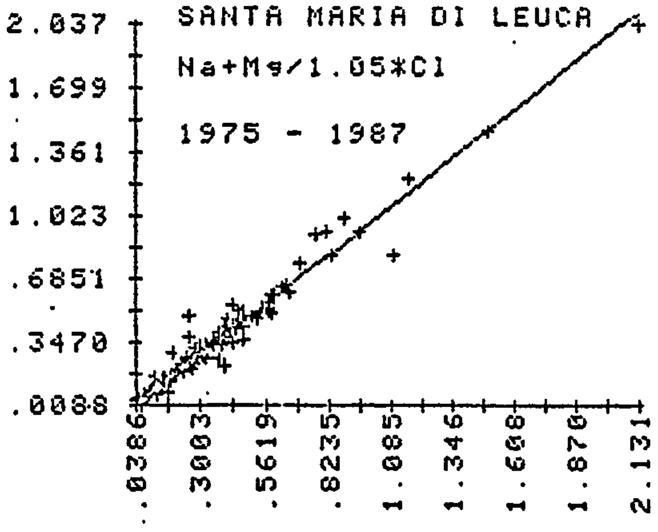
Figs. 14 and 15 - Correlations for all the stations using eq. <2>, valid for seawater



```
  ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL109       2.3
REG     1      2.1      2.1 999.9
RESID108       0.1      0.0
R QUADRATO=         0.941

YHAT =      0.022 +       0.697 X
```

FIG. 16

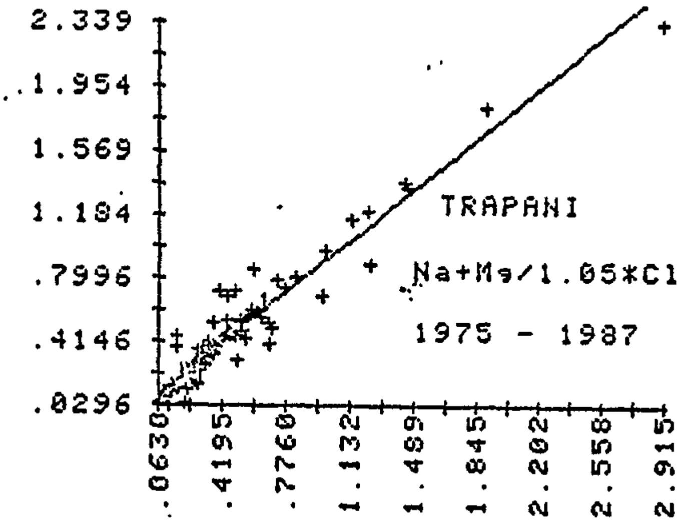


```
  ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL113      10.6
REG     1     10.2     10.2 999.9
RESID112       0.4      0.0
R QUADRATO=         0.964

YHAT =     -0.004 +       0.987 X
```

FIG. 17

Figs. 16 and 17 - Correlations for all the stations using eq. <2>, valid for seawater



```
   AOV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ        SM      F
TOTAL107      13.5
REG    1      12.4      12.4 999.9
RESID106       1.0       0.0
R QUADRATO=         0.924

YHAT =      0.044 +      0.858 X
```

FIG. 18

Fig. 18 - Correlations for all the stations using eq. <2>, valid for seawater

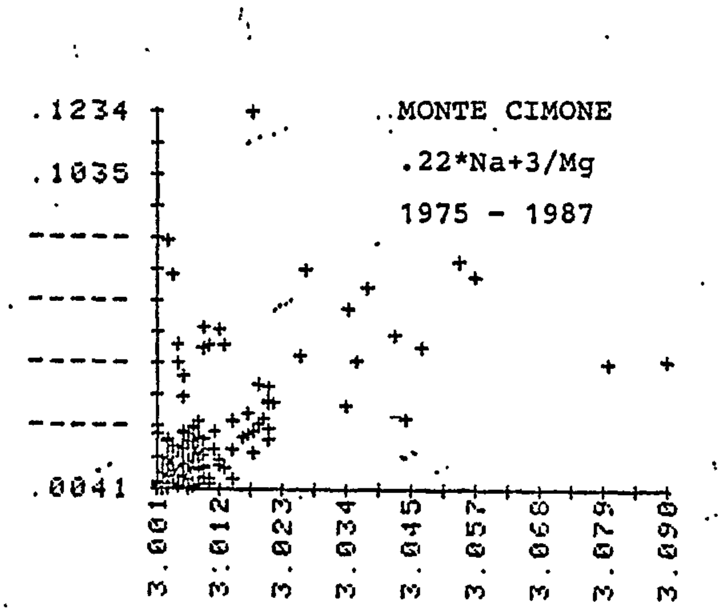


FIG. 19

Fig. 19 - Correlations for all the stations using eq. <3>, valid for rainwater

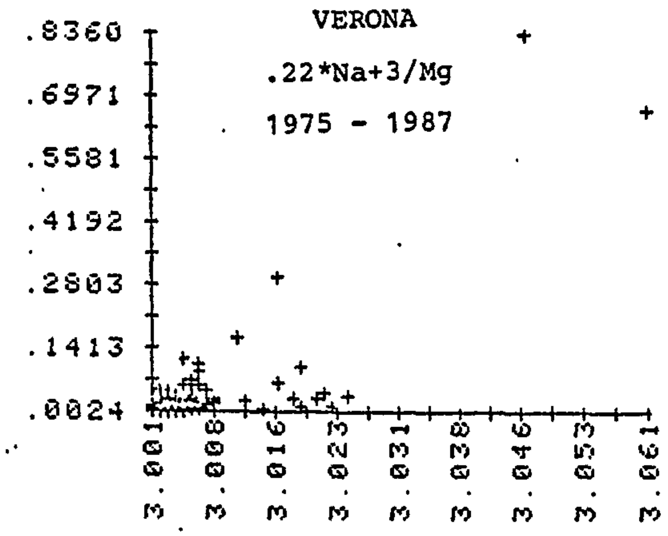
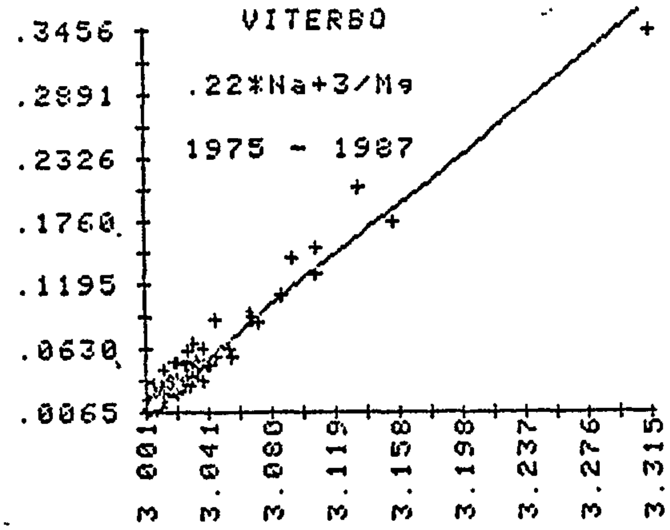


FIG. 20

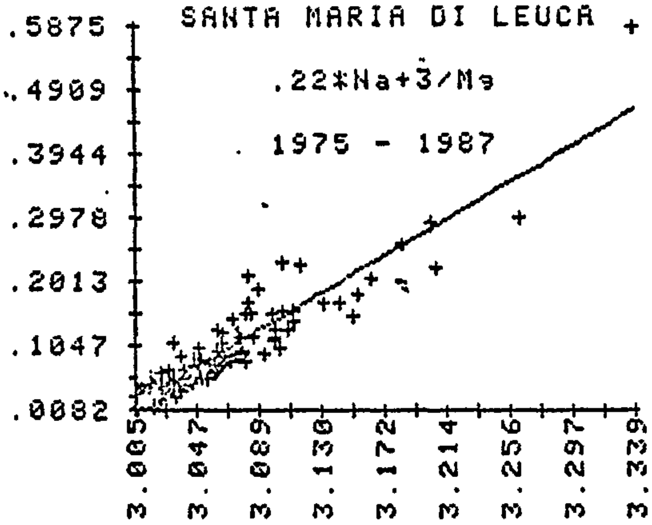


```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ      SM      F
TOTAL104      0.2
REG     1     0.2      0.2 999.9
RESID103      0.0      0.0
R 'QUADRATO=       0.952

YHAT =     -3.418 +      1.142 X
```

FIG. 21

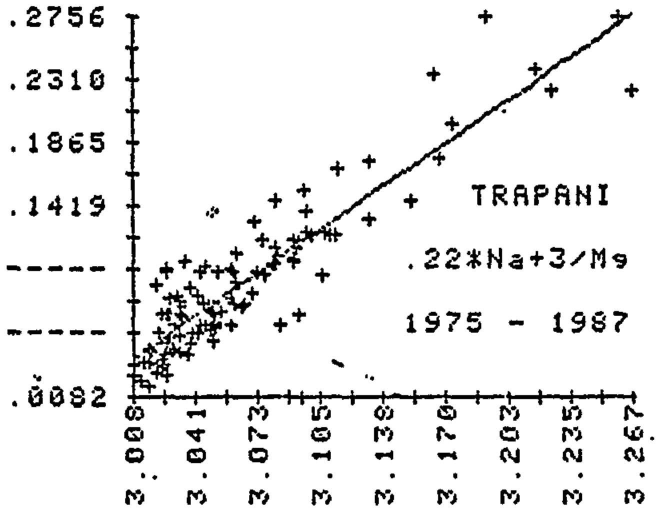
Figs. 20 and 21 - Correlations for all the stations using eq. <3>, valid for rainwater



```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL118      0.7
REG    1      0.6      0.6  768.2
RESID117      0.1      0.0
R QUADRATO=        0.868

YHAT =     -3.985 +      1.331 X
```

FIG. 22

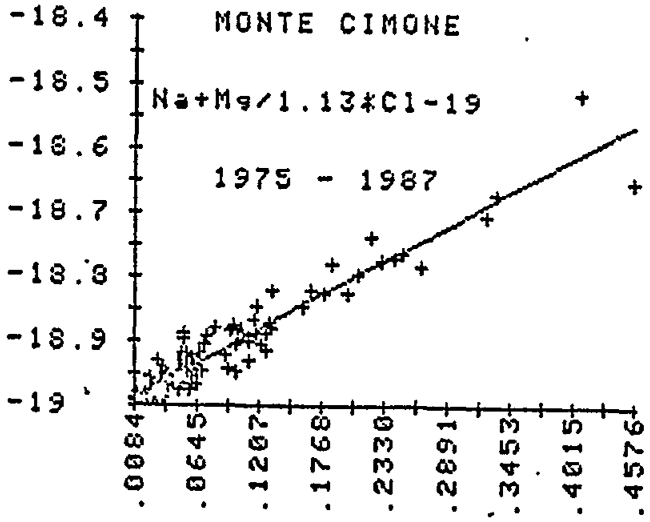


```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ       SM      F
TOTAL107      0.3
REG    1      0.3      0.3  437.0
RESID106      0.1      0.0
R QUADRATO=        0.805

YHAT =     -2.783 +      0.936 X
```

FIG. 23

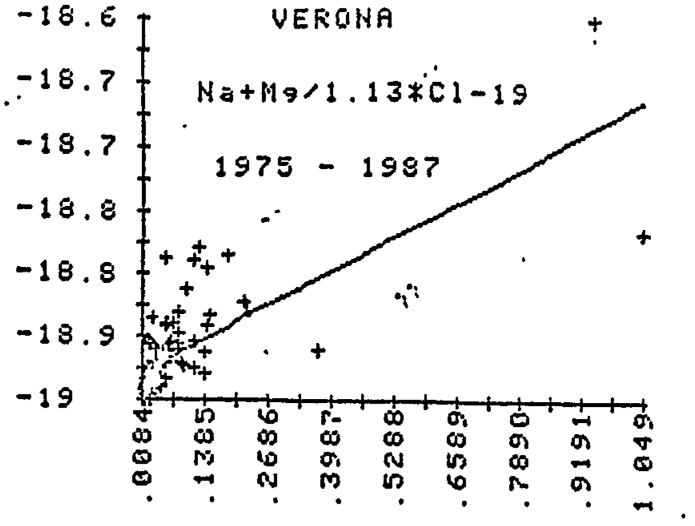
Figs. 22 and 23 - Correlations for all the stations using eq. <3>, valid for rainwater



```
    ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL      SQ       SM       F
TOTAL128         0.6
REG      1       0.6      0.6 999.9
RESID127         0.1      0.0
R QUADRATO=          0.915

YHAT =    -18.996 +       0.871 X
```

FIG. 24

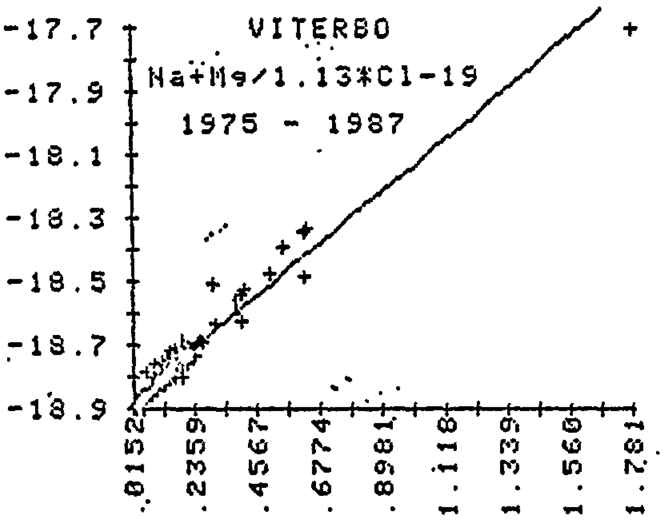


```
    ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL      SQ       SM       F
TOTAL132         0.2
REG      1       0.1      0.1 172.0
RESID131         0.1      0.0
R QUADRATO=          0.568

YHAT =    -18.977 +       0.246 X
```

FIG. 25

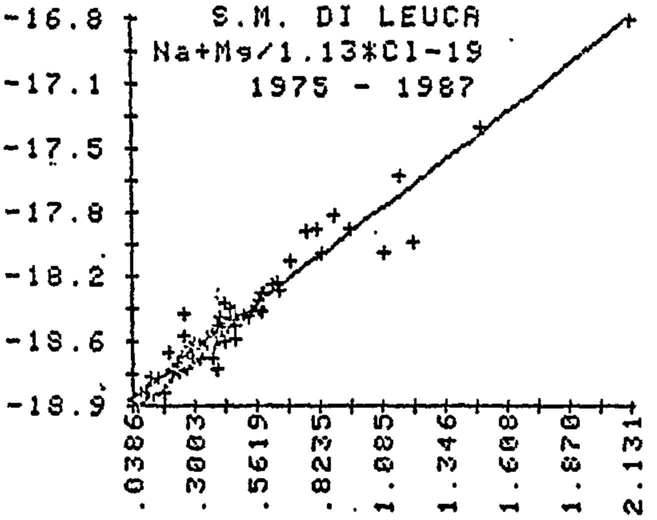
Figs. 24 and 25 - Correlations for all the stations using eq. <4>, valid for rainwater



```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL     SQ      SM     F
TOTAL107        2.7
REG     1       2.5      2.5 999.9
RESID106        0.2      0.0
R QUADRATO=          0.940

YHAT =    -18.973 +        0.759 X
```

FIG. 26

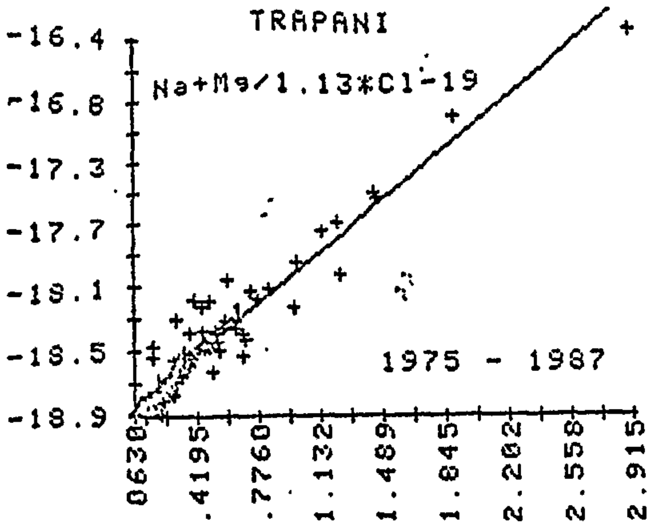


```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL     SQ      SM     F
TOTAL114       12.6
REG     1      12.0     12.0 999.9
RESID113        0.6      0.0
R QUADRATO=          0.955

YHAT =    -18.998 +        1.035 X
```

FIG. 27

Figs. 26 and 27 - Correlations for all the stations using eq. <4>, valid for rainwater



```
   ADV: REGRESS. LINEARE :COD. 1
SORGENTE/GL    SQ      SM.     F
TOTAL109      15.8
REG     1     14.5     14.5 999.9
RESID108       1.3      0.0
R QUADRATO=          0.918

YHAT =    -18.950 +      0.923 X
```

Fig. 28 - Correlations for all the stations using eq. <4>, valid for rainwater

THE VARIABILITY OF THE ATMOSPHERIC INPUT IN THE NORTH WESTERN MEDITERRANEAN BASIN

Paper presented by Jacques Morelli

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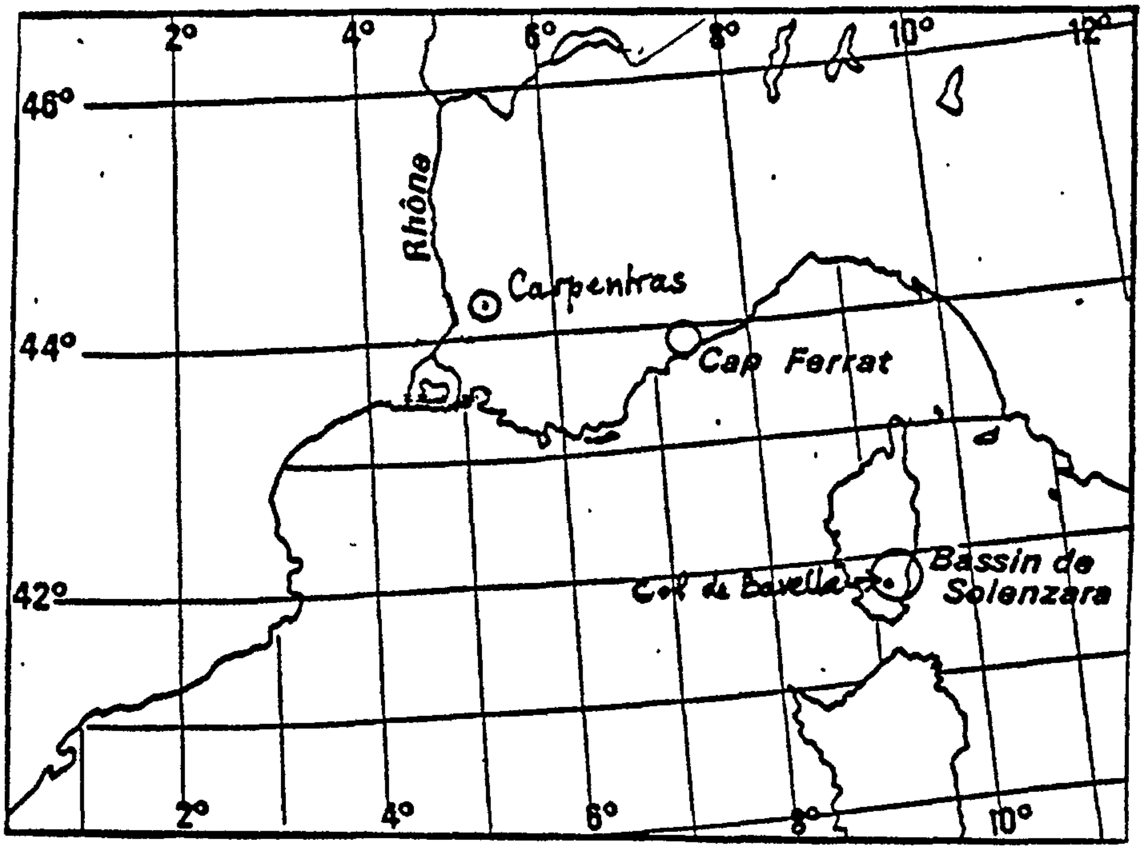
INTRODUCTION

Long-term investigations of the input of airborne material have been carried out in the North Western Mediterranean Basin within the framework of the CNRS Land-Sea Interactions Coordinated Group - CRECO ICO (Groupement de Recherches Coordonnées "Interactions Continent - Océan" du Centre National de la Recherche Scientifique). Since 1980, a geochemical study on atmospheric deposition of major components has been conducted at the Bavella Pass, in a undeveloped area of south Corsica. This work was completed by observations on trace metal and nutrient atmospheric input carried out since 1986 at the site of Cap Ferrat, on the French Riviera. The study at the Cap Ferrat atmospheric sampling station was supported within the research component of MEDPOL. More recently a similar study of atmospheric trace metal input was undertaken in 1987 close to the Rhône delta region, at a site at the Carpentras Meteorological Station. The locations of the various sampling stations around the north western Mediterranean Basin are given in Figure below.



Most of the results presented here are related to chemical investigations of rain in South Corsica. In addition, preliminary data on observations at the Cap Ferrat coastal stations are also briefly given.

I - RESULTS RELATED TO RAIN CHEMISTRY IN SOUTH CORSICA*

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ABSTRACT

Tremendous variations in the relative abundances of major ions in rain water have been observed at a undeveloped location in south Corsica (Bavella Pass). From selected data combined with air mass back trajectories reaching the sampling zone, these variations can be explained by antagonistic influences of well-differentiated aerosols mainly originating in the continental environment of the Mediterranean Basin. The impact of the marine source is significant in all cases. Episodes of acid rain are observed when incoming air masses pass over various remote European industrial regions (lowest pH values close to 4), and can be particularly attributed to pollution by sulphuric acid which contributes significantly to the ionic balance. By contrast, air masses arriving from arid regions of north Africa correlate with the highest pH values (6 to 7) and correspond to red rain episodes of high solid particulate matter contents of up to 30% calcite. Owing to the partial dissolution of this component, the red rains are responsible for very high enrichments in dissolved calcium and bicarbonate, which may account for the major part of the ionic concentration of rain water. In situations involving the mixing of Saharan and European air masses, the intermediate pH values observed may be a consequence of a neutralizing effect of the incoming desert aerosol on the atmospheric acidity. It appears therefore that Saharan dust may counterbalance the effects of acidic rains in Mediterranean regions. Such interaction in the atmosphere and also at ground and sea level after atmospheric deposition may have implications for the marine and terrestrial ecosystems of these areas.

---

* The text presented here has been accepted for publication in the Journal of Aerosol Science (Vol. 19, n° 6, 1988) under the title "Fluctuations of ionic composition of precipitation collected in Corsica related to changes in the origins of incoming aerosols" and is reproduced with the permission of the Editor.

MATERIALS AND METHODS

Systematic observations of the chemical composition of atmospheric deposition have been carried out since 1980 in a station located in an uninhabited area of South Corsica at the Bavella Pass (41° 50 N, 9° 10 E). A plastic gauge of 400 cm^2 aperture was used for the collection. According to the intensity of precipitations, their frequencies, duration and site accessibility in winter, the sampling times ranged from several hours to one week. Samples were sometimes taken within rainfall episodes and were thus not mixed with dry deposition. In the other cases, they represent bulk deposition and we estimated that the contribution of dry deposition to their content in dissolved and solid matter is low compared to that of wet deposition (less than 10%). The liquid samples, which were infrequently produced from melting snow, were filtered indoors close to the field, using 0.4 µm Nucleopore filters in order to evaluate their content in solid particulate matter. The pH was measured immediately after sampling by potentiometric method. Filtered solutions were analyzed by atomic absorption spectrometry for the determination of their concentrations in Na^+, K^+, Ca^{++}, Mg^{++} and by colorimetry for that of the ions Cl^-, SO_4^{--}, NO_3^- and NH_4^+.

RESULTS AND DISCUSSION

From selected data from the years 1981, 1984 and 1985 recorded in Table 1, we have related the fluctuations of the ionic composition of collected samples to changes in the origins of incoming aerosols incorporated into clouds and precipitations. In a previous work on the geochemistry of coastal aerosols, air masses back trajectories appeared as a helpful tool for the identification of their sources (Morelli et al., 1983, Morelli et al., 1985). That is why we call on this method in this study, using trajectories established by the French National Meteorology. On this basis, we distinguish in Table 1 situations with atmospheric input from the European continent, episodes with influence of Saharan dust and situations with mixing of Saharan and European air masses. For the considered precipitation samples, back trajectories at 2 pressure levels are represented in Figs. 1 to 11 (A:700 hPa, B:850 hPa). In these Figures, the time origins were taken 4 days before the arrival of air masses in the sampling zone and the segments of the trajectories correspond to runs of 6 hours.

The ionic balance of our liquid samples was determined taking into account the contributions of the analyzed ionic species in % of the total ionic concentrations evaluated in microequivalent per litre. We noted that the sum of the contributions of anions and cations are both in the range 50±1%. As examples, results corresponding to the three kinds of meteorological situations considered in Table 1 are given in Figs. 12, 13 and 14.

Due to the insularity of Corsica and to the fact that incoming air masses pass over the Mediterranean, the impact of the marine source on the chemical composition of precipitations is generally significant though very variable. With regard to sea salt particles derived from bursting bubbles (Blanchard, 1963) and assuming the conservation of the ionic ratios of sea water and the marine origin of all the collected sodium, it may be calculated that they represent 3-47% of the total ionic concentrations of the samples of Table 1. This marine contribution accounts for a large amount of the chlorides and magnesium and for a relatively small part of the sulphates, at the most about 10% for the episodes of March 8 1984 and November 20-25 1985. Another undetermined part of the marine sulphates probably originates from transformations of biogenic organosulphur gases emitted at the sea surface (Bonsang et al., 1980; Carlier et al. 1984; Turner and Liss, 1985). A volcanic contribution in sulphates also cannot be excluded when arriving air masses have been influenced by sulphur emissions from the volcanoes of southern Italy (Haulet et al., 1977). If we look at air masses trajectories of Figs. 1 to 11, this seems not to be the case for the results presented in this paper.

When air masses pass over various remote European industrialized regions (Figs. 1 to 4), the pH of water samples is relatively acid and close to 4. Precipitation samples then have high concentrations of sulphate and to a lesser extent of nitrate and ammonium (Table 1). Although there are natural processes leading to rain acidification (Charlson and Rodhe, 1982; Legrand et al., 1984), this result may be explained by the preponderant influence of polluted aerosols containing sulphuric acid and lower quantities of nitric acid. As shown in Fig. 12, they contribute largely to the ionic content of the collected water.

In cases of typical Saharan dust input (Figs. 5 to 8), the ionic composition of samples undergoes a noticeable change and is associated with pH values close to 7, with a very high content of calcium and bicarbonate (Table 1). Such situations correspond to red rain episodes, observed by many authors over the Mediterranean and southern Europe (Clement et al., 1972; Bucher and Lucas, 1975; Prodi and Fea, 1979; Ganor and Mamane, 1979; Tomadin et al., 1984; Chester et al., 1984). These events are very frequent in Corsica; for example, we observed 19 red rains on 60 precipitations collected during 1984 (Loye-Pilot et al., 1986). If we consider their high content in solid particulate matter including up to 30% of calcite, it appears that the partial dissolution of this component is responsible for their enrichment in dissolved calcium (Loye-Pilot et al., 1986) and in bicarbonate. These species may then account for the major part of the ionic concentrations of the collected water (Fig. 13). On the other hand, the relatively high content in sulphate of red rains (Table 1) could partly be attributed to the dissolution of desertic gypsum particles.

In situations of interactions of air masses coming both from the Saharan and European continents (Figs. 9 to 11), we observed intermediate pH values (Table 1). Sulphates are then the most abundant ionic species (Table 1 and Figure 14). These probably result from the addition of two effects: inclusion in rain water of sulphur derived from polluted aerosols and possible dissolution of gypsum desertic particles. Most of the dissolved calcium can be linked with the Saharan input and the European pollution may contribute to the content of the samples in nitrates and ammonium. In such mixed situations the pH values may be explained by the neutralization of the acidity of polluted air masses by desertic particles (Loye-Pilot et al., 1986, 1987).

Finally, very large fluctuations of ionic composition of precipitations have been observed in Corsica. They can be related to antagonistic influences of natural and man-made aerosols derived from various remote sources of the African and European continents, in addition to those of the marine sources. An important fact to be emphasised concerns the neutralizing effect of incoming desertic aerosol on the rain acidity due to the spreading of the European air pollutants over Mediterranean regions. Taking into consideration the impact of precipitations on terrestrial and marine ecosystems (Likens, 1981; Bolin and Cook, 1983; Duce, 1986), this interaction in the atmosphere and also at ground and sea level after atmospheric deposition is a factor of some importance for the Mediterranean environment.

ACKNOWLEDGMENTS

This work was carried out with the support of ENSJF Biology-Geology Laboratory and of the CNRS Land-Sea Interactions Coordinated Group (GRECO-ICO) and ATP Aerosols désertiques. We thank J. M. Gros and B. Strauss from the French National Meteorology for the establishment of air masses trajectories and J. A. Lefèvre and N. Kielbasa for technical assistance.

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Table 1

Chemical composition of precipitations collected at the Bavella Pass (South Corsica)

N° of sample	Sampling date	Air masses origin	Rainfall (mm)	pH	Concentrations (mg.l^{-1})				Concentrations (mg.l^{-1})				
					Cl^-	$SO4^{--}$	$HCO3^-$	$NO3^-$	Na^+	K^+	Ca^{++}	Mg^{++}	$NH4^+$
SITUATIONS WITH ATMOSPHERIC INPUT FROM THE EUROPEAN CONTINENT													
1	20 Feb. 1981	See Fig. 1	7 (<u>snow</u>)	4,10	1,60	7,55	0,00	0,63	0,74	0,23	0,30	0,16	1,11
2	7- 8 Nov. 1981	See Fig. 2	11,8	4,07	2,00	4,50	0,00	3,10	0,87	0,21	0,32	0,10	0,90
3	8 Mar. 1984	See Fig. 3	28,7	4,16	5,50	5,53	0,00	2,89	2,67	1,29	0,38	0,36	1,12
4	20-25 Nov. 1985	See Fig. 4	3,1	3,89	18,60	10,90	0,00	8,10	9,12	4,52	9,75	1,05	1,15
SITUATIONS WITH INFLUENCE OF SAHARAN DUST													
5	28-29 June 1981	See Fig. 5	6,0	7,18	3,22	7,50	22,20	n.d.	1,60	0,43	8,48	0,10	n.d.
6	4- 5 May 1984	See Fig. 6	42	6,81	3,14	3,95	11,10	1,28	1,04	0,16	5,72	0,26	0,15
7	12-13 May 1985	See Fig. 7	15	7,14	1,50	4,40	22,30	1,38	0,96	0,32	7,90	0,23	0,20
8	18-20 May 1985	See Fig. 8	8	6,82	1,10	4,10	10,40	2,10	0,50	0,25	3,32	0,22	0,37
MIXED SITUATIONS													
9	15-16 Nov. 1985	See Fig. 9	27,7	5,84	0,48	1,74	0,50	0,74	0,10	0,22	0,62	0,05	0,32
10	16-18 Nov. 1985	See Fig. 10	18,9	5,80	0,58	2,31	0,40	0,86	0,15	0,30	0,60	0,04	0,54
11	18-20 Nov. 1985	See Fig. 11	18	4,46	1,04	2,30	0,00	1,16	0,37	0,45	0,11	0,06	0,31

n.d.= not determined

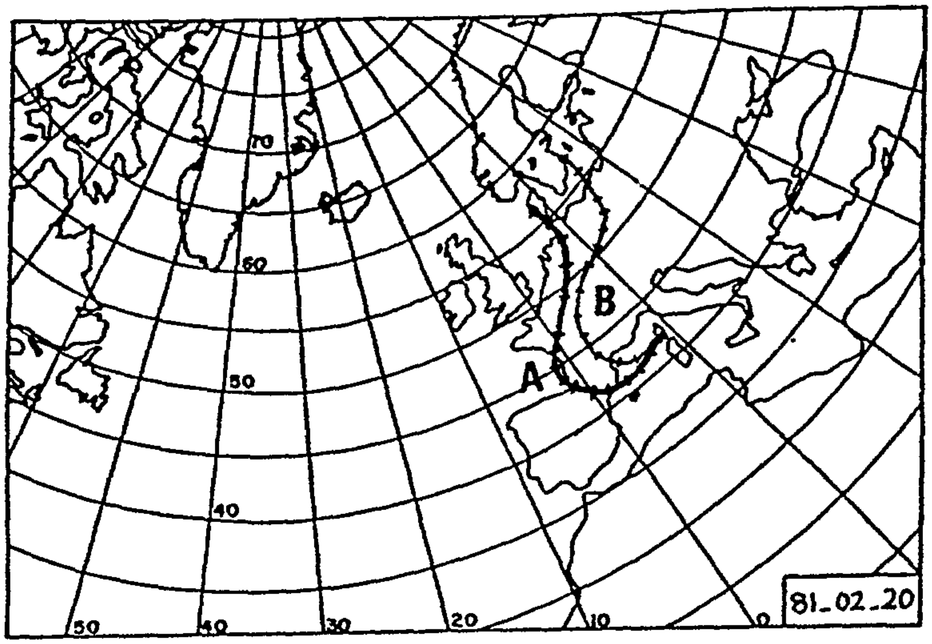

Fig. 1 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on February 20, 1981 at 6 h UT

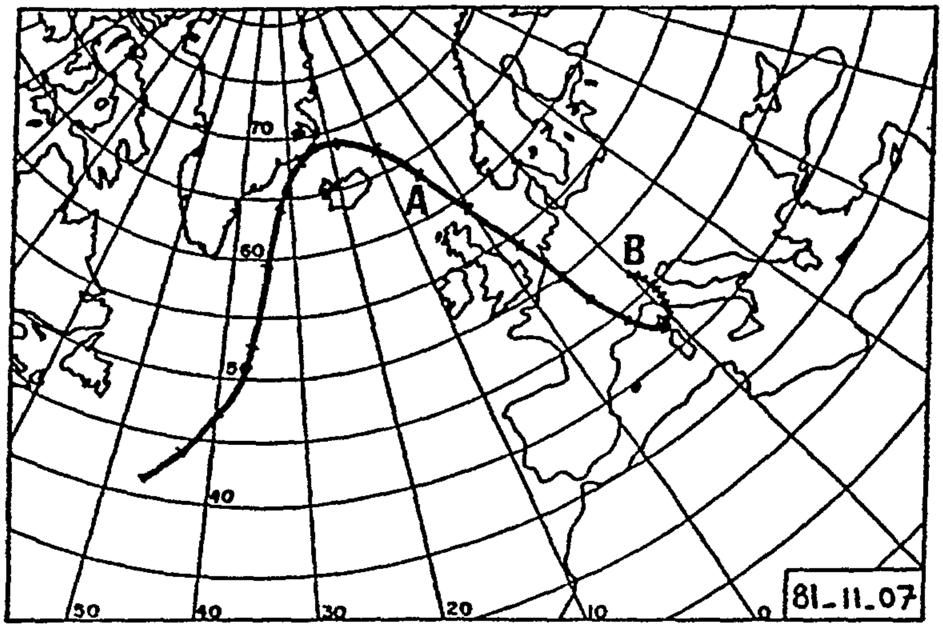

Fig. 2 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on November 7, 1981 at 18 h UT

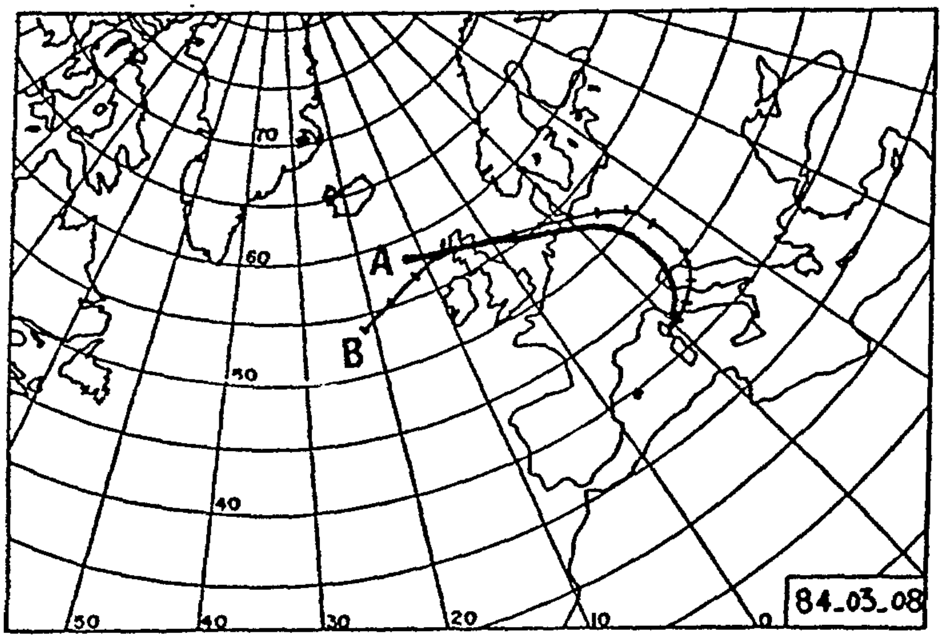

Fig. 3 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on March, 8, 1984 at 18 h UT

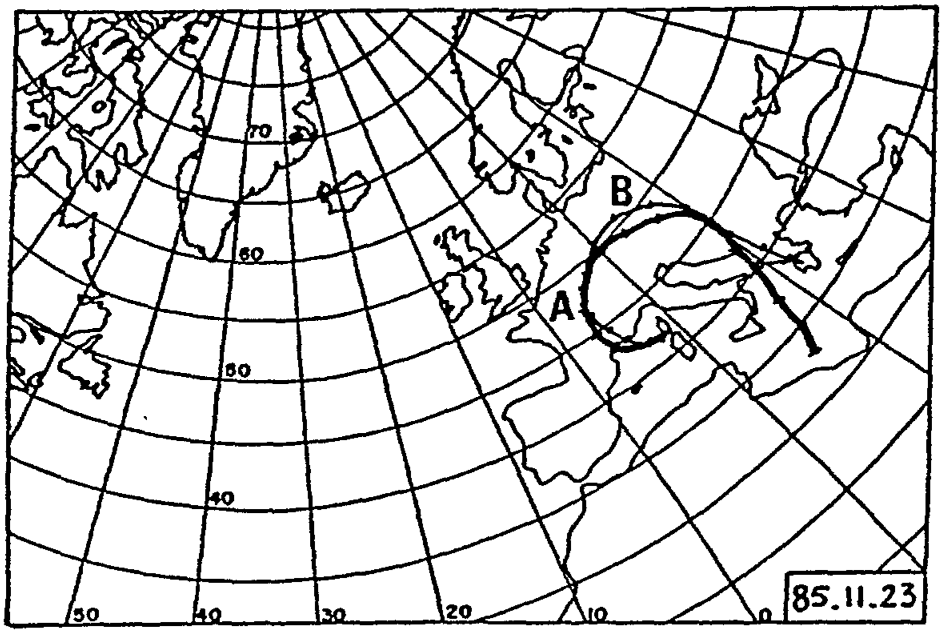

Fig. 4 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on November 23, 1985 at 6 h UT

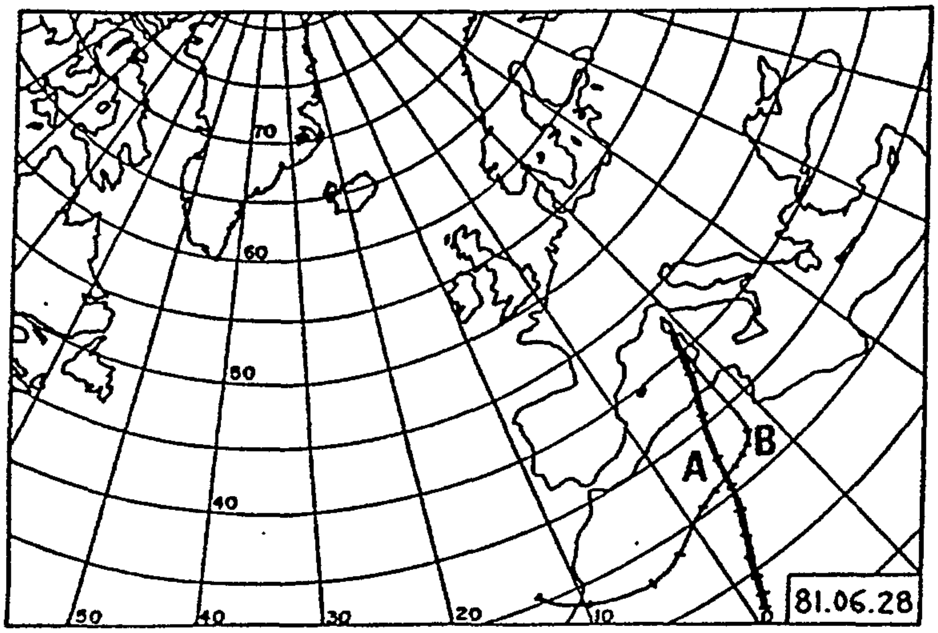

Fig. 5 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on June 28, 1981 at 12 h UT

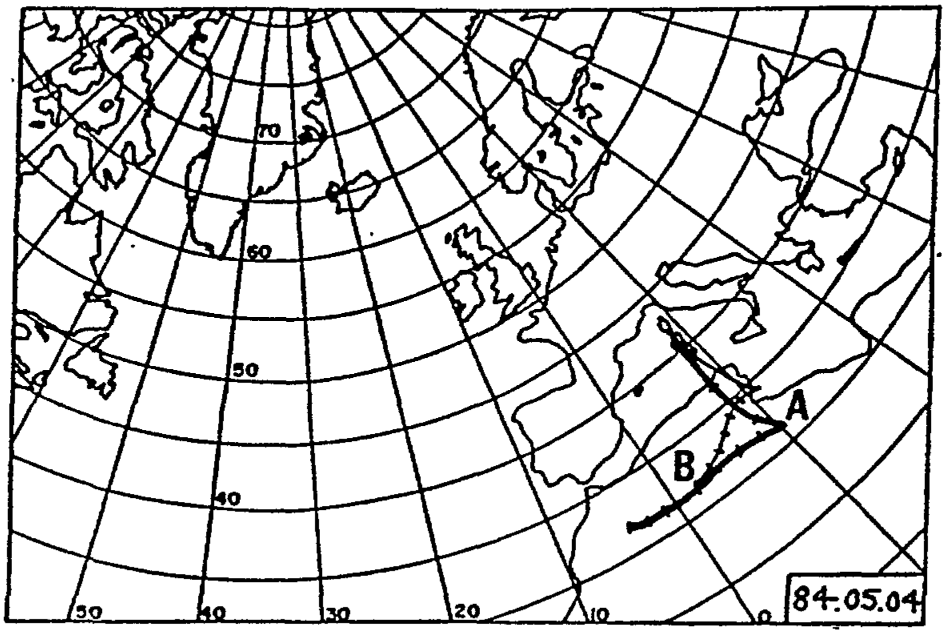

Fig. 6 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on May 4, 1984 at 0 h UT

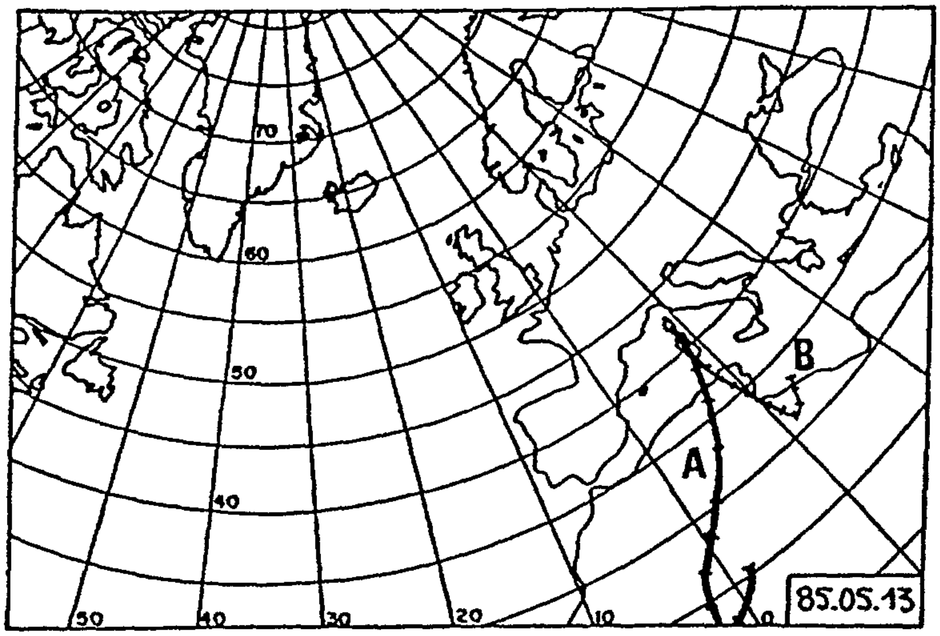

Fig. 7 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on May 13, 1985 at 12 h UT

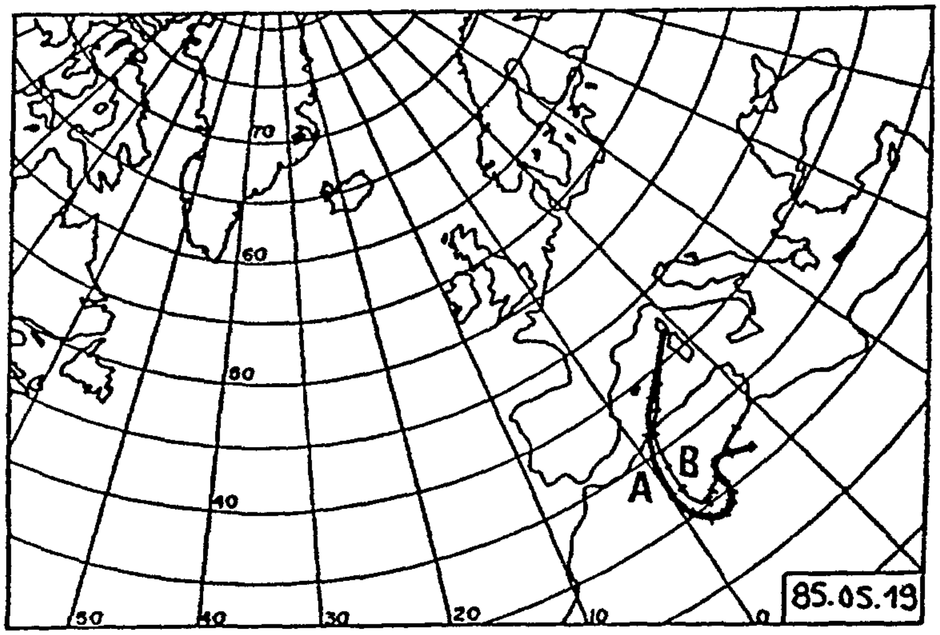

Fig. 8 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on May 19, 1985 at 0 h UT

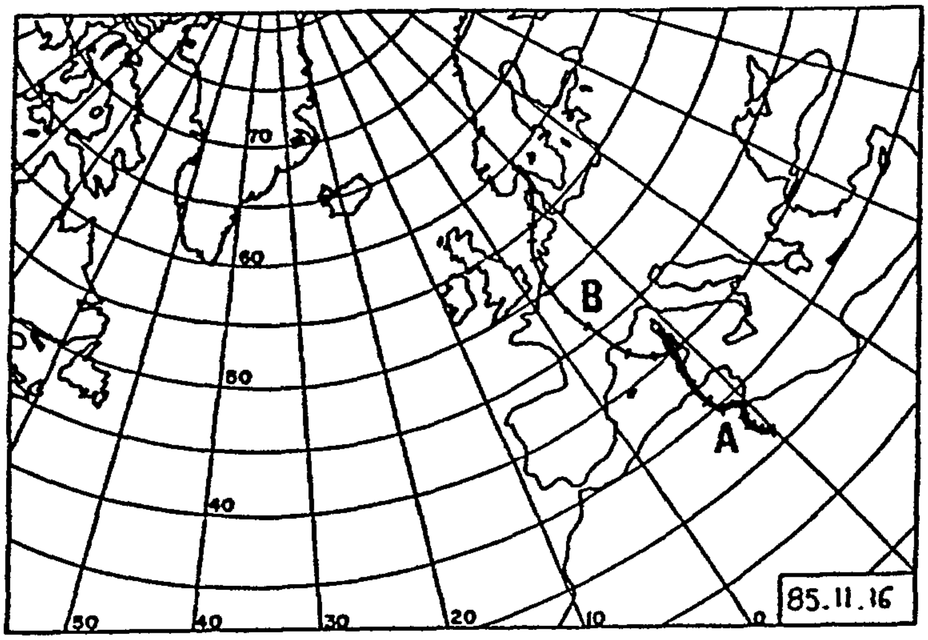

Fig. 9 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on November 16, 1985 at 0 h UT

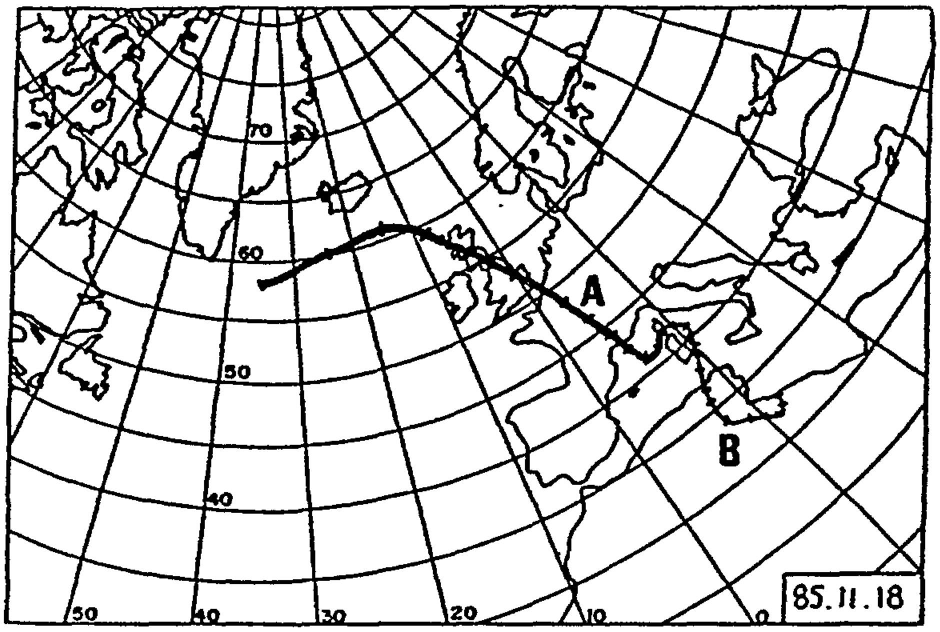

Fig. 10 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on November 18, 1985 at 12 h UT

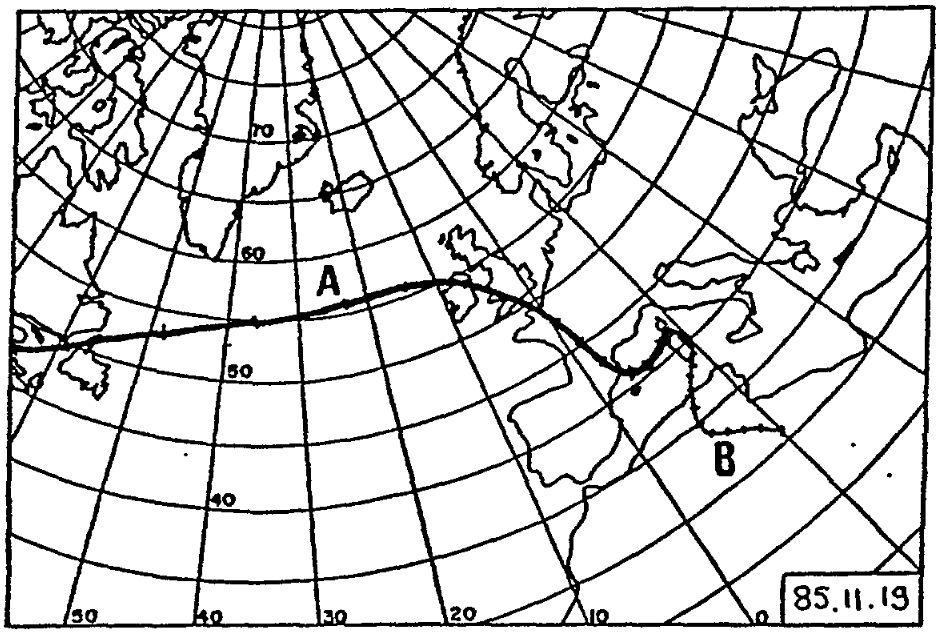

Fig. 11 - Air-masses backtrajectories - A: 700 hPa; B: 850 hPa.
Situation on November 19, 1985 at 0 h UT

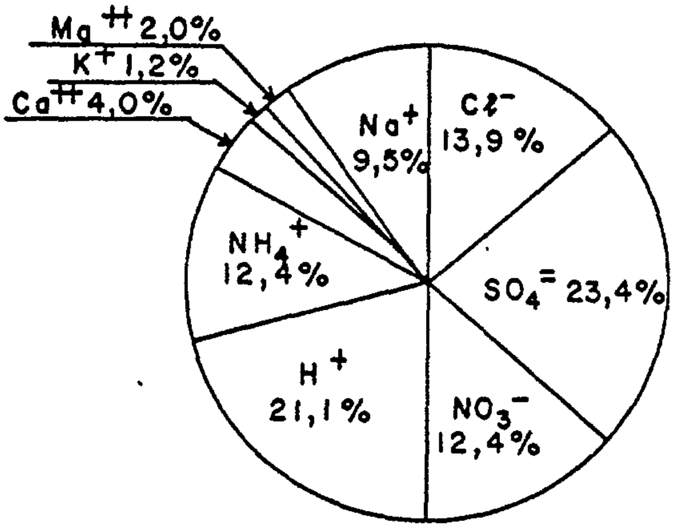

Fig. 12 - Ionic balance of a situation with atmospheric input from the European continent (November 7-8, 1981)

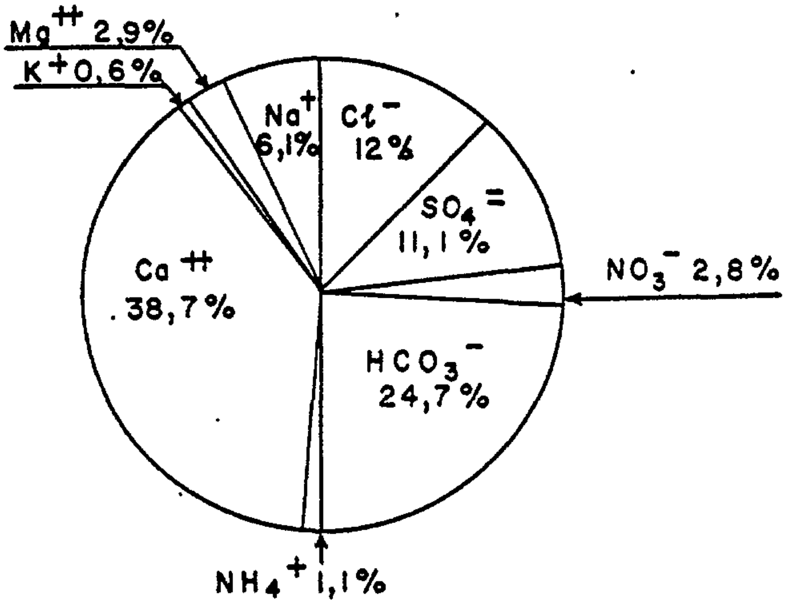

Fig. 13 - Ionic balance of a situation with Saharan dust influence
(May 4-5, 1984)

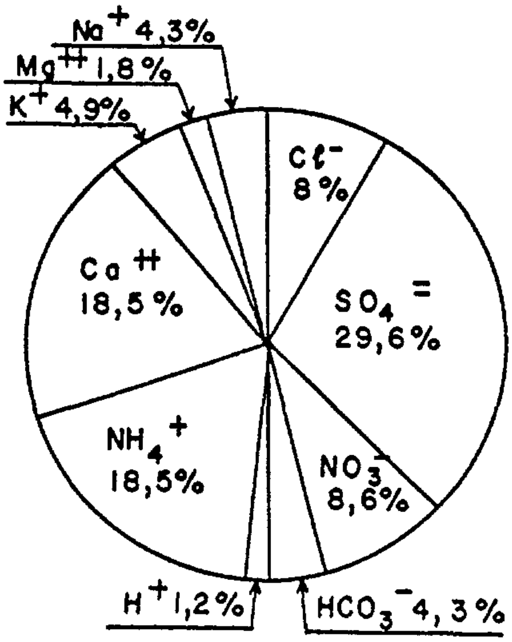

Fig. 14 - Ionic balance of a mixed situation
(November 16-18, 1985)

II - PRELIMINARY DATA ON OBSERVATIONS AT THE CAP FERRAT ATMOSPHERIC SAMPLING STATION (FRANCE)

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The main objectives of ongoing investigations carried out since 1986 on the French Riviera at the Cap Ferrat atmospheric sampling station are as follows:

i) to give basic information on temporal fluctuations of the atmospheric input of trace metals and nutrients from long-term monitoring of the chemical composition of aerosols and precipitation;

ii) to specify source areas of the collected material, taking into account the origins of incoming air masses;

iii) to evaluate the elemental fluxes associated with the atmospheric deposition and the relative contributions of wet and dry deposition;

iv) to compare atmospheric and riverine input of the measured components to the North Western Mediterranean;

v) to provide relevant data in order to improve the geochemical mass balance of these components in the Mediterranean Basin.

On the basis of annual observations on trace metals, the following results may be highlighted.

1. The observed atmospheric concentrations of Pb, Cd, Cu and Zn are in the ranges of 5-100, 0.05-1.5, 2-20 and 5-120 ng.m^{-3} respectively.

2. The concentrations of Pb, Cd, Cu and Zn in rain water are variable and in the ranges 1-30, 0.05-1.5, 1-20 and 1-100ppb respectively.

3. The measured annual wet deposition fluxes of Pb, Cd, Cu and Zn are 6, 0.3, 2.7 and 1 2 $kg.km^{-2}.y^{-1}$ respectively.

4. These values are in good agreement with those derived from similar observations of F. Elbaz-Poulichet and C. Guieu in Provence, at the Carpentras Meteorological station located about 200 kilometres east of Cap Ferrat.

5. An extrapolation of the observed elemental deposition fluxes to the North Western Mediterranean Basin (zone II of the UNEP inventory of pollutant sources in the Mediterranean Sea), leads to an atmospheric input of Pb, Cd, Cu and Zn higher than the riverine discharge of these elements by the Rhône and Ebro (these two main rivers contribute respectively 63% and 20% of the fresh water input to marine zone II), especially for Pb (at least 1 order of magnitude higher in this case).

The following conclusions concerning the atmospheric wet deposition of nutrients may also be made.

1. There are marked temporal fluctuations in rain water concentrations of inorganic nitrogen (nitrate + ammonium ion), with relatively low values frequently being associated with persistent heavy precipitation and higher values associated with brief weak rains.

2. The average annual rain water concentration of inorganic nitrogen during the year 1986 (about 80 $\mu mol.N.1^{-1}$) is approximately twice that observed over the same time period in south Corsica at the Bavella Pass.

3. The annual wet deposition flux of inorganic nitrogen at the Cap Ferrat site was estimated at 610kg $N.km^{-2}.y^{-1}$ for the year 1986. This value corresponds relatively well with those measured at the Bavella Pass where the average annual rainfall is about two times higher.

4. As for trace metals, the depositional flux of inorganic nitrogen extrapolated to the north western Mediterranean Basin represents an atmospheric input of the same order of magnitude as the riverine inorganic nitrogen discharge in that marine area.

Thus the atmospheric contribution to the input of trace metals and inorganic nitrogen to the north western Mediterranean appears to be very significant compared to that of the riverine discharge. A more accurate evaluation of the associated depositional fluxes, of the impact of man-made emissions, and of long-range atmospheric transport will require extended regional studies implying simultaneous monitoring at various coastal stations bordering the Mediterranean Basin. The biogeochemical significance of airborne pollutants in marine Mediterranean ecosystems will have to be considered carefully in the future. This will necessitate a reinforcement of the close cooperation between specialists in atmospheric pollution, meteorology and marine chemistry and biology.

ATMOSPHERIC TRANSPORT AND DEPOSITION OF TRACE ELEMENTS TO THE WESTERN MEDITERRANEAN SEA

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ABSTRACT

Beginning in 1985 a continuous aerosol and deposition sampling programme was launched at a coastal location in Northwestern Corsica. This site is about 300m above sea-level and at least 20km from local pollution sources. It is exposed during 80% or more of the time to maritime air masses which have travelled over the western Mediterranean from southern, western and northern directions. Twenty-four-hour aerosol samples were collected on 0.4 µm pore size Nuclepore filters from a 10m high tower and analyzed for Al, Si, S, Mn, Zn by X-Ray Fluorescence and by flameless atomic absorption for Na, Cu and Pb. Total deposition samples were collected in a "Crapal" sampler and analyzed for Al, Si, Mn and Pb.

So far the data obtained from April 1985 to April 1986, show that the temporal variability of the elemental concentrations in aerosols displays two distinctive patterns. First, a seasonal pattern is observed for the elements of continental origin, either natural (e.g. Al, Si) or anthropogenic (e.g. S, Pb). This pattern is inversely related to the frequency and amount of rainfall so that the highest concentrations are observed between May and October. This seasonal pattern is not observed for locally produced sea-salt aerosol particles (index Na), whose concentration is related to local wind-speed. Elements associated with mineral particles exhibit sporadic but intense concentration peaks that are superimposed on this general pattern. Twenty of these events were recorded during our sampling period and three-D air mass trajectories show that all these events are associated with transport of soil dust from Africa.

The total deposition (wet and dry) measurements indicated that the input of matter from the atmosphere to the western Mediterranean is very discontinuous in relation with changes both in the source strengths (Saharan dust for example in the case of Al and Si) and in scavenging efficiency.

INTRODUCTION

Au cours des dernières années, un intérêt croissant a été porté à l'étude de la contamination du milieu marin par des contaminants d'origine atmosphérique. En Méditerranée, divers programmes ont été mis en oeuvre pour apprécier l'impact de la retombée atmosphérique sur la "qualité" de l'eau et le degré de perturbation ainsi engendrée. La plupart des études menées ont été basées sur des prélèvements d'air effectués en bateau lors de campagnes en mer (Chester et al., 1981; Arnold, 1985; Dulac et al. 1987). A partir de ces données, ces auteurs ont tous souligné l'extrême variabilité temporelle des concentrations des éléments constitutifs de l'aérosol atmosphérique méditerranéen. Cette variabilité des concentrations, qui peuvent fluctuer d'un facteur 5 en l'espace de 48 heures, rend extrêmement délicate toute approche quantitative du flux atmosphérique transféré de l'atmosphère vers le milieu marin.

Cette constation nous a conduits à développer un programme de recherche visant à la fois à quantifier de façon fiable ce transfert de matière et à comprendre les processus qui contrôlent sa variabilité temporelle.

La démarche adoptée est basée sur un suivi en continu des concentrations atmosphériques de certains éléments d'intérêt et sur une collecte également continue de la retombée atmosphérique totale (dépôt humide + dépôt sec).

Nous présentons ici les premiers résultats obtenus, relatifs à la période avril 1985-avril 1986.

PRELEVEMENTS ET ANALYSES

Echantillonnage

Le site de prélèvement choisi est le Capo Cavallo (42°31N, 8°40 E) au nord-ouest de la Corse. Ce site est à environ 20 km de toute source de pollution et est exposé plus de 80% du temps à des masses d'air d'origine maritime venant du nord, de l'ouest et du sud.

Les prélèvements d'aérosol sont effectués quotidiennement sur des membranes en polycarbonate de type Nuclepore et de porosité 0,4 µm. Leur durée de 24 heures et un débit de prélèvement de l'ordre d'un m^3/ heure assure des volumes échantillonnés d'environ 20-25 m3 par jour. Les prélèvements d'aérosol sont effectués au sommet d'une tour météorologique de 10 mètres.

La retombée atmosphérique totale, c'est à dire l'ensemble dépôt sec et dépôt humide, est échantillonnée par pas d'environ 15 jours à l'aide d'un collecteur de type CRAPAL. Il s'agit d'une coupelle hémisphérique surmontée d'une couronne cylindrique de diamètre 35,7cm et d'une hauteur de 10cm dont le bord supérieur biseauté définit exactement une surface de collecte de 0,1m2. Le décrochement ainsi créé permet de limiter les éventuels rebonds lors de pluies violentes ou de grêle ainsi que les réentrainements trop importants. L'ensemble est en plexiglass et monté sur un trépied calculé de façon que l'ouverture se trouve exactement à un mètre du sol. Il est recouvert par une toile en nylon (à maille d'un mm), régulièrement changée, permettant de s'affranchir de l'apport d'insectes ou de feuilles. Ce collecteur est relié par un entonnoir en polyéthylène à une bonbonne de cinq litres. Cette bonbonne est protégée des rayons du soleil par une boîte-étui doublée de polystyrène. Lors de sa mise en place, chaque bonbonne contient un litre d'acide nitrique Probalo Normatom 0,1 N. L'ensemble de ces précautions a pour but d'éviter la prolifération d'algues dans la bonbonne et d'assurer une conservation correcte de l'échantillon jusqu'à son rapatriement au laboratoire. Une seconde dose d'acide nitrique est utilisée lors du retrait de la bonbonne pour rincer le collecteur et récupérer les éventuelles particules encore déposées sur les parois de celui-ci.

La représentativité des mesures de pluie par ce collecteur a pu être testée comparativement à une jauge météorologique. Des blancs de manipulation ont été faits périodiquement tant pour la collecte des aérosols que pour la retombée atmosphérique. Des détails complémentaires peuvent être trouvés dans Bergametti (1987).

Analyse

Aérosols

L'analyse des éléments contenus dans l'aérosol atmosphérique nécessite le recours à deux techniques analytiques : la spectrométrie de fluorescence X (SFX) et l'absorption atomique en four (AA).

La spectrométrie de fluorescence X étant une méthode non-destructive, nous avons tout d'abord analysé par cette technique Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe et Zn. Les procédures utilisées ont déjà été largement décrites (Elichegaray et al., 1981; Losno et al., 1987).

L'analyse du plomb, du cuivre et du sodium dans les aérosols a été effectuée par spectrométrie d'absorption atomique en four (Perkin-Elmer 400 avec four HGA 500). Préalablement à l'analyse, les échantillons sont dissous par attaque acide. Le filtre est placé dans une bombe téflon de 8 ml possédant un couvercle à vis hermétique. Dans ces bombes, on ajoute 4 ml d'acide nitrique Prolabo Normatom et 1 ml d'acide perchlorique Prolabo Normatom. Ces bombes sont placées dans un bain thermostaté à 80°C pendant 4 jours. Une journée supplémentaire de séjour dans le bain thermostaté, bouchon posé mais non vissé, est alors nécessaire pour permettre une évaporation douce afin d'obtenir un volume final de l'ordre d'un ml. Le résidu est alors pesé et repris par un volume d'eau Milli-Q d'environ 4 ml, déterminé précisément par pesée. Des blancs sont bien évidemment effectués à chaque niveau de la chaîne de traitement.

Retombée atmosphérique

Après collecte, les échantillons de retombée atmosphérique sont filtrés au laboratoire, en salle blanche et analysés en Al, Si, Mn, P et Pb. Dans le cas du plomb et du phosphore, la fraction insoluble n'est pas dosée, des mesures ayant montré qu'elle représentait moins de 5% du plomb total et moins de 7% du phosphore. Les solutions sont alors dosées par spectrométrie d'absorption atomique en four (pour Al, Mn et Pb). Le phosphore dissous est dosé par colorimétrie selon la méthode décrite par Murphy et Riley (1962). Le silicium dissous est également dosé par colorimétrie selon la procédure décrite par Krauskofp (1956), Staiton et al., (1977) et Strickland (1952).

La fraction insoluble est dosée par SFX selon la même procédure que celle utilisée pour le dosage des aérosols.

VARIABILITE TEMPORELLE DES CONCENTRATIONS D'AEROSOL

(a) Mise en évidence d'événements sporadiques

La Fig. 1 illustre la variation quotidienne des concentrations en silicium sur une période d'environ un an. Cette Figure, typique des éléments d'origine détritique (Al, Fe, Ti), confirme visuellement ce qui a été dit précédemment, à savoir des niveaux de concentrations notablement différents pour des échantillons très voisins dans le temps (le cas extrême étant observé entre le 29/12/85 et le 01/01/86, les concentrations de Si étant divisées par un facteur 200 en 3 jours).

Ces variations brutales de concentrations apparaissent de façon totalement irégulière durant l'année : des pics de concentrations ressortent, fréquemment au printemps et en été, plus épisodiquement en automne et en hiver. De même, des concentrations extrêmement basses sont couramment observées durant l'automne et l'hiver, plus rarement en été et au printemps.

La Fig. 2 qui illustre la variation quotidienne des concentrations du soufre, élément principalement lié à la source de pollution, ne fait pas ressortir de tels pics positifs de concentration. La différence de comportement de ces deux éléments signifie donc qu'il existe une source naturelle particulière, susceptible d'engendrer des épisodes où les concentrations des éléments d'origine détritique sont extrêmement élevées. L'étude des trajectoires des masses d'air associées à ces épisodes nous montrera que ces épisodes résultent quasi-systématiquement d'un transport de matière en provenance d'Afrique et correspondent à des apports de poussières sahariennes.

A l'inverse, les épisodes à basses concentrations sont en phase pour ces deux éléments dont les sources sont notablement différentes. Ceci nous a conduits à penser que, plus qu'un terme source, c'était un processus d'abattement commun qui devait être responsable de ces basses concentrations. En effet, comme le montre la courbe de pluviosité au bas des Figs. 1 et 2, ces épisodes à basse concentration correspondent à des échantillons collectés lorsque l'atmosphère locale a été lessivée par des précipitations. Celles-ci ont pour effet de ramener les concentrations à un niveau extrêmement bas et ceci de façon relativement identique pour tous les éléments.

En conclusion, les courbes de variation quotidienne des concentrations sur une période d'une année font ressortir principalement deux types d'événements susceptibles d'affecter les teneurs sur une échelle de temps très courte. Les concentrations des éléments, ayant en totalité ou en partie une origine détritique, peuvent être multipliées par un facteur 100 en l'espace de quelque(s) jour(s) lors de transports de poussières sahariennes. A l'inverse, les processus d'abattement par les précipitations ramènent localement les concentrations journalières de presque tous les éléments à un niveau minimal, créant ainsi des "anomalies" négatives de concentration.

(b) Mise en évidence d'un cycle saisonnier

Grâce à cette identification des principaux événements responsables des fluctuations à court terme des concentrations, il nous a été possible d'effectuer un lissage des courbes précédentes par écrêtement afin de dégager d'éventuels phénomènes de plus faibles amplitudes. Les Figs. 3 et 4 mettent ainsi en évidence un cycle saisonnier des concentrations. On observe en effet l'existence de deux périodes différenciées : l'une correspondant à l'été méditerranéen, fait ressortir un niveau élevé des concentrations (moyenne géométrique : 1100 ng/m3 pour le silicium ; 2660 ng/m3 pour soufre); l'autre, intervenant en automne et en hiver, est caractérisée par des niveaux moyens nettement plus bas (237 ng/m3 pour le silicium; 1360 ng/m3 pour le soufre). Ces deux périodes sont reliées par deux périodes intermédiaires (une au printemps, l'autre au début de l'automne) au cours desquelles les concentrations croissent (printemps) ou décroissent (automne) progressivement.

Ces niveaux de concentration différents semblent traduire l'abattement de l'aérosol local via les précipitations comme l'atteste la courbe de pluviosité donnée au bas des Figs. 3 et 4. En effet, les concentrations minimales apparaissent durant la saison pluvieuse alors que les niveaux élevés de concentration sont consécutifs à des périodes sans précipitation. Ceci nous conduit à invoquer l'existence d'un cycle saisonnier des concentrations dans la mesure où celles-ci sont en relation avec un paramètre météorologique, les précipitations, dont le caractère saisonnier est bien établi.

Ce caractère saisonnier demande, bien évidemment, une année de mesure supplémentaire pour être parfaitement mis en évidence mais son existence est certaine puisqu'il dépend d'un paramètre (les précipitations) à caractère cyclique.

(c) Conséquence de l'existence d'un cycle saisonnier sur l'origine et le transport des aérosols

La Fig. 5 nous montre l'existence d'une variation temporelle des concentrations du même type pour tous les éléments, à l'exception du chlore et du sodium. Il semble même exister une relation inverse pour ces deux éléments, relation que nous allons essayer d'expliquer.

Cas des éléments d'origine marine : Na et Cl

Nous avons vu que les concentrations de ces deux éléments dans l'aérosol atmosphérique de la Méditerranée Occidentale résultaient en grande partie des sels de mer émis par "bubbling". Les Figs. 6 et 7 nous montrent effectivement que les concentrations de ces deux éléments sont grandement dépendantes de l'état de la mer ou de la vitesse du vent, les deux paramètres étant intimement liés. On retrouve d'ailleurs pour ces éléments des relations du même type que celle proposée par Lovett (1978) entre vitesse du vent et concentrations des sels de mer (Fig. 7). Le comportement particulier de ces deux éléments doit donc s'expliquer par référence à leur mode de génération. Une confirmation est apportée par la Fig. 8 sur laquelle est reportée la vitesse moyenne mensuelle du vent local à 10 mètres du sol. On observe que les vents moyens les plus forts apparaissent plus fréquemment durant la période humide (d'octobre à avril). On peut donc penser, au vu de la relation de la Fig. 7, qu'à cette période la production de sels de mer est plus intense en Méditerranée Occidentale. Ceci explique donc parfaitement les concentrations plus élevées que nous observons pour ces éléments en automne et en hiver par rapport à celles du printemps et de l'été.

Néanmoins, bien qu'il y ait cette émission plus intense de sels de mer durant la période humide, les précipitations ne ramènent pas ces concentrations, comme celles des autres éléments, à un niveau minimum. Ceci ne peut s'expliquer qu'en relation avec le caractère local des émissions de Na et Cl : l'existence d'une source marine très proche permet une réalimentation très rapide du réservoir atmosphérique en ces éléments après une pluie.

Conséquences sur le transport

Ce comportement particuler de Na et de Cl nous autorise à penser que les concentrations des autres éléments résultent donc très majoritairement d'un transport à longue distance de matière émise loin des côtes corses. En effet, les éléments non-marins présentant un faible niveau moyen de concentration durant la période humide, on doit en conclure que, dans leur cas, le réservoir atmosphérique n'a pas le temps de se réalimenter totalement entre deux précipitations. Ceci implique donc que leur source d'émission n'est pas locale mais, qu'au contraire, les concentrations observées pour ces éléments en Corse résultent d'un transport à longue distance à partir de sources continentales.

En nous appuyant sur cette différence de comportement, il est possible de déterminer le temps moyen nécessaire à la réalisation du réservoir après une pluie.

Le niveau moyen des concentrations de ces éléments en période humide étant relativement stable, on peut admettre, en première approximation, que le temps moyen séparant deux événements pluvieux durant cette période est inférieur au temps moyen nécessaire à la réalimentation du réservoir en ces éléments. Ce temps (calculé en divisant la durée de la période humide par le nombre de journées de pluie) est de l'ordre de deux jours. Une confirmation de ce chiffre peut être obtenue en étudiant les événements pluvieux séparés par un intervalle de temps supérieur à deux jours. On obtient alors une durée de deux à trois jours pour que les éléments soumis au transport à longue distance retrouvent un niveau de concentration proche de celui précédant l'événement pluvieux étudié. On peut donc en déduire que, pour les éléments dont l'origine est autre que marine, les sources atmosphériques de matière se trouvent à au moins deux jours de temps de transport du site de prélèvement.

Pour des vents moyens de l'ordre de 6 m/s, ce temps de transport correspond à une distance d'environ 1000 km, ce qui est approximativement la distance séparant la Corse des côtes espagnoles ou africaines desquelles, nous le verrons, proviennent environ 70% des masses d'air échantillonnées.

(d) Conclusion de l'étude de la variabilité temporelle

Il ressort de cette étude de la variabilité annuelle des concentrations un certain nombre de faits marquants. Tout d'abord, nous avons pu montrer que, pour les éléments d'origine détritique, les épisodes de transport de poussière saharienne constituaient le phéonomène essentiel permettant d'expliquer les pointes de concentration observées. Leur caractère aléatoire dans le temps justifie *a posteriori* la stratégie de suivi en continu que nous avons choisie. Nous avons également pu montrer l'existence d'un cycle saisonnier des concentrations et en expliquer l'origine par l'alternance d'une période sèche et d'une période humide. Nous avons également pu démontrer que les concentrations des éléments non marins dans l'atmosphère méditerranéenne résultaient bien d'un transport à longue distance dont on a pu estimer la durée moyenne à deux jours.

ROLE DES REGIONS-SOURCES SUR LA VARIABILITE DES CONCENTRATIONS : APPROCHE TRAJECTOGRAPHIQUE

Nous venons de voir que le facteur intervenant au premier ordre sur les concentrations des aérosols en Méditerranée occidentale était le taux de précipitations locales, celles-ci donnant l'allure générale de la courbe annuelle.

Nous allons maintenant montrer que le terme source est un facteur susceptible d'expliquer une part importante de la variabilité résiduelle des concentrations.

Pour traiter ce problème, nous avons choisi d'identifier des régions-sources en ayant recours à des trajectographies des masses d'air échantillonnées.

Sommairement, le principe de reconstitution de la trajectoire est que le déplacement instantané de la masse d'air est égal au vecteur vent en son centre. Celui-ci est calculé de cinq minutes en cinq minutes par interpolation linéaire, spatiale et temporelle (Imbard 1983) à partir des champs tridimensionnels de vent, analysés et archivés au Centre Européen pour les Prévisions Météorologiques à Moyen

Terme de Reading (G.B.), (Lorenc et al., 1977). Ces données sont disponibles par échéances de six heures à neuf niveaux différents (compris entre 1000 et 50 hPa) et pour une grille dont le pas vaut 1.875 degré en latitude comme en longitude. Le modèle permet d'établir, sur cinq jours au maximum (quatre dans notre cas), des trajectoires commençant ou finissant à n'importe quel endroit du globe.

L'avantage de ce modèle est d'être tridimensionnel et donc de prendre en compte la composante verticale du vent, en général de l'ordre de quelques centimètres par seconde. Cette vitesse verticale est supérieure d'un ordre de grandeur environ à la vitesse de chute théorique en atmosphère calme de particules de 1 ou 2 µm.

Martin et al. (1987) ont montré l'importance de ce facteur dans le calcul des trajectoires, en particulier lors de transports subsidents dans l'atmosphère libre en régime anticyclonique ou de transports dans la couche limite en système dépressionnaire.

Nous disposons pour chaque échantillon (donc chaque jour) de deux trajectoires tridimensionnelles finissant à Capo Cavallo, aux niveaux 925 et 700 hPa, généralement pour l'heure médiane de l'échantillon. Notre échantillonnage sur le plan de l'origine des masses d'air est en bon accord avec le flux moyen annuel déduit de la climatologie sur six ans des masses d'air arrivant à Ajaccio à 850 hPa et à Medpoint (40°N, 6 ° E) (Fig. 9).

Dans un premier temps, ces trajectoires vont nous permettre d'identifier pour chaque élément les régions-sources pour lesquelles sont observés les niveaux de concentration maxima et minima. Néanmoins, pour que cette identification soit significative, il est nécessaire d'intégrer un certain nombre des conclusions de l'étude précédente sur la variabilité temporelle des concentrations. Ainsi, nous avons vu que la pluviosité sur le site était un facteur essentiel pour expliquer le niveau des concentrations observées et que le temps de réalimentation du réservoir après une pluie pouvait être estimé à environ deux jours. Il est clair que, sour peine de mélanger des phénomènes différents (abattement, région-source), les échantillons pour lesquels une pluie locale est intervenue dans les deux jours précédant la collecte doivent être écartés pour la recherche des régions-sources. C'est donc sur un fichier a priori exempt de l'influence des précipitations locales que portera cette recherche. Nous avons tenu à nous assurer que le retrait de ces échantillons n'affectait pas la représentativité climatologique de notre banque de données. La Fig. 10 nous montre que les fréquences des trajectoires arrivant à 925 hPa à Capo Cavallo, avec ou sans les épisodes pluvieux à échéance de deux jours, sont voisines.

Enfin, nous ne considérerons, pour cette étude, que les trajectoires à 925 hPa, l'étude à 700 hPa ayant été menée et montrant une dispersion importante de l'information. Ceci laisse à penser, comme on pouvait le prévoir, que l'échantillon recueilli au sol traduit davantage la concentration des masses d'air circulant dans les basses couches que celle des masses d'air voyageant en altitude.

Mise en évidence des régions-sources

Notre importante banque de données nous a permis de recourir à une approche originale du problème de la mise en évidence des régions-sources. Pour chaque secteur de 22,5° d'une rose des vents centrée sur Capo Cavallo et pour chaque élément, nous avons calculé la moyenne géométrique des concentrations et l'écart-type associé. Il est alors possible d'effectuer un regroupement des secteurs homogènes en concentration. On obtient alors une sectorisation définitive, dont on observera qu'elle diffère notablement selon l'origine de l'élément étudié.

Concentrations moyennes des éléments en fonction des secteurs d'origine

Cette étude a été menée pour tous les éléments analysés à l'exception du chlore et du sodium qui ont une source d'émission locale dont l'intensité dépend de la vitesse du vent et de l'état de la mer. D'autre part, les résultats relatifs au potassium ne seront pas présentés dans le mesure où nous avons été dans l'impossibilité de dégager une sectorisation quelconque des concentrations de cet élément en fonction de l'origine des masses d'air, et ceci bien que le potassium n'ait probablement pas qu'une origine locale.

1. Les éléments d'origine détritique : Al, Si, Fe, Ti

Pour ces quatre éléments, les sectorisations définitives obtenues sont très voisines (Fig. 11). Elles font toutes ressortir l'existence de concentrations élevées pour le secteur Sud. Celles-ci bien évidemment sont à relier à des épisodes de transport de poussières sahariennes.

On notera que les masses d'air associées au secteur ouest-nord ouest présentent, compte tenu de leur caractère atlantique, les plus basses concentrations (environ 3 fois plus faibles que pour le secteur sud). A l'interface de ces deux secteurs se trouve une zone de transition marquée par des concentrations intermédiaires et des écarts-types importants. A l'évidence, ceci résulte du mélange de trajectoires s'orientant soit au sud, soit à l'ouest à échéance supérieure à deux jours.

Le secteur nord-est présente quant à lui des concentrations un peu plus élevées (ce qui est logique compte tenu de son caractère plus continental) mais celles-ci restent malgré tout inférieures de près d'un facteur deux à celles du secteur sud.

On notera simplement pour mémoire que les épisodes associés à des trajectoires courtes (regroupées dans le secteur circulaire médian) présentent des concentrations relativement élevées.

2. Les polluants : S, Mn, Zn, Cu, Pb

Les classifications obtenues pour ces éléments font toutes apparaître l'existence d'une région source très intense correspondant aux masses d'air en provenance des secteurs nord et est (Fig. 12). Les concentrations observées y sont généralement près de deux fois supérieures à celles associées à des masses d'air venant de l'ouest.

Ceci est relativement logique si l'on se réfère aux cartographies des émissions de Pacyna (1984). En effet, les bassins industriels lorrains, allemands, belges et ceux des pays de l'est sont répertoriés comme étant les plus gros émetteurs de métaux-traces en Europe.

On notera également que les niveaux les plus faibles pour les polluants sont observés généralement pour le secteur sud. Ce résultat semble a priori logique compte tenu de la faible industrialisation des pays africains (bien que les normes sur les rejets y soient moins sévères qu'en Europe). Cependant, ce résultat est notablement en désaccord avec les observations de Dulac (1986) qui observait des concentrations maximales en Cd et en Pb pour ce secteur. On indiquera simplement que certains échantillons de Dulac correspondant à ce secteur ont été collectés très près des côtes : ceci a pu conduire à des teneurs élevées liées à la proximité des sources.

Enfin, le secteur ouest présente des concentrations intermédiaires traduisant une origine mixte : à sa composante atlantique, s'ajoutent les polluants émis lors du survol de l'ouest de la France ou de l'Espagne. Dans ce secteur, on se doit également de relever une zone correspondant au nord de l'Espagne pour laquelle sont observées des concentrations importantes de polluants. Il est probable que, outre les zones urbaines espagnoles, on retrouve sur ces épisodes les contributions des importants bassins sidérurgiques du Pays Basque et de Catalogne.

On notera également que, si l'on excepte le soufre, les concentrations correspondant aux trajectoires "courtes" ne présentent pas, pour ces éléments, de différences notables par rapport à celles observées dans les secteurs Nord-Nord Est ou Nord-Nord Ouest.

FLUX ATMOSPHERIQUES A LA MEDITERRANEE OCCIDENTALE

Flux de retombée totale

Le Tableau 1 rassemble les valeurs du flux de retombée atmosphérique totale (sèche + humide) en µg/cm²/an de cinq éléments à Capo Cavallo pour la période d'échantillonnage ainsi que les valeurs obtenues par d'autres auteurs pour diverses régions marines.

On retrouve une variation de ces flux de retombée entre les différentes régions marines très voisine de celle observée pour les concentrations d'aérosol. On notera cependant l'écart important pour les flux d'aluminium entre les valeurs mesurées en Corse et en Mer du Nord, très probablement en raison des épisodes d'apports de poussières sahariennes en Méditerranée occidentale. Dans le Pacifique Nord, les faibles concentrations d'aluminium dans l'air (21 ng/m3; Duce et al., 1983) se répercutent au niveau du flux, lequel est environ 40 fois plus faible qu'en Méditerranée occidentale.

Les flux de plomb sont près de deux fois supérieurs en Mer du Nord comparativement à la Méditerranée occidentale, comme le laissaient prévoir les concentrations respectives de cet élément dans les aérosols de ces deux régions.

Une certaine cohérence existe donc entre ces différentes données de flux de retombée et les concentrations d'aérosol associé, bien que le rapport de proportionnalité ne soit pas toujours conservé entre les différentes régions marines.

Ceci se vérifie sur le Tableau 2 où sont reportées les vitesses apparentes de dépôt total calculées en divisant le flux de retombée par la concentration moyenne arithmétique des éléments dans l'aérosol. Il faut indiquer que cette vitesse totale n'a pas de sens physique précis puisqu'elle intègre des phénomènes d'abattement différents (dépôt sec + dépôt humide). Elle fournit néanmoins une valeur moyenne de la vitesse de dépôt des particules, laquelle est généralement utilisée pour estimer ces flux de retombée lorsque l'on ne dispose que de mesures d'aérosol.

On notera un bon accord d'ensemble entre ces données si l'on excepte l'amplitude importante de variation de la vitesse de dépôt total de l'aluminium entre le Pacifique Nord et la Mer du Nord. Les valeurs de vitesse de dépôt total pour le plomb sont également près de trois fois plus élevées en Méditerranée occidentale qu'en Mer du Nord.

On signalera que ces vitesses de dépôt total mesurées sont assez éloignées des valeurs généralement admises (de l'ordre de 1 cm/s), valeurs souvent déduites de la mesure d'éléments radioactifs (Pb 210, Turekian et al. 1977); ou Be 7, Silker, 1974).

Rôle des apports de poussières désertiques

Pour les éléments d'origine détritique, la variabilité des flux de retombées totales résulte en grande partie des apports sporadiques mais intenses de poussières désertiques.

Parmi nos échantillons de retombée, six au moins sont fortement soumis à des apports sahariens : le Tableau 3 les indique en rappelant les dates des épisodes mis en évidence par l'utilisation conjointe des aérosols et des trajectoires de masses d'air (Bergametti, 1987).

Ces six échantillons correspondent à des flux de silicium moyennés sur la période d'échantillonnage (constituant donc des limites inférieures), de 1 à 6,5 microgrammes/cm2/j. La masse apportée par ces seuls échantillons représente plus de 55% de la masse totale de Si et d'Al transférée dans l'année alors que ces six échantillons ne représentent que 64 jours de dépôt. Pour des éléments comme le phosphore ou le manganèse qui possèdent dans l'atmosphère une composante anthropogénique non négligeable, ces six épisodes sahariens représentent tout de même encore 35 et 45% de leur flux annuel respectif. A l'inverse, un polluant comme le plomb n'est pas notablement affecté par ces épisodes, son dépôt pour ces six épisodes représentant 18,8% de son dépôt total soit l'équivalent du temps de collecte.

Le cas extrême est observé entre le 1er et le 15 mars 1986 où près de 30% du flux annuel de Si et d'Al retombent durant cette seule période.

D'autre part, même si la mise en évidence est moins aisée, d'autres échantillons sont également soumis à des apports d'origine saharienne et l'on peut raisonnablement penser qu'en réalité au moins 70% des flux de silicium et d'aluminium résultent d'apports en provenance d'Afrique. Ceci correspond à un flux de poussières sahariennes moyen d'environ 12 tonnes/km2 an (calculé en considérant que l'aluminium représente 8% de la masse totale des poussières) ce qui est en accord avec les résultats obtenus au col de Bavelle (Corse) par Löye-Pilot et al. (1986) (14 tonnes/km2/an). Ces auteurs indiquent par ailleurs que la masse de poussières sahariennes apportées au bassin méditerranéen occidental correspond presque exactement à la masse de matière solide apportée par le Rhône (4,3 10^6 tonnes).

Le dépôt des poussières désertiques s'effectue très probablement en grande partie par voie humide, la plupart de ces épisodes (5 sur 6) prenant fin consécutivement à une pluie.

Les périodes d'apports intenses

Il est intéressant de regarder comment l'intervention successive ou simultanée des différents facteurs contrôlant la variabilité de l'apport atmosphérique en Méditerranée occidentale se répercute dans le temps. En particulier, nous allons essayer de définir les saisons où se produisent les apports les plus intenses pour les différents éléments.

La Fig. 13 montre que plus de 70% de l'apport atmosphérique en éléments d'origine détritique (Si, Al) s'effectuent durant le printemps et l'hiver où l'effet combiné de transport de poussières sahariennes et de précipitations importantes conduit à des flux élevés. L'hiver, à lui seul, représente plus de 50% du flux annuel de ces éléments. Ceci est presque uniquement dû à l'épisode très intense de début mars 1986 et seule une série temporelle plus longue nous permettrait de proposer une généralisation statistiquement significative de ces apports saisonniers.

En été, les faibles flux mesurés s'expliquent par le fait qu'aucun évènement de poussières sahariennes n'est immédiatement suivi de pluie. En automne, l'apport est minimal malgré une pluviosité élevée.

Le plomb présente un histogramme de ses dépôts saisonniers très différent : les deux tiers du dépôt se produisent durant le printemps et l'été. L'influence des épisodes sahariens est quasi-inexistante pour cet élément et cette répartition saisonnière traduit presque exclusivement l'existence de coefficients d'abattement total plus forts en période chaude qu'en automne ou en hiver (Bergametti, 1987).

Le manganèse et plus encore le phosphore présentent peu de variations saisonnières de leur apport. Ceci résulte probablement de leur comportement mixte de polluant et d'élément détritique.

L'apport n'est donc pas identique dans le temps pour tous les éléments. On observe ainsi des situations aussi paradoxales que celle du plomb: malgré une liaison évidente entre les flux de cet élément et la pluviosité, l'essentiel de son apport s'effectue durant la saison peu pluvieuse où les taux d'abattement sont beaucoup plus élevés. De même, l'apport saisonnier en éléments détritiques est difficilement prévisible dans la mesure où un seul événement de transport de poussières désertiques peut représenter à lui seul 30% du flux annuel. En fonction du moment où il interviendra, l'histogramme des apports saisonniers sera complètement modifié.

On peut tirer de ces résultats un certain nombre d'informations quant à la dynamique de l'apport atmosphérique à la Méditerranée Occidentale. La première évidence concerne le caractère très pulsé de ces apports, en pariculier pour les éléments détritiques où nous avons pu montrer qu'un seul épisode saharien était susceptible d'apporter près de 30% du flux annuel de ces éléments.

Les apports de Si et d'Al permettent d'estimer l'apport que constitue potentiellement la source atmosphérique pour la sédimentation marine. On peut déduire de nos données (en considérant que l'aluminium représente 8% de la masse de l'apport atmosphérique) un flux de matière d'origine atmosphérique de l'ordre de 1,2 mg/cm2/an. En admettant pour cette matière une densité de l'ordre de 1,5 (Yaalon, 1985), ce flux atmosphérique correspond à un dépôt annuel de l'ordre de 8 microns. Cette valeur représente entre 8 et 16% de la sédimentation pélagique en Méditerranée occidentale (50 µm/an, Eriksson, 1979; 100 µm/an, Chamley, 1971) laquelle est grandement dominée par le matériel biogénique marin (environ 50%, Paterne, communication personnelle). C'est donc une part importante du sédiment non-biologique (de l'ordre de 25%) que représente cet apport atmosphérique en Méditerranée occidentale.

Plus étonnant encore: on observe pour les polluants un apport également pulsé, de plus faible amplitude. La raison n'en est pas tant la sporadicité des émissions mais plus probablement des processus d'abattement plus efficaces au printemps et en été durant lesquels s'effectuent 70% des apports en plomb. Ceci est d'autant plus important que l'apport atmosphérique en cet élément au bassin occidental méditerranéen (277 000 km2), calculé d'après nos données, représente 8300 tonnes/an, soit plus de cinq fois les apports telluriques (1600 tonnes/an, UNEP, 1984).

A l'inverse, l'apport atmosphérique global en phosphore (9200 tonnes/an) a une importance limitée comparée aux 140000 tonnes/an d'origine tellurique (UNEP, 1984). On peut cependant s'interroger sur les conséquences pour l'activité biologique marine des épisodes sahariens durant lesquels une large part de cet apport en phosphore s'effectue en des temps très courts.

CONCLUSION

Au cours de cette étude, nous avons cherché à identifier les facteurs responsables de la variabilité temporelles des flux de matière apportée par l'atmosphère à la Méditerranée Occidentale.

Grâce à une stratégie de suivi en continu des concentrations élémentaires de l'aérosol par pas d'un jour sur une période de plus d'une année, il a été possible de mettre en évidence les principaux paramètres responsables de la variabilité de ces concentrations.

Nous avons tout d'abord montré l'existence d'un cycle saisonnier des concentrations des éléments. Ce cycle, contrôlé par la pluviosité, fait apparaître des niveaux moyens de concentrations 3 à 5 fois plus élevés en période sèche qu'en période pluvieuse pour tous les éléments à l'exception du sodium et du chlore. Pour ces deux éléments, nous avons montré, comme d'autres auteurs l'avaient déjà fait, que leurs concentrations dans l'atmosphère résultaient de l'émission des sels de mer, gouvernée par la vitesse du vent local et l'état de la mer. Ces résultats ont permis de démontrer que la matière présente dans l'atmosphère méditerranéenne (à l'exception de Cl et de Na) résultait d'un transport à longue distance (d'une durée moyenne d'environ deux jours) à partir de sources continentales.

Nous avons ensuite tenté d'identifier, grâce à la trajectographie des masses d'air, ces régions-sources continentales. Le nombre important d'échantillons dont nous disposions nous a permis d'adopter sur ce point une approche moins empirique que celle habituellement utilisée. Après avoir montré la représentativité climatologique de notre échantillonnage, nous avons ainsi pu définir des secteurs, différents selon l'origine des éléments, correspondant à des niveaux de concentration homogène. Les concentrations maximales des polluants correspondent à des transports en provenance des pays industrialisés du nord et de l'est européen. A l'inverse, les concentrations maximales en éléments détritiques se sont trouvées associéss à des transports en provenance d'Afrique.

L'étude de la retombée atmosphérique nous a montré que plus de la moitié des apports d'éléments détritiques se faisait en cinq ou six évènements de transport de poussières désertiques: certains événements pouvant à eux seuls représenter 30% du flux annuel d'aluminium ou de silicium. Finalement, nous avons montré qu'environ 70% du flux de ces éléments et environ 40% du flux de manganèse et de phosphore résultaient de ces seuls apports d'origine désertique. Consécutivement, l'apport atmosphérique à la Méditerranée occidentale semble en mesure d'expliquer au moins 25% du flux de sédiment non biogénique.

De même pour les polluants, nous avons montré que les apports en plomb par voie atmosphérique dominaient à l'échelle du bassin occidental les apports telluriques d'un facteur cinq. Il est à noter que ces apports de polluants présentent également un caractère pulsé en relation avec leur concentration maximale en période de pluies à forte efficacité de nettoyage.

Sur le plan méthodologique, les conclusions que l'on peut tirer se situent à deux niveaux : le suivi en continu effectué tant pour les aérosols que pour la retombée est le seul moyen actuellement d'obtenir un bilan relativement précis ds apports atmosphériques. Mais surtout, il montre très clairement la variabilité de ces apports dans le temps et le risque qu'il y a à raisonner sur des valeurs moyennes à l'échelle annuelle alors que l'essentiel de l'apport se trouve expliqué par quelques événements très brefs dont on estime encore très mal l'influence sur la vie marine.

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Tableau 1

Flux de retombée atmosphérique totale (en µg/cm2/an)
dans diverses régions marines

	Capo Cavallo[1] (Med. Occid.)	Petten[2] (Mer du Nord)	Cedar Key[3] (Floride)	Enewetak[4] (Pac. Nord)	Ninety Miles Beach[5] (Nelle Zélande)
Al	97	47.5	-	2.5*	-
Si	307	-	-	-	-
P	3.2	-	3.1	-	1.5
Mn	2.2	-	-	0.009**	-
Pb	2.9	4.5	-	0.007**	-

[1]: la présente étude
[2]: Cambray _et_ _al_., 1975
[3]: Hendry _et_ _al_., 1981
[4]: * Uematsu _et_ _al_., 1985; ** Arimoto _et_ _al_., 1985
[5]: Chen _et_ _al_., 1985

Tableau 2

Vitesses apparentes de retombée atmosphérique totale (en cm/s)
dans diverses régions marines

	Capo Cavallo[1] (Med. Occid.)	Petten[2] (Mer du Nord)	Enewetak[3] (Pac. Nord)	Ninety Miles Beach[4] (Nelle Zélande)
Al	8.8	9.7	3.1	-
Si	10.9	-	-	-
P	7.6	-	-	12
Mn	9.5	-	-	-
Pb	4.1	1.5	-	-

[1]: la présente étude
[2]: Cambray _et_ _al_., 1975
[3]: Hendry _et_ _al_., 1985
[4]: Chen _et_ _al_., 1985

Tableau 3

Echantillons de retombée atmosphérique les plus fortement soumis à des apports de poussières désertiques

Dates de collecte	Date de l'épisode saharien	Flux de retombée Si (/ug/cm2/j)
07/05/85-17/05/85	12-14/05/85	2,14
11/06/85-21/-6/85	19-20/06/85	1,16
01/07/85-11/07/85	03-04/07/85	1,07
15/12/85-01/01/86	28-29/12/85	1,13
01/03/86-15/03/86	01-02/03/86	6,58
06/04/86-09/04/86	06-07/04/86	5,16

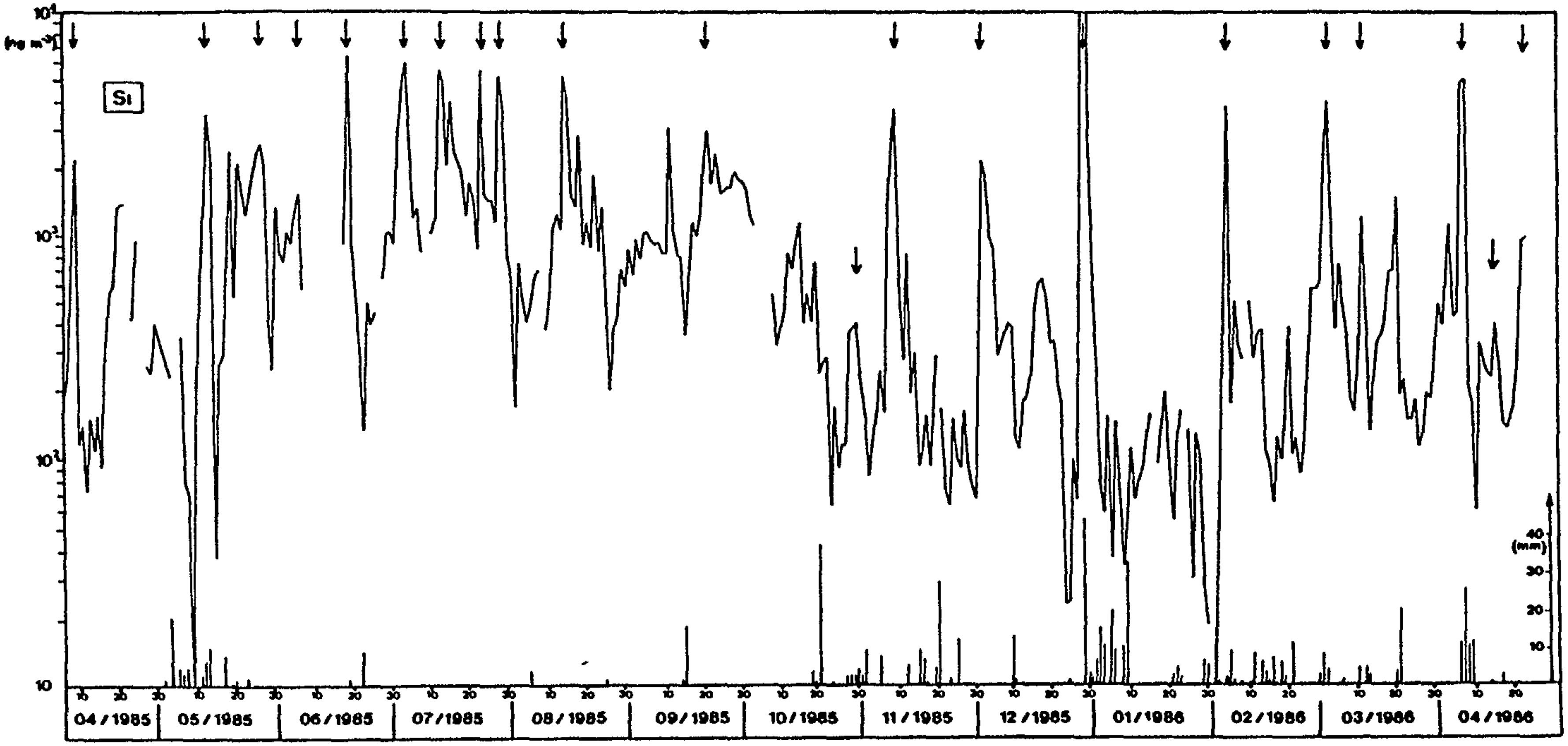


Fig. 1 - Concentrations journalières de Silicium à Capo Cavallo du 06/04/85 au 23/04/86.
(les flèches indiquent des transports de poussières en provenance d'Afrique: la pluviosité journalière est reportée au bas de la courbe)

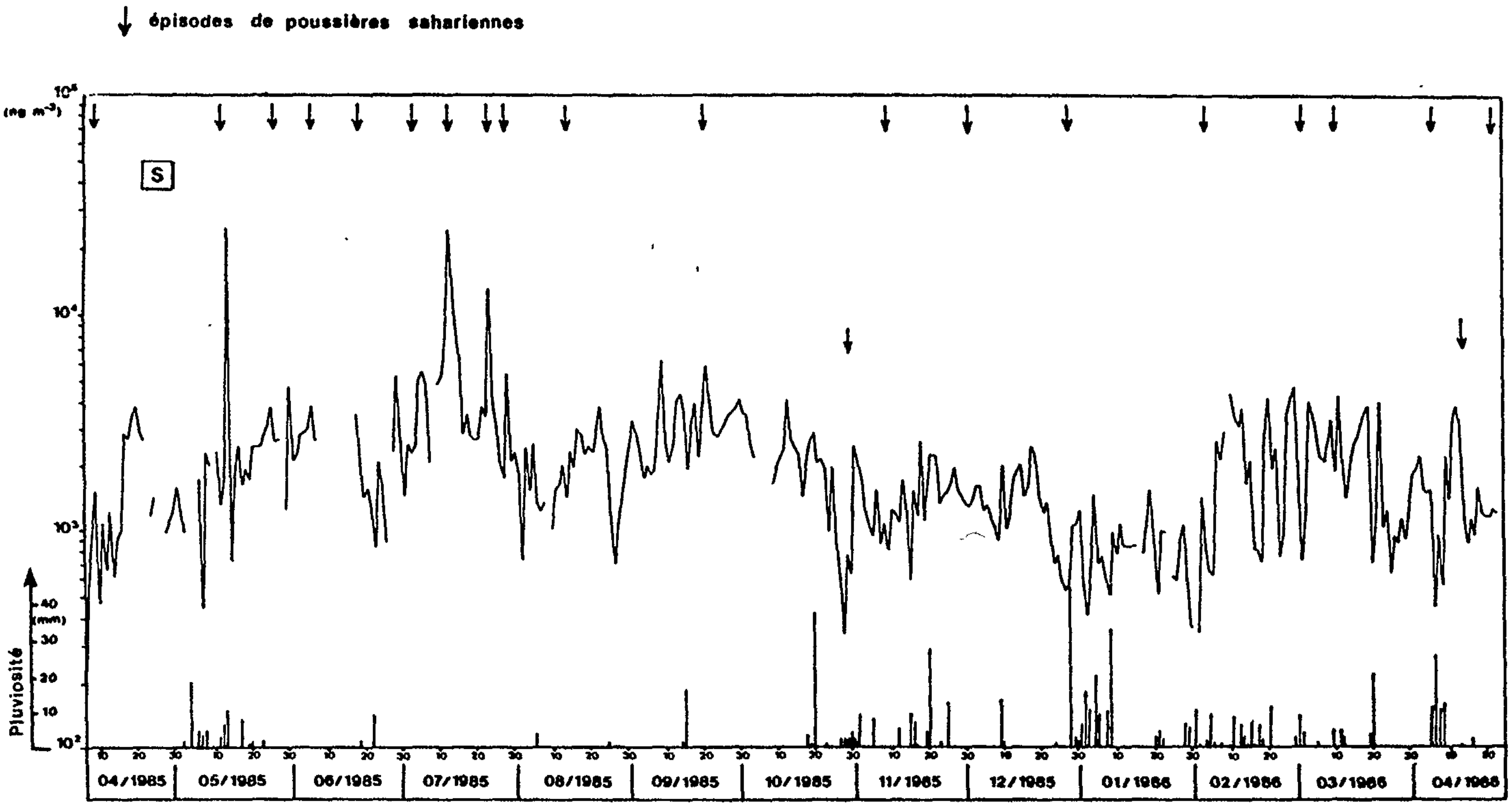


Fig. 2 - Concentrations journalières du Soufre particulaire à Capo Cavallo pour la période du 06/04/85 au 23/04/86.

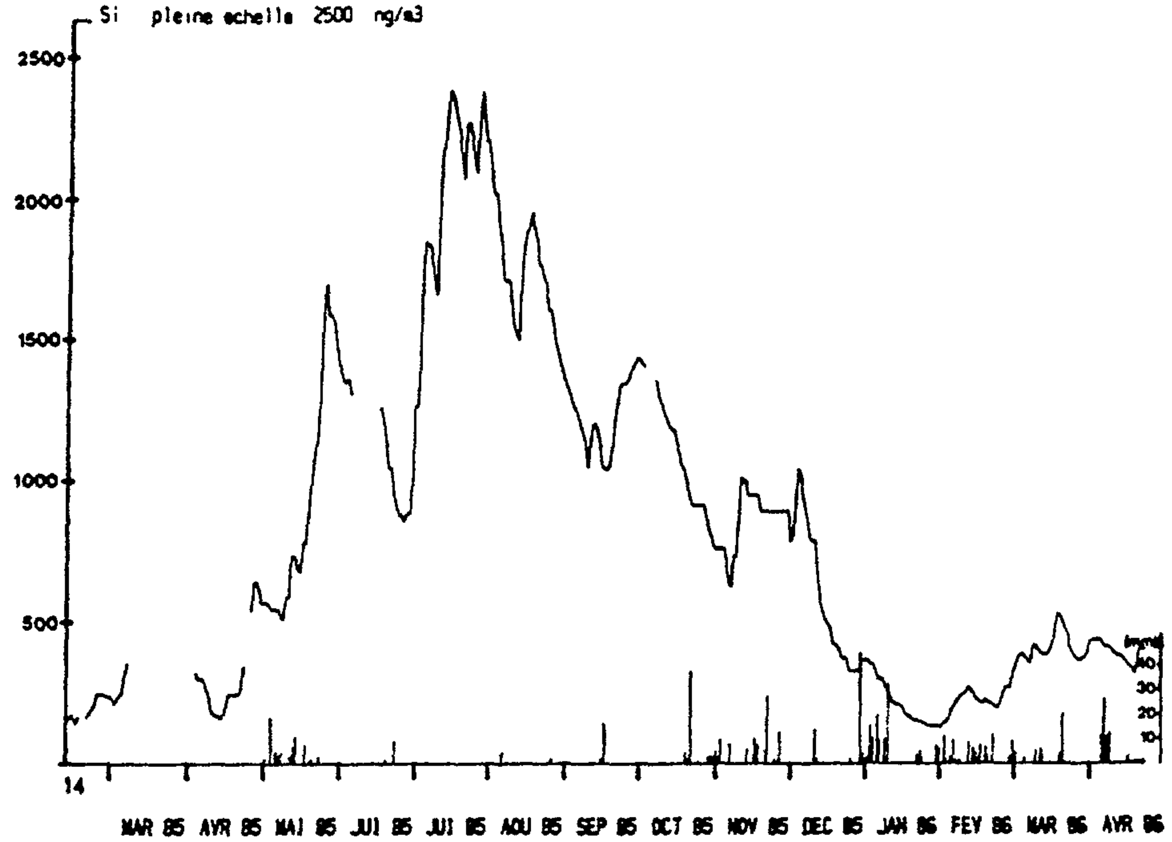


Fig. 3 - Courbe lissée des variations journalières des concentrations de Silicium

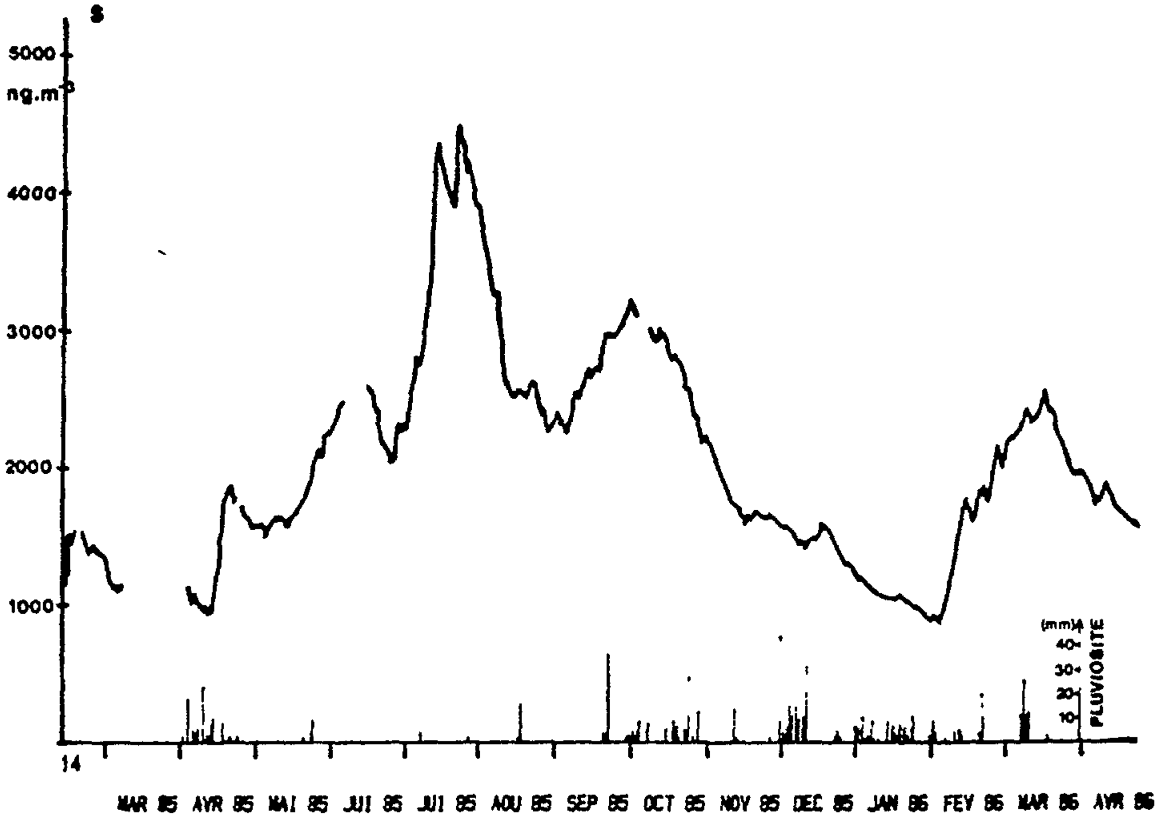


Fig. 4 - Courbe lissée des variations journalières des concentrations de Soufre particulaire

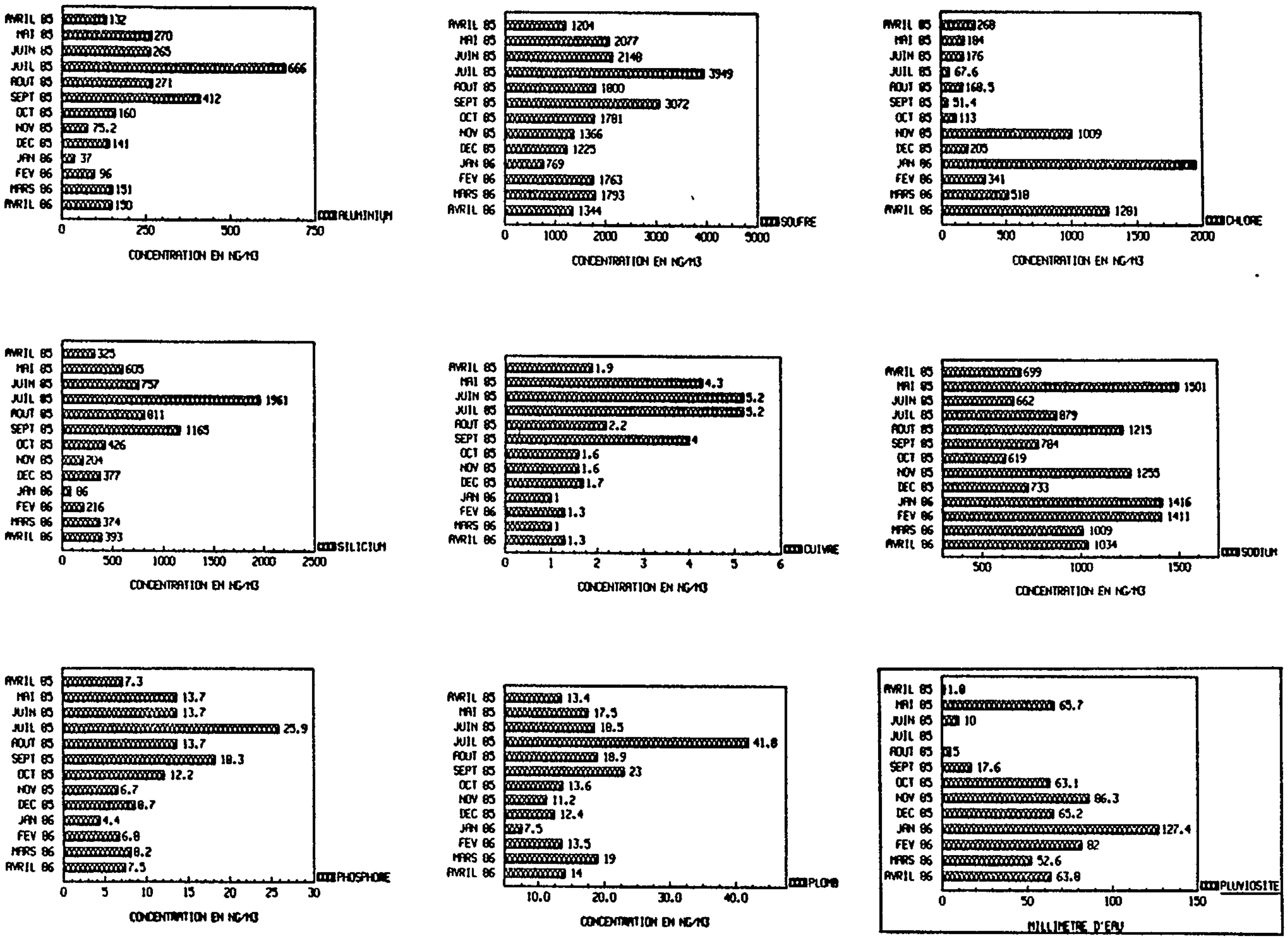


Fig. 5 - Evolution mensuelle des concentrations des éléments et relation avec la pluviosité

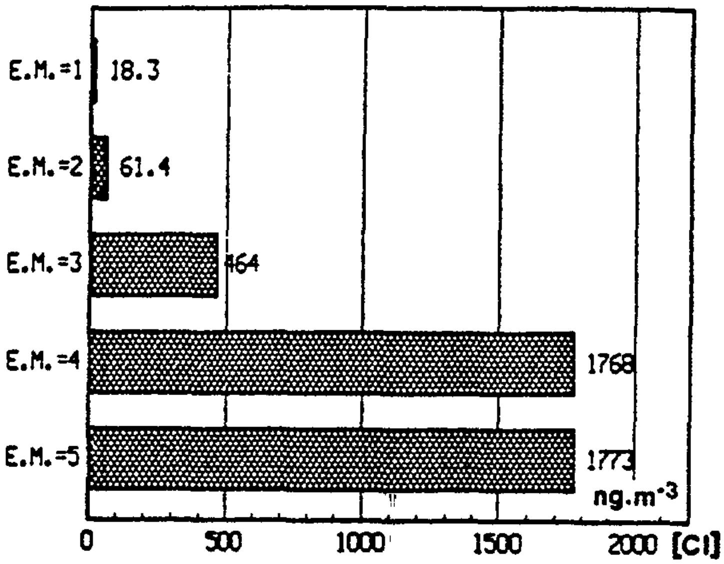


Fig. 6 - Relation entre les concentrations en Cl à Capo Cavallo
et l'état de la mer

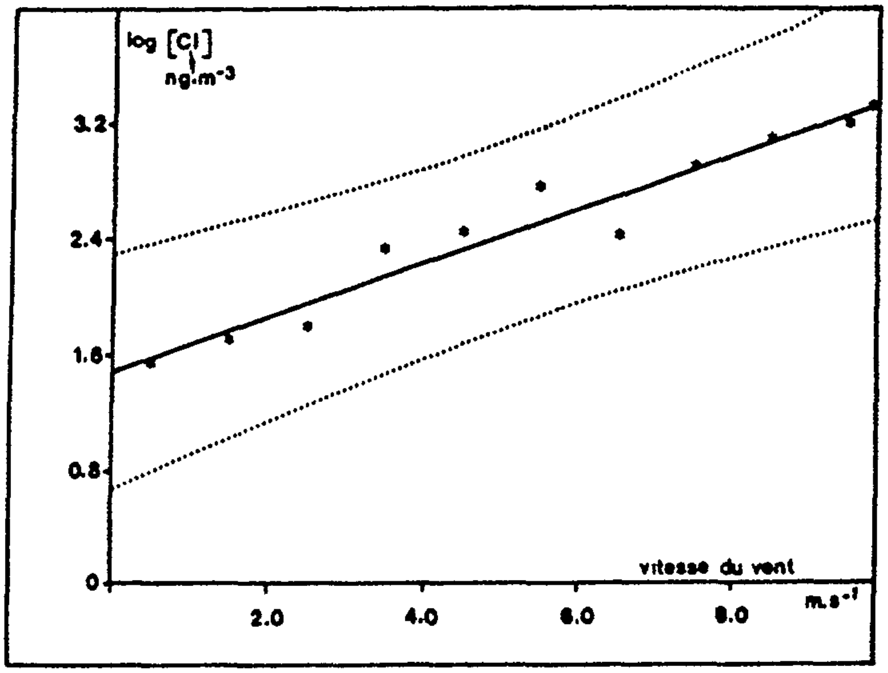


Fig. 7 - Relation entre les concentrations en Cl à Capo
et la vitesse du vent local

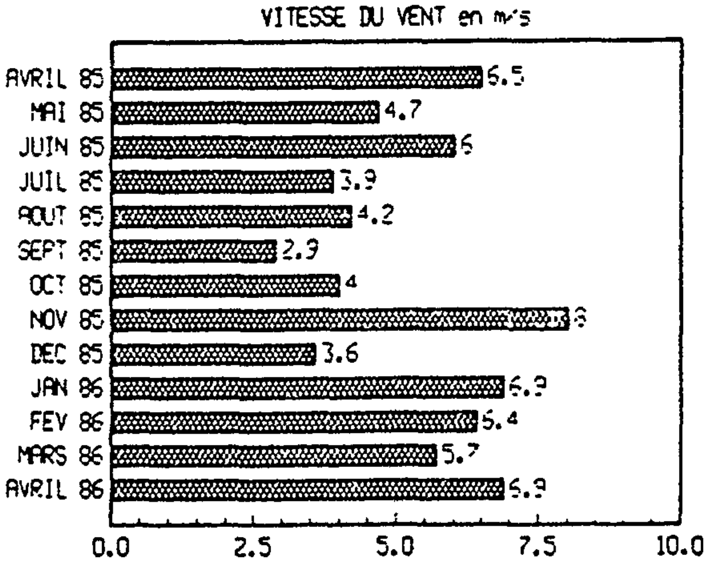
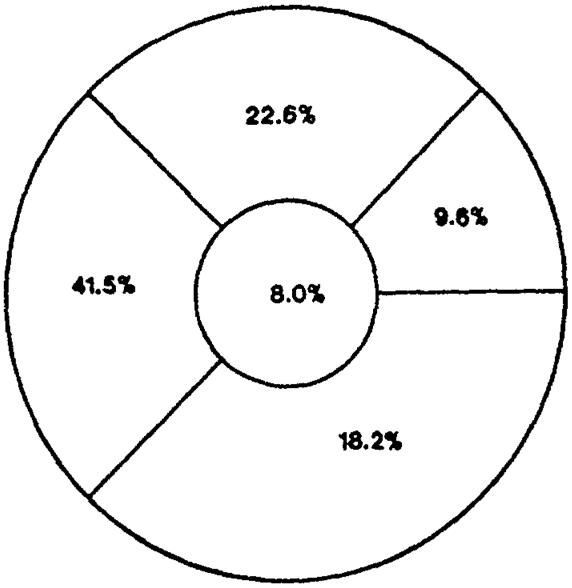
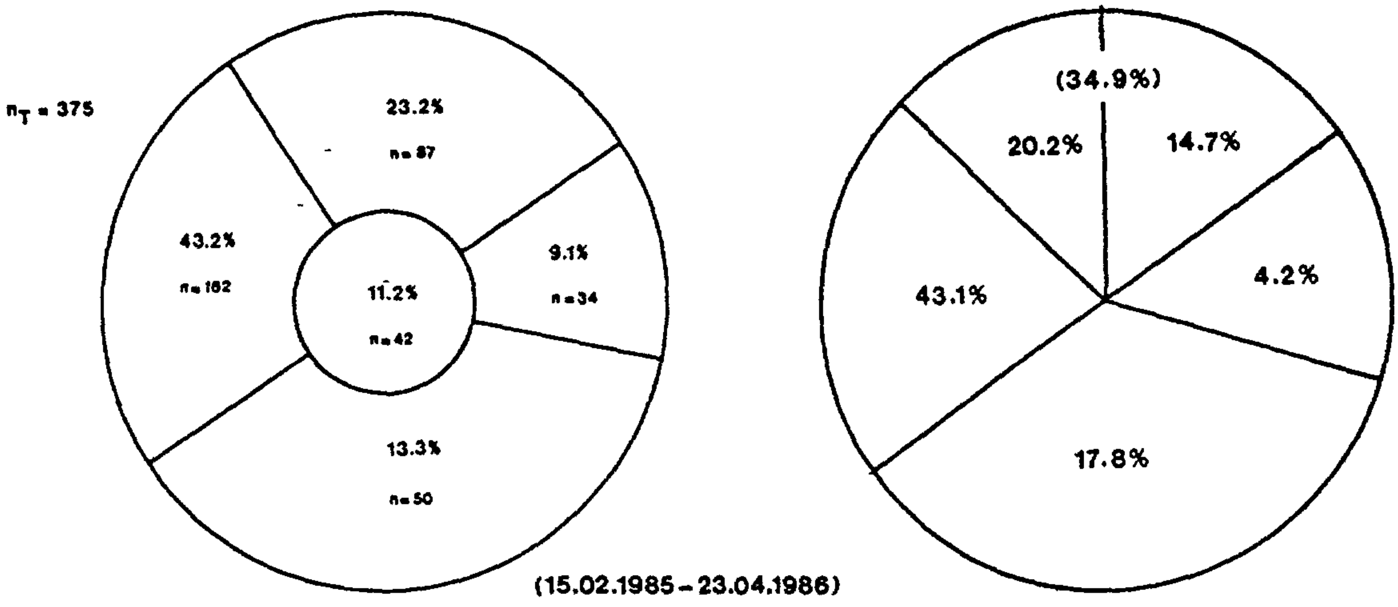


Fig. 8 - Moyennes mensuelles de la vitesse du vent local à 10 mètres
à Capo Cavallo



CLIMATOLOGIE DES TRAJECTOIRES
ARRIVANT A 850 hPa A AJACCIO (1975-1980)



(15.02.1985 - 23.04.1986)

TRAJECTOGRAPHIE 925 hPa
épisodes pluvieux inclus
CAPO CAVALLO

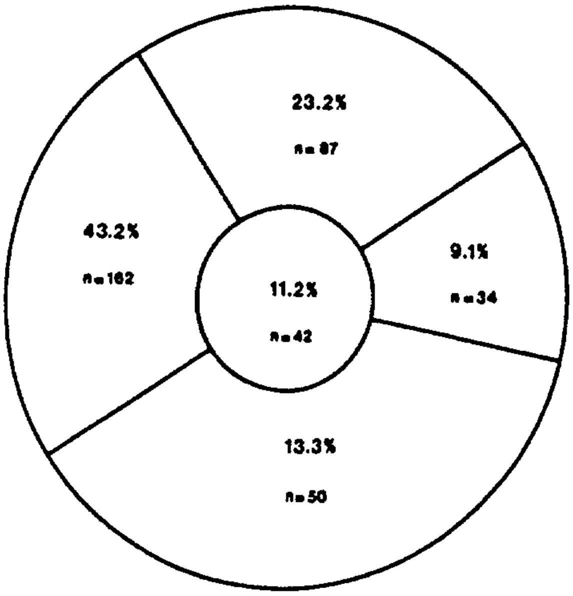
MEDPOINT

Fig. 9 - Fréquence par secteur de l'origine des masses d'air échantillonnées à Capo Cavallo (à 925 hPa) et comparaison avec une climatologie sur six ans des flux d'air arrivant à Ajaccio à 850 hPa et une climatologie pour Medpoint (40° N, 6° E)

TRAJECTOGRAPHIE 925 hPa

épisodes pluvieux inclus

CAPO CAVALLO



TRAJECTOGRAPHIE 925 hPa

épisodes pluvieux éliminés

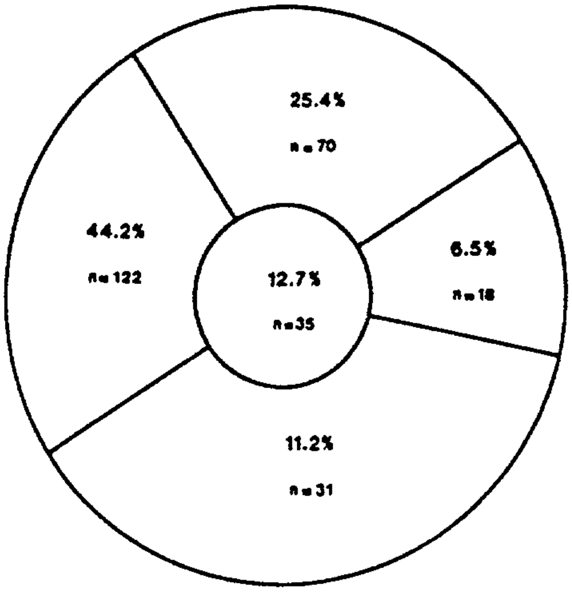


Fig. 10 - Comparaison entre l'origine des masses d'air arrivant à Capo Cavallo à 925 hPa avec ou sans prise en compte des épisodes associés à une pluie locale

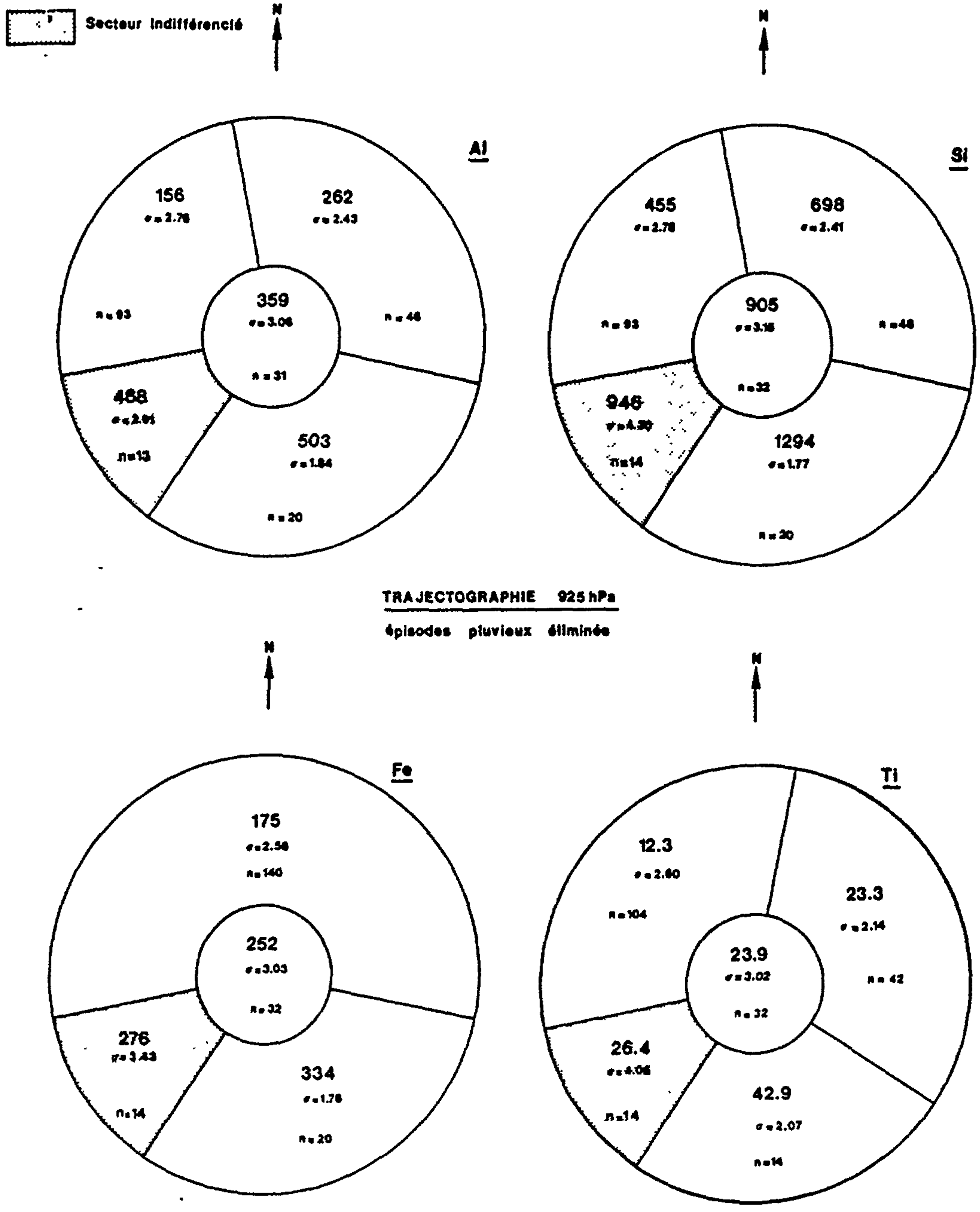


Fig. 11 - Sectorisation des concentrations des éléments détritiques
en fonction de l'origine des masses d'air
(valeurs en ng/m³)

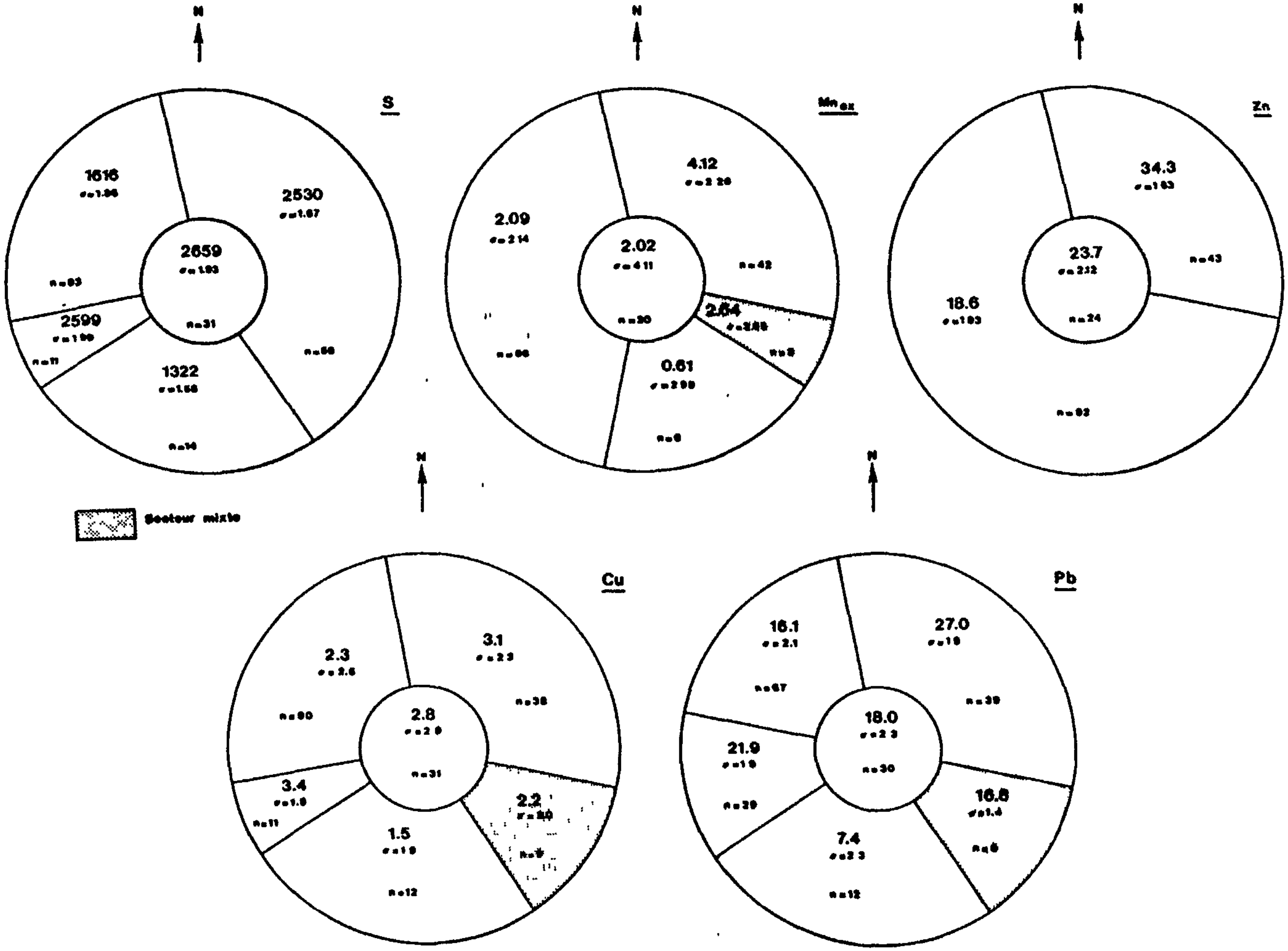


Fig. 12 - Sectorisation des concentrations des polluants en fonction de l'origine des masses d'air (valeurs en na/m^3).

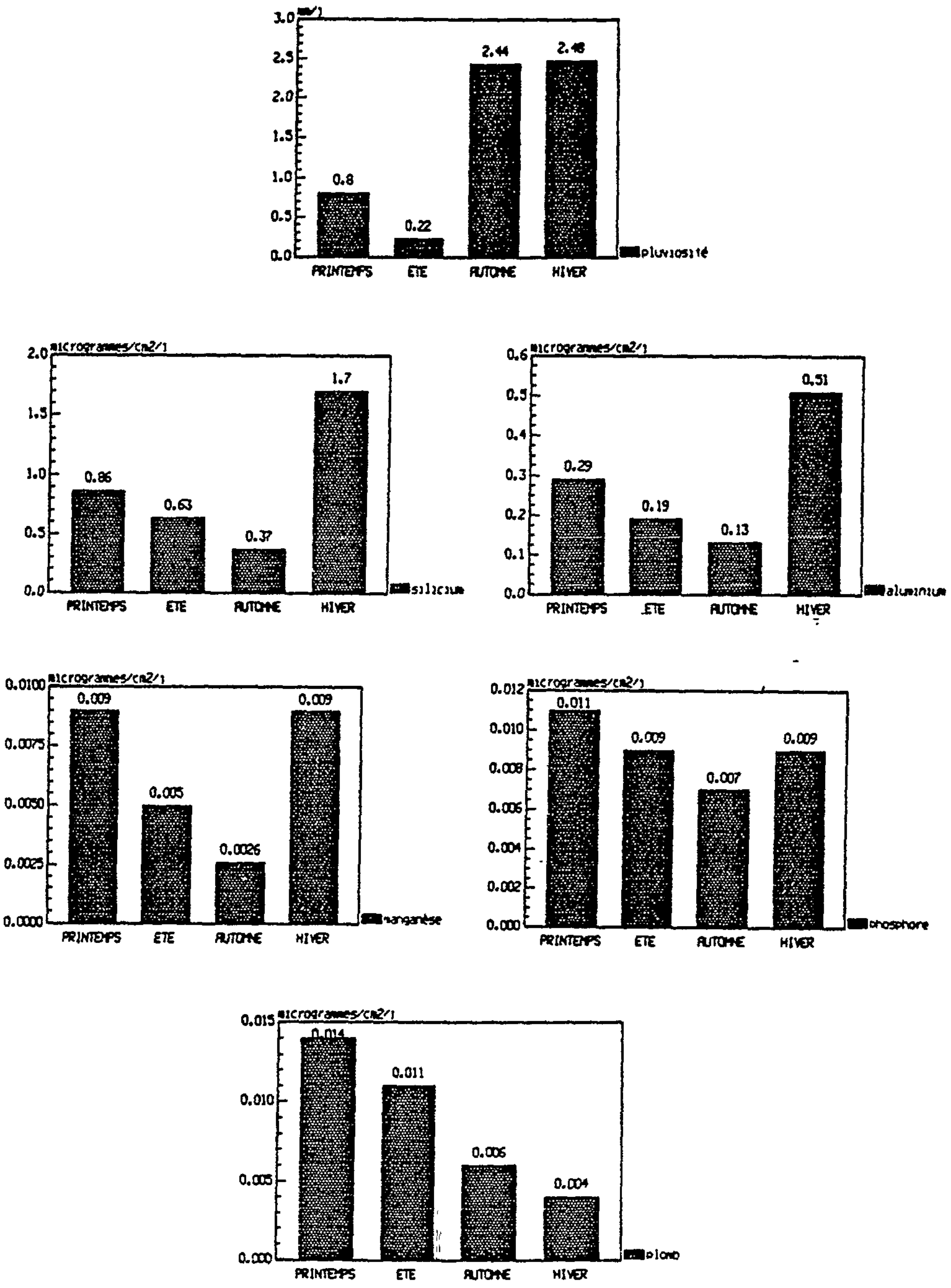


Fig. 13 - Apports atmosphériques saisonniers en Si, Al, P, Mn et Pb

TROPOSPHERIC OZONE PRODUCTION AND TRANSPORT IN THE MEDITERRANEAN

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INTRODUCTION

There are basically two types of urban air pollution. One is associated with a wet and cool climate, its constituents being predominantly particulates and sulphur dioxide, and is usually called London-type smog after the notorious fogs of London in the forties and early fifties (Cvitas and Güsten, 1977). Chemically speaking this type of pollution is on the decline. The other, so-called Los Angeles type smog, or photochemical smog (Leighton, 1961), is associated with a dry, warm climate, its main constituents being nitrogen oxides, ozone and hydrocarbons. This is chemically oxidizing. On the basis of climate, photochemical smog is expected to be the dominant kind of air pollution in the Mediterranean. Some reports for this area have shown that ozone concentrations in urban sites have reached levels in excess of air quality standards (Ganor et al., 1978; Dezeljin et al., 1981; Giovanelli et al., 1982; Lalas et al., 1983; Cvitas et al., 1985). We report here on an extensive study of photochemical pollution carried out in Greater Athens during the summer of 1984.

MATERIALS AND METHODS

Ozone was monitored at five sites in Athens and its surroundings, as shown on the map in Fig. 1, using commercial monitors Dasibi AH 1003 and 1008 (sites O, A, K, I) based on UV absorption and Bendix 8002 (site L) based on the chemiluminescent reaction of ozone with ethylene. The Dasibi instruments have a reliable internal calibration system and the Bendix instrument was calibrated against one of the Dasibi and the neutral potassium iodide method (Hodgeson et al., 1971). Ozone concentrations were plotted continuously with chart recorders and hourly average values were determined therefrom.

The sites were chosen so as to obtain an insight into ozone formation and transport in the area of Greater Athens. The reference site O at the National observatory is a typical urban site. Air was sampled from near the room of the Observatory building at an altitude of 107 m. This is also the site of continuous meteorological data acquisition. The second site, L, was on the hill of Lykabetos in the centre of Athens at an altitude of approximately 200 m. For six days ozone was monitored simultaneously on two locations on the hill - one on the summit (altitute 263 m) and one about 50 m lower near the open-air theatre. As no significant differences were found, the higher site was abandoned. Site I was near the summit of the 1024 m high mountain Hymettos. Site K was at Kastella in the urban part of Piraeus. This is close to the sea and about 8 km south-west of central Athens. Site A was on the north-eastern part of the island Aegina at an altitude of approximately 190 m on a treeless open slope facing Athens. It was completely isolated from traffic and anthropogenic sources of pollution. The site was approximately 30 km to the south west of central Athens.

RESULTS

Site O: At the National Observatory ozone was monitored from 1st June till 23rd July. A total of 1204 hourly average values was obtained. Out of those, 29 values which represent 2.4% of the total time, exceeded the US Air Quality Standard of 120 ppb. 67 values (5.6% of total time) were in excess of 100 ppb. The average diurnal variation of ozone volume fraction computed from the collected data is shown in Fig. 2a.

Site L: On the hill of Lykabetos ozone was monitored for a total of 2001 hours over the period 8th June to 6th September. Hourly average values seldom exceeded 120 ppb-for 4 hours only, which represents 0.2% of the time. 64 hourly values (3.2% of total time) exceeded 100 ppb, while values over 80 ppb comprise 9.7% of the data (194h). A substantial fraction 29.7% (589 h) consists of values below 30 ppb. The average diurnal variation at this site is shown in Fig. 2b.

Site I: At the 1000m high site on the mountain Hymettos only low ozone concentrations were found. Out of the 1542 h of the measuring period (2nd June-6th August) only during 19 hours (1.2% of total time) did the hourly average volume fractions exceed 40 ppb. For 1127 hours representing 73.1% of the time the values stayed below 20 ppb. By plotting the average diurnal variation (Fig. 2c) it becomes obvious that at this altitude the ozone concentration in the atmosphere is practically constant.

Site K: At Kastella in Piraeus close to the sea, ozone was monitored for a total of 978 hours over the period 19th July to 30th August. Most of the hourly average volume fractions fell between 20 and 80ppb, 911h or 93.1% of the time. Only for 41h (4.2% of time) the values were below 20ppb and 26h (2.7% of time) above 80ppb. The average diurnal variation is shown in Fig. 2d.

Site A: At the monitoring site on the island of Aegina, chosen to study the effect of transport, ozone concentrations were recorded from 16th June till 7th September for a total of 1746 hours. This rural site does not show as great a variation as the urban sites mainly for the lack of low concentrations during the night and peak concentrations which are occasionally encountered in the city. Thus 63.7% of the time (for 1111h) the ozone volume fractions were between 40 and 60ppb only for 55 h (3.2% of time) below 30ppb and 14h (0.8% of time) above 80ppb. The average diurnal variation is given in Fig. 2e.

DISCUSSION

By comparing the average diurnal variation of ozone concentration at different sites (Figs. 2-6) it immediately becomes obvious that site 1 on the 1000m high mountain Hymettos shows completely different patterns to the other sites. It is clear that ozone concentrations at an altitude of about 1000m are almost constantly at a level of 20ppb. On a few occasions only is the pronounced variation in the city reflected at this altitude. An example is shown in Fig. 3 for 30th June. The unusual variation with a dip in the midday maximum is seen at the two sites in the city and at a lower level on Hymettos.

The National Observatory is representative of a typical urban site with a pronounced maximum in ozone concentrations at about noon (12-17h), and a minimum in the early morning due to high emissions of ozone-destroying pollutants (predominantly NO). On the somewhat higher hill of Lykabetos, an almost identical pattern is observed, proving it also to be a site representative of the city. The extremely high values as reported for 1982 (7) were not obtained in 1984.

The most interesting site from which to study possible transport of photochemical smog was on the 30 km distant island of Aegina (Site A). It is interesting to note that the average maximal daily concentrations at this rural site (Fig. 2e) are very similar to those in the centre of Athens (sites O and L, Figs. 2a and 2b). The more pronounced differences are seen during the night when ozone concentrations drop by more than 50% from the noon value in the city but only by about 25% at the site on Aegina which has hardly any local pollution sources.

At Site K in Piraeus, a pattern midway between the city and the island Aegina was observed (Fig. 2d).

Since the main aim of our study was to find out to what extent the metropolitan area of Athens affects its surroundings in terms of photochemical pollution, we examined the data from Site A in greater detail. It is difficult to see what can be attributed to transport and what to local ozone production just by looking at daily variations of ozone concentrations. The curves for individual days are seldom as smooth as the one for the average day (Fig. 2e). It is difficult to define what might the typical pattern for any one site and even more so for the discrepancies in such patterns and their interpretation.

If we assume that the discrepancies almost cancel out, we can take the average diurnal variations shown in Fig. 2e as representing typical patterns during the day. We therefore examined in greater detail the deviations from this average pattern by plotting the relative deviations of hourly average volume fractions in percents $(100^{\circ}(\varphi-\varphi)/\varphi)$ against time of the day for each day. A typical day in this representation would be one which shows only small deviations, as for instance 7th July in Aegina (Fig. 4). Above average values can be attributed to transport, as for instance on 2nd August (Fig. 4), when transport of ozone precursors favoured its excessive formation on the previous day (see text below). Since the consumption of ozone at this rural site is low, it stayed here for the whole of 2nd August. Negative deviations are probably due to meteorological conditions preventing photochemical smog formation such as cloudy and rainy weather, strong wind, low temperature etc. Such negative deviations were found on 9th July (also shown in Fig. 4).

In all these cases the diurnal variation of ozone concentrations was similar to the typical pattern but at different levels. There were however days when the pattern itself was qualitatively different. An example is shown in Fig. 5a. On 1st August, during the early hours of the day, lower than average ozone concentrations were measured, while in the afternoon and evening the deviations were both large and positive. Such a pattern can be explained in terms of transport of pollutants in the late hours of the previous day whioch continued over night. These pollutants destroyed ozone as at an urban site, which explains the negative deviations in the early hours. However, the many ozone precursors in the air favoured its enhanced formation after sunrise. The high levels of ozone persisted on Aegina over night and on the following day (Fig. 4). Further support for this interpretation can be found by examining the pattern at site K between Athens and Aegina. Here an even more pronounced decrease in ozone concentrations during the early hours was observed (Fig. 5b). The drop occurred after 21h on 31th July and lasted till noon of 1st August, indicating the presence of large amounts of ozone-destroying pollutants in this area. Some of them obviously reached Aegina. Such a pattern was observed on the following days: July 11, 17, 18; August 1, 11, 16, 17, 19, 23; September 5.

An opposite pattern of positive deviations in the early hours of the day, changing to negative in the later hours as shown for 12th August in Fig. 6 can be rationalized in terms of changed meteorological conditions. Ozone formed in excess the preceding day stayed in the area only during the early hours and then was substituted by cleaner air masses.

CONCLUSION

The present study based on observations in the region of Athens showed that photochemical pollution can indeed greatly affect air quality in and near urban sites in the Mediterranean. In the area of Athens the primary pollutants are sometimes carried into the Saronikos Bay region where they generate secondary pollutants under the influence of solar irradiation. Such photochemical pollution can subsequently be blown back into the city by sea breezes.

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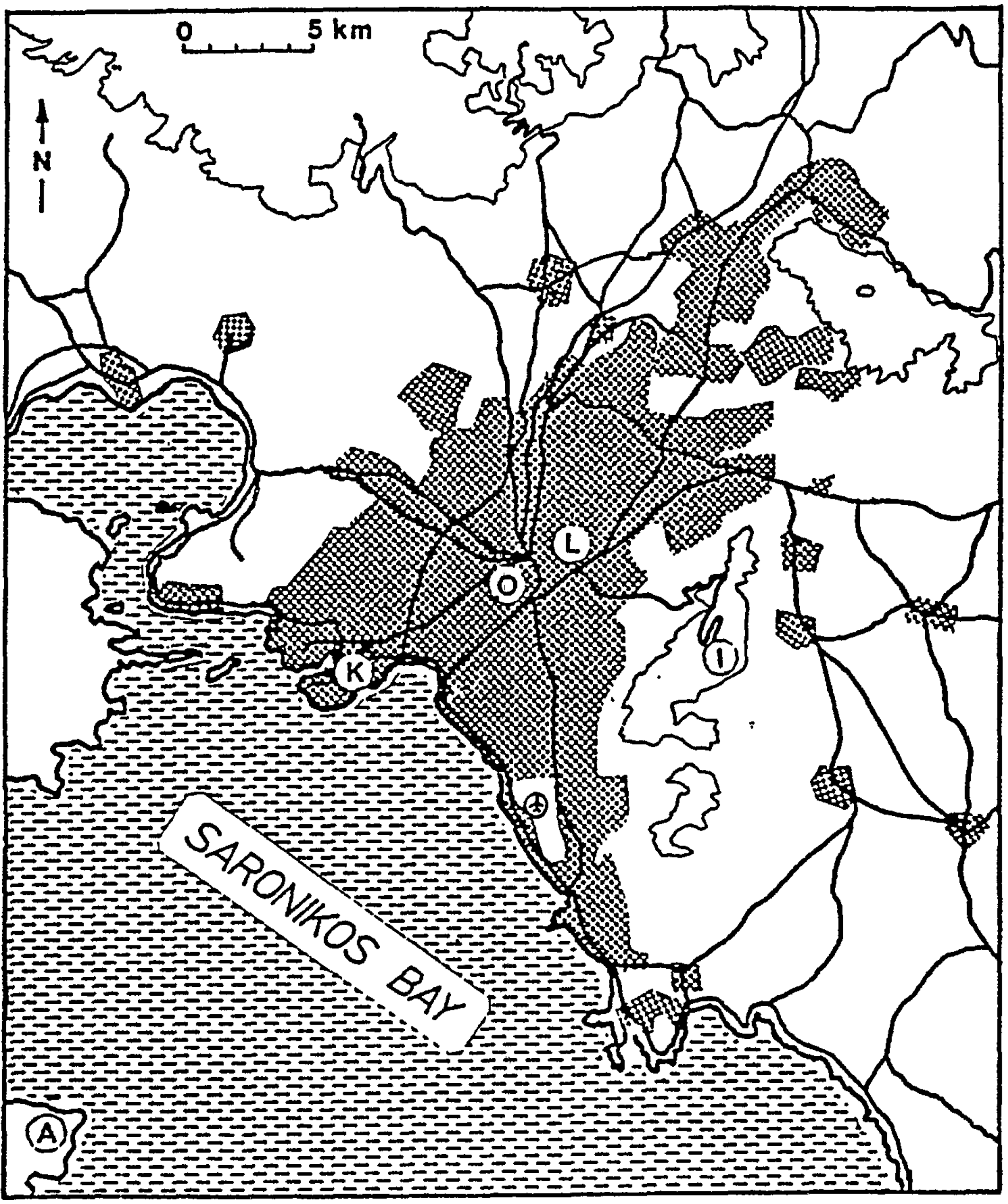

Fig. 1 - Map of Greater Athens with indicated monitoring sites:
O - National Observatory, L - hill of Lykabetos, I - mount Hymettos,
K - Kastella (Piraeus), A - island of Aegina

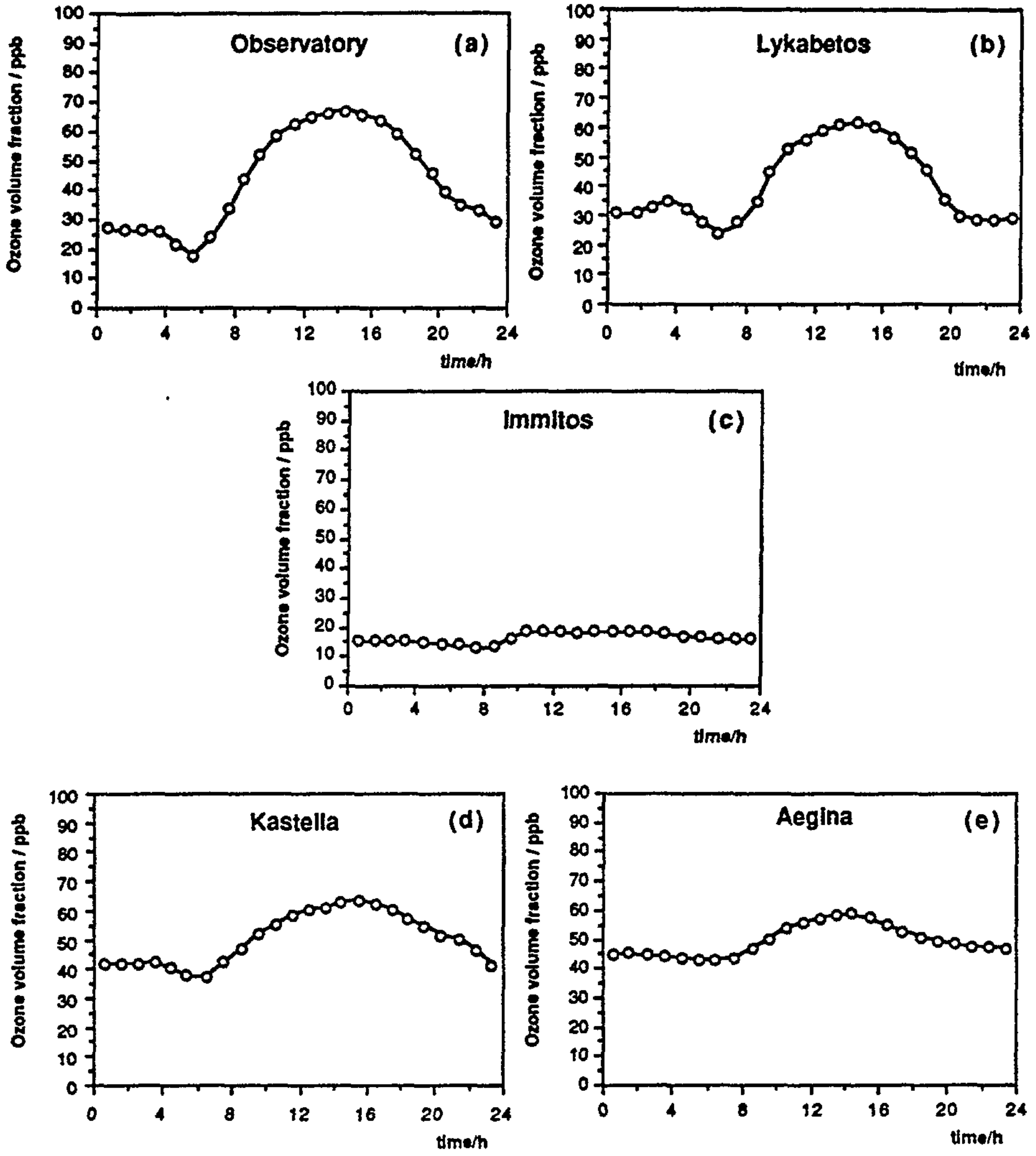

Fig. 2 - Average diurnal variation of hourly ozone volume fractions at various monitoring sites

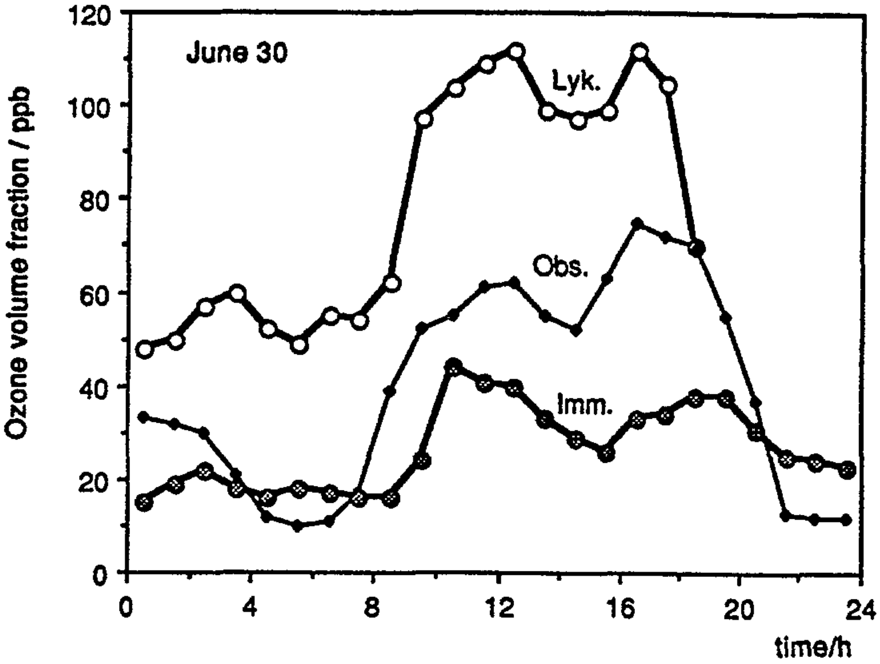

Fig. 3 - Diurnal variation of hourly ozone volume fractions at three sites on 30th June 1984

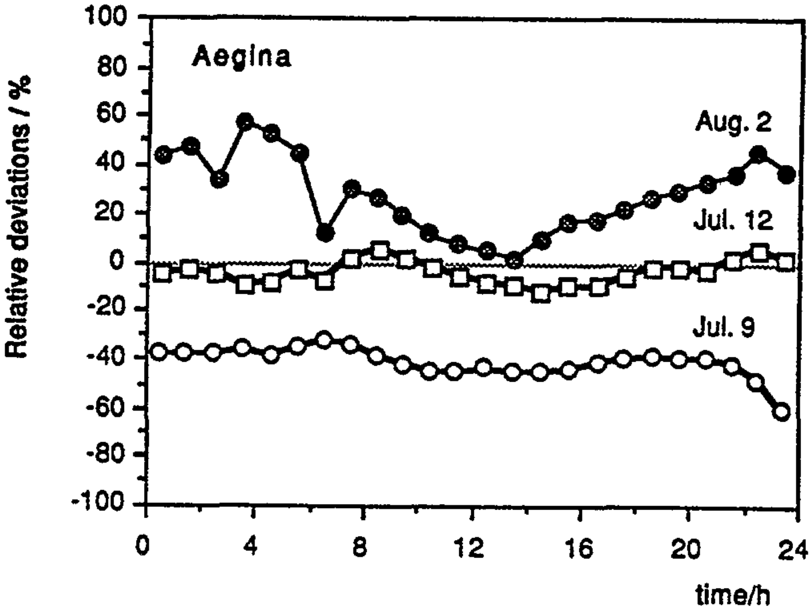

Fig. 4 - Relative deviations of ozone volume fractions on selected days

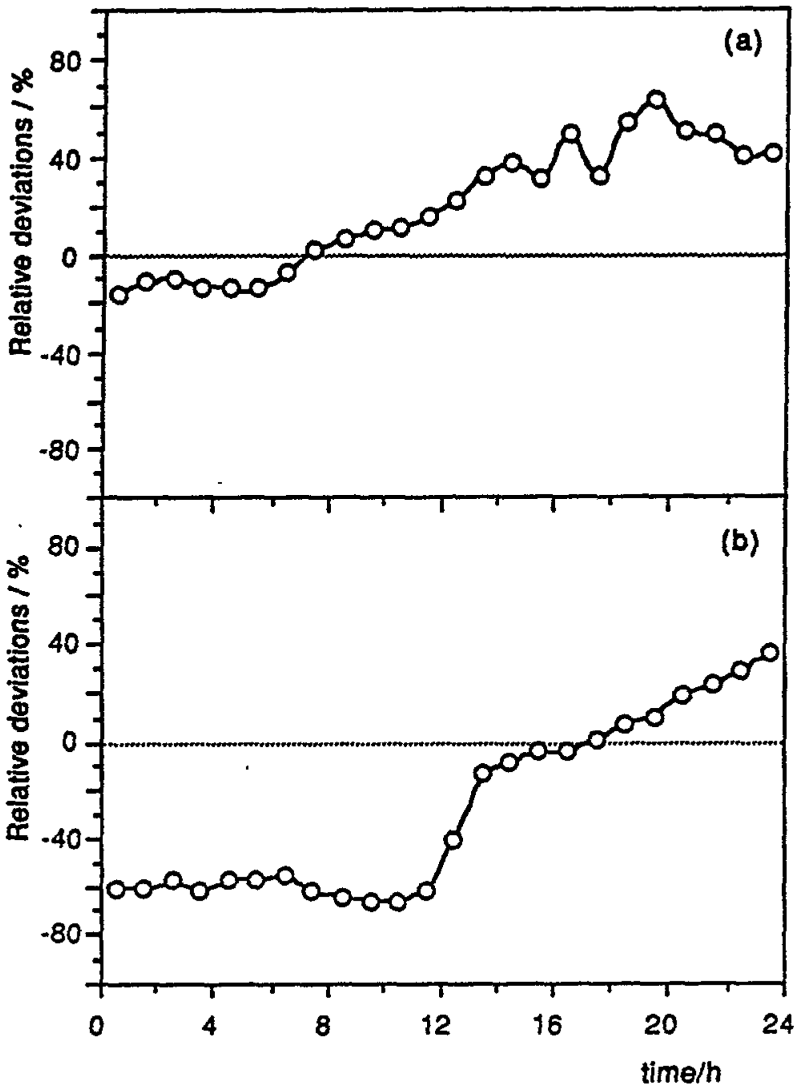

Fig. 5 - Relative deviations of ozone volume fractions on 1st August (a) on Aegina and (b) in Kastella

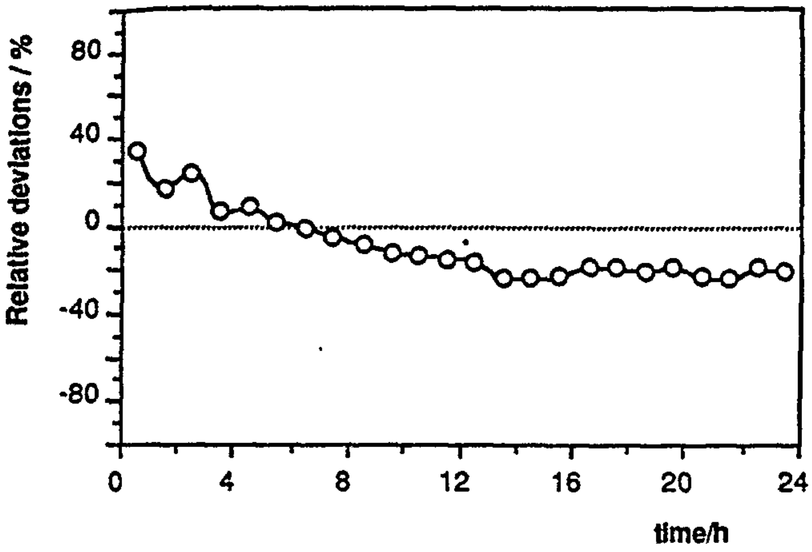

Fig. 6 - Relative deviations of ozone volume fractions on 12th August 1984 at the monitoring site on Aegina

METEOROLOGICAL AND CLIMATOLOGICAL DATA FOR THE ASSESSMENT OF ATMOSPHERIC TRANSPORT OF POLLUTANTS IN THE MEDITERRANEAN BASIN*

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[2] Air Resources Laboratory, National Oceanic and Atmospheric Administration, U.S.A.

ABSTRACT

This article presents the essential results of a comprehensive report prepared for the GESAMP Working Group as one of the activities on the Interchange of Pollutants between the Atmosphere and the Oceans. An overview of the meteorological measurements that are pertinent in describing the transport and deposition of pollutants into the Mediterranean region is given. The assessment of the contribution of different source areas to the pollutant concentrations and their deposition in the region requires not only an analysis of the meteorological data to be made but also to input these data into models whose calculations can be used for a more sophisticated evaluation. Procedures such as an innovative statistical method for mapping trajectory flow climatology were applied. For evaluations of convection processes in the Mediterranean region, long range transport model outputs of boundary layer heights are analyzed along with Heffter's independent method. Routinely measured meteorological parameters also provide information to determine the relative importance of the dry and wet deposition processes. This includes monthly average precipitation amounts, duration and intensities of precipitation,, cloud amounts, etc. Suggestions are made for further analysis of meteorological data that would help in the understanding of the polluting of the Mediterranean via the atmosphere.

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* This paper was published in its extended form as MAP Technical Reports Series No. 30, UNEP, Athens, 1989.

INTRODUCTION

In this report the Mediterranean Sea, being a semi-enclosed basin, is thought to be particularly vulnerable to atmospheric pollution and was therefore chosen.

The overwater meteorological data necessary for offshore dispersion in the Mediterranean basin are different from overland meteorological data. For example, Pasquill-Gifford stability categories of overland turbulence levels which have been successfully parameterized as a function of solar radiation and wind speed only can be used without considering surface temperature or humidity. This is not the case with the Boundary Layer over water surfaces where diurnal temperature changes are quite small, response times long and latent heat fluxes important. Overwater turbulence levels are largely governed by the air-water temperature difference, overwater wind speed and the specific humidity.

MATERIALS AND METHODS

The parameters mentioned in the report are obtained from surface and upper air routine observations around the region. Therefore, our data source consists of measurements and not of results derived from numerical forecasting models, suggested as an alternative source by Klug (1984).

RESULTS AND DISCUSSION

General Synoptic Weather Patterns over the Mediterranean Basin

Synoptic weather patterns are essential as a first tool to understand the overall flow configurations for evaluation of the pathways of contaminants to the Mediterranean region. A brief description of the five main synoptic weather patterns is given below:

Type A: An anticyclone or ridge of high pressure lies over the northeastern Atlantic or the British Isles. During the presence of this blocking anticyclone, a quasi-permanent low pressure trough in the midtroposphere (about 500 hpa) extends along the axis of the Mediterranean Basin. This trough line leads to cyclogenesis when vorticity maxima move into its region of influence to form cyclogenesis. This major synoptic feature is the cyclogenesis in the Bay of Genova and the subsequent cyclone's movement eastward, especially during the winter period (Miller *et al*., 1987) (Fig. 1).

Type B: Northern Europe is dominated by an anticyclone. Pressure is relatively low over the whole Mediterranean (Fig. 2).

Type C: Westerly type. A deep depression (or a sequence of depressions) dominates the middle latitudes of Europe, and westerly winds prevail over most of the Mediterranean (Fig. 3). Types A, B and C are the most common types of winter in the Mediterranean Basin.

Type D: Easterly type. An anticyclone dominates central and southern Europe giving easterly winds over most of the Mediterranean. Pressure is relatively low over northern Europe (Fig. 4).

Type E: Anticyclonic type. An anticyclone or ridge of high pressure covers the greater part of the Mediterranean area giving generally light winds, mainly westerly in the north, easterly in the south and northerly in the east. Pressure is relatively low over central or northern Europe (Fig. 5).

Types D and E, which are the most frequent during the summer in the Mediterranean, are classified as a short-fetch, northwesterly type in the eastern Mediterranean Basin (Dayan, 1986). When types D or E prevail, the high pressure over the Mediterranean decreases toward the east, the prevailing wind is northwesterly and the weather is warm. These easterly patterns are almost continuous in July and August, but very infrequent from November to April. Although the Grosswetterlagen classifications are very useful to get the overall picture, each individual weather system has its own unique characteristics and may greatly influence the transport of pollutants to the region. Thus other more specific methods must be applied. Some of these are described in the next chapter.

Meteorological Parameters Pertinent in Describing Atmospheric Transport and Removal of Pollutants in the Mediterranean Basin

A. Horizontal Transport

1. Sea-Surface Winds

In order to give the simplest picture of the flow in the basin, the following chart (Fig. 6) depicts the general air movement at 10 metres above sea level. The arrows in each square are the mean vector of all observed winds. Length and thickness of arrows represent the relative constancy of the general wind pattern in four intervals. By "relative constancy" is meant the ration of the force of the mean resultant wind to the mean wind force, regardless of direction, i.e. the ration of the vectorial mean to the scalar mean.

In regions where the wind usually comes from the same direction, the ration will be near 100%, but when there is little constancy the direction of the wind arrow depends on variable winds. Noteworthy is the strong stability of the winds in summer in the eastern Mediterranean.

2. Monthly horizontal flow patterns at the 850 hPa level

Another method of viewing the transport is to look directly at the data from the upper air soundings. The 850 hPa (approximately 1500m) standard level was chosen as the most representative of the top of the transport layer. This level is taken as the approximate boundary between the surface wind regime and the regime of the upper winds relatively free from local surface effects.

One of the most obvious features of upper air data is the small number of observations that are available compared with surface data. It is essential therefore that all the available data be used, especially in areas such as the Mediterranean where there are so few soundings. For this reason we have used two different data bases to construct the monthly horizontal flow patterns at 850 hPa expressed as averaged U and V values, the zonal and meridional components respectively. The following data bases were used in the full report: (1) Radiosonde data collected for the period 1957-1964 (Newell et al., 1972); and (2) Radiosonde data collected for the period 1946-1950 (Air Ministry, Meteorological Office, 1962).

In Figs. 7 (a) (b) and 8 (a) (b) the zonal westerly component (U) is defined as positive, whereas for the meridional component (V), south is defined as positive. It is noteworthy that the U component is the major one in these latitudes for which its seasonal and spatial distribution are governed by synoptic weather patterns.

3. Backtrajectory Analysis - The Visual Classification

Since the wind field is known to be the most important factor affecting the transport of pollutants (over distances of the order of 500km), flow climatologies based on a one-layer backward trajectory model were constructed to represent the seasonal transport paths in the eastern and western parts of the region. Studies of Lagrangian models for long-range transport of pollutants are numerous in the scientific literature (Eliassen, 1984). The gridded trajectory model of the Air Resources Laboratory (ARL) was used to develop these climatologies for the Mediterranean (Harris, 1982). Such flow studies have been constructed in the past for remote sites such as the island of Bermuda; Barrow, Alaska; and Mauna Loa, Hawaii (Miller, 1981 a, b; Miller et al., 1985) and for some receptor locations within the Mediterranean region (Dayan, 1986; Miller, et al., 1987). The ARL operational model uses wind data acquired from the National Meteorological Centre. These data consist of gridded wind components at standard pressure levels from 1000 hPa to 100 hPa, twice a day over the whole globe.

The essential air flow patterns for both the Eastern (Dayan, 1986) and the Western (Miller, et al., 1987) receptors were evaluated in conjunction with seasonal synoptic weather types characterizing the Mediterranean basin. The most interesting feature of the frequency distribution of air parcel trajectories for both sites is the relatively high frequency of trajectories arriving from the west during winter months and trajectories arriving from a north-northwesterly component during the summer season (Fig. 9).

4. Automatic Classification - Statistical Flow Climatology

Miller et al., (1987) compared the visual method of classification against an automated method for a concurrent time and site using two different LRT models and found similar results, which give some justification for the use of automatic categorization methods in this review.

4.1. Frequency of air-parcel pathways

Constant level trajectories from a receptor site were computed in the atmospheric layer (1000-850 hPa) using archived gridded wind field (1978-1982). Each trajectory of 5 days' duration was identified by segment and end-point positions.

Maps showing the percentage of trajectories crossing a location of interest in the Mediterranean basis and arriving at a certain receptor are displayed.

In Fig. 10, which displays the month of December, about 40% of all trajectories calculated between 1000 and 850 hPa crossed Cyprus on their way to Israel whereas only about 20% of the same trajectories traversed South Italy on their way to Israel. The same examples for the western receptor are displayed in Fig. 11.

4.2 Arrival time (days) at the western and eastern receptor in the Mediterranean basin

Heffter's programme was applied to determine the minimal time of arrival at the receptor (in days) from any location on the map. For example, the minimal time of arrival to Israel from Greece is less than 3 days for August (Fig. 12), whereas for December (which represents a typical winter month) it would take less than 2 days for a parcel of air to reach Israel. A possible application of this method might be a valuable tool in emergency planning purposes following an accidental pollutant release in the atmosphere above the Mediterranean basin

B. Convective Processes

Air pollution simulation models are most sensitive to changes in the mixing depth (Bhumralkar et al., 1981; Maul, 1982; Eliassen, 1983; Van Dop, 1986).

In this report, monthly climatological mixing depth values were calculated for two typical summer and winter months (July and January 1984).

In order to prepare these mixing depth means, data from over 150 radiosonde stations around the Mediterranean area were processed (Fig. 12a) using two criteria for the detection of the lowest stable layer of the atmosphere defined as the lid of the mixing depth:

1. $\delta\Theta/\delta z \geq 0.005^\circ$ K/m

2. $\theta_{top} - \theta_{Base} \geq 2^\circ K$

The average calculated mixing depth for winter (Jan. 84) and summer (July 84) is displayed in Figs. 13 and 14 respectively. As expected, the main result was that the mixing height was found to be generally higher over land and probably at its minimum thickness above the Mediterranean Sea.

C. Deposition

After entering the Mediterranean area, pollutants such as heavy metals are mixed into the atmosphere, transported by winds and finally removed or deposited by dry and wet deposition processes. Wet deposition includes both within and below cloud scavenging. Therefore, monthly mean low cloud amounts (oktas) for day and night time were prepared and presented for every month. Figs. 15 and 16 present such a display for a typical winter and summer month respectively.

Maximum daily rainfall was computed for wash-out effect calculations and simulations within the Mediterranean basin. Such maximum daily rainfall charts for January (Fig. 17) and July (Fig. 18) are displayed here.

CONCLUSIONS

In this paper the necessary parameters for understanding the atmospheric transport of pollutants to the Mediterranean Basin has been described. In so doing, the authors have provided an answer to the leading questions raised by the GESAMP Working Group (GESAMP, 1985) i.e.:

"What are the major atmospheric pathways for contaminants reaching the Mediterranean?"

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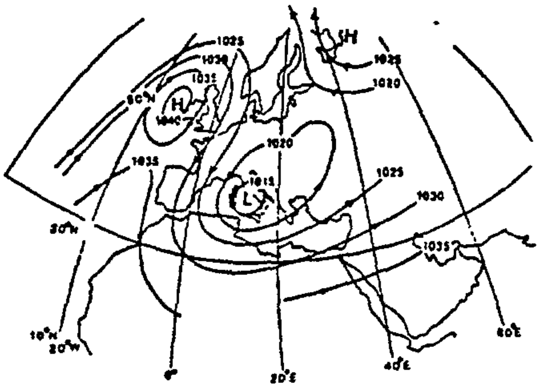


Fig. 1 Synoptic Weather Pattern - Type A

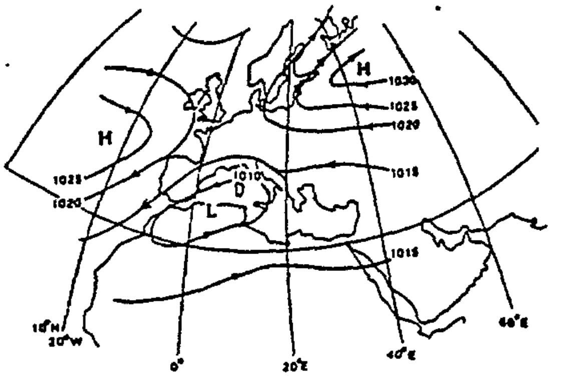


Fig. 2 Synoptic Weather Pattern - Type B

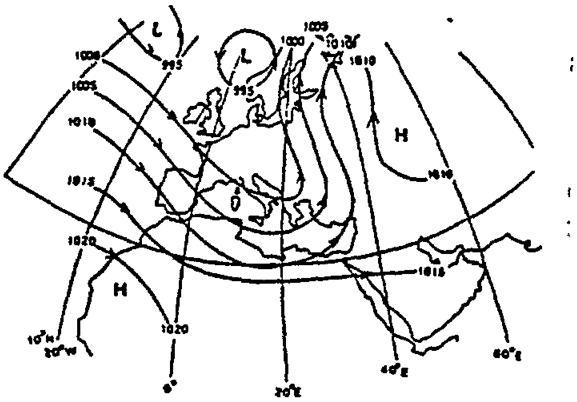


Fig. 3 Synoptic Weather Pattern - Type C

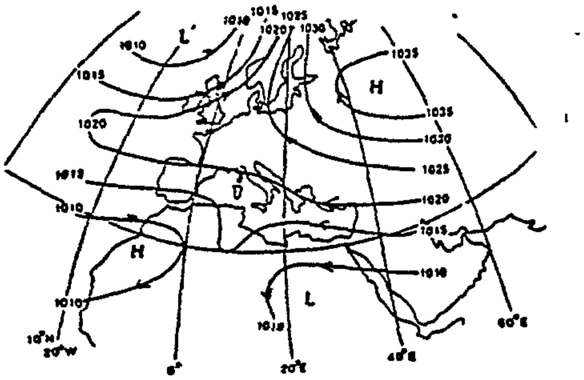


Fig. 4 Synoptic Weather Pattern - Type D

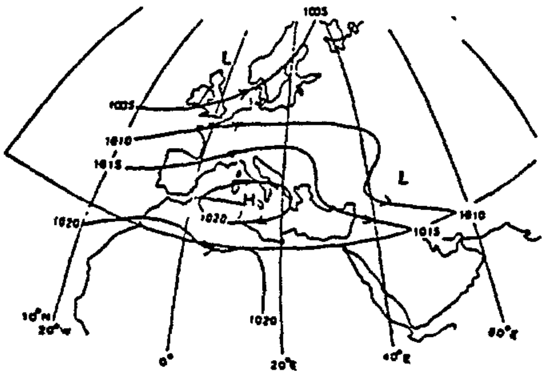


Fig. 5 Synoptic Weather Pattern - Type E

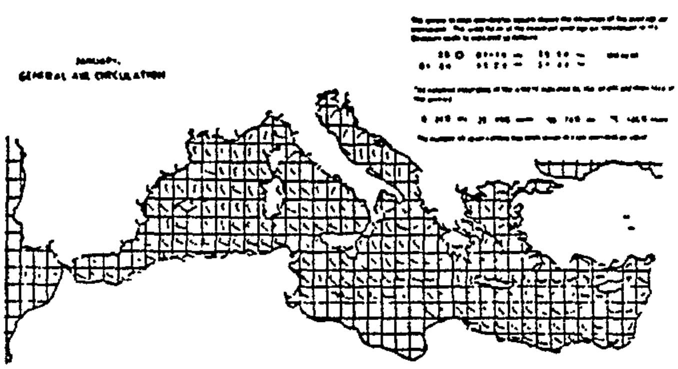


Fig 6

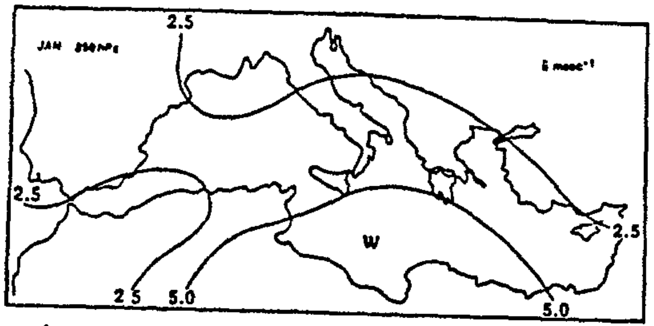


Fig. 7a

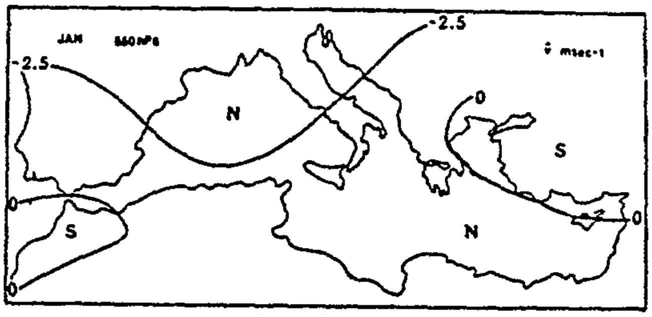


Fig. 7b

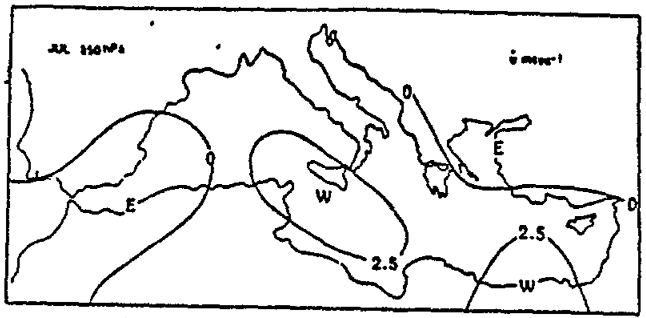


Fig. 8a

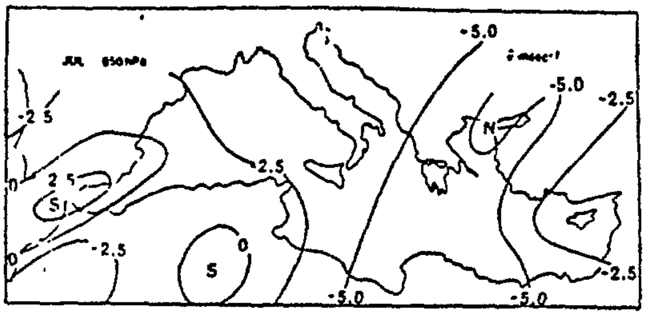


Fig. 8b

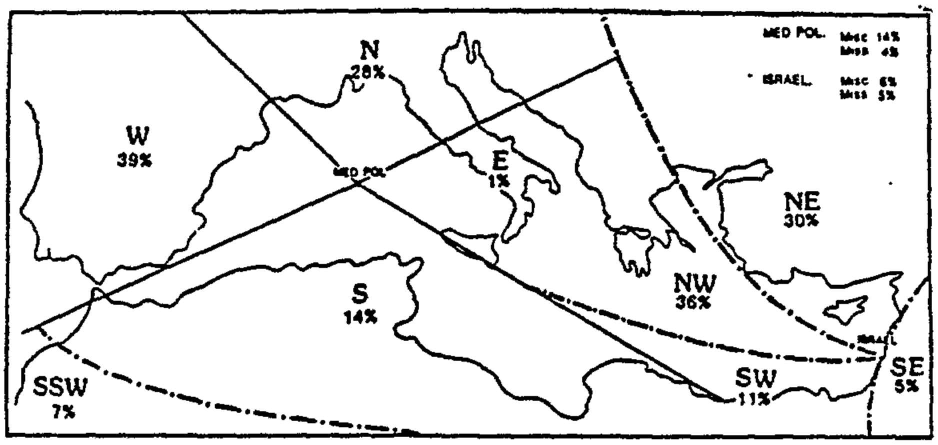


Fig. 9

Fig. 7a - Mean zonal (u) winds (m s^{-1}) at the 850 hPa level for January

Fig. 7b - Mean meridional (v) winds (m s^{-1}) at the 850 hPa level for January

Fig. 8a - Mean zonal (u) winds (m s^{-1}) at the 850 hPa level for July

Fig. 8b - Mean meridional (v) winds (m s^{-1}) at the 850 hPa level for July

Fig. 9 - Locations of the western (Med Pol) and easter (Israel) receptors in the Mediterranean Basin. Sectors NW, NE, SE, SW and SSW separated by broken lines, are trajectory directions for the western Mediterranean: sectors N, E, S and W, separated by solid lines, are trajectory directions for the eastern Mediterranean. The percentage of flow from each sector is indicated. The percentages of miscellaneous and missing data are also given.

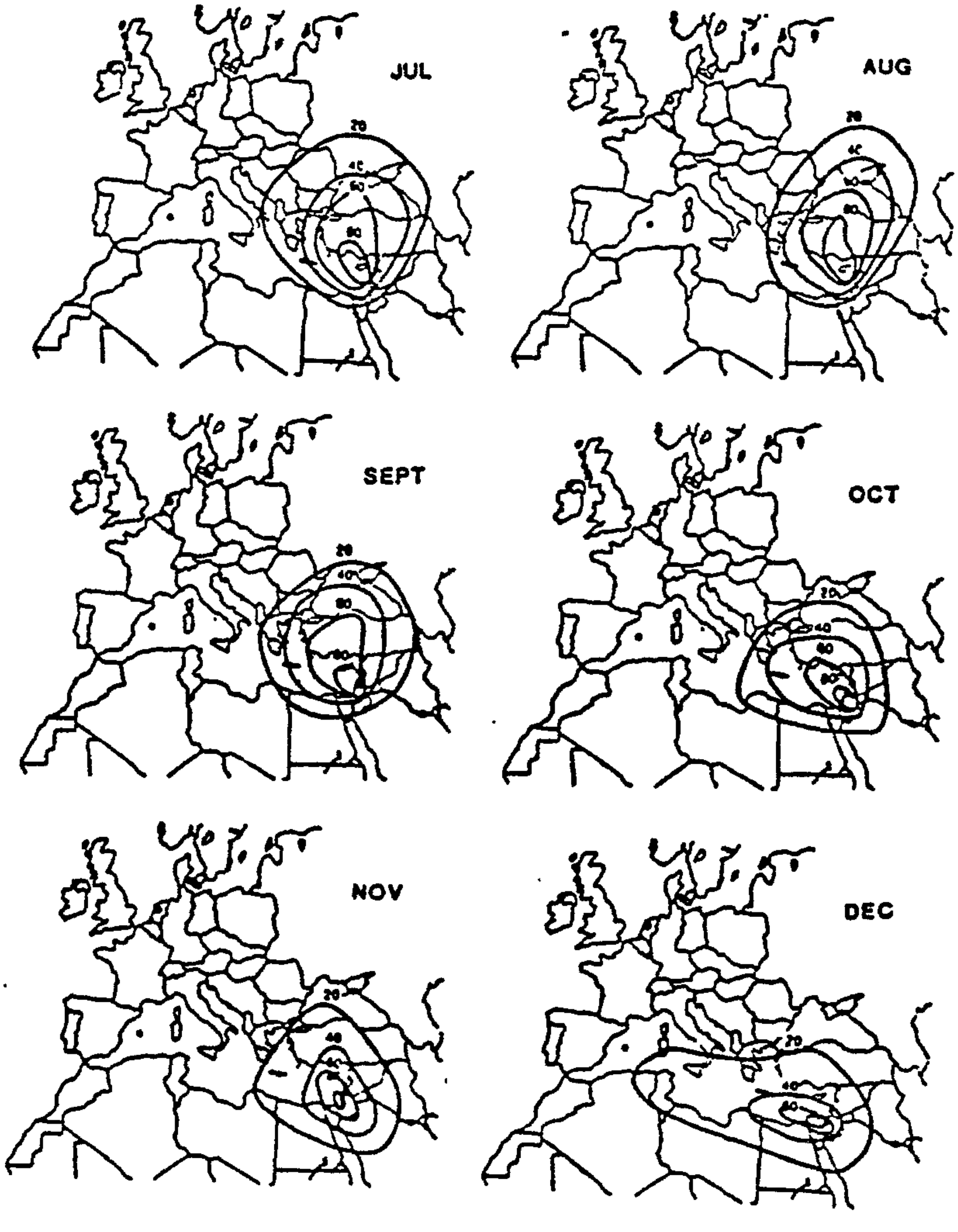


Fig. 10 - Trajectory statistics at the eastern Mediterranean (Israel) point for July-December, 1978-1987. The values shown are the percentages of boundary layer trajectories (1000-850 hPa) that had arrived at Israel and had traversed a given location on the map.

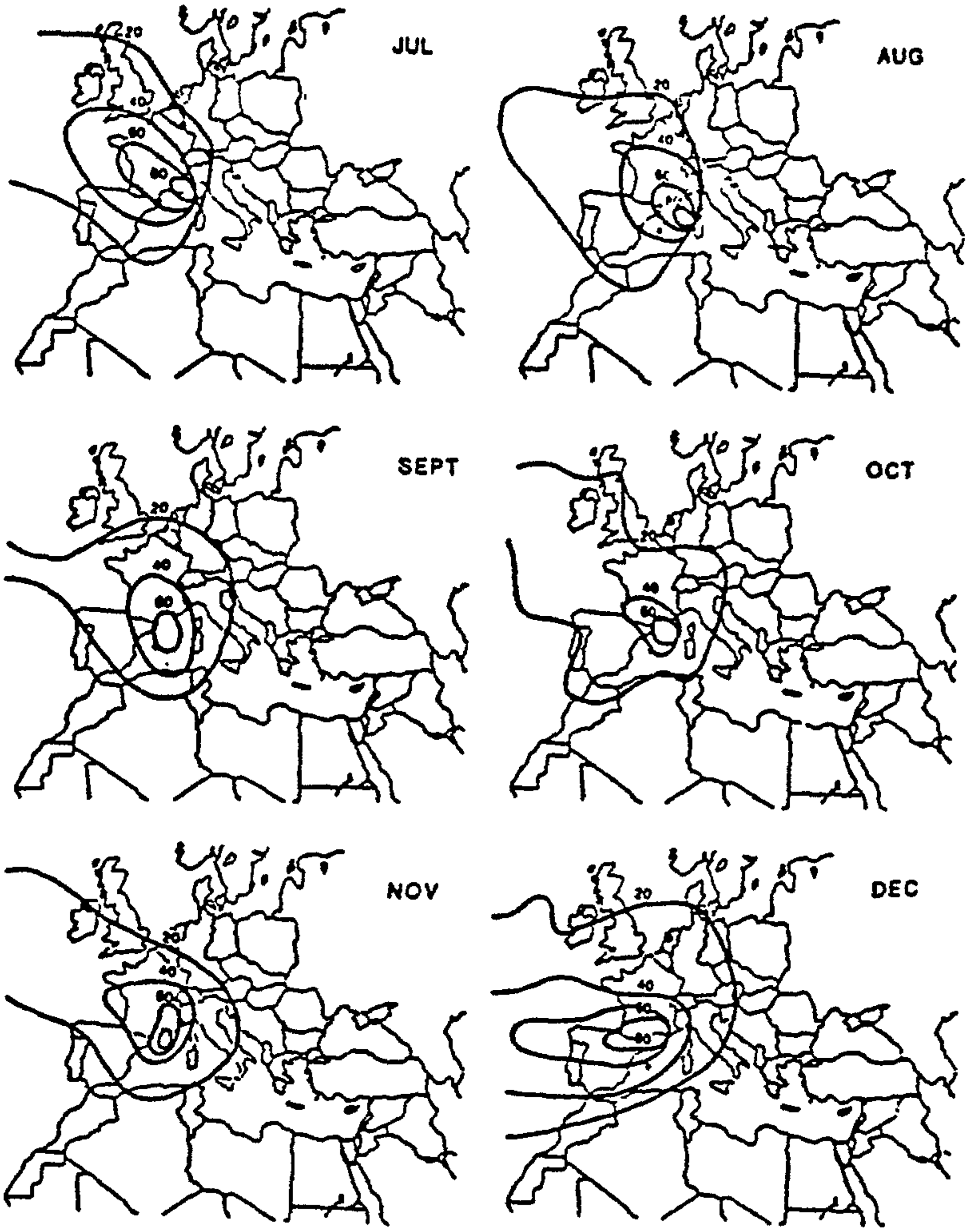


Fig. 11 - Trajectory statistics at the westerb Mediterranean (Med Pol) point for July-December, 1975-1984. The values shown are the percentages of boundary layer trajectories (1000-850 hPa) that had arrived at Med Pol and had traversed a given location on the map.

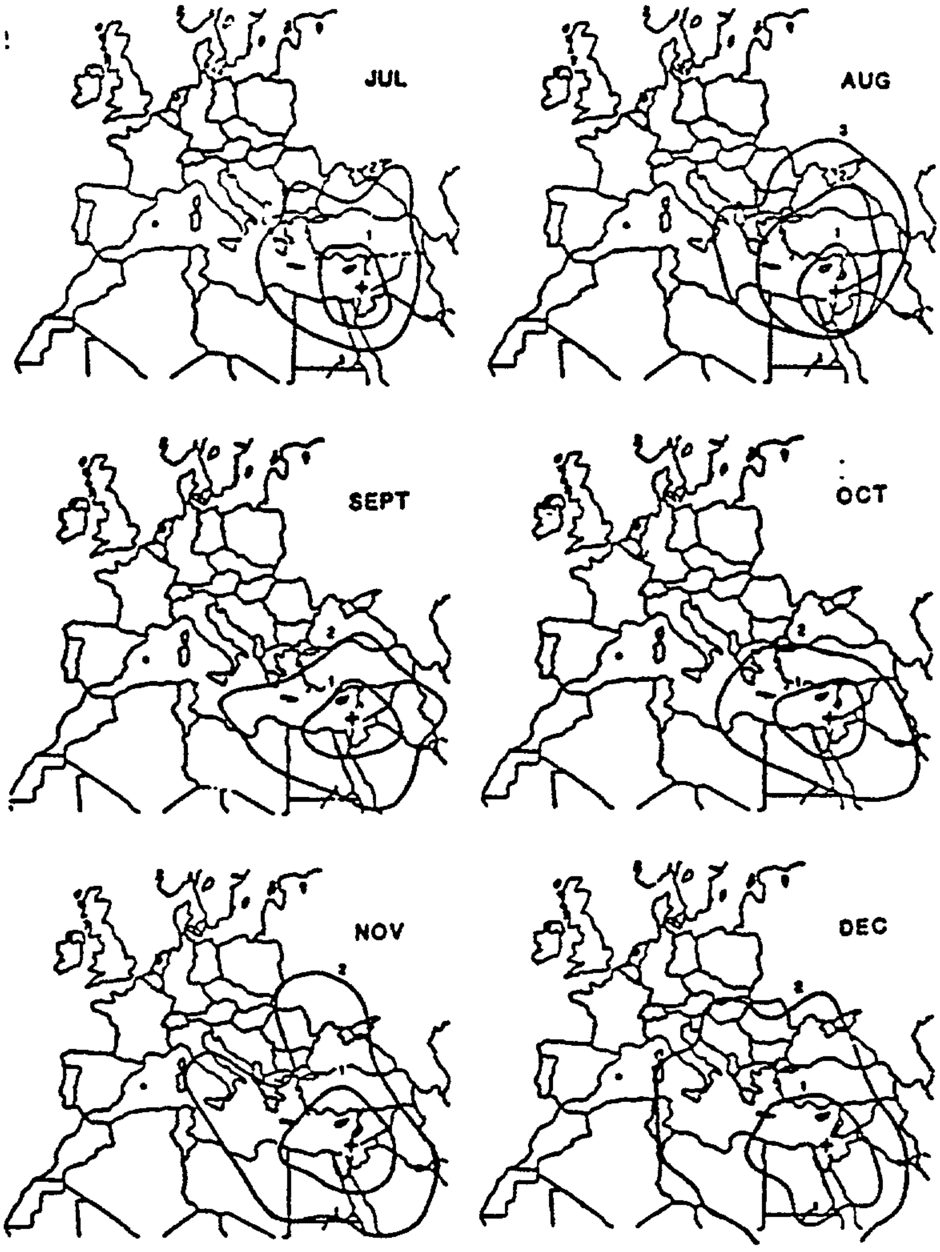


Fig. 12 - Arrival time (days) to the eastern site for July-December, 1978-1982.

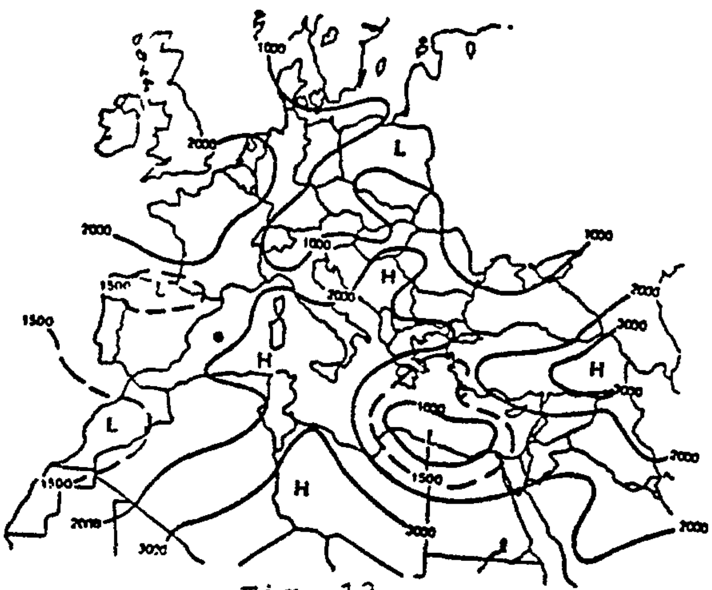


Fig. 13

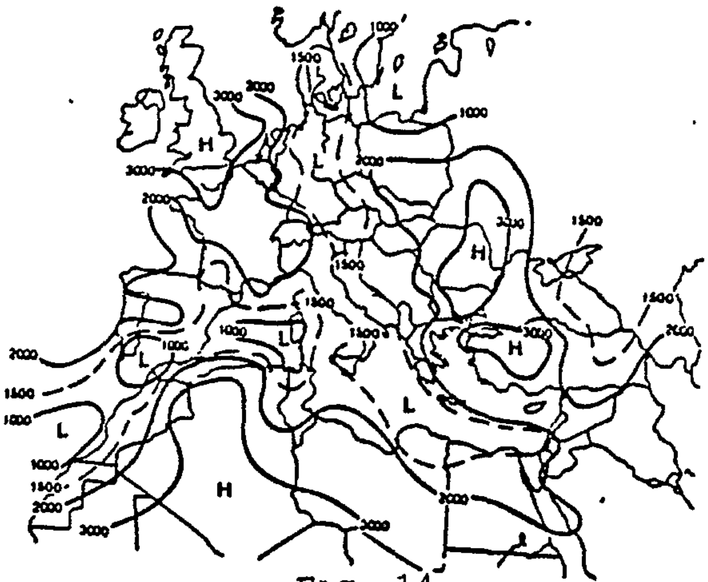


Fig. 14

Fig. 14a

Fig. 13 - Average calculated mixing height (m) for winter exemplified by January 1984.

Fig. 14 - Average calculated mixing height (m) for summer exemplified by July 1984.

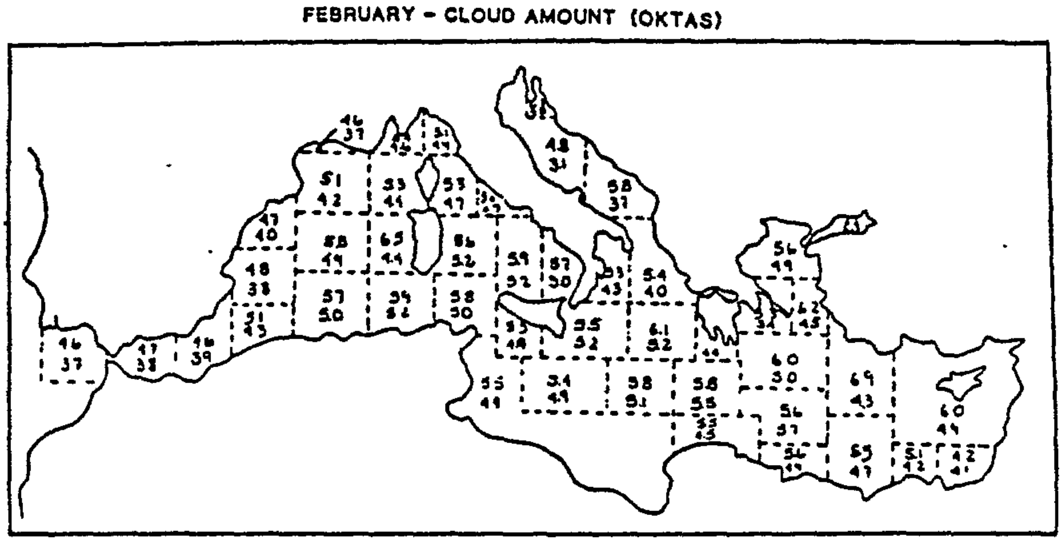

FEBRUARY - CLOUD AMOUNT (OKTAS)

Fig. 15

▦ day
■ night

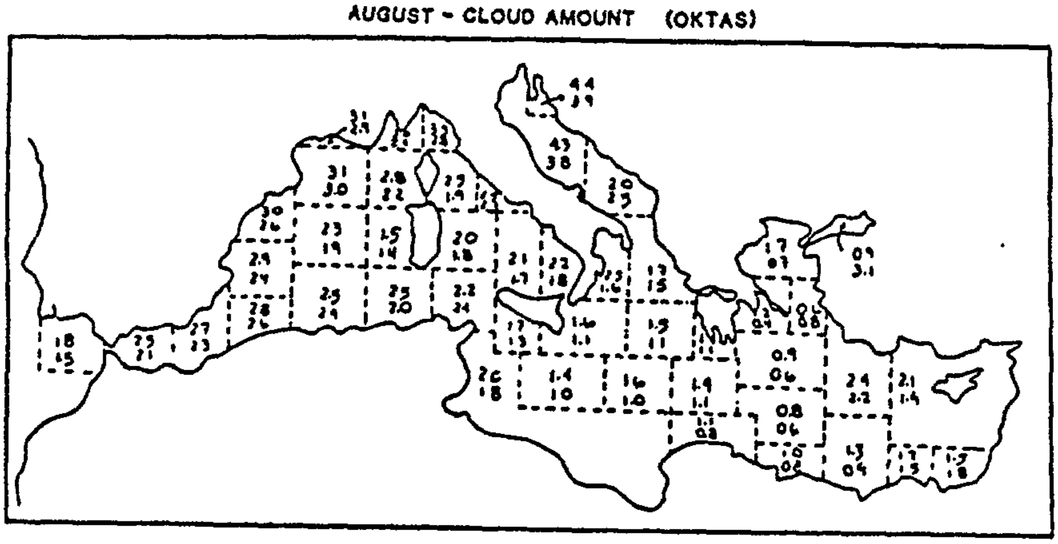
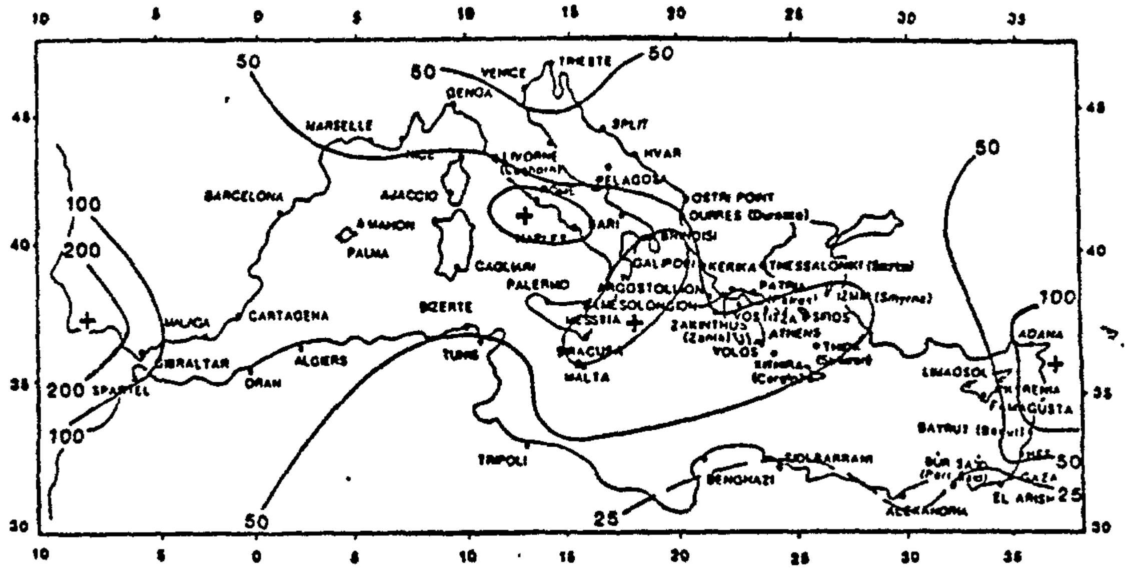

AUGUST - CLOUD AMOUNT (OKTAS)

Fig. 16

■ day
■ night



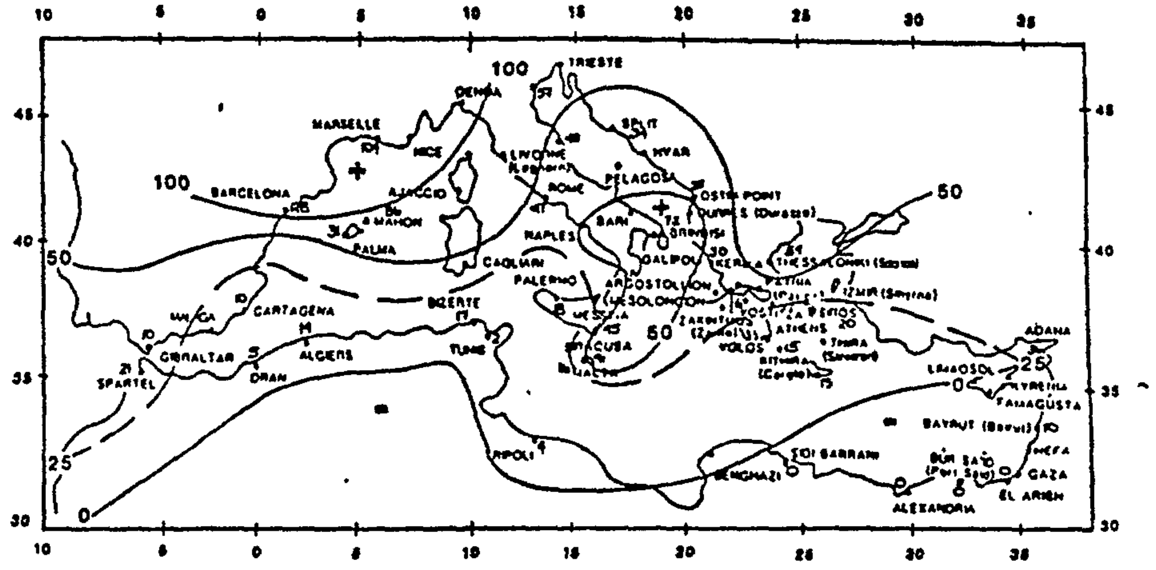


Fig. 17 - Distribution of maximum daily fall for January (mm)
Fig. 18 - Distribution of maximum daily fall for July (mm)

SYNOPTIC-SCALE MODEL SIMULATION OF TRANSPORT OF PASSIVE SUBSTANCES OVER THE EUROPEAN REGION

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ABSTRACT

A primitive equation limited area model with grid-box mountains is used to calculate back trajectories relevant for the transport of passive contaminants into the Mediterranean Basin.

INTRODUCTION

Simulation of the long-range (synoptic scales) transport presents two or three major problems. The first is an advected treatment of the planetary boundary layer since sources of contamination are usually located within PBL. When the contaminants move out of the PBL an accurate flow pattern simulation is necessary to get the correct long-range transports. Finally, if the contaminant is soluble, then a "wet" model is needed.

The present study deals with possible trajectories of a passive substance, and therefore a version of the model without physics has been used. For future studies we plan calculations of the trajectories with full physics model that has shown considerable success in forecasting.

A 36-hour flow simulation was made starting with an analysis from the Alpex data set. Boundary values were updated every 12 hours. During the run, check points were made every hour. From these check points collection back trajectories were then calculated. In order to assess the importance of the mountains, the same calculation of the trajectories was repeated with a vertical velocity set to zero.

METHODOLOGY

Model description

(a) Step-like mountains

The main problem of the mountains representation with sigma system primitive equation models is that of the non-cancellation of errors in the two terms of the pressure gradient force (Smagorinsky *et al.*, 1967). Many ideas aimed at understanding the origin and reduction of the error have been put forward (cf., for example, the review paper by Mesinger and Janjic, 1985).

In view of the ever-increasing horizontal and vertical resolution, and a need to have more realistic model mountains, we feel that the step-like mountain representation is a natural replacement for the sigma system which might have been suited for the low-resolution models of the sixties and seventies.

The synoptic scale transport of passive substances is clearly dependent on atmospheric flows on those scales resulting from the effect of mountains. Since the representation of mountains is a major feature of the differences among possible choices of vertical coordinates, the capacity of a model to simulate correctly atmospheric flows may offer guidance as to how successful a particular choice actually is.

A remarkably successful idealized simulation of the Genoa lee cyclogenesis was achieved in an early effort by Egger (1972). He used the sigma system for gentle terrain slopes and a blocking approach with vertical walls to represent steep mountains.

The pressure gradient force problem of the terrain-following coordinates as well as other additional inconveniences (Simmons and Burridge, 1981) are all a consequence of the slope of coordinate surfaces. The Egger method achieved approximately horizontal coordinate surfaces, but suffered from two imperfections. It was unable to accommodate properly the three-dimensional geometry of steep mountains and it had steep mountains change their elevation as a function of time.

Recently, Mesinger (1984) has pointed out a method of achieving approximately horizontal coordinate surfaces using a coordinate free of these problems. It can be written as

$$\eta = \frac{p - p_T}{p_S - p_T} \eta_S \qquad (2.1)$$

with

$$\eta_S = \frac{p_{rf}(z_S) - p_T}{p_{rf}(0) - p_T} . \qquad (2.2)$$

Here p is pressure, the subscripts T and S stand for the top and the ground surface values of the model atmosphere respectively; Z is geometric height and Prf(Z) is a suitably defined reference pressure as a function of Z. Furthermore, the ground surface heights Z_s are permitted to take only a discrete set of values, chosen so that mountains are constructed from the three-dimensional grid boxes in the model (Mesinger and Janjic, 1985). If this is felt to be advantageous, Prf(0) in (2.2) can be replaced by Prf(Z_b), with Z_b representing a base elevation defined so as to include gentle slopes of the surface topography.

A schematic picture of the representation of mountains using this "step-mountain" coordinate is shown in Fig. 1. In this figure, u, T and PS represent the u velocity component, temperature and surface pressure grid points respectively. The circled u grid points would be the points with zero values of the velocity components normal to sides of the mountain shown in the Figure.

An attractive feature of (2.1) is that, once a model code using (2.1) has been written, an option of having all grid points at = 1 can easily be included.

For an extension of the step-mountain approach, as well as of some of the schemes considered earlier (Mesinger, 1984) to two horizontal dimensions, several factors need to be considered. This will be done in the following three sections. Along the way, a number of additional details will be given for the model used in experiments carried out to test the performance of the system.

(b) Horizontal grid, hydrostatic equation and the vertical grid and definition of mountains

The horizontal model has the semi-staggered E grid. For simulation of the slowly changing quasi-geostrophic motion, horizontal advection scheme of Janjic (1984) was chosen. Its main feature is the control of energy cascade towards smaller scales. Also the E grid scheme conserves momentum and imposes a more stringent constraint on the false cascade of energy towards smaller scales. Specifically within the non-divergent part of the flow it completely prevents the false cascade of energy into the two grid interval wave.

For our part, we have introduced the step-mountain coordinate into the latest version of the E grid limited area model which two of us have been developing over a number of years (Mesinger, 1977; Janjic, 1977, 1979; Mesinger and Strickler, 1982; Janjic, 1984).

Now that the coordinate surfaces are approximately horizontal, hydrostatic equation can be simplified to the following:

$$\Delta\Phi = -\,(RT/\overline{p}^{\eta}\,)\,\Delta p. \qquad (2.3)$$

Here represents the increment of geopotential across an eta layer, R the gas constant and the overbar the simplest two-point averaging along the axis indicated by the accompanying subscript.

Specification of the top pressure surface of the model and of the layer thicknesses is needed in order to complete the definition of the vertical grid. The top pressure surface of the model was chosen to coincide with the highest pressure level for which analyses were available.

In defining the model mountains. one requirement is similar to that found in the sigma system framework, namely the specification of terrain heights so as to represent adequately the barrier effect of real topography (e.g. Mesinger, 1977; Wallace et al., 1983). With the step-mountain system, additional considerations may be made. For example, a straightforward discretization of "input" grid point terrain elevations to nearest reference interface elevations may produce some temperature points surrounded on all four sides by wall wind points. Such "wind-less" valleys seem undesirable since they are insufficiently resolved by the horizontal resolution used. Still another consideration we made was a practical one: for expedience and/or comparison against earlier results rather than use one of the available very high resolution terrain tapes, we wanted to use grid point terrain fields already prepared for earlier experiments or for other models. For these and other reasons explained below we chose the mountain specification procedure consisting of five consecutive steps, as follows:

(i) "input" grid point terrain heights are prescribed or prepared by space interpolation. For the European region (Alpine lee cyclogenesis) experiments these were the mountains used for one of the cases (that of December 1969) by Mesinger and Strickler. They were obtained after a "valley filling" and an additional moderate envelope-type (0.5 of the standard deviation) enhancement;

(ii) To avoid the creation of isolated temperature points in subsequent discretization steps, terrain elevations were made equal for groups of four neighbouring terrain points. We have attempted to do this without reducing the barrier effect present in input heights as would have happened were a simple-four point averaging to be carried out. Thus, instead, "silhouette" averaging (Mintz, personal communication) of terrain elevations of the groups of four neighbouring points is carried out. This is done so as to provide them with an elevation equal to the average height of the silhouette they present to the horizontal air flow. In other words, area-averaging of four neighbouring heights is performed in vertical planes rather than horizontal. For consistency with the horizontal advection scheme of the model (Janjic, 1984), average silhouette heights are first calculated for four orientations of the vertical plane. These are the four orientations normal to each of the grid lines passing through the centre of the four-point grid box. The four average silhouette heights are then averaged using weights 2/3 and 1/3 as appropriate in view of the above-mentioned advection scheme of the model.

As an exception to this four-point averaging, if two or more of the four input points happen to be over the sea, the four-point box is defined to represent a sea box. This is done in order to prevent spreading of continents, as happened for example with the ad hoc procedure used by Bleck (1977).

Each of the four point grid boxes has a wind point in its centre, and is discretized in the steps to follow to the same reference interface elevation. Hence the possible appearance of isolated temperature points is precluded.

One might be concerned about the loss of detail through this four-point grouping of the terrain points. On the other hand it may be that the forcing within the "4 to 2 Δ x" scale to an extent that can easily be avoided is not desirable in a grid point model because of the aliasing and other errors that occur in that range. Thus, the four-point grouping may be beneficial, irrespective of the considered step-mountain issue of isolated temperature points. It should be stressed, however, that the four-point averaging is by no means required by the finite difference schemes used in the model and need not be done if one prefers not to do so. Alternative procedures could, of course, be devised to prevent the creation of isolated temperature points.

As already pointed out, a separate definition of single grid point input terrain heights done within step (i) was followed here for practical reasons. In other words, it was not meant to serve the interests of the representation of mountains. Ideally, with very high resolution terrain data available, silhouette averaging would have been performed immediately on the four-point mountain boxes, without going through step (i) listed here.

The silhouette aspect of the four-point grouping discussed here was, of course, only one factor in the problem of arriving at elevations preserving the barrier effect present in given higher-resolution terrain data. Lately, this problem has typically been handled by the introduction of the so-called envelope orography (Wallace et al., 1983; Tibaldi, 1986). The silhouette averaging should be distinctly superior, since it is based on the actual and not on an assumed shape of the higher resolution terrain. Specifically, the envelope technique assumes a biharmonic shape of sub grid scale mountains. With the actual shape of sub grid scale orography known, there is no reason to make an assumption about this shape. Examples are easily found of shapes for which the envelope technique is clearly inappropriate. Thus, a plateau-like mountain of a scale larger than the grid scale - not a rare shape among real world mountains - may through the envelope procedure acquire awkward fence-like additions along its edges. Indeed, this has been noticed in the case of Tibet (Manabe, personal communication). The silhouette averaging leaves such a mountain essentially unchanged.

(iii) Discretization is performed to the nearest of the elevations the model interfaces would have if pressure were equal to the reference pressure, chosen to be the standard atmosphere. For the European region, with the top pressure and layer thicknesses as stated, this has resulted in interface elevations of 0, 290, 1112, 2433, ...m.

(iv) Substantial mountain gaps (saddle points) are restored if these have been closed in the preceding two steps. The idea underlying this effort is the possibility that in discretization done on a four-point by four-point basis, gaps might be closed between mountains that one would not have wanted closed considering the original higher resolution ("input") terrain field. Details of this procedure will be omitted here. Essentially, they required the saddle shape to have been of a sufficient "amplitude" defined in terms of the reference layer thickness. For our European region, the gap restoration rules, as defined, have restored one four-point mountain gap, that between the Pyrenees and the Alps.

(v) Finally, in our experiments, four-point mountain boxes are removed if they are located, completely or partly, in a given number of the outermost rows of grid points along the boundaries of the integration domain. The number of "no mountain" lines was six for the European region and five for the North American region experiments.

RESULTS

Since velocity fields were saved at a given time interval during the forecast, trajectories were calculated in two steps. The first step was a calculation that utilises velocities from the n-th check point to obtain a preliminary position x_{n+1}^*, y_{n+1}^* and η_{n+1}^*:

$$
\begin{aligned}
x_{n+1}^*(t_n+\Delta t) &= x_n(t_n) + u_n(t_n)\Delta t, \\
y_{n+1}^*(t_n+\Delta t) &= y_n(t_n) + v_n(t_n)\Delta t, \qquad (3.1) \\
\eta_{n+1}^*(t_n+\Delta t) &= \eta_n(t_n) + \dot{\eta}_n(t_n)\Delta t.
\end{aligned}
$$

Then the final result was obtained from both n-th and n+1-th check point:

$$
\begin{aligned}
x_{n+1}(t_{n+1}+\Delta t) &= x_{n+1}^*(t_n+\Delta t) + .5{*}[u_{n+1}(t_{n+1})+u_n(t_n)]\Delta t, \\
y_{n+1}(t_{n+1}+\Delta t) &= y_{n+1}^*(t_n+\Delta t) + .5{*}[v_{n+1}(t_{n+1})+v_n(t_n)]\Delta t, \qquad (3.2) \\
\eta_{n+1}(t_{n+1}+\Delta t) &= \eta_{n+1}^*(t_n+\Delta t) + .5{*}[\dot{\eta}_{n+1}(t_{n+1})+\dot{\eta}_n(t_n)]\Delta t.
\end{aligned}
$$

Since after the first step that starts from a grid point trajectory will reach a point away from a grid point velocities at these points were calculated using the bilinear interpolation in x and y direction and linear interpolation in vertical.

In Fig. 2 results are presented from the three calculations of back trajectories with check points taken every hour, two hours and finally three hours. In these Figures a part of the integration domain is represented with grid point numbers as x and y axis. Trajectories were also calculated without vertical velocities. These trajectories are presented together with the respective 3-D trajectories so that comparison is straightforward. Differences between 2-d trajectories from one panel to another are less pronounced than the difference between the 3-D trajectories. Apart from that, a comparison of the terrain heights and heights of the points along the trajectory shows the occasionally a trajectory "goes" under mountains. This difference, 3-D versus 2-D trajectories, depends on the vertical and horizontal shear and changes from case to case and within a case show regional variability.

CONCLUSIONS

From the comparison between 3-D and 2-D trajectories it can be seen that there is a difference that remains even with the finest time resolution with check points every hour. This difference varies with an increase of the time interval between the check points but not in a monotonic way and is probably due to some small scale flow field characteristics.

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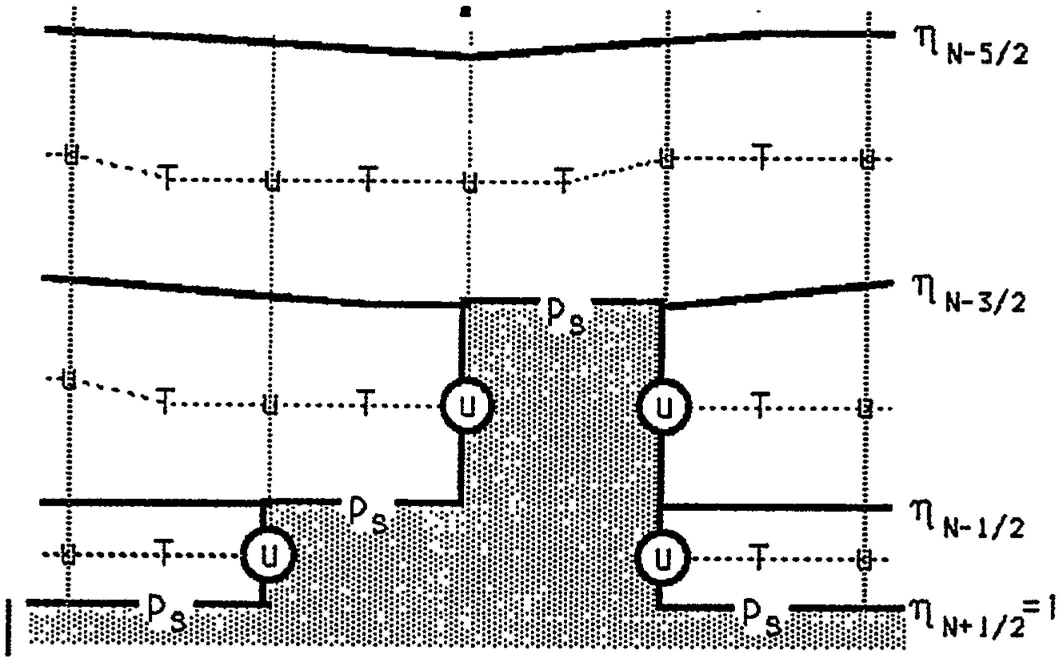

Fig. 1 - A schematic picture of the representation of mountains using this "step-mountain" coordinate

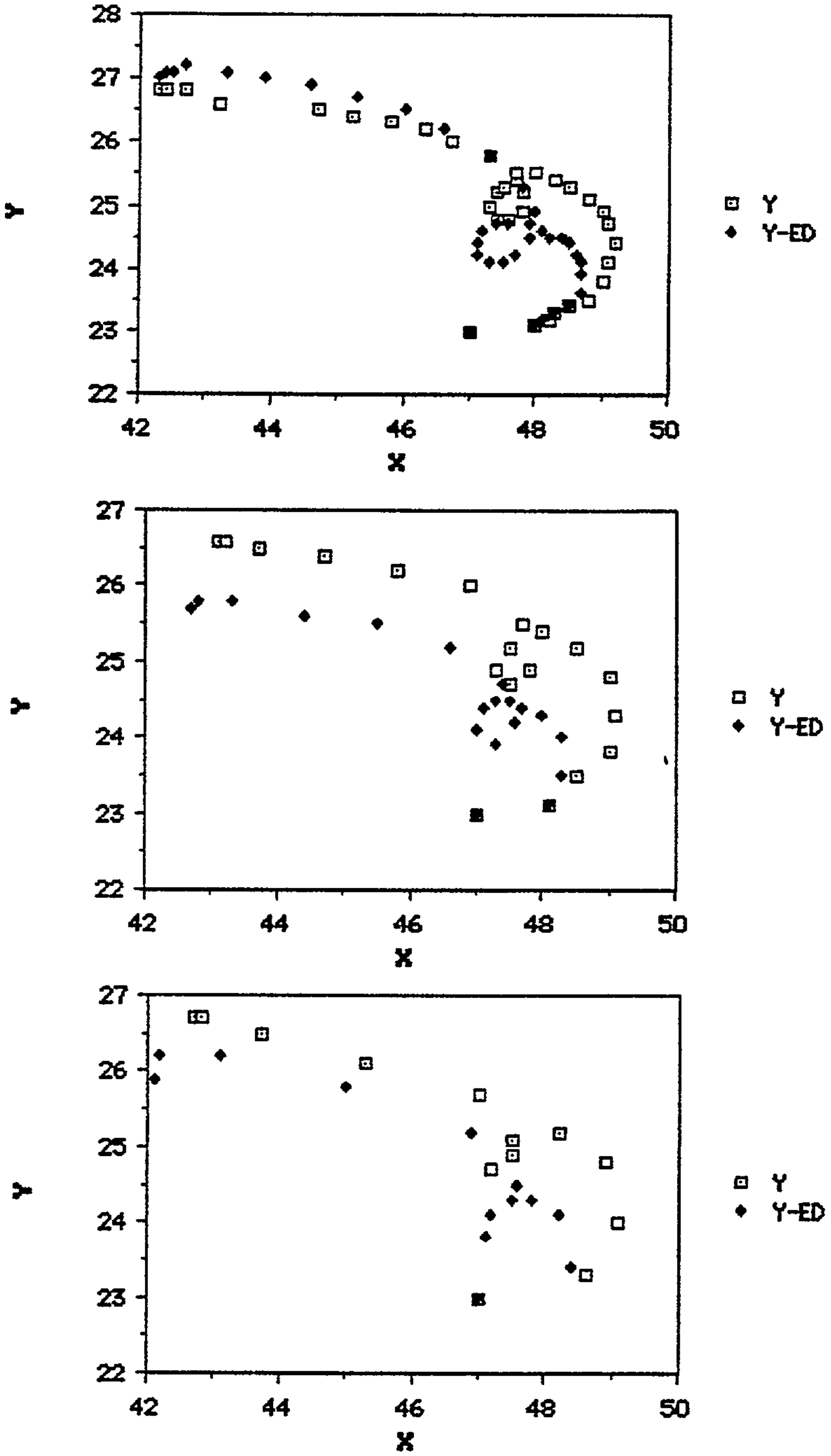

Fig. 2 - Trajectories calculated every hour, top panel. The middle panel shows trajectories calculated at two hours'interval and the bottom panel shows trajectories calculated at three hours'interval. Open square are 2-D trajectories while closed squares are 3-D trajectories.

MATHEMATICAL MODEL OF UNSTEADY DIFFUSION OF POLLUTANTS OVER COMPLEX TERRAIN

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INTRODUCTION

The diffusion processes in the atmosphere over complex terrain are governed by atmospheric turbulence and its related surface properties. In some cases buoyancy-driven air motions coupled with the air motions due to mechanical turbulence complicate the process of atmospheric diffusion.

In the case of coastal regions there can be an interaction of land-sea breeze and mountain-valley winds, which results in a complex flow field of one typical diurnal cycle with daily varying circulating flows and variations of mixing layer depth.

This paper presents a three-dimensional mathematical model of the Eulerian type, in which the basic three-dimensional equation is solved numerically. The model is intended to be as general as possible so as to include unsteady change of concentration due to both diffusion and advection processes as well as temporal and spatial variation of the strength of the pollution sources. The model is suited for computation and prediction of concentration field in the case of unsteady mezo-scale diffusion of pollutants over complex terrain.

METHODS

Mathematical formulation

The diffusion of the pollutant whose concentration is denoted by C can be seen in the Eulerian framework described by the following equation.

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} + V\frac{\partial C}{\partial y} + W\frac{\partial C}{\partial z} = -\frac{\partial \overline{u'c'}}{\partial x}\;\frac{\partial \overline{v'c'}}{\partial y} - \frac{\partial \overline{w'c'}}{\partial z} + R + S \qquad (1)$$

The turbulent concentration fluxes $\overline{u'c'}$, $\overline{v'c'}$, $\overline{w'c'}$ were modelled by using the first order closure model:

$$\overline{u'c'} = -K_{xx}\frac{\partial C}{\partial x} \quad \overline{v'c'} = -K_{yy}\frac{\partial C}{\partial y} \quad \overline{w'c'} = -K_{zz}\frac{\partial C}{\partial z} \tag{2}$$

An introduction of the terrain-following coordinate system requires the transformation of the vertical coordinate system (Mahrer and Pielke, 1976):

$$x^{*} = \overline{H}\;\frac{z - Z\,(x,y)}{H(x,y,t) - Z(x,y)}$$

so that the transformed form of the transport equation is:

$$\frac{\partial(\Delta HC)}{\partial t} + U\frac{\partial}{\partial x}(\Delta HC) + V\frac{\partial}{\partial y}(\Delta HC) + \frac{\partial}{\partial z^{*}}(W^{*}C) + \frac{\partial}{\partial x}\left(K_x\Delta H\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y\Delta H\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z^{*}}\left(K_z\frac{\partial C}{\partial z^{*}}\right) + R\Delta H + S\Delta H \tag{4}$$

where:

$$W^{*} = W - U\left(\frac{\partial Z}{\partial x} + z^{*}\frac{\partial \Delta H}{\partial x}\right) - V\left(\frac{\partial Z}{\partial y} + z^{*}\frac{\partial \Delta H}{\partial y}\right) - z^{*}\frac{\partial \Delta H}{\partial t} \tag{5}$$

$$\text{and } H = H\,(x,y,t) - Z(x,y) \tag{6}$$

The corresponding initial and boundary conditions are:

$$\begin{array}{lll}
\text{at} & t = o & C(x,y,z) = o \qquad \forall\, x,y,z \\
\text{at} & z^{*} = o & K_z\dfrac{\partial C}{\partial z^{*}} = V_d C \\
\text{at} & z^{*} = H & K_z\dfrac{\partial C}{\partial z^{*}} = o \\
\text{at} & x = x_W \text{ and } x = x_E, & K_h\dfrac{\partial C}{\partial x} = o \\
\text{at} & y = y_S \text{ ad } y = y_N, & K_h\dfrac{\partial C}{\partial y} = o
\end{array} \tag{7}$$

<u>Numerical procedure</u>

For the solution of the different equations (4) with the corresponding initial and boundary conditions the numerical finite - the volume method (Patarker 1980) was employed. The method entails the numerical integration of the full partial differential equation over the control volume formed around each grid point of the three-dimensional mesh that represents the computation domain. For treating the unsteady term the fully implicit procedure was used. The system of discretization equations is then solved by employing the line-by-line iteration method which is based on the solution of any horizontal or vertical line of points along which the TDMA algorithm is applied (Ivanovic, 1981 and Ivanovic, 1986).

Input data for the model

(a) Topography of the relief

The dispersion model is designed for mezo-scale transport. In the test example shown, the domain was of the size 300 x 200 km covered by the uniform mesh of 60 x 50 grid points (one quadrant 5 x 5 km). The non-uniform vertical distribution of grid points was selected to be fine near ground and gradually expanding towards the top of the mixing layer.

(b) Emission inventory

The data on air pollution sources and their rates of emission for the given domain of interest were taken from the detailed emission inventory containing the information on all major point sources (coordinates of their location, height of stack, emission rate and regime of emitting).

(c) Wind field data

For the purpose of testing the model the meteorological data were taken from the detailed climatological studies for the selected region and period of time. The prevailing wind comes from the south-west. The detailed wind field in the horizontal plane was reconstructed by employing $1/r^2$ interpolation scheme while the vertical component had to satisfy the continuity condition (mass consistent wind field).

(d) Coefficient of turbulent diffusivity

The coefficient of turbulent diffusivity in the vertical direction was determined as a function of friction velocity u_* and the Monin-Obukhov length L (Shir and Shieh 1974)

for stable conditions: $K_z = U_* K_o Z e^{-4z/H}$
for unstable conditions: $K_z = U_* K_o Z e^{-4z/H} / \phi n$, $\phi n = f(z/L)$.

Horizontal eddy diffusivity in stable conditions can be taken as constant.

RESULTS

After a series of elementary numerical tests of the model with known analytical solutions, the physical behaviour of the model was tested for one mezo-scale region of the north-eastern part of Yugoslavia, the relief of which is presented in Fig. 1. The emission rates of major point sources according to one of several possible scenarios are given in the table below:

Source	U	K	T	O	K	Z	M
Emission rate (10^3 t/a)	180	83	50	110	22	76	10
Height of stack (m)	300	100	150	300	100	100	100

The ground level concentration distribution for the given meteorological conditions of one selected day are presented in Fig. 2.

CONCLUSIONS

The model presented is capable of computing concentration fields in any given complex terrain including coastal regions provided that the appropriate meteorological input is available.

By careful modelling of chemical reactions, it will be possible to compute the concentration field of other chemical compounds like NO_x, ozone etc.

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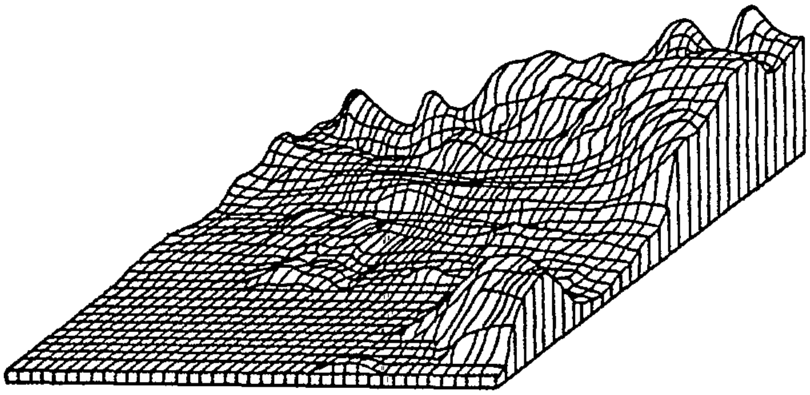

Fig. 1 - Relief of the domain of interest

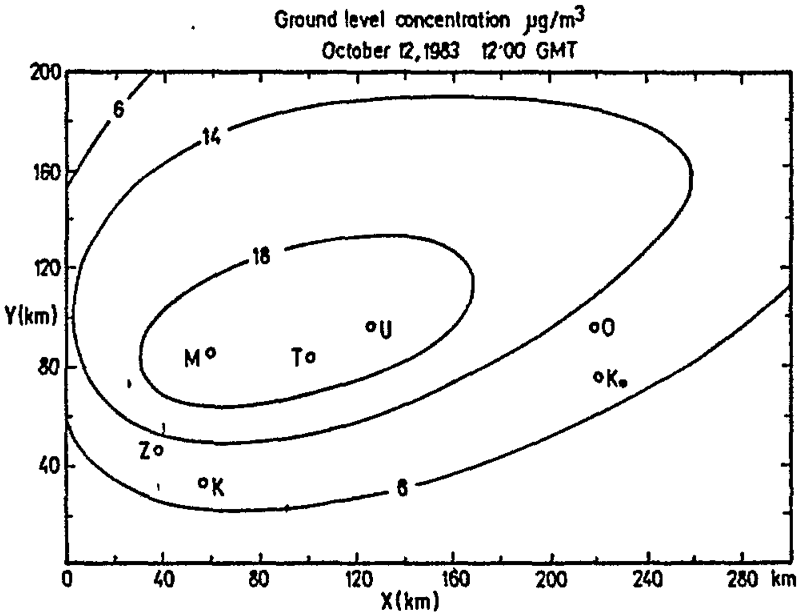

Fig. 2 - Ground level concentration distribution for the selected domain

ASSESSMENT OF ATMOSPHERIC POLLUTION SOURCES OF THE EASTERN MEDITERRANEAN SEA AND THE COASTAL AREA OF ISRAEL

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The Mediterranean Sea occupies a narrow latitudinal belt of an inland marine domain, which separates the humid European continent from the arid zone of North Africa. Eastward, the Mediterranean borders the Israeli-Levant coastal plain and its mountainous backbone, followed to the east by the deserts of Arabia and Mesopotamia.

Migration of atmospheric pollutants of natural and anthropogenic origin to the eastern Mediterranean Sea and the coastal plain of Israel is taking place according to the following air trajectories (Publs. Israel Meteo. Survey: Gagin and Neumann, 1974; Dayan, 1986):

i) air masses from the Atlantic and northwest Europe, moving mostly over the Mediterranean Sea;

ii) air masses from north and northeastern Europe, moving mostly over the central European continent;

iii) air masses from the south, moving mostly over the African continent;

iv) air masses from the south east, originating over the Arabian peninsula.

Transportation of dust constituents into the considered area is carried out from Sahara and throughout the arid land mass of Arabia, Jordan and Iraq.

Volcanic activity within the Mediterranean basin, as in Greece and Italy, might contribute too to the local atmospheric pollutant load, according to the intensity of the eruptive events.

The effects of the sea and land breezes on pollutant concentration, including man-made inputs due to local and long-fetched sources, in the coastal and offshore regions of the Mediterranean Sea, will be studied with a three-dimensional numerical mesoscale model. In the current study, the Mahrer and Pielke (1977) mesoscale model will be coupled with an advection-diffusion air quality model (Doron, 1981), and applied to the Mediterranean coastal area of Israel, in order to evaluate pollutant dispersion associated with the sea and land breeze circulation. During the night, when the land breeze and the down slope flows from the inland mountain range are dominant in the lower atmosphere (up to 300m approximately), pollutants from the coastal area are advected offshore. These pollutants can be either washed into the Mediterranean Sea or recirculated towards land with the onset of the land breeze.

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APPLICATION OF LIGHT SCATTERING TECHNIQUES TO THE CHARACTERIZATION OF AIR POLLUTANTS

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INTRODUCTION

If an obstacle, for example an aerosol, is illuminated by radiation (Fig. 1) it scatters the radiation in all directions (scattered wave). Scattering is often accompanied by absorption, and is common in materials such as coal or soot particles. In natural environments one recurring problem is to describe, by suitable analysis of the scattered field, the particles or particles responsible for the scattering. The measurements usually available for analysis are irradiance of scattered light for a set of directions and the polarization properties of the scattered light.

This paper describes the theoretical part of a previous experimental study. An instrument for angular scattering measurements was used (Fig. 2), whose essential elements are: a collimated light source; an arm that can be rotated about the sample; and a detector system mounted on the arm which includes optical elements to collect light scattered. The light source may be a lamp with suitable collimators or a laser (a He - Ne laser was used in this study). Intersection of the incident beam with the detector field of view determines the scattering volume which consequently changes with angle. Therefore, the measured signal must be corrected by the multiplicative factor sin θ. Soot particles were produced by air profane diffusions flames.

MATERIALS AND METHODS

Mie Theory

The scattering of light by a homogeneous sphere can be treated by the Mie Theory. The Mie Theory used for this mathematical model makes the following assumptions:

- scattering of plan monochromatic wave;
- independent scattering; the scattering by well-defined separate particles such as occur in a fog, water drops and dust grains in atmospheric air;
- the effects of multiple scattering will not be considered;
- spherical homogeneous particles are considered with radius R (diameter d), the origin of the coordinates being chosen at the centre of the particle.

The most important property of the scattered wave is the intensity I:

$$I = I\ (\theta,\ \varphi,\ d,\ \lambda, m\ (\lambda)).$$

The direction of scattering is characterized by the angle θ which it makes with the direction of propagation of the incident light and azimuth angle (Fig. 3).

λ is the wave length and m the refractive index of the particle. Absorbing particles (soot particles) are characterized by a complex refractive index: $m = n - ik$
For non-absorbing particles ($k = 0$) m is real.

Instead of the radius R, was chosen the dimensionless parameter $\alpha = 2\ \pi R/\lambda$, the size parameter.

The point of departure of the Mie theory is the Maxwell equations. The solution of Maxwell's equations gives the intensities I_1, I_2 of the scattered polarized light.

I_1 is the perpendicular and I_2, the parallel component of the electric field of the scattered wave.

$$I_1 = \frac{Io}{2} \cdot \frac{\lambda^2}{4\ \pi^2\ D^2} \cdot i_1 \qquad I_2 = \frac{Io}{2} \cdot \frac{\lambda^2}{4\ \pi^2\ D^2} \cdot i_2$$

where:

$$i_1 = S_1\ (\theta)\ 2 \qquad \text{and} \qquad i_2 = S_2\ (\theta)\ 2$$

S_1 $(\theta,\ \varphi)$ and S_2 $(\theta,\ \varphi)$ are the scattering functions; they describe amplitude and phase of the scattered wave and are calculated through i_1 and i_2.

$$i_1 = f\ (m,\ \alpha,\ \theta) \qquad \text{and} \qquad i_2 = f\ (m,\ \alpha,\ \theta)$$

i_1 and i_2 have been written as a series of N terms of Legendre functions with coefficients expressed directly in terms of the Mie coefficients a_N, b_N. These were determined using the Riccati bessel-functions and their derivatives.

All these functions were determined for different values of α as functions of N and computer programmes developed to calculated all these functions as functions of α and θ.

$\alpha = \alpha\ (R, \lambda)$. In practical problems, the case λ = constant and R variable are of great interest, because in air pollution problems the particles are of different sizes.

The determined scattered intensities have been normalized to the intensity of incident light lo, so that relative Intensities (dimensionless) are determined:

$$Is = \frac{I}{Io} \cdot \frac{1}{\sin\theta} .$$

RESULTS AND DISCUSSION

Single spherical particles

The results of computations of angular scattering by a sphere using computer programmes are shown in the following Figures. The incident light is polarized parallel (dotted curves) or perpendicular (solid curves) to the scattering plane. Figs 4 and 6 show the angular distribution of the scattered light for large resp. small absorbing particles and figure 5 for non-absorbing particles.

For absorbing particles Is_1 is always greater than Is_2, so that the degree of polarization P is always positive. P is described by the expression:

$$P = \frac{i_1 - i_2}{i_1 + i_2} \quad , \quad |P| \leq 1$$

For large particles (Fig. 4), the increased complexity of scattering is an indicator of its extreme sensitivity to size. Thus, comparison of measured scattering with sets of calculations is a possible means of accurately sizing spheres.

For a given refractive index, the number of peaks in the scattering pattern gives a fairly good measure of the sphere radius.

For small size parameters (Fig. 6), the familiar Rayleigh scattering patterns are obtained. The scattering pattern is perfectly symmetric and the light scattered at right angles is fully polarized ($i_2 = o$ for $\theta = 90°$).

For larger particles, the deviations from the Rayleigh theory appear as forward-backward asymmetry, with more light being scattered in forward directions. As the size increases, the asymmetry becomes more pronounced and the dominant forward-scattering lobe narrows.

For non-absorbing particles (Fig. 5) such as fog and rain, the plots of the two components of the scattered light show also the existence of a sequence of peaks. However, in this case, the two curves frequently intersect; this corresponds to a change of sign in polarization.

For absorbing and non-absorbing particles and for all sizes, $i_1 = i_2$ at 0° and 180°. The two polarizations are indistinguishable in these directions because of symmetry. In other directions, the scattering plane enforces a distinction.

Mixtures of spherical particles

The mathematical model has also been adapted for mixtures of spherical particles with a given size distribution. Mixtures of waterdrops (H_2O), SiO_2 - and Fe - spheres in different proportions have been considered.

The results (Fig. 7) are similar to those of single particles. However, the forward-backward asymmetry becomes more pronounced (10^4). Moreover, the intensities of scattered light seem to be independent of the direction of the vibration of the electric field vector. The curves show how the typical features are washed out if particles of a wide range of sizes are present.

Non-spherical particles

As non-spherical particles, long (L) circular (R) cylinders of a homogeneous material were considered ($L \gg R$).

When exposed to a plane wave of radiation, they present a somewhat similar scattering problem as homogeneous spheres. The problem is quite comparable to the Mie problem if the incident light travels perpendicularly to the cylinder axis. This case has been solved in detail.

The curves (Fig. 8) show the same general behaviour as was found for spheres. As the size increases, the asymmetry becomes more pronounced and the number of peaks increases. Though forward scattering is predominant, I_1 and I_2 have different values (the difference becomes important for larger particles). Forward scattering can be used to size non-spherical particles of unknown optical properties. On the other hand, polarization tends to be positive over a wide range of angles for non-spherical particles. It can be used as a measure of non-sphericity (depolarization ratio).

CONCLUSIONS

The electromagnetic scattering theory for a sphere, Mie theory, was developed and applied to single particles. Computer programmes were run for soot particles and larger spheres. The intensities of scattered light were calculated and their variations with optical and physical properties of the particles discussed.

Application of the theory to a mixture of spherical particles of an exponential size distribution was also investigated, and a two-component mixture (Fe, H_2O resp. Fe, SiO_2) was used. To determine the extent to which the theory is applicable to non-spherical particles (in air pollution many particles are not spheres), computer tests were run for long circular cylinders.

From the comparison of the calculated curves with given measured curves and experimental date, the particle size distribution, the spherical particles and deviations from sphericity and the densities could thus be determined.

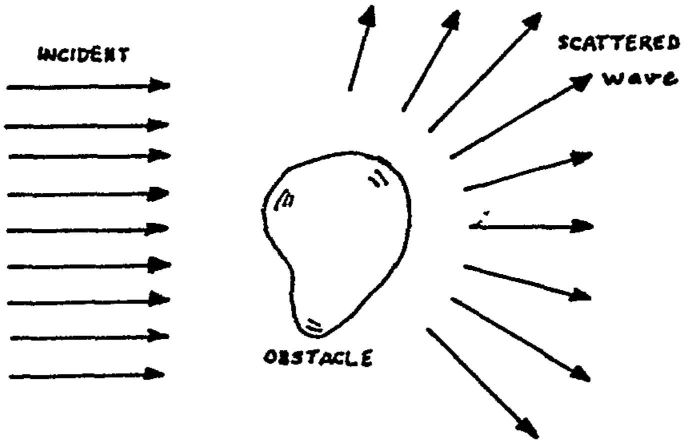

Fig. 1 - Scattering by an obstacle

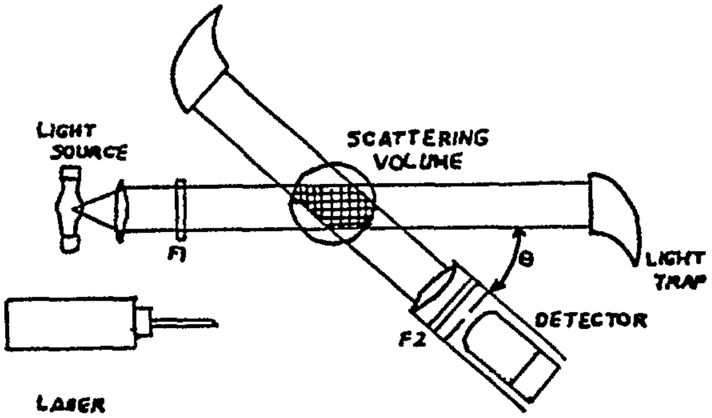

Fig. 2 - Schematic diagram of a nephelometer
for measuring angular scattering

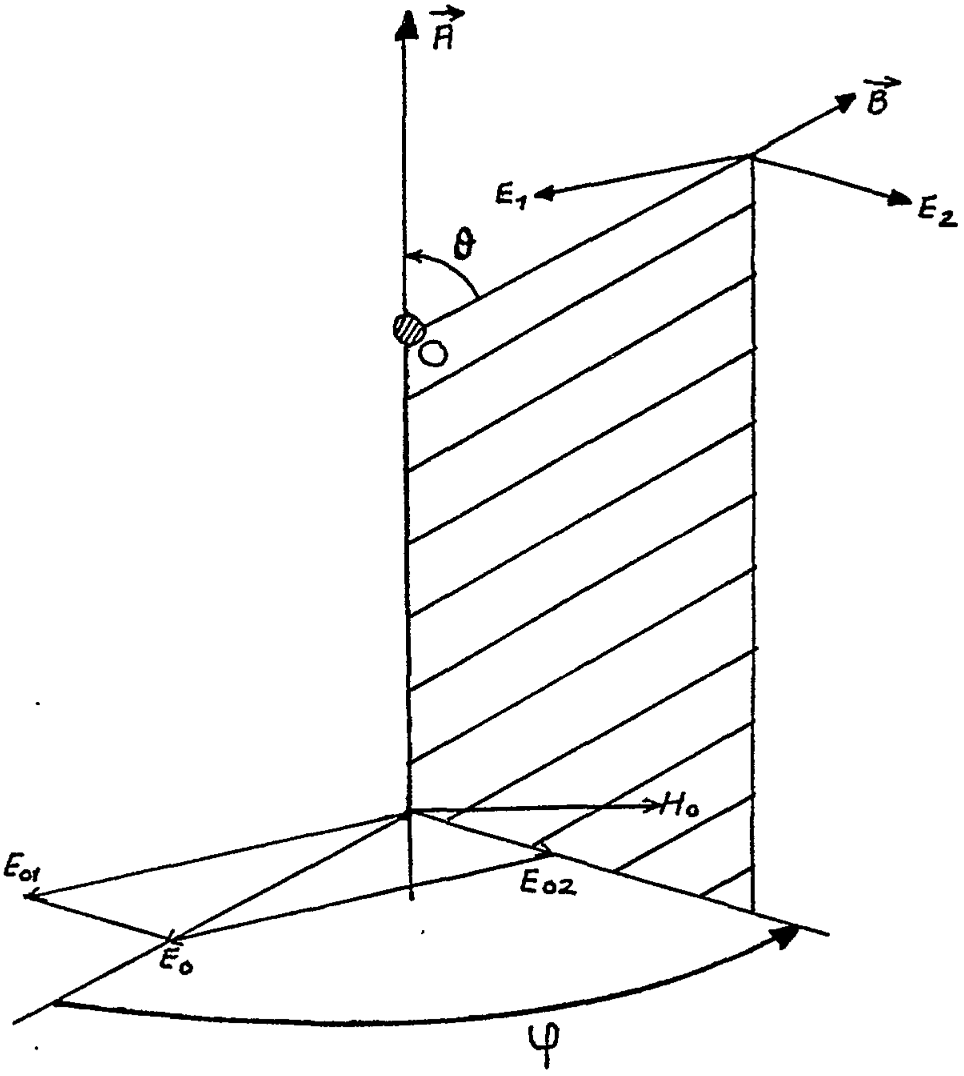

Fig. 3 - Decomposition of electric vectors of incident (E_{01}, E_{02}) and scattering (E_1, E_2) waves.

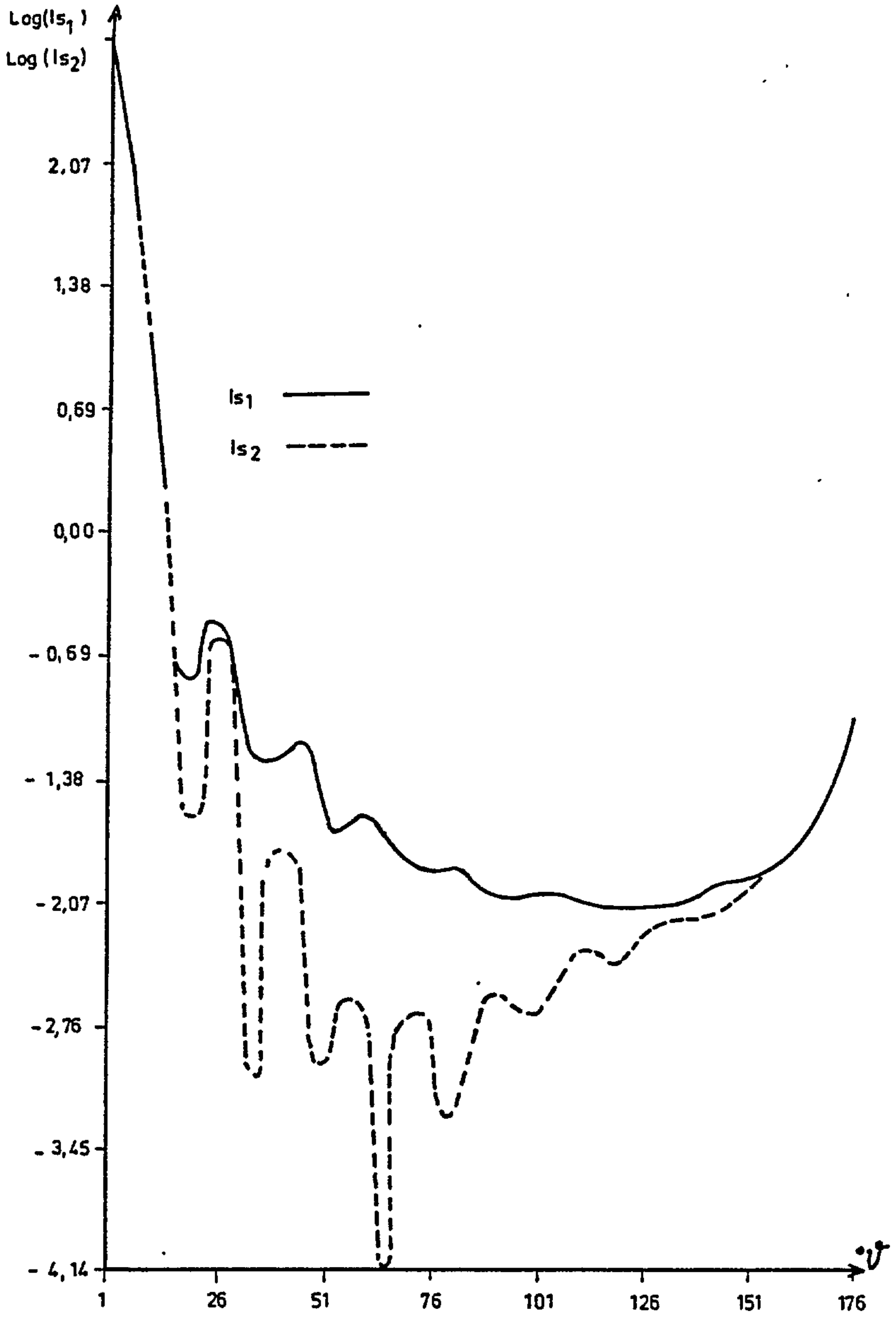

Fig. 4 - Angular scattering by spheres with:
m = 1.60-0.60i and α = 10.00

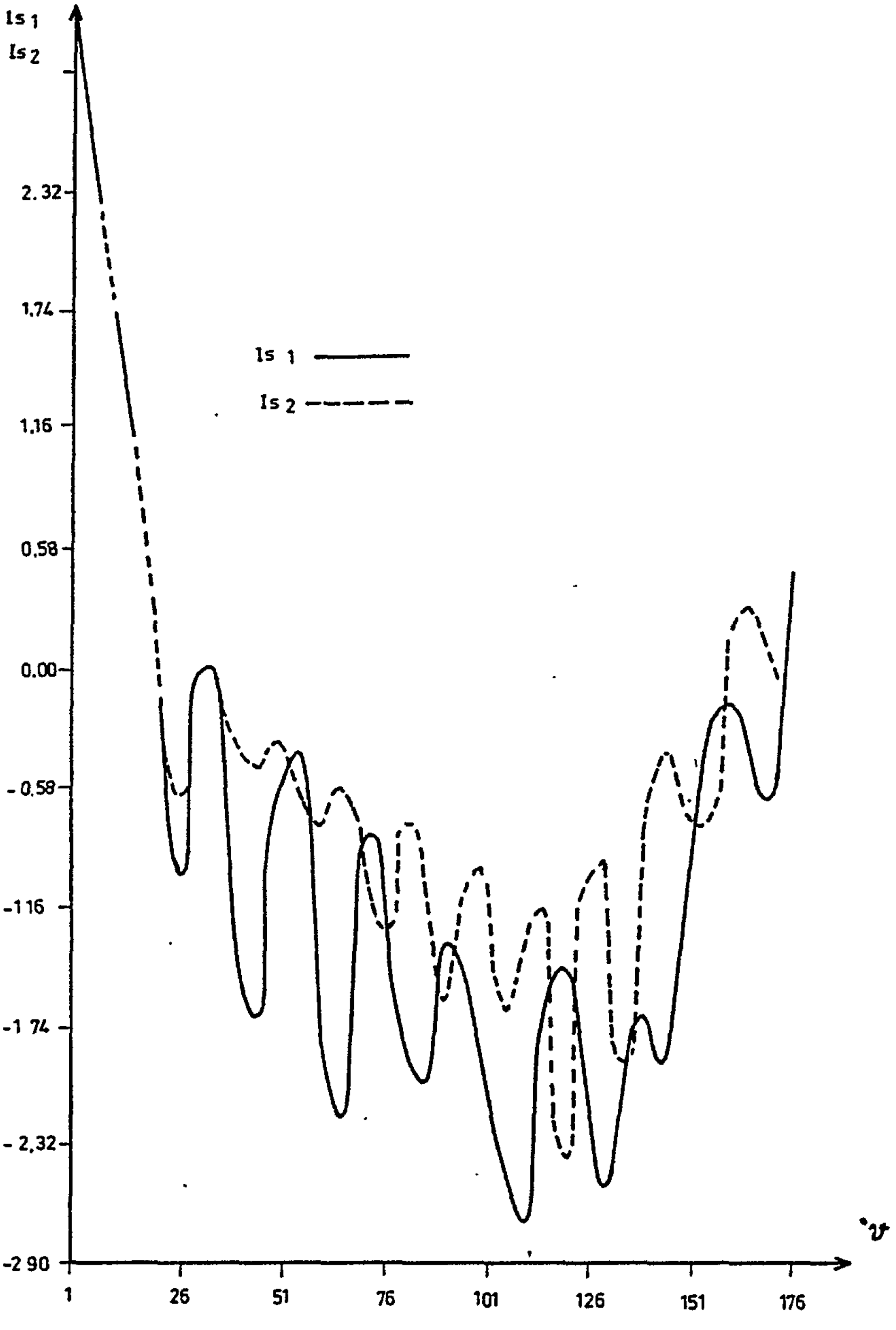

Fig. 5 - Is₁ resp. Is₂ as function at √ with:
m = 150 - 0i and α = 10.00

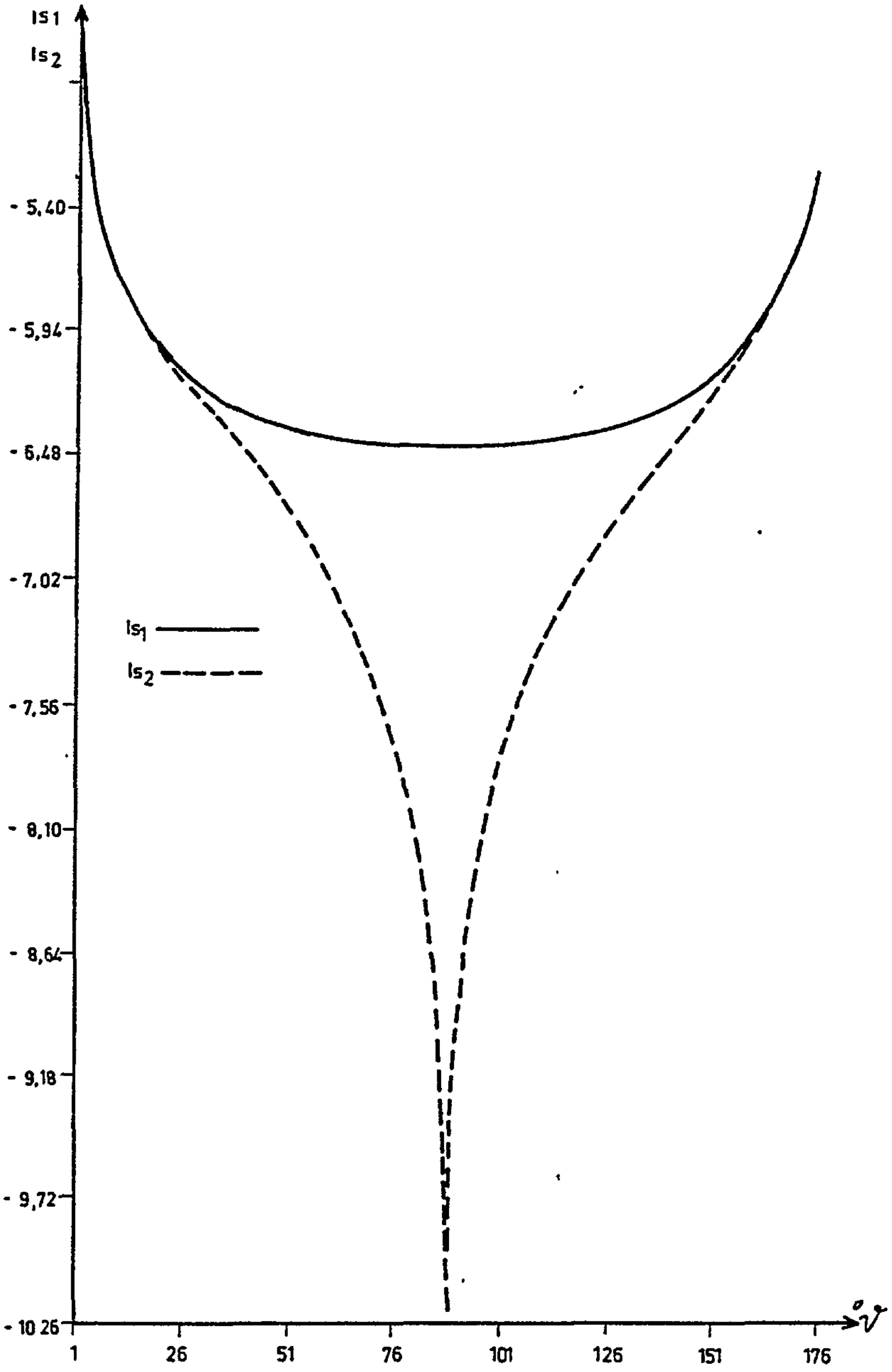

Fig. 6 - Rayleigh - Scattering
m = 2.28 - 1.20 i and α = 0.25

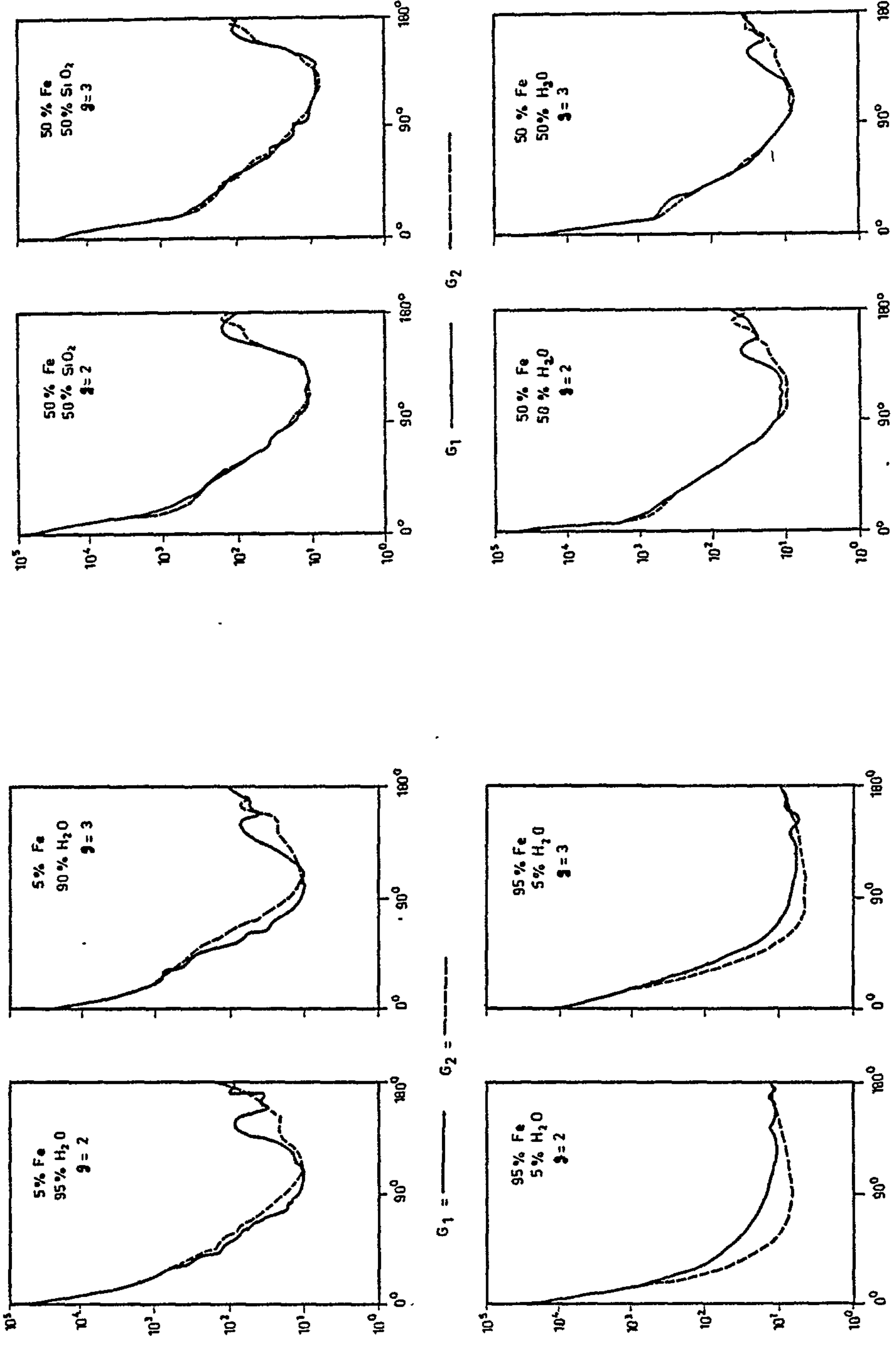

Fig. 7 - Angular Scattering by mixtures of particles with:
m = 1.27 - 1.30 i (Fe), m = 1.33 (H_2O) and m = 1.55 (SiO_2)

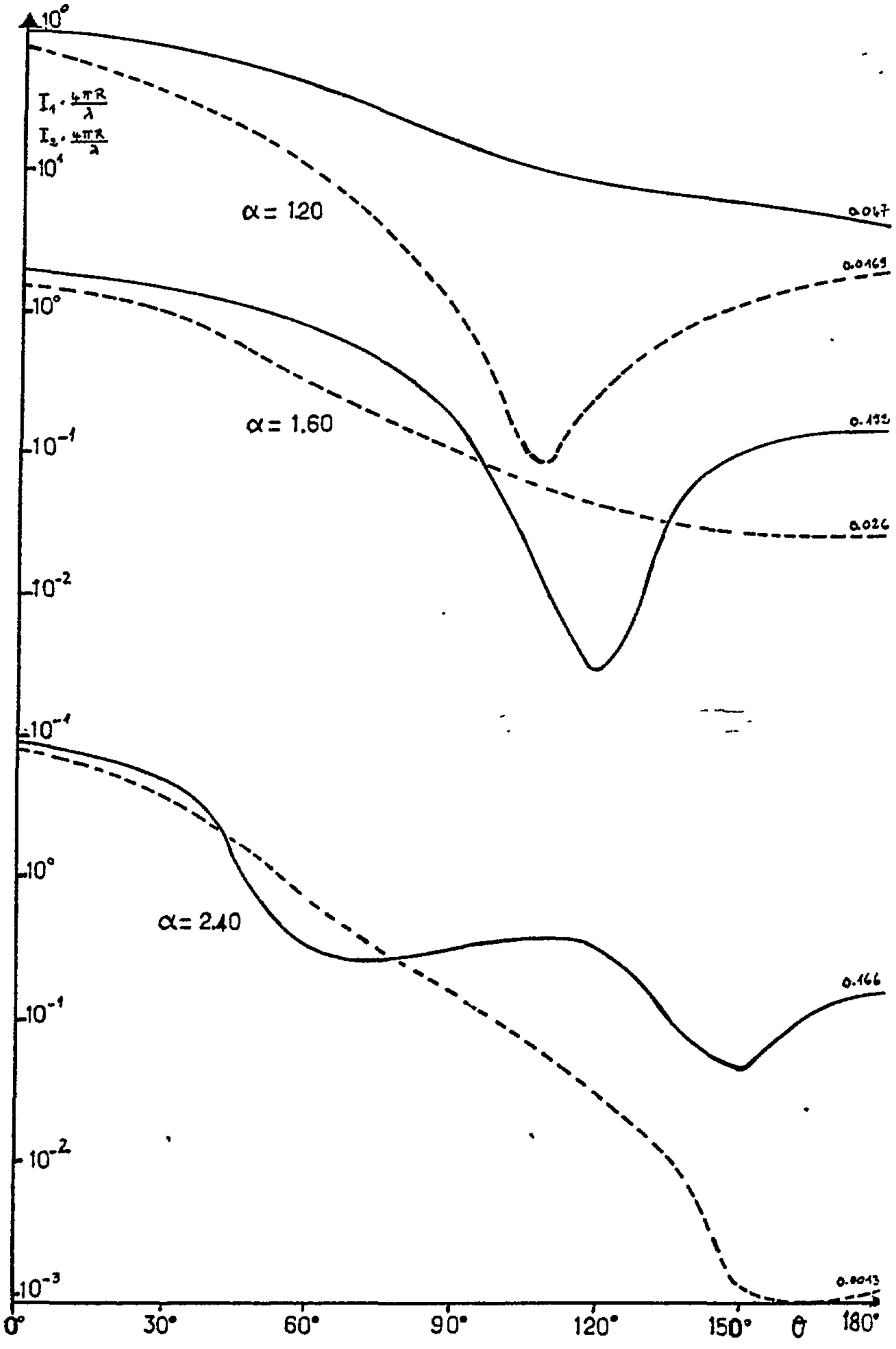

Fig. 8 - Angular Scattering by cylinder with m = 1.50

LICHENS AS BIOINDICATORS FOR ATMOSPHERIC POLLUTION BY CHLORINATED HYDROCARBONS

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ABSTRACT

Lichen samples from Southern France were analyzed for chlorinated hydrocarbons. The concentrations were in the same range as in industrial areas in Italy and Norway but higher than results reported from remote areas in Sweden and especially in the Antarctic. PCB concentrations were also compared with atmospheric concentrations in the same area. A concentration factor of $2\text{-}10^5$ for PCB between lichen and atmosphere is of the same order as that calculated for Antarctic samples. Lichens are suggested as suitable bioindicators for the study of atmospheric pollution by chlorinated hydrocarbons.

INTRODUCTION

Lichens are slow-growing plants with a large surface area and are thus prone to absorb pollutants from the atmosphere. These plants have been studied for their uptake of different kinds of compounds such as radionuclides (Liden and Gustafson, 1967; Mattsson, 1972; Mattsson, 1975; Persson, 1968; Persson, 1969; Persson, 1971; Holm and Persson, 1975; Miettinen and Hasanen, 1967), metals (Nygard and Margo, 1983; Pakarinen et al., 1983; Johnsen et al., 1983) and organic compounds (Bacci et al., 1986; Villeneuve et al., 1985; Carlberg et al., 1983) both in industrialized areas and in areas remote from anthropogenic influence. In a previous study (Villeneuve, 1986) concentrations of polychlorinated biphenyls (PCBs) in the atmosphere at a fixed station (Oceanographic Museum) located in Monaco on the Mediterranean coast of France were reported.

For this study, lichens were sampled in the mountains facing the Mediterranean Sea in the same area, close to Monaco, in order to compare the organochlorine content (insecticides in the DDT series, PCBs and toxaphene) with those reported in other parts of the world and to calculate concentration factors for PCBs between lichen and air, respectively.

MATERIALS AND METHODS

Samples of lichen (Usnea barbata) were collected in May 1986 at two sites on the mountain facing the Mediterranean Sea in the Monaco area; Peira Cava, a ski station at an altitude of 1200m, and Turini at an altitude of 1800m.

Lichen samples were freeze-dried and ground. The green parts of the plants were soxhlet extracted for 8 hours with hexane. The extracts were concentrated in a rotary evaporator to a volume of 10ml. The column chromatography procedure used for separation of PCBs, DDTs and Toxaphene was that described by Risebrough et al., (1983). The extracts were analyzed by gas chromatography and electron capture detection. An internal standard, 2,4,5-trichlorobiphenyl, was added to the samples for the estimation of the recovery throughout the analysis. The chlorinated hydrocarbons for standard solutions were supplied by Analabs Inc., USA. The hexane used as solvent was quartz glass distilled (Burdick and Jackson quality, Fluka, Switzerland). The Florisil for column chromatographic clean-up was also supplied by Analabs Inc., USA.

The gas chromatographic analyses were performed on a Hewlett Packard 5890A instrument equipped with a Ni-63 electron capture detector. The column was a 25m fused silica capillary, i.d. 0.3m, coated with a 0.33 um film of crosslinked SE-54. Nitrogen was used both as carrier gas and detector scavenger gas at flow rates of 1.7 and 30ml/min respectively. The oven temperature was kept at 70° for 2 minutes after injection and then raised with 3°/min to 260°. Chromatogrammes were recorded on a Spectraphysis 4200 integrator.

RESULTS AND DISCUSSION

The concentrations of chlorinated hydrocarbons in the lichen samples are given in Table 1. A general conclusion of these results is that the concentrations of the insecticides and toxaphene are higher at the highest altitude, while the individual compounds of PCBs are more irregularly distributed.

The insecticides, used mainly for agricultural purposes, may have been transported by winds from the agricultural areas in the Rhône Valley. Turini is more exposed to these air masses than Peira Cava. The adsorption of chlorinated compounds could be dose dependant as is the adsorption of these compounds by worms (Fowler et al., 1978), fish (Veith et al., 1979) and mussels (Langston, 1978). In Table 2 the concentrations obtained in different parts of the world are given as reported by different authors. It can be noted that the concentrations levels are of the same order of magnitude in Italy, Norway and France, where lichen samples were collected in industrialized areas, when compared to results reported from northern Sweden and especially the Antarctic, where the levels are significantly lower, the only exception being PCBs in the Swedish samples.

The concentrations measured in lichens reflect an adorption which is integrated over a long time period and should be correlated with the mean atmospheric burden over the period. Based on an earlier study of the atmospheric concentration of PCB in Monaco (Villeneuve, 1986) and on the fact that the distribution of PCBs is not altitude-dependant considering such a variation of 1000m, an estimate of the concentration factor between lichen and atmosphere was made. The mean atmospheric concentration of Aroclor 1254 over two and a half years in 1975-1977 was 0.34 ng/m^3 (Villeneuve, 1986) or 0.27 pg/g moist air at the mean temperature of 12°C. Compared to the corresponding concentration in the lichen samples this gives a concentration factor of $3\text{-}10^5$ for the Turini area and $1\text{-}10^5$ in Peira Cava. A concentration factor in the same range, $1\text{-}10^5$ can be calculated from Antartic studies on PCBs in the atmosphere (Tanabe, 1983) and in lichens (Bacci *et al.*, 1986). This indicates that lichens are potentially suitable as bioindicators in studies of atmospheric pollution by organochlorine compounds. In fact, these factors are in the same range as the corresponding factor for mussels as compared to seawater which is $2\text{-}10^5$ (Marchand *et al.*, 1976; Elder, 1976).

Although nothing is known about the kinetics of adsorption of organochlorine compounds by lichens, it is likely to be a fairly rapid process. For a better understanding of the distribution between air and lichens, studies should be conducted on the kinetics of adsorption as well as desorption of the organochlorine pollutants.

CONCLUSIONS

The results obtained show that the concentrations of chlorinated hydrocarbons in lichen collected in southern France are of the same order of magnitude as in industrial areas in Italy and Norway, and higher than those reported from remote areas in Sweden and especially in the Antarctic.

Accumulation factors calculated from lichen and atmospheric concentrations of PCBs are in the same range in Southern France and in the Antarctic. They are also in the same range as for mussels in relation to seawater. Lichen appear to be a valuable potential bioindicator for studies of the atmospheric pollution by chlorinated hydrocarbons.

ACKNOWLEDGEMENT

The International Laboratory of Marine Radioactivity operates under an agreement between the International Atomic Energy Agency and the Government of the Principality of Monaco. The Laboratory gratefully acknowledges this support in the conduct of the work reported here. We thank also Drs. A. Walton, L.D. Mee and S.W. Fowler for their useful comments on the manuscript.

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Table 1

Concentrations (in ng/g dry weight) of chlorinated hydrocarbons in lichen (Usnea barbata) collected in southern France.

	TURINI 1800m	PEIRA-CAVA 1200
HCB	7.1	3.9
Lindane	130	24
a-HCH	126	28
d-HCH	9.4	2.1
pp'-DDE	13.3	2.5
pp'-DDD	1.4	0.7
pp'-DDT	12.2	8.7
op-DDD	4.4	3.8
op-DDT	4	4.7
Aroclor 1248	19	25
Aroclor 1254	87	28
Toxaphene	190	130
Polychlorobiphenyl congeners:		
3,3'	6.3	11
2,2',3,3'	0.4	0.3
2,2',5,5'	3.6	2.2
2,2',3',4,5	0.3	0.4
2.2',4,5,5'	3	4.5
2,2',3,4,4',5'	13.3	17.7
2,2',3,3',6,6'	0.5	0.5
2,2',4,4',5,5'	1.9	2

Table 2

Comparison of chlorinated hydrocarbon concentrations (in ng/g dry weight) in lichens collected in different regions.

Lichen species	Location	Year	HCB	a-HCH	Lindane	pp'-DDE	pp'-DDT	Aroclor 1248	Aroclor 1254	Reference
Cladonia alpestris	Sweden	1975	0.26	3.3	1.24	0.18	1.75	18.9	15.3	(13)
Lobaria pulmonaria Xanthoria parietina	Italy	1984	1.5	27	10	8.5	12.5	n.d.	n.d	(23)
Hypogymnia physodes	Norway	1979	5.8	54	35.4	2.6	10.3	52		(14)
Usnes sulphurea	Antartica	1985	0.72	0.34	0.69	0.25	0.38	6.7		(12)
Usnea barbata	France	1986	5.5	77	78	7.9	10.5	22	57	This study

REMOTE SENSING OF AIRBORNE POLLUTION OVER THE MEDITERRANEAN SEA

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The direct determination of the air-sea surface flux of pollutants and the elaboration of numeric simulation models requires up-to-date observations of the concentration of the atmospheric pollutants and of all meteorological inputs above the sea surface.

The diffusion of atmospheric pollutants has been studied over the last few years mostly on land and particularly in urban areas (Pasquill and Smith, 1983), whereas very little attention has been paid to the open sea where the thermodynamic is very different from above land; the exchange of large water masses plays a dominant role.

Palumbo and Mazzarella (1985) have recently observed that the annual variation of the evaporation-precipitation along the Mediterranean Basin is equal to the annual cycle of marine flow crossing the Straits of Gibraltar so that the sea-air mass exchange cannot be ignored.

The above does not allow the extrapolation to the open sea, even along the coast line, of the results obtained on the land and concerning the pollutant's flux from the air to the sea. Similarly the introduction of thermodymamic inputs observed on the land for modelling atmospheric diffusion above the sea provides simulated fictitious results; this is because the reliability of computed data is related to the significance level of the environmental inputs, in this case very low and because of the unavailability of data observed above the sea.

It thus appears to be necessary to propose a monitoring programme of the physical and chemical data concerning airborne pollution of the open sea by means of remote sensing systems in addition to routine observations.

DIAL (DIfferential Absorption Lidar*) remote sensing systems were investigated in depth and developed during the last decade (Van de Hulst, 1957; Asano *et al*., 1975; Byer *et al*., 1973; Collins *et al*., 1976; Schwemmerg *et al*., 1982; Bocchiola *et al*., 1983; Draghi *et al*., 1983).

The atmospheric distribution and concentration of many gases can be determined by a mobile DIAL system with emissions in the U.V.-Visible range, primarily intended for SO_2 monitoring. Its application can be extended to other gases (NO_2, Cl_2, I_s, H_6O etc.) and to atmospheric parameters (Lebow *et al*., 1982).

With emission in IR (continuously tunable from 1.5 to 4 μm) many pollutant gases (CO, CO_2, CH_4) and some other carbons (HCl, H_2S, H_sS, NH_3 etc. can be probed (Baumgartner *et al*., 1978; Federiksson *et al*., Rothe *et al*., 1983).

DIAL method is based on the measurement of the different atmospheric absorption at two wavelengths on and off corresponding to the peak and to the trough of the absorption spectrum of the gases.

There are two ways in which a DIAL can be used: the first utilizes the distributed scattering of molecules and aerosols (Fig. 1a), while the other (Fig. 1b) utilizes the scattering of topographic targets (hills, buildings etc.) as retroreflectors. The first method provides range resolution of concentration measurements, the second gives only the average concentration in the optical path between the LIDAR and the target. The Italian National Power Organization (ENEL) has committed to the CISE laboratory two mobile DIAL systems for real time pollutants concentration measurements.

The first system with emissions in the U.V/ visible and near IR uses Mie and Raileigh scattering as retroreflector (BYER *et al*., 1973). It has fifteen metres of spatial resolution. The second one, with emissions in IR, uses topographic targets as retroreflectors. In both systems a 20 Hz Nd-YAG laser with 700mj of energy in 20ns was utilized.

The system which experimented over a path of a few kilometres can be extended to larger paths. Techniques based on fluorescence can be operated for the detection of heavy metals suspended in the air. The DIAL mobile system may be installed in an aeroplane for large-scale investigations above the whole Mediterranean area.

The cost of a complete DIAL system is estimated at around US$ 500,000, about three times higher than a conventional monitoring station.

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* LIDAR: **LI**ght **D**etection **A**nd **R**anging

The main advantages of remote sensing compared to direct physical and chemical observation above the sea surface are:

(a) the determination of the atmospheric concentration of Hg which is difficult to observe by means of the land monitoring station;

(b) the possibility of cruises along the main trajectories of air flows and during types of weather typical of the Mediterranean Basin;

(c) the acquisition of physical information that allows water flux sea surface-air and vice-versa to be estimated;

(d) the vertical profiles of pollutants concentration and of meteorological data;

(e) the U.V.-visible DIAL system can provide spatial resolution since it can rotate over a solid angle of 2 with high precision.

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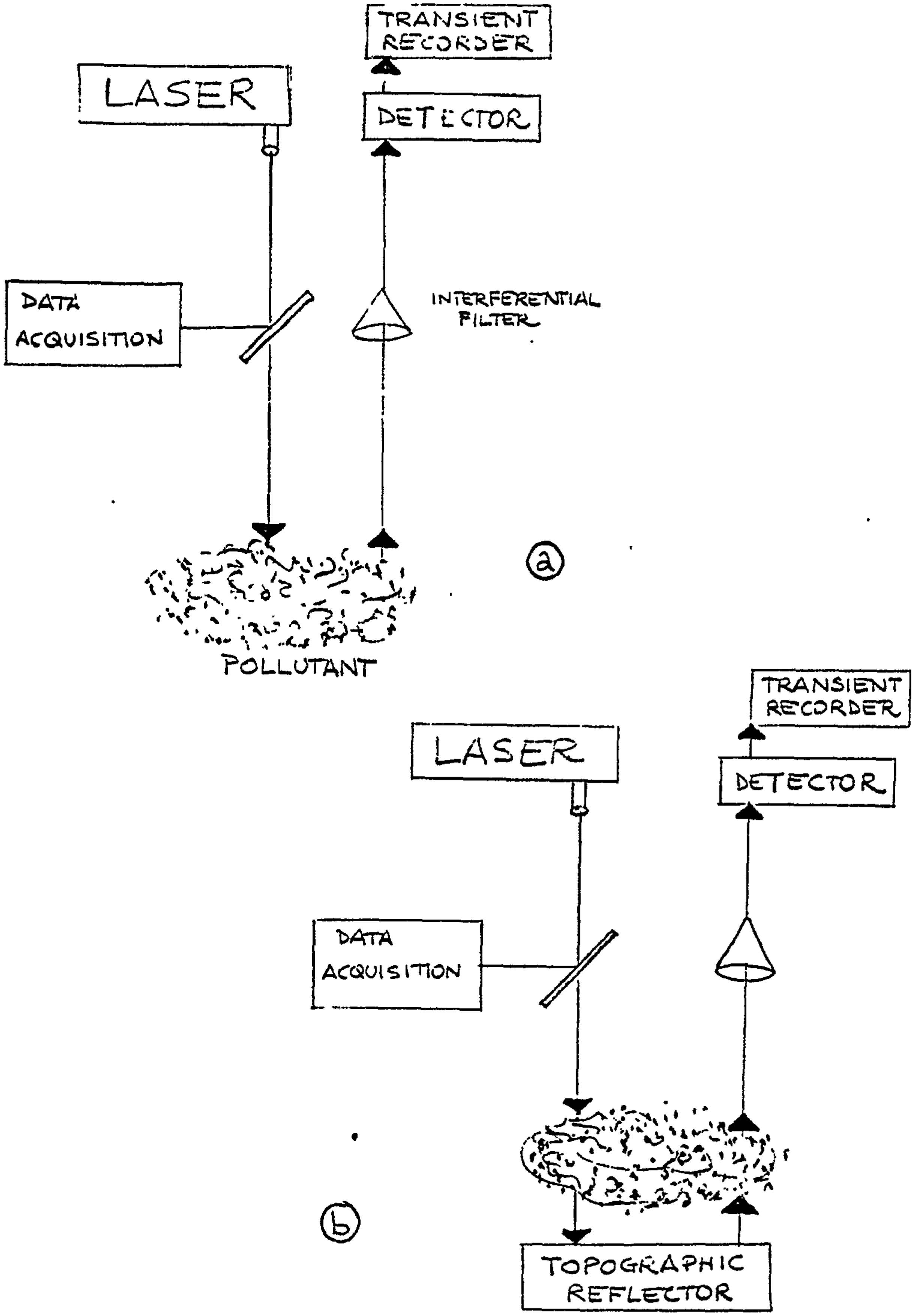

Figs. 1a and 1b - Two different ways of using DIAL method

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Publié et imprimé par:

Plan d'action pour la Méditerranée
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