UNITED NATIONS ENVIRONMENT PROGRAMME
MEDITERRANEAN ACTION PLAN
MEDPOL

ATMOSPHERIC TRANSPORT AND DEPOSITION OF POLLUTANTS INTO THE MEDITERRANEAN SEA

Final reports on research projects

WORLD METEOROLOGICAL ORGANIZATION

MAP Technical Reports Series No. 133

UNEP/MAP
Athens, 2001

P.O. Box 18019, Athens, Greece.

ISBN 92-807-2070-8

For bibliographic purposes this volume may be cited as:

UNEP/MAP/MEDPOL: Atmospheric Transport and Deposition of Pollutants into the Mediterranean Sea: Final Reports on Research Projects. MAP Technical Reports Series No. 133, UNEP/MAP, Athens, 2001.

The thematic structure of the MAP Technical Series is as follows:

- Curbing Pollution
- Safeguarding Natural and Cultural Resources
- Managing Coastal Areas
- Integrating the Environment and Development

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 (BP), Priority Actions Programme (PAP), Specially Protected Areas (SPA), Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea (REMPEC), Environment Remote Sensing Centre (ERS), and Cleaner Production Centre (CP).

ATMOSPHERIC TRANSPORT AND DEPOSITION OF POLLUTANTS INTO THE MEDITERRANEAN SEA

FOREWORD

The MED POL Programme, initially designated as the environmental assessment component of the Mediterranean Action plan, has been operational since 1975. Its first phase (MED POL-Phase I) was implemented from 1975 to 1980 and it comprised seven basic baseline studies covering the major marine pollution problems in the Mediterranean including the study of pollutant-transfer processes at river/sea and air/sea interfaces.

An important role in initiating airborne pollution studies in the Mediterranean belonged to the report on "Atmospheric Transport of Contaminants into the Mediterranean Sea" prepared in 1985 by the WMO-led GESAMP* Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans. The report reviewed the knowledge on the levels of atmospheric contaminants over the Mediterranean, emissions, climatology pertinent to atmospheric transport and deposition. Despite a limited database existing at that time for the region it was possible to conclude that the levels of atmospheric contamination over the Mediterranean were comparable to those over other European regional seas. Since that time all the MED POL activities related to the airborne pollution have been co-ordinated by the World Meteorological Oragnization (WMO).

Within MED POL-Phase II (1981-1996) the first MED POL airborne pollution monitoring and modelling programme was prepared in November 1987 at the WMO/UNEP Workshop on Airborne Pollution of the Mediterranean Sea held in Belgrade (MAP TRS No. 31). The major goals of the programme were identified as follows: to evaluate the importance of the atmospheric transport and deposition of land-based contaminants to coastal and open Mediterranean waters, to asses the airborne contamination levels of potentially harmful substances, to identify sources and source areas for these atmospheric contaminants, and to develop predictive models for assessing airborne pollution load. For routine monitoring, the programme recommended by the workshop included measurements of the following parameters: in precipitation - pH, conductivity, SO_4, NH_4, NO_3, Na, K, Mg, Ca, Cd, Pb, Cu and Zn; in air - Cd, Pb and total particulate matter, and surface ozone. The second WMO/UNEP Workshop on Airborne Pollution of the Mediterranean Sea held in Monaco in April 1991 (MAP TRS No. 64) recommended that the priority measurement parameters should also include nutrients (N and P compounds) which may cause eutrophication.

The Programme for the Assessment and Control of Pollution in the Mediterranean Region (MED POL-Phase III) was adopted by the Extraordinary Meeting of the Contracting Parties to the Barcelona Convention held in Montpellier in July 1996. One of the specific objectives of this programme is "to identify the sources, assess the present levels and keep under periodic review the trends in the load of contaminants reaching the Mediterranean Sea from marine and land-based sources including point and non-point sources and airborne contaminants". The main recommendations on the MED POL-Phase III activities related to monitoring, modelling, assessment and control of pollution of the Mediterranean Sea through the atmosphere were developed at the WMO/UNEP Expert Meeting on airborne Pollution of the Mediterranean Sea held in Paris in October-November 1994 (ENV/MED POL/ AP/2). The objectives of these activities were identified as follows: to assess airborne pollution of the Mediterranean Sea and its sub-regions; to identify long-distance area sources of airborne pollution; to provide scientific rational for formulation of regional measures to protect the sea against pollution through the atmosphere; to monitor the trends of airborne pollution levels and inputs for evaluating the compliance with the adopted control measures; to ensure the required quality of monitoring data, and to promote the increased involvement of national institutions in the programme through direct assistance, training and advisory expert missions. An amended measurement programme was also developed as well as requirements for quality assurance and quality control and for further research.

---

[*] GESAMP = IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

During MED POL-Phase II and the beginning of MED POL-Phase III more than 30 national MED POL research projects and studies were supported from the Mediterranean Trust Fund. The results of these studies and assessments were published in the Mediterranean Action Plan Technical Reports Series:

- "Meteorological and climatological data from surface and upper measurements for the assessment of atmospheric transport of pollutants in the Mediterranean Basin (MAP TRS No. 30),
- "Assessment of airborne pollution of the Mediterranean Sea by sulphur and nitrogen compounds and heavy metals" (MAP TRS No. 85),
- "The input of anthropogenic airborne nitrogen to the Mediterranean Sea through its watershed" (MAP TRS No. 118),
- "Atmospheric input of mercury to the Mediterranean Sea" (MAP TRS No. 122),
- "MED POL manual on sampling and analysis of aerosols and precipitation for major ions and trace elements" (MAP TRS No. 123) and
- "Atmospheric input of persistent organic pollutants to the Mediterranean Sea" (MAP TRS No. 130).

In the result of measurements, modelling and assessments of the atmospheric transport and deposition of pollutants into the Mediterranean Sea and its sub-regions it was shown that the atmospheric inputs of nutrients, some heavy metals and organic pollutants are equal or even exceed the inputs of these pollutants through the rivers and that finding is of great importance not only from the scientific point of view but primarily for the development of pollution control measures. The importance of the atmospheric input of pollutants into the Mediterranean Sea and its effects on the marine environment and biogeochemistry was also stressed by the MED POL Consultation Meeting on the Identification of Mediterranean Environmental and Pollution Emerging Issues held in Rome, Italy in May-June 2000 which recognised the atmospheric deposition as one of the six presently emerging environmental issues in the Mediterranean (UNEP(OCA)/MED WG.168/3).

The present publication contains five papers summarising the results of the research projects implemented in some Mediterranean countries in 1999-2000 and supported from the Mediterranean Trust Fund through WMO. They are devoted to the measurements and assessments of atmospheric fluxes of some heavy metals, major ions, nutrients and the Sahara dust to the western and eastern parts of the Mediterranean and the Adriatic Sea.

TABLE OF CONTENTS

WET AND DRY DEPOSITION FLUXES OF MAJOR IONS IN THE EASTERN MEDITERRANEAN, BLACK SEA AND CENTRAL ANATOLIA.

Gurdal Tuncel

Middle East Technical University, Dept. Environmental Engineering, 06531 Ankara, Turkey

ABSTRACT

Concentrations of trace elements and major ions were measured in daily precipitation samples at permanent rural stations located at the Mediterranean and Black Sea coast of Turkey and at Central Anatolia, for 2, 6 and 6 years, respectively. The most important outcome of this study is the detection of high concentrations of pollution-derived elements and ions at different parts of Turkey. Since these high concentrations are measured at stations separated by at least 400 km from each other, it should be a regional phenomenon. Concentrations of trace elements and ions measured in this study are compared with corresponding concentrations at more than 80 EMEP stations. Concentrations of anthropogenic ions such as SO_4^{2-}, NO_3^- and NH_4^+ are among the highest reported in whole Europe. Same conclusion is also reached when concentrations of anthropogenic trace elements are compared with literature data. Unlike the concentrations of other anthropogenic ions, H^+ ion concentration at Turkish stations is among the lowest values reported in Europe, suggesting an extensive neutralization of acidity in rainwater, either at Anatolia or during transport. Neutralization is more extensive at the central Anatolia station than at the coastal stations. Primary neutralizing agents in precipitation are $CaCO_3$ and NH_3, but Na and Mg also contribute to the neutralization of acidity. Neutralization is more complete during summer due to high abundance of soil particles containing $CaCO_3$ in the atmosphere. An important characteristic of chemical composition of rainwater at Anatolia is episodic and seasonal variations in the concentrations of elements and ions. Short-term variations in the concentrations of crustal and marine elements are due to short-term, wind-induced variations in sea salt and soil particle generation. The episodic variations in the concentrations of anthropogenic elements, on the other hand, are due to variations in the upper atmospheric air-mass transport. Unlike concentrations, wet deposition fluxes of measured elements and ions at Turkish stations are not high compared to corresponding fluxes reported for various regions in Europe due to small annual rainfall in the region.

1. INTRODUCTION

Chemical compositions of aerosols and precipitation in the Mediterranean region and factors affecting these compositions are fairly well established through studies performed since 1980's, particularly in the west part of the basin. There are two main sources that strongly affect the composition of atmospheric particles and precipitation in the Mediterranean area. One of these is the eolian dust transported from North Africa (Guerzoni et al., 1999; Kubilay and Saydam, 1995) and the other one is the pollution aerosol transported from Europe (Dulac et al., 1987; Bergametti et al., 1989; Gullu et al., 1998). Compositions of aerosol and the precipitation in the Mediterranean basin are determined by relative abundances of these two components (Chester et al., 1993; Guerzoni et al., 1999). Composition is modified to a certain extent by contributions from other sources, such as biogenic emissions (Mihalopoulos et al., 1997; Simo and Grimalt; 1998), sea salt generation (Piazzola and Despiau, 1997; Gullu et al., 1998; Hacisalihoglu et al., 1992) and local anthropogenic emissions (Gullu et al., 1998).

Since the Mediterranean is a semi-enclosed sea, deposition of both anthropogenic and crustal components in aerosol by dry (Dulac et al., 1998; Kuloglu, 1998) and wet (Hernandez et al., 1996; Herut et al., 1999; 2000; Al-Momani et al., 1995; 1998) scavenging mechanisms strongly affect chemistry, biochemistry and sedimentation in the aquatic environment (Guerzioni et al., 1999; Guieu et al., 1997; Davies and Buart Menard, 1990; Quetel et al., 1993).

Although transport of pollution aerosol from industrialized European countries is well documented, rain water in the Mediterranean region is not acidic, because the most important characteristic of precipitation in the region is extensive neutralization of acidity, particularly by $CaCO_3$, which originates from calcareous soil in North Africa, Middle East and along the coasts of the Mediterranean Sea (Loye-Pilot et al., 1986; LeBalloch and Guerzioni, 1995; Camerara and Catalan, 1996; Al-Momani et al., 1998; El-Agha, 2000; Herut et al., 2000).

Most of the data generated in the Mediterranean region are confined to the western part of the basin. However, the data base for the Eastern Mediterranean have significantly expanded in recent years for both aerosols (Kubilay and Saydam, 1995; Luria et al., 1996; Kubilay et al., 2000; Gullu et al., 1998; 2000; Mihalopoulos et al., 1997; Ganor and Mamane, 1982; Ganor et al., 1998) and precipitation (Glavas, 1988; Herut et al., 1999; 2000; Al Momani et al., 1995; 1998). Improvements in the existing database can allow for identification of similarities and differences in both levels of chemicals and their transport to various sub-basins in the region, such as Western Mediterranean, Eastern Mediterranean, Middle East, Black Sea, Anatolia and North Africa. Although the existing database is adequate for a comparison between Eastern and Western Mediterranean, data on the chemical composition of aerosol and precipitation is scarce at North Africa, Black Sea and the Anatolian plateau.

In this study chemical composition of precipitation and wet deposition fluxes of major ions and trace elements at three stations located on the Mediterranean coast, Black Sea coast and central Anatolia will be discussed.

2. EXPERIMENTAL

Daily, wet-only rain samples were collected at three permanent stations located on the Mediterranean and Black Sea coasts of Turkey and at the Central Anatolia for different duration between 1992 and 1998.

The station at the Mediterranean coast is located at a rural area approximately 20 km to the west of the city of Antalya (36°80'N and 31°00'E). The station is designated MED POL station for Turkey and operated by the Middle East Technical University and the Ministry of Forestry. It is on the coast and approximately 20 m from sea surface.

The Central Anatolia station is located approximately 50 km to the North of the city of Ankara (40°10'N and 33°10'E). The station is the only EMEP station in Turkey and operated by the Ministry of Health. The Black Sea station is located approximately 20 km to the east of the town of Amasra (41°47'N and 32°29'E), three kilometers inland from the coast line and operated in coordination between the Middle East Technical University and the Ministry of Forestry.

Standard EMEP procedures (EMEP, 1996) are used for sampling and analysis of precipitation at the Central Anatolia station. At the Black Sea and Mediterranean stations the samples are collected and analyzed using procedures recommended for the MED POL program. Sampling and analysis protocols used at the three stations were fairly similar, because siting, sampling and analysis procedures used by both the EMEP and MED POL programs are not significantly different.

Detailed procedures used in collection of samples and subsequent analysis are described elsewhere (Tuncer, 2000; Al-Momani et al., 1998; El-Agha, 2000). Only a brief summary of instrumentation and procedures will be given in this manuscript.

At the central Anatolia station, rain samples were collected between March 1993 and June 1998 at a permanent station in a rural area, at an altitude of approximately 1000 m. Sampling was continuous and rarely interrupted due to instrument malfunction. Since the station is an EMEP station (TR0001), site selection criteria, sampling, analysis and data quality control protocols are the same as that employed in the EMEP network (EMEP, 1996).

Samples were collected using a Walter Eigenbrodt Model NSA181 wet-only rain sampler. Precipitation amount was also determined using a recording rain gauge. Collected samples were analyzed for Conductivity and H^+, SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, Mg^{2+}, Ca^{2+} and K^+ ions in the Ministry of Health laboratories located at the city of Ankara, which is approximately 50 km from the station.

Conductivity is measured using a WTW, model LF 96-A conductivity meter equipped with WTW Tetracon 96 electrode. The pH of the samples was measured using a WTW, model 523 pH meter, equipped with a Sentix 96 glass electrode. Sulfate, NO_3^- and Cl^- ions were measured using a Dionex, Model DX-100 ion chromatograph equipped with HPIC AS3 separation and AMMS-II suppressor columns. Ammonium ion was measured by the Indophenol-blue method (EMEP, 1996) and cations were measured by a Perkin Elmer 1100B atomic absorption spectrophotometer.

Completely identical sampling and analysis protocols are used at the Black Sea and Mediterranean stations. At the Mediterranean, samples were collected in a permanent station, which is located 20 km to the West of the town of Antalya. Sampling was started in January 1992 and has continued without interruption since then. Precipitation samples for trace element analysis were collected using a Karlbe automatic wet-only sampler. Sampling bottles were acidified by adding 10 mL of 10% subboiled HNO_3 before they were installed in the sampler. The precipitation samples for ion analysis were collected using a "modified" ANDERSEN, acid precipitation sampler. In both samplers, rainwater was first collected by a high-density polyethylene funnel, which has 40.0 cm internal diameter, then passed through a filtration unit containing 47 mm diameter and 0.45 µm pore size membrane filter and finally collected in a sampling bottle with 1 L capacity. The funnel, filtration unit and sampling bottle are connected by high-density polyethylene tubing. Filtration units and polyethylene tubing were replaced with clean fresh ones after the collection of each rain sample. The used tubing was discarded, and filtration units were sent to the central laboratory for cleaning. At the Laboratory all sample processing, such as volume and pH measurement, digestion of filters containing insoluble fractions of samples by HNO_3 – HF mixture are carried out in a Class 100 clean area.

Since rain samples are filtered during collection, soluble and insoluble fractions of measured parameters are determined separately. Precipitation samples were analyzed for Na, Ca, K, Mg, Al, Pb, Cu, Cd, Ni, V, Cr, Fe, Zn, SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+ by atomic absorption spectrometry (AAS) and ion chromatography (IC) using a Perkin Elmer, HGA 700 graphite furnace atomizer, coupled to a Perkin Elmer 1100B atomic absorption spectrophotometer. Ions in rainwater were measured using a Varian 2010 IC equipped with a Vydac 302 anion exchange column and a JASCO model 875, UV-VIS detector.

Field and laboratory blanks were routinely analyzed along with the collected samples to monitor sample contamination (one field blank and several laboratory blanks were prepared and analyzed every month). Field blanks were generated by pouring 250 mL of double-distilled, deionized water through the sampling funnel in the sampler. The water was allowed to pass through the filter and was collected in the sample bottle which was preacidified with 10 mL of 10% subboiled HNO_3 as in the samples. The field blanks for ion analysis were prepared in the same way, except water was collected in a regular sampling bottle that was not acidified. Laboratory blanks consisted of aliquots of water and subboiled HNO_3 used in the analytical system.

The water used in analysis was first double distilled and then deionized using a Bernstead Nanopure 550 deionization system. The HNO_3 used in the acidification of sample bottles and the digestion of filters was prepared by subboiling distillation of analytical grade acid. The HF used in the digestion of filters was commercial suprapure grade (Merc).

The accuracy of analytical measurements was checked by routine analysis of National Institute of Standards (NIST) standard reference materials SRM 1646 (estuarine sediment), SRM 2704 (Buffolo river sediment) and SRM 2694 (simulated rain water). Methods of standard additions were used in all AAS analysis.

The ratio of total anions to that of total cations ($\sum$anions/$\sum$cations) is an indicator of the completeness of the measured parameters. If all important parameters are included in measurements and if measurements are done correctly, then this ratio should be equal to unity. Deviation from unity indicates that either some of the parameters were measured incorrectly or some important anion or cation is not included in the measurement protocol.

The average ∑anion-to-∑cation ratio was approximately 0.8 at the Mediterranean and Black Sea samples and 0.65 in samples collected at the Central Anatolia station, owing to exclusion of HCO_3^- ion from measurements. At pH values around 5, which is the average pH measured at the Mediterranean and Black Sea stations, the bicarbonate ion accounts for approximately 20% of the ionic mass [*Losno et al*., 1991; *Khwaja and Husain*, 1990. Lower anion-to-cation ratio at the Central Anatolia is due to higher pH of rainwater. Expected HCO_3^- ion concentration was calculated using the measured concentrations of acidic and basic species in rainwater samples. After correcting for HCO_3^- ion concentration, the anion-to-cation ratio increased from 0.8 to 0.95, confirming that most of the important anions and cations were included in measurements.

Size separated aerosol samples, which were used to calculate dry deposition fluxes of elements and ions were collected only at the Mediterranean station using a Sierra Instruments High Volume Cascade Impactor Series 230 attached to General Metal Works Model GMWL 2000 High Volume Air Sampler. The operating flow-rate was kept constant at 25 SCFM (0.84 m^3 min^{-1}), and the total volume of sampled air was measured with a high-volume dry-gasmeter. Particles were separated into seven size groups with 50% cut-points of >10.2 μm, 4.2 μm, 2.1 μm, 1.4 μm, 0.73 μm, 0.41 μm, and <0.41 μm. Whatman-41 cellulose substrates placed on each stage were used as collecting media. Particles smaller than the cut-off diameter of the last stage (0.41 μm) were collected on a Whatman-41 cellulose back-up filter.

Collected samples were sent to Ankara at every 15 days and analyzed for trace elements using AAS and instrumental neutron activation analysis (INAA) and major ions by IC (Kuloglu, 1998).

Backward trajectories that are used in trajectory statistics were calculated by the General Directorate of Meteorology, using the ECMWF isentropic 3D trajectory model.

3. RESULTS AND DISCUSSION

3.1 Average concentrations of ions and elements

Volume weighted average concentrations of measured ions and elements in the three stations are given in Table 1. Trace elements are measured at the Mediterranean and Black Sea stations, but not in the Central Anatolia station. Major ions are measured at all stations.

Concentrations of sea salt elements such as Cl and Na are the highest in Mediterranean coast and lowest in the central Anatolia. Concentrations of sea salt elements depend on the relative distances of stations to the coast. Their concentrations are the highest on the Mediterranean coast, where the station is located at the coast. Concentrations are lower on the Black Sea coast, because the station is approximately 3 kms from the coastline, which is long enough distance for the coarse sea salt particles to scavenge out by dry deposition. The Central Anatolia station is approximately 400 km away from the nearest coast. Consequently, elements, which have marine source at the coastal stations, originate from crustal material at the central Anatolia.

Concentrations of crustal ions, such as Ca, K are comparable at the Black Sea and Mediterranean, but significantly smaller at the central Anatolia. Concentrations of crustal ions depend on the composition of soil around stations and their relative concentrations at three stations indicate their different abundance in the soils at different parts of the country.

Concentrations of the H^+ ion are comparable at the Mediterranean and Black Sea. However, H^+ ion concentration measured at the central Anatolia is significantly lower than concentrations measured at the coasts, indicating more extensive neutralization of acidity at the central Anatolia as will be discussed later.

Concentrations of SO_4^{2-} and NO_3^- are the highest at the Mediterranean coast and comparable at the Black Sea coast and central Anatolia. Ammonium concentrations on the other hand are fairly similar in all three stations.

Concentrations of anthropogenic elements Zn, Ni, Cr, Pb and Cd are not dramatically different at the Black Sea and Mediterranean coasts. Zinc and Ni concentrations are slightly higher at the Mediterranean coast, whereas concentrations of Cr, Pb and Cd are slightly higher at the Black Sea coast.

The only anthropogenic element that shows a significant difference between the two coasts is Cu. Copper concentration is approximately a factor of 20 higher on the Black Sea coast, suggesting an important Cu source at the Black Sea. The most likely source of Cu in the Black Sea region is the Cu smelter at the city of Samsun, which is located approximately 300 km to the east of the sampling point. However, general similarity in the concentrations of most pollution-derived elements at two stations, which are separated by approximately 700 km indicates that their sources are regional.

Ionic composition of precipitation shows substantial differences between different parts of the country. The contribution of ions to the total inorganic mass in precipitation at the three stations are given in Figure 1. Most of the inorganic mass consists of sea salt ions, namely Na and Cl at the Mediterranean station. These two ions account for approximately 60% of the inorganic mass in precipitation. Contribution of sea salt ions to the total inorganic mass in the Black Sea precipitation is 9%.

Crustal component dominate the inorganic mass at the Black Sea coast. Magnesium, K and Ca accounts for approximately 53% of the mass. Contribution of crustal ions to the total inorganic mass at the Mediterranean and Central Anatolia stations are 10% and 23%, respectively.

Percentages of marine and crustal contribution to inorganic mass given above are only rough estimates, because Na and Cl are assumed to be purely marine, Ca, K and Mg are assumed to be purely crustal to calculate marine and crustal contribution to inorganic mass at each region. However, significant fractions of Mg, K and even Ca have sea salt origin at the Mediterranean station and most of Na in the Central Anatolia originates from crustal material rather than sea salt.

At the central Anatolia, anthropogenic ions SO_4^{2-}, NO_3^- and NH_4^+ dominate the inorganic mass, accounting for 66% of the ionic mass. The contributions of anthropogenic ions to inorganic mass at the Mediterranean and Black Sea stations are 28% and 31%, respectively.

3.2 Comparison with literature

Although comparison of ionic and elemental composition of rainwater in different parts of Turkey provides information on the similarities and differences in the composition of precipitation in the Black Sea, Mediterranean and central parts of the country, such a comparison does not give information on the pollution level in the region. Comparison of measured concentrations of elements and ions at the three stations with levels reported for polluted and unpolluted regions at Europe can be used as a preliminary indication for the magnitude of pollution transport to the Anatolia. Annual volume weighted average concentrations of ions measured at the Black Sea, Mediterranean coasts and at the central Anatolia are compared with the corresponding data reported for 83 EMEP stations in Europe for the years 1996, 1997 and 1998. The results are depicted in Figure 2a. The EMEP data were used for comparison because, (1) all stations in the network have the same site selection, sampling and analytical protocols which are fairly similar to the stations used in this study, (2) the network of stations covers the Europe fairly well and hence the ranges used in comparison are representative for both polluted and unpolluted regions in the continent and (3) the data were readily accessible through internet.

Concentrations of marine elements and ions such as Na and Cl^- measured in the Mediterranean coast are among the highest reported in Europe. High concentrations of marine elements at the Mediterranean station are expected, because the station is influenced by the sea and the sea salt generated via bubble bursting, particularly during frontal storms, is subsequently washed out by rain. The levels of the same elements measured at the central Anatolia and Black Sea are comparable with the concentrations reported in other parts of Europe, because these two stations are not in the immediate vicinity of the sea.

Concentrations of crustal elements Ca, K and Mg measured at the Mediterranean and Black Sea coasts are very high compared to values reported for EMEP network. Concentrations of these elements reflect composition of both the soil at the receptor site and soil transported to the region. Contribution of Saharan dust transported to the Mediterranean to Ca and other base-cation levels at the southern Europe had been reported (Semb et al., 1995). However, soil in most parts of Turkey is calcareous and contains high concentrations of Ca, K and Mg. Consequently, high concentrations of these ions in our samples do not necessarily imply transport from North Africa.

Concentrations of pollution-derived elements and ions at the three stations in Turkey are expected to be lower than their concentrations at European sites, which are significantly closer to the Western Europe where emissions are high due to extensive industrialization and to Eastern European countries where emissions are high due to lack of emission control. However, comparison of SO_4^{2-}, NO_3^- and NH_4^+ concentrations measured at the Black Sea, Mediterranean and Central Anatolia stations with EMEP data reveals unexpectedly high concentrations of these pollution derived ions at all three sites in Turkey.

Concentrations of nss-SO_4^{2-} and NH_4^+ measured in Black Sea, Mediterranean and central Anatolia precipitations are among the highest reported in whole Europe, indicating that the eastern Mediterranean and Black Sea regions are under strong influence of pollution transport. Nitrate concentration at the Mediterranean station is also among the highest reported values in EMEP network, but concentrations measured at central Anatolia and Black Sea sites are lower and comparable with the values reported from EMEP stations.

Similar conclusions can be reached when anthropogenic trace elements measured at our stations are compared with data reported in literature. Since trace elements in precipitation are not included in the EMEP measurement protocol, trace element data generated in this study are compared with data reported for various remote and rural sites. Data used in the comparison are from remote sites including Enewetak, (Arimoto et. Al., 1985), Bermuda (Church et al., 1984), Jungraujoch (Tschiersch et al,. 1996), Greenland (Galloway et al., 1982), W. Atlantic (Church et al., 1984), South Atlantic (Helmers and Schremes, 1995), Paradise Island (Helstead et al., 2000), from rural sites including, Western Switzerland (Atteia et al., 1994), Netherlands (Daalen, 1991), Aberdeen (Balls et al., 1989), Sweden (Galloway et al., 1982), Aspvertin (Ross, 1990), La Castania (Rodrigo, et al., 1999), Cumbria (Nimmo, et al., 1997), Paris (Garnaud et al, 1999), Gottingen Germany (Galloway et al., 1982), Kollo, Africa (Freydier et al., 1998), North Sea (Baeyens et al, 1990), Jeziory, Poland (Wala et al, 1999), Rural Average (Galloway et al., 1982), Hiroshima, Japan (Takeda et al, 2000), Cap Ferrat (Chester et al., 1997), Sardinia, Italy (Guerzioni et al., 1996) and from urban sites including, Urban Average (Galloway et al., 1982), W. Massachusetts (Wolf, 1989), F.R.G (Valenta et al., 1986), Vosges, (Tschiersch et al, 1996), Munich (Tschiersch et al., 1996), Germany (Gromping et al., 1997), Sudbury, Canada (Chan et al., 1984), Saxonia (Matschullat and Bozau, 1996), Bombay (Ashawa et al., 1984), Belgium (Komy et al., 1988), Chernogolovka (Hoffmann et al., 1997), Fiordland (Helstead et al., 2000), Tennessee (Lindberg, 1982). The results are depicted in Figure 2b.

Concentrations of elements with anthropogenic sources, namely Cd, Pb, Mn, V, Ni, Cr and Cu measured at the Black Sea and Mediterranean coast are high compared to concentrations reported for both remote and rural sites. Concentrations of Cd, Ni, Pb, Cu and Cr measured at both Mediterranean and Black Sea stations are among the highest values reported in literature. Concentrations of Mn and V measured at the Black Sea station is also among highest values, but levels of these two elements at the Mediterranean station is not known, as they are not measured in the Mediterranean samples. High concentrations of pollution-derived elements measured at the Mediterranean and Black Sea coasts of Turkey are in agreement with high concentrations of SO_4^{2-}, NO_3^- and NH_4^+ measured at the same stations.

Comparison of anthropogenic element and ion concentrations with literature data clearly demonstrates that Anatolia, including Mediterranean and Black Sea coasts is under the influence of pollution transport from high emission areas, both in and outside the country. Although discussion of aerosol data is not included in this manuscript, similar high concentrations of anthropogenic trace elements and ions at the Black Sea and Mediterranean coasts of Turkey are also observed in atmospheric particle data.

3.3 Neutralization of acidity

Since data suggest the pollution transport to the Eastern Mediterranean, Anatolia and Black Sea regions, one would expect to measure high concentrations of H^+ ion in all three stations as well. However, concentration of H^+ at the Black Sea, Mediterranean and central Anatolia precipitations are among the lowest values reported in the EMEP network. Such low H^+ concentrations suggest an extensive neutralization of rainwater acidity at all three regions.

Precipitation is expected to be acidic in regions that are under the influence of anthropogenic emissions. However, the pH of the rainwater is determined not only by transport of acid precursors, but also acid base reactions in cloud and rain droplets. Two important bases that neutralize acidity in rainwater are NH_3 and $CaCO_3$. The $CaCO_3$ is particularly important for the Mediterranean region, because soil along the coasts is calcareous and contains high concentrations of $CaCO_3$. Neutralization of rainwater acidity is frequently reported in both eastern and western parts of the Mediterranean basin, particularly when the airflow is from south (Camarero and Catalan, 1996; Loye-Pilot, et al., 1986; Plaisence et a., 1997; Avila et al., 1996)

Frequency distribution of pH values measured at the Black Sea, Mediterranean and Central Anatolia are given in Figure 3. Annual average pH in these three sites are 4.99, 5.10 and 6.10, respectively. Both the frequency distributions and annual average pH values show that the rainwater in different parts of Turkey are not acidic. Since it was shown in the previous section that the levels of pollution-derived ions are among the highest in Europe, these high pHs indicate extensive neutralization of acidity in the Anatolian Plateau.

The pH frequency distribution for the central Anatolia is shifted to higher pH values than the corresponding distributions at the Black Sea and Mediterranean regions, suggesting more complete neutralization of rainwater acidity in the Central parts of the country compared to coastal regions. This is also reflected in the higher annual average pH measured in the central Anatolia station.

High annual average pH values at the three stations do not necessarily imply complete absence of acidic rains. Approximately 30% of rain events sampled at the Black Sea and Mediterranean coasts have pH smaller than 5.0 and can be considered acidic. However, only 5% of rain events in the central Anatolia can be classified as acidic ($pH<5.0$). Most of the acidic rains are associated with 850 mb air mass transport from N and NW wind sectors, where the high emission areas both in Turkey and at Europe are located.

Sulfate-to-nitrate equivalent ratio in precipitation can be an indicator for the form of pollution transported to a receptor area. There are two main emission regions in Europe. One of these regions includes western European countries where emissions are high owing to heavy industrialization and the second emission area is the eastern European countries, where emissions are high due to lack of emission control. Sulfate-to-nitrate ratios from these two source regions are expected to be different. In the Western Europe, SO_2 emissions decreased significantly in recent years with the sulfur reduction protocol, which became effective in mid 80's. But NO_x emissions are not reduced at the same time and to the same level with SO_2 due to the nature of NO_x and SO_2 control technologies. Consequently, the emissions at the Western Europe should have low SO_2/NO_x ratio, which should transform to low SO_4^{2-}/NO_3^- ratio after long-range transport. Since there is no significant control on both SO_2 and NO_x emissions in the Eastern Europe, the SO_4^{2-}/NO_3^- ratio in long-range transported emissions from Eastern Europe is expected to be high. Sulfate-to-nitrate ratio in emissions from Balkan countries and Turkey should be similar to ratio in emissions at the Eastern Europe.

Based on this argument, the potential of the SO_4^{2-}/NO_3^- ratio to be used as a tracer for the source regions of the pollutants that are being transported to the Black Sea, Central Anatolia and eastern Mediterranean was investigated. Sulfate-to-nitrate ratio in EMEP stations and stations used in this study are depicted in Figure 4. The EMEP stations are separated into two groups depending on their locations. The stations in the western European countries are indicated as "Group 1 EMEP stations" and stations in the eastern European countries are indicated as "Group 2 EMEP stations".

As can be seen from the figure, although there is significant overlap, probably due location characteristics of individual stations, SO_4^{2-}/NO_3^- ratio in Group 1 stations varies between <1 and 2 (mean 1.23 ± 0.37) and most of the ratios higher than 2 are observed in group 2 stations (group 2 mean ratio is 2.55 ± 1.02). This fair difference in the SO_4^{2-}/NO_3^- ratios measured in two groups of

EMEP stations indicate that the ratio has potential to be used as tracers of source regions in Europe.

Average SO_4^{2-}/NO_3^- ratios measured at the Central Anatolia and Black Sea precipitation are 2.41 ± 1.2 and 2.40 ± 1.2, respectively, which resembles the ratio from Eastern European countries, Balkan countries and Turkey. However, SO_4^{2-}/NO_3^- measured at the Mediterranean station is 1.3 ± 1.5, which resembles the ratio in Group 1 EMEP stations. Although discussion of source regions is beyond the scope of this manuscript, the difference in the SO_4^{2-}/NO_3^- ratios at the Mediterranean coast and central and northern parts of Turkey may imply that these regions can be under the influence of different source areas.

However, it should be noted that SO_4^{2-}/NO_3^- ratio is not constant but decrease approximately 30% in summer as shown in Figure 5. Lower ratio in summer is due to more effective scavenging of NO_3^- in summer with dry deposition mechanism. A well-known feature of the Eastern Mediterranean climatology is a dry and long summer season. Approximately 20% of the annual precipitation occurs between April and October. Since dry deposition of submicron SO_4^{2-} particles is not as effective as the dry deposition of coarse NO_3^- particles, the SO_4^{2-}/NO_3^- ratio in atmospheric aerosols and hence in precipitation decrease during summer season.

The ratio of the H^+ ion concentration to the sum of the concentrations of SO_4^{2-} and NO_3^- ions [$(H^+)/(SO_4^{2-}+NO_3^-)$ ratio] is a good indicator for the extent of neutralization of acidity in precipitation. The ratio is unity if HNO_3 and H_2SO_4 in precipitation are not neutralized and deviation from unity is a measure of the extent of neutralization. The average $(H^+)/(SO_4^{2-}+NO_3^-)$ ratios at the Mediterranean, Black Sea and Central Anatolia stations are 0.30 ± 0.28, 0.25 ± 0.23 and 0.04 ± 0.06, respectively, indicating that approximately 70% - 75% of rainwater acidity at the coastal regions, and 95% at the central Anatolia is neutralized.

The $(H^+)/(SO_4^{2-}+NO_3^-)$ ratio also show a well-defined seasonal pattern as depicted in Figure 6. The ratio is smaller in summer season, indicating more extensive neutralization during summer months at all three stations. More than half of the rainwater acidity at the Mediterranean is in the form of free acidity in January, February, November and December, but approximately 80% - 90% of the acidity is neutralized in summer. In the Black Sea station, approximately 50% - 70% of the rainwater acidity is neutralized in winter and 80% - 95% in summer. The neutralization is more extensive at the central Anatolia, where more than 90% of the acidity is neutralized in winter and practically no free acidity is found in summer.

It is clear that the acidity in the region is neutralized, particularly in the summer season. The most likely neutralizing agents are NH_3 and $CaCO_3$. Ammonia is a common neutralizing agent for the acidity in precipitation, particularly in the northern parts of Europe where other base cations are not abundant (Semb et al., 1995). Since NH_4^+ concentrations measured at the Black Sea, Mediterranean and Central Anatolia are among the highest measured in whole Europe, NH_3 is a potential neutralizing agent. However, NH_3 is not the only neutralizing agent, because soil in the Eastern Mediterranean is rich in $CaCO_3$, which also neutralizes acidity in rainwater.

The variation of Ca and NH_4^+ concentrations with H^+ concentrations in Mediterranean, Black Sea and Central Anatolia rainwater are depicted in Figure 7. In all three stations, H^+ ion concentrations clearly decrease with increasing concentrations of both NH_4^+ and Ca, indicating that NH_3 and $CaCO_3$ are the primary species that neutralize rainwater acidity in different parts of Turkey.

Although NH_3 and $CaCO_3$ are the main neutralizing agents, minor contributions of other ions such as Na and Mg to the neutralization of rainwater acidity are reported (Al-Momani et al., 1998; Tuncer, 2000). A stepwise multiple linear regression analysis was performed on the concentrations of SO_4^{2-} and NO_3^- to determine all ions that participate in the neutralization process. Concentrations of SO_4^{2-} and NO_3^- were used as dependent and concentrations of H^+, Ca^{2+}, NH_4^+, Na^+, Mg^{2+} and K^+ were used as independent variables. The regression equations calculated for Mediterranean, Black Sea and Central Anatolia regions are given in Table 2.

In all stations concentrations of SO_4^{2-} and NO_3^- ions are correlated with Ca^{2+} and NH_4^+ showing that NH_3 and $CaCO_3$ are the main neutralizing agents, as expected. Nitrate ion concentrations at all stations are correlated with Ca^{2+} and NH_4^+, but not with Na^+, Mg^{2+} or K^+, implying that HNO_3 in precipitation is neutralized by NH_3 and $CaCO_3$, and other ions do not significantly participate in the neutralization. Sulfate ions, on the other hand, in addition to Ca^{2+} and NH_4^+, are also correlated with Na^+ and Mg^{2+} ions, suggesting that Na^+ and Mg^{2+}ions also participate in the neutralization of H_2SO_4 in rainwater.

It should be noted that at all three stations the correlation between NO_3^- and H^+ ions is stronger than the correlation between SO_4^{2-} and H^+ ions. Such difference between correlation coefficients gives the impression that most of the free acidity in the Black Sea, Central Anatolia and Mediterranean regions is in the form of HNO_3 rather than H_2SO_4. Reasons for such selective neutralization of H_2SO_4 are not clear.

3.4 Temporal variations in concentrations of elements and ions

Concentrations of elements in rainwater show strong short-term (episodic) variations in all stations. Such episodic changes in the concentrations of elements and ions with both anthropogenic and natural sources in the Mediterranean region are well documented (Remuadaki et al., 1991; Bergametti et al., 1989; Gullu et al., 1998; Al-Momani et al., 1998). The source of marine elements and ions in precipitation is sea salt particles generated on the sea surface by the bubble bursting process. The mechanism depends on the surface wind speed (Hacisalihoglu et al., 1992) and storm activity before frontal systems generate large quantity of sea salt particles which are subsequently washed out by rain generating an episode in the concentrations of marine elements and ions, such as Na, Cl^-, Mg, Br (Al-Momani et al., 1998; Gullu et al., 1998).

The episodes in the concentrations of crustal elements and ions in precipitation are generated either by wind induced resuspension of local soil (Al-Momani et al., 1998; Tuncer, 2000; Al-Agha, 2000), or by transport of dust from North Africa (Kubilay and Saydam, 1995; Guerzoni et al., 1996), both of which are highly episodic in nature.

Short-term variability in the concentrations of anthropogenic elements and ions are due to changes in the upper atmospheric air mass transport. Emission sources are distributed unevenly around the study area. Most of the countries with high emissions, either due to heavy industrialization or due to lack of emission control are located in the W, NW and N wind sectors. Emissions in other sectors are not significant, because countries lying in S, SW, E, SE and SW sectors are not heavily industrialized. Preferential transport of pollutants from certain wind sectors is depicted in Figure 8, where back trajectories corresponding to SO_4^{2-} episodes in the Black Sea and Central Anatolia precipitation are plotted. In both cases, episodic high SO_4^{2-} concentrations in the Black Sea and Central Anatolia are transported from W and NW sectors. Episodes in the concentrations of anthropogenic elements and ions are generated by change in the air mass transport direction in time scale of a few days.

Monthly average concentrations of typical crustal (Ca), marine (Na), and anthropogenic (SO_4^{2-} and H^+) ions are depicted in Figure 9. Calcium is used as a typical crustal element, because elements like Al and Fe are measured at the Black Sea and Mediterranean stations, but not at the Central Anatolia and seasonal variations in Ca concentrations are similar to variations in Al and Fe concentrations. Concentrations of marine and crustal elements and ions show consistent seasonal patterns in the Black Sea, Mediterranean and Central Anatolia. Concentrations of crustal elements are high during summer season at all stations, due to easier resuspension of soil particles during dry summer season. Resuspension of soil is more difficult in winter (although winds are stronger), because surface soil is either ice or snow covered, as in the central Anatolia or damp, as in the Black Sea and Mediterranean, during winter months.

With the exception of H^+, seasonal variations in the concentrations of anthropogenic elements are not the same at all stations, as shown in Figure 9 for SO_4^{2-}. Concentrations of Cr, Ni, Cu, nss-SO_4^{2-} and NH_4^+, are higher in summer season in the Mediterranean station. The most likely explanation for high concentrations of these anthropogenic elements in summer months would be the seasonal variations in the transport pattern. If the air mass movements to the Black Sea, Mediterranean and central Anatolia are predominantly from W, NW and N sectors during summer season and from other sectors in winter, it would result in high concentrations of anthropogenic elements during summer months.

Upper atmospheric transport of air masses to the eastern Mediterranean region is extensively investigated by various researchers, using different backtrajectory models (Dayan, 1986; Kubilay and Saydam, 1995; Güllü et al., 1998; Katsoulis and Whelpdale, 1993). These climatological studies have revealed that the air mass transport from the W quadrant is approximately the same in the summer and winter seasons. The difference between summer and winter frequencies is found to be 7% (Dayan et al., 1989), 5% (Kubilay and Saydam, 1995), 2% (Gullu et al., 1998) and 1% (Katsoulis and Whelpdale, 1993). These observations common in most climatologiacal studies, suggest that the seasonal variations in the concentrations of anthropogenic elements cannot be explained by seasonal variations in the transport pattern, because the difference in the transport frequency in the W, NW and N sectors between the summer and winter seasons is not large enough to explain approximately a factor of 2 difference in the concentrations of anthropogenic elements and ions. Similar results are also obtained in the Black Sea region (Gunaydin, 2000).

High concentrations of some of the anthropogenic elements during summer season at the Mediterranean station are explained by more extensive scavenging of particles from the atmosphere during winter. Elements and ions measured in the Mediterranean, Black Sea and central Anatolia precipitation are transported to these receptors from distant source regions. During long-range transport, pollutants are removed from the atmosphere by wet deposition, which is more frequent in winter. Consequently, air masses arriving to the receptor areas in winter are fairly cleaned up by wet deposition during their 3-4 day long transport. Scavenging is not as extensive in summer due to infrequent rains, both at the sampling point and at regions over which air masses pass through. Similar seasonal behaviors of elements and ions are also observed in aerosol studies in the eastern Mediterranean atmosphere (Gullu et al., 1998; Kubilay and Saydam, 1995).

Concentrations of Cd, Zn and Pb in the Mediterranean precipitation are comparable in summer and winter seasons, which indicates that the sources for these elements are close to the receptor. The concentrations of long-range transported elements and ions are higher in summer due to more extensive scavenging in winter. An element can have comparable concentrations in summer and winter, or higher concentration in winter only if it is not scavenged as extensively as the first group, which is possible when the emission sources are close to receptor.

Seasonal variations in the concentrations of anthropogenic elements in the Black Sea are the same with their seasonal behavior in the Mediterranean. Concentrations of Cd, Pb, Ni, Cr, V, and NH_4^{2-} have higher concentrations during summer season in the Black Sea precipitation, suggesting that they are transported to the Black Sea atmosphere from distant sources, whereas concentrations of Zn, Cu, SO_4^{2-} and NO_3^- during summer months are comparable or higher than their average winter concentrations, indicating that sources of Zn, Cu, SO_4^{2-} and NO_3^- are close to the sampling site.

Concentrations of crustal ions, such as Ca, K, Mg are higher during summer at the central Anatolia, in comparison with the other two stations. However, concentrations of SO_4^{2-} and NO_3^- are comparable in both seasons. Although similar concentrations of SO_4^{2-} and NO_3^- ions during summer and winter months may indicate nearby sources, seasonal variation in the rain intensity in the Central Anatolia can also be responsible for such seasonal pattern.

Concentrations of ions decrease with increasing precipitation amount due to such processes as diffusive aerosol capture, initial rain evaporation and dilution (Khwaja and Husain, 1990; AlMomani et al., 1998). Consequently, if the intensity of rain is significantly higher in summer season, it can result in lower-than-expected average concentrations of elements and ions in that period. Monthly total rainfall and monthly average rain intensities (in mm per event) for the Mediterranean, Black Sea and Central Anatolia are depicted in Figure 10. Rainfall is higher during winter months at all three stations as expected. The difference between summer and winter rainfall is the highest for the Mediterranean site. Intensity of rain, on the other hand, is higher during winter season in the Mediterranean and Black Sea regions and higher during summer season in the Central Anatolia, showing that the rain events in the Central Anatolia are less frequent, but more intense during summer.

Higher rain intensity at the coastal stations suggests that higher concentrations of SO_4^- and NO_3^- in the Black Sea precipitation during winter season are not due to variations in rain intensity. However, comparable concentrations of SO_4^- and NO_3^- in the central Anatolia in summer and winter seasons may not be necessarily due to local sources, but can also be explained by higher rain intensity during summer season.

In order to test this hypothesis, monthly average concentrations of SO_4^{2-} and NO_3^- in samples with less than 1.5 mm and higher than 9.0 mm rain amount are calculated for the Central Anatolia. The precipitation amount in each sample changes between 0.02 mm and 22 mm. There were 87 samples with precipitation amount less that 1.5 mm and 55 samples with precipitation amount higher than 9.0 mm. By using these small ranges of precipitation in monthly average concentrations, the influence of rain intensity on the seasonal variability is minimized, if not completely eliminated. The monthly average SO_4^{2-} concentrations in the two data subsets are depicted in Figure 21. It should be noted that uncertainty in some of the bars in the figure are fairly high due to small number of samples used in the average calculations. In both figures higher concentrations during summer months are clear, confirming that lack of the seasonal behavior in the concentrations of SO_4^{2-} and NO_3^- is due to higher intensity of rains in summer season, rather than local sources at the Central Anatolia station.

Hydrogen ion is the only parameter that shows similar seasonal variations at all three sites. Concentrations of H^+ ion are higher in winter at all stations. Difference between summer and winter concentrations of H^+ is more pronounced than the difference observed in other anthropogenic elements. Seasonal variations in the concentrations of H^+ ion are determined by seasonality of the neutralization process as well as by the transport to the receptor. Since the concentrations of both NH_4^+ and Ca^{2+} ions are higher during summer at all sites, more complete neutralization of rainwater acidity and hence lower H^+ concentrations are expected during summer season at all stations.

3.5 Deposition fluxes

Soluble and insoluble wet deposition fluxes of elements and ions in the Mediterranean, Black Sea and Central Anatolia regions are given in Table 3. Sulfate and NO_3^- are the dominating fraction of deposited inorganic mass in the Blacks Sea and Central Anatolia. They together account for 32% and 52% of deposited mass at these two stations, respectively. Sulfate and NO_3^- deposition accounts only for 24% of deposited mass at the Mediterranean station, because Na and Cl dominate wet deposition at that station owing to close proximity of the station to the Mediterranean Sea. Trace elements account for 3% and 4% of total wet deposition at the Mediterranean and Black Sea stations, respectively.

Most of the major ion deposition occurs in soluble form at all stations, as expected. Crustal elements Fe and Al deposit mostly in insoluble form. Their soluble fluxes vary between 10% and 15% at both the Black Sea and Mediterranean sites. Fraction of metals deposited in soluble forms is comparable at both stations, except for Cd and Zn. Almost all of the Zn and Cd wet deposition at the Mediterranean occur in soluble form, whereas only 45% of Cd and 68% of Zn deposition are in the soluble form in the Black Sea region.

Magnesium is another element, which showed significantly different solubility at the two stations. Almost all of the Mg wet deposition in the Mediterranean is in soluble form, but only 60% is in soluble form in the Black Sea precipitation. This is probably due to different forms of Mg at these two stations. Since the station at the Mediterranean coast is close to the sea, approximately 70% – 90% of Mg have sea salt origin, which is highly soluble. Since the Black Sea station which is approximately 3 km from the coast is not under strong influence of sea salt particles, most of the Mg at the Black Sea station has crustal origin, which is not as soluble as marine Mg.

Wet deposition fluxes of elements and ions measured in this study are compared with the corresponding fluxes in the EMEP network in Figure 3. As discussed previously, concentrations of elements and ions measured in the Black Sea, Central Anatolia and Mediterranean regions of Turkey are among the highest values reported for Europe. However, wet deposition fluxes of the same elements and ions are not as high as concentrations when compared with EMEP data. Wet deposition fluxes of H^+, nss-SO_4^{2-}, NO_3^-, NH_4^+ and K are among the lowest deposition values in the EMEP program. Chlorine and Na deposition fluxes at the Mediterranean are high due to close proximity of the station to the coast. The main reason for low wet deposition fluxes of elements and ions in this study is fairly low annual precipitation in the region. Annual rainfall at the three stations is among the lowest 10 values in all EMEP stations used in the comparison.

Elements and ions measured in this study have fairly similar seasonal patterns in their deposition fluxes. Monthly wet deposition fluxes of H^+, nss-SO_4^{2-} and Ca are given in Figure 4. Approximately same monthly variations are observed in all elements and ions and at all stations. No matter what are the seasonal variations in concentrations, deposition fluxes of all measured parameters are high during winter and low in summer. Summer to winter differences are the largest at the Mediterranean station.

Well-defined seasonality in the deposition fluxes of elements and ions and low annual deposition fluxes in the Mediterranean, Central Anatolia and Black Sea regions of Turkey are due to strong dependence of wet deposition fluxes of elements on the precipitation volume and seasonal variations in rainfall amount. Since wet deposition fluxes of elements and ions depend strongly on the precipitation volume, as depicted in Figure 54 for nss-SO_4^{2-} in the Central Anatolia, monthly variation of precipitation have strong influence on the seasonal behavior of the deposition fluxes of elements and ions. Due to this dependence of deposition fluxes on precipitation amount, monthly variations of deposition fluxes of elements are similar to the monthly variations of rainfall.

Dry deposition fluxes of elements and ions are measured only at the Mediterranean station using size separated concentration data (Kuloglu, 1998) and a model developed by Slinn and Slinn (1980). Dry deposition fluxes of measured elements and ions are included in Table 3. In most parts of Europe wet deposition fluxes of elements and ions dominate over dry deposition fluxes. However, this is not the case in the Eastern Mediterranean and Black Sea regions. Dry deposition fluxes of NH_4^+, SO_4^{2-}, NO_3^-, K, Na and Cr are comparable with their wet deposition fluxes. Dry deposition fluxes of crustal and marine elements, which are associated with coarse particles in the atmosphere, are a factor of 2 to 3 higher than corresponding wet fluxes. Wet deposition fluxes of only Cd and Ni are significantly higher than their dry deposition fluxes. Similarities in wet and dry deposition fluxes of elements in the Eastern Mediterranean is also due to low annual rainfall in the region.

4. CONCLUSIONS

In this study precipitation samples collected at three permanent stations at different parts of Turkey were analyzed for 18 parameters including major ions, H^+, NH_4^+, SO_4^{2-}, NO_3^-, Cl, Mg, Ca, K, Na and trace elements, Cd, Cu, Pb, Al, Ni, Cr, Zn, Fe and V.

Sampling stations were located in rural areas at the Black Sea and Mediterranean coast of Turkey and approximately at the center of the Anatolian plateau. In all stations, rainwater samples were collected daily using automated wet-only and wet-and-dry samplers. Standard samplers at the Mediterranean and Black Sea stations were modified to collect soluble and insoluble fractions of precipitation separately.

The most important observation in this study is unexpectedly high concentrations of both major ions and trace elements at three Turkish stations. Ion data generated in this study are compared with corresponding concentrations reported at more than 80 EMEP stations covering whole Europe. Concentrations of ions with anthropogenic origin, such as SO_4^{2-}, NO_3^-, and NH_4^+ in Mediterranean, Black Sea and Central Anatolia precipitation are among the highest concentration values reported in Europe. Since trace elements are not measured at EMEP stations, trace metal data are compared with literature data from urban, rural and remote stations. This comparison also showed that anthropogenic trace element concentrations at Turkish stations are among the highest values reported in literature.

With such high concentrations of anthropogenic parameters, one would expect fairly high concentrations of H^+ in the Central Anatolia, Black Sea and Mediterranean regions. However, H^+ concentrations at all three stations are among the lowest values reported in the EMEP network, indicating extensive neutralization of acidity in rainwater reaching to Anatolia. The annual average pH in the Black Sea, Mediterranean and Central Anatolia are 5.1, 4.9 and 6.13, respectively, suggesting more complete neutralization of rain acidity in the central Anatolia.

The investigation of [$(H^+)/(SO_4^{2-} + NO_3^-)$] has revealed that approximately 50% - 70% of acidity in rainwater in coastal regions and 90% of acidity in the central parts of the Anatolia plateau is neutralized. Neutralization shows a well-defined seasonal pattern with more extensive neutralization during summer season.

Main bases that neutralize acidity in Anatolian precipitation are found to be $CaCO_3$ and NH_3. However, a multiple linear regression exercise performed on the data has suggested that Mg and Na also participate in the neutralization process. Free acidity at all three sites is in the form of HNO_3 rather than H_2SO_4. The reason for selective neutralization of sulfate acidity is not clear.

Measured parameters show well-defined short- (episodic) and long-term (seasonal) variations. Episodic changes in the concentrations of crustal elements are due to sudden increase in the resuspension of surface soil with increases in wind speed. Such episodes in crustal element concentrations are more frequent during summer, as the surface soil is ice covered or highly moist during winter. Episodes in the concentrations of marine elements such as Na and Cl are attributed to short-term enhancement of sea salt generation at the surface of the sea by storm activity. Such episodes in the concentrations of marine elements are more frequent during winter, due to more frequent storm activity. Episodic increases in the concentrations of anthropogenic elements and ions is due to changes in the direction of upper atmospheric air mass movements.

Concentrations of crustal elements at the all three stations are higher in summer due to dry conditions of surface soil during summer. Concentrations of marine elements in the Black Sea and Mediterranean regions are higher in winter, owing to more frequent storm activity and subsequent sea salt generation during winter.

Seasonal behaviors of trace elements and ions with anthropogenic sources are different at different stations. Concentrations of anthropogenic elements that are carried to the region by long-range transport are higher in summer period at all stations, due to more extensive wet scavenging in winter. Concentrations of some of the anthropogenic elements and ions are comparable at both seasons, because of the less efficient wet scavenging of elements which are emitted to the atmosphere from sources close to sampling points. However, seasonal variation of rain intensity in the Central Anatolia also affects differences between summer and winter concentrations of ions.

Unlike the concentrations, the wet deposition fluxes of elements and ions measured in this study are fairly low when compared with deposition fluxes at different parts of Europe due to strong dependence of wet deposition fluxes of elements on annual rainfall and low annual rainfall in the region.

***Acknowledgement**. We thank General Directorate of Meteorology for computing backtrajectories. Also to Mr. Feruzan Malci, Grürel Sirin, Erdal Örtel, Ünal Eler and Suat Tosun for their assistance in sampling and Mr. Ramazan Demir and Mrs. Ayfer Esen for their assistance in the laboratory.*

REFERENCES

Al-Agha O., Chemical Composition of precipitation in Black Sea region, Ph.D. Thesis, Middle East Technical University, Ankara, Turkey (2000)

Al-Momani, I. F., Aygun, S., and Tuncel G., Wet deposition of major ions and trace elements in the eastern Mediterranean basin. *J. Geophysical Research*, 103, 8287-8299 (1998)

Al-Momani, I. F., Tuncel, S. G., Eler, U., Ortel, E., Sirin, G., and Tuncel, G., Major ion composition of wet and dry deposition in the Eastern Mediterranean basin. *The Science of the Total Environment*, 164, 75-85 (1995)

Arimoto, R., R. A. Duce, R. A., Ray, B. J., Hewitt, A. D., Williams, J., Trace elements in the atmosphere of American Samoa: concentrations and deposition to the tropical south Pacific. *J. Geophysical Research*, 92, 8465-8479 (1987)

Ashawa, S. C., Kelkar, D. N. and Mishira, U. C, Wet deposition of Cd, Pb and Cu at Donar (Bombay) and its relationship with rainfall. Water, Air and Soil Pollution, 25, 63-71 (1985)

Atteia, O., Major ions and trace elements in precipitation of Wetern Switzerland. *Atmospheric Environment*, 28, 3617-3624 (1994)

Avila A., Time trends in the precipitation chemistry at a mountain site in northeastern Spain for the period 1983 – 1994. *Atmospheric Environment,* 30, 14363-1373 (1996)

Balls, P., Trace metals and major ions composition of precipitation at a North Sea coastal site. *Atmospheric Environment*, 23, 2751-2759 (1989)

Beayens, W., Dehairs, F., and Dedeurwaerder, H., Wet and dry deposition fluxes above the North Sea. *Atmospheric Environment*, 2, 1693-1703 (1990)

Bergametti, G., Dutot, A. L., Buart-Menard, P., Losno, R., and Remoudaki E., Seasonal variability of elemental composition of atmospheric aerosol particles over the Northwestern Mediterranean. *Tellus*, 41b, 353-361 (1989)

Camarero, L., and Catalan, J., Variability in the Chemistry of Precipitation in the Pyrenees (Northeastern Spain) - Dominance of Storm Origin and Lack of Altitude Influence. *J. Geophysical Research*, 101, 29491-29498 (1996)

Chan, W., Vet, R., Ro, C., Tang, A. and Lusis, M., Long-term precipitation quality and wet deposition fields in the Sudburry basin. *Atmospheric Environment*, 18, 1175-1188 (1984)

Chester, R., Nimmo, M., Alarcon, M., Saydam, C., Murphy, K. J. T., Sanders, G. S., and Corcoran, P., Defining the chemical character of aerosols from the atmosphere of the Mediterranean-Sea and surrounding regions. *Oceanologica Acta*, 16, 231-246 (1993)

Chester, R., Nimmo, M., Corcoran, P.A., “Rain Water-Aerosol Trace Metal Relationships at Cap Ferrat: A Coastal Site in the Western Mediterranean”, *Marine Chemistry,* 58, 293-312 (1997)

Church, T., Tramontano, J. and Scudluark, J., The wet deposition of trace metals to the western Atlantic ocean at the Mid-Atlantic coast and on Bermuda. *Atmospheric Environment*, 18, 2657-2664 (1984)

Daalen, J. V., Air quality and deposition of trace elements in the province of South Holland. *Atmospheric Environment*, 25, 691-698 (1991)

Davies, J., and Buart-Menard, P., Impact of atmospheric deposition on particulate Mn and Al distribution in Northwestern Mediterranean surface water. *Paleogeography, paleoclimatology, paleoecology*, **89,** 35-45 (1990)

Dayan, U., Climatology of backtrajectories from Israel, based on synoptic analysis. *J. Climatology and Applied Meteorology*, 25, 591-595 (1986)

Dayan U., Heffter J. L., Miller J. M., Seasonal distribution of planatery boundary layer depths over the Mediterranean basin. *MAP Technical Report Series No 30 Part* b (1989)

Draaijers, G. P., Van Leeuven, E. P., De Jong, P. G. H. and Erisman, J. W., Base cation deposition in Europe, Part II. Acid neutralization capacity and contribution to forest nutrition. Atmospheric Environment, 31, 4159-4168 (1997)

Dulac, F., Buart Menard, P., Ezat, U., Melki, S., and Begametti, G., Atmospheric input of trace metals to the Western Mediterranean: Uncertainties in modeling and dry deposition from cascade impactor data. *Tellus*, 41B, 362-378 (1989)

Dulac, F., Buart-Menard, P., Arnold, M., Ezat, U., and Martin D., Atmospheric input of trace metals to the Western Mediterranean sea: 1. Factors controlling the variability of atmospheric concentrations. *J. Geophysical Research*, 92, 8437-8453 (1987)

EMEP manual for sampling and analysis, NILU CCC 1/95 (1996)

Freydier, R., Dupre, B. and Lacaux, J., Precipitation chemistry in Intertropical Africa. *Atmospheric Environment*, 32, 749-765 (1998)

Fujita, S., Takahashi, A., Weng, J., Huang, L., Kim, H., Li, C., Huang, F. T. C., Jeng, F., Precipitation chemistry in East Asia. *Atmospheric Chemistry*, 34, 525-537 (2000)

Galloway, J. N., Thornton, J. D., Norton, S. A., Volchok, H. L. and McLean R. A. N., Trace metals in atmospheric deposition: a review and assessment. *Atmospheric Environment*, 16, 1677-1700 (1982)

Ganor, E., and Mamane, Y., Transport of Saharan dust across the Eastern Mediterranean. *Atmospheric Environment*, 16, 581-587 (1982)

Ganor, E., Levin, Z., and Van Grieken, R., Composition of individual aerosol particles above the Israelian Mediterranean coast during the summer time, *Atmospheric Environment*, 32, 1631-1642 (1998)

Garnaud, S., Mouchel, J.M., Chebbo, G., Thevenot, D. R., Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff. The *Science of the Total Environment,* 235, 235-245 (1999)

Glavas, S., A Wet only precipitation study in a Mediterranean site, Patras, Greece. *Atmospheric Environment*, 22, 1505-1507 (1988)

Gromping, A., Ostapczuk, P. and Emons, H., Wet deposition in Germany: Long-term trends and the contribution of heavy metals. *Chemosphere*, 34, 2227-2236 (1997)

Guerzoni S., Quarantotto G., Cesari G., Trace metal composition and grain size of particulates in aerosols and precipitation collected in NW Mediterranean (39N, 9E): A multivariate analysis. in *The Impact of African Dust Across the Mediterranean*. R. Chester, S. Guerzoni eds., pp 333 - 338, Kluwier (1996)

Guerzoni, S, Chester, R., Dulac, F., Herut, B., Loye-Pilot, M., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, S., and Ziveri, P., The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea*. Progress in Oceanography*, 44, 147–190 (1999)

Guieu, C., Chester, R., Nimmo, M., Martin, J. M., Guerzoni, S., Nicolas, E., Mateu, J., and Keyse, S., Atmospheric input of dissolved and particulate metals to the Northwestern Mediterranean*. Deep-Sea Research Part II-Topical Studies In Oceanography*, 44, 655-674 (1997)

Gullu, G., Olmez, I., Aygun, S., and Tuncel, G., Atmospheric trace element concentrations over the Eastern Mediterranean sea: factors affecting temporal variability, *J. Geopysical Research*, 103, 21943-21954 (1998)

Gullu, G., Ölmez, I., and Tuncel, G., Temporal variability of atmospheric trace element concentrations over the eastern Mediterranean Sea, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 55, 1133-1148 (2000)

Gunaydin, C. G., M.Sc Thesis, Middle East Technical University, Ankara, Turkey (2000)

Hacisalihoglu, G., Eliyakut, F., Balkas, T. I., and Tuncel, G., Chemical composition of particles in the Black Sea aerosols. *Atmospheric Environment*, 26, 3207-3218 (1992)

Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Buttler, T. J., and Rodhe, H., Steep declines in atmospheric base cations in regions of Europe and North America. *Nature*, 367, 351-354 (1994)

Helmers, E. and Schrems, O., Wet deposition of metals to the tropical North and South Atlantic Ocean, *Atmospheric Environment***,** 29, 2475-2484 (1995)

Helstead, M. R., Cunningham, R. and Hunter, K., Wet deposition of trace metals to a remote site in Fiortland, New Zeland. *Atmospheric Environment*, 34, 665-676 (2000)

Hernandez, E., Gimeno, L., Sanchez, M., Rua, A., and Mendez, R., Relationship Between Rain Composition in Spain and Its Sources*. J. Geophysical Research-Atmospheres*, 101, 23381-23387(1996)

Herut, B., Krom, M. D., Pan, G., and Mortimer, R., Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact, *Limnology and Oceanography*, 44, Issue 7, 1683-1692 (1999)

Herut, B., Starinsky, A., Katz, A., and Rosenfeld, D., Relationship between the acidity and chemical composition of rainwater and climatological conditions along a transition zone between large deserts and Mediterranean climate, Israel. *Atmospheric Environment*, 34, 1281-1292 (2000)

Hoffman, P., Karandashev, V. K., Sinner, T. and Ortner, H. M., Chemical analysis of rain and snow samples from Chernogolovka/Russia by IC, TXRF and ICP-MS. *Fresenius J. Analytical Chemistry*, 357, 1142-1148 (1997)

Katsoulis, B. D. and Whelpdale, D. M., A climatological analysis of four day backtrajectories from Aliartos, Greece. *Theoretical and Applied Climatology,* 47, 93-103 (1993)

Khwaja, H. A., and Husain, L., Chemical characterization of acid precipitation in Albany, New York. *Atmospheric Environment*, 24, 1869-1882 (1990)

Komy, Z., Vangrieken, R. and Roekens, E., Analysis of rain water by differential-pulse stripping voltammetry in nitric-acid medium. *Analytica Chimica Acta*, 204, 179-187 (1988)

Kubilay, N., Nickovic, S., Moulin, C., and Dulac, F., An illustration of the transport and deposition of mineral dust onto the eastern Mediterranean. *Atmospheric Environment,* 34 1293-1303 (2000)

Kubilay, N., Saydam, A. C., Trace elements in the atmospheric particulates over the eastern Mediterranean; Concentrations, sources and temporal variability. *Atmospheric Environment*, 29, 2289-2300 (1995)

Kuloglu, E., Dry deposition fluxes and size distribution of elements in Eastern Mediterranean. M.Sc. Thesis, Middle East Technical University, Ankara, Turkey (1998)

Lebolloch, O., and Guerzoni, S., Acid and alkaline deposition in precipitation on the western coast of Sardinia, Central Mediterranean (40-Degrees-N, 8-Degrees-E). *Water Air And Soil Pollution*, 85, 2155-2160 (1995)

Lindberg, S. E., Factors influencing trace metal, sulfate and hydrogen ion concentrations in rain. Atmospheric Environment, 16, 1701-1709 (1982)

Loye-Pilot, M. D., Martin, J. M., and Morelli J., Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature*, 321, 427-428 (1986)

Luria, M., Peleg, M., Sharf, G., Tovalper, D. S., Spitz, N., Benami, Y., Gawii, Z., Lifschitz, B., Yitzchaki, A., and Seter, I., Atmospheric sulfur over the East Mediterranean region. *J. Geophysical Research-Atmospheres*, 101, 25917-25930 (1996)

Matschullat, J. and Bozau, E., Atmospheric Element Input in the Eastern Ore Mountains. *Applied Geochemistry*, 11, 149-154 (1996)

Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P., Tropospheric eerosol ionic composition in the Eastern Mediterranean region. *Tellus*, 49, 314-326 (1997)

Nimmo, M., and Fones, G. R., The Potential Pool of Co, Ni, Cu, Pb and Cd Organic Complexing Ligands in Coastal and Urban Rain Waters. *Atmospheric Environment*, 31, 693-702 (1997)

Piazzola, J., and Despiau, S., Contribution of marine aerosols in the particle size distributions observed in Mediterranean coastal zone. *Atmospheric Environment*, 31, 2991-3009 (1997)

Plaisance, H., Coddeville, P., Roussel, I. and Guillermo, R., A qualitative determination of the source locations of precipitation constituents in Morvan, France. *Environmental Technology*, 17, 977-986 (1996)

Quetel, C. R., Remoudaki, E., Davies, J. E., Miquel, J. C., Fowler, S. W., Lambert, C. E., Bergametti, G., Buatmenard, P., Impact of atmospheric deposition on particulate iron flux and distribution in Northwestern Mediterranean waters. *Deep-Sea Research*, 40, 989-1002 (1993)

Rodrigo, A., Avila, A., Gomez, B. A., Trace metal concentration in Parmelia Cepertata (L) Arc compared to bulk deposition, throughfall and leaf wash fluxes in two holm oak forests in Montseny (NE Spain). *Atmospheric Environment*, 33, 359-367 (1999)

Ross, H. B., Trace metal wet deposition in Sweden: Insigth gained from daily wet only collection. *Atmospheric Environment*, 24, 1929-1938 (1990)

Semb, A., Hanssen, J. E., Francois, F., Maenhaut, W. and Pacyna, J. M., Long-range transport and deposition of mineral matter as a source for base cations. *Water Air And Soil Pollution*, 85, 1933-1940 (1995)

Simo, R., and Grimalt, J.O., Spring-summer emission of dimethyl sulfide from the Northwestern Mediterranean Sea. *Estuarine, Coastal and Shelf Science,* 47, 671-677 (1998)

Slinn, S. A. and Slinn, W. G. N., Modelling of atmospheric particulate deposition to natural waters, in *Atmospheric Pollutants in Natural Waters*, S. J. Eisenreich Ed., pp 25-53, Butterworth, Stoneham, Mass (1981)

Takeda,, K., Marumoto, K., Minamikawa, T., Sakugawa, H. and Fujiwara, K., Three-year determination of trace metals and the lead isotope ratio in rain and snow depositions collected in Higashi-Hiroshima, Japan. *Atmospheric Environment*, 34, 4525-4535 (2000)

Tschiersch, J., Hietel, B., Maier, B., Schulz, F. and Trautner C., Trace element analysis of precipitation samples by preconcentration and PIXIE measurements. *Nuclear Instruments and Methods in Physics Research B*., 109, 526-529 (1996)

Tuncer, B., M. Sc. Thesis, Middle East Technical University, Ankara, Turkey (2000)

Valenta, P., Nguyen, V. D. and Norburg, H. W., Acid and heavy metal pollution by wet deposition. *The Science of the Total Environment*, 55, 311-320 (1986)

Wala, B. and Siepak, J., Research on the variability of physico-chemical parameters characterising acid precipitation at the Jeziory Ecological Station in the Wielkopolski National Park Poland. *The Science of the Total Environment,* 239, 173-187 (1999)

Wolff, T. L. and Korsok, P. E., Atmospheric concentrations and regional source apportionment of sulfate, nitrate and sulfur dioxide in the Berkshire Mountains in Western Massachsetts, *Atmospheric Environment*, 23, 55-65 (1989)

Table 1. Volume weighted average concentrations of ions and elements at the Mediterranean, Central Anatolia and Black Sea stations

		Black Sea	Mediterranean	Central Anatolia
Cl	mg L^{-1}	1.32	16	0.62
NO_3^-	mg L^{-1}	1.44	5.1	1.75
SO_4^{2-}	mg L^{-1}	2.26	5.9	2.67
NH_4^+	mg L^{-1}	1.31	1.2	1.15
pH		4.99	5.1	6.13
Ca	mg L^{-1}	2.43	2.2	1.47
K	mg L^{-1}	4.15	0.72	0.33
Mg	mg L^{-1}	2	1.5	0.12
Na	mg L^{-1}	0.11	10	0.37
Al	mg L^{-1}	10.1	0.58	
Cu	µg L^{-1}	100	4.9	
Fe	mg L^{-1}	7.54	0.53	
Mn	mg L^{-1}	3.44		
Zn	µg L^{-1}	100	137	
Ni	µg L^{-1}	18.7	24	
Cr	µg L^{-1}	11.7	9	
Pb	µg L^{-1}	12.3	10	
V	µg L^{-1}	8.39		
Cd	µg L^{-1}	5.17	4.5	

Table 2. ***Elements that participate in the neutralization of H_2SO_4 and HNO_3 at the three stations***

CENTRAL ANATOLIA

$[NO_3^-] = -0.35 + 0.16[H^+] + 0.56[Ca^{2+}] + 0.24[NH_4^+] + 0.13[Na]$

$[SO_4^{2-}] = 1.9 + 0.08[H^+] + 0.19[Ca^{2+}] + 0.11[NH_4^+] + 0.22[Mg^{2+}] + 0.15[Na]$

MEDITERRANEAN

$[SO_4^{2-}] = 14 + 0.01[H^+] + 0.19[Ca] + 0.14[NH_4^+] + 0.64[Mg]$

$[NO_3^-] = -1.1 + 0.85[H^+] + 0.6[Ca] + 0.72[NH_4^+]$

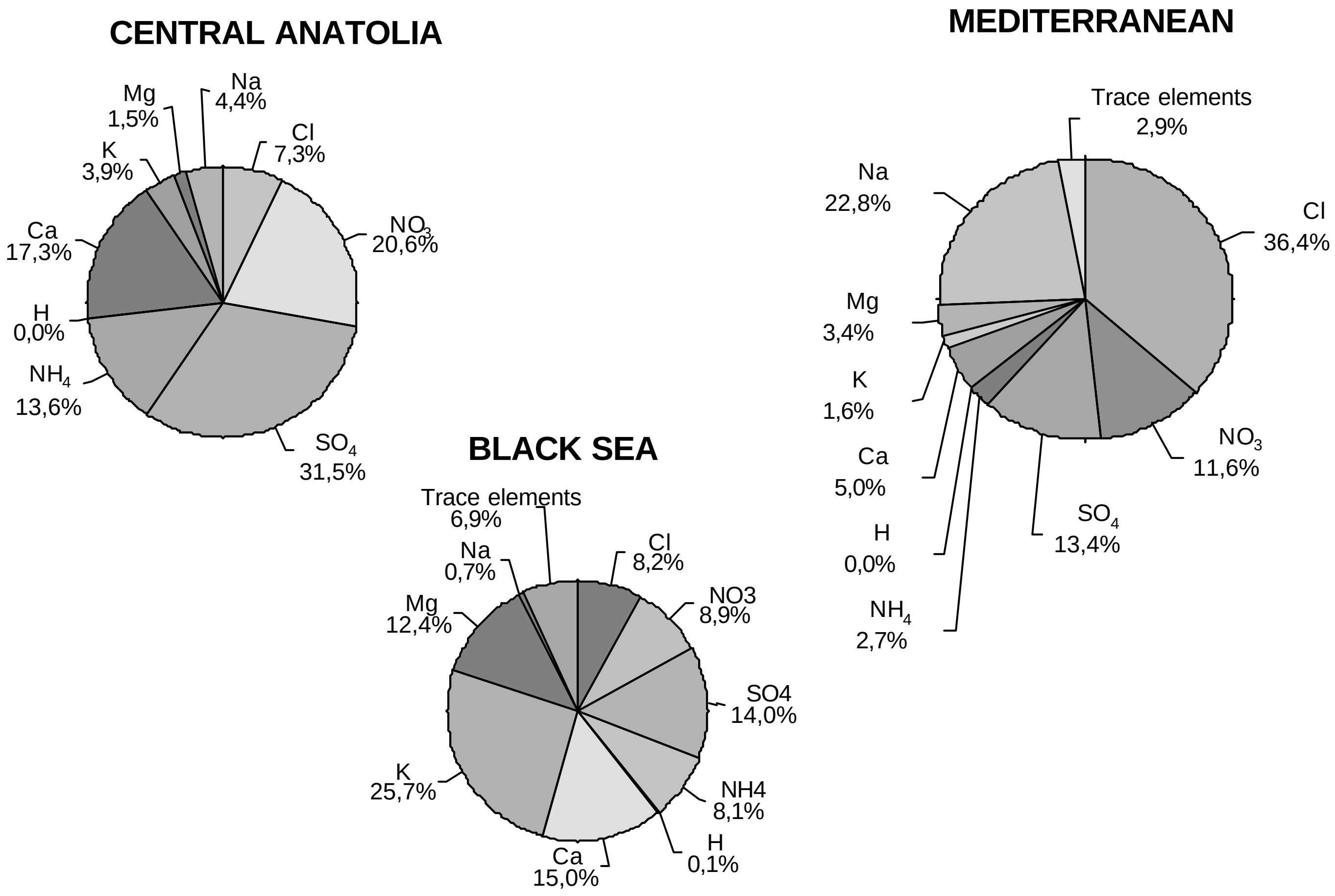
BLACK SEA

$[SO_4^{2-}] = 1.4 + 0.06[H^+] + 0.15[Ca] + 0.25[NH_4^+] + 0.04[Mg]$

$[NO_3^-] = -7.1 + 0.22[H^+] + 0.11[Ca] + 0.27[NH_4^+]$

Table 3. Wet deposition fluxes of ions and elements in the Eastern Mediterranean region

	Mediterranean			Black Sea			Central Anatolia
	Soluble Flux	Insoluble Flux	TOTAL Flux	Soluble Flux	Insoluble Flux	TOTAL Flux	TOTAL Flux
H^+			8.0			4.56	1.36
NH_4^+			190			573	337
SO_4^{2-}			920			916	806
NO_3^-			770			578	527
Cl			2,600			509	185
Mg	230	18	250	85	753	839	39
Ca	340	14	350	313	6.10	319	449
K	98	15	110	147	14.8	162	100
Na	1,600	21	1,621	509	8.85	518	111
Cd	0.69	0.032	0.722	0.85	1.02	1.87	
Cu	0.49	0.3	0.79	22	18	40	
Pb	1.0	0.62	1.62	0.21	4.53	4.74	
Al	11	81	92	14.2	37.5	51.7	
Ni	1.7	2.0	3.7	2.2	5.24	7.39	
Cr	0.59	0.86	1.45	0.55	0.52	1.07	
Zn	19	2.0	21	23.2	10.9	34.1	
Fe	28	53	81	6.1	2.52	31.25	
V				0.69	2.65	3.34	


CENTRAL ANATOLIA

MEDITERRANEAN

BLACK SEA

Figure 1. Contribution of ions to the total inorganic mass in precipitation.

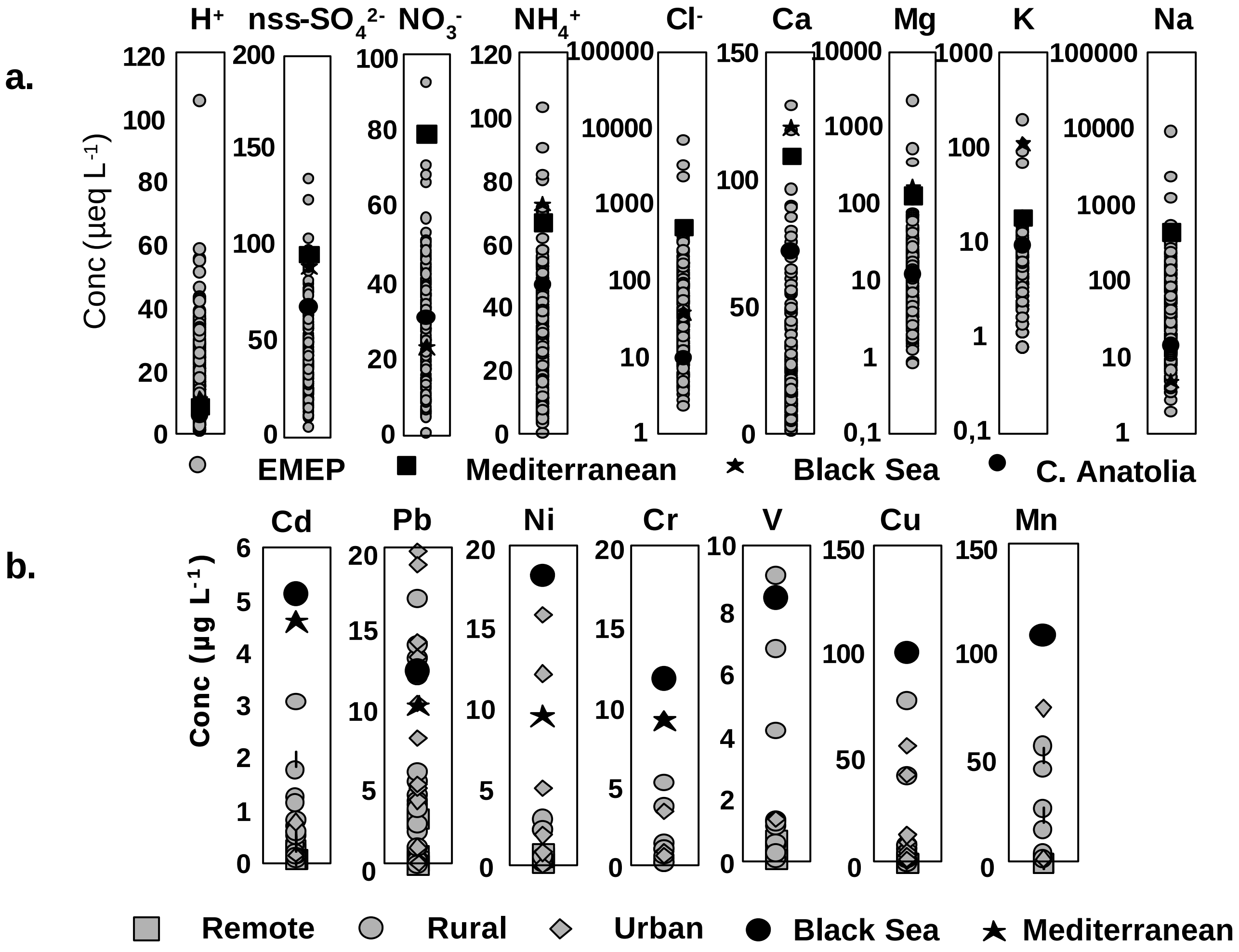
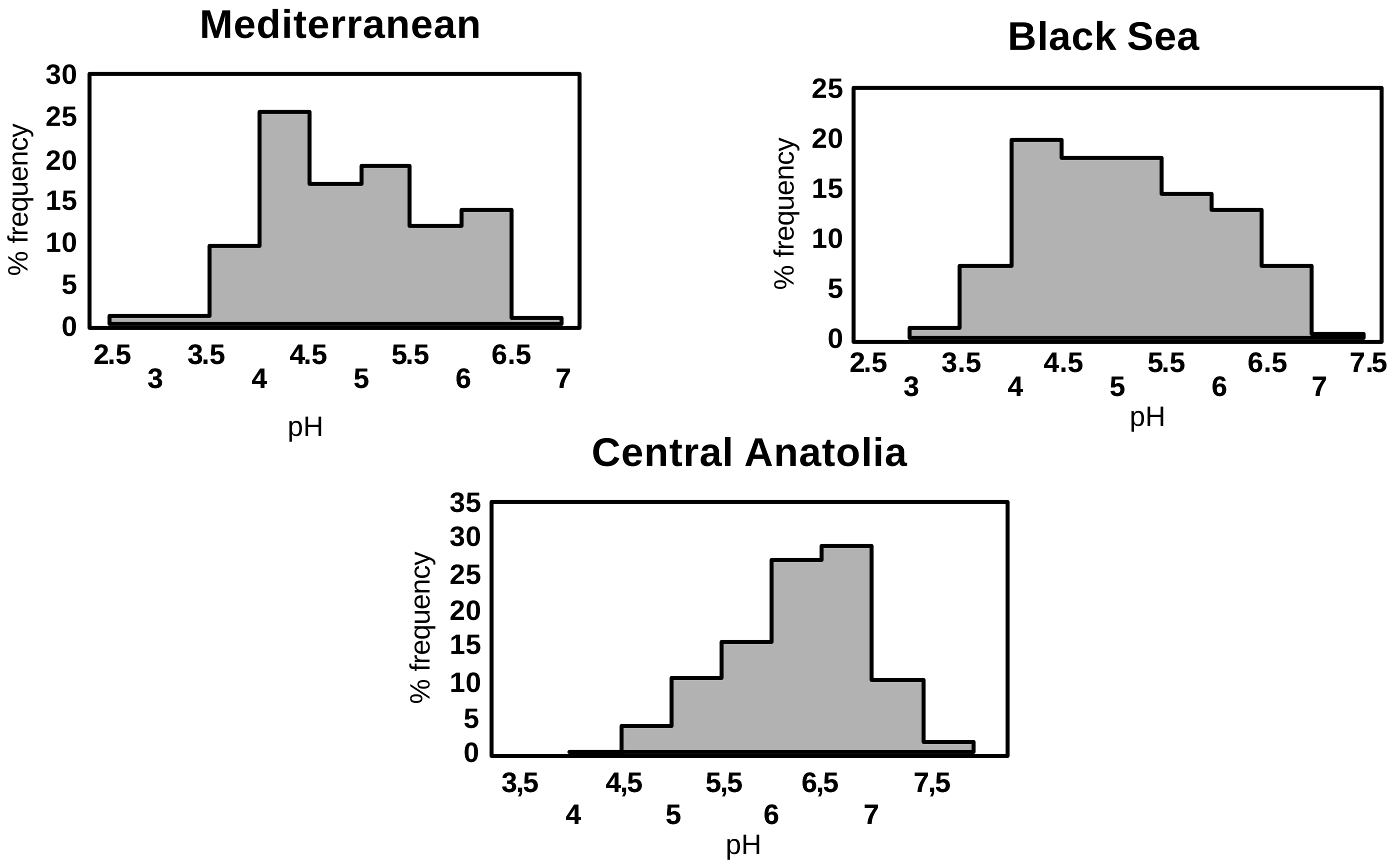


Figure 2. Comparison of annual volume weighted average concentrations of ions measured at the Black Sea, Mediterranean coasts and at the central Anatolia with Literature data. a. Ion concentrations are compared with the corresponding data reported for 83 EMEP stations in Europe for the years 1996, 1997 and 1998 and b. Concentrations of elements are compared with data reported for comparable sites in literature



Mediterranean

Black Sea

Central Anatolia

Figure 3. Frequency distribution of pH values measured at the Black Sea, Mediterranean and Central Anatolia Stations

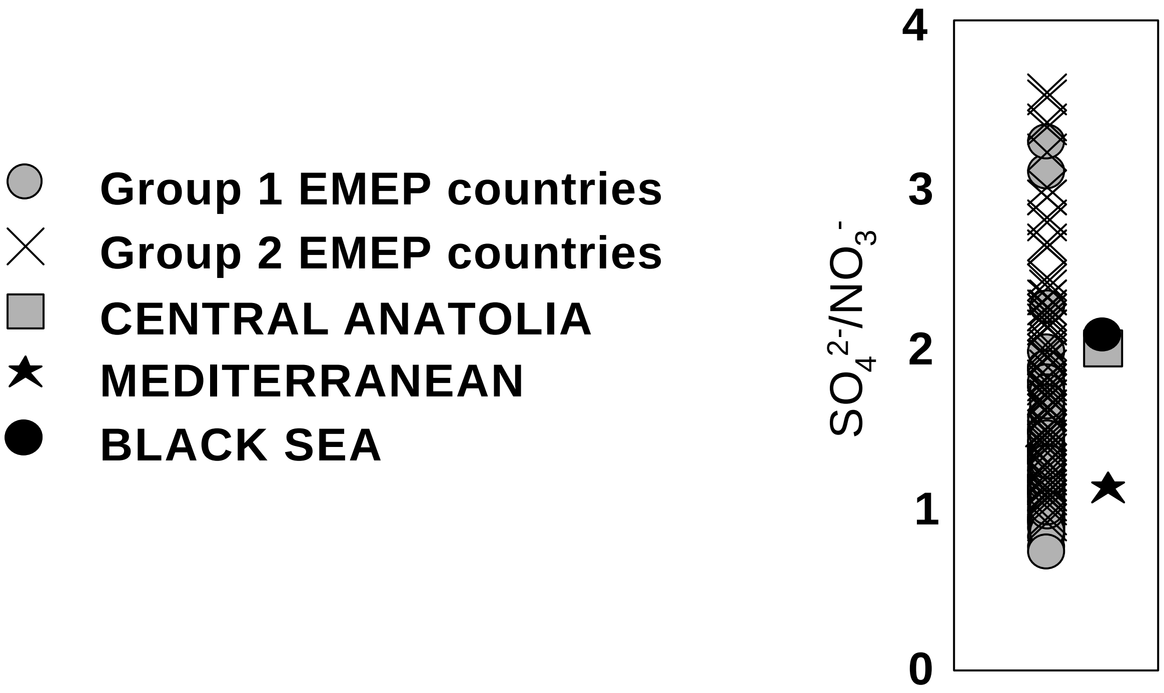


Figure 4. Comparison of nss-sulfate-to-nitrate ratio measured in this study with EMEP data for the years 1996, 1997 and 1998

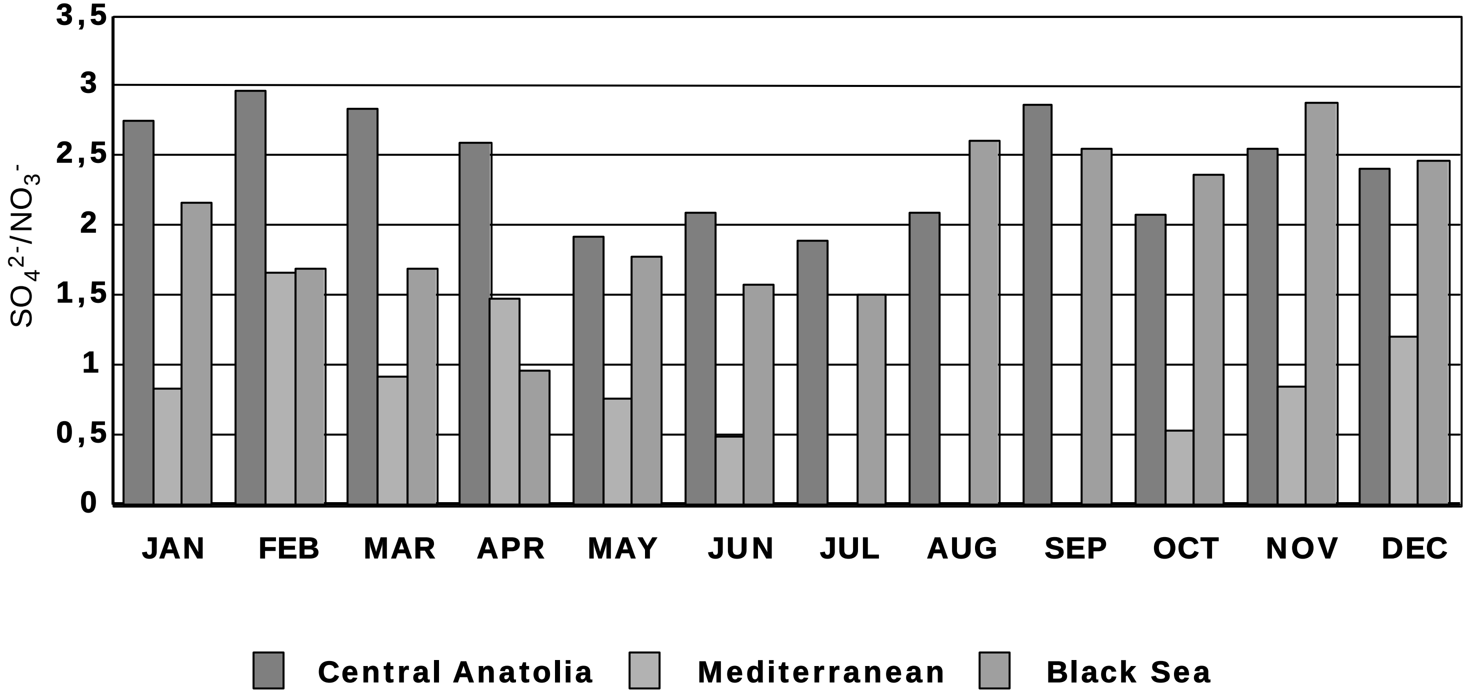


Figure 5. Seasonal variation of SO_4^{2-}/NO_3^- ratio.

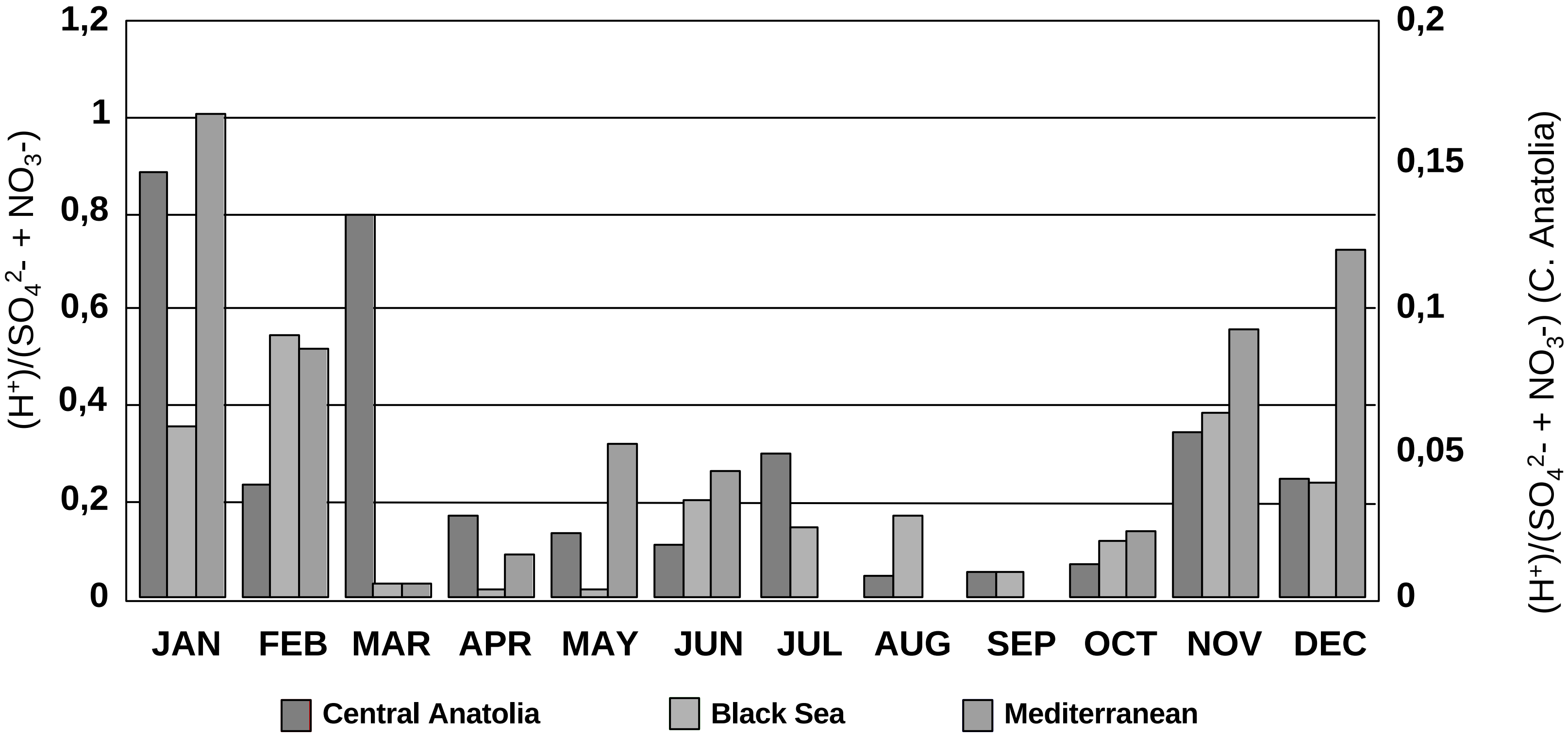


Figure 6. Seasonal variation of $(H^+)/(SO_4^{2-}+NO_3^-)$ ratio.

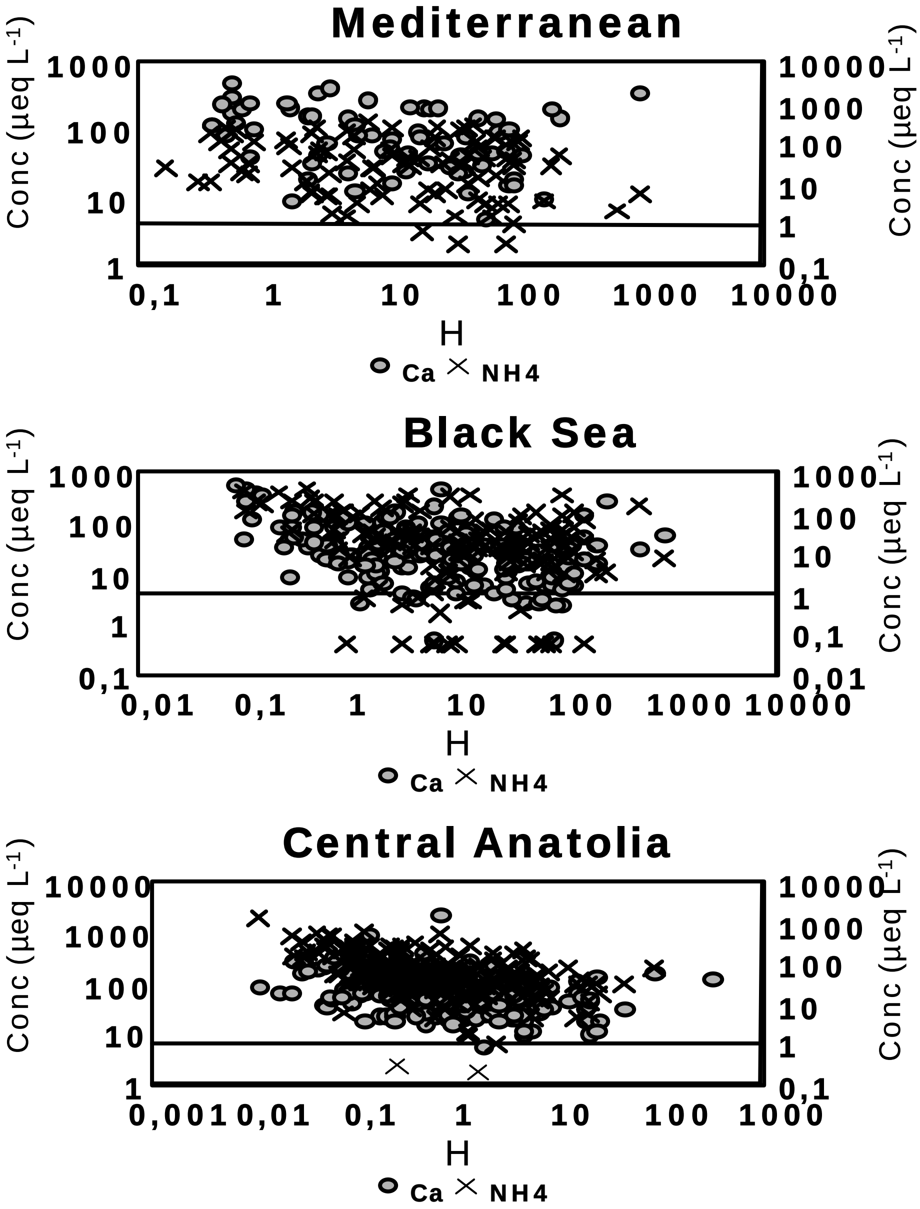


Figure 7. Variation of Ca and NH_4^+ concentrations with H^+ concentration in Mediterranean, Black Sea and Central Anatolia rainwater

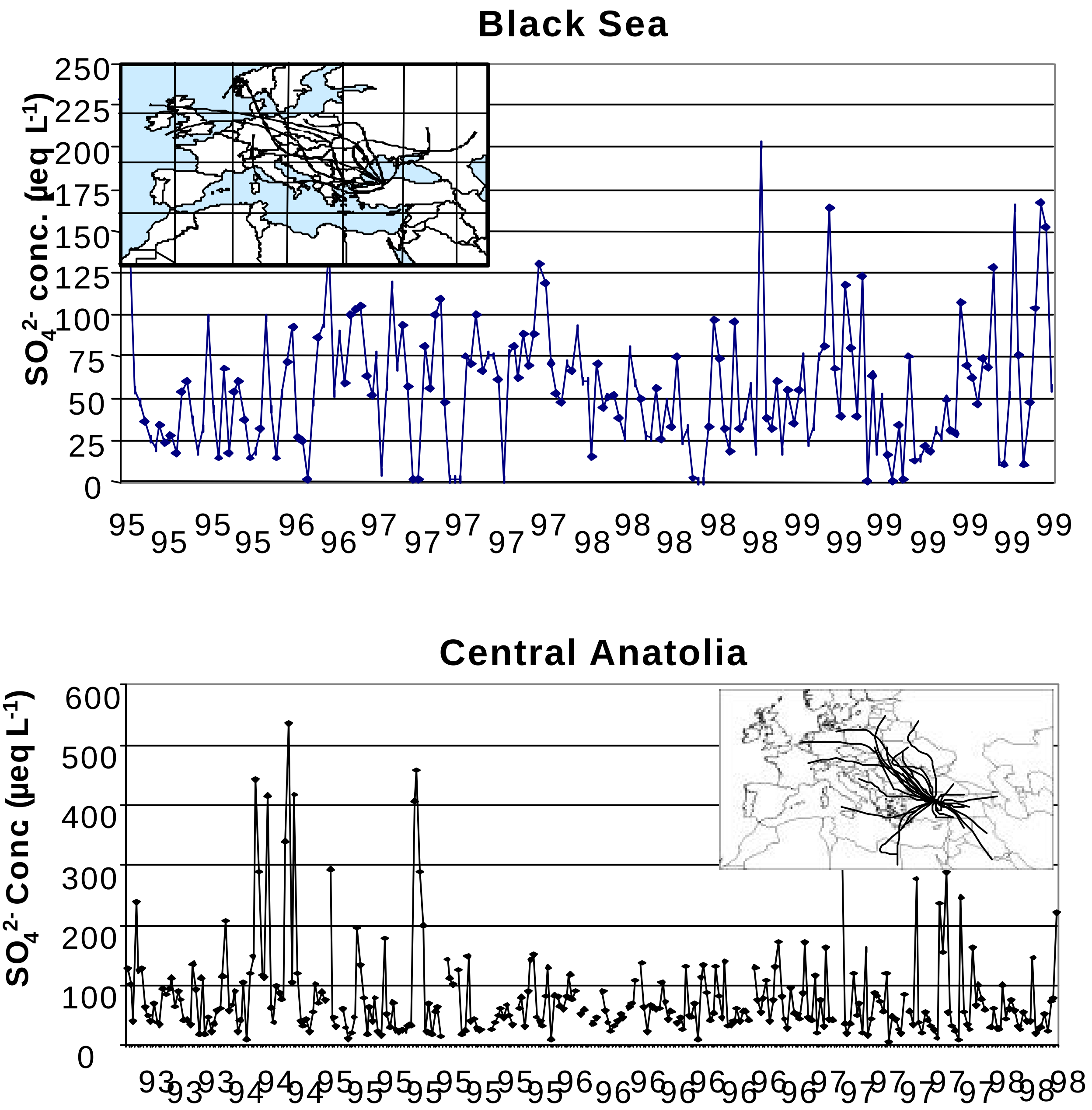


Figure 8. Backtrajectories corresponding to SO_4^{2-} episodes at the Black Sea and Central Anatolia stations

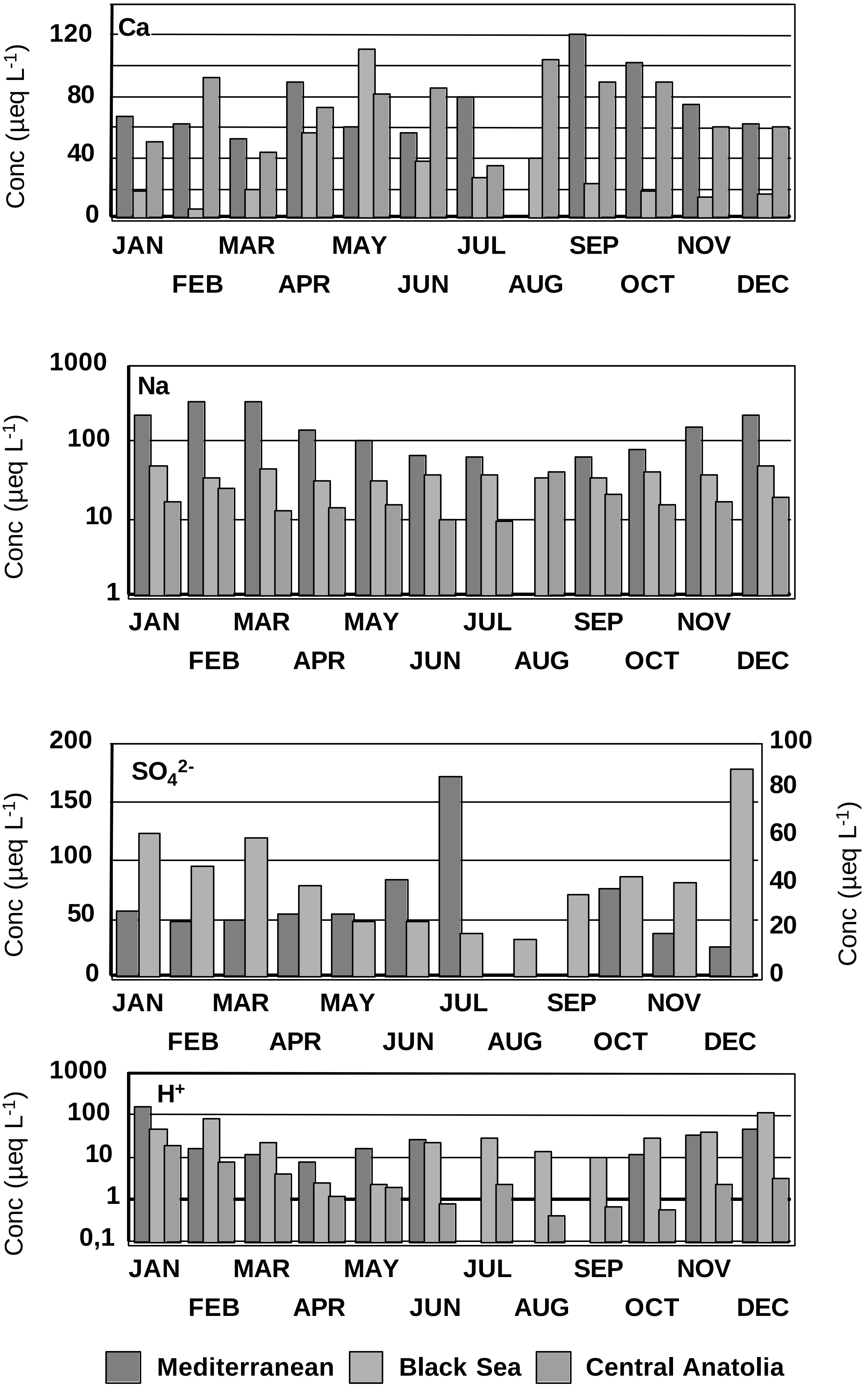


Figure 9. Monthly average concentrations of Ca, Na, SO_4^{2-}, and H^+ ions

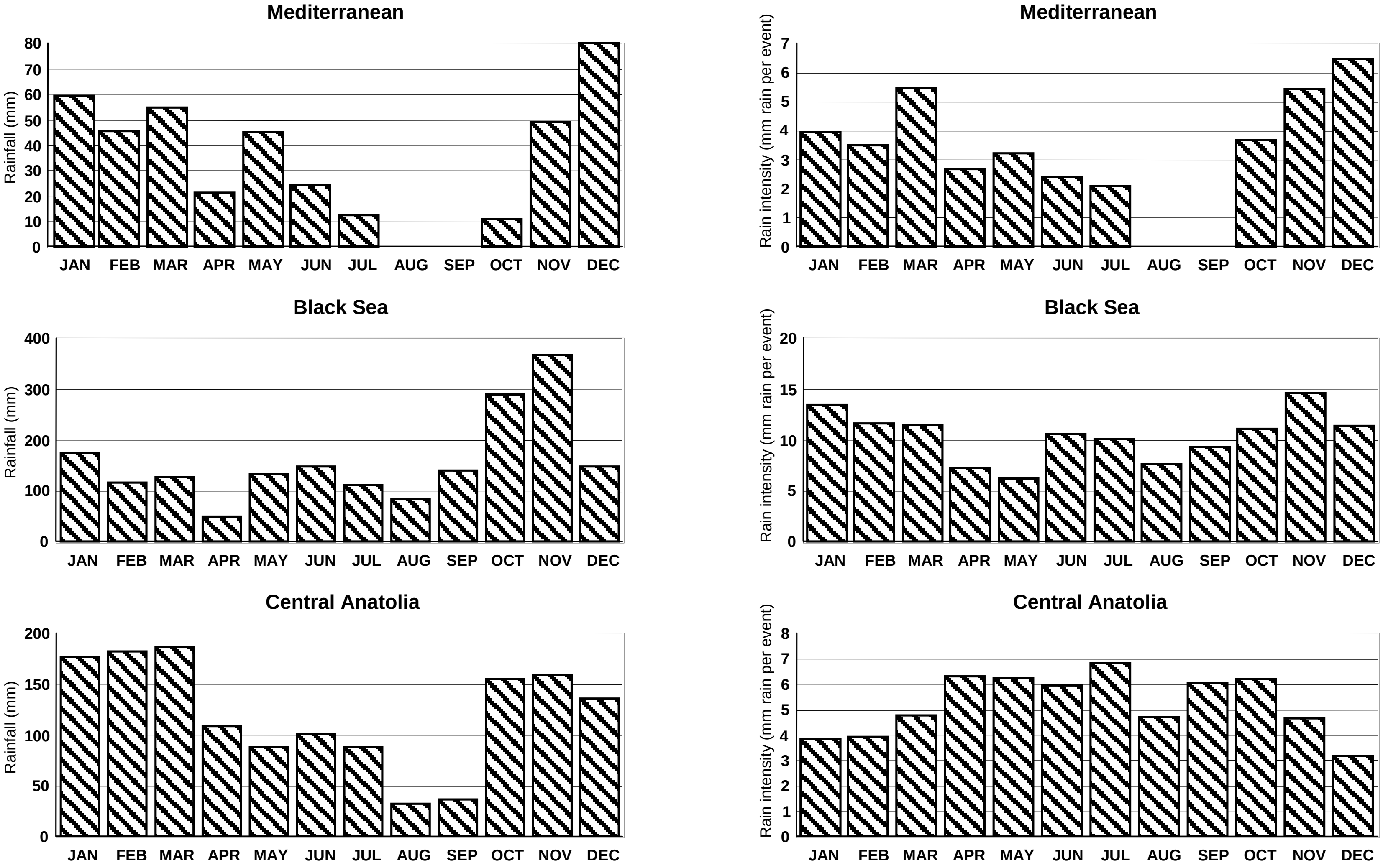


Figure 10. Monthly total rainfall and monthly average rain intensity at the Mediterranean, Black Sea and Central Anatolia stations

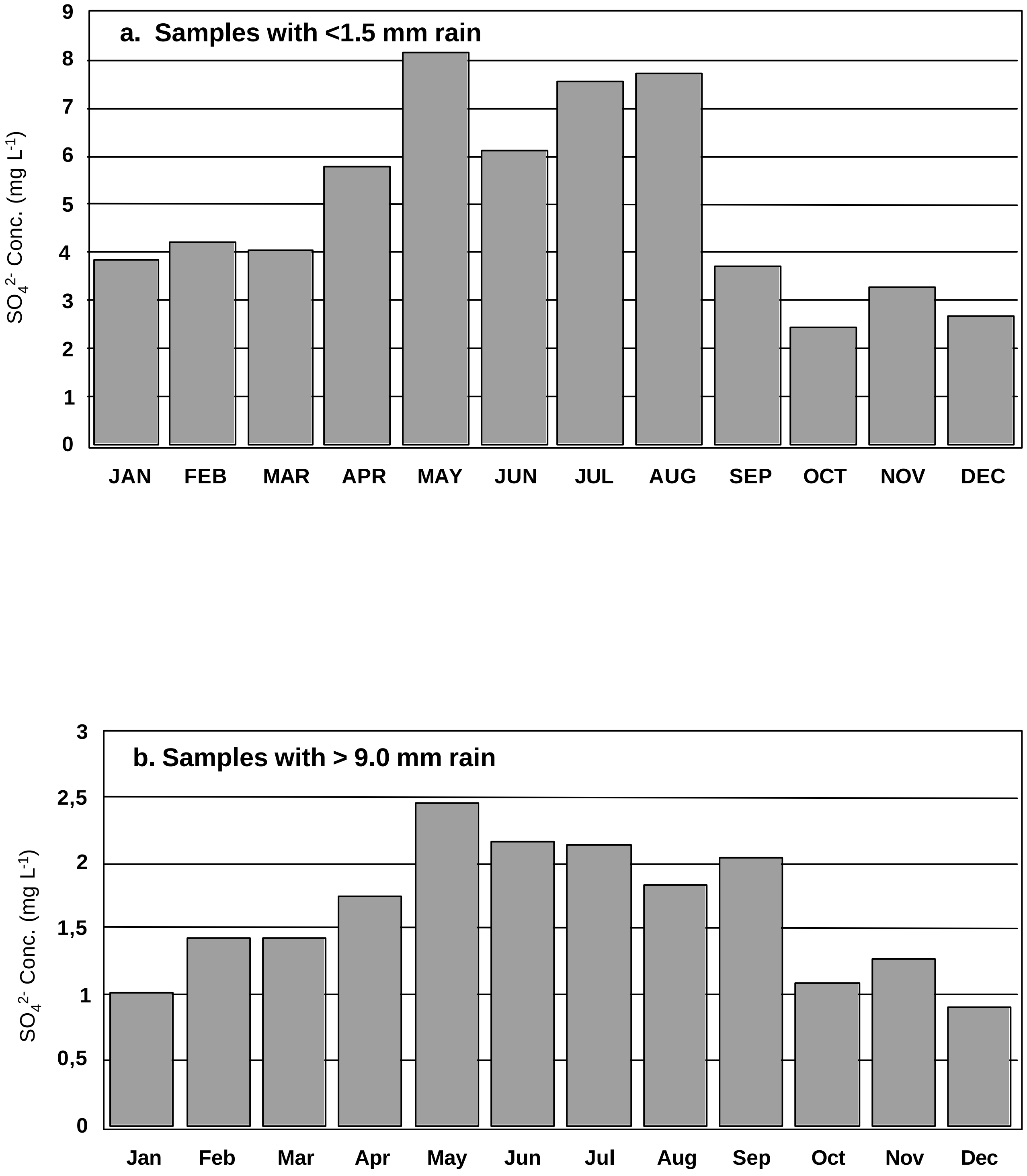


Figure 11. Monthly average SO_4^{2-} concentrations in the events with less than 1.5 mm and more than 9.0 mm rain

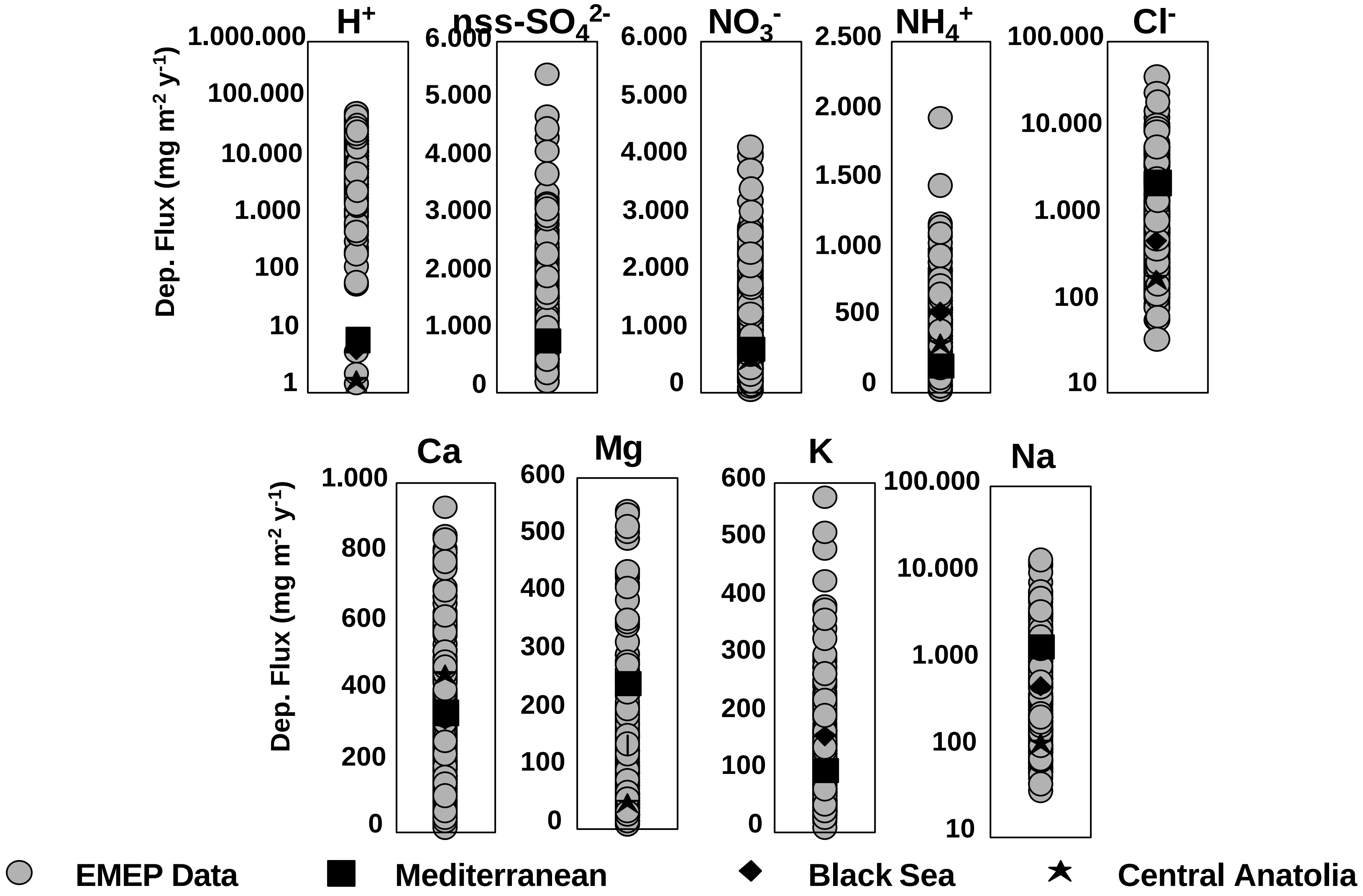


Figure 12. Comparison of wet deposition fluxes of ions measured in this study with EMEP data for the years 1996, 1997, and 1998

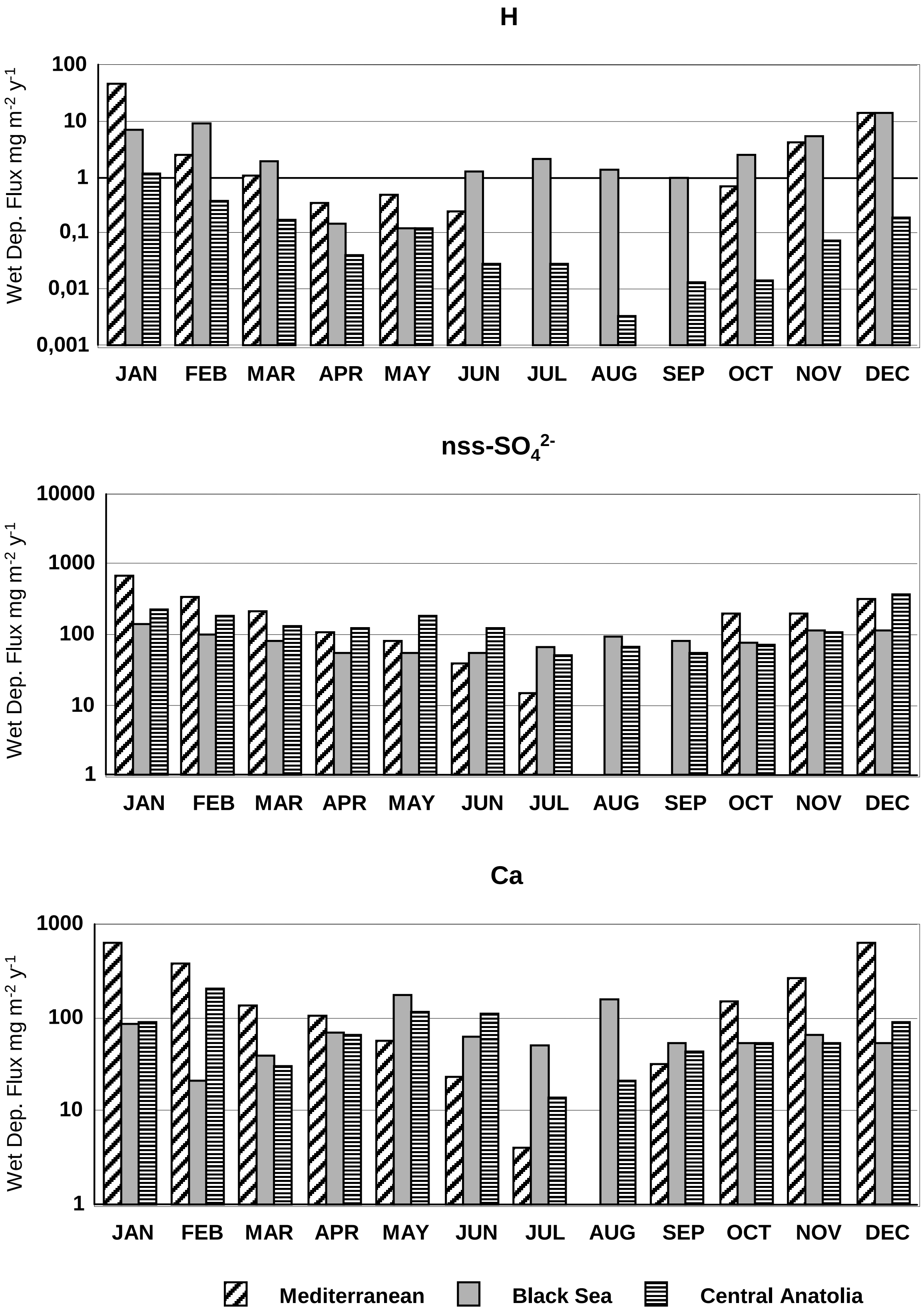


Figure 13. Monthly wet deposition fluxes of H^+, nss-SO_4^{2-} and Ca

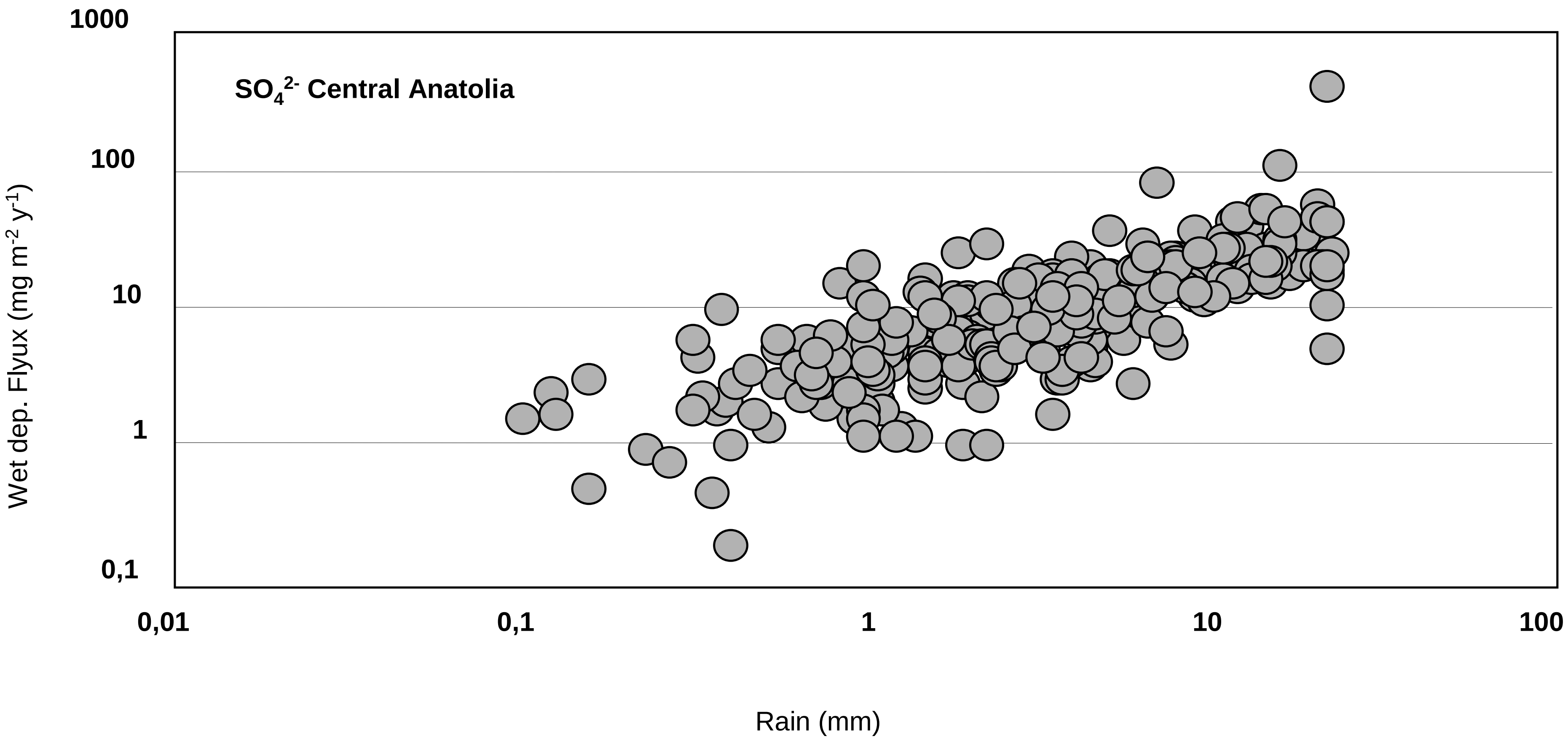


Figure 14. Dependence of wet nss-SO_4^{2-} deposition on precipitation amount in the Central Anatolia

ATMOSPHERIC BULK FLUXES OF NATURAL AND POLLUTANT METALS TO THE NORTH WESTERN MEDITERRANEAN: THEIR TREND OVER THE PAST 15 YEARS (1985-2000)

M.D. Loÿe-Pilot [£], C. Guieu [§] and C. Ridame. [§]

[£] : Unité de Biogéochimie Marine, Ecole Normale Supérieure, 1 rue M. Arnoux, 92120 Montrouge, France

[§] : Laboratoire d'Océanographie de Villefranche (LOV), BP 08, Quai de la Darse, 06238 Villefranche-sur-Mer, France.

ABSTRACT

The total atmospheric deposition of Al, Fe, Pb, Zn and Cd was measured during 18 months on the northwestern coast of Corsica. The sampling station (Pirio), chosen for its isolation from any local and regional contamination sources, was already used for monitoring during the two previous years. The interannual variability of the total atmospheric deposition was found to be high (up to a factor of 2, for Al, Fe, and Pb). Using Al as a crustal tracer indicates that Pb, Cd and Zn are mainly associated with anthropogenic aerosols (> 85% for Cd and Zn) and Fe with crustal aerosols. However, natural lead mainly brought by Saharan dust is not negligible in the case of important dust fallout, its contribution increases with the decrease of anthropogenic emissions. In order to determine the spatio-temporal variability of the trace metals over the North Western Mediterranean Sea, the observed fluxes are compared to those previously found in the past decade using the same methodology. The variation of Al and Fe since 1985 (by a factor of 4 to 6) can be related to the variation of the Saharan dust fallout.

The limitation in the use of lead additives in gasoline has resulted in a decrease of the European atmospheric lead emissions of about a factor of 3 since 1985 and in a maximum decrease of the total atmospheric flux of a factor of 6 when taking into account the natural interannual variability of atmospheric deposition in this region. So the recorded decrease in the lead atmospheric flux since 1985 (~a factor of 30) reveals a slight local contamination at the previous Corsican station, the recorded decrease since 1989 matching the lowering of emissions. The total lead fluxes to the North Western Mediterranean seem to decrease very slowly since 1995, resulting from a presently small decrease of the emissions counterbalanced by the increase of natural lead brought by Saharan dust.

In the case of Cd and Zn, the difference by a factor of 30 and 23 respectively between the data obtained at La Tour du Valat (7/1988 - 6/1989) and those at Pirio (3/1995 - 3/1997, 5/1999 - 11/2000) indicates a local or regional contamination at La Tour du Valat. The same type of contamination occurred for Zn at Cap Ferrat. Indeed Cd and Zn fluxes did not vary much since 1993 and the fluxes measured at Pirio are representative of the long-range transport of these anthropogenic contaminants over the North Western Mediterranean.

1. INTRODUCTION

In recent years, several studies have shown that the atmosphere is the main transport route of trace metals to marine waters (Patterson and Settle, 1987, Martin *et al.*, 1989; Bergametti *et al.*, 1989; Duce *et al.*, 1991; Jickells, 1995). The atmospheric input of these components has an impact on biological processes in the sea (see for example (Fitzwater *et al.*,1982, Duce and Tindale, 1991) and on marine chemical cycling.

The atmospheric input of different substances to the water column is particularly important in the case of the Mediterranean Sea as it is an almost-enclosed system (Martin *et al.*, 1989, Elbaz-Poulichet *et al.* in press). Moreover the Mediterranean environment is a very interesting case-study as the atmospheric input is dominated by the antagonistic influences of the natural terrigenous source from the Saharan desert in the South and the anthropogenic sources from the European continent in the North (Loÿe-Pilot *et al.*, 1986; Dulac *et al.*, 1987; Loÿe-Pilot and Morelli, 1988; Bergametti *et al.*, 1989; Chester *et al.*, 1993; Guieu *et al.*, 1993, 1997; Migon and Caccia, 1998; Guerzoni *et al.*, 1999). The composition of the atmosphere in the North Western Mediterranean is dominated by the anthropogenic signature upon which Saharan outbursts are superimposed (Martin *et al.*, 1989; Chester *et al.*, 1993; Guieu *et al.*, 1997). This is reflected in the relative homogeneity of average aerosol concentrations over the North Western Mediterranean Sea (Guieu *et al.*, 1997).

In order to characterize the atmospheric fluxes of metals to the North Western Mediterranean, several studies were undertaken at coastal sites in the last decade, covering variable sampling time and methodologies (Bergametti 1987; Migon 1988; Chester *et al.*, 1990; Guieu 1991; Remoudaki 1990; Migon *et al.*, 1997). The comparison of the data from four Mediterranean stations has shown high variations of the total deposition flux for some metals such as Zn and Cd (Guieu *et al.*, 1997), suggesting a specific local or regional contamination in cadmium and zinc for the sites having the highest fluxes. This fact lead us to choose a remote island site in order to determine the actual fluxes of metals, especially trace metals, to the open waters of the North Western Mediterranean. The sampling site was also selected to be near a site which was used for monitoring in the late eighties (Bergametti 1987, Remoudaki 1990) in order to establish temporal trends.

The aims of this study were to evaluate, at a remote station, the bulk atmospheric fluxes of such metals as Al, Fe, Zn, Cd and Pb and to determine the spatio-temporal variability of these fluxes in the North Western Mediterranean Sea by comparing our results with previously published data over the past decade.

2. MATERIAL AND METHODS

2.1 The sampling station

The sampling site was established at Pirio (42°21' N, 8°44' E, and 350 meters above sea level) on the northwestern coast of Corsica (Figure1). This station was chosen because of its isolation from any contamination sources (road, wire fence, smoke, automobile traffic) and because it was far away from any industrialized area and an intensive agriculture zone. The site that is located 9 km from the sea, is under marine influence. The marine fraction makes up to 65% of major elements` inputs (Loÿe-Pilot, 1995). The soil surface is composed of hard rocks (rhyolite) or is covered by vegetation, hence local dust from soil re-suspension is negligible. The Pirio station represents a quite good observatory for the air quality in the North Western Mediterranean Sea (Loÿe-Pilot, 1995).

2.2 Sample collection

The bulk atmospheric deposition was collected from 1 May 1999 to 6 November 2000 in 12 samples representing time periods ranging from 26 to 77 days.

The collector was made of a 4 litre polyethylene bottle, placed on a 1.7 m high wood stack. A polyethylene funnel was placed on top of the bottle (surface = 113 cm²). A nylon mesh (porosity = 40 µm) covered the funnel in order to avoid insects and organic debris to fall inside the bottle. The collector was acidified in the field with 100 ml of ultrapure HNO_3 1% at the beginning of the sampling time in order to desorbe metals that may have stuck on the bottle walls and also to avoid an algae development. The funnel was rinsed at the end of the sampling period with 100 or 200ml of HNO_3 0.1% -which was added to the sample - in order to collect dry deposited material or rain particulate matter present on the funnel wall.

After collection, the samples were carried back to the laboratory in Villefranche where they were transferred to a clean room and weighted.

Due to aerodynamic considerations, the dry deposition could be underestimated in such collector. However the intercomparison between such device and other bulk collectors used in other sites (Tour du Valat, Capo Cavallo) indicates that the efficiency is the same in both cases

(Remoudaki *et al.*, 1991). Our conclusions on the spatial and temporal trends are then valid in spite of a probable slight underestimation of the total fluxes reported here.

Field blank. A field blank was made in order to estimate a possible contamination during the transport, and/or generated by the reagents and/or by the operator. In the field, a given volume of ultrapure water was poured in a clean collector. The metal content was found to be negligible as it represents only 10% of the lowest value measured for the samples.

Cleaning procedure. All the plastics used were made of high density polyethylene (Nalgene); the material was prepared inside a clean room : the bottles and funnels were soaked in a Decon bath for 1 week, then they were soaked for 2 weeks inside a 50% HCl bath, then they were rinsed with ultrapure water. For the transport to and from the sampling station, the bottles were stored inside double plastic bags.

2.3 Preparation of the samples and analysis

In order to solubilize the particulate phase before the analysis by AAS, the samples were entirely evaporated inside a one-liter Teflon beaker on a hot plate (T°≈ 220 °C). The evaporation protocol is described in Ridame, 1997. Acid digestion (HF, HNO3) was performed according to the protocol described by Journel, 1998. The MESS-2 reference material (National Council of Canada) was used to evaluate the reliability of the evaporation phase and of acid digestion. Reagent blanks were performed to test the contamination effect of the nitric acid used for the digestion. The samples were analyzed by graphite furnace atomic absorption spectrometer (Varian AAS 800 Spectra) in order to determine the metals concentrations. The standard addition method was used for Cd measurements, and the Al, Fe, Zn and Pb concentrations were calculated from calibration curves. Triplicate measurements were performed and the reproducibility was found to be between 0 and 5% for all metals.

Results obtained on the certified reference material indicate a good accuracy of the analyses: the mean recovery for Al, Fe, Pb, Zn and Cd were respectively 87±8, 96±3, 107±5, 95±6 and 99±11%. The low standard deviations (within about ±10%) demonstrate a good reproducibility of results. The blank values were below the detection limit.

The pH data used in the discussion are from the simultaneous collection of bulk deposition of major elements in a separate collector at Pirio.

2.4 Selection of comparable data

In order to assess the spatial and the temporal variability of the metal fluxes in the North Western Mediterranean Sea, the fluxes obtained during a survey in our remote site were compared with the 2 year previous survey at the same site from January 27th, 1995 to March 18th, 1997 (Ridame 1997, Ridame *et al.* 1999) and with the surveys performed for various Mediterranean sites (Tables 1 and 3). In this discussion, we have only considered datasets obtained on a representative sampling period and using comparable sampling protocols. Similar bulk fluxes have been determined since 1985 at only 3 coastal stations : an island one, Cap Cavallo (Bergametti 1987, Remoudaki 1990, Remoudaki *et al.* 1991) in Corsica; and two continental ones, Cap Ferrat (Migon *et al.*, 1997) on the French Riviera coast and Tour du Valat (Guieu 1991, Guieu *et al.*, 1993, 1997) in the Rhone delta (Figure1). The various devices used and the sampling protocols at each site are described in Table 1.

In the discussion concerning the terrigenous elements (Al, Fe), data from the Pirio station are compared with the Saharan dust input recorded at another Corsica station - Ponte Leccia (42° 21' N, 9° 12' E) (Figure 1). The protocol used for the determination of the Saharan dust input at this site is described in Loÿe-Pilot *et al.* 1986 and Loÿe-Pilot and Martin, 1996.

3. METALS FLUXES AT PIRIO in 1999/2000

The bulk deposition fluxes for each sample measured for 18 months are given in Table 2 and are expressed in $mg.m^{-2}$ and $\mu g.m^{-2}$; daily fluxes are computed and are expressed $mg.m^{-2}.d^{-1}$, µg.m^{-2}.d^{-1} or ng.m^{-2}.d^{-1}. In order to compare our results with those previously published and to discuss the temporal evolution, we consider the fluxes for a one-year period . For this reason, two annual fluxes were derived from the present data (annual flux year 1: P14→P21 (30 May 1999 to 27 May 2000); and the annual flux year 2: P18 →P24 (6 November 1999 to 6 November 2000)). Fluxes recorded at the other sites and in the previous study at Pirio were also recast in a 1-year period (Table 3).

3.1 Temporal variability of the atmospheric fallout

Daily fluxes were computed for the 12 sampling periods in order to discuss the intra-annual variability (Table 2 and Figure 2). Al and Fe display the maximum variability of daily fluxes with factor higher than 300. The variability of daily lead fluxes is an order of magnitude lower (34), like those of zinc and cadmium which are still lower (19 and 11 respectively).

The terrigeneous elements, Al and Fe, present the highest values of annual fluxes 644-1010 and 340-545 mg.m^{-2}.y^{-1} respectively and a high interannual variability (factor 1.6). The fluxes of Pb present also a significant interannual variability with a factor of 2.1. At the opposite, annual fluxes of Zn and Cd are stable with a factor of 1.1.

The distinct variability of the different metals reflects their different origins.

3.2 Origin of the metals

Each sample represents an integration of the total atmospheric fallout for periods of various durations (from 26 to 77 days). In these conditions, a single sample represents the mixing of fallout from air masses of different origins, with different loads of pollutants and natural aerosols. In order to identify the main sources of metals, aluminum is used as a tracer of the crustal particles. However in this study, we will not use only the crustal Al content as the reference since it is not representative of surface soils which are the source of atmospheric terrigeneous components (Schütz and Rahn 1982, Hong *et al.*, 1996). In Corsica, as in the open North Western Mediterranean, the terrigeneous component is made of Saharan dust which represents more than 90% of the total particulate input (Loÿe-Pilot and Martin, 1996). Hence the Western Mediterranean reference values for Al concentration (7.09%), Fe/Al (0.63), Pb/Al (3.4.10^{-4}), Zn/Al (10.3.10^{-4}) and Cd/Al (1.7.10^{-6}) ratios in the Saharan crustal end member were taken from Guieu & Thomas (1996) and Guieu et al. (submitted). As a comparison, Upper Crust ratios of elements concentrations taken from Wedepohl (1995) were tested (Pb/Al=2.2.10^{-4}, Zn/Al=6.7.10^{-4} and Cd/Al=1.32.10^{-6}).

Iron is well correlated to aluminum (Figure 3), indicating that it is associated with terrigenous particles originating from the Sahara desert.

The Metal/Al ratios for Pb, Cd and Zn are much higher than those found in the Saharan end-member (Figure 3) hence indicating that they are borne by aerosols generated by human activities. The contribution of anthropogenic fraction for each metal (Me) is calculated as the excess fraction Xs, expressed in percentage.

$$Xs= (Me_{sample}- (Me/Al_{ref} \times Al_{sample}))/ Me_{sample} \times 100$$

For some samples the crustal fraction of Pb is not negligible (Table 3, Figure 3) especially during periods of high Saharan dust inputs (high Al inputs). The Sahara desert is thus a potential source of «natural» lead in the case of a major input of dust. The Pb excess fraction for the whole period represents from 52 % (Saharan reference) to 72 % (Upper crust reference). The contribution of anthropogenic sources is highest during the winter period when Saharan dust input is very low (Al input lower than 0.2mg.m^{-2}), which also corresponds to the weakest pH (Figure 4), due to the occurrence of acid rains.

Cd and Zn are typically associated with non-crustal aerosols with an excess fraction of 96-100% and 84-90% respectively (Figure 2 and Table 4).

These results are in good agreement with the emission inventories of anthropogenic sources of metals (Nriagu, 1989, Pacyna, 1984, 1998) and with previous results established at various coastal sites of the North Western Mediterranean (Guieu *et al.*, 1997, Ridame *et al.* 1999). The present results confirm that Mediterranean aerosols have an important man-made background (Martin *et al.*, 1989; Chester *et al.*, 1993, Guieu *et al.*, 1997, Guerzoni et al., 1999).

4. EVOLUTION OF THE FLUXES OVER THE PAST DECADE

In order to assess the spatial and the temporal variability of the metal fluxes in the North Western Mediterranean Sea, the two annual fluxes obtained in our remote site, are compared with those previously established during the 2-year survey at the same site and for the selected Mediterranean sites (Tables 1 and 3). Considering the whole data set (Table 3), the mean fluxes present important variations from one site to another. We will discuss the case of the terrigeneous components (Al and Fe) and the case of the anthropogenic components (Cd, Zn and Pb).

4.1 The terrigeneous components : Al and Fe

The annual fluxes of Al (642-1014 $mg.m^{-2}.y^{-1}$) obtained in this study are of the same order of magnitude as the fluxes measured at Cap Cavallo for 1985-86 (516-1036 $mg.m^{-2}.y^{-1}$) and Tour du Valat (845-990 $mg.m^{-2}.y^{-1}$), but much higher than those determined in the previous survey -in the years 1995 and 1996 (171-270 $mg.m^{-2}.y^{-1}$) and those reported by Journel (1998) for Cap Ferrat (283 ± 520 $kg.km^{-2}.y^{-1}$) for 1995 (Figure 5).

Spatial variations are not likely between the two Corsican sites (Cap Cavallo and Pirio). Then the measured fluxes show a very high temporal variability of the Al input (up to a factor of 6). This reflects the temporal variability of the Saharan dust fallout that is the source of aluminum in the open Mediterranean. In fact the Saharan dust monitoring in Corsica (Loÿe-Pilot and Martin 1996) has shown a decrease of the dust fallout in the nineties as compared to the end of the eighties (Figure 6). The higher Al fluxes measured at Pirio during 18 months in the years 1999/2000 could perhaps indicate a reverse trend, the significance of which is to be looked for in the short-term climatic variability.

These data also show that there is no significant spatial variability of the Saharan dust input between Corsica and the French coast.

4.2 Anthropogenic components: Zn, Cd and Pb.

The annual fluxes of lead (1.0 and 0.5 $mg.m^{-2}.y^{-1}$) are very near of those measured at the same site in the years 1995-1996 (1.1 and 0.7 $mg.m^{-2}.y^{-1}$). They are 3 or 4 times lower than those measured in the period 1988-1989 at Cap Ferrat and much lower (by a factor of 15 to 30) than measured at Cap Cavallo in the years 1985-1986 (Table 3).

The annual fluxes of Zn (5.4-5.6 $mg.m^{-2}.y^{-1}$) and Cd (0.03 $mg.m^{-2}.y^{-1}$) at the Pirio station are similar to those previously measured in 1995-1996 (6.1-4.2 $mg.m^{-2}.y^{-1}$ and 0.04-0.07 $mg.m^{-2}.y^{-1}$) and among the lowest values published for this region (Table 3).

For Cd, the flux is lower but of the same order of magnitude as that one found at the Cap Ferrat site (no data are available for the Cap Cavallo site). The flux at Tour du Valat is 20-40 times higher than at the Pirio site (Table 3 and Figure 7).

For Zn, the flux at Tour du Valat and Cap Ferrat is of the same order of magnitude and about 20 times higher than that at Pirio (Table 3 and Figure 8) (no data are available for Cap Cavallo).

The observed differences can be related to (1) the spatial variability, and/or (2) the temporal variability related to the actual evolution of the concentrations in the atmosphere over the past decade, (3) the possible contamination at the previous stations.

4.2.1 Spatial variability

The hypothesis of a spatial variability of the fluxes between the different regions is not in agreement with results of an inter-comparison that took place during a one month period simultaneously at 3 sites: Tour du Valat, Cap Ferrat and a site near Ajaccio in Corsica. This inter-comparison showed that the total atmospheric fluxes measured were the same (Guieu *et al.*, 1997). Moreover, the fact that the Ni, Cu, Cd fluxes are of the same order of magnitude at Cap Ferrat and Pirio (previous survey, Ridame et al., 1999) indicates that there is no clear decreasing trend of metal fluxes with respect to the distance of the sampling site from the continental pollution sources between the French coast and Corsica. This still confirms the existence of a rather homogenous polluted background over the North Western Mediterranean (Martin et al 1989, Chester et al 1993).

The two annual Pb fluxes measured at the Pirio station are (1.0 and 0.5 $kg.km^{-2}.y^{-1}$) are similar to those measured in 1995-1996 and appear to be lower than the fluxes recorded at the other Mediterranean sites (Table 3 and Figure 9). The recorded decrease of the atmospheric flux of lead from 1985 (Cap Cavallo) up to present time (Pirio) (Figure 9) can be estimated to be a factor of about 30. Since the two sites are quite close to each other (~25 km), the spatial variability is not a realistic assumption; a possible variability between Pirio and Cap Cavallo due to a different rainfall pattern has been ruled out (Ridame et al 99). The difference observed should be attributed to the temporal variability, related to the reduction of emissions, or partly to a possible contamination at the Cap Cavallo site.

4.2.2 The temporal variability related to the actual evolution of the concentrations in the atmosphere over the past decade

In the following discussion, we will examine if the acute decrease observed between the fluxes of Cd, Zn, Pb over the past decade can be the result of a reduction in the metals` emissions. The emissions in Europe are known for the period between 1955 and 1990 (Pacyna 1998, 1997) and up to 1998 (EMEP 2001).

Cd. For Cd**,** a diminution of emissions by factors of 1.1, 1.4 and 1.5 are recorded for the periods 1985/1990, 1990/1995 and 1990/1998 respectively. These low values result from the averaging of emissions from the European countries with the effective emission reduction policy (Germany: decrease x 1.8 for 1985/1990 and x 2.8 for 1990/1998) and the European countries where emissions are still increasing (Spain: increase x 3.4 for 1985/1990 and x 1.1 for 1990/1998). For Germany, where data on emissions are available up to 1995 and the reduction policies are effective, a diminution by a factor of 3.3 is recorded between 1985 and 1995 (Karl *et al.*, 1997): hence, a factor of 4 represents the maximum value at a European scale of the decreasing factor. The decreasing factor of 30 found between Tour du Valat and Pirio (Table 3 and Figure 7) is thus totally unrealistic with the knowledge of the evolution of the emissions in Europe. This fact confirms the existence of a local or regional source of Cd at the Tour du Valat site.

Zn. As the evolution of the Zn emissions are of the same order of magnitude that those for Cd - decreasing factor of 1.5 between 1990 and 1998 - (Pacyna, 1998; EMEP 2001), the decreasing factors of 16 and 23 recorded respectively between Cap Ferrat, Tour du Valat and Pirio have to be explained by a local or regional source of contamination at the two continental sites (Table 3 and Figure 8). This finding demonstrates that the Cd and Zn fluxes measured at La Tour du Valat and Zn at Cap Ferrat cannot be extrapolated to the North Western Mediterranean. For this reason, these data were not taken into account in the global budget presented by Guieu *et al.* (1997) and Elbaz-Poulichet *et al.* (2001).

In fact the decrease of the emissions of Cd and Zn between 1995 and 1998 is only of a factor of 1.1 at the European scale: it is then normal that the fluxes measured at Pirio in 1995 and 1996 and during 1999/2000 are in the same range. The interannual variability related to the weather variability is higher than the variation of emissions and is responsible for the differences observed between the annual fluxes.

Pb. The important decrease of lead in the atmospheric flux could be the consequence of the limitation in the use of lead additives in gasoline. As a consequence of this limitation (in effect in France since 1988), a decreasing factor of the atmospheric lead concentrations of 1.3 and 1.4 in aerosols and rainwater respectively was observed between 1986 and 1992 at Cap Ferrat (Migon *et al.* 1993, 1994). Marine lead concentrations measured in the North Western Mediterranean basin from 1983 to 1992 seem to decrease by a factor of 2 in the surface waters (Nicolas *et al.*, 1994). In 1990, while northern Europe had already started to use intensively unleaded gasoline, 72% of atmospheric lead was still coming from the use of leaded gasoline at the European scale (Pacyna, 1998).

Between 1985 and 1990, the decrease of lead emissions is highly variable depending on the country considered: at the global European scale, the decrease is a factor of 1.1 (EMEP 2001) to 1.6 (Pacyna 1998); in France it is a factor of 2.9 while, in Eastern Europe, emissions are constant or increasing slightly. This trend means that between 1985 and 1990, the maximum diminution that could be recorded at the coastal French sites could only be a factor of about 3.

The diminution recorded between 1985-1987 (Cap Cavallo) and 1990 (Tour du Valat) indicates a factor of 4 to 9: consequently, this decrease cannot be explained by the emission reduction policy alone. Other anthropogenic sources of Pb in the atmosphere (stationary emissions) decreased by a factor of 2.2 between 1985 and 1995 in Germany (Karl *et al.*, 1997) where environmental policies are the most demanding. Thus the evolution of these sources cannot explain the measured decrease either.

In France where the substantial decrease of emissions has occurred since 1985, the cutting-down of lead emission resulted both from the use of unleaded gasoline and the increase of the number of diesel cars led to a diminution by a factor of 8.5 in the period between 1985 and 1995 and 11.1 between 1985 and 1998 (EMEP 2001).

This reduction is still much smaller than the factor recorded between the Cap Cavallo (1985-1987) and the Pirio first survey (1995-1996) which is of 14-44.

The Figure 9 shows that the decrease of the total atmospheric flux of lead observed since 1989 in the North Western Mediterranean corresponds to the decrease of the leaded gasoline consumption and stationary sources emissions, while only a part of the observed flux decrease since 1985 can actually be attributed to the decrease of emissions, the other part being due to a likely local contamination at the previous Corsican sampling station.

The lowest annual flux of the last 15 years (0.5 $mg.m^{-2}.y^{-1}$) which was recorded at Pirio from November 1999 to November 2000 may perhaps indicates the still decreasing trend of emissions in the near Italy and some countries of Northern Europe, which was counterbalanced in 1999 by the input of natural lead by Saharan dust.

5. CONCLUSIONS

In addition to the results of the previous 2-years survey in Corsica, an 18 months dataset of atmospheric deposition of metals allows to reassess the total atmospheric fluxes over the North Western Mediterranean. The comparison with the previous data obtained in the same area with the same methodology allows an interpretation of the possible changes in composition or intensity of the deposition over the past decade.

For the terrigeneous components Al and Fe, the flux at the Pirio station in 1999/2000 is in the same range as the fluxes measured during the end of the eighties, whilst they are much higher than those measured at the same site in 1995-1996 or at the French coast in 1995. These metals are originating from the Saharan source and the observed variation corresponds to the variation of the Saharan dust fallout. The 1995 and 1996 Saharan dust fluxes (measured and derived from aluminum measurements) confirm the decreasing tendency of the Saharan dust fallout recorded in the nineties in Corsica and the French Riviera.

When considering the anthropogenic elements, the mean fluxes of Zn and Cd (5.5 and 0.03 $mg.m^{-2}$) at the Pirio station are among the lowest values published for this region (data available since 1989). For Cd, the flux is lower but of the same order of magnitude as the one measured at the Cap Ferrat site. The flux at Tour du Valat, 20-40 times higher than at Pirio, reveals a local or regional contamination. For Zn, the flux at Tour du Valat and Cap Ferrat are of the same order of magnitude and about 20 times higher than that at Pirio, still indicating a local or regional contamination at the two continental coastal sites. The recorded decrease of the atmospheric flux for lead from 1989 (Tour du Valat) up to present time (Pirio) fits with the decrease of emissions at the European level. But the acute decrease (by a factor of about 30) between the fluxes measured in Corsica at Cap Cavallo in the years 1985-1986 and at Pirio in the years 1995-1996 and 1999/2000 indicates that a local contamination occurred at the previous Corsican site.

No clear downward trend of metal fluxes as a function of the distance of the sampling site from the continental pollution sources between the French coast and Corsica can be observed.

ACKNOWLEDGMENTS

This study was conducted as a contribution to the Programme for the Assessment and Control of Pollution in the Mediterranean Region (MED POL) implemented in the framework of the Barcelona Convention, and was partly supported from the Mediterranean Trust Fund through a contract with the World Meteorological Organization.

REFERENCES

Bergametti, G., 1987. Apports de matière par voie atmosphérique à la Méditerranée Occidentale : aspects géochimiques et météorologiques. Thèse de Doctorat, Université de Paris VII, 296 pp.

Bergametti, G., Buat-Ménard, P. and Martin, D., 1988. Trace metals in the Mediterranean atmosphere. In: S. Beilke, J. Morelli and G. Angeletti (eds), Field Measurements and Their Interpretation, Air Pollution Report, 14, CEC, Brussels, 88-95.

Bergametti, G., Dulot, A.L., Buat-Ménard, P., Losno, R., and Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the Northwestern Mediterranean, *Tellus*, 41B, 353-361.

Chester, R., Saydam, A.C. and Sharples E.J, 1981. An approach to the assessment of local trace metals pollution in the Mediterranean marine atmosphere, *Marine Pollution Bulletin*, 12, 426-431.

Chester, R., Sharples E.J., Sanders, G.S. and Saydam, A.C., 1984. Saharan dust incursion over the Tyrrhenian Sea, *Atm. Env*. 18, 5, 929-935.

Chester, R., M. Nimmo, K.J.T. Murphy and E. Nicolas, 1990. Atmospheric trace metals transported to the western Mediterranean : data from a station on Cap Ferrat. *In: 2nd EROS 2000 Workshop, Blanes (Espagne), 6-9 Fevrier 1990, Water Pollution Research Report, 20,* CEC, Brussels, 597-612.

Chester R., M. Nimmo, M. Alarcon, M. Saydam, C. Murphy, G. S. Sanders and P. Corcoran, 1993. Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions, *Oceanologica Acta*, 16, 3, 231-246.

Duce R.A. and Tindale N., 1991. Atmospheric transport of iron and its deposition in the ocean, *Limnology and Oceanography*, 36, 8, 1715-1726.

Duce, R.A., Liss P.S., Merrill J.T., Atlas E.L., Buat-Ménard P., Hicks B.B., Miller J.M., Prospero J.M., Arimoto A., Church T.M., Ellis W., Gallowy J.N., Hansen L., Jickells T.D., Knap A.H., Reinhardt K.H., Schneider B., Soudine A., Tokos J.J., Tsunogai S., Wollast R. and Zhou M., 1991. The atmospheric input of trace species to the world ocean, *Global Biogeochemical Cycles*, 5, 3, 193-259.

Dulac, F., Buat-Ménard, P., Arnold, M., Ezat, U., and Martin, D., 1987. Atmospheric input of trace metals to the Western Mediterranean Sea : 1. Factors controlling the variability of atmospheric concentrations, *J. Geophys. Res*., 92, 8437-8453.

Elbaz-Poulichet F., Guieu C., and Morley N., 2001. A reassessment of trace metals budgets in the Western Mediterranean Sea, *Marine Pollution Bulletin*, in press.

EMEP, 2001. Data from the EMEP web site -www.emep.int - (february 2001).

Fitzwater, S.E, Knauer, G.A. and Martin, J.H., 1982. Metal contamination and its effects on primary production measurements, *Limnol. Oceanogr*., 27(3), 544-551.

Guerzoni, S., Lenaz, R., and Quarantotto, G., 1988. Field Measurements at sea : atmospheric particulate trace metals "end-members" in the Mediterranean, *Air Pollution Research Report,* 14, CEC, Brussels, 96-100.

Guerzoni S., Chester R., Dulac F., Herut B., Loÿe-Pilot M.D., Measures C., Migon C., Molinaroli E., Moulin C., Rossini P., Saydam C., Soudine A., Ziveri P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Progress in Oceanograph*y, 44, 147-190.

Guieu C., 1991. Apports atmosphériques à la Méditerranée Nord-Occidentale. Thèse de Doctorat, Université de Paris VI, 225 p.

Guieu C., J. M. Martin, A. J. Thomas and F. Elbaz-Poulichet, 1991. Atmospheric versus river input of metals to the Gulf of Lions: total concentrations, partitioning and fluxes, *Marine Pollution Bulletin*, 22, 4, 176-183.

Guieu C., J. Zhang, A. J. Thomas, J. M. Martin and J. C. Brun-Cottan, 1993. Significance of the atmospheric fallout upon the upper layer water chemistry of the North Western Mediterranean, *Journal of Atmospheric Chemistry*, 17, 45-60.

Guieu, C. and Thomas, A.J., 1996. Saharan aerosols: from the soil to the ocean, *In: S. Guerzoni and R. Chester (eds.), The Impact of desert dust across the Mediterranean*, Kluwer Acad. Publ., 207-216.

Guieu, C., Chester, R., Nimmo, M., Martin, J.M., Guerzoni, S., Nicolas, E., Mateu, J. and Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean, *Deep-Sea Research II*, 44, 3-4, 655-674.

Guieu C, Loÿe-Pilot M.D., Ridame C., and Thomas C. Chemical characterization of the Saharan end-member; some biogeochemical implications in the Western Mediterranean. Submitted to *Journal of Geophysical research.*

Jickells, T., 1995. Atmospheric inputs of metals and nutrients to the oceans : their magnitude and effects. Marine Chemistry 48 : 199-214.

Journel B., 1998. Etude géochimique des apports atmosphériques de métaux en Mer Ligure, Thèse de Doctorat, Université Aix-Marseille III, 250pp.

Hong S., Candelone J.P., Turetta C. and Boutron C.F., 1996. Changes in natural lead, copper, zinc and cadmium concentrations in central Greenland ice from 8250 to 149100 years ago: their association with climatic changes and resultant variations of dominant source contributions, *Earth Planet. Sci .Let*., 143, 233-244.

Karl U., Sasse H., Veaux Ch., Rentz O., 1997. Heavy metals emissions in Germany-Emissions sources and emission evaluation methodologies. *In: Report and proceedings of the workshop on the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development,* EMEP/MSC-E report 1/97 (volume II), WMO-GAW report n°117. WMO, Genève, 134-144.

Loÿe-Pilot, M.D., Martin, J.M., Morelli, J., 1986. Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature*, 321, 6088, 427-728.

Loÿe-Pilot, M.D. and Morelli, J., 1988. Fluctuations of ionic composition of precipitations collected in Corsica related to changes in the origins of incoming aerosols. *J. Aerosol Sci.*, 19, 5, 577-585.

Loÿe-Pilot, M.D., Martin, J.M. and Morelli, J., 1990. Atmospheric input of inorganic nitrogen to the Western Mediterranean, *Biogeochemistry*, 9, 117-134.

Loÿe-Pilot, M.D., 1995. Suivi de l'évolution du dépôt atmosphérique total de plomb, soufre, azote et de poussières sahariennes en milieu méditerranéen, Rapport MAB-Reserve de Biosphere du Fango, 105 pp.

Loÿe-Pilot, M.D. and Martin, J.M., 1996. Saharan dust input to the Western Mediterranean : an eleven years record in Corsica. *In: S.Guerzoni and R.Chester (eds.), The impact of desert dust across the Mediterranean*, Kluwer Acad. Publ., 191-199.

Loÿe-Pilot, M.D., Ridame, C., Guieu, C., 1998. Suivi de l'évolution du dépôt atmosphérique total de plomb, soufre, azote et de poussières sahariennes en milieu méditerranéen, Rapport final du programme 1995-1996, Réserve de Biosphère du Fango, MAB France, 40 pp.

Martin, J.M., Elbaz-Poulichet, F., Guieu, C., Loÿe-Pilot, M.D. and Han, G., 1989. River versus atmospheric input of material to the Mediterranean Sea : an overview. *Marine Chemistry*, 28, 159-182.

Martin J-M. and Whitfield M., 1983. The significance of the river input of chemical elements to the ocean, in Trace metals in sea water, ed., C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg , pp 265-296, Plenum, New York.

Migon, C., 1988. Etude de l'apport atmosphérique en métaux-traces et sels nutritifs en milieu côtier méditerranéen; implications biogéochimiques. Thèse de Doctorat, Université de Nice, 217 pp.

Migon, C., and Caccia, J.L., 1990. Separation of anthropogenic and natural emissions of particulate heavy metals in the Western Mediterranean atmosphere, *Atmospheric Environment*, 24A, 2, 399-405.

Migon, C., Morelli, J., Nicolas, E., and Copin-Montégut, G., 1981. Evaluation of total atmospheric deposition of Pb, Cd, Cu and Zn to the Ligurian Sea, *Sci. Total Environ*., 105, 135-148.

Migon, C., 1993. Riverine and atmospheric inputs of heavy metals in the Ligurian Sea, *Sci. Total. Environ*., 138, 289-299.

Migon C., Jourdan E., Nicolas E., and Gentilli B., 1994. Effects of reduced leaded fuel consumption on atmospheric lead behaviour, *Chemosphere*, 28, 1, 139-144.

Migon, C., Journel, B. and Nicolas, E., 1997. Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea, *Atmospheric Environment*, 31, 6, 889-896.

Nicolas E., Ruiz-Pino D., Buat-Ménard P. and Béthoux J-P., 1994. Abrupt decrease of lead concentration in the Mediterranean sea: a response to antipollution policy, Geophysical Research Letters, vol. 21, N° 19: 2119-2122.

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals, *Nature*, 338, 47-49.

Pacyna, J., 1984. Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europe, *Atmospheric Environment*, 18, 1, 41-50.

Pacyna, J., 1997. Emissions inventories for heavy metals and persistent organic pollutants in Europe. *In: Report and proceedings of the workshop on the assesment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development,* EMEP/MSC-E report 1/97 (volume I), WMO-GAW report n°117. WMO, Genève, pp. 4-17.

Pacyna J., 1998. Source inventories for atmospheric trace metals*, In: R.M. Harrison and R. Van Grieken, Atmospheric particles*, J. Wiley & Sons Ltd., 386-423.

Patterson, C.C and Settle, D.M.,1987. Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale, *Marine Chemistry*, 22, 137-162.

Remoudaki, E., 1990. Etude des processus contrôlant la variabilité temporelle des flux atmosphériques de polluants et de poussières minérales en Méditerrannée Occidentale. Thèse de Doctorat, Université de Paris VI, 224 pp.

Remoudaki E., G. Bergametti and P. Buat-Ménard, 1991. Temporal variability of atmospheric lead concentrations and fluxes over the Northwestern Mediterranean Sea, *Journal of Geophysical Research*, 96, 1043-1055.

Ridame C. 1987. Les apports atmosphériques de métaux traces en Méditerranée Nord-Occidentale : résultats de 2 ans de mesure dans la Réserve du Fango (Corse). Rapport de DEA Océanographie, Météorologie et Environnement-Option : Géochimie Marine, Université P. et M. Curie (Paris 6). 41 p,.

Ridame C., Guieu C., Loÿe-Pilot M.D., 1999. Total atmospheric fluxes of aluminium, iron and trace metals in the North Western Mediterranean for a two year measurement period (1995 to 1997) at a remote coastal station (Corsica). *Journal of Geophysical research*, 104, 23, 127-138.

Schutz L. and Rahn K.A., 1982. Trace element concentrations in erodible soils, *Atmospheric Environment*, 16, 171-176.

Wedepohl K.H., 1995. The composition of the continental crust, *Geochimica and Cosmochimica Acta*, vol. 59, No.7, 1217-1232.

Table 1. *Characteristics of the sampling and analytical protocols used at the different sites in the North Western Mediterranean where bulk sampling was performed.*

	Capo Cavallo	Tour du Valat	Cap Ferrat	Pirio
Type of device	"Crapal" acidified to pH 1	"Crapal" acidified to pH 1	Filtration kit filled-up with acidified seawater	4 l bottle with funnel
Surface cm	1020	1020	50	113
Analysis	acid soluble fraction + insoluble fraction* AAS + XSF	evaporation of an aliquote/digestion AAS	acid soluble fraction AAS	total evaporation/digestion AAS
Duration of one sample (days)	4 to 75	15 to 31	7	96-97: 28 to 132 99-2000: 26 to 77

(1) Bergametti, 1987. Remoudaki, 1990

(2) Guieu, 1991

(3) Migon *et al.*, 1997

*: only acid soluble fraction for Pb

XSF= X fluorescence spectrometry, AAS = atomic absorption spectrometry

Crapal: device used originally by the French Commissariat à l'Energie Atomique, made of plexiglass.

Table 2. Bulk inputs of metals at Pirio -Corsica and corresponding daily fluxes.

	Sampling dates	Sample label	Sampling duration	Rainfall	*pH*	**Al**		**Fe**		**Pb**		**Zn**		**Cd**	
			days	mm		mg/m	mg/m/d	mg/m	mg/m/d	mg/m	µg/m/d	mg/m	µg/m/d	µg/m	ng/m/d
	5-1/5-30	**13**	28.7	44.6		46.4	1.62	35.1	1.22	0.052	1.81	0.14	4.73	1.5	53
1	5-30/7-8	**14**	39.0	33.7	*6.08*	55.4	1.42	33.5	0.86	0.062	1.59	0.28	7.28	2.1	54
	7-8/8-26	**15**	49.0	36.0	*6.90*	452.9	9.24	243.5	4.97	0.211	4.31	1.60	32.6	4.1	83
	8-26/9-30	**16**	35.0	123.8	*5.58*	167.5	4.79	93.6	2.67	0.201	5.74	1.23	35.3	6.2	177
	9-30/11-6	**17**	37.0	230.6	*5.19*	46.3	1.25	24.7	0.67	0.126	3.41	0.42	11.3	4.5	122
	11-6/12-15	**18**	39.0	216.3	*4.77*	6.4	0.16	3.9	0.10	0.099	2.53	0.78	19.9	2.4	61
	12-15 99/1-17	**19**	33.0	12.1	*5.01*	0.8	0.02	0.5	0.02	0.025	0.77	0.06	1.93	0.5	16
	1-17/3-12	**20**	55.3	33.5	*4.79*	1.5	0.03	2	0.04	0.107	1.94	0.35	6.34	3.1	57
	3-12/5-27	**21**	76.0	176.9	*6.97*	278.7	3.67	143.4	1.89	0.124	1.63	0.91	12.0	8.0	105
2	5-27/7/26	**22**	59.9	68.6	*6.14*	71.9	1.20	38.4	0.64	0.010	0.17	1.30	21.8	3.6	60
	7-26/10-11	**23**	76.9	165.0	*6.01*	116.4	1.51	64.4	0.84	0.055	0.71	1.05	13.7	5.2	68
	10-11/11-6	**24**	26.1	193.3	*6.17*	168.3	6.46	87.1	3.34	0.046	1.78	0.94	36.1	5.5	210
	Total on sampling period		555	1334		**1413**	2.55	**770**	1.39	**1.12**	2.02	**9.07**	16.3	**47**	84
	5-30 99/5-27 00	**Year 1**	363.3	863		**1010**	2.78	**545**	1.50	**0.96**	2.63	**5.6**	15.5	**31**	85
	11-6 99/11-6 00	**Year 2**	366.1	866		**644**	1.76	**340**	0.93	**0.47**	1.27	**5.4**	14.7	**28**	77

Table 3. Comparison of annual bulk fluxes of metals (in mg.m-2.y-1.) at Piro – Corsica – with others published values for the North Western Mediterranean Sea

	Corsica		**Rhone delta**		**French Riviera**	**Corsica**			
Station	Cap Cavallo	Cap Cavallo	Tour du Valat	Tour du Valat	Cap Ferrat	Pirio	Pirio	Pirio	Pirio
sampling period	3/25/85-3/22/86	3/22/86-4/16/87	5/11/88 -5/6/89	7/1/88 - 7/19/89	10/1/92-9/30/93	3/14/95-3/13/96	3/13/96-3/18/97	5/30/99-5/27/00	11/6/99-11/6/00
reference	a	b	c	c	d	e	e	this study	this study
Al	1036	516	990	845		171	270	1010	644
Fe	679	325	945	851		118	156	545	340
Pb	31	15	3.5	3.4	3.1	1.1	0.7	1.0	0.5
Zn			115.5	96.1	80.3	6.1	4.2	5.6	5.4
Cd			1.6	1.2	0.07	0.07	0.04	0.03	0.03

(a) Bergametti 1987

(b) Remoudaki 1990

(a) and (b) Remoudaki et al. 1991 (in the case of Pb)

(c) Guieu 1991.

(d) Migon et al. 1997

(e) Ridame 1997, Ridame et al 1999

Table 4. Anthropogenic fraction expressed as excess fraction of iron, lead, zinc and cadmium.
The excess fraction ([Met $_{sample}$- Met/Al $_{ref}$ x Al $_{sample}$]/Met $_{sample}$x100) was computed using 2 different references for the terrigenous component: a= Saharan end-member, b= Upper Crust.

Sampling dates	Sample label	*pH*	**Al**	**Fe**	***Excess***		**Pb**	***Excess***		**Zn**	***Excess***		**Cd**	***Excess***	
			mg/m	mg/m	*%*	*%*	mg/m	*%*	*%*	mg/m	*%*	*%*	µg/m	*%*	*%*
					a	*b*		*a*	*b*		*a*	*b*		*a*	*b*
5-1/5-30 99	**13**		46.4	35.1	*17*	*47*	0.052	*70*	*80*	0.14	*65*	*77*	1.5	*100*	*96*
5-30/7-8 99	**14**	*6.08*	55.4	33.5	*0*	*34*	0.062	*70*	*80*	0.28	*80*	*87*	2.1	*100*	*97*
7-8/8-26 99	**15**	*6.90*	452.9	244	*0*	*26*	0.211	*27*	*53*	1.60	*71*	*81*	4.1	*100*	*86*
8-26/9-30 99	**16**	*5.58*	167.5	93.6	*0*	*29*	0.201	*72*	*82*	1.23	*86*	*91*	6.2	*100*	*97*
9-30/11-6 99	**17**	*5.19*	46.3	24.7	*0*	*25*	0.126	*88*	*92*	0.42	*89*	*93*	4.5	*100*	*99*
11-6/12-15 99	**18**	*4.77*	6.4	3.9	*0*	*35*	0.099	*98*	*99*	0.78	*99*	*99*	2.4	*100*	*100*
12-15 99/1-17 00	**19**	*5.01*	0.8	0.5	*0*	*36*	0.025	*99*	*99*	0.06	*99*	*99*	0.5	*100*	*100*
1-17/3-12 00	**20**	*4.79*	1.5	2.0	*0*	*70*	0.107	*100*	*100*	0.35	*100*	*100*	3.1	*100*	*100*
3-12/5-27 00	**21**	*6.97*	278.7	143	*0*	*22*	0.124	*24*	*51*	0.91	*69*	*80*	8.0	*100*	*96*
5-27/7/26 00	**22**	*6.14*	71.9	38.4	*0*	*25*	0.010	*0*	*-58*	1.30	*94*	*96*	3.6	*100*	*97*
7-26/10-11 00	**23**	*6.01*	116.4	64.4	*0*	*28*	0.055	*28*	*53*	1.05	*89*	*93*	5.2	*100*	*97*
10-11/11-6 00	**24**	*6.17*	168.3	87.1	*0*	*23*	0.046	*0*	*20*	0.94	*82*	*88*	5.5	*100*	*96*
Total on sampling			**1413**	**770**	***0***	***27***	**1.12**	***57***	***72***	**9.07**	***84***	***90***	**46.7**	***100***	***96***

a: Guieu & Thomas 1996 Guieu et al. submitted
b: Wedepohl 1995 (Upper Continental Crust)

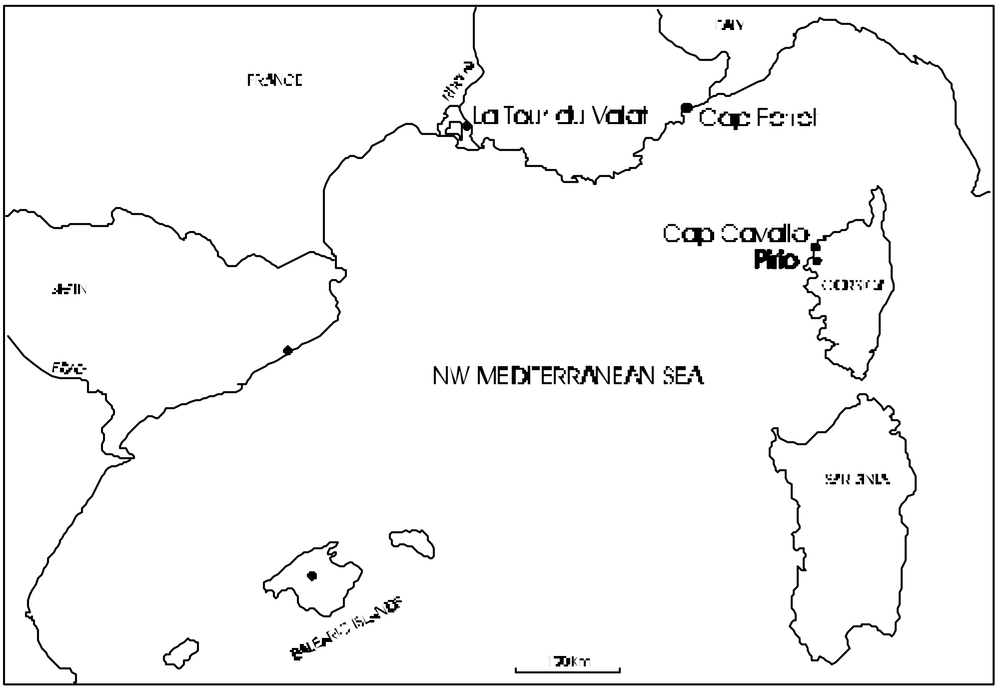


Figure 1. Location of the Pirio sampling site along with the other sites discussed in the paper.

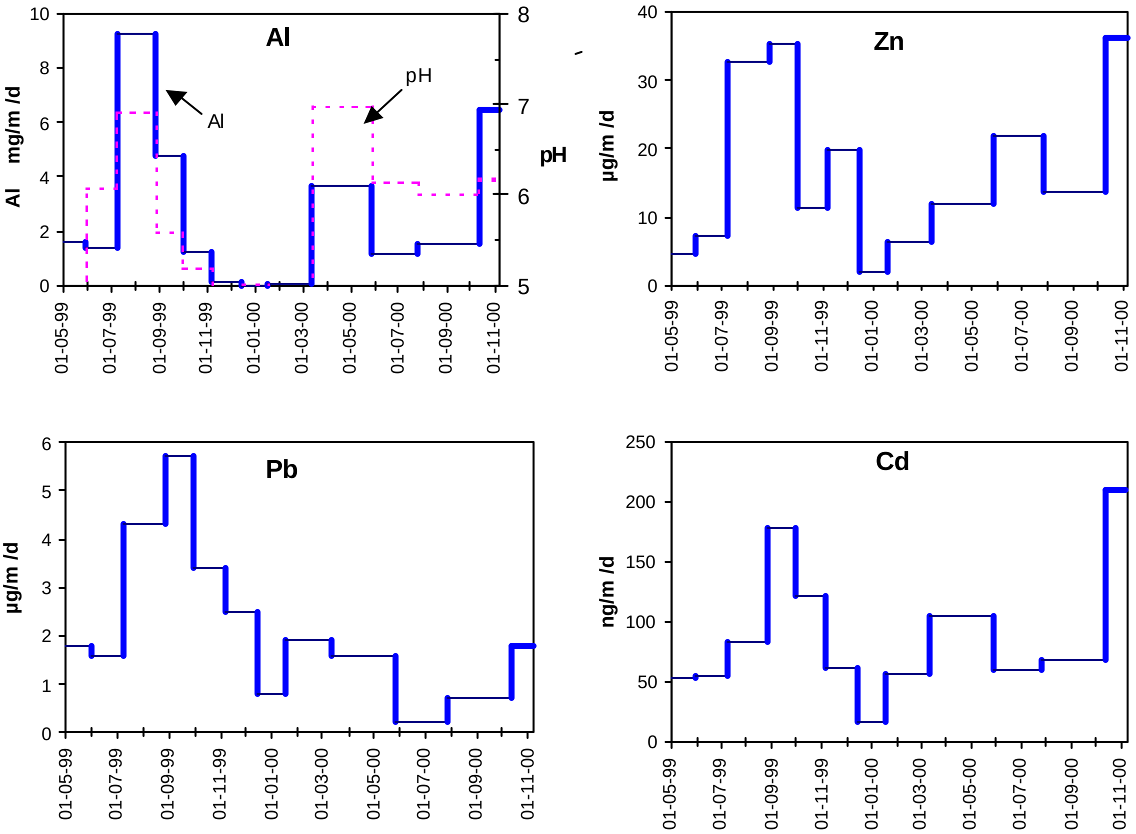


Figure 2. Temporal variability of the bulk atmospheric inputs of Al, Pb, Zn, Cd measured at the Pirio station from May 1st, 1999 to November 6th, 2000. Al input is plotted against pH.

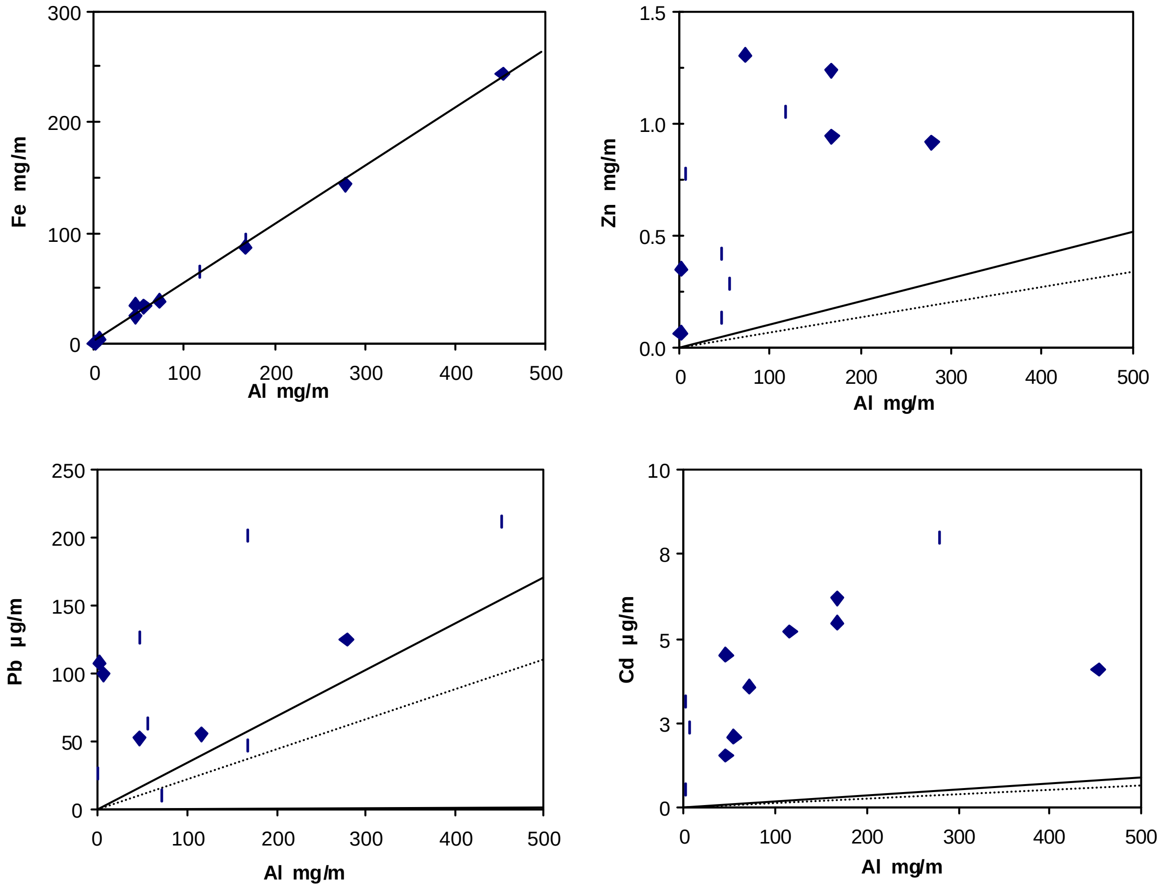


Figure 3. Metal vs. Aluminium in the bulk atmospheric deposition. The lines indicate the Metal/ Al ratio in the Saharan end member reference (continuous line) and in the Upper Crust reference (dotted line), except for Fe vs. Al where it represents the regression line.

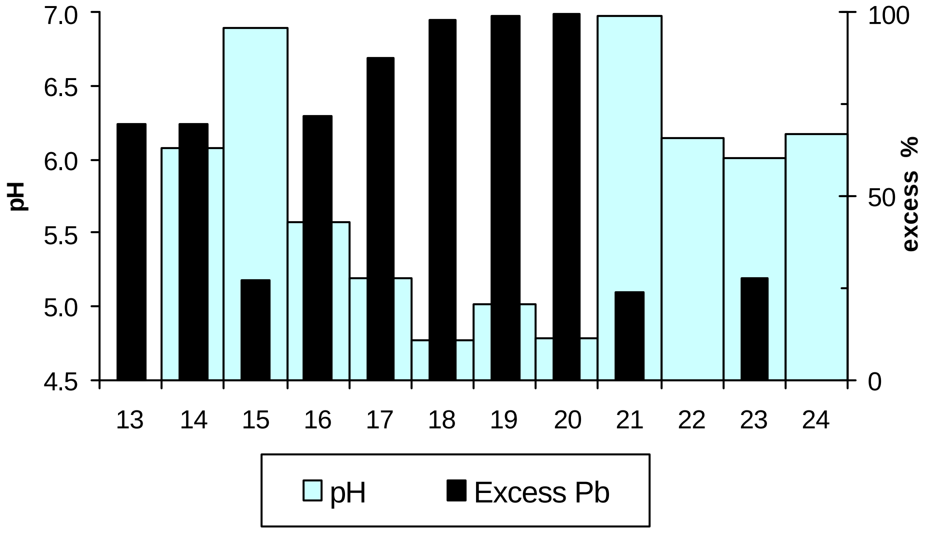


Figure 4. Temporal variability of pH and excess Pb (see text and table 4). Excess Pb corresponds to anthropogenic lead.

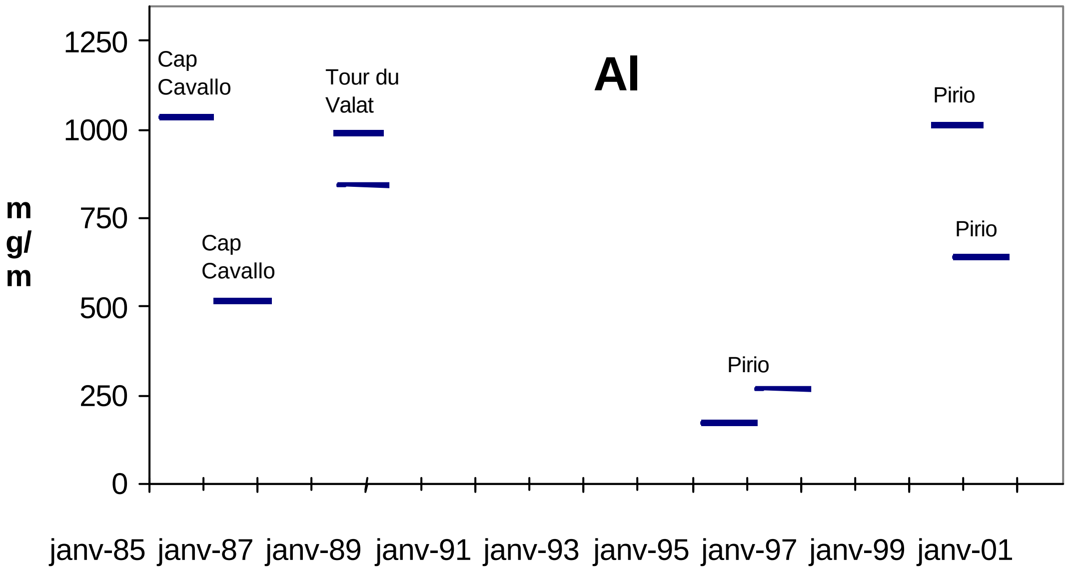


Figure 5. Evolution of the total atmospheric flux of aluminum between 1985 and 2000 in the North Western Mediterranean environment.

References: Cap Cavallo 3/85-3/86 : Bergametti, 1987; Cap Cavallo 3/86-4/87 : Remoudaki, 1990; Tour du Valat 5/88-6/89: Guieu, 1991; Cap Ferrat 10/92-9/93: Migon et al., 1997; Pirio 3/95-3/97: Ridame et al. 1999.

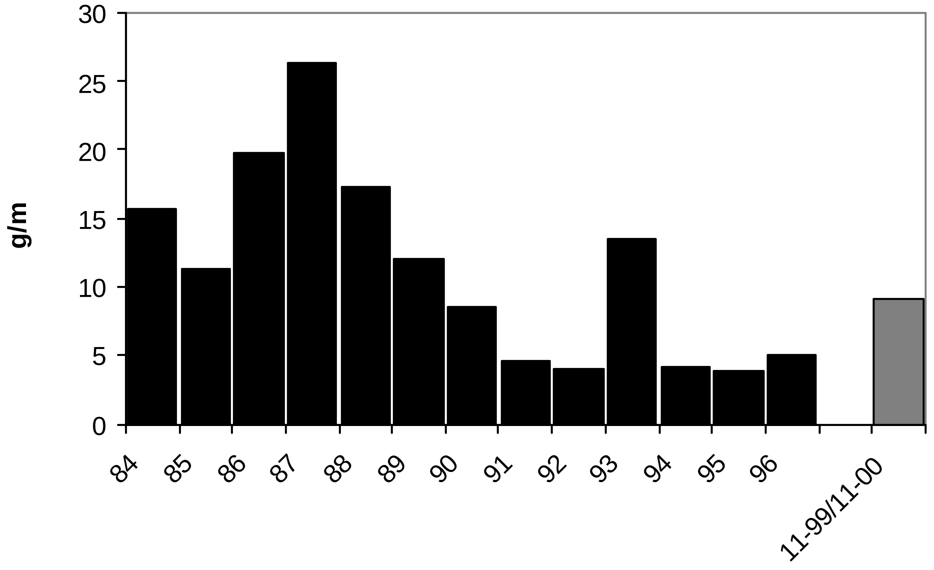


Figure 6. Evolution of the annual Saharan dust flux in Corsica (g.m^{-2}). 1984-1996, in black: measured (from Loÿe -Pilot and Martin, 1996 and unpublished values); (2) 11-99/11-00: calculated from the Al flux determined at Pirio using an Al concentration in Saharan dust of 7.09%.

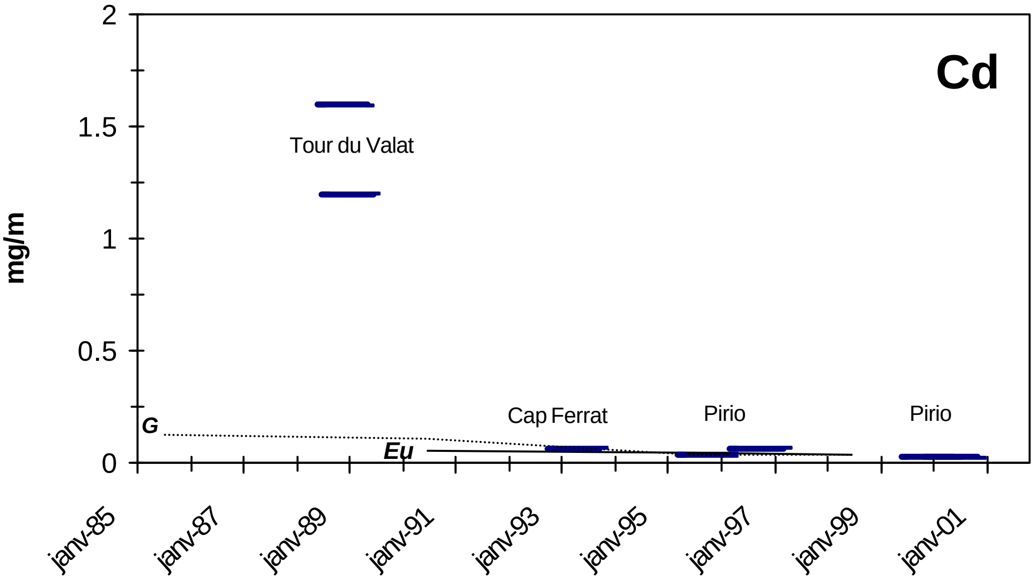


Figure 7. Evolution of the total atmospheric flux of cadmium between 1985 and 2000 in the North Western Mediterranean environment.
The lines represent the expected fluxes in the North Western Mediterranean if the fluxes vary in te same proportion as the emissions. ***Dotted line: fluxes following the emissions trends for Germany:G; continuous line: fluxes following the emissions trends for total Europe: Eur. References: Cap Cavallo 3/85-3/86 : Bergametti, 1987; Cap Cavallo 3/86-4/87 : Remoudaki, 1990; Tour du Valat 5/88-6/89: Guieu, 1991; Cap Ferrat 10/92-9/93: Migon et al., 1997; Pirio 3/95-3/97: Ridame et al. 1999.***

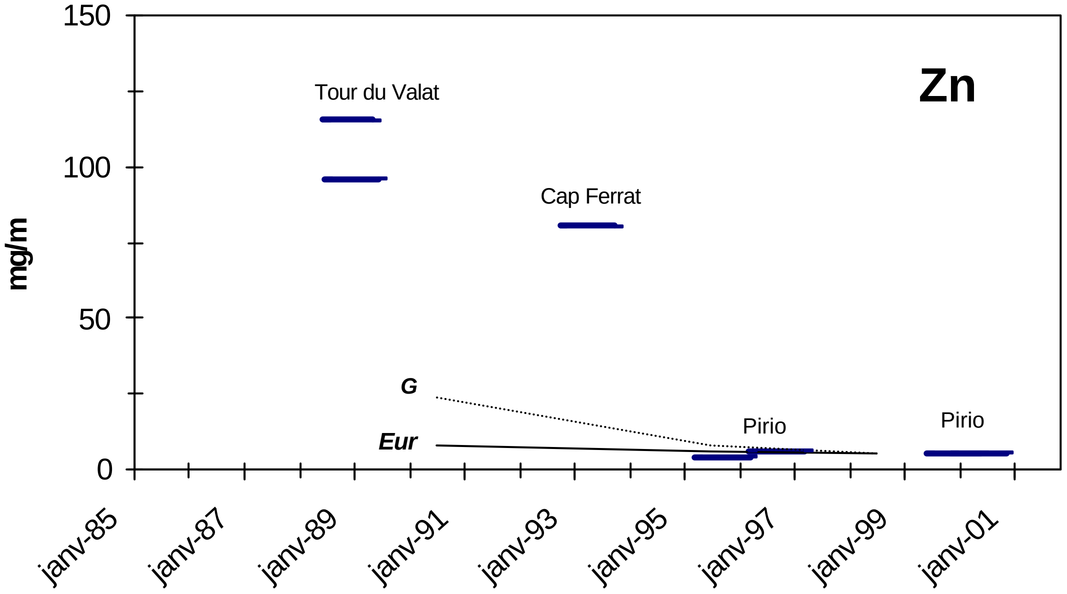


Figure 8. Evolution of the total atmospheric flux of zinc between 1985 and 2000 in the North Western Mediterranean environment.
The lines represent the expected fluxes in the North Western Mediterranean if the fluxes vary in te same proportion as the emissions. ***Dotted line: fluxes following the emissions trends for Germany:G; continuous line: fluxes following the emissions trends for total Europe: Eur. References: Cap Cavallo 3/85-3/86 : Bergametti, 1987; Cap Cavallo 3/86-4/87 : Remoudaki, 1990; Tour du Valat 5/88-6/89: Guieu, 1991; Cap Ferrat 10/92-9/93: Migon et al., 1997; Pirio 3/95-3/97: Ridame et al. 1999.***

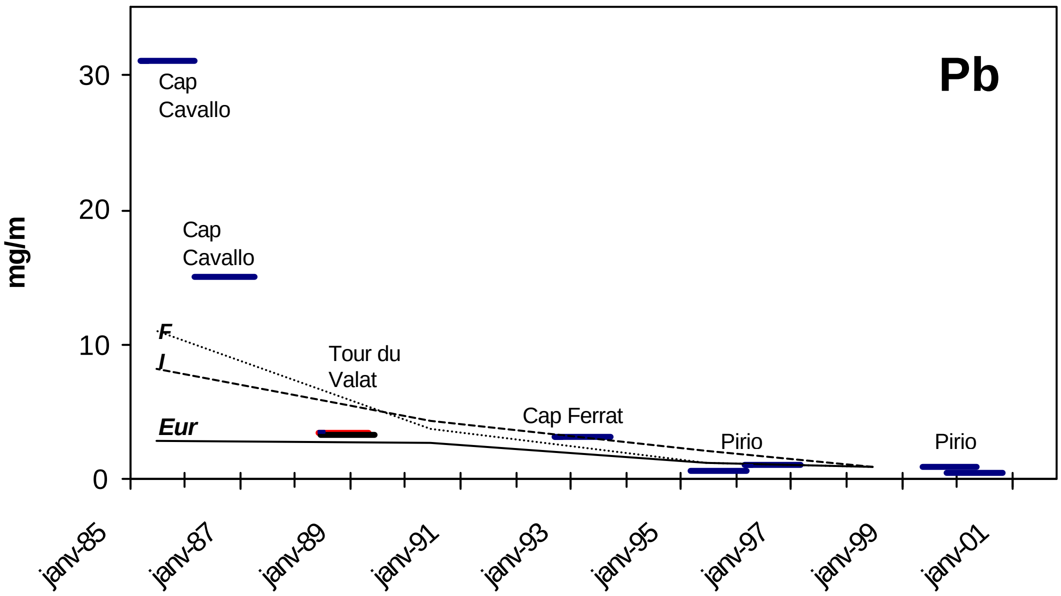


Figure 9. Evolution of the total atmospheric flux of lead between 1985 and 2000 in the North Western Mediterranean environment.

The lines represent the expected fluxes in the North Western Mediterranean if the fluxes vary in te same proportion as the emissions. Dotted line: fluxes following the emissions trends for France:F and Italy: I; continuous line: fluxes following the emissions trends for total Europe: Eur. References: Cap Cavallo 3/85-3/86 : Bergametti, 1987; Cap Cavallo 3/86-4/87 : Remoudaki, 1990; Tour du Valat 5/88-6/89: Guieu, 1991; Cap Ferrat 10/92-9/93: Migon et al., 1997; Pirio 3/95-3/97: Ridame et al. 1999.

ATMOSPHERIC INPUTS OF TRACE METALS (DRY) AND NUTRIENTS (WET) AT THE MEDITERRANEAN COAST OF ISRAEL: SOURCES, FLUXES AND POSSIBLE IMPACT

Barak Herut

Israel Oceanographic & Limnological Research., National Institute of Oceanography, Haifa 31080, Israel

1. INTRODUCTION

The large atmospheric inputs of natural and anthropogenic trace elements and nutrients to the oceans were emphasized in recent studies (Duce et al., 1991). The export of massive desert dust from the Sahara and surroundings to the North Atlantic Ocean and the Mediterranean Sea (Begametti, 1989; Moullin, 1997) and the long-range transport of anthropogenic substances is expected to be particularly important in adjacent semi-enclosed, oligotrophic seas such as the Mediterranean (Martin et al., 1989). Moreover, atmospheric deposition plays a role in both the release of elements to surface waters and their scavenging from the water column (Jickells, 1995).

The Mediterranean has been the subject of considerable internationally coordinated effort, to study and deal with the threats of various types of airborne pollutants to the area (GESAMP, 1989; UNEP/WMO, 1992). However, most of the data are limited to the northwestern basin (Dulac et al., 1987; Bergametti et al., 1989; Martin et al., 1989; Chester et al., 1996; Guerzoni et al., 1997, 1999; Guieu et al., 1997; Migon et al., 1997) and much less is available for the eastern part (Herut and Krom, 1996; Herut et al., 1999, in press; Kubilay and Saydam, 1995; Kubilay et al., 1997; Gullu et al., 1998).

Dayan (1986) investigated the climatology of back trajectories for Israel. Air masses reach Israel from three major directions: (a) WNW to NNW representing a long fetch of maritime air masses from north-west Europe crossing the Mediterranean Sea, (b) N to NE mostly inland flows from eastern Europe crossing Turkey, and (c) SW to SE air flows from inland North Africa and the Arabian Peninsula. The first represent air masses with higher contributions of the aersol populations from European and marine sources whilst the third is likely to have aerosol populations strongly influenced by mineral components from the deserts of North Africa (Sahara), Sinai and Arabian Peninsula. These major sources have been shown previously to influence the chemical composition of rainwater over Israel (Herut et al., 1993; 1995; 1999, 2000).

This report combines recent publications (Herut et al., 1999; in press) and some additional data, which present the first concerted effort to obtain information on aerosol concentrations, sources and fluxes of trace elements and nutrients along the Israeli Mediterranean coastline (SE Mediterranean). It also provide estimates of the bioavailable aerosol flux (wet and dry) of nutrients into the SE Mediterranean in order to develop a clearer understanding of the atmospheric contribution to the new production in the Levantine basin and its possible effect on the unusual N/P ratios and nutrient limitation. This summary is based on long-term measurements of particulate atmospheric trace metals (Pb, Cd, Cu, Zn, Cr, Mn, Fe and Al) and nutrients in rainwater (PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+) carried out at sites along the Mediterranean coast of Israel.

2. METHODS

2.1 Sampling of total suspended particles

Total suspended particles (TSP) in air were collected by high volume samplers located on the roof of the National Institute of Oceanography (NIO) at Tel-Shikmona (TS, Fig. 1) (located on the shore, 22m above sea level) and at Maagan Michael (MM, about 900 m from shore, 13 m above sea level). Sampling was carried out predominantly at weekends for about 60 hours (mostly in days without rain). In addition the sampling was also carried out on 4 occassions during special meteorological conditions of ‘Hamsins’ characterized by the influence of air masses from the southern deserts. Two selected dust event samples (on February 6th and November 15th, 1996) were collected at Ashdod (ASH, about 2.5 km from shore, 30 m above sea level) and were used as reference samples representing crustal dominated aerosol populations. Additionally, dry deposited materials were collected from a plastic surrogate collector at Eilat (Gulf of Aqaba), Israel on May 28th, 1998, and from the top of a solar panel at Beit Yannay, Israel, following a dust storm.

TSP were collected at TS from October 1994 to December 1997 and at MM from March 1996 to December 1997 following the UNEP/WMO (1992) recommendations. At TS a total of 61 samples were collected on Whatman QM-A quartz microfibre and 35 on Whatman 41 filters (both 20.3 x 25.4 cm^2), and at MM a total of 66 samples were collected on Whatman QM-A quartz microfibre. The filters were stored in a desiccator for 24h and weighted before sampling. After collection the filters were dried in a desiccator 72 hours before being re-weighed. The Whatman #41 filter weights were inaccurate owning to their tendency to immediately adsorb humidity. Approximately 1/8 of each filter was used for the trace metals analysis. Other sub-samples of the same filters were used to determine nutrient content (see hereafter).

Surface (1000 mb) air mass back trajectories (3-5 days) for 50 samples from TS and MM, collected during 1996, were calculated using the software Trajplot (Canadian Atmospheric Environmental Agency).

2.2 Sampling of rainwater

The sampling of the rainfall was performed at TS, ASH and MM (Fig. 1). In TS and ASH, rain was collected on an event basis while in MM rainwater samples were retrieved on a weekly basis. Rainwater samples were collected at TS from 1992 until March 1998, at MM from January 1996 until March 1998 and at ASH from November 1995 until March 1998. A total of 187, 36 and 67 rainwater samples were collected at each site, respectively.

Rainwater samples were collected using plastic funnels (25 cm diam.) and bottle-type collectors (100 cm height) as recommended by UNEP/WMO (1992). At ASH station the rain was collected using a Graseby automatic collector. Sub-samples were immediately frozen for nutrient determination and pH was measured on a further sub-sample. The samples for nutrients were collected in 15 ml plastic scintillation vials that had been prewashed with 10% hydrochloric acid and rinsed thoroughly with double distilled water. The total amount of rain collected in each event was measured. The remaining rainwater samples were then filtered (through Whatman #42) and stored in a refrigerator at 4 °C for major element analyses (Na^+, Ca^{2+}, Cl^-, SO_4^{2-}).

2.3 Chemical analysis of TSP

Analysis of Cd, Pb, Cu, Zn, Cr, Mn, Fe, Al, Ca and Na in TSP were carried out after total digestion with HF following the procedure of ASTM (1983). The digested samples were diluted by double distilled water. The concentrations were measured on a Perkin Elmer 1100B atomic absorption spectrometer (AAS) and graphite furnace AAS (GFAAS). The filter blanks were usually less than 10% of the total concentrations (except for Na in Whatman QM-A filters). The analytical precision was estimated to be within 4% of the values reported increasing towards 8% for Zn and Cd. The accuracy of the methods were evaluated on the basis of analyses of International Standard Reference Materials: Estuarine Sediment 1646 (NIST), MESS-2 Sediment (NRCC) and Coal Fly Ash. All elemental results were within 5% of the certified values.

To further validate the analysis an inter-laboratory study was carried out between IOLR (Israel) and the Plymouth University (UK). Eleven Whatman 41 filter samples from TS were selected to represent a range of particulate metal concentrations. For all elements applying a paired t-test to the aerosol concentrations determined by the two laboratories there were no significant differences at the 95% confidence interval, between the two datasets. This further validates the observed concentrations. Replicate analyses of portions of Whatman 41 filters yielded precision <5% for all elements except Cd, which was 8%. This illustrates that the collected aerosol material is evenly distributed across the filter media.

The comparison between the trace metal chemical composition of aerosols with different air mass origin was made using the Mann-Whitney test.

2.4 *Rainwater chemical determinations*

pH in rainwater was determined immediately after retrieving the sample using a Radiometer pH Meter. Dissolved nutrients (PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+) were determined by a segmented flow Technicon System II auto analyzer (Krom et al., 1991). The precisions for NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-} were 0.04, 0.04, 0.7 and 0.01 M, respectively. Cations (Na^+ and Ca^{2+}) were measured after suitable dilution using an ICP-EAS. Anions (Cl^- and SO_4^{2-}) were analysed using a Dionex DX100 Ion Chromatograph with AS14 column, AS3500 autosampler and AI450 computer interface and software. Precision was 1.7% for Cl^-, 0.6% for SO_4^{2-}, 8.6% for Ca^{2+}, and 2.2% for Na^+. Accuracy was checked using I.A.P.S.O. standard seawater stock solution, which gave results within 0.5% of the expected values.

2.5 *Leaching experiments*

Leaching experiments were performed to evaluate the amount of seawater leachable inorganic phosphorous (LIP) and total IP from TSP collected on Whatman 41 filters by high volume sampler at TS between March and December, 1996. After collection the filters were dried in a desiccator for 72 hours before being re-weighed. The filter weights were inaccurate due to their tendency to immediately adsorb humidity. Twenty dust filter sub-samples (2 cm^2) were soaked and shaken for 3 hours in 15 ml of 0.2 m filtered SE Mediterranean surface seawater (collected by the R.V Shikmona during 1997, 20 km off the Israeli coast). Another sub-sample (2 cm^2) was shaken for 4 days with 15 ml of 1N HCl to estimate total IP and Ca content. The Al concentrations were measured on a third sub-sample (10 cm^2) by total digestion with HF following the procedure of ASTM (1983). The filter blank and bottle adsorption effect were calculated as <5% of the total IP concentrations and insignificant (undetected) in the seawater LIP. Prior to the experiments it was estimated that the leaching process (kinetics) reaches close to equilibrium after two hours.

Total IP concentrations were also measured on additional 22 Whatman Ultra-pure Quartz Microfibre (QMA) filters collected by the same high volume sampler at TS during February 1995 to November 1996. Fifteen of the filters were collected together with the Whatman 41 filters (during 1996) but at different dates. The weights of TSP for the QMA filters were measured as given above and were found accurate. The total IP measurements were performed on sub-samples (2 cm^2) that were shaken for 4 days with 15 ml 1N HCl. The filter blanks were found too high to perform the seawater LIP measurements. The filter blanks in the HCl digestion procedure for the determination of total IP were approximately 50% of the total IP concentrations.

Surface (1000 mb) air mass back trajectories (3-5 days) for the TS high volume samples, both Whatman 41 and QMA, were calculated using the software Trajplot (Canadian Atmospheric Environmental Agency). We classified the air masses into two geographical categories: (a) West-East European and (b) N Africa and the Arabian Peninsular.

2.6 *Estimate of fluxes*

The wet atmospheric deposition fluxes (F_W) were calculated from the annual amount of precipitation (P) and the volume-weighted mean concentration (C) of the substance of interest (eq. 1). Samples from MM had a longer exposure time and contained dry fallout as well as rainwater. These samples were not used for the wet flux estimates. We will use these samples to examine the influence of dry fallout on the nutrient content in the rain. Similar results were obtained calculating the flux for all individual rain events and correcting it for the annual amount of precipitation (60-89% of the total annual amount was collected).

$$(1)\ F_W = C \times P$$

The dry atmospheric deposition fluxes (F_d) were calculated by multiplying the geometric mean particulate concentration in air of the element of interest C_i by the elemental dry settling velocity (V_d):

$$(2)\ F_d = C_i \times V_d$$

The velocity V_d varies with particle size (from gravitational settling of large particles to impaction and diffusion of small particles (submicrometer)) and is dependent on climatological and physical conditions in the troposphere, especially in coastal environments. The values used here follow the mean values used by Duce et al. (1991). For Cd, Pb, Zn, Cu and Cr which are found primarily associated with submicrometer particles a mean value of 0.1 cm s^{-1} was applied, and for Al, Fe, Mn and P which are present primarily in the coarse fraction a mean value of 2 cm s^{-1} was adopted. These values fall close to the V_d range given in other studies (Rojas et al., 1993; Migon et al., 1997 and references therein). It should be emphasized, however, that the flux calculations might vary by approximately an order of magnitude due to the uncertainties in V_d.

3. DRY ATMOSPHERIC INPUTS OF TRACE METALS: SOURCES AND FLUXES

3.1 Total suspended particles in air

TSP concentrations in air were calculated for the QMA filter samples. TSP concentrations at TS ranged from 22 to 191 g m^{-3} with a mean±std deviation value of 71±33 g m^{-3} and at MM from 30 to 183 g m^{-3} with a mean value of 70±35 g m^{-3}. It should be noted that the TSP contained recycled seasalts. Assuming that all Na is of marine origin and using its composition in seawater (Na constitutes 31% of the Mediterranean seawater salts; Herut et al., 1990), the amount of seasalts contribution to the aerosol population may be estimated. The Na concentrations in the blank QMA filters were too high to allow them to be used to calculate the seasalt fraction. Therefore, we used the average Na concentration measured on representative Whatman 41 samples at TS and MM. Based on the average Na concentration at TS and MM (11482±3173 and 385±281 ng m^{-3}, respectively) the TSP contains 3.7 and 1.2 g m^{-3} of seasalt, approximately 5 and <2% of the TSP, respectively. Thus, the influence of seasalt on the TSP concentrations was estimated as minor. It is assumed that for the trace metals considered in this study it is even more insignificant. The concentration of these trace metals in the non-seasalt fraction (mainly mineral dust) is three to four orders of magnitude higher than in the seasalt fraction (seaspray) and therefore seasalt contribution of these trace metals is negligible (Weisel et al., 1984). Such minor seasalt contribution was also found in the western Mediterranean Sea for some trace elements (Dulac et al., 1987).

To estimate mineral dust concentrations in air the concentration of Al may be used assuming that this element represents on average a known % by weight of the mineral aerosol. Such an approach was used by Duce et al. (1991) using the Al concentration in average crust material (8.04 % by weight, Taylor and McLennan, 1985). The scatter plot of Ca vs. Al concentrations in air in the present study indicates that the Ca/Al ratios (as proxy of carbonates/alumino-silicates ratio) vary from 0.3 to 50 probably attributed to differential local soil/rock contribution. It is therefore likely that the use of Al concentration alone in dust events of Saharan origin (~4.5 % by weight) will underestimate the mineral dust concentration at this region because of the presence of variable amounts of carbonate. Indeed, the calculated average Ca concentrations in dust collected at TS is 7.4±2.9 % by weight, higher than the average concentration in crustal material (4.15 % by weight, Taylor and McLennan, 1985).

3.2 Particulate trace metals in air

The statistical summary of the particulate trace metal concentrations in air at TS and MM is presented in Table 1. At TS similar trace aerosol elemental concentrations were found for both Whatman 41 and Quartz filters although they represent different sampling dates. Similar concentrations of crustal derived metals (Al, Fe, Mn and most Cr) and of Cd and Cu were observed at both MM and TS. The somewhat higher Zn concentrations at TS (although not having statistically significant difference to that observed at MM) may represent the influence of local unidentified anthropogenic sources. The higher Pb concentrations at MM may also reflect local source contributions to the collected aerosols during sampling in 1996. The variability of Fe, Mn, Pb and Cd concentrations in air during contemporaneous sampling at TS and MM stations is given in Fig. 2. Similar concentrations (data fall along the 1:1 line) of the dust-born elements were attributed to regional or remote (southern Negev, Sinai and North African deserts) dust transport events, while the local site contribution is minor. Plotting the Pb and Cd concentrations in air for contemporaneous samples from TS and MM shows higher concentration variability (Fig. 2). Samples that fall approximately to the 1:1 line represent regional or remote sources, while samples that fall below the 1:1 line show enriched concentrations at MM attributed to possible local contribution.

A comparison of the aerosol trace metal concentrations from the present study with those observed at another Eastern Mediterranenan coastal site (Erdemli, Turkey), Table 2 (Kubilay and Saydam, 1995), would indicate generally slightly elevated concentrations of Al and Fe aerosol concentrations and comparable concentration values for Pb and Cd. Whereas Zn is enriched, especially at TS, in comparison to the Erdemli sampling site. The source of Zn enrichment along the Israeli coast is not clear and might be related to local traffic sources. The relatively high Cr concentrations in Erdemli were attributed to contamination by local ophiolitic rocks (Kubilay and Saydam, 1995). Comparing trace metal aerosol concentrations with typical values quoted in the literature for coastal sites at the western basin (Table 2; Chester et al., 1993; Guieu et al., 1997) it is evident that the crustal elements are enriched (between 2 to 3 times) in the Eastern Mediterranean aerosol population. This is not surprising owing to the greater dominance and proximity of surrounding arid regions to the Eastern Basin. Considering the predominantly anthropogenically derived trace elements, comparable concentrations were detected at TS and MM similar to those quoted for the western Mediterranean basin (Table 2; Chester et al., 1993, Migon et al., 1997), but their anthropogenic fraction is higher at the European coastal sites (see further below).

Common factors influencing the variations between aerosol trace metal concentrations at both collection stations (TS+MM) were examined by principle component analysis (PCA, SAS software). The application of PCA on the present dataset may facilitate (a) an understanding of inter-relationships between elements in the aerosols (Fones, 1996) and hence indicate common transport/removal mechanisms and/or emission source identification (e.g. Massart et al., 1988; Schaug et al., 1990). Datasets are reduced to a small number of representative vectors or Principal Components (PC's), which represent the entire variability in the dataset. Each PC is composed of a loading weight for each variable. Three main PC's (eigenvectors with eigenvalues > 1) were responsible for about 70% of the variance in the current trace metal aerosol dataset variability. PC1 (describes 32% of the variance) depicts similar loading to all elements while PC2 (describes 23% of the variance) depicts opposite loading of anthropogenic derived (Cd, Cu, Pb, Zn) versus natural derived elements (Al, Fe, Mn, Cr) (see further below in the discussion on EF_{crust} values), elucidating the different behavior and origin of these two groups of elements (Fig. 3).

Fe, Mn and Al concentrations had similar seasonal variability at both sampling sites attributed to their crustal origin. In contrast, smaller concentration variability and sometimes-different temporal variability were observed for Pb, Cd and Zn, attributed to their dominant anthropogenic origin. The seasonality was tested statistically using Duncan's Multiple Range Test (SAS software) and was found to be significant ($p<0.05$) for the crustal derived elements. Higher concentrations were recorded during spring and autumn as compared to those of summer and winter (e.g., mean Fe concentrations in TS+MM during spring and autumn were 1117 and 1502, respectively, whereas in winter and summer amounted to 639 and 729 ng m^{-3}). Similar seasonal patterns of desert dust pulses elevating the concentrations of crustally derived elements such as Al and Fe in the aerosol were regularly observed at sampling sites in the Western Mediterranean (e.g. Guieu et al., 1997). The high concentrations peaks (>1500 ng Al m^{-3}) were attributed to dust storms ('pulses') moving from N African and surrounding desert regions as previously documented (Ganor and Mamane, 1982). Seasonal variability in crustal elemental aerosol concentrations, with enhanced concentrations (by 2-3 times) in the summer period have also been noted at collection sites located on the Turkish Mediterranean coast (Gullu et al., 1998). The enhancement was attributed to greater resuspension of soil particles during the dry summer months and minimum aerosol generation from damp soil surfaces in the winter. In addition, Gullu et al., (1998) stressed the importance of Saharan dust transport episodes occurring in May and April as well as September and October. Both these periods fall in their defined “summer “ period.

Defining the aerosol trace metal concentrations into different air mass groupings may provide preliminary information on elemental source regions. This approach has been adopted by a number of studies (e.g. Kubilay and Saydam, 1995; Gullu et al., 1998). For the current study the characteristics of contrasting air masses and hence aerosol sources were examined by calculating surface (1000 mb) air mass back trajectories (3-5 days) for 50 samples collected during 1996 at TS and MM. We classified the air masses into two geographical categories: (a) West-East European airmass (EAM) and (b) North Africa and the Arabian (Saudi) Peninsular airmass (ASAM). This classification is based on Dayan’s (1986) categorization, but combines his two European sources (see Introduction) into one category (EAM). Using this categorization and then calculation of the associated mean aerosol trace metal concentration significantly higher concentrations of Al and Fe were observed in ASAM (median ≈1100 ng m^{-3}) compared to EAM (median ≈500 ng m^{-3}). There were little differences between the concentrations of the other considered trace metals between the two defined air masses categories (mean concentration of Cd and Pb were 0.24 and 59 ng m^{-3}, respectively, in ASAM and 0.29 and 62 ng m^{-3} in EAM), which would indicate the importance of regional sources rather than solely long range transported material.

The mass of trace elements in a given volume of air derived from crustal and oceanic sources can be estimated from reference elements such as Al (or Fe) and Na (after correcting for crustal contribution), respectively (Chester et al., 1993; Weisel et al., 1984). Al was used here to estimate the enrichment factors relative to crustal composition according to the equation:

$$(3)\ EF_{crust} = (Tr/Al)_{air}/(Tr/Al)_{crust}$$

where $(Tr/Al)_{air}$ is the concentration ratio of the trace element to Al in the air suspended particles and $(Tr/Al)_{crust}$ is the ratio in average crustal material. Equation (3) was applied using the average chemical composition of the upper continental crust given by Taylor and McLennan (1985). This upper crust average contains lower trace/Al ratios by approximately a factor of two as compared to this ratio in regional natural dust samples (Table 3). This difference is mainly attributed to the higher (almost twice) Al concentration in average continental crust than in collected dust samples, while other natural elements (Fe and Mn) showed similar concentrations (Table 3). Thus, the EF_{crust} values probably overestimate the anthropogenic imprint (by a factor of ~2) but are useful for site comparisons across the Mediterranean Basin.

High EF_{crust} values (>>10, Table 2) were calculated for Cd, Pb and Zn due to their dominant anthropogenic source (representing the group so-called anomalously enriched elements - AEEs). Minor enrichment was calculated for Cu. Relatively low median EF_{crust} values (<10) were calculated for Fe, Mn and Cr (they belong to the non-enriched elements - NEEs). Although Cr and Mn may originate from a combination of sources they exhibit here a dominantly crustal source. The sequence of EF_{crust} is Cd>Pb>Zn>Cr>Mn>Fe for TS while at MM Pb enrichment was higher than that of Cd, probably due to the local contamination during 1996.

The EF_{crust} values for Cd and Pb (as AEEs) are higher by factor of 3-8 for the European sites compared to those in the eastern basin. The EF_{crust} values for Zn at both sites are lower than at the European coastal sites. Both East Mediterranean sites have similar Pb:Cd ratios of 140-150 (Table 2), higher than those observed at the European sites or the western and eastern European emissions (46-52, Pacyna et al., 1984). The value quoted from Sandroni and Migon, (1997) and Migon et al. (1997) (Table 2) is perhaps the most reliable ratio as the aerosol concentrations were evaluted after the significant decline with time of Pb emissions during the late

80’s and early 90’s, especially in western Europe and to a lesser degree of Cd. The differences between the Pb:Cd ratios for the east and northwest Mediterranean sites are probably attributed to the combination of the following processes: (a) compartively different regional rates of emissons of contaminants with regard to the eastern basin, (b) differential settling between Cd and Pb during their passage from Europe to the Eastern Mediterranean, and (c) eastward enrichment of crustal material with Pb:Cd ratios of ~200. This eastward crustal enrichment is also reflected by higher Zn:Cd ratios of >190 at the Israeli coast and in crustal material (~720) as compared to the European sites (58-100) or the western and eastern European emissions (26-34, Pacyna et al., 1984). Similarly the Zn:Pb at the Israeli coast and crustal material (>1.3) are higher than at the European sites (~1) or the western and eastern European emissions (0.54-0.65, Pacyna et al., 1984).

Desert type events (ASAM, category b), classified by air mass back trajectories, contain significantly ($p<0.05$) lower EF_{crust} values for Cd and Pb as compared to air masses from Europe (EAM) (Fig. 4). The geometric mean EF_{crust} values of Cd and Pb of EAM (category a) events (453 and 280, respectively) were significantly ($p<0.01$) higher than in ASAM events (110 and 133, respectively). This general difference is likely to be attributed to the degree to which the anthropogenic aerosol components are “diluted” with local and long range tranported crustal material, as there were no significant difference in the concentrations of the anthropogenically derived trace elements between air mass sectors. Individual events showed differences in EF_{crust} values attributed to different contamination intensities from a combination of European and local sources. For example, in ASAM events during 29/4/96 and 14/11/96 EF_{crust} values of Cd and Pb were between 29-107 and 33-85, respectively. In EAM events during 11/3/96 and 21/5/96 these values ranged between 1460-442 and 996-619, respectively. It is difficult to quantify the local versus external contribution of these contaminants. Somewhat higher Pb:Cd ratios were associated with ASAM probably attributed to their higher ratios in crustal material (~200, Table 2) compared to their ratios in the European ‘background’ or emissions (see above).

3.3 Mixing of anthropogenic and crustal aerosol end-members

The total mass of certain particulate AEE in a given volume of air (Tr_{air}) is composed of

$$(4)\ Tr_{air} = Tr_{crust} + Tr_{anth}$$

where the subscripts *crust* and *anth* designate its crustal (natural) and anthropogenic fractions. Assuming all the Al in the air is of crustal origin,

$$(5)\ Al_{air} = Al_{crust}$$

then the mass of Tr_{crust} in aerosol population is given by

$$(6)\ Tr_{crust} = Al_{air} \times (Tr/Al)crust$$

Substituting equations (5) and (6) into (4) we obtain,

$$(7)\ (Tr/Al)_{air} = (Tr/Al)_{crust} + Tr_{anth}/Al_{air}$$

Substituting equation (3) into (7) we obtain,

$$(8)\ EF_{crust} = 1 + Tr_{anth}/Al_{air} \times (Al/Tr)_{crust}$$

Equation (8) describes a linear mixing between two possible end-members: (a) a 'clean' crustal-derived particles characterized by $EF_{crust} = 1$ and, (b) anthropogenic-derived particles. Within the EF_{crust} vs. $1/Al_{air}$ relationship the slope of the line represents the term $Tr_{anth} \times (Al/Tr)_{crust}$ (Fig. 5) from which Tr_{anth} can be estimated, similar to composite enrichment factor diagrams presented by Rahn (1976) and Chester et al. (1993). Thus, polluted samples will exhibit higher slopes than relatively clean samples. The dilution of clean crustal material in air is represented by the horizontal line along EF = 1 (Tr_{anth} -->0) or as defined here when EF<10. This behavior was clearly exhibited by Fe while for trace elements as Pb (Fig. 5) and Cd the data fall in-between various mixing lines between crustal particles and anthropogenic Pb or Cd concentrations of about 10 to 250 ng m^{-3} of air. In general, TS samples showed somewhat lower Pb_{anth} concentrations as compared to samples from MM. The latter is attributed to contamination of Pb from local traffic and the nearby power plant during 1996.

The anthropogenic end-member is probably derived from two main sources, local and European emissions. At present (as given above) it is impossible to quantify the variations of these two fractions.

3.4 *Estimation of dry fluxes*

The estimation of dry deposition fluxes of each trace element is problematic due to the use of different sampling methodologies, poor knowledge of the elemental mass-size distribution and other effecting factors (Guerzoni et al., in press). Nevertheless, large amount of data was published mainly for the western and central Mediterranean (Guieu et al., 1997). The average mineral flux into the coastal zone was estimated using eq. (1). The calculated mean flux was 21 g m^{-2} yr^{-1} for TS and MM. Our estimate is quite similar to dust sedimentation rates of 20-40 g m^{-2} yr^{-1} calculated for the East Mediterranean by Ganor and Mamane (1982) or 30-60 g m^{-2} yr^{-1} estimated by Ganor and Foner (1996). These calculated fluxes are higher by almost an order of magnitude than those estimated over the Northern Hemisphere Oceans (Duce *et al.*, 1991).

The estimated dry fluxes of the trace elements are presented in Table 4. The Fe and Al fluxes are higher (by a factor of >2) than fluxes to the Atlantic and Pacific Oceans (Duce et al., 1991). The fluxes of AEEs are significantly lower than those estimated for the North Sea (Rojas et al., 1993) or the central and western Mediterranean (Guieu et al., 1997; Migon et al., 1997), but higher than those estimated for the Atlantic and Pacific Oceans (Duce et al., 1991).

3.5 *Conclusions*

1. Two main associations of particulate anthropogenic (Cd, Cu, Pb, Zn) and natural elements (Al, Fe, Mn, Cr) were detected (using principal component analysis). The composition of Pb, Cd, Zn and Cu in air indicated their dominant anthropogenic origin, exhibited by their high EF_{crust} values (>>10).
2. A statistically significant seasonal pattern of higher concentrations of crustal derived elements (Fe, Al, Mn and partly Cr) during spring and autumn as compared to summer and winter was observed.
3. Higher concentrations (by a factor of 2-3) of crustal derived elements and comparable concentrations of anthropogenic elements (e.g. Pb, Cd) were detected at the Israeli coast and the eastern Mediterranean Basin compared to the northwestern Mediterranean.
4. Different ratios of Pb:Cd and Zn:Cd were calculated at the Israeli coast compared to northwestern Mediterranean sites. It is speculated that these differences are attributed to the mixing of crustal material with local and European emissions. At present it is impossible to quantify the latter two fractions.
5. The use of the back trajectory analysis and the subsequent categorization of aerosol populations enabled the differences in the trace metal aerosol characteristics to be evaluated. The two main populations, European and North Africa – Arabian, exhibited a significant different geochemical imprint on the aerosol composition. European-born air masses contained significant higher EF_{crust} values for Cd and Pb due to the greater anthropogenic character of the aerosol population, with a dilution by crustal material leading to comparatively lower EF_{crust} values associated with the North African – Arabian air masses.

4. WET ATMOSPHERIC INPUTS OF NITROGEN AND PHOSPHORUS: SOURCES, FLUXES AND POSSIBLE IMPACT

4.1 *Rainwater*

The chemical composition of the rainwater is similar at all three sites and is mainly Na-Cl. This is typical for the Israeli coastal zone area (Herut et al., 2000). The rainwater salinity is higher at TS compared to MM and ASH. This is attributed to a higher input of seaspray (SS) components (e.g., Na and Cl) caused by the proximity to the sea. In most of the rains Na^+ vs. Cl^- showed a clear marine ratios (0.87) as presented in Fig. 6. The amount of SS and non-seaspray (NSS) for each ion was calculated from the major ion to chloride ratio assuming no fractionation alters the seawater ratios during, or after, the injection of seaspray into the atmosphere. Ca^{2+} and SO_4^{2-} showed the most significant enrichment relative to the marine ratio, having significant NSS contribution (Fig. 6).

pH values in the rainwater samples ranged from 3.6 to 8.2, with volume-weighted mean value of 5.2. The relative contribution of NO_3^- versus $SO_4^{2-}{}_{nss}$ to the rainwater acidity based on their volume-weighted mean concentration, was approximately 1:4. A similar contribution for nitrate (of about 20%) was estimated in European precipitation (Berner and Berner, 1996). However, no significant correlation was found in this study between H^+ and NO_3^- or NO_3^--NH_4^+ concentrations or between H^+ and $SO_4^{2-}{}_{nss}$.

No correlation was found between the nutrients (PO_4^{3-}, NO_3^-, NH_4^+) and Na^+ or Cl^- concentrations ($r^2 < 0.046$), indicating a non-marine origin for the nutrients. The SS contribution to the dissolved nutrients in the rainwater samples has been calculated to be insignificant. Less than 0.05% of the dissolved inorganic phophorous (DIP) and 0.09% of the dissolved inorganic nitrogen (DIN) in the rainwater could be attributed to SS assuming that no fractionation occurred during the passage from seawater to SS. Even if the P was enriched by 150 in the surface microlayer (Graham and Duce, 1979), the fraction of marine derived phosphate would still be less than 10% of the total amount in the rain.

In general, high temporal variability of the nutrient concentrations was observed (Fig. 7). A dim seasonal pattern exists in the PO_4^{3-} behavior at ASH and TS with high concentrations occurring predominantly in the beginning and the end of each winter, while no seasonal pattern was exhibited by the NO_3^- (or NH_4^+, not shown) concentrations. This PO_4^{3-} seasonal pattern is probably related to higher concentrations of local dust being washed out of the air with the first rains in the autumn and to dust storms moving from N African and surrounding deserts which occurs mostly in spring (Ganor and Mamane, 1982). There was a positive correlation between PO_4^{3-} and $Ca^{2+}{}_{nss}$ concentrations for rainwater samples from ASH and MM. The relatively lower $PO_4^{3-}/Ca^{2+}{}_{nss}$ ratios in TS rains indicates lower dissolution of phosphate from the dust (by rainwater) at this site. These differences might be attributed to the longer exposure time of the MM samples to dust particles and higher dust concentrations in the air at ASH (Herut, 1998). However, without simultaneous measurements of dust concentrations in air it is difficult to assess the relationship between the nutrient concentrations and the latter.

At TS the main dissolved inorganic nitrogen (DIN) specie was usually NO_3^- while at ASH NH_4^+ was dominant (Table 5). NO_2^- concentrations were negligible and constituted <2% of the DIN. Volume-weighted mean DIN concentrations were higher at TS than ASH, mainly due to higher NO_3^- concentrations. Two possible hypotheses have been suggested to explain the markedly different NO_3^-:NH_4^+ ratios at TS and ASH. One possible explanation for this observation is that TS is more affected by occasional local anthropogenic contribution of NO_3^- while ammonia derived from animal wastes and fertilizers, is more dominant at ASH. TS is adjacent to the city of Haifa while ASH is adjacent to areas of intensive agriculture. In this model the NO_3^- flux at ASH plus the NH_4^+ flux at TS represent the total DIN flux of the European ‘background’ rainfall. This more conservative model was chosen for the flux calculations carried out below. The alternative model is that the entire DIN in ASH comes from Europe and that there was no significant local input of NO_3^- or NH_4^+. This model requires that the European rain started off with a significant NH_4^+ content part of which was subsequently transformed via atmospheric oxidation to NO_3^-. The more northerly rain then has undergone greater oxidation of NH_4^+ than the southerly rains. With the data available it is not possible to decide which of these hypotheses is correct.

4.2 Leachability of phosphorus from dry fallout by surface seawater

Leaching experiments using SE Mediterranean surface seawater were performed on twenty Whatman 41dust filters from TS to evaluate the amount of seawater LIP. The mean total IP concentration in the dust was 0.13 0.11 % (geomean = 0.09 %). A mean of 387 205 g IP per g of dust was leached by seawater. However the concentrations of phosphate in the dust on the Whatman 41 filters may contain relative large errors because the weight of the dust on the filters was inaccurate (see methods). Similar leachable values (LIP per g of dust) were obtained using dust weights that had been estimated from the Al concentrations assuming that this element represents on average 4.5 % by weight of the mineral aerosol (Herut, 1998) or by using both Ca and Al concentrations assuming they represent the calcium carbonate and alumino-silicate fractions in each sample. Somewhat lower mean total IP concentration of 0.07 0.04% was calculated in the dust samples collected by QMA filters (22 samples). Applying the average seawater leachable fraction of LIP (38% in the Whatman 41 filters, see hereafter) to the mean total IP of the QMA filters, an average of 260 g LIP per g of dust was leached by seawater. Fig. 8 shows that the seawater LIP accounted for 6-85 % of the total IP (mean of 38%), and it varied between samples and probably dust sources. While total IP concentrations in air were linearly correlated to the particulate Ca (or Al, not shown) concentrations, no such relationship was observed with seawater LIP (Fig. 9). Most of the total IP peaks (Fig. 10) represent desert type dust events as estimated using the air mass back trajectories for the TS high volume samples. This conclusion was based on back trajectory categorization of all the dry deposition samples into two air mass populations: (a) from North Africa and the Saudi Peninsular, and (b) from West and East Europe. While the desert type events usually contain higher P and Ca concentrations in air (similar behavior was observed for the QMA filters) their IP solubility in seawater, expressed as a percentage of total IP, was usually lower (median value of ~25% as compared to ~45% in European type events). Although Saharan dust events exhibited lower IP solubility in seawater, such dust events may still contribute high amounts (load) of P to the surface waters due to their relatively high deposition rates and high total IP concentrations (0.36-0.44%, Guieu and Thomas, 1996; Ganor and Foner, 1996). The solubility of IP in ‘remote’ loess particles (aeolian deposits) collected at the Negev Desert (Israel) was approximately 11% in seawater (Herut et al., 1999), similar to the dust events here. Over the NW Mediterranean, Bergametti et al. (1992) and Migon and Sandroni (in press) observed similar trend of lower P solubility in rainwater during Saharan type events.

4.3 Fluxes and possible impact

The annual rainfall, and the fluxes of PO_4^{3-} (DIP) and the various inorganic nitrogen species in rainwater are presented in Table 5. These flux estimates might contain uncertainties related to the analytical error of the volume-weighted mean concentrations (<±7% for PO_4^{3-}, NO_3^-, NH_4^+ and 30% for NO_2^-) and to the fact that the latter were calculated based on 60-89% of the total amount precipitated (see Methods). The DIN flux in TS (~0.48 g N m^{-2} yr^{-1}) was higher than in ASH and significant differences exist between the NO_3^- and NH_4^+ fluxes due to their different concentrations in the rain (Table 5). Using the more conservative hypothesis to explain this observation (see above), the NO_3^- fluxes in ASH (~0.10 g N m^{-2} yr^{-1}) and NH_4^+ fluxes at TS (~0.18 g N m^{-2} yr^{-1}) represent the total DIN flux of the European ‘background’ (0.28 g N m^{-2} yr^{-1}). The average NH_4^+:NO_3^- ratio of this ‘background’ flux (1.8) is in the range of ratios typically found in polluted air masses (1.1-2.8) and higher than those associated with African air masses (<0.9) in the northwestern Mediterranean (Loye-Pilot et al., 1990). The flux variations between years were not related to the amount of precipitation and were probably attributed to variations in air mass climatology as observed for the western Mediterranean (Loye-Pilot et al., 1990). The increasing pattern of NH_4^+ fluxes at TS may indicate larger anthropogenic contributions over the past several years. However, since this is the first such estimate of the DIN flux to the region, it is not possible to determine conclusively whether this flux is increasing systematically with time and if so, by how much.

In order to calculate the flux of DIN to the SE Mediterranean basin it is necessary to allow for the lower rainfall amounts at the sea (350-450 mm yr^{-1}; Martin et al., 1989) and probably lower DIN concentrations due to local inland contribution. It was therefore assumed that the DIN fluxes over the SE Mediterranean Basin were attributed to the European 'background' (as defined above) and were 15% lower due to reduced precipitation. The calculated DIN fluxes (~0.24 g N m^{-2} yr^{-1}) are much higher than the estimates for remote clean areas or for the Southern Hemisphere oceans (0.03-0.04 g N m^{-2} yr^{-1}) (Duce et al., 1991). They are lower, however, than the fluxes calculated for areas such as the North and Baltic Seas (~1 g N m^{-2} yr^{-1}) (Duce et al., 1991) or for the NW Mediterranean (0.51 g N m^{-2} yr^{-1}) (Loye-Pilot et al., 1990) which are immediately adjacent to areas of significant anthropogenic input. Assuming that the fluxes in the Southern Hemisphere represent the natural "background" level, nearly the whole DIN flux into the Mediterranean is of anthropogenic origin.

At present, no estimates are available of the inorganic nitrogen (IN) content of dry fallout in the eastern Mediterranean. The estimated ratio of the wet/total (i.e. both wet and dry) IN deposition in the West Mediterranean is approximately 0.75 (Martin *et al.,* 1989; Guerzoni et al., in press), which is similar to that of other oceanic areas (Duce *et al.,* 1991). Based on the latter, we estimated the total IN deposition as ~0.37 g N m^{-2} yr^{-1} and ~0.32 g N m^{-2} yr^{-1} for the Israeli Mediterranean coast and the SE Mediterranean, respectively. Higher total IN fluxes of 0.66-0.77 g N m^{-2} yr^{-1} were estimated for the NW Mediterranean (Loye-Pilot et al., 1990; Guerzoni et al., in press and references therein).

The calculated average DIP flux via rainfall into the Mediterranean coastal zone of Israel was estimated as 0.009 g P m^{-2} yr^{-1} (Table 5) and somewhat lower in the SE Mediterranean (0.008 g P m^{-2} yr^{-1}). Applying equatioin 2 we calculated the total IP dry fluxes and the seawater LIP fluxes (Fig. 10). It was estimated that the average (geomean) dry total IP flux was 0.031 g P m^{-2} yr^{-1} and the geomean dry LIP flux was 0.01 g P m^{-2} yr^{-1}. If we use an estimated deposition flux of 20 g m^{-2} yr^{-1} for the Saharan dust over the SE Levantine Basin (Ganor and Mamane, 1982), and a mean total IP and LIP as calculated in this study (0.13% and 387 ppm), similar fluxes of 0.008 and 0.026 g P m^{-2} yr^{-1} were obtained. Using these data, the ratio of the wet/total IP (i.e. both wet and dry) deposition was calculated to be 0.2. This value is somewhat smaller than the estimate of 0.3 for the West Mediterranean (Martin et al., 1989) probably because the SE Mediterranean receives only ~450 mm yr^{-1} of rainwater distributed over sporadic 20-30 rain days. The total (wet and dry) IP flux over the Mediterranean coast of Israel was estimated to be 0.04 g P m^{-2} yr^{-1} and was probably somewhat lower over the SE Mediterranean Basin (0.039 g P m^{-2} yr^{-1}). Similar fluxes were estimated in the NW Mediterranean (0.034 g P m^{-2} yr^{-1}; Loye-Pilot et al., 1996) and in Corsica (0.04 g P m^{-2} yr^{-1}; Bergametti et al., 1992). Lower fluxes by a factor of 3 were estimated for the North Atlantic and Pacific (0.0056 and 0.0076 g P m^{-2} yr^{-1}, respectively), and by about a factor of 20 for the South Atlantic and Pacific (Duce *et al.,* 1991).

Table 6 summarizes the estimated wet, dry and leachable IN and IP atmospheric fluxes and their ratios over the SE and NW Mediterranean. It is reasonable to suggest that the dissolved IP plus seawater LIP fluxes represent the amount of phosphate, which is bioavailable in the surface waters. This assumes that there is no significant adsorption onto or desorption from inorganic particles after they reach the surface waters. The DIN:DIP and also the dissolved plus the seawater leachable IN:IP ratios in the atmospheric precipitates were well above the Redfield ratio (N:P = 16:1) and also higher than the measured N:P ratios in Levantine deep waters (N:P = 27:1; Krom et al., 1991). This estimated ratio may increase even further due to the unknown contribution of seawater leachable N from dry fallout. It is estimated that these ratios are higher in the NW Mediterranean as compared to the SE basin mainly due to higher total IN fluxes. These data suggest that the atmospheric input of nitrogen could potentially support higher amounts of productivity by a factor of approximately 2-3 than does the input of phosphorus. By using the N:C ratios of Redfield (16:106) or that evaluated by Takahashi et al. (1985) (16:122), the atmospheric input of DIN estimated here (0.24 g N m^{-2} yr^{-1}) supplies 8% of the total new production (16.7-19.2 g C m^{-2} yr^{-1}, Krom et al., 1992) to the eastern Mediterranean, but a minimum of 20% if the production recycled from the previous year (Krom et al., 1992) is removed. In comparison, the atmospheric total IN inputs account for 10-50% of the total new production in the western Mediterranean Sea (Martin et al., 1989). By using the P:C ratios of Redfield (1:106), the total bioavailable IP flux of 0.018 g m^{-2} yr^{-1} (Table 6) accounts for 0.74 g C m^{-2} yr^{-1} (4-11% of the total new production), about half that of DIN. Thus, the atmospheric contribution to new production may be less than the above DIN assessment. However because the surface waters are so oligotrophic, it is nevertheless possible that particular rainfall or dust storm events may still trigger measurable blooms of phytoplankton (Buat-Menard et al., 1989; Bergametti et al., 1992; Migon and Sandroni, in press). For example, the dust event in May 7th, 1996 contributed seawater LIP in the order of 117 ng m^{-2} d^{-1} (Fig. 10). This input is equivalent to 4.8 mg C m^{-2} d^{-1} which corresponds to 96 g Chl-a m^{-2} d^{-1} (using C/Chl-a = 50 (23-79) by weight, Parsons and Takahashi, 1975). Although this amount constitutes less than 1% of the total integrated Chl-a in the euphotic zone (0-120m) during spring (12 mg Chl-a m^{-2}, Herut et al., in press), it represents a significant fraction (~8%) of the upper mixed layer (~20m with mean chl-a concentration of 0.06 g l^{-1}). A second example is the major dust event during May 15th, 1998. We calculated that during May 15th 170 mg Al settled on 1 m^2 (flux of 170 mg Al m^{-2} d^{-1}) which is ~30% the mean yearly flux (~500 mg Al m^{-2} y^{-1}, see above). Assuming that Al represents on average 4-10% by weight of the mineral aerosol it represents a load of 1500-4000 mg dust per m^2. This event contributed approximately 200 g m^{-2} d^{-1} of seawater leachable PO_4-P and a total PO_4-P flux of 2400 g m^{-2} d^{-1}. The leachable input could support 8.5 mg C m^{-2} d^{-1} which corresponds to 170 g Chl-a m^{-2} d^{-1}. This amount represents ~1.5% of the total integrated Chl-a in the euphotic zone (0-120m) measured during June 1996 and May 1997 (10-13 mg Chl-a m^{-2}, Herut et al., in press) and ~17% of the Chl-a in the upper mixed layer (~20m with mean chl-a concentration of 0.05 g l^{-1}). This input is probably a minimum estimate because the event lasted for about 3 days. It is still unknown if that dust may eventually scavange phosphate from the water, especially after descending into the deep water mass, owning to its relatively high (~29) Fe/P ratio (molar) as suggested by Blomqvist (1999).

The calculated atmospheric N and P fluxes suggests that the atmospheric input to the basin causes an imbalance of N:P, which at the very least reinforces the possible P limitation (Krom et al., 1991; Zohary and Robarts, 1998). Moreover, global atmospheric N fluxes have increased during the last 100 years (Galloway et al., 1995). It is likely that in this basin the emissions from anthropogenic sources of N to the atmosphere are increasing faster than those of P. This suggests that anthropogenic changes in the atmospheric nutrient flux will also reinforce the P limited nature of the basin, as has been suggested for other oceanic areas (Fanning, 1989). However, in coastal areas of N limited waters it may enhance primary production (Paerl, 1985) or trigger the development of harmful algal blooms (Paerl, 1997 and others).

Acknowledgements

This report presents recently and soon to be published data of the following co-authors: Michael D. Krom, Gang Pan, Robert Mortimer, Malcolm Nimmo, Angela Medway and Roy Chester. The authors would like to express their gratitude to the collaboration of Hadera Association of Towns for Environmental Protection and Ashdod-Yavneh Regional Association for Environmental Protection. We wish to thank Y. Gertner and G. Fainstein for their technical assistance in the dust filters analyses and sample collection. We would like to thank Dr. J.I. Hongwei and Dr D. Banks for the analyses of cations in rainwater by ICP-EAS, and Dr. M. Nimmo for the analyses of the air mass back trajectories. This study was supported in part by the Israeli Ministry of Environment, UNEP/WMO (MEDPOL Program, projects 13.181, 8.072, 5.116), the Israeli Ministry of Infrastructure and by UK NERC grant no: GR3/10016.

References

ASTM (1983) Designation - D3683-78. Standard test method for trace elements in coal and coke ash by atomic absorption*. American Society for Testing and Materials Publisher.* Pennsylvania, USA .pp.472-475.

Bergametti G., Dutot A.L., Buat-Menard P., Losno R. and Remoudaki E. (1989) Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. *Tellus*, 41B, 353-361.

Bergametti, G., E. Remoudaki, R. Losno, E. Steiner and B. Chatenet. 1992. Source, transport and deposition of atmospheric phosphorus over the northwestern Mediterranean. *J. Atmos. Chem*.,14: 501-513.

Berman, T., D.W. Townsend, S.Z. El sayed, C.C. Trees and Y. Azov. 1984. Optical transparency, chlorophyll and primary productivity in the Eastern Mediterranean near the Israeli coast. Oceanol. Acta, 9: 439-447.

Berner, E.K. and R.A. Berner. 1996. Global Environment: Water, Air, and Geochemical Cycles. Prentice Hall, New Jersey, 376 pp.

Bethoux, J.P., P. Morin, C. Chaumery, O. Connan, B. Gentili and D. Ruiz-Pino. 1998. Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change. *Mar. Chem.,* 63: 155-169.

Buat-Menard, P., J. Davis, E. Remoudaki, J.C. Miquel, G. Bergametti, G. Lambert, C.E. Ezat, C. Quetel J., La Rosa and S.W. Fowler. 1989. Non-steady-state biological removal of atmospheric particles from Mediterranean surface waters. *Nature,* 340: 131-134.

Chester R., Nimmo M., Alarcon M., Saydam C., Murphy K.J.T., Sandres G.S. and Corcoran P. (1993) Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions. *Marine Chemistry*, 42, 107-126.

Chester R., Nimmo M. and Keyse S. (1996) The influence of Saharan and middle eastern desert-derived dust on the trace metal composition of Mediterranean aerosols and rainwaters: An overview. In: Impact of Desert Dust Across the Mediterranean (eds. S. Guerzoni and Chester R.). *Kluwer Academic Publishers*, The Netherlands, 253-273.

Cornell, S., A. Rendell and T. Jickells. 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. Nature, 376: 243-246.

Dayan U. (1986) Climatology of back trajectories from Israel based on synoptic analysis. *J. Climate Appl. Met.*, 25, 591-595.

Duce R.A., Liss P.S., Merril J.T., Atlas E.L., Buat-Menard P., Hicks B.B., Miller J.M., Prospero J.M., Arimoto R., Church T.M., Ellis W., Galloway J.N., Hansen L., Jickells T.D., Knap A.H., Reinhardt K.H., Schneider B., Soudine A., Tokos J.J., Tsunogai S., Wollast R., and Zhou M. (1991) The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles*, 5, 193-259.

Dulac F., Buat-Menard P., Ezat U., Melki S. and Bergametti G. (1987) Atmospheric input of trace metals to the western mediterranean Sea, 1, Factors controlling the variability of atmospheric concentrations. *J. Geophys. Res*., 92, 8437-8453.

Fanning, K.A. 1989. Influence of atmospheric pollution on nutrient limitation in the ocean. *Nature,* 339: 460-463.

Galloway, J.N., R.W. Howarth, A.F. Michaels, S.W. Nixon, J.M. Prospero and F. Dentener. 1996. Nitrogen and phosphorus budgets of the North Atlantic Ocean and its watershed. Biogeochemistry, 35: 3-25.

Galloway, J.N., W.H. Schlesinger, H. Levy II,, A.F. Michaels and J.L. Schnoor. 1995. Nitrogen fixation: Anthropogenic enhancement-environmental response. *Global Biogeochemical Cycles,* 9: 235-252.

Ganor, E., and Mamane Y. (1982) Transport of Saharan dust across the eastern Mediterranean. *Atmos. Environ*., 16, 581-587.

Ganor, E. and Foner H.A. (1996) The mineralogical and chemical properties and the behaviour of aeolian Saharan dust over Israel, p. 163-172. *In* S. Guerzoni and Chester R. [eds.], Impact of Desert Dust Across the Mediterranean. Kluwer Academic Publishers, the Netherlands.

GESAMP (1989) IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution. The Atmospheric Input of Trace Species to the World Ocean,1989. Rep. Stud. GESMAP (38).

Graham, W.F. and R.A. Duce. 1979. Atmospheric pathways of the phosphorus cycle. *Geochim. Cosmochim. Acta,* 43: 1195-1208.

Guerzoni S., Molinaroli E. and Chester R. (1997) Saharan dust inputs to the western Mediterranean Sea: depositional patterns, geochemistry and sedimentological implications. *Deep-Sea Res. II*, 44, 631-654.

Guerzoni S., Chester R., Dulac F., Moulin C., Herut B., Loye-Pilot M-D., Measures C., Migon C., Rossini P., Saydam C., Soudine A. (1999). The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Progress in Oceanography*, 44, 147-190.

Guieu, C. and A.J. Thomas. 1996. Saharan aerosols: from the soil to the ocean, p. 207-216. *In* S. Guerzoni and Chester R. [eds.], Impact of Desert Dust Across the Mediterranean. Kluwer Academic Publishers, the Netherlands.

Guieu C., Chester R., Nimmo M., Martin J.M., Guerzoni S., Nicolas E., Mateu J. and Keyse S. (1997) Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean. *Deep-Sea Res. II*, 44, 655-674.

Gullu G. H., Olmez I., Aygun S., Tuncel G. (1998) Atmospheric trace element concentration over the eastern Mediterranean Sea: Factors affecting temporal variability. *J. Geophys. Res.,* 103, 21,943-21,954.

Herut, B. 1998. Monitoring the atmospheric input of trace species along the Mediterranean coast of Israel in 1997. IOLR Rep. H43/98.

Herut B., A. Starinsky, A. Katz and Bein A. (1990) The role of seawater freezing in the formation of subsurface brines. *Geochim. Cosmochim. Acta*, 54, 13-21.

Herut B., Starinsky A. and Katz A. (1993) Strontium in rainwater from Israel: Sources, isotopes and chemistry. *Earth Planet. Sci. Lett.*, 120, 77-84.

Herut B., Spiro B., Starinsky A. and Katz A. (1995) Sources of sulfur in rain water as indicated by isotopic ^{34}S data and chemical composition, Israel. *Atmos. Environ*., 29, 851-857.

Herut B. and Krom M.D. (1996) Atmospheric input of nutrients and dust to the SE Mediterranean. In: Impact of Desert Dust Across the Mediterranean (eds. S. Guerzoni and Chester R.). *Kluwer Academic Publishers*, The Netherlands, 349-358.

Herut, B., T. Zohary, R.D. Robarts and N. Kress. 1999. Adsorption of dissolved phosphate onto loess particles in surface and deep Eastern Mediterranean water. *Mar. Chem.,* 64, 253-265.

Herut B., Krom M.D., Pan G., Mortimer R. (1999) Atmospheric input of nitrogen and phosphorus to the SE Mediterranean: sources, fluxes and possible impact. *Limnol. & Oceanog.,* 44, 1683-1692*.*

Herut B., Starinsky A., Katz A., and Rosenfeld D. (2000) Relationship between the acidity and chemical composition of rainwater and climatological conditions along a transition zone between large deserts and Mediterranean climate, Israel. *Atmos. Environ*.**,** 34, 1281-1292.

Jickells T. (1995) Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. *Marine Chemistry*, 48, 199-214.

Kubilay, N.N. and Saydam C. (1995) Trace elements in atmospheric particulates over the eastern Mediterranean; concentrations, sources, and temporal variability. *Atmos. Environ*., 29, 2289-2300.

Kubilay, N.N., Saydam C., Yemenicioglu S., Kelling G., Kapur S., Karaman C., Akca E., (1997) Seasonal chemical and mineralogical variability of atmospheric particles in the coastal region of the Northeast Mediterranean. *Catena*, 28, 313-328.

Krom, M.D., S. Brenner, N. Kress, A. Neori and L.I. Gordon. 1992. Nutrient dynamics and new production in a warm-core eddy from the E Mediterranean. *Deep-Sea Res*., 39, (3/4), 467-480.

Krom, M.D., N. Kress, S. Brenner and L.I. Gordon. 1991. Phosphorus limitation of primary productivity in the Eastern Mediterranean Sea. *Limnol. Oceanogr.,* 36, 424-432.

Loye-Pilot, M.D., J.M. Martin and J. Morelli 1990. Atmospheric input of inorganic nitrogen to the western Mediterranean. *Biogeochemistry,* 9, 117-134.

Martin J.M., Elbaz-Poulichet F., Guieu, Loye-Pilot M.D. and Han G. (1989) River versus atmospheric input of material to the Mediterranean Sea: an overview. *Marine Chemistry*, 28, 159-182.

Massart, D. L., Vandeginste, B. G. M., Deming, S. N., Michotte, Y., and Kaufman, L., (1988) Chemometrics : a Textbook, Elsevier, Amsterdam,

Migon C., Journel B. and Nicolas E. (1997) Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea. *Atmos. Environ*., 31, 889-896.

Migon, C., G. Copin-Montegut, L. Elegant, and J. Morelli 1989. Atmospheric input of nutrients to the coastal Mediterranean area. Biogeochemical implications. *Oceanol. Acta*, 12, 187-191.

Migon, C. and V. Sandroni. 1999. Phosphorus in rainwater: partitioning, inputs and impact on the surface coastal ocean. *Limnol. Oceanogr*., 44, 1160-1165.

Moulin, C., C.E. Lambert, F. Dulac and U. Dayan. 1997. Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation. *Nature,* 387**,** 691-694.

Owens, N.J.P., J.N. Galloway and R.A. Duce. 1992. Episodic atmospheric nitrogen deposition to the oligotrophic oceans. *Nature,* 357, 397-399.

Pacyna J.M., A. Semb and J.E. Hanssen (1984) Emissions and long-range transport of trace element in Europe. *Tellus*, 36B, 163-178.

Paerl, H.W. 1985. Enhancement of marine primary production by nitrogen-enriched acid rain. *Nature,* 315, 747-749.

Paerl, H.W. 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as “new” nitrogen and other nutrient sources. *Limnol. Oceanogr.,* 42, 1154-1165.

Parsons, T. and M. Takahashi. 1975. Biological Oceanographic Processes. Oxford, Pergamon Press, 186 pp.

Prospero, J.M., K. Barrett, T. Church, F. Dentener, R.A. Duce, J.N. Galloway, H. Levy II, J. Moody and P. Quinn. 1996. Atmospheric deposition of nutrients to the North Atlantic Basin. *Biogeochemistry,* 35, 27-73.

Rahn K.A. (1976) The chemical composition of the atmospheric aerosol. Tech. rep., Graduate School of Oceanography, Univ. of Rhode Island, Kingston, R.I.

Rojas C.M., Injuk J., Van Grieken R.E. and Laane R.W. (1993) Dry and wet deposition fluxes of Cd, Cu, Pb and Zn into the southern Bight of the North Sea *Atmos. Environ*., 27A, 251-259.

Salihoglu I., C. Saydam, O. Basturk, K. Yilmaz, D. Gocmen, E Hatipoglu and A Yilmaz 1990. Transport and distribution of nutrients and chlorophyll-a by mesoscale eddies in the Northeastern Mediterranean. *Mar. Chem.,* 29, 375-390.

Sandroni V and Migon C. (1997) Significance of trace metal medium-range transport in the western Mediterranean, *Science of the Tot. Env*., 196, 83-90.

Schaug, J., Rambaek, J. P., Steinnes E., Henry R. C. (1990) Multivariate analysis of trace element data from moss samples used to monitor atmospheric deposition. *Atmos. Environ*., 24, 2625-2631.

Takahashi, T., W. S. Broecker, and S. Langer. 1985. Redfield ratio based on chemical data from isopycnal surfaces. *J. Geophys. Res*., 90 C4, 6907-6924.

Taylor S.R. and McLennan (1985) The continental crust: its composition and evolution. Blackwells, Oxford, England, 312 pp.

UNEP/WMO (1992) Airborne pollution of the Mediterranean Sea. Report and Proceedings of the Second WMO/UNEP Workshop. MAP Technical Reports Series No.64, UNEP, Athens.

Weisel C.P., Duce R.A., Fasching J.L. and Heaton R.W. (1984) Estimates of the transport of trace metals from the oceans to the atmosphere. *J. Geophys. Res*., 89, 11607-11618.

Zohary, T. and R.D. Robarts. 1998. Experimental study of microbial P-limitation in the eastern Mediterranean. *Limnol. Oceanogr*., 43, 387-395.

Table 1: Statistical summary of particulate trace metal concentrations in air (ng m^{-3}) at stations along the Mediterranean coast of Israel.

Station	Parameter	Cd	Cu	Pb*	Zn	Mn	Cr	Fe	Al
Maagan Michael QMA filters	arithmetic mean	0.26	8.9	47.8 (61.2)	104	21.7	4.7	950	1163
	std	0.13	5.2	35.2 (42.7)	100	14.8	2.3	890	1244
	geometric mean	0.23	7.2	38.2 (48.9)	63	18.1	4.0	685	788
	median	0.22	8.7	35.3 (50.4)	51	16.4	4.9	635	646
	min	0.07	0.7	11.9 (11.9)	11	6.5	1.1	90	102
	max	0.69	22.4	177 (226)	334	68.8	10.0	3911	5659
	n	66	66	46 (66)	66	66	65	65	65
Tel Shikmona QMA filters	arithmetic mean	0.32	6.8	42.8	156	27.5	2.8	1096	1409
	std	0.22	3.5	30.0	142	45.1	2.4	1184	1603
	geometric mean	0.27	5.8	34.6	91	16.4	2.1	781	969
	median	0.28	6.5	35.2	91	14.5	2.2	715	913
	min	0.07	0.5	6.9	0.2	1.3	0.5	161	46
	max	1.51	18.3	143.8	553	240.3	12.2	6742	8139
	n	61	44	61	61	61	55	61	56
Tel Shikmona WH41 filters	arithmetic mean	0.29	8.7	43.9	164	20.4	3.5	1084	995
	std	0.27	7.1	33.9	291	17.7	1.9	1008	853
	geometric mean	0.19	5.4	33.6	85	14.5	2.9	798	720
	median	0.24	5.7	35.5	72	16.2	3.2	846	694
	min	bb	bb	4.2	20	0.7	0.4	122	36
	max	1.14	30.1	183.9	1607	86.4	7.8	5135	4276
	n	35	32	35	35	33	31	35	35
Tel Shikmona **All**	geometric mean	0.24	5.7	34.2	89	15.7	2.4	787	865
	n	96	76	96	96	94	86	96	91

na = not analysed due to contamination by the high-volume sampler motor. *excluding 1996 samples (see text), in parenthesis all samples (1996+1997)

Table 2: Particulate trace element concentrations and enrichment factor values (EFcrust) in air over the Israeli Mediterranean coastline, Turkey (Erdemli) and European coastal sites.

Element	**northern Israel (TS)[1]**		**Turkey Erdemli[2]**		**European Coastal Sites[3]**	
	ng m^{-3}	EF	ng m^{-3}	EF	ng m^{-3}	EF
Al	865	1	685	1	318	1
Fe	787	2.3	685	2.5	275	2.2
Mn	15.7	2.4	12.6	2.5	11	4.6
Cr	2.4	6.4	8.5	29	2.9	21
Cu	5.7	21	na	na	5 (3.6)[4]	51
Zn	89*	117	19	31	41 (27)[4]	146
Pb	34.2	159	30	176	40 (33)[4]	506
Cd	0.24	228	0.19	228	0.7 (0.28)[4]	1806
Pb:Cd	143		158		57 (80[4], 116[5])	
Zn:Cd	371		100		59 (~100[4,5])	
Zn:Pb	2.6		0.63		1 (1.3[4], 0.8[5])	

na = not analysed; * = possible contamination problem.

[1] Present study.

[2] Kubilay and Saydam, 1995.

[3] Chester et al., 1993; Guieu et al, 1997.

[4] Migon et al., 1997.

[5] Sandroni and Migon, 1997.

Table 3: Trace element concentrations (g g^{-1} dry wt.; Al and Fe in %) and EF$_{crust}$ values for samples of regional dust event and loess deposits from the Negev desert.

Site / Sample	**Parameter**	**Cd**	**Pb**	**Zn**	**Cu**	**Cr**	**Mn**	**Al**	**Fe**
Eilat Dust 28 May 1997	Concentration	1.4	21.5	na	na	na	711	4.25	3.45
	EF$_{crust}$	27	2				2	1	1.9
BY Dust March 1996	Concentration	na	na	na	na	na	530	5.00	3.17
	EF$_{crust}$						2	1	1.6
Netivot loess	Concentration	0.12	8.7	65	23	70	595	4.50	3.2
	EF$_{crust}$	2	1	2	1.6	3.6	2	1	1.6
Ashdod Feb. 2nd, 1996	Concentration	1.1	227	270	na	91	617	4.75	3.56
	EF$_{crust}$	20	19	6	-	4	1.7	1	1.7
Ashdod Nov. 11th, 1996	Concentration	1.0	86	128	243	54	517	4.13	3.07
	EF$_{crust}$	19	8	4	19	3	1.7	1	1.7
Upper Crust*	Concentration	0.098	20	71	25	35	600	8.04	3.2

na = not analysed; * Taylor and McLennan, 1985.

Table 4: Estimates of trace element dry fluxes (g m^{-2} y^{-1}; Fe, Mn and Al in mg m^{-2} y^{-1}) to the Israeli Mediterranean coast and to the southern coast of France (Migon et al., 1997).

Station	Cd	Cu	Pb	Zn	Cr*	Mn	Fe	Al
Maagan Michael	7	226	1542	1979	127	11	432	497
Tel Shikmona	8	178	1080	2806	75	10	496	545
Cap Ferrat (France)	33	1606	2555	41610	na	na	na	na

na = not analysed; * probably underestimated due to association with large crustal particles

Table 5: Estimates of wet nutrient fluxes (g m^{-2} yr^{-1}) and volume-weighted mean concentrations (M) along the Israeli Mediterranean coast.   All fluxes were calculated based on the annual or total (all years) volume-weighted mean concentrations (see text).

Site	**Year**	**Precipitation** (m)	**Units**	**P-PO_4^{3-}**	**N-NO_3^-**	**N-NH_4^+**	**N-NO_2^-**	**DIN**
Ashdod	1995/6	0.516	flux	0.015	0.069	0.217	0.002	0.284
Ashdod	1996/7	0.543	flux	0.006	0.107	na	0.005	nc
Ashdod	1997/8	0.552	flux	0.009	0.108	0.301	0.004	0.413
Ashdod	all years	0.537	flux	0.009	0.097	0.269	0.004	0.364
			volume-weighted mean	0.56	12.94	35.80	0.48	48.47
			n	57	57	45	57	45
Tel Shikmona	1992/3	0.557	flux	0.008	0.161	nc	na	nc
Tel Shikmona	1993/4	0.321	flux	0.010	0.339	0.076	na	0.432
Tel Shikmona	1994/5	0.435	flux	0.008	0.183	0.144	0.002	0.325
Tel Shikmona	1995/6	0.620	flux	0.008	0.239	0.223	0.003	0.465
Tel Shikmona	1996/7	0.412	flux	0.011	0.470	0.211	0.003	0.684
Tel Shikmona	1997/8	0.647	flux	0.008	0.298	0.257	0.004	0.558
Tel Shikmona	all years	0.499	flux	0.009	0.284	0.177	0.003	0.482
			volume-weighted mean	0.58	40.62	25.40	0.44	69.04
			n	179	179	160	118	160

na = not analysed; nc = not calculated due to partial NH_4^+ analyses; DIN = total dissolved inorganic N.

Table 6: Calculated values of the flux of dissolved inorganic nitrogen and phosphorus in rainfall (DIN & DIP), seawater leachable from dry fallout (LIN & LIP) and the total nutrient input (total dry and wet IN & IP) in units of g m^{-2} yr^{-1}, and their ratios over the Israeli Mediterranean coast (IMC), the SE Mediterranean (SEMED) and the NW Mediterranean (NWMED). The bioavailable IP (BIP) flux was estimated by DIP + LIP. Unknown data is marked by ?.

Parameter	**IMC**[a]	**SEMED**[b]	**NWMED**[c]
DIN	0.28	0.24	0.51[c]
LIN^	?	?	?
Total dry and wet IN	0.37[&]	0.32[&]	0.7[d]
DIP	0.009	0.008	0.005[e] - 0.016[d] (avg. 0.01)
LIP^	0.01	0.01	0.01[#]
Total dry and wet IP	0.040	0.039	0.034[d] -0.04[f] (avg. 0.037)
Bioavailable IP (BIP)	0.019	0.018	0.02
Total dry and wet IN/IP (molar)	20	18	42
DIN/DIP (molar)	70	66	113
DIN/BIP (molar)	33	30	56

[a] This study; [b] Extrapolation of 85% IMC fluxes for DIN and DIP (see text);

[c] Loye-Pilot et al., 1990; Migon et al., 1989; [d]Guerzoni et al., 1999; [e]Migon and Sandroni, 1999, [f]Bergametti et al., 1992.

[&] Calculated assuming wet IN = 3 dry IN (see text).

^ Seawater leachable IN and IP from dry fallout (bioavailable).

[#] Calculated assuming similar leachability (LIP/Total IP ratio) as in IMC.

LIN = leachable inorganic nitrogen

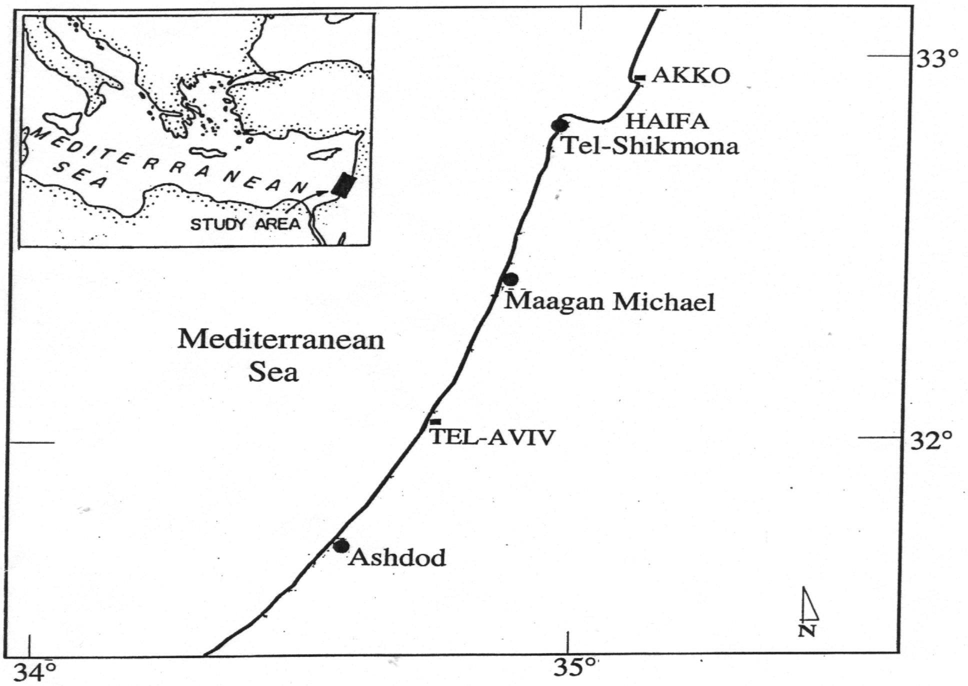


Figure 1: Location of sampling stations along the Mediterranean coast of Israel.

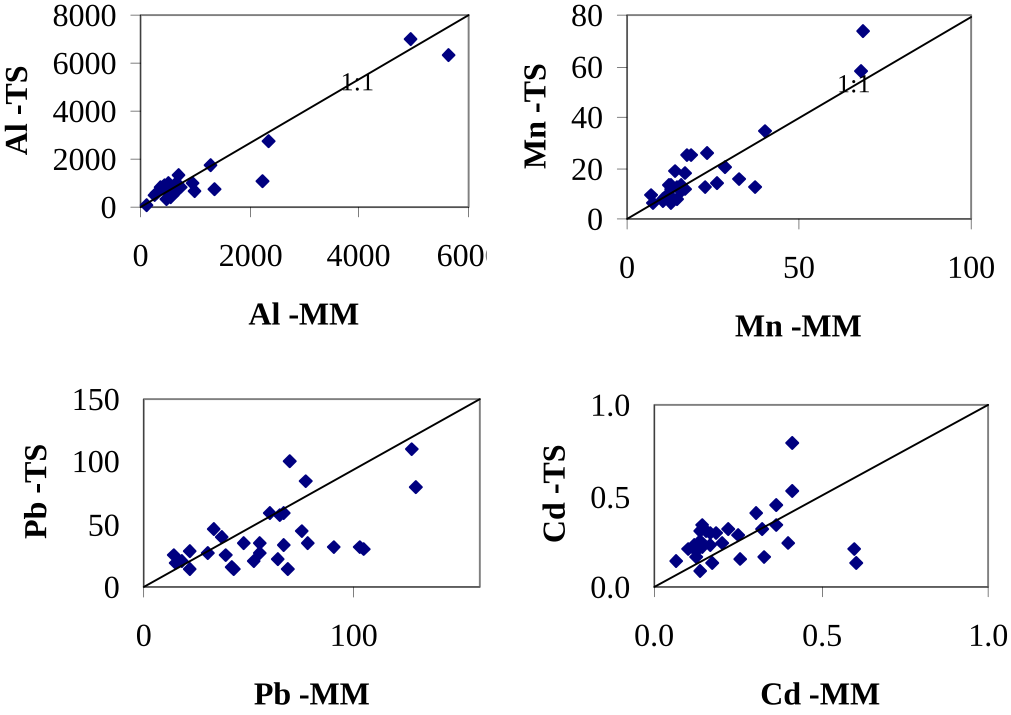


Figure 2: Particulate Al and Pb concentrations in air samples collected contemporaneously at Tel-Shikmona (TS) and Maagan Michael (MM).

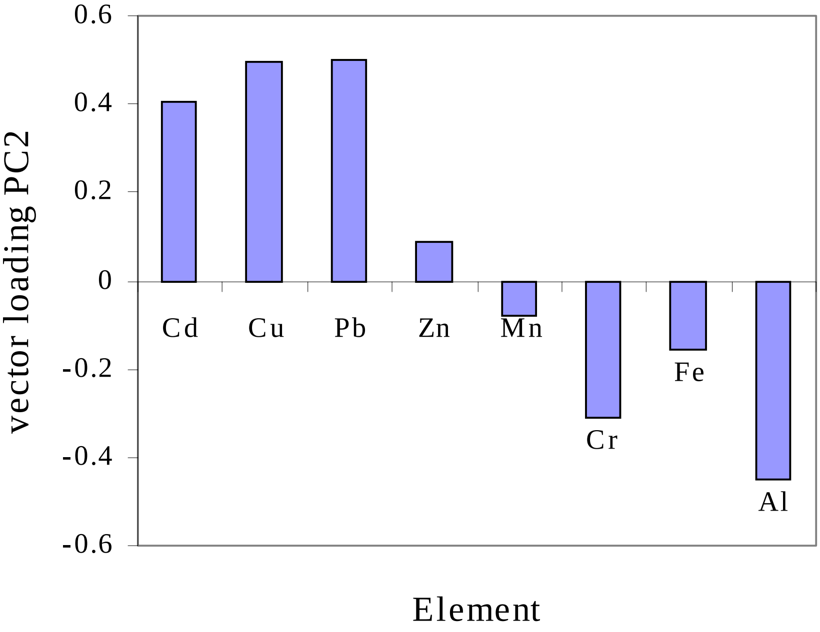


Figure 3: The adverse loading of anthropogenic (Cd, Cu, Pb, Zn) versus natural elements (Al, Fe, Mn, Cr) as depicted by principal components analysis (eigenvector 2) on TS and MM samples.

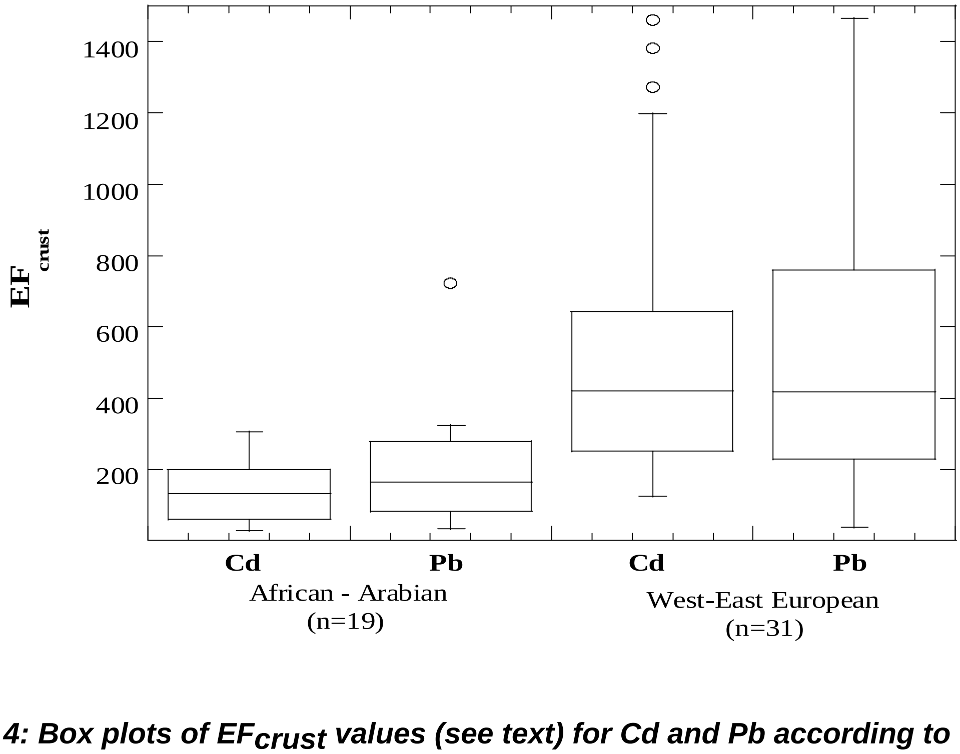


Figure 4: Box plots of EF_{crust} values (see text) for Cd and Pb according to the origin of the associated air masses. Two geographical sectors were classified, European and Afro-Arabic (see text). The bottom and the top of each box are located at the 25 and 75 precentiles. The central horizontal line is drawn at the sample median.

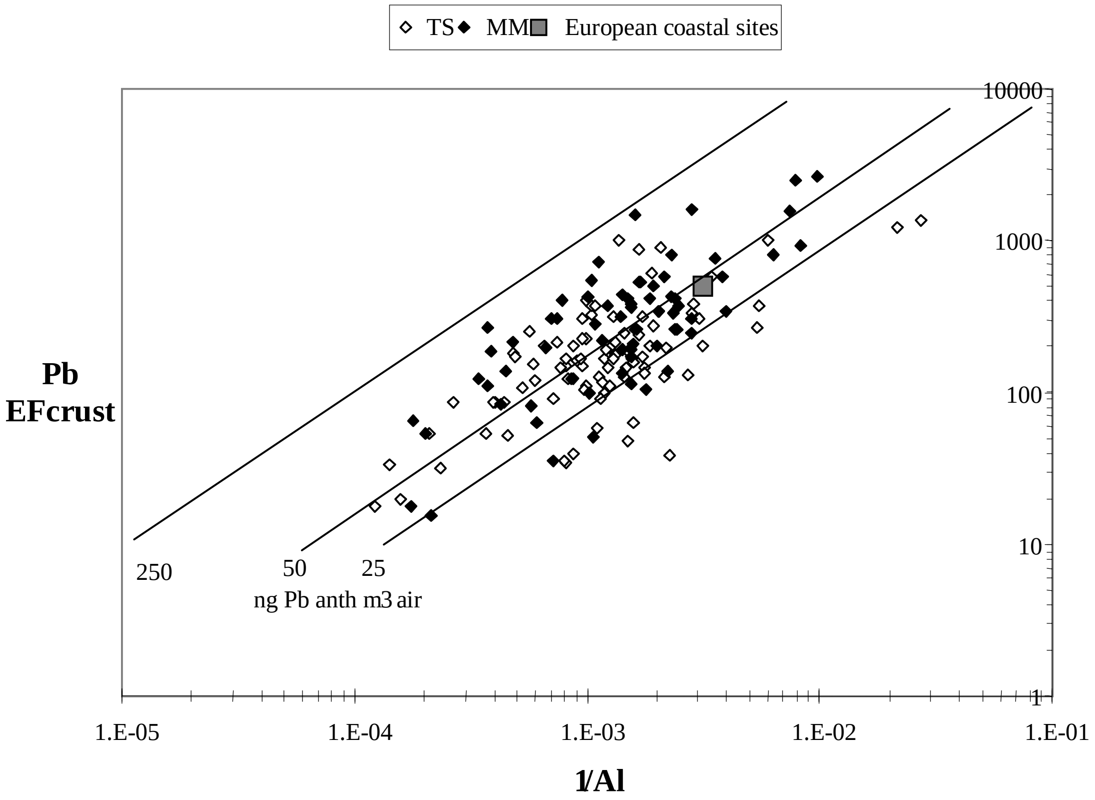


Figure 5: Plot of Pb EF_{crust} vs. 1/Al_{air}. The position of the data points is explained by the mixing between a 'clean' crustal aerosol end-member and an anthropogenic end-member (see text). The slope of the line represent the term Tr_{anth} x $(Al/Tr)_{crust}$ from which Tr_{anth} can be estimated. Higher slopes exhibit more polluted sites. The dilution of clean crustal material in air is represented by an horizontal line along EF = 1 (Tr_{anth} -->0). Contamination by anthropogenic trace element will cause a vertical shift to the data. The mixing between the latter two end-members will distribute the data along 45° downwards range.

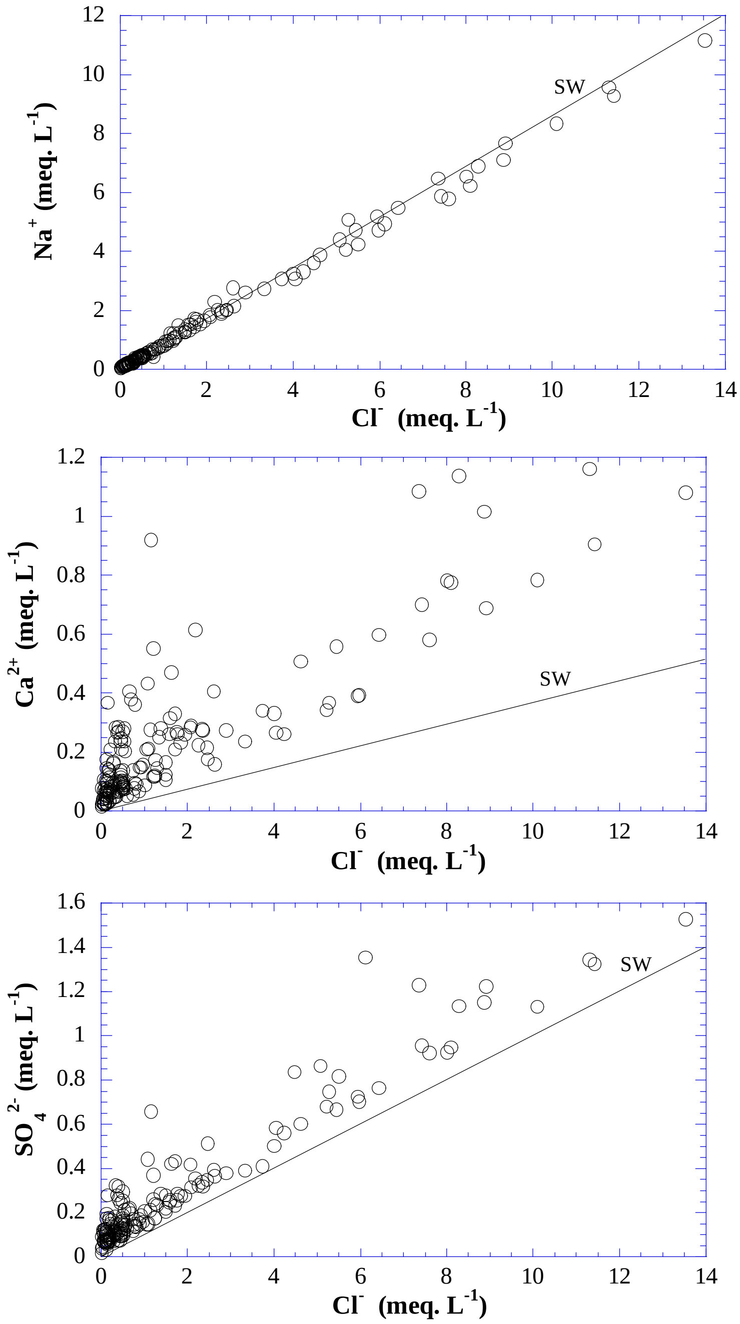


Figure 6: The relationship between Na^+, Ca^{2+}, SO_4^{2-} and Cl^- in rainwater. Cl^- vs. Na^+ display a clear marine ratio (seawater (SW) line) indicating their introduction into all rain samples as seaspray while Ca^{2+} and SO_4^{2-} display a large non-seaspray fraction.

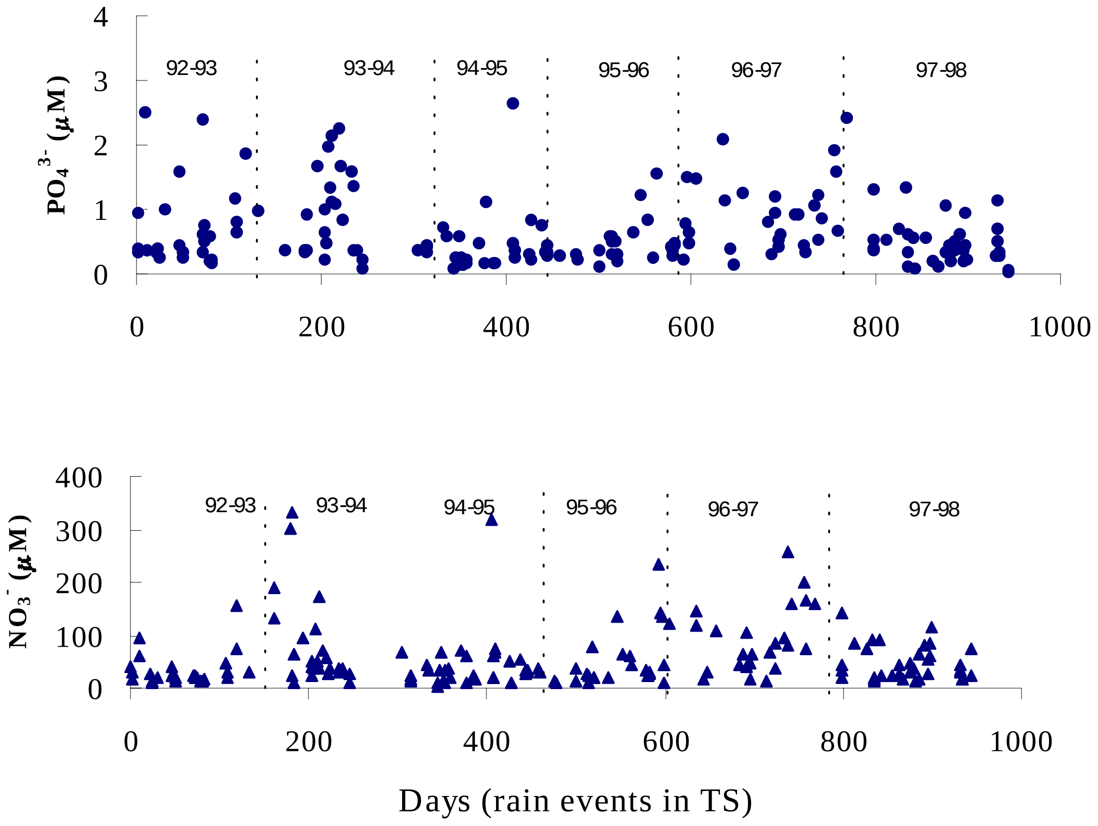


Figure 7: Temporal variability of PO_4^{3-} and NO_3^- concentrations (M) in rainwater samples collected at Tel-Shikmona (TS) and at Ashdod (ASH). Data points of 5 rain events from TS, which had PO_4^{3-} concentrations >4 M are out of scale (not marked by a symbol).

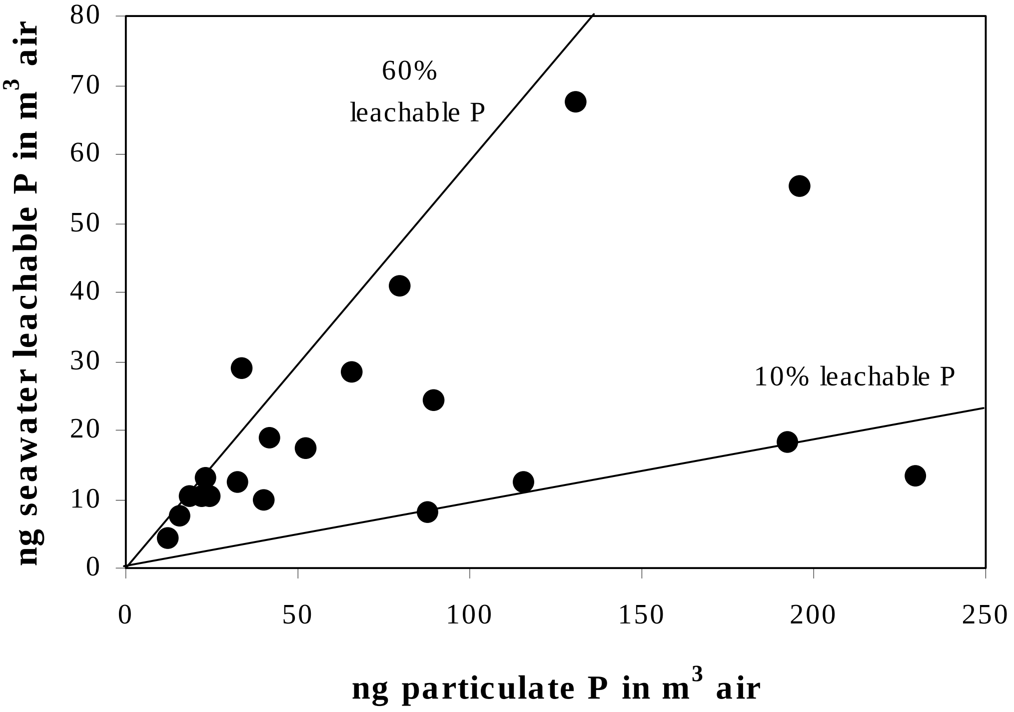


Figure 8: The relationships between seawater leachable and HCl leachable (total) particulate inorganic P concentrations in m^3 air. Total and seawater leachable concentrations were measured in dust collected on Whatman 41 filters at Tel-Shikmona during 1996.

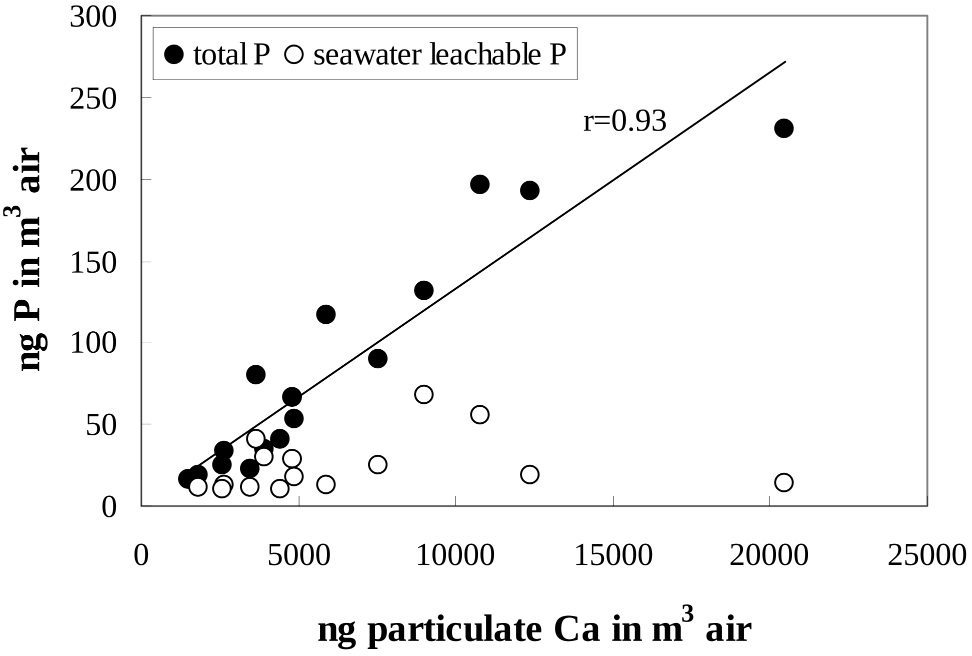


Figure 9: The relationships between seawater leachable and HCl leachable (total) particulate inorganic P concentrations in m^3 air and particulate Ca concentrations in m^3 air. The linear regression line calculated for the total inorganic P data is included ($p<0.05\%$).

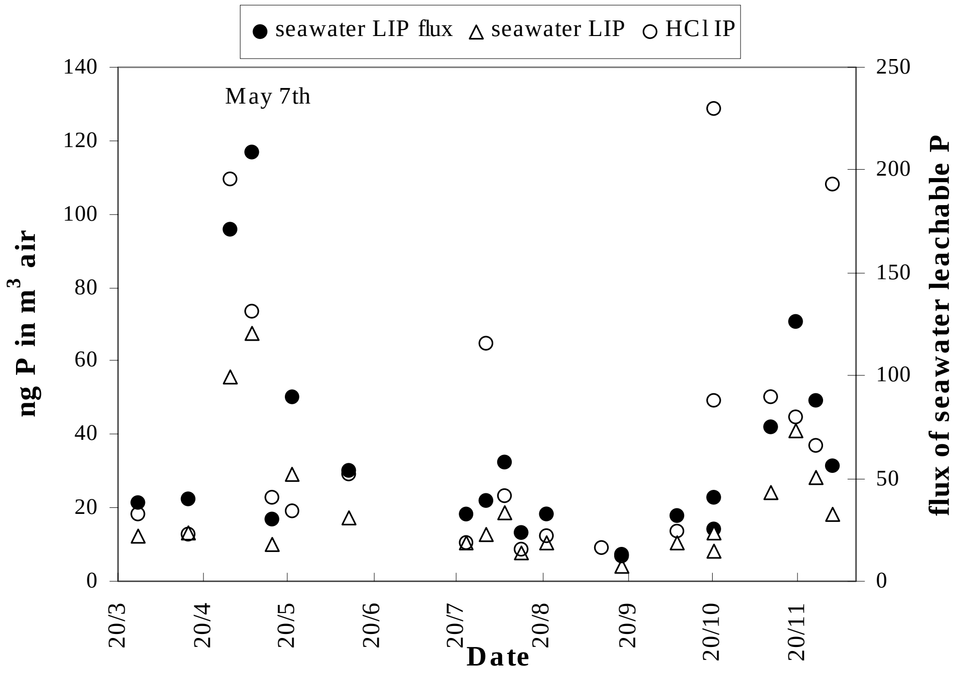


Figure 10: Temporal variability of seawater leachable (LIP) and HCl leachable (total) particulate inorganic P (IP) in m^3 air, and of seawater LIP fluxes (g m^{-2} d^{-1}).

ATMOSPHERIC INPUT OF INORGANIC NITROGEN TO THE ADRIATIC SEA

***Vesna Djuricic*[1], *Visnja Sojat*[1], *Sonja Vidic*[1], *Stefano Guerzoni*[2]**

[1] Meteorological and Hydrological Service of Croatia, Gric 3, 10000 Zagreb, Croatia
[2] Istituto di Geologia Marina, CNR, Via Gobetti 101, 40129 Bologna, Italy

1. INTRODUCTION

Man can disturb the natural environment in many ways, particularly when disposing the wastes resulting from his activities. A prime example of this is the influx of man-made nutrients, mainly in the form of nitrogen and phosphorus compounds, to estuary and coastal areas, which may result in the long-term decline of marine life. Though we often think of nutrients as being beneficial to life, an overabundance may cause perceptible water quality deterioration as well as chronic or intermittent health hazards, including toxicity and the loss of aesthetic and hence recreational values of affected waters (Pearl, 1988). Recent investigations of the biogeochemical cycles of trace elements in marine systems have placed increased significance on the atmospheric input of nutrients (Eskinja et al, 1996). It has been suggested that in open–ocean waters, the flux of growth-limiting macronutrients, such as nitrogen, and micronutrients, such as iron, may constrain the marine productivity (Pearl, 1985; Knap et al., 1986; Fanning, 1989; Pearl et al., 1990; Willey and Cahoon, 1990; Owens et al., 1992; Michaels et al., 1993). Studies of coastal estuaries, such as Chesapeake Bay (US), have shown that atmospherically derived dissolved inorganic nitrogen (NO_3^- + NH_4^+, components of acid rain) contributes 25-35% of the total loading of this primary nutrient (Fisher and Oppenheimer, 1991; Hinga et al, 1991; Scudlark and Church, 1993).

In the northern Adriatic, the predominant sources of anthropogenic atmospheric nitrogen emission are attributed to fossil fuel combustion, the oil and petroleum industry and transportation, while in the southern and mid Adriatic mainly to agricultural production. The reported effects are extensive algal blooms and oxygen depletion (Enviro, 1990). It has been discussed that eutrophication on a regional level occurs in the northern Adriatic, and also, at a local level, in several coastal areas with periodic extremely negative consequences for the ecosystem and various human activities. Furthermore, a series of undesirable events occurred in the past decade: invasions of jellyfish and other species, hypertrophic formations of mucilaginous aggregates, and, more recently, an increased frequency of toxic dynoflagellate appearance (Smodlaka, 1994).

It is well known that precipitation is a very efficient scavenger of pollutants. Changes in the chemical composition of precipitation reflect changes in the chemical composition of the atmosphere, resulting in deposition. It has been discussed that the atmospheric input of pollutants to the Mediterranean Sea is of the same order of magnitude as the riverine input for many species (Erdman, 1994). Since the Mediterranean Sea is a semi-enclosed sea, the effects of atmospheric transport and deposition are expected to be higher than in regions like the open oceans. The complexity of the problem needs detailed studying in order to understand and assess the atmospheric input of inorganic nitrogen to the Adriatic coastal area.

In Croatia, the Meteorological and Hydrological Service (MHSC) monitors and studies the atmospheric precipitation quality and air pollution. The chemical composition of precipitation on the Adriatic coast has been monitored since the beginning of the MED POL programme as part of the National Atmospheric Precipitation Chemistry Programme (NAPCP). Three national stations are included in the MED POL. Over the last decade, the MHSC have taken an active part in the investigation of pollutant deposition. Research has been focused on the effects of acid rain, particularly those of sulphuric (H_2SO_4) and nitric (HNO_3) acids on forests (Bajic, Djuricic, 1995; Vidic, 1995; Alebic-Juretic, Sojat, 1997; Sojat et al, 1996; Pozar-Domac et al, 1998; Sojat, Borovecki, 1995).

The aim of this paper is to address the problem by focusing on nitrogen wet deposition. For that purpose, nitrogen compounds and the pH values of daily, bulk precipitation samples for the period 1981-1995 have been analysed. The results are shown as basic statistic parameters of concentration and wet-deposition. The paper contains the analysis of meteorological parameters that may significantly influence environmental issues in the region: weather types, wind regime and precipitation. Trend and trajectory analysis have been investigated, too.

2. INVESTIGATED AREA

Six of the stations along the Adriatic coast considered in this paper (Fig. 1) belong to the monitoring network for precipitation chemistry, established and maintained by the Meteorological and Hydrological Service of Croatia. All of them are located at meteorological stations.

Rijeka (φ=45° 20´ N, λ=14° 27´E, h=120 m asl) is the largest Croatian shipyard and harbour on the Adriatic coast, situated in the Kvarner Bay in the Northern Adriatic. In addition, a great number of pollution sources are assembled here: an oil refinery and petroleum industry, a cokery, a thermal power plant, local industries, heavy traffic, domestic heating. The meteorological station is situated on a hill slope in the northern part of the city, about 2 km from the city centre.

Because of its position (both on a micro and regional scale), this station is classified as an “impact” station. It is under the influence of local and regional pollution sources.

Pula (φ=44° 52´ N, λ=13° 51´E, h=30 m asl) is the southernmost city on the Istra peninsula. It is surrounded by the sea from NW through S to NE, and therefore is under the sea influence. Local pollution sources are a shipyard and domestic heating, which is not very strong, because of the mild climate. The climatological station is situated on flat terrain, in the city centre, inside a pine tree park. Pula is classified as an “impact” station.

Senj (φ=44° 59´ N, λ=14° 54´E, h=26 m asl) has a very specific location under the Velebit mountain, the largest mountain along the coast, which is the natural boundary between the Croatian inland and the Adriatic Sea. It is under the influence of strong *bura* wind (NE wind), which is the result of a strong chanelling effect of the wind stream over the Vratnik pass. The meteorological station is situated in the northern part of the urban area. Local pollution is mainly from traffic. Although there are no big industries in the region, because of its microlocation, this station could also be classified as an “impact” station.

Zadar (φ=44° 8´ N, λ=15° 13´E, h=5 m asl) is in mid Adriatic. Local pollution sources in Zadar are the local industry (sawing machines, foodstuff), traffic and, in a small amount, domestic heating. The meteorological station is in the suburb, about 150 m from the sea, under the sea influence. Zadar is classified as an “impact” station.

Zavizan (φ=44° 49´ N, λ=14° 59´E, h=1594 m asl) is the highest station in Croatia, placed at the top of the Velebit mountain. There are no local pollution sources nearby. The height of the station is practically the average hight of the 850 hPa level surface. Zavižan is classified as a “rural” station.

Dubrovnik (φ=42° 39´ N, λ=18° 5´E, h=42 m asl) is a southern Adriatic station. It is open to the sea in all directions except to the west, and under the strong sea influence, especially in cases with *jugo,* a strong southern wind. There are no significant anthropogenic pollution sources in the region. Dubrovnik is classified as a “rural” station.

3. DATA AND METHODS

3.1. Chemical data

Concentration of nitrogen from nitrates (NO_3^--N) and ammonia (NH_4^+-N), as well as precipitation acidity (pH value) from bulk daily precipitation samples are statistically analysed. Wet deposition of nitrogen from nitrate and ammonium is calculated, too.

3.2. Meteorological data

Meteorological parameters have been measured at the same locations as precipitation quality. We have analysed: daily precipitation amount, wind direction and strength (generally and in precipitation days) observed in climatological terms, daily weather types and 72 hours backward trajectories from three of the considered locations.

3.3. Sampling methods

The precipitation samples are bulk daily samples collected from 07 to 07 UTC. The samples are stored in bottles in which they will be transported to the laboratory (without filtering at the station). At the stations, the bottles are stored in a cold and dark place, not always at the recommended temperature of 4°C. The samples are transported to the laboratory within one or two weeks.

Comparison of one year parallel measurements with bulk and wet-only method, made at one of our stations, shows that some neutralisation processes occurred in bulk samples. In that particular year, the percentage of acid rain in bulk samples was less than 30%, indicated only in three months. Wet-only sampling method gave acid precipitation in all seasons, except summer. Between 8 and 64% of precipitation was acid.

Some experiments of ionic stability of precipitation samples have shown that pH values of bulk samples which stay in original sampling bottle in the room temperature for 9 days significantly increase (Peden, Skowron, 1978). Dust in precipitation samples increases pH value by neutralisation with calcium. Some of our sampling sites are under the influence of dust. Also, sample analysis is delayed sometimes for about 2 weeks which both influence pH value.

Comparison of nitrogen compounds in precipitation shows that nitrate bulk concentrations were generally higher than wet-only, while differences for ammonium ions were not so expressive. Peden and Skowron (1978) showed that insects and bird droppings in precipitation sample could influence ammonium concentrations in irregular way. Impurities from trees could influence most major ions in precipitation, except ammonium. Urban influence raises most of major ion concentrations, too. All those influences are present every now and than at our stations.

Reported nitrate (and sometimes ammonium) concentrations and pH values in precipitation at our stations are a little bit higher than real values, because of the measuring method used. That has to be taken into account in comparing our results with some other's.

3.4. Analytical methods

Chemical analyses are performed in the central laboratory at the Meteorological and Hydrological Service in Zagreb. Measurement techniques and equipment are: pH–meter 93, Radiometer (pH); electrical conductivity method, CDM 210, Radiometer (el. conductivity); standard titrimetric method (HCO_3^-); ion-selective electrode method, Orion Research 901 (Cl^-, F^-, NH_4^+-N); UV/VIS-spectrophotometric method, Perkin Elmer Lambda 1 (SO_4^{2-}-S, NO_3^--N); atomic absorption method, Perkin Elmer (Na^+, K^+. Ca^{2+}, Mg^{2+}).

Quality control of the data includes visual inspection and ion balance checking. Because of many failures in sampling, transport, storing and chemical analysis methods, a number of samples did not satisfy the ion balance criteria. Only samples which fulfil the ion balance criteria (about 21–40% of total precipitation amount per station) were taken into consideration for further statistic analyses.

4. PRECIPITATION QUALITY

4.1. Precipitation acidity

The major statistic parameters for the pH values of samples that fulfil the ion balance criteria are given in Table 1. Precipitation is acid on average at all stations except Pula. The most acid precipitation is measured in Rijeka, which was already shown in some previous papers (Djuricic, 1989; Djuricic, Vidic, 1992; Djuricic, Bajic, Sojat, 1996; Sojat et al, 1996). Rijeka is under the influence of both long–range and local pollution sources, which is reflected in the precipitation pH value. More than 50% of the samples in Rijeka are acid. Other “impact” stations have about 20% of acid precipitation. The two ”rural” stations have 34-39% of acid precipitation. In Dubrovnik, the sea influence could be a significant reason. Zavizan is supposed to show the influence of long–range pollution. However, in certain weather conditions, when air pollution from the Kvarney Bay enters mixing layer which is so high that Zavižan is inside it, it is possible that this pollution is wet deposited there.

Table 1. Statistic parameters of precipitation pH values from samples that fulfil ion balance criteria, 1981-1995 (N = number of samples; x_{vw} = volume-weighted mean; σ = standard deviation; variab. (%) = standard deviation expressed in percentage of mean value; min = minimum value; max = maximum value).

Parameter	Rijeka	Pula	Senj	Zavizan	Zadar	Dubrovnik
N	353	176	257	749	119	213
x_{vw}	4,75	6,34	5,40	5,26	5,50	5,12
σ	0,90	0,72	0,77	0,75	0,78	0,77
variab. (%)	18,90	11,40	14,30	14,30	14,20	15,00
min	3,68	4,20	3,95	3,71	4,01	4,08
max	8,25	7,69	7,83	7,63	7,60	8,24

The lowest individual pH value, as well as the highest, are also measured in Rijeka. Variability (standard deviation divided by mean value, in percentage) and standard deviation are the greatest at Rijeka, too.

The most frequent individual pH values are between 6 and 7 at four of the locations considered. At the same time, at those locations volume-weighted means are less than 6. The reason is that the samples with greater precipitation amount had lower pH, which contributes more to the volume-weighted average. On the other hand, many of the samples with pH 6–7 were those of small precipitation amount.

The temporal variation of the precipitation pH values can be seen from the annual volume-weighted means (Figure 2). The smallest year to year variations are shown at the two “rural” stations Zavizan and Dubrovnik and the “impact” station Rijeka. The difference is in the fact that at Zavizan and Dubrovnik annual pH is between 5 and 6, while at Rijeka between 4 and 5.

Precipitation pH values and their variability at Croatian Adriatic coast are quite comparable with those at an Italian site (Ciattaglia and Cruciani, 1989). In Italy, more acid precipitation was also found in industry developed regions in Northern Italy than in the middle or in the south.

4.2. Nitrogen compounds in precipitation

Nitrogen compounds in precipitation are from nitrates (NO_3^--N) and ammonia (NH_4^+-N). On average, at all stations except Zavizan, nitrate concentration is greater than that of ammonia (Table 2). Concentrations of nitrates and sulphates are always slightly higher than the ammonia concentrations (Samb, 1998). From 70 to 80% of ammonium concentrations are below 1 mg/l at all stations. For nitrate this is true only for Zavizan. At all other stations, the frequency of nitrate concentrations below 1 mg/l varies between 37 and 63%. Nitrate concentrations of 1-2 mg/l appear in 24 to 42% of cases. Both, nitrate and ammonium concentrations are higher at "impact" stations under the influence of traffic, industry or the sea, than at "rural" ones.

Day to day concentrations of both nitrogen compounds, vary a lot, what could be seen from a big standard deviation and variability (more than 100%) at all stations.

The maximum concentration could be really high, more than 10 times higher than the mean value, especially for nitrate.

Table 2. Statistic parameters of nitrogen concentration (mg/l) from nitrates (NO_3^--N) and ammonia (NH_4^+-N) from samples that fulfil ion balance criteria, 1981-1995 (N = number of samples; x_{vw} = volume-weighted mean; σ = standard deviation; variab. (%) = standard deviation expressed in percentage of mean value; min = minimum value; max = maximum value).

	Rijeka		Pula		Senj		Zavizan		Zadar		Dubrovnik	
	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N
N	349	321	173	167	250	234	732	704	116	70	202	202
x_{vw}	0,94	0,88	1,23	0,73	1,24	0,48	0,42	0,45	1,33	0,60	0,78	0,50
σ	1,36	1,03	1,52	1,38	1,16	0,78	0,73	0,50	1,80	0,86	1,29	0,88
variab. (%)	145	117	124	189	94	163	174	111	135	143	165	176
min	0,02	0,02	0,17	0,01	0,12	0,02	0,01	0,01	0,08	0,03	0,07	0,01
max	12,10	5,40	11,00	14,90	9,43	8,90	8,26	3,61	11,10	4,22	10,00	7,31

Loÿe-Pilot et al. (1989) reported that the concentrations of dissolved nitrogen compounds for polluted rain samples are greater than 1.5 mg/l and the typical value is around 2.9 mg/l. Our results are in that range. However, we have to remember that because of the sampling, storing and transportation methods, reported concentrations are a little bit higher than they really are.

Temporal variations of both nitrogen compounds are small at two "rural" stations (Zavizan and Dubrovnik) and greater at the “impact” stations, especially in Zadar (Figure 3). A small variation is a characteristic of “rural” stations. Simultaneous nitrate and ammonia annual mean concentrations are very similar at "rural" stations. At Zavizan, the annual NH_4^+-N is even greater than NO_3^--N, in many cases. On the other hand, at "impact" stations, the annual mean concentration of NO_3^--N is greater than NH_4^+-N almost every year. Time courses of nitrate and ammonium annual means differ quite a lot. That indicates on the different source behaviour of those pollutants.

The annual course of nitrates in precipitation is not very evident (Figure 4). At the mountain "rural" station Zavizan the nitrate concentrations are almost the same through the whole year. The annual course of ammonium ion concentrations shows higher concentrations in the vegetation period, what is to be expected.

4.3. Deposition of nitrogen

The Rijeka area gets the greatest amount of nitrogen wet deposition (Figure 5). Although the mountain station Zavizan receives more precipitation, wet deposition of nitrogen is not the greatest, because of lower concentrations. Going from the north to the south of the Adriatic coast, the deposition amount declines (Figure 5).

The total nitrogen wet deposition at Zavižan was higher in the period from 1993 to 1995. In those three years, the concentrations of both nitrogen compounds were rather high, as well as precipitation amount. High concentrations might reflect the increase of anthropogenic emissions of ammonia in some regions in Europe (EMEP/MSC-W Report 1/99).

Wet deposition is the product of ion concentration and precipitation amount. Wet deposition of nitrate is more under the influence of precipitation behaviour. Greater nitrate wet deposition in autumn reflects the greater precipitation amount in autumn at all stations, although nitrate ion concentrations are not very high in that season (Figure 6).

On the other hand, wet deposition of ammonia is more under the influence of the ion concentration course. Higher ammonia concentrations in the vegetation period cause higher wet ammonia deposition values, despite relatively low precipitation amount (Figure 6).

The July minimum in precipitation amount is evident for wet deposition of both nitrogen compounds.

As Zavizan is not under direct influence of local pollution sources, it predominantly shows the effects of regional and long-range pollution transport. According to the Zavizan records, we could say that most of the deposited nitrogen, approximately between 1 and 2 g/m^2 per year, comes to the northern Adriatic by the long-range transport. According to the Rijeka records, another 1 to 2 g/m^2 per year are contributed by the local pollution sources in Northern Adriatic, especially in the Kvarner Bay. The deposition in Senj is in agreement with that. Pula, which is closer to the sea, is less loaded by nitrogen deposition.

The Middle Adriatic, represented by Zadar, in the 15-years period considered, got approximately 2.4 times less precipitation than Rijeka. The total wet nitrogen deposition is still, in some years, almost the same as in Rijeka. Because of its location, we suppose that the Zadar station shows a combined influence of local and long-distant pollution sources.

The total nitrogen deposition in Dubrovnik, in Southern Adriatic, was the smallest, and similar to Zavizan. Since Dubrovnik is, like Zavizan, considered as a “rural” station, we could suppose that most of the measured nitrogen deposition originates from long-distance sources. Unfortunately, because of the war operations in Croatia, there were no measurements in Dubrovnik in 1993 -1995, to compare them with the highest deposition levels at Zavizan.

Greater depositions in some years (for instance, in 1984 in Pula, Senj, Zadar and Dubrovnik) coincide with greater precipitation amounts, while in other years (in 1982 in Rijeka and in 1990 in Zadar) with higher nitrate or ammonia concentrations.

In Zavizan and Dubrovnik, the deposition of nitrates is similar to that of ammonia. In Dubrovnik, in most of years, the nitrate deposition is slightly higher, while in Zavizan it is the opposite. At the other locations, the nitrate deposition is often higher than that of ammonium.

Model calculations for last several years show that 88–97% of oxidised and 58–78% of reduced nitrogen come to Croatia from neighbouring countries (EMEP, 1997). On the other hand, 81–95% of oxidised and 56–67% of reduced nitrogen from Croatian sources deposited in Croatia. About 10–15% of the total deposition deposited on the sea.

According to the measured deposition at six stations along the Adriatic coast, it seems that 1-2 g N /m^2 per year reach the Adriatic Sea from long-distance sources. In addition, another 1-2 g N /m^2 per year comes to the northern and mid Adriatic from local pollution sources. It seems to be rather high load of the environment, comparing to some other regions (for instance, wet deposition of inorganic nitrogen at the Cap Ferrat (France) in 1986 was 0.61 g/m^2 (Migon et al, 1989). It has to be mentioned again that these reported values are overestimated, because of sampling, storing and analyzing methods.

5. METEOROLOGY

5.1. Weather types – general description

Weather type gives the first, rough selection of weather patterns that influence meteorological, ecological and other parameters. Classification of weather conditions is based on the surface pressure field and wind flow, and by the geopotential field at 1.5 or 5.5 km of height (AT 850 or AT 500 hPa). Each type is characterised by specific meteorological conditions (Loncar, Bajic, 1994). There are six main weather types over Croatia, valid also for the Adriatic coast.

Precipitation weather type (PWT) is characterised by strong winds, frontal passages and convergence of horizontal air flow and air lifting along the axis or in the centre of low pressure activity over western and north-western Europe. PWT is more frequent in the cold part of the year (Figure 8). This type is characterised by stratum cloudiness and long-lasting precipitation episodes.

Radiation weather type (RWT) is characterised by zero pressure gradient fields, accompanied by weak winds of variable directions. In this type the precipitation is mainly convective and effects of local pollution prevail. RWT is more frequent in the warm part of the year (Figure 8). It has to be mentioned that the dominant factor for a particular weather type could have different effects on weather, depending on the part of the year. This is most obvious in the radiation weather type: maximum turbulent vertical exchange occurs during summer, while the most stable conditions with temperature inversions and no mixing is characteristic for that type in winter time.

Advection from SE Europe (SE adv.) is characterised by cold advection in wintertime, with weak winds and long-lasting stable conditions accompanied with temperature inversions. It is more frequent in the cold part of the year.

Advection from the NW Europe (NW adv.) is mainly connected with frontal passages and therefore with mostly fast advection of cold air from NW Europe over the warm land, which results in convective cloudiness and precipitation. Frequency of this type is similar during the whole year.

Wind weather type (WWT) is characterised by very fast advection of cold air, strong winds and good horizontal and vertical air exchange. It is a little bit more frequent during the cold part of the year.

High-pressure ridge (HPR) is connected mainly with anticyclone over Western Europe or Azores and with low-pressure activity over south-eastern Europe. HPR is almost the dominant weather type during summer, especially in southern Adriatic (Figure 8). It is characterised by weak winds, mainly from NE direction and small precipitation amount. Regional transport of air mass from inland to the sea with dominant NE wind (although weak) is possible.

In general, radiation weather type was the most frequent in the 15 years period from 1981 to 1995 (Figure 7). Precipitation weather type and high-pressure ridge have followed it. If only days with precipitation are under consideration, then the precipitation weather type prevailed, while the radiation weather type had lower frequency. The same conclusion is valid along the whole Adriatic coast. Although the radiation weather type is generally the most frequent (about 40% of all days) it gives less than 20% of the total precipitation amount. More precipitation (50-60% of total amount) gives the precipitation weather type which frequency is about 20%. The high-pressure ridge, which occurs in about 15% of time, gives only 2-5% of precipitation.

Annual course of the three most frequent weather types is almost the same for northern and mid Adriatic, while for southern Adriatic it differs slightly (Figure 8). The precipitation weather type is more frequent in cold part of the year. Minimum is in July while maximum in April or December (northern and mid Adriatic), or in October and November (southern Adriatic). Annual course of precipitation amount is very similar to it. The radiation weather type has the opposite annual course, with higher frequency in warm part of the year. There are some reductions in its frequency in June and November in southern Adriatic probably because of higher frequency of the high-pressure ridge. The high-pressure ridge does not have well-defined annual course.

Described weather types are typical for the region. However, they have similar characteristics as five main synoptic weather patterns for the Mediterranean Sea, based on the Grosswetterlagen classification applied by Hess and Brezovski (1969) (Dayan and Miller, 1989).

5.2. Weather types and deposition of nitrogen compounds

Connection between weather types and nitrogen concentrations as well as wet deposition were investigated. The Dubrovnik station was not considered, because of the lack of comparable data due to interruptions caused by the war in the investigated period.

Nitrate concentrations in Rijeka and Zavizan are almost independent on weather types (Figure 9). At the other three locations the highest nitrate concentrations were observed during the weather type with fast advection of cold air from NW Europe, connected mainly with frontal passages. In this, not very frequent weather type, accompanied with small precipitation amount, the air masses come from polluted regions in west, north-west and north Europe. Higher nitrate concentrations are connected with the high-pressure ridge, too. Slight transport from inland to the sea is possible in that weather type. According to this, the influence of inland nitrate sources on regional scale should be taken into account in Rijeka, Pula and Zadar.

Ammonium concentrations in Zadar are also high in the NW advection weather type (from only six samples). The highest ammonium concentrations in Rijeka are connected with the wind weather type and high-pressure ridge. The high-pressure ridge is important for ammonium concentrations in Zadar, too. In these two weather types the influence of regional and distant pollution sources might be of significant influence.

When only two prevailing weather types are taken into consideration, slightly higher concentrations in the radiation weather type are found for both, nitrate and ammonium, at all stations. Differences are small, but stil could indicate the importance of local pollution sources. It is the most frequent type and its importance is not negligible for about 20% of the total amount of precipitation.

On the other hand, in individual samples higher concentrations are connected with the precipitation weather type showing the influence of distant pollution sources. Top ten highest concentrations are connected mainly with this precipitation weather type, especially in northern Adriatic. As this type brings approximately 60% of precipitation, its importance is even greater. Combination of influences for long-distant, regional and local pollution sources is obvious from these analyses.

Deposition of nitrates and ammonia is the greatest in the precipitation weather type mainly because of higher precipitation amount (Figure 10).

The analysis of nitrogen in the atmosphere in connection with general weather conditions shows that concentrations and deposition levels along the Adriatic coast are the combination of local, regional and long-distance nitrogen sources. Prevailing influence is pertinent to each particular case. Large-scale weather patterns coupled with local circulation and maritime conditions in a complex orography in a number of cases explain observed conditions, but in many cases more detailed analysis is needed.

5.3. Wind regime

Wind is the most important factor affecting the transport of pollutants. Together with other meteorological parameters it reflects atmospheric processes under different weather conditions. It is well known that weather conditions in mid latitudes vary considerably. In Croatia, there is a lot of different weather conditions followed by intense and frequent changes between them.

Main factors influencing the surface airflow are: turbulence (irregular and accidental local air movements caused by mechanic and thermal conditions), characteristics of the ground over which the air flows, warming and cooling of the ground during day and night, topographic characteristics of the ground and small obstacles like houses, trees etc. and atmospheric disturbances of meso and macro scale. In orographically developed regions, like Croatian coast, wind is affected by local conditions in a very high degree.

It is evident from annual wind rose (Figure 11) that the most frequent winds along the Adriatic coast are *bura* (NE wind) and *jugo* (SE wind, sirocco). *Bura* (often referred to as ‘bora’) is more significant in the northern Adriatic, while *jugo* in the mid and southern Adriatic. *Bura* has the greatest frequency in Senj (35% of ENE wind). Investigations of wind regime in Croatia showed that in the areas where *bura* blows its relative frequency varies between 12 and 30% (Bajic, 1997). Depending on local ground characteristics, at some location *bura* has stronger north component (Rijeka, Dubrovnik), while at the others east component is stronger (Senj). In Zadar and mountain station Zavizan, *bura* is of minor significance.

On some stations along the Adriatic, seasonal wind *ethesia* has influence, too (NW wind resulting from general circulation between the Azores anticyclone and the Karachi depression).

The greatest frequency of *bura* and *jugo* in the cold part of the year is the consequence of the pressure distribution with high pressure over the land and low pressure over the sea. On the other hand, during summer dominant influence on wind along the Adriatic coast has the Azores anticyclone and *maestral* (NW wind) which is the resultant wind from ethesia and sea breeze. Among the considered stations, *maestral* is the most frequent in Zadar.

A specific wind rose in Zavizan, with almost only E and W wind, is connected mainly with the local orography.

Seasonal variations of the wind direction are not very strong. The frequency of *bura* is higher in winter and autumn in Rijeka, Senj and Dubrovnik. *Jugo,* which is the most evident in

Dubrovnik and Zadar, is more frequent in spring than in other seasons. *Maestral* is the main wind in Zadar during summer.

More than 50% of wind (independent on direction) is not stronger than 3 Beauforts (≤5.4 m/s). Strong wind (6 B and more) blows in less than 5% of cases. It is more frequent in the cold part of the year. Strong or severe *bura* in Senj is the consequence of specific location of Senj under the Velebit mountain and the Vratnik pass with strong channelling effect of wind stream (Luksic, 1975; Makjanic, 1966; Makjanic, 1978; Bajic, 1989; Vucetic, 1993). The situations with strong *bura* in Senj in winter could last very long. The frequency of calms decrease along the coast from the north to the south. Calms are more frequent in warm part of the year at all stations.

The described wind regime allows significant transport in the lower boundary layer from inland toward the coast.

Precipitation wind roses

Ordinary wind roses give the general picture of the wind regime at specific location. The main subject of this investigation is the atmospheric input of inorganic nitrogen to the Adriatic Sea by precipitation. Precipitation wind roses give additional information about wind regime in days with precipitation, which could differ from general ones.

In days with precipitation, the significance of *jugo* comes out, while frequency of *bura* and the western wind decreases. The differences vary depending on location, but generally become greater going toward south. *Bura* is still prevailing wind in northern Adriatic, while in mid and southern Adriatic *jugo* prevails during the whole year.

According to Dubrovnik data, the most frequent daily precipitations amounting to 1–5 mm (28%) contribute most to the precipitation wind rose. Small precipitation amounts (≤ 0.5 mm daily, with frequency of 18%) are connected with *bura* in cold part of the year, while with *jugo* in summer and specially in spring. On the contrary, great daily precipitation amounts (≥50.1 m, with frequency of only 1.8%) are connected with *jugo* in cold part of the year, and with *bura* in warm.

5.4. Precipitation

The precipitation regime results from distribution of atmospheric circulation systems and frontal passages. In summer, a subtropical high-pressure zone reaches the south of Croatia, while circulation systems pass more to the north. Therefore the main cause of precipitation are the cold frontal systems, which bring rain in July. These cold fronts come mainly from northern Alps, reaching first the north-western part of Croatia and the northern Adriatic coast. Going toward south-east, they become weaker giving less precipitation. On the other hand, during autumn and early winter, a great number of circulation systems pass over the Mediterranean and Adriatic Sea toward the inland. The mountains on the coast (Dinarides, Velebit) are the obstacles on which air masses have to rise, resulting with convective cloudiness and precipitation.

The annual course of precipitation amount is similar at all stations along the coast (Figure 13), with maximum in autumn (October and November) and minimum in summer (July). That kind of annual course in known as maritime. Zavizan and Rijeka receive the highest precipitation amount in all seasons. Zadar and Pula receive less precipitation in winter, spring and late autumn, but Dubrovnik receives the least precipitation in July. The explained path of cold fronts (with rains in July) along the Adriatic, on which they become weaker going to the south, can explain well-defined minimum in Dubrovnik.

The annual course of precipitation day's number is similar for all stations, too. Although more precipitation falls in autumn, number of days with precipitation has maximum in spring or early summer (April, June) in northern Adriatic, while in winter or spring (December, March) in mid and southern Adriatic (Figure 13). The precipitation amount per event is greater in autumn than in winter, spring or summer.

Zavizan and Rijeka received the highest precipitation amount during the whole period of investigation (Figure 14). Zavizan is the mountain station on the height of about 1600 m and receives high precipitation amounts. Rijeka gets a lot of precipitation because of its position on the way of frontal passages and a lot of precipitation is locally enhanced by orography. Pula and Zadar received less precipitation.

6. TREND ANALYSIS

In order to investigate the trend of nitrate and ammonium concentrations three types of analysis have been performed: 1) time series for all observed ion concentrations (outlayers greater than arithmetic mean plus three times standard deviation were excluded), 2) time series for samples which satisfied ion balance criteria and 3) those for volume-weighted annual mean values calculated from all data. Linear regression was estimated and correlation coefficients were calculated for all three cases. Significance of the linear trend for annual mean values and values that satisfied criterion of ion balance was checked with the Kendall tau test. On Figure 15 only time series and trends of volume-weighted annual means are presented, but all three types of investigation will be discussed.

Time series of nitrate ions in all observed values as well as those from samples that satisfied ion balance criteria, show slight decreasing tendency at all stations, except Zavizan. Correlation coefficients are significant at 95% confidence level only at Pula and Senj for decrease and at Zavizan for increase. Precipitation volume weighted annual means of nitrate concentrations show a decreasing linear trend, significant on 95% confidence level at Rijeka and Senj, while an increasing trend at Zavizan (Figure 15). At Pula, Zadar and Dubrovnik nitrate concentrations also decrease, but not significantly.

Time series of ammonium ions in all samples show small decreasing tendency at Pula and Zavizan, while increasing at other stations. The subset of samples that satisfied ion balance criteria shows increasing tendency, significant on 95% confidence level, only at Rijeka and Senj, and not significant at Zavizan and Zadar, as well as slightly decreasing tendency at Pula and Dubrovnik. Precipitation volume weighted annual means of ammonium concentrations show significant increasing trend at Senj and Zadar (Figure 15). Not significant increasing trend is found at Rijeka, Zavizan and Dubrovnik, and decreasing at Pula.

Increasing trend of nitrogen compounds which has been noticed in many regions in Europe and North America is evident only in Zavizan for nitrates and Senj and Zadar for ammonia. Zavizan is the only real rural station in Croatia, far away from industrial and other local pollution sources. Therefore we could say that Zavizan reflects the nitrate trend in this part of Europe. All the other stations are more or less under influence of some local or regional pollution sources. General trends are therefore not so evident. Decreasing trend of nitrates in Rijeka and Senj may reflect decreasing industry and traffic activities in the period from 1990 to 1995, caused by war in Croatia.

7. TRAJECTORY ANALYSIS

Computation of air parcel trajectories is a very powerful tool to estimate the long-range transport of substances. Combined with diffusion and deposition processes it can provide an estimate of the fluxes over the sea of substances of particular interest, such as nutrients.

Dry adiabatic (isentropic) trajectories are a good approximation of three-dimensional transport of air-masses. To study the atmospheric transport to the northern, mid and southern Adriatic coast, 72-hours backward isentropic trajectories were computed for Rijeka, Zadar and Dubrovnik from 10 m asl once a day, beginning at 00 UTC, for the one year period October 1998 – September 1999. HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model (Draxler and Hess, 1997), developed in NOAA Air Resources Laboratory (Web address: http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, MD) was used. Trajectories were calculated for each day, except 1, 2, 16 and 17th day of the month, because of lack of meteorological input data.

Seasonal and yearly cluster analyses were made for each station using the cluster program developed by Stunder (1996). Mean trajectories for each cluster are presented in Figures 16-18. In addition, cluster analyses of trajectories in precipitation days were also made. For each of those clusters volume-weighted average pH values, nitrate and ammonium concentrations, as well as nitrogen wet deposition were calculated.

The main differences between cluster-mean trajectories are in their length and direction, depending particularly on whether the trajectories come from inland or the sea. The percentage of the length of a trajectory crossing over the sea is also important for transport of pollution.

At all three stations there are short, medium, long and very long cluster-mean trajectories. Short (local or regional) are 50–400 km long, medium 500–1600, long 1500–2500, while very long 2000–5000 km. The differences between them are greater with regard to shorter trajectories.

Short trajectories are very frequent (about 50%) at all stations, during all seasons. They are connected with the zero pressure gradient field, typical for summer or for the case of stationary low pressure field over the north Adriatic. Characteristics of these situations are weak winds of a variable direction, maximum turbulent vertical exchange in summer, but very stable conditions with temperature inversions and no mixing in winter. This kind of synoptic situations are classified as the radiation weather type. Short trajectories are characteristic for local and regional transport of pollution. Directions of short trajectories depend on concrete location, but more frequently they come from inland in warm part of the year and from the sea in cold part of the year.

Medium long cluster-mean trajectories from inland represent regional and long-distance transport of pollution to the Mediterranean. Trajectories come mainly from N–NE. In these situations the west or central Europe is under the influence of a high pressure field, while east and south-east of Europe under low (situations classified as the high pressure ridge weather type). Most of trajectories belonging to these clusters cross over high polluted industrial regions in west, central or eastern Europe, or over the Balkan peninsula come even from the Black Sea.

The main characteristic of SW and W cluster-mean trajectories is that they are crossing over the Mediterranean Sea and coming to the measurement site from the sea side. They are connected mostly with the Genoa low pressure field. The region they cross over is not very polluted, so they do not bring a lot of anthropogenic air pollution. These clusters contain sometimes several trajectories from Sahara, bringing Saharan dust to the Mediterranean.

Long and very long trajectories come from NW-W. Very long ones are rather rare, but because of their speciality they make separate cluster at each station. In that situation south-west Europe is under the high pressure filed, while north-east under the low pressure. Strong wind is mainly connected with frontal passages and fast advection of cold air over the warm land (NW advection weather type). Usually there are two very long cluster-mean trajectories: one more northerly, coming from the north of the Atlantic Ocean, Iceland or Greenland, and the other from the mid Atlantic, Azori Islands, or even from the eastern US or Canadian coast. Very long trajectories are connected with strong wind. They cross over the sea with natural sulphur emission (affecting chemical composition of precipitation, especially pH) along a significant part of their length. They also cross over the west and north-west Europe with high anthropogenic pollution emissions. Therefore, chemical composition of precipitation transported that way is very complex.

Generally, trajectories from the northern and eastern quadrant are more frequent in cold part of the year, while from S-SW in warm.

Most of trajectories curve and very often the main direction of the cluster differs from the direction the trajectories arrive to the site. Sometimes different cluster-mean trajectories come with the same wind direction. Local and regional conditions (meteorological, and specially orographic) cause turning of the general west and north-west airflow, which is the most common for Croatia, to local north-east. For instance, with NE wind (*bura*), which is very often along the Adriatic coast, very different trajectories may come from NW to E direction (Figures 16-18). Similarly, with the SE wind (*jugo*) different trajectories may come from E to SW directions.

In the considered one year period precipitation was acid only in Rijeka, while the greatest nitrogen deposition was at the Dubrovnik area. The influence of high polluted regions with ammonium in northern Italy, France, Netherlands, northern Germany and Denmark (EMEP/MSC-W Report 1/95) could be seen at all three stations in higher NH_4^+-N concentrations connected with the air flow from NW.

Table 3. Number of trajectories per cluster for Rijeka, Zadar and Dubrovnik, for the period October 1998 - September 1999. (72 hours isentrophic backward trajectories)

cluster	**short**	**N**	**NE**	**E**	**SE**	**S**	**SW**	**W**	**NW_l**	**NW_{vl}**
season	**RIJEKA**									
spring	32		3		5		21+1	8	8+2	
summer	26	20				15	3+5		9	2
autumn		20	7	6		16	19		5	4
winter	29	7		14					19+6	3
year	163		31				55		28+27	9
	ZADAR									
spring		19	2		26	2		19	9	2
summer			19		25		20+2	1	10+3	
autumn		10	5		16		24	11+1	8	3
winter		10		15				29+5	13	4+2
year			74	18		83	42	25	49+16	8
	DUBROVNIK									
spring	32	14	2			19	5+1	5		
summer	38	15	5				9+4	6		2
autumn	20		10	16		9	11		10	2
winter	16	8	10					5+22	12+1	4
year	118	44	26				60	33	20	12

This analysis is made for one particular year. The conclusions cannot be generalised. However, they agree with similar investigation for the GAW regional station Zavizan (Bajic, 1998/99) and for several stations in Croatia (Tudor, 2000).

Number of trajectories in particular cluster per season and year for each station is shown in Table 3. Cluster-mean trajectories for the whole year (a) and for precipitation days (b) are shown on Figures 16-18. Despite some common characteristics, each station has several pecularities.

Rijeka

The cluster analysis includes 313 trajectories, resulting in 6 cluster-mean trajectories (Figure 16a). Short trajectories are the most frequent (52%) in all seasons, except autumn (Table 3). They come from the land (E or SE) in warm part of the year, while from the sea (SW) in winter. There are three cluster-mean trajectories of medium length (Figure 16a), from SW, NE and NW, and long and very long ones are from NW.

Precipitation days

The cluster analyses includes 116 trajectories resulting in 8 cluster-mean trajectories (Figure 16b). Most of them (73%) are generally from the west. The most frequent (27%) are short trajectories parallel to the Adriatic coast. Up to 26% of total precipitation amount which is acid and has the highest ammonium concentration and deposition (Table 4), mostly of local and regional origin, is associated with these trajectories.

The greatest precipitation amount (30%) comes with the cluster-mean trajectory from S (or SW), connected mostly with the Genoa low pressure field. Precipitation coming that way is the most acid and has the highest nitrate concentration and deposition. Trajectories belonging to this cluster circulates over industrially developed European regions, northern Italy, the Mediterranean and northern Adriatic (Kvarner Bay). All these regions are polluted, both from anthropogenic and natural sources.

Significant precipitation amount comes also from W (14%) and SW (10%). It is also acid on average and loaded with nitrogen compounds.

Table 4. Characteristics of wet deposition in different trajectory clusters at Rijeka, for the period Oct. 1998. to Sept. 1999. (N = number of days; Σ RR = total precipitation amount in cluster, in mm; pH_{vw} = prec. volume-weighted average pH; $(NO_3^- \text{-} N)_{vw}$ = prec. volume-weighted nitrate concentration (mg/l); $(NH_4^+ \text{-} N)_{vw}$ = prec. volume-weighted ammonium concentration (mg/l); Dep.NO_3 = nitrogen from nitrates wet deposition (in g/m^2); Dep. NH_4 = nitrogen from ammonia wet deposition (in g/m^2); numbers in brackets are from one or two samples).

Cluster	short	S	W	SW	NW_l	NW	N	NW_{vl}
N	31	28	22	12	5	6	10	2
Σ RR (mm)	428,3	500,9	223,9	157,3	54,1	13,6	38,6	3,8
pH_{vw}	5,39	4,98	5,47	5,41	5,33	6,70	6,10	6,10
$(NO_3^- \text{-} N)_{vw}$	0,86	1,06	0,68	0,75	0,70	(2,16)	0,79	(1,44)
$(NH_4^+ \text{-} N)_{vw}$	0,91	0,67	0,87	0,61	0,48	(2,18)	0,81	(1,15)
Dep. NO_3 (g/m^2)	0,37	0,53	0,15	0,12	0,04	0,03	0,03	0,005
Dep. NH_4 (g/m^2)	0,39	0,33	0,20	0,10	0,03	0,03	0,03	0,004

Zadar

The cluster analysis includes 315 trajectories resulting in 8 clusters (Figure 17a). Clusters from southern directions are counter clockwise curved, while those of northern directions are clockwise curved. In both "halfs" there are short, medium, long and very long cluster-mean trajectories. Shorter ones are curved more. 50% of trajectories are short, coming from two almost opposite directions, S-SW and N-NE. About 30% of trajectories are of medium length, from NW and SW. The rest are long and very long trajectories from NW and E. The main difference between two short clusters is that the S-SW cluster crosses over the sea water, and the N-NE one over the land (high polluted regions).

About 35% of precipitation amount belong to the SW cluster, which includes only 13% of trajectories. The cluster with the most trajectories (26%) gives only 20% of precipitation. More precipitation is connected with clusters that come to Zadar from the sea side.

Precipitation days

The cluster analysis includes 100 trajectories resulting in 6 clusters (Figure 17b). 58% of them are short, 26% medium and 16% long or very long.

Short trajectories come to Zadar with the most frequent SE wind, in two completely different clusters. One is from NE-E, crossing over the land. It brings 14% of total precipitation amount which is not acid on average, but has a lot of nitrates (industry and traffic pollution sources are dense in the region it crosses over, Table 5). The short cluster-mean trajectory from S-SW (crossing over the sea with almost all its length) brings two times greater precipitation amount (29%) which is not acid on average, but have a lot of ammonia.

The most precipitation (38%) belongs to the NW cluster-mean trajectory. In this cluster the volume weighted average pH is the smallest (Table 5). This cluster crosses partly over the sea, partly over the land. Mostly because of high precipitation amount, wet deposition of nitrogen from nitrates is the greatest in this cluster.

Long and very long clusters include small number of trajectories and bring small precipitation amount. The highest ammonium concentration in the long NW cluster is related to the high anthropogenic ammonia pollution in NW Europe (Samb, 1998).

Table 5. Characteristics of wet deposition in different trajectory clusters at Zadar, for the period Oct. 1998. to Sept. 1999. (N = number of days; Σ RR = total precipitation amount in cluster, in mm; pH_{vw} = prec. volume-weighted average pH; $(NO_3^-\text{-}N)_{vw}$ = prec. volume-weighted nitrate concentration (mg/l); $(NH_4^+\text{-}N)_{vw}$ = prec. volume-weighted ammonium concentration (mg/l); Dep.NO_3 = nitrogen from nitrates wet deposition (in g/m^2); Dep. NH_4 = nitrogen from ammonia wet deposition (in g/m^2).

Cluster	short NE	short SW	NW_l	NW	NW_{vl}	W
N	29	29	11	26	4	1
Σ RR (mm)	108.8	227.6	127.3	293.2	15.8	0.4
pH_{vw}	6.4	6.3	6.1	5.7	6.7	7.8
$(NO_3^-\text{-}N)_{vw}$	0.94	0.85	0.72	0.74	0.70	/
$(NH_4^+\text{-}N)_{vw}$	0.48	0.57	0.73	0.40	0.54	/
Dep. NO_3 (g/m^2)	0.10	0.19	0.09	0.22	0.01	/
Dep. NH_4 (g/m^2)	0.05	0.13	0.09	0.12	0.01	/

Dubrovnik

The cluster analysis of 313 trajectories results in 7 cluster-mean trajectories (Figure 18a). Short trajectories are the most frequent (38%) in all seasons except winter (Table 3), especially in warm part of the year. They come from inland (only in spring from the Adriatic Sea) and reach Dubrovnik from SE. About 20% of trajectories belong to the medium long cluster-mean trajectory from SW and 14% from N-NE. Long trajectories come from W (11%) and E (8%). The rest (10%) are long or very long trajectories from NW.

It is very interesting that there is no cluster from SE, although SE wind is very frequent in Dubrovnik. However, NE trajectories in winter, E and S in autumn and S in spring, turn around in the vicinity of Dubrovnik and come to the station with SE wind. The most frequent wind directions in Dubrovnik are NNE, SE, NNW and SW–W. Short trajectories come to Dubrovnik from those directions.

The highest precipitation amount belongs to cluster-mean trajectories from the sea side (SW 36% of precipitation amount and only 19% of trajectories). The cluster with the greatest number of trajectories (118, i.e. 38%) brought less than 20% of total precipitation amount.

Precipitation days

The cluster analysis includes 89 trajectories. There are two different short cluster-mean trajectories, both coming with SE wind (Figure 18b). One is from NE, bringing 15% of precipitation amount, not acid, but with the highest concentrations and deposition of nitrates and ammonia. The other is from S, bringing 18% of non acid precipitation, with a little bit lower, but still high concentration of nitrogen compounds. The same wind direction is connected also with the longer E cluster-mean trajectory, crossing over inland, bringing the greatest precipitation amount (22%) with the lowest nitrate and ammonium concentrations (Table 6).

Besides the SE (*jugo*) wind, very frequent wind direction is NE (*bura*), but there are no trajectories from that direction. Bura brings to Dubrovnik mostly small amounts of precipitation.

About 12% of trajectories in precipitation days are very long, mostly from NW, coming to the station from W or SW. They bring only small amount of precipitation.

Table 6. Characteristics of wet deposition in different trajectory clusters at Dubrovnik, for the period Oct. 1998. to Sept. 1999. (N = number of days; Σ RR = total precipitation amount in cluster, in mm; pH_{vw} = prec. volume-weighted average pH; $(NO_3^- \text{-} N)_{vw}$ = prec. volume-weighted nitrate concentration (mg/l); $(NH_4^+ \text{-} N)_{vw}$ = prec. volume-weighted ammonium concentration (mg/l); Dep.NO_3 = nitrogen from nitrates wet deposition (in g/m^2); Dep. NH_4 = nitrogen from ammonia wet deposition (in g/m^2), concentrations in brackets are from small number of samples).

Cluster	short NE	short S	E	E_I	W	SW	NW	NW_I	NW-N_M
N	15	17	17	3	13	6	7	8	3
Σ RR (mm)	143,9	164,6	203,9	34,2	151,5	107,4	58,3	55,4	15.3
pH_{vw}	6,06	6,23	5,76	5,85	5,74	6,50	5,97	6,38	6,38
$(NO_3^- N)_{vw}$	1,28	0,95	0,41	(0,42)	0,75	0,92	1,07	0,76	1,51
$(NH_4^+ \text{-} N)_{vw}$	3,79	0,82	0,47	(0,19)	0,66	1,12	1,66	0,42	1,12
Dep. NO_3 (g/m^2)	0,184	0,156	0,084	0,014	0,114	0,099	0,062	0,042	0,023
Dep. NH_4 (g/m^2)	0,545	0,135	0,096	0,006	0,099	0,120	0,097	0,023	0,018

8. CONCLUSIONS

Analysis of meteorological conditions at the stations (prevailing weather type, wind and precipitation regime), and the analysis of the atmospheric transport to the stations demonstrated by single back trajectories, together with statistical analysis of nitrogen compounds in precipitation and their wet-deposition results in several conclusions:

- The Adriatic coast is under the combined influence of local, regional and long-distant pollution sources. On the average, higher nitrogen concentrations were in the weather type which reflects mainly the influence of local pollution sources, whose frequency is about 20% of time with precipitation and gives about 20% of total precipitation amount. However, higher individual concentrations were connected with the weather type which reflects mainly the influence of distant sources and whose frequency is about 45% of time with precipitation and gives 60% of total precipitation amount.
- Atmospheric transport of nitrogen compounds from inland toward the sea is significant, especially in the northern and southern Adriatic coast.
- Calculated wet deposition of total nitrogen (oxidised and reduced) ranges from 1 to almost 4 g/m^2 along the Adriatic coast. Comparison of bulk and wet-only methods for precipitation sampling has showed that the bulk method gives almost 50% higher monthly mean nitrate concentrations than wet-only. That also indicates the importance of dry deposition and local influences on a daily scale.
- Increasing trend for nitrogen concentrations, that has been found in Europe, has been confirmed at the rural station Zavizan, too. Two of stations along the Adriatic coast show increasing trend in ammonium concentrations, while at all the other locations decreasing tendency have been found for both nitrate and ammonium.

References

Alebic-Juretic, A., V. Sojat, 1997, *Chemical Composition of Rainwater Collected at Two sampling Sites Within the City of Rijeka,* Proceedings of 1st Croatian Conference on Air Protection ′′97, Crikvenica, Croatia, 16.–18. October 1997, 409–413.

Bajic, A., 1989, *Olujna bura na sjevernom Jadranu (Severe bura on the Northern Adriatic), Part I: Statistics analysis,* Croatian meteorological Journal, Vol. 24, 1–10.

Bajic, A., V. DJuricic, 1995, *Precipitation Chemistry and Atmospheric Processes in the Forested Part of Croatia,* Water, Air and Soil Pollution, Vol 85(1-4), 1955–1960.

Bajic, A. et al, 1997, *Meteoroloske podloge za proracun moguce proizvodnje elektricne energije iz energije vjetra na odabranim makrolokacijama u Republici Hrvatskoj (Meteorological basis for possible electric energy production from wind energy for the chosen macro-locations in Croatia),* A Study under the contract between Croatian Electricity Company and Meteorological and Hydrological Institute of Croatia, DHMZ, Zagreb, 111 pp.

Bajic, A., 1998/99, *Atmospheric transport to the GAW regional station Zavizan and related precipitation chemistry,* Croatian Met. Jour., Vol. 33, Cro. Met. Soc., Zagreb, (in print)

Ciattaglia, I., and L. Cruciani, 1989, *Review of chemical data by the Italian Meteorological Service,* Airborne pollution of the Mediterranean Sea. Report and Proceedings of the First WMO/UNEP Workshop, MAP Technical Reports Series No.31, UNEP, Athens 1989, 101–122.

Dayan, U., J. M. Miller, 1989, *Meteorological and climatological data from surface and upper air measurements for the assessment of atmospheric transport and deposition of pollutants in the Mediterranean Basin; A Review,* MAP Technical Report Series, No. 30, UNEP, Athens, 134 pp.

Draxler, R.R., G.D. Hess, 1997, *Description of the HYSPLIT_modeling system*, NOAA Technical Memorandum ERL AARL-224.

Djuricic, V., 1989, *Some precipitation chemistry characteristics of selected stations along the Adriatic coast,* Airborne pollution of the Mediterranean Sea. Report and Proceedings of the First WMO/UNEP Workshop, MAP Technical Reports Series No.31, UNEP, Athens 1989, 81–101.

Djuricic, V., S. Vidic, 1992, *Acid precipitation at the northern Adriatic,* Airborne pollution of the Mediterranean Sea, Report and Proceedings of the Second WMO/UNEP Workshop, MAP Technical Reports Series No.64, UNEP, Athens 1992, 137–155.

Djuricic, V., A.Bajic, V. Sojat, 1996, *Precipitation quality characteristics in different synoptic situations at the area of Rijeka,* Scientific Symposium “Natural science researches of the Rijeka area”, Rijeka, Croatia, 23.-26. October 1996, 181–189.

EMEP/MSC-W Report 1/95.

EMEP/MSC-W Report 1/97.

EMEP/MSC-W Report 1/99.

EMEP Report 1/99, *Transboundary Acid Deposition in Europe*, Edited by Tarrason, L.and J. Schaug, July 1999, 246 pp.

Erdman, L. et al, 1994, *Assessment of Airborne Pollution of the Mediterranean Sea by Sulphur and Nitrogen Compounds and Heavy Metals in 1991*, MAP Technical Reports Series No.85, UNEP, Athens, 303 pp.

Eskinja, I., Z. Soljic, S. Svel-Cerovecki, M. Eskinja, V. Sojat, 1996, *Sources and Fate of Polycyclic Aromatic Hydrocarbons in Ambient Air of Urban and Rural Croatian Sites,* Intern. Journ. Environ. Analytical Chem., Vol. 63, 251–268.

Fanning, K., 1989, *Influence of atmospheric pollution on nutrient limitation in the ocean*. Nature 339: 460–463.

Fisher, D. C. and M. Oppenheimer, 1991, *Atmospheric nitrogen deposition at the Chesapeake Bay estuary*. Ambio 20: 102–108.

Hinga, K. R., A. A. Keller and C. A. Oviatt, 1991, *Atmospheric deposition and nitrogen inputs to coastal waters*. Ambio 20: 256–260.

Knap, A., T. Jickells, A. Pszenny, and J. Galloway, 1986, *Significance of atmospheric-derived nitrogen on productivity of the Sargasso Sea*. Nature 320: 158–160.

Loncar, E., A. Bajic, 1994, *Tipovi vremena u Hrvatskoj (Weather types in Croatia),* Croatian Meteorological Journal, Vol. 29, 31–41.

Luksic, I., 1975, *Bura u Senju (Bura in Senj),* Senjski zbornik, Vol. 6, 467–494.

Loÿe-Pilot, M. D., J. M. Martin and J. Morelli, 1989, *Atmospheric input of particulate matter and inorganic nitrogen to the Northwestern Mediterranean,* Water Pollution Research Reports, EROS 2000, Eds. J.M. Martin and H. Barth, pp 453.

Makjanic, B., 1966, *Prilog poznavanju klime grada Senja (Contribution to the knowledge of the climate of Senj),* Pomorski zbornik, Vol. 4, 603–624.

Makjanic, B., 1978, *Bura, jugo, etezija, (Bora, Sirocco, Ethesia)*, Contribution to the knowledge of weather and climate of SFRJ, 117 pp.

Michaels, A. F., D. A. Siegel, R. Johnson, A. H. Knap and J. N. Galloway, 1993, *Episodic inputs of atmospheric nitrogen to Saragosso Sea: Contribution to new production and phytoplankton blooms*. Global Biogeochemical Cysles 7: 339–351.

Migon,C., G.Copin-Montegut, L.Elegant and J.Morelli, 1989, *Prelimainary data on observations at the Cap Ferrat atmospheric sampling station (France),* Airborne pollution of the Mediterranean Sea. Report and Proceedings of the First WMO/UNEP Workshop, MAP Technical Reports Series No.31, UNEP, Athens 1989, 139–140.

Owens, N. J. P., J. N. Galloway, and R. A. Duce, 1992, *Episodic atmospheric nitrogen deposition to oligotrophic oceans*. Nature 357: 397–399.

Pearl, H. W., 1985, *Enhancement of marine production by nitrogen-enriched acid rain*. Nature 315: 747–749.

Pearl, H. W., 1988, *Nuisance phytoplankton blooms in coastal, estaurine, and inland waters*. Limnol. Oceanogr. 33 (4, part 2): 823–847.

Pearl, H. W., J. Rudek and M. A. Mallin, 1990, *Stimulation of phytoplankton production in coastal waters by natural rainfall inputs: Nutritional and trophic implications*. Marine Biology 107:247–254.

Peden, M. E., L. M. Skowron, 1978, *Ionic stability of precipitation samples*, Atm. Env., Vol. 12, 2343–2349.

Pozar-Domac, A. et al, 1998, *The Silba Marine Park – preliminary research of the main characteristics of the area, establishment of specially protected area, and marine park managing organisation,* Periodicum Biologorum, Vol. 100, No. 1, 7–18.

Scudlark, J. R. and T. M. Church, 1993, *Atmospheric input of inorganic nitrogen to Delaware Bay Estuaries*, Vol. 16, No. 4: 747–759.

Semb, A. et al, 1998, *Pilot measurements of nitrogen containing species in air,* EMEP/CCC-Report 5/98, NILU, Norway, 58 pp.

Smodlaka, N., 1994, *Outlines for a proposal of the Croatian monitoring programme*, Report of the consultation meeting on the evaluation of the Croatian monitoring programme, UNEP (OCA)/ MED WG. 80/2., Anex VIII, 1994.

Stunder, B., 1996, *An assessment of the quality of forecast trajectories,* Jour. Appl. Met., Vol. 35, 1319-1331.

Sojat, V., D. Borovecki, 1995, *Chemical Composition and Characteristics of Precipitation in Rijeka, Senj and Sibenik Raingauge Stations,* 1st Croatian Conference on Waters Sustainable Development and Water Management, Dubrovnik, Croatia, 24.–27. May 1995, 561–568.

Sojat, V., S. Vidic, G. Hrabak-Tumpa, D. Borovecki, 1996, *Acid Precipitation in the Kvarner Area Region,* International Congress, Energy and the Environment, 15th Scientific Conference, Opatija, Croatia, 23.–25. October 1996., 471–478.

Tudor, M., 2000, *Atmospheric transport to Croatia* (B.Sc. thesis, in Croatian), University of Zagreb, 53 pp.

Vidic, S., 1995, *Deposition of Sulphur and Nitrogen Compounds in Croatia,* Water, Air and Soil Pollution, Vol. 85(1-4), 2179–2184.

Vucetic, V., 1993, *Severe bora on the Mid-Adriatic*, Croatian Meteorological Journal, Vol. 28, 19–36.

Willey, J. D. and L. B. Cahoon, 1991, *Enhancement of chlorophyll production in Gulf Stream surface seawater by rain-water nitrate*. Marine Chemistry 34: 63–75.

Figure 1. Investigated area with marked positions of Rijeka, Pula, Senj, Zavizan, Zadar and Dubrovnik

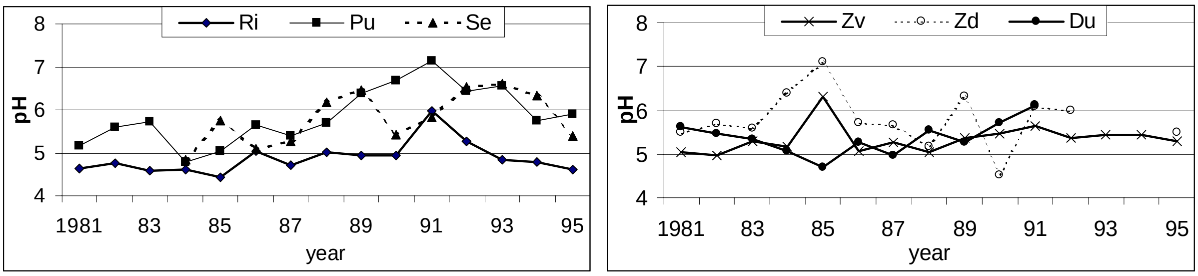


Figure 2. Volume-weighted annual pH values for Rijeka (Ri), Pula (Pu), Zavizan (Zv) and Zadar (Zd) for the period 1981-1995, Senj (Se) 1984–1995, and Dubrovnik (Du) 1981–1991.

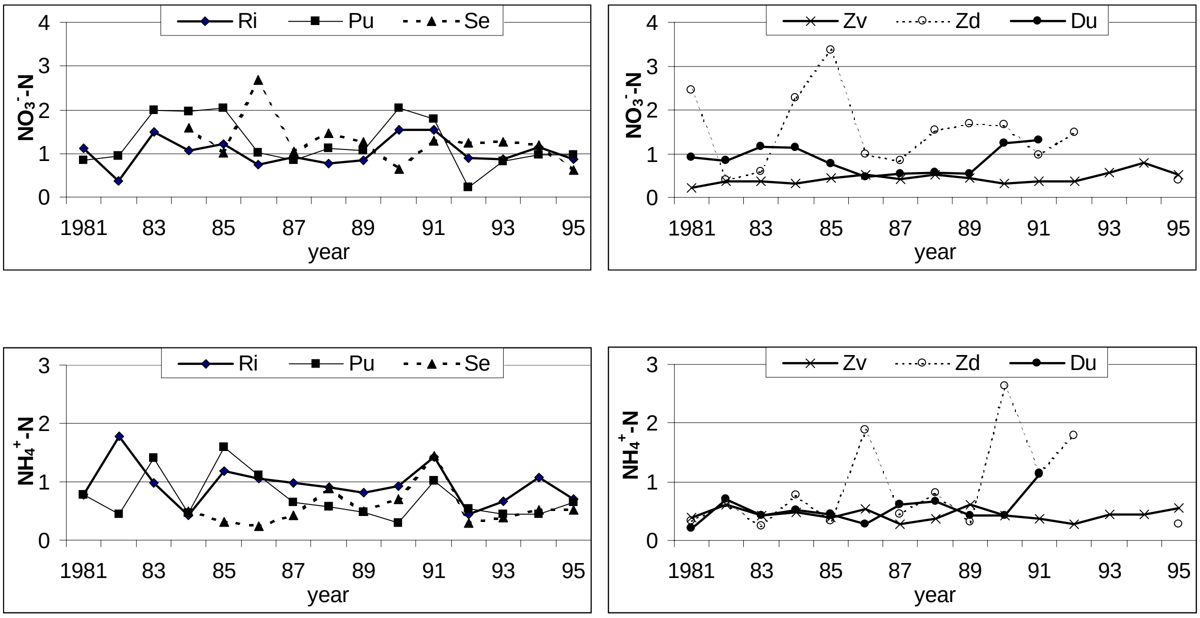


Figure 3. Nitrate and ammonia volume-weighted annual means for Rijeka (Ri), Pula (Pu), Zavizan (Zv) and Zadar (Zd) for the period 1981-1995, Senj (Se) 1984–1995, and Dubrovnik (Du) 1981–1991.

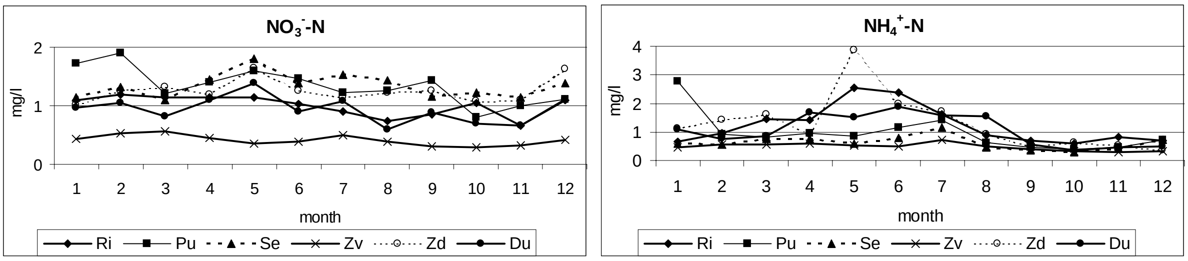


Figure 4. Annual course of nitrate and ammonium concentrations in precipitation (mg/l) in Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv), Zadar (Zd) and Dubrovnik (Du), for the period 1981-1995.

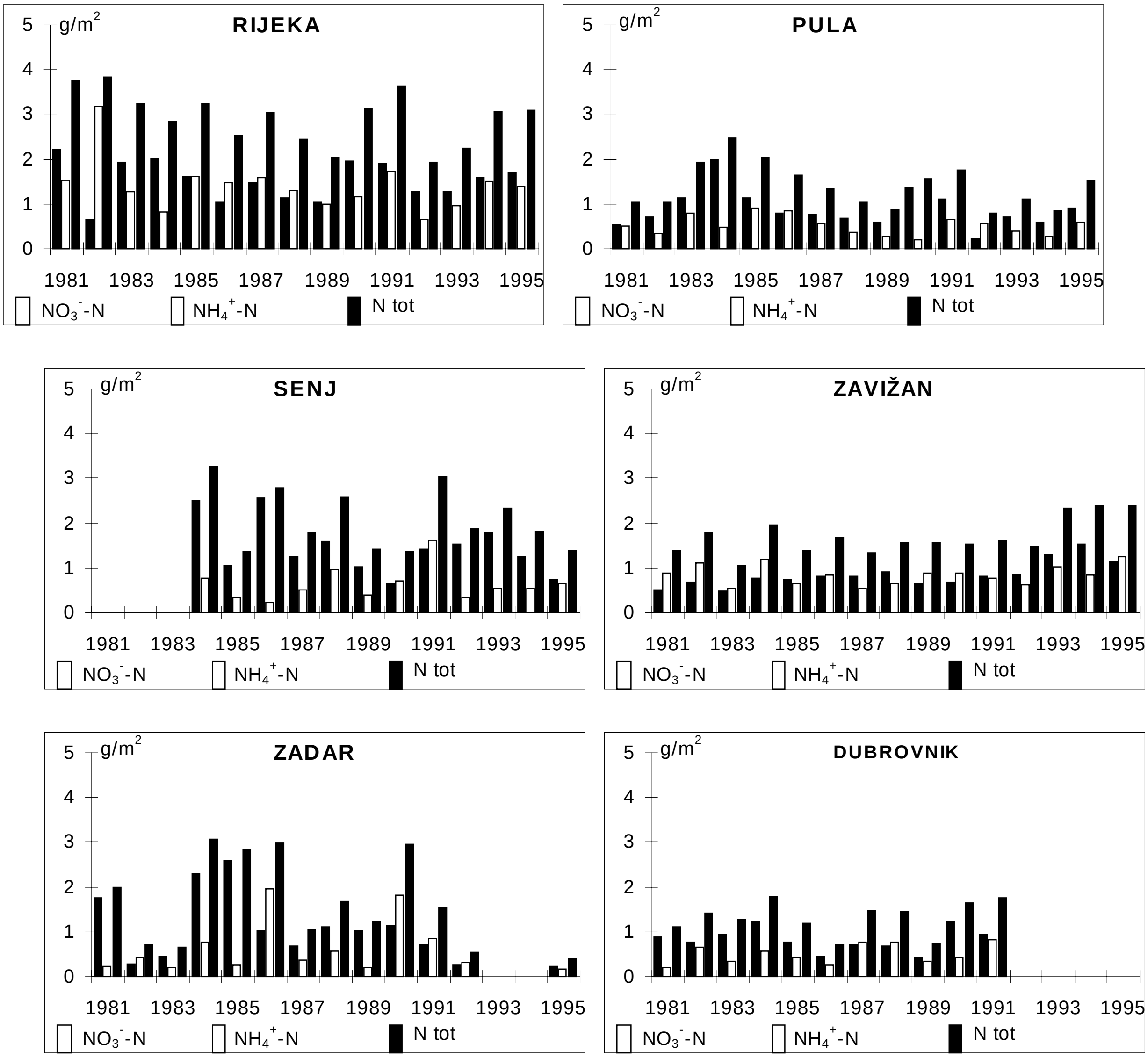


Figure 5. Deposition of nitrogen from nitrate, ammonium and total (g/m^2) in Rijeka, Pula, Zavizan and Zadar for the period 1981-1995, Senj 1984–1995, and Dubrovnik 1981–1991

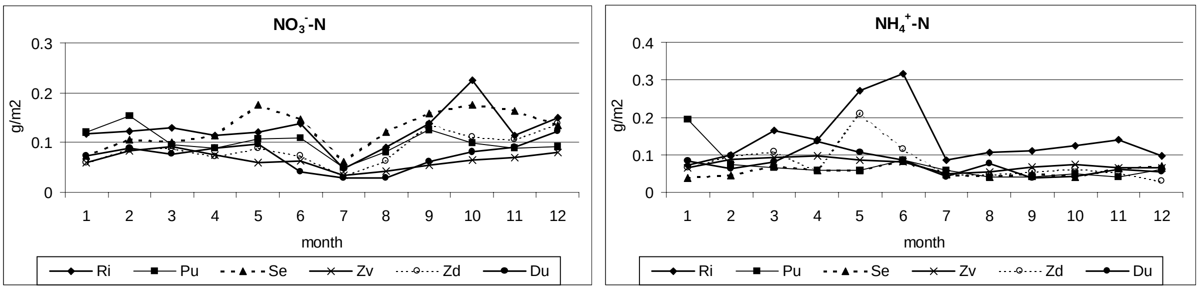


Figure 6. Annual course of nitrate and ammonium wet deposition (g/m^2) in Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv), Zadar (Zd) and Dubrovnik (Du), for the period 1981-1995. (volume weighted monthly mean concentration times monthly mean precipitation amount).

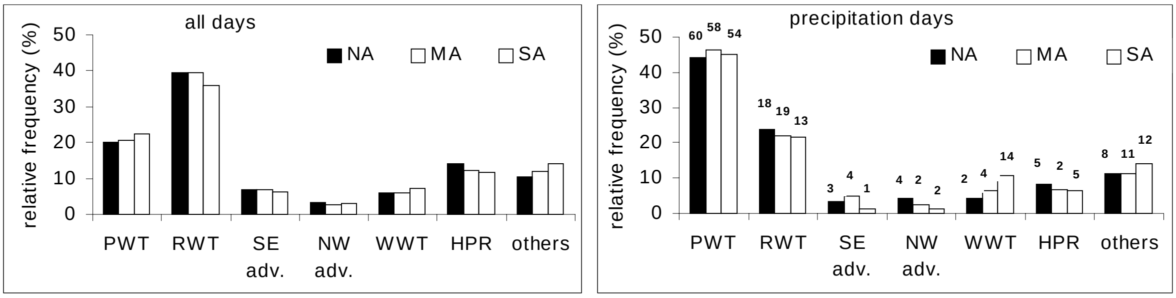


Figure 7. Frequency distribution of weather types over the northern (NA), mid (MA) and southern (SA) Adriatic, for the period 1981–1995 (NA and MA) and only 1991 (SA), for all days and days with precipitation (PWT = precipitation weather type; RWT = radiation weather type; SEadv. = advection from SE; NWadv. = advection from NW; WWT = wind weather type; HPR = high pressure ridge; others = other untypical weather types). Numbers above columns are percent of total precipitation amount for particular weather type.

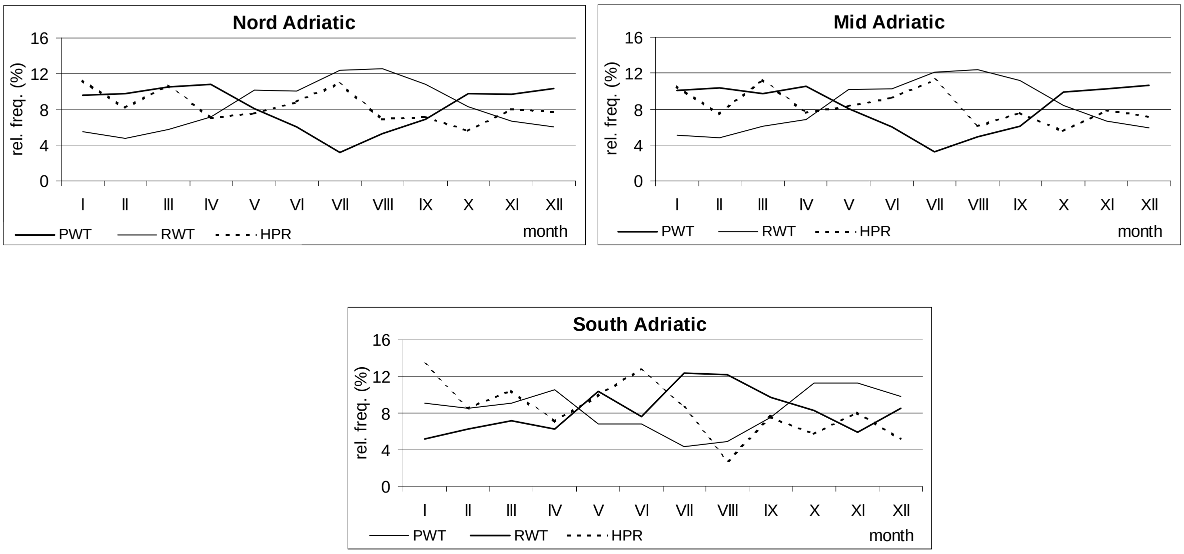


Figure 8. Annual course of relative frequencies (%) of three prevailing weather types over the northern and mid Adriatic in the period 1981–1995 and southern Adriatic in the period 1991–1995.

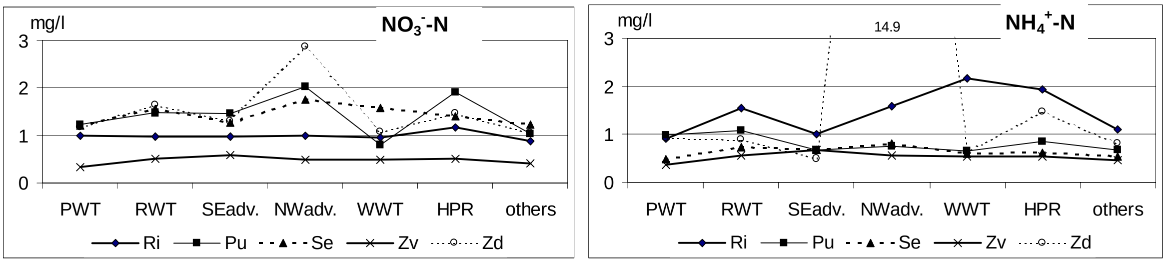


Figure 9. Precipitation volume weighted mean concentrations of NO_3^--N and NH_4^+-N ions (mg/l) from all samples in six main weather types in Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv) and Zadar (Zd) in the period 1981–1995.

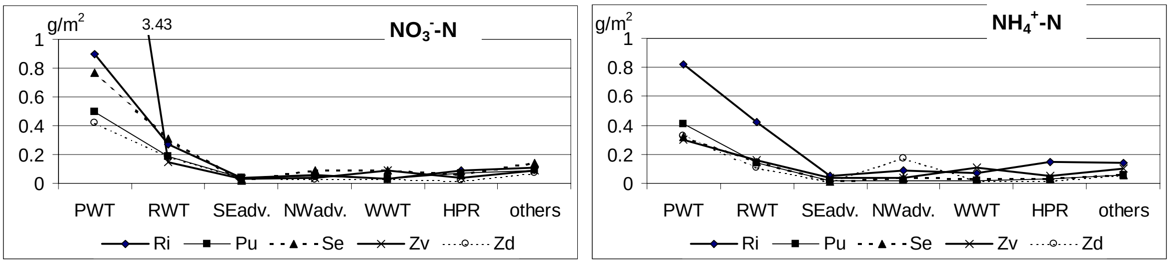


Figure 10. Average yearly wet deposition of nitrates and ammonia for six main weather types in Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv) and Zadar (Zd) in the period 1981–1995.

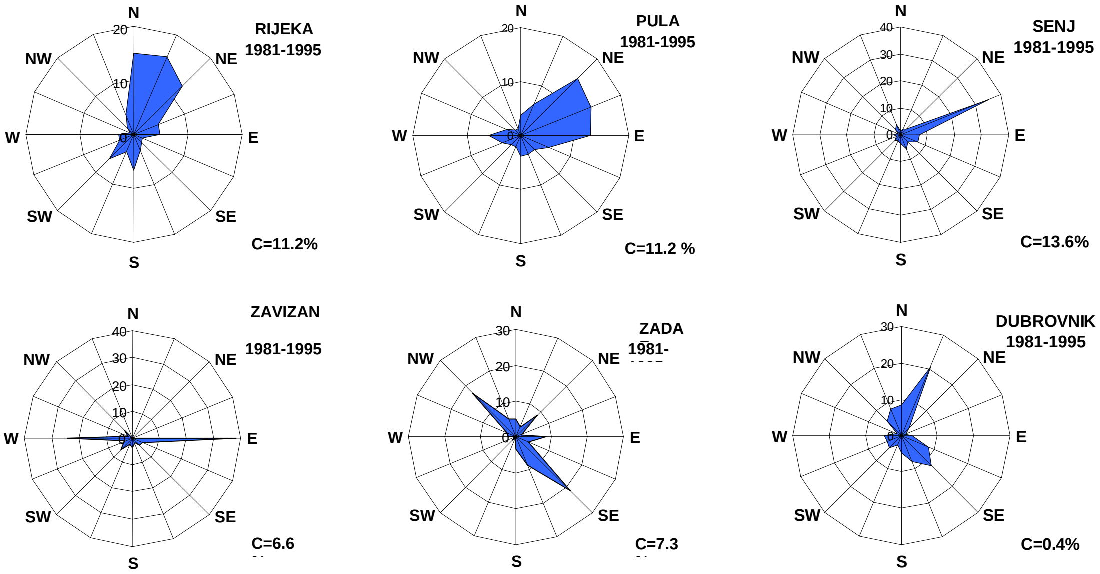


Figure 11. Annual wind roses with different scales for selected stations along the Adriatic coast

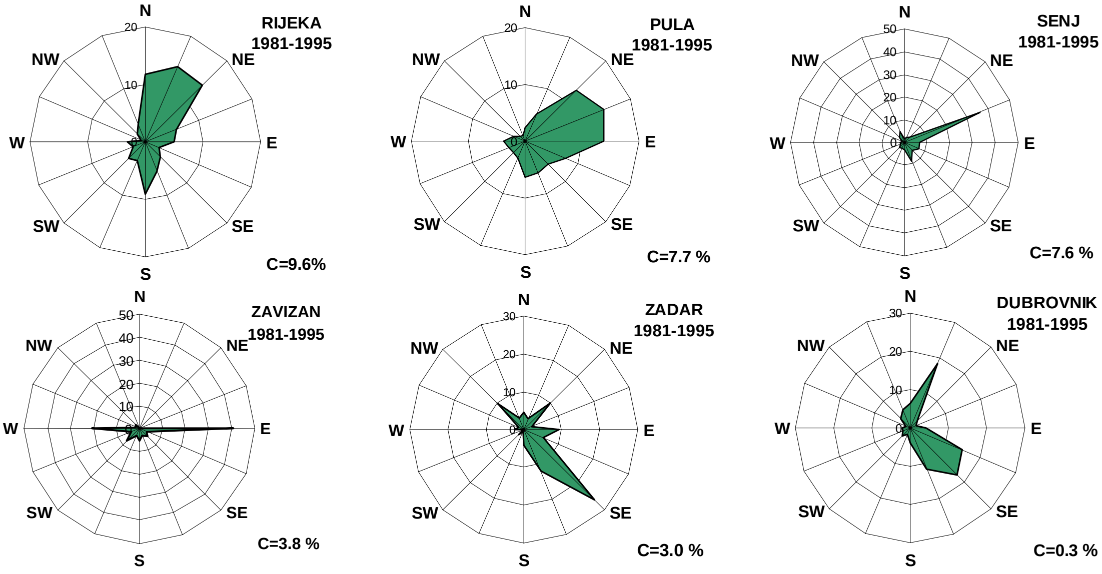


Figure 12. Annual precipitation wind rose for selected stations along the Adriatic coast

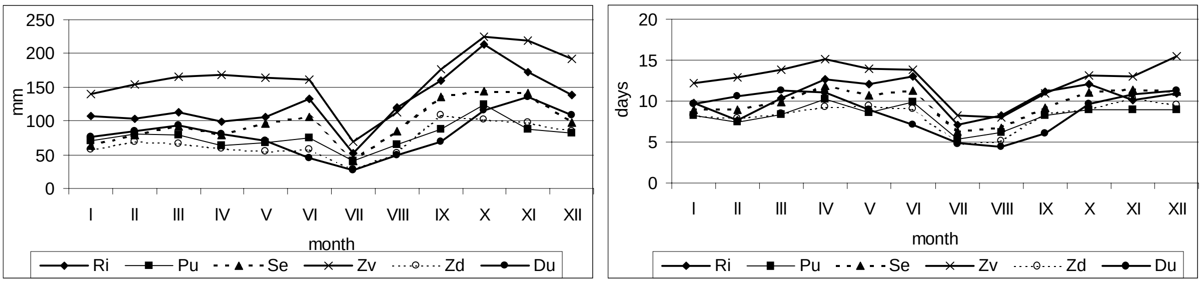


Figure 13. Annual course of precipitation amount (mm) and number of days with precipitation ≥ 0.1 mm, for Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv), Zadar (Zd) and Dubrovnik (Du), for the period 1981-1995.

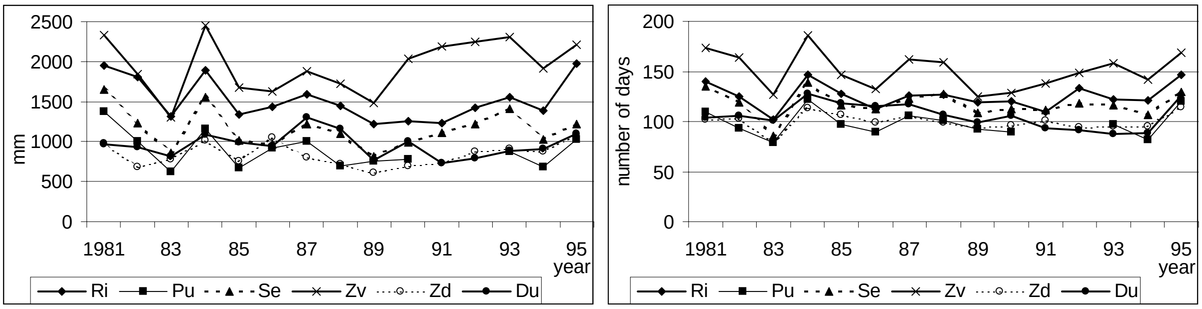


Figure 14. Annual precipitation amount (mm) and annual number of days with precipitation ≥0.1 mm for Rijeka (Ri), Pula (Pu), Senj (Se), Zavizan (Zv), Zadar (Zd) and Dubrovnik (Du), for the period 1981-1995.

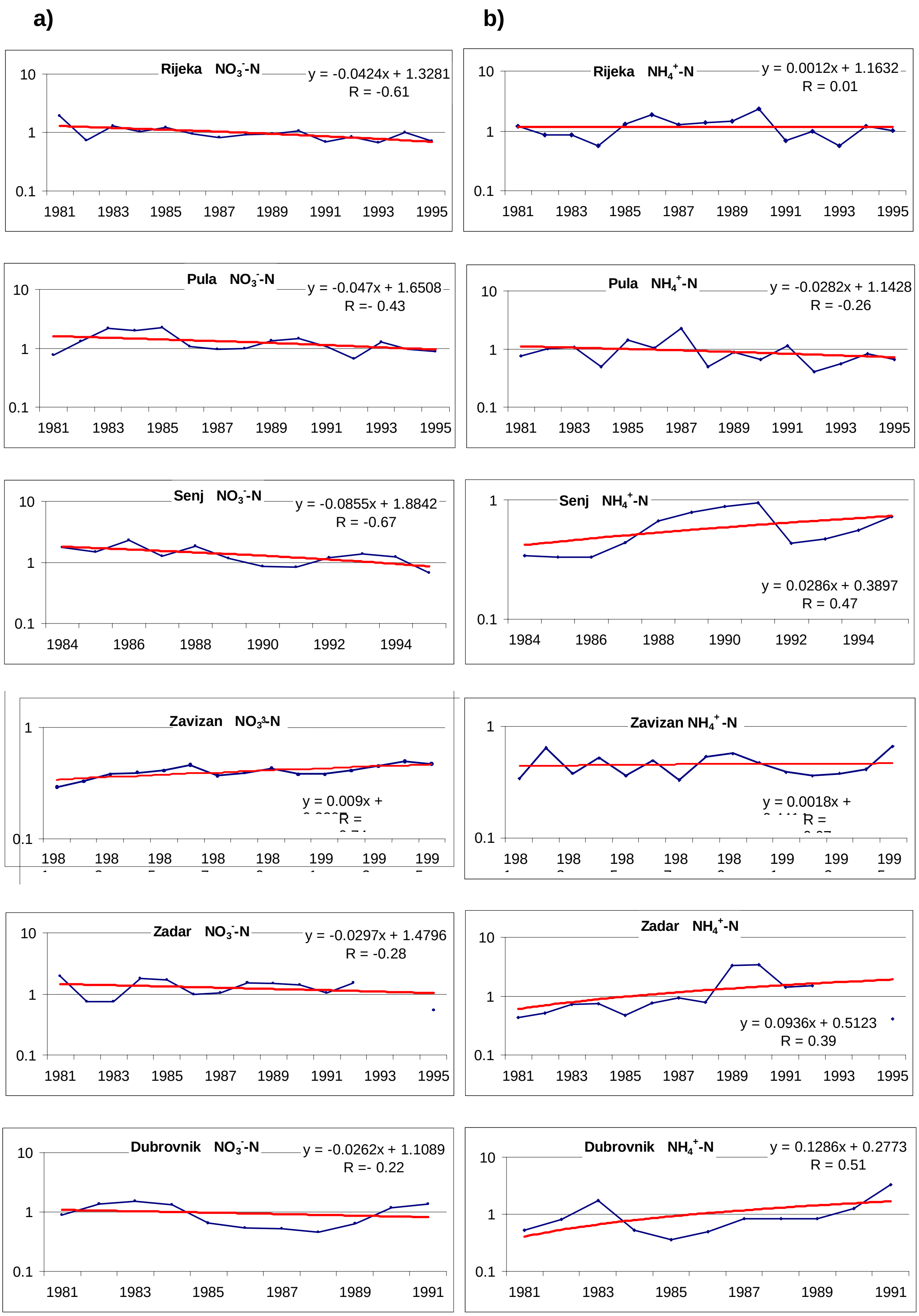


Figure 15. Time series with estimated linear regression for precipitation volume weighted annual means of a) NO_3^--N and b) NH_4^+-N concentrations using a logarithmic scale, for the stations along the Adriatic coast, for the period 1981–1995.

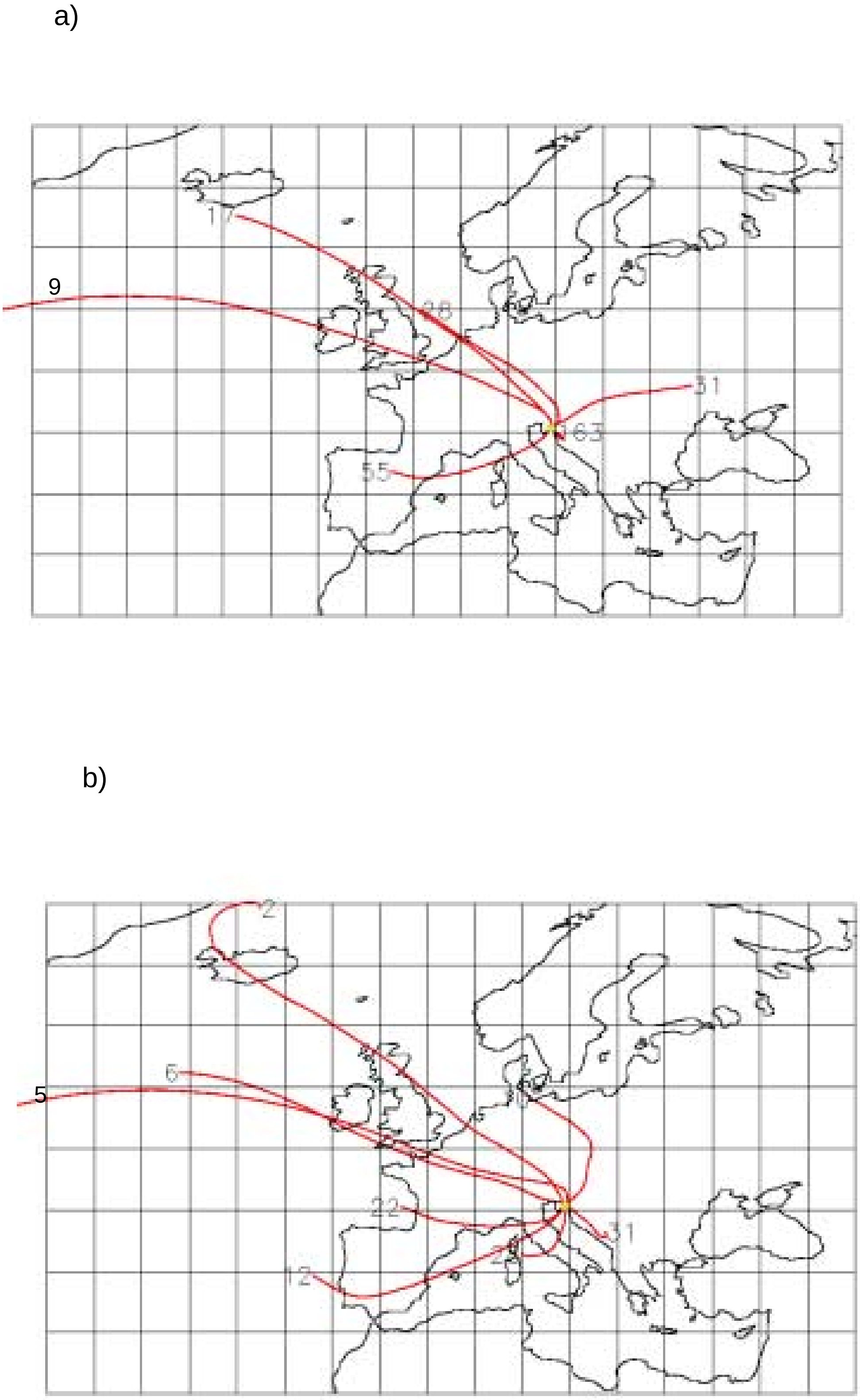


Figure 16. Cluster-mean trajectories to Rijeka in the period October 1998 - September 1999. a) for the whole year, b) in precipitation days (number at the end of cluster-mean trajectory indicates the number of belonging single trajectories)

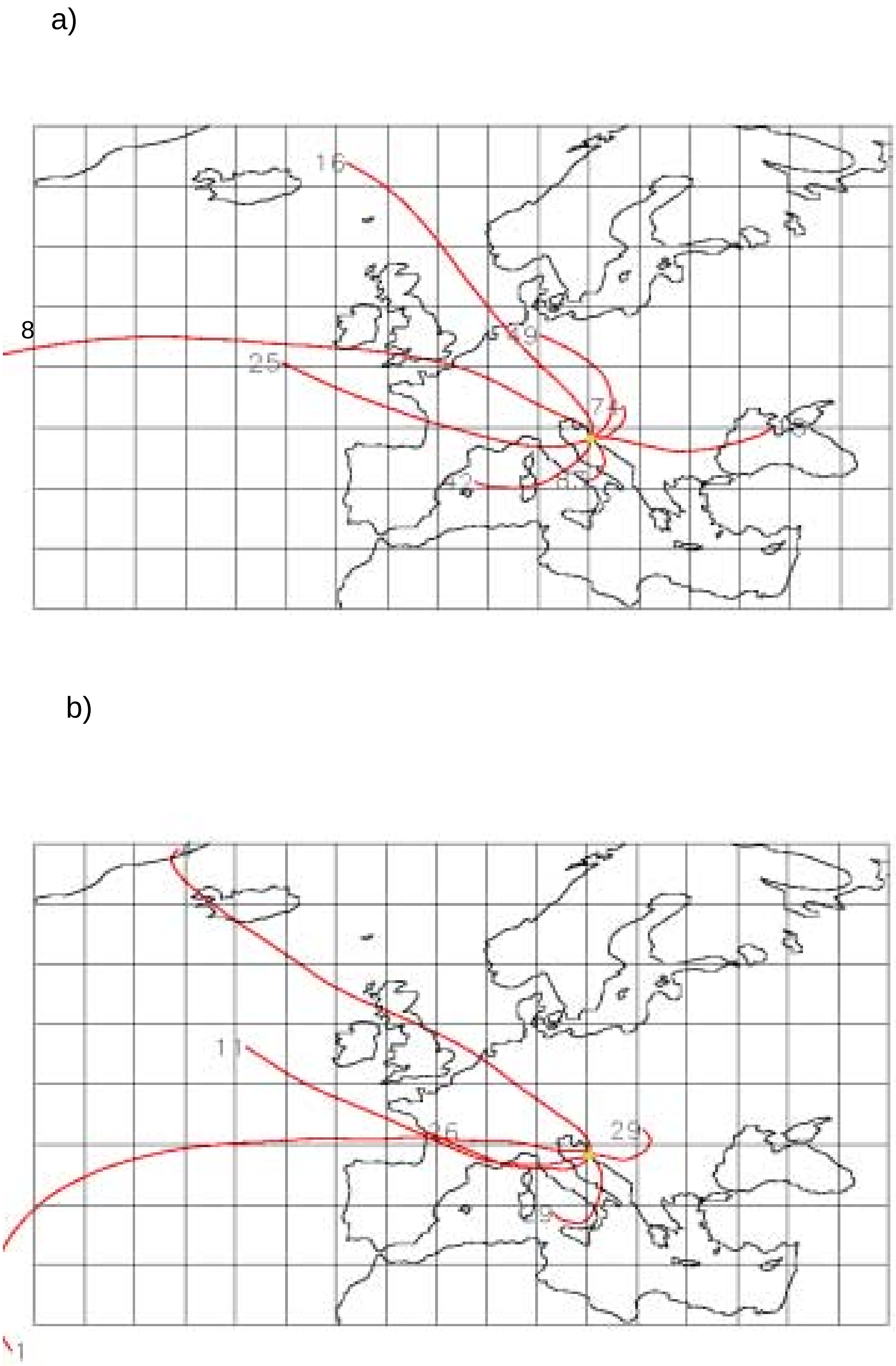


Figure 17. Cluster-mean trajectories to Zadar in the period October 1998 - September 1999. a) for the whole year, b) in precipitation days (number at the end of cluster-mean trajectory indicates the number of belonging single trajectories)

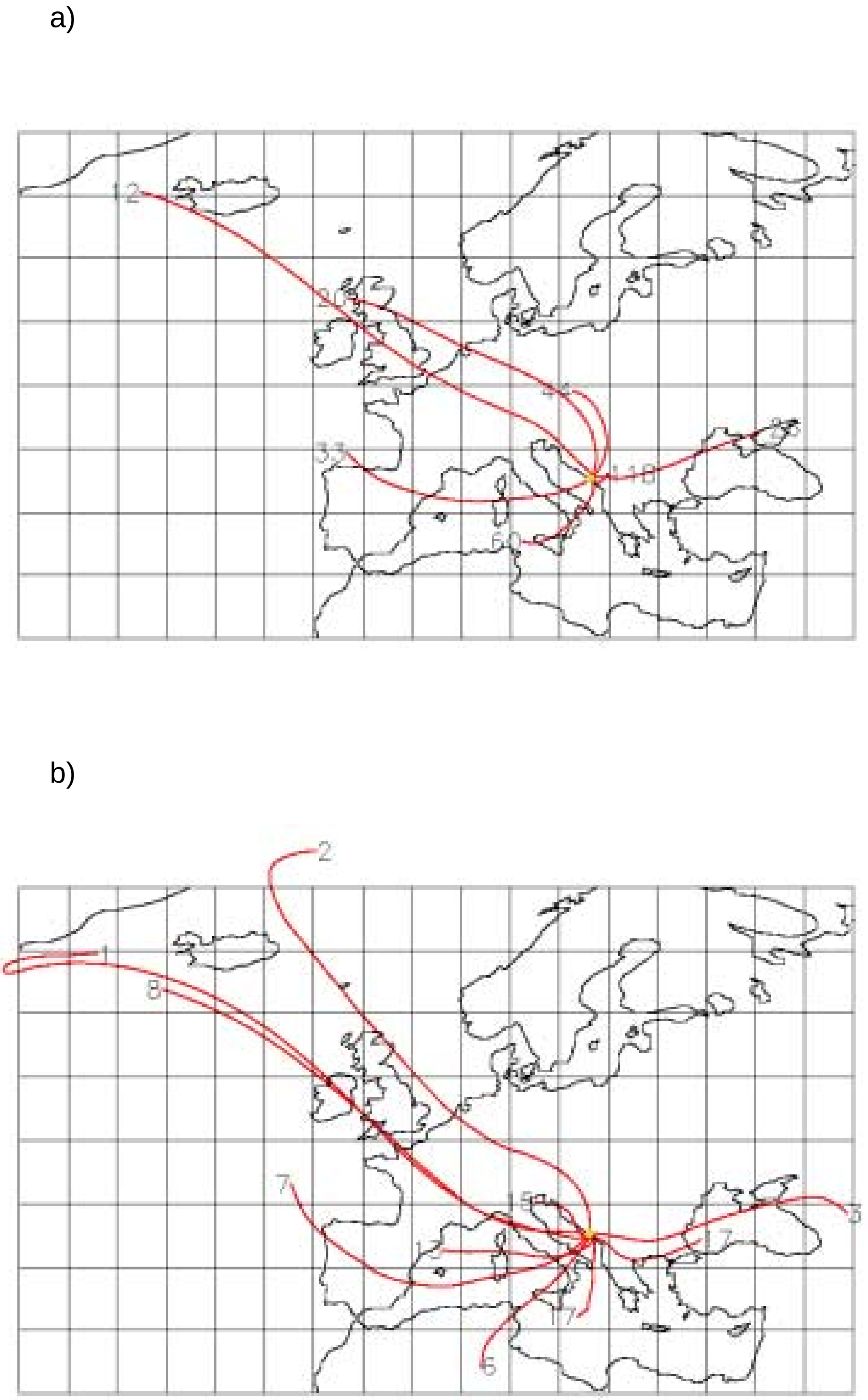


Figure 18. Cluster-mean trajectories to Dubrovnik in the period October 1998 - September 1999. a) for the whole year, b) in precipitation days (number at the end of cluster-mean trajectory indicates the number of belonging single trajectories)

FACTORS CONTROLLING THE VARIABILITY OF AEROSOL TRACE METAL CONCENTRATIONS IN THE NORTH-EASTERN MEDITERRANEAN TROPOSPHERE: WITH SPECIAL EMPHASIS ON SAHARAN DUST TRANSPORT

Nilgün Kubilay[1], Mustafa Koçak[1], Emin Özsoy[1], Malcolm Nimmo[2]

[1]Institute of Marine Sciences, Middle East Technical University, Erdemli-Icel, Turkey
[2]Department of Environmental Sciences, The University of Plymouth, Plymouth, UK

ABSTRACT

Long-term, land-based sampling of the aerosols above the Turkish coast of the north-eastern Mediterranean Sea (36.6. N°, 34.4°E) has demonstrated the dominance of mineral dust particles over the basin. Aerosol samples, collected by a hi-volume pump through filtration on Whatman-41 filter papers, were analysed for trace metals by AAS. Analysis of 739 samples collected during the periods of August 1991 – December 1992 and January 1996 – December 1998 has shown that pulses of desert particles invade the region during the transitional season (March through May) and during such events the aerosol Al concentrations (indicator of mineral dust) increase by an order of magnitude. Three days backward, three dimensional air-mass trajectory analyses have confirmed the invasion of the basin by sporadic and intense concentrations of mineral dust originating from Sahara. A transport event in the first half of April 1998 is studied through combined analyses of ground based and satellite observations and modelling results.

1. INTRODUCTION

From recent reviews it is apparent that the atmosphere is not only a significant, but in some cases, the dominant pathway by which metals and nutrients reach the ocean (Duce *et al*., 1991; Jickells, 1995, 1999). Atmospheric processes appear to play a primary role in supplying trace metals (Martin *et al*., 1989; Guieu *et al*., 1997; Guerzoni *et al*., 1999; Ridame *et al*., 1999), as well as nitrogen and phosphorus (Herut *et al*., 1999a) to the Mediterranean Sea. For example, trace metal inputs from the atmosphere are quantitively significant, and in some cases exceed riverine inputs (e.g. for Pb, Cu, Cd in the western Mediterranean; Guieu *et al*., 1991a). Quantitative evaluation of trace metal fluxes to the Mediterranean Sea are therefore of great importance. In addition, an understanding of the impact of those inputs on marine biogeochemical cycles is essential for the management of marine systems. Dust deposition from the atmosphere is an important factor influencing the functioning of the Mediterranean ecosystem, as it carries many trace elements (e.g. Fe, Mn and Al) which serve as micronutrients in the sea.

There is an increasing gradient of dust deposition from the western towards the eastern Mediterranean (Guerzoni *et al*., 1997). The dust transport to the eastern Mediterranean occurs in the form of "pulses" and the annual dust flux may be a result of only a few Saharan outbreaks (Kubilay *et al*., 2000). Despite a large daily variability, the general pattern of dust export from Africa over the Mediterranean begins over the eastern Mediterranean in spring and covers the western Mediterranean in summer (Moulin *et al*., 1998). Contrasting views suggest that the deposition of the Saharan dust plays a role either in the enhancement of the productivity of the pelagic system by supplying nutrients (Bergametti *et al*., 1992; Herut *et al*. 1999a; Migon and Sandroni, 1999; Ridame and Guieu, 2000) or by, contributing to the development of an oligotrophic system via the removal of phosphorus through adsorption onto deposited dust particles (Krom *et al*., 1991; Herut *et al*., 1999b).

As atmospheric inputs may potentially affect the marine environment, it is therefore necessary to determine the magnitude, timing and geographical distribution of the atmospheric concentrations and fluxes of these compounds in coastal and open sea regions. The large variations in daily aerosol trace metal concentrations over the western and the eastern basins of the Mediterranean (Bergametti *et al*., 1989; Kubilay and Saydam, 1995; Güllü *et al*., 1998), highlight the importance of the Programme for the Assessment and Control of Pollution in the Mediterranean Region (MEDPOL-Phase III), in parallel with a continuos sampling strategy for assessing the inputs of trace elements over the Mediterranean basin (UNEP/WMO, 1992). Satellite observations and modelling offer an opportunity to make spatial extrapolations of local measurements from coastal sites into the rest of the domain of interest, making it possible to further assess the biogeochemical significance of the deposition events on a regional basis (Kubilay *et al*., 2000).

2. MATERIALS AND METHODS

2.1 Sampling Location

The sampling station used for the current study is located (36.6°N and 34.3°E) on the Turkish coast of the eastern Mediterranean (Figure 2). The two nearest urban centres are Erdemli (a small town with a population of 25,000) and Mersin (a big and industrialised city with more than 500,000 inhabitants) located 7 and 45 km east of the sampling site, respectively. Agricultural and touristic activity can be found in close vicinity, while a limited number of industrial activities such as petroleum refinery and soda production, non-ferrous metal (chromium), thermal power and fertiliser plants, pulp and paper production occurs along the coast at distances of more than 50 km to the east and west of the sampling tower.

2.2 Sample Collection and Elemental Analysis

Aerosol samples were collected by a Hi-Volume GMWL-2000 (General Metal Works Inc., rate: 1 m^3 min^{-1}) sampler at a height of 22 m above sea level, located on the harbour jetty at the Institute of Marine Sciences. Collections were carried out over two periods: from 1 August 1991 to 31 December 1992 (339 samples), and from 1 January 1996 to 31 December 1998 (400 samples). The samples collected during the first collection period were analysed for 13 trace metals and the results have been published elsewhere (Kubilay and Saydam, 1995). The samples collected during the second period have been analysed only for Al (indicator of mineral dust) and will be examined together with Al results from the previous sampling period (on total 739 samples). The Al concentrations allow an assessment of the seasonality of the long-range desert dust transport to the eastern Mediterranean. The aerosols were collected on 20 x 25 cm Whatman 41 filters. Blank filters were passed through the handling procedure, without exposure to the air, and the blanks from the same batches as those used for the collections were run through the analytical techniques. The procedure for the trace element analyses of the aerosol samples have been described elsewhere (Kubilay, 1996; Kubilay and Saydam, 1995; Kubilay *et al*., 1995). Briefly, one quarter of each filter was cut off in a clean, laminar-flow bench with the use of Teflon coated forceps and disposable nylon gloves, then placed in a PTFE beaker, digested with HF/HNO_3 acid mixture at 120°C and subsequently made up to 25 mL volume with 0.1 N HNO_3. Milli-Q double distilled water (DDW) was used throughout the analysis. Digested samples were analysed for their trace metal contents by a computer controlled GBC-906 model (GBC Scientific Equipment Pty Ltd., Australia) atomic absorption spectrometer (AAS) equipped with a deuterium lamp. Both flame and flameless modes of AAS were utilised with the attachment of FS3000 and PAL3000 autosamplers, respectively. The substruction of the blanks did not contribute significantly to uncertainties in the final concentrations as a result of the relatively high elemental concentrations of atmospheric particulate over the eastern Mediterranean.

2.3 Air-mass Back Trajectories

Kinematic air mass back trajectories were calculated daily at 1200 UT for 1989 through 1998. Trajectories were calculated 3 days back, a sufficient duration to diagnose long-range transport. Using a 10 year trajectory database, we examined the climatological airflow patterns and the differences in transport patterns for four arrival elevations and we will subsequently discuss the role of the vertical component of the transport.

The European Centre for Medium Range Weather Forecast (ECMWF, Reading, UK) global wind analyses are used for the computation of backward trajectories based on integration of the archived three-dimensional wind field at every 6-hr intervals interpolated with a small (one hour) time increment (Mc Grath, 1989). The accuracy of the trajectories used in this work has been assessed by Kubilay *et al*. (2000) using mineral dust as a geochemical tracer.

We selected four arrival elevations: 900, 850, 700 and 500hPa. These levels represent flow below, near and above the planetary boundary layer (PBL) depth in the eastern Mediterranean basin (Dayan *et al*., 1996). To establish climatology of trajectories, cluster analysis, a multivariate statistical technique, is used to group trajectories according to wind speed and direction. This procedure uses a mathematical criterion to ensure similarity among the trajectories in each group or cluster. Each transport cluster can then be described by a mean trajectory or “cluster mean” that best represents all the trajectories in that cluster. In this way, many trajectories can be efficiently summarised (Harris and Kahl, 1990).

2.4 Model utilized for mineral dust transport forecast

The atmospheric forecast model (ETA model), developed at the National Centre for Environmental Prediction (NCEP) (Mesinger *et al*., 1988) modified by Nickovic *et al*. (1997) includes dust production/transport/deposition processes and has been successfully tested for the selected Mediterranean dust intrusion cases (Nickovic and Dobricic, 1996; Özsoy *et al*., 1998; Kubilay *et al*., 2000), and is used to forecast dust transport events in the Mediterranean basin. The model uses land surface data to determine the dust flux at the surface based on soil water content and land surface type. In the model, single sized particles are introduced into a turbulent atmospheric boundary layer in the form of a flux of particles. The transport module of the system consists of a conservation equation for dust concentration, which is integrated in time, together with the other prognostic equations of the ETA model. The dust is considered as a passive substance with a unique particle size. The model is initialised with the daily analyses fields at 1200 UT and supplied with boundary data every 6 hours, both produced by the NCEP global model, and forecasts are performed for periods of up to 48 hours. The forecast data are saved at the Institute of Marine Science.

2.5 Seawater Solubilty Studies

Portions of two selected aerosol samples (one representing a predominantly “Saharan”, aerosol population collected on the 14th April 1998, and one representing an “European” aerosol, collected on 5th March 1998) were equilibrated in sterile, organic and particulate free seawater buffered at a pH of 8.0. The equilibration time of the aerosol samples in the seawater was fixed at one hour. During the experiments the seawater temperature will be kept constant at 25^{o}C which represents the average surface seawater temperature of the Eastern Mediterranean shallow coastal water. Subsequent analyses for all sample manipulations were carried out in a Class 100 clean room. The reaction vessel for the current study was a Teflon container. It was acid washed to minimise sample contamination. Equilibrated seawater was then filtered through a 0.45 m membrane filter to terminate any further particulate / dissolved reactions and the filtrate was then retained after acidification to await trace metal analysis for the dissolved trace metal fraction. Soluble trace metal fractions in the seawater were then determined directly by the ultra sensitive technique stripping voltammetry. Zn, Cu and Pb were determined by ASV (Anodic stripping voltammetry) and Ni, and Co by ACSV (Adsorptive cathodic stripping voltammetry). The remaining filter sample retained on the 0.45 m membrane filter undergo a total acid digestion with metal concentrations being determined by ICP-MS enabling the soluble fraction to be calculated.

3. RESULTS AND DISCUSSION

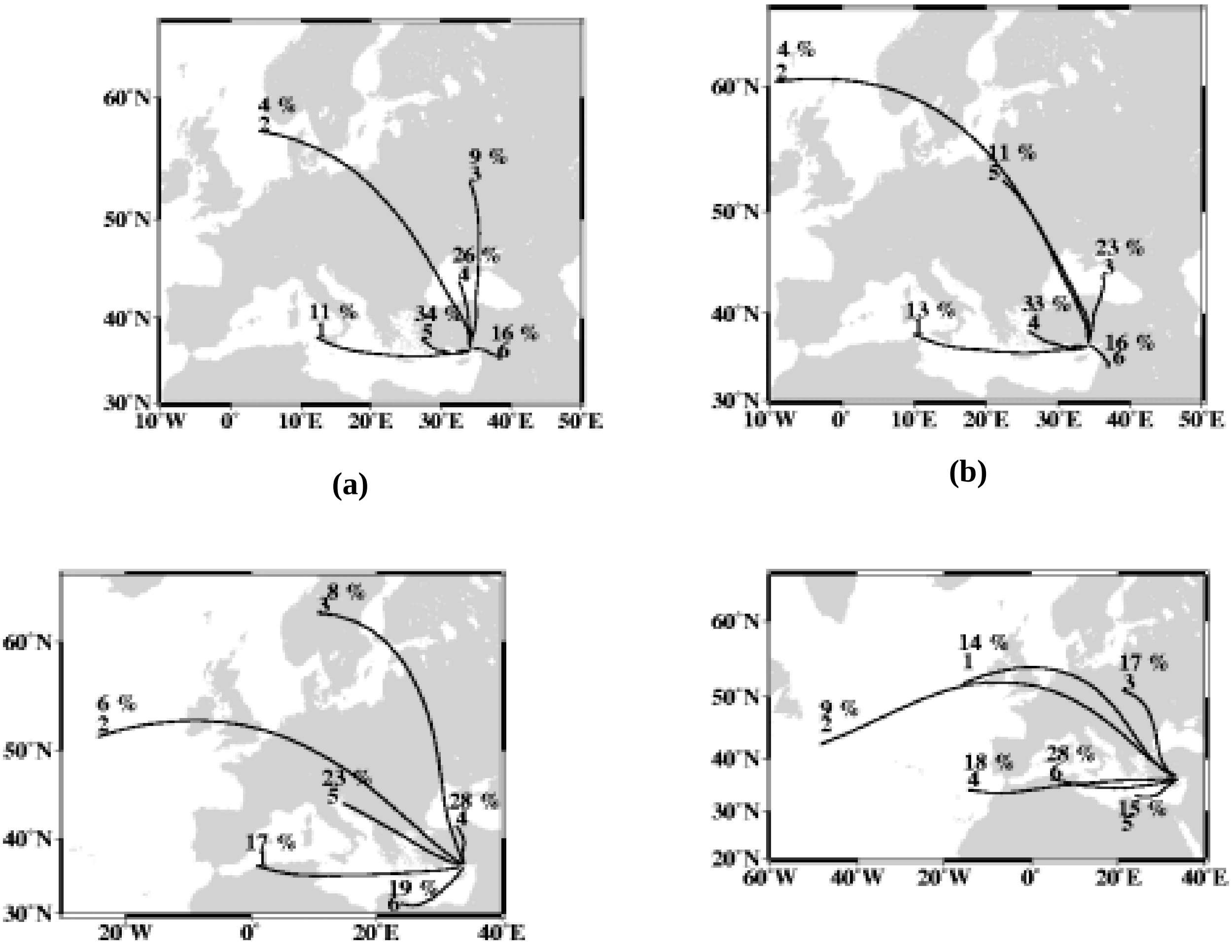
3.1 Air Flow Climatology at the Erdemli Site

Climatically, the Mediterranean region is characterised by generally warm winters (November - February) dominated by rainfall and dry summers (June-September). The transitional seasons, spring and autumn are of very different length. The relatively long spring season (March through May) is noted for periods of unsettled winter-type weather associated with an increased occurrence of North African cyclones; the rest of this period is very similar to that in the summer. Autumn usually lasts only one month (October) and is characterised by an abrupt change from the summer to the unsettled weather of winter (Brody and Nestor, 1980).

Our 10-year database of daily 3-day back trajectories allows us to quantify the frequency with which specific source regions (of aerosols) contribute to the material transported across the eastern Mediterranean. Figure 1 shows cluster-mean trajectories at the four different atmospheric levels for the period 1989-1998. The cluster-mean plots contain the following information: (1) the mean trajectory for each cluster and paired numbers, (2) showing the percent of all complete 3-day back trajectories in each cluster (top); and (3) the assigned cluster numbers (bottom).

The lower layer trajectories (Figure 1a,b) indicate a dominating group of clusters (4,5,6) originating from the west, north and east and accounting for 76 % at 900 hPa and (3,4,6) accounting for 72 % of the trajectories at 850 hPa, respectively. Cluster 1 from the west occurs 11 and 13 % of the time, representing long fetch maritime air masses from the western Mediterranean Sea at both pressure levels. The remaining clusters presenting north-north east continental flow pattern (2 and 3 at 900 hPa) and (2 and 5 at 850 hPa), respectively occurs 13 % and 15 % of the time.

Clusters indicating rapid transport from the south-southwesterly sector (the North African continent) have frequencies of 36 % (1+6) at 700 hPa and 61 % (4+5+6) at 500 hPa over the 10 year period (Figure 1c,d). Slower northerly flow originating from the Black Sea accounts for 28 % of the time (cluster 4, Figure 1c) at 700 hPa. It appears from Figure 1 that the transport from Europe mostly occurs above the boundary layer as well as the transport originating from North African continent. The easterly component in winds arriving at Erdemli diminishes at 700 and 500 hPa levels.



(a) (b)

(c) (d)

Figure 1. Atmospheric flow patterns for the period 1989-1998, depicted by cluster-mean trajectories arriving at Erdemli; (a) 900, (b) 850, (c) 700 and (d) 500 hPa. The numbers show the percent of complete trajectories occuring in that cluster (top) and cluster number (1-6) (bottom).

3.2 Comparison with other studies

Before attempting to explain the temporal variability of the elemental aerosol concentrations for the present study, a comparison is presented with those from other land-based atmospheric sampling programs carried out in European coastal sites (Figure 2). The other studies were conducted at different time periods and, with different sampling and analytical methodologies, it must therefore be stressed that the data in Table1 should be regarded as no more than an indication of trace metal concentrations expected in the lower atmosphere. The comparison of the concentrations measured at Erdemli with those reported elsewhere in the Mediterranean could serve to demonstrate the differences between the patterns of transport in the eastern and western parts of the Mediterranean.

The mean concentration of each element in aerosols exhibits substantial spatial variations. The geometric mean concentrations are presented when comparing our data with other measurements, as they are more representatives of the lognormal distributed datasets. On the other hand, the arithmetic mean would certainly have to be used in the calculation of average deposition during a specified measurement period. In terms of total deposition (flux) the arithmetic mean is more useful because in this case the occasional extreme values may contribute significantly.

The elemental concentration in atmospheric particulate at any site differs by several orders of magnitude, depending on geographic location, the local meteorological conditions (rain, long-range transport of air masses) and the seasonal changes in the intensity of emission rates. As many factors affect the atmospheric concentrations of elements over short time and space scales, it is difficult to characterise aerosol composition based on regional averages of atmospheric concentrations. One way to overcome this difficulty and at the same time to evaluate the principal sources of trace metals in aerosols is to calculate elemental enrichment factors, incorporating a comparison of elemental aerosol concentrations with those of reference elements which are indicators of a specific type of source. For the crustal source, Al is normally used as the indicator element, and the EF_{crust} value is calculated according to the equation given below:

$$EF_{crust} = (X/Al)_{aerosol} / (X/Al)_{crust}$$

in which $(X/Al)_{aerosol}$ is the concentration ratio of the trace element to Al in aerosol, and $(X/Al)_{crust}$ is the ratio in average crustal material. The equation was applied using the average elemental crustal ratios given by Wedepohl (1995). Usually, an arbitrary EF_{crust} value of < 10 is accepted to indicate that a trace metal in the aerosol has a dominant crustal source and these elements are classed as the “non-enriched elements” (NEEs). In contrast, an EF_{crust} value of >10 is considered to indicate that a significant proportion of an element has a non-crustal source and would be termed as “anomalously enriched elements” (AEEs).

Data for the geometric means of the concentrations and the EF_{crust} values of the trace metals in aerosols from coastal collection sites in the Mediterranean, Black and Irish Seas (Figure 2) are given in Table 1 and 2, respectively. In order to compare the data with other studies reported in the literature, the EF_{crust} values in Table 2 have been calculated directly from the geometric averages, rather than computing them from the average EF_{crust} of individual samples.

Aerosols from the two eastern Mediterranean coastal sites, Erdemli and Tel Shikmona, have generally similar concentrations of the trace metals except for Zn. The source of Zn enrichment at Israeli site is most likely due to urban ‘hot spot’ source(s) in close vicinity to the sampling site. Lower concentrations of soil related elements (Al, Fe) at Antalya and Amasra relative to the other two eastern Mediterranean sites (Erdemli and Tel Shikmona) probably result from the differences in the sampling techniques. A pre-impactor with 10 µm cut point is used in the sampling procedure of the Antalya and Amasra sites (Güllü *et al*., 1998; Karaka, 1999). It has been shown that during wet and dry deposition of Saharan dust at Sardinia the dust particle diameters show a bimodal structure, with maxima at < 10 µm and > 10 µm particle diameters (Guerzoni *et al*., 1997). Accordingly the lower concentrations found at Antalya and Amasra could be a result of the size selective sampling method used at the sites partially missing the aerosols originating from Saharan outbreaks. At Amasra there is no any sharp winter-summer differences in terms of rain amounts and rain event frequency and temperature differs as at the northeastern Mediterranean stations (Antalya and Erdemli). The elemental concentrations are similar in two remote coastal sites (Corsica and Sardinia). Aerosols from European coastal sites (Liverpool, Blanes, Tour du Valat and Cap Ferrat) have generally similar characteristics with respect to their trace metal concentrations.

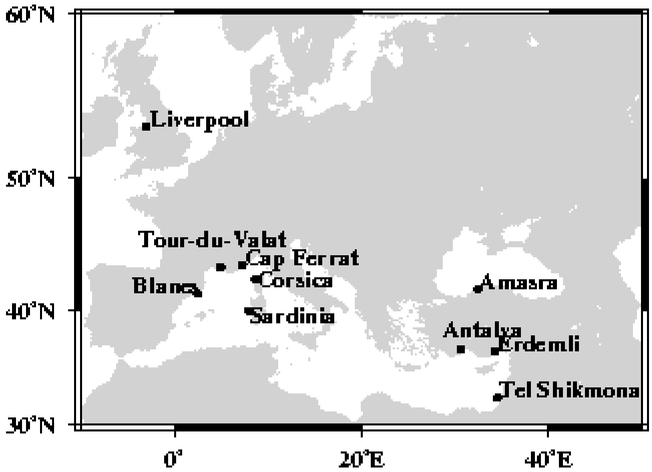


Figure 2. Location of the land-based collection sites for aerosol samples.

A number of features may be identified from the data listed in Table 1 and 2.

The major difference in the aerosol concentrations observed in this study and Tel Shikmona with regard to those located in the western basin, is higher observed concentrations of crustal elements, specifically, Al and Fe. Although the aerosol concentrations of crustal elements Al and Fe in the atmosphere of the Erdemli site are about the twice high as at the western stations, the concentration of Mn is comparable for both basins. This element has a mixed origin; its concentration being affected by both crustal and anthropogenic sources. It has been shown that the main contribution to the aerosol Mn concentration at Erdemli is from the crust whereas it is from anthropogenic emissions at the western Mediterranean sites (Kubilay, 1996).

On the basis of the average EF_{crust} values, the trace metals in aerosols of the coastal sites given in Figure 2 may be divided in two general groups:

(1) Fe and Mn behave as NEEs at all sites.

(2) Zn, Pb and Cd are characterised as AEEs at all sites, although there are differences in their EF_{crust} values. The EF_{crust} values of Pb and Cd are significantly lowered at eastern Mediterranean sites relative to that of European coastal sites.

It may be concluded, therefore, that the aerosols in the lower troposphere of the eastern Mediterranean basin contain higher NEEs (Al, Fe) and lower AEEs (Pb and Cd) than the western basin.

Table 1. Geometric average trace metal concentrations for particulate aerosols from a number of sites (refer to Figure 2).

Element	Liverpool[1]	Blanes[2]	Tour du Valat[3]	Cap Ferrat[4]	Corsica[5]	Sardinia[6]	Amasra[7]	Antalya[8]	Erdemli[9]	Tel Shikmona[10]
Al	317	390	380	370	168	480	210	300	685	720
Fe	340	316	275	320	144	278	200	230	685	798
Mn	8.4	10	13	11	5.3	7.4	8.7	6.11	12.6	14.5
Zn	36	50	60	41	19	21	10	11.3	19	85
Pb	43	50	56	58	16	14	12	13	30	33.6
Cd	-	0.60	0.51	0.36	-	0.3	0.21	-	0.19	0.19

[1] Chester *et al*. (2000); [2] Chester *et al*. (1991); [3] Guieu (1991b); [4]Chester *et al*. (1990); [5]Bergametti *et al*. (1989); [6]Guerzoni *et al*. (1999); [7]Karakaş (1999); [8]Güllü *et al*. (1998); [9]Kubilay and Saydam (1995); [10]Herut *et al*. (*in press*)
Concentrations are given in ng m^{-3} of air, (-) indicates no data reported.

Table 2. Average EF_{crust} values, based on the geometric averages given in Table 1.

Element	Liverpool	Blanes	Tour du Valat	Cap Ferrat	Corsica	Sardinia	Amasra	Antalya	Erdemli	Tel Shikmona
Al	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Fe	2.7	2.0	1.8	2.2	2.1	1.5	2.4	1.9	2.5	2.8
Mn	3.9	3.8	5.0	4.4	4.6	2.3	6.1	3.0	2.7	3.0
Zn	169	191	235	165	168	65	71	56	41	176
Pb	618	584	671	714	434	133	260	197	199	212
Cd	-	1168	1019	739	-	475	759	-	211	200

3.3 Daily variations of the atmospheric concentrations

The daily variations of concentrations between August 1991 and December 1992 for Na, Fe, Ca, Mn, Pb, Zn and Cd are presented in Figure 3. The complete data set may be found in Kubilay (1996). The figure also depicts local rainfall, clearly demonstrating the dramatic decreases in elemental concentrations following rain in winter, spring and autumn – but not during the dry summer period. High variability of atmospheric concentrations is observed on time scales of the order of one day.

Na, which is universally used as an index for seasalt particles in the atmosphere, shows peaks in winter periods, associated with storms. A classical linear relationship between local wind speed and the atmospheric concentration of Na in aerosols has been demonstrated at coastal sites of the western (Corsica) and eastern (Erdemli) Mediterranean (Bergametti *et al*., 1989; Karakoc, 1995).

Atmospheric concentrations of the major elements (Al, Fe, Si, Ca) in the marine environment mostly related to the long-range transport of crustal alumino-silicate particles (commonly referred as dust or mineral aerosol) over the marine environment (Rahn, 1976). In fact, Al concentration can be used as a direct chemical indicator (see next section) for the intrusion of dust from surrounding desert areas, which are primary sources of mineral aerosol. Fe, Ca and Mn depict similar seasonal dependence, with minimum concentrations during winter, when increased soil moisture inhibits dust suspension. During the same period the weathering of crustal material and consequently the atmospheric concentrations of derived elements decreases. During the transitional seasons of spring and autumn, intense episodes occur and result in increased values of major elements. Between these peaks the concentrations diminish to the background values observed in winter. During summer, the concentrations of these elements had less variation (Kubilay and Saydam, 1995), and were generally higher than those in winter as a results of more favourable conditions for soil particles to become airborne.

Concentrations of Pb, Zn and Cd, which originate from pollution sources, did not show the significant seasonal trends as observed for crustal elements.

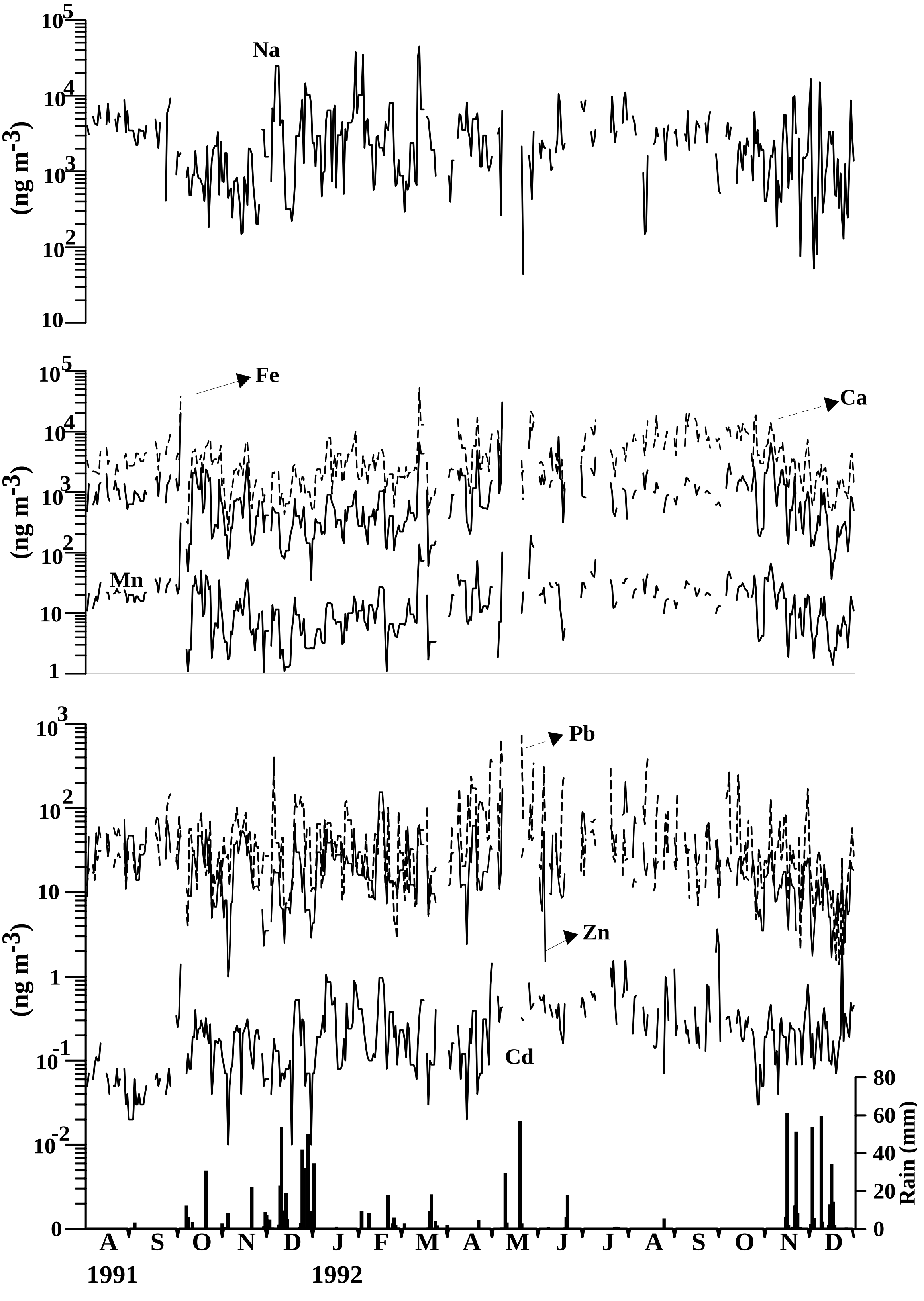


Figure 3. Time series of daily atmospheric concentrations of Na, Ca, Fe, Mn, Pb, Zn and Cd at Erdemli. The daily precipitation is shown at the bottom.

3.4 The variability in aerosol Al concentration in the Northeastern Mediterranean atmosphere and controlling meteorological factors

Time series of aerosol Al concentration (indicator of mineral dust) is displayed in Figure 4, together with local precipitation corresponding to wet deposition. Substantial variability is apparent on both daily and seasonal time scales. During the extreme events of mineral dust intrusions, atmospheric concentrations occasionally exceed the background levels by up to two orders of magnitude. It is also evident that the precipitation is usually followed by an abrupt decrease in Al concentration due to washout by rain. For example, during a Sahara dust intrusion in October 1991 (the first sharp peak in Figure 4) a high value (22568 ng m^{-3}) was followed by a rather low concentration (430 ng m^{-3}) accompanied by rainfall. During the same event the concentrations of Fe, Ca and Mn were decreased from 20047, 37600 and 306 ng m^{-3} to 113, 326 and 2.5 ng m^{-3} respectively (Kubilay *et al.*, 1994).

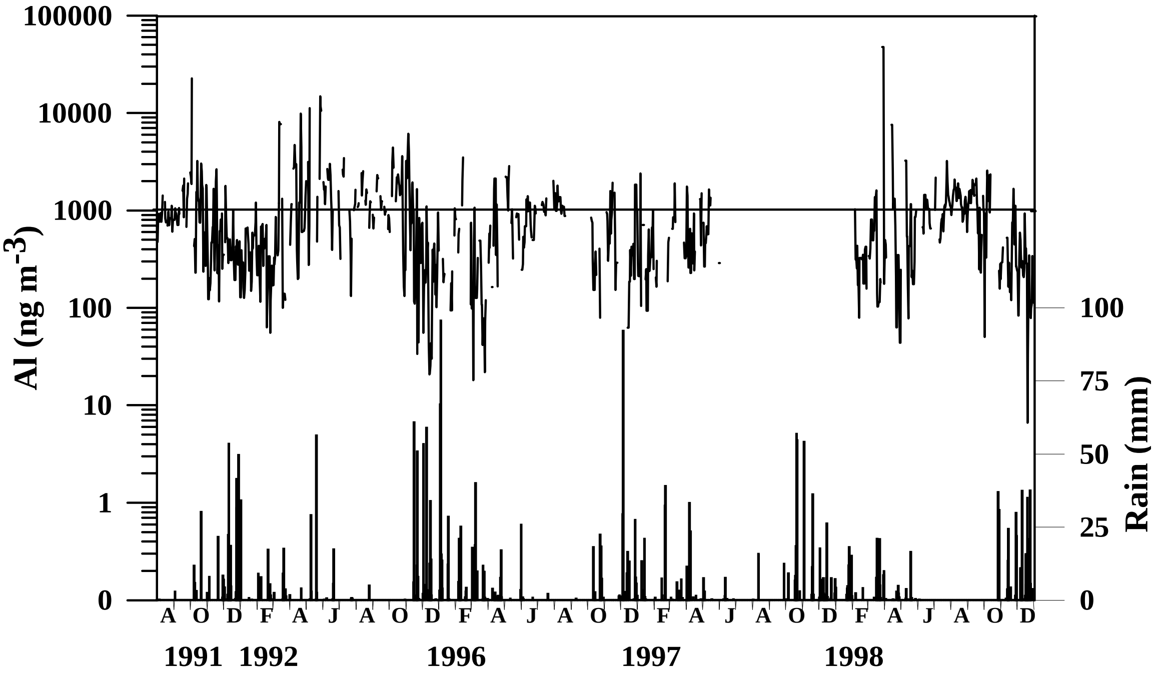
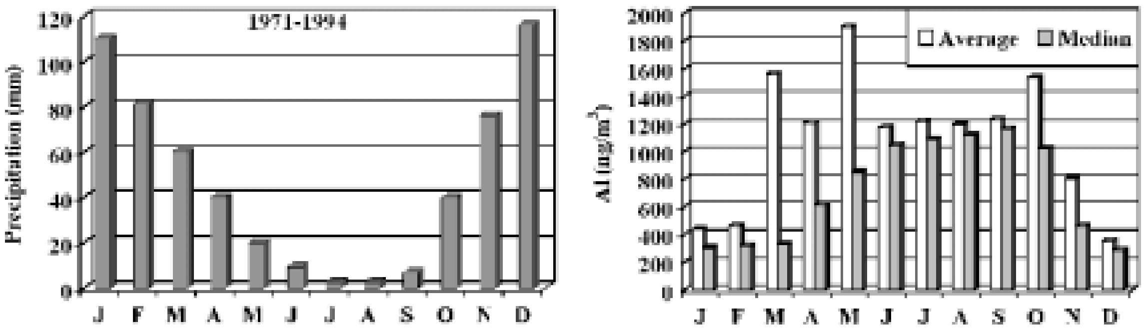


Figure 4. Variations in aerosol Al concentrations during August 1991-December 1992 and January 1996-December 1998 at Erdemli , illustrating the large-scale short-term variability. Local daily precipitation amounts are indicated at the bottom.

To demonstrate more clearly the relationship between local precipitation and the aerosol Al concentration at Erdemli, a histogram for the monthly climatological precipitation and Al concentrations is presented in Figure 5. The 24 years' (1971-1994) climatological monthly mean precipitation (Figure 5a) indicates very little precipitation in the months of June, July, August and September, as compared to the main rainfall season of January, February, November and December.

The monthly mean and median concentrations of aerosol Al present similar values during the dry months (June, July, August and September), which indicate that there are no substantial changes in daily atmospheric Al concentrations in these months. The minimum monthly Al concentrations are observed in the months of January, February and December when high precipitation washes out the atmosphere and results in decreased concentrations. The greatest differences between the mean and median concentrations of Al were observed in March, April and May (Figure 5b). Although precipitation scavenging was still effective in these periods (Figure 5a) the Al concentration was increased by mineral dust transport with cyclones originating from North Africa (Kubilay *et al.*, 2000).

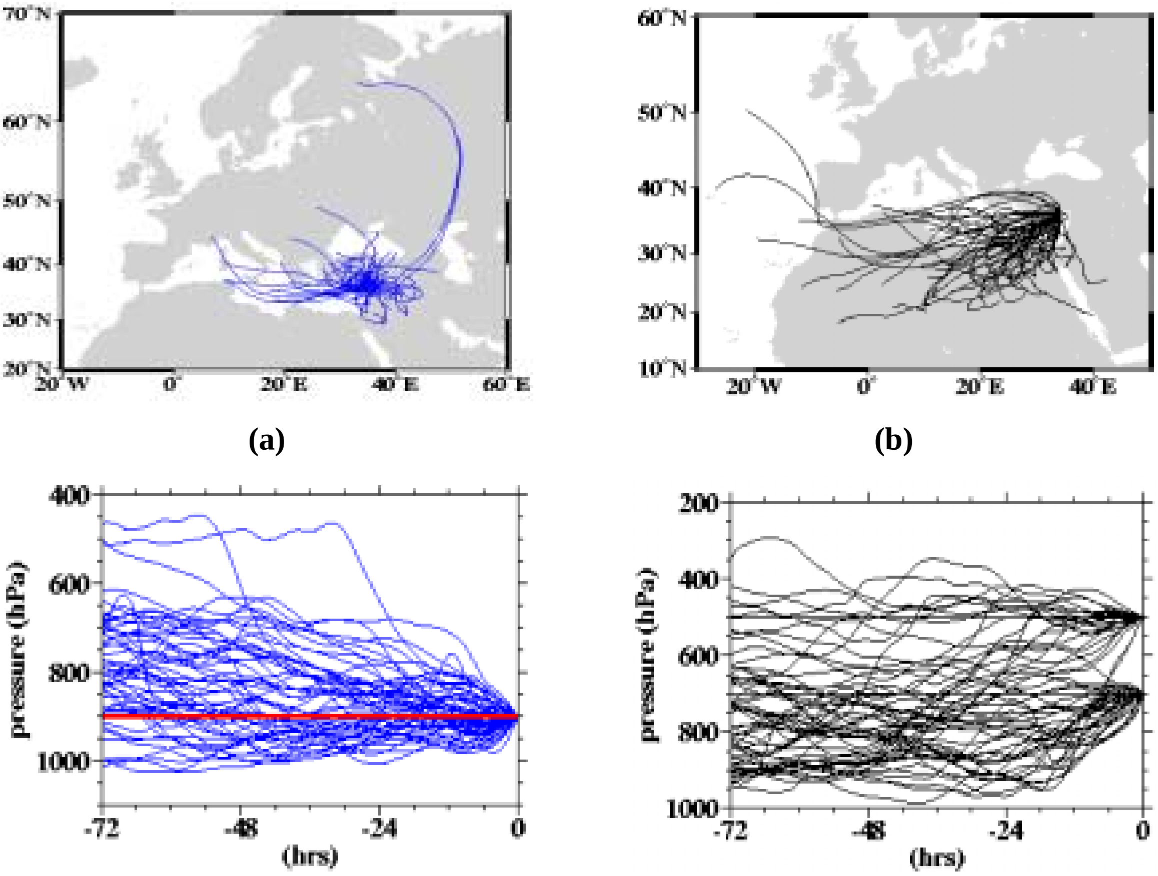


(a) (b)

Figure 5. Monthly variation of precipitation (a) and aerosol Al concentration (b) at the Erdemli station.

Much of the Saharan and Middle Eastern mineral dust is transported in pulses, superimposed on a background reflecting the trace metal composition of local sources. Chester *et al*. (1996) made an arbitrary assumption, that a peak with particulate Al concentration > 1000 ng m^{-3} of air corresponds to a desert derived “pulse” at any site in the Mediterranean Sea. The identification of these pulses was used together with air mass back trajectory analyses to select major events. During the sampling period of March-May, various samples with Al concentration of ≥ 1000 ng m^{-3} were identified. The computed trajectories (Figure 6) for selected days pointed to the origins of the air masses arriving at the selected final barometric levels. The shallower trajectories (arriving at 900 hPa) of the identified air masses originated from non-desert sources, excluding a few cases (Figure 6a). On the other hand, the trajectories arriving at the upper barometric levels (700 and 500 hPa) mostly originated from Africa, except a few cases which originated from the Arabian Peninsula (Figure 6b).

The slope of the vertical component of trajectories shown in the lower panel of Figure 5 provides information on the prevailing meteorological conditions during transport (Martin *et al*., 1990; Kubilay *et al*., 2000). It is observed that the trajectories arriving at 900 hPa start from the upper levels, typically representing anticyclonic motion, and the trajectories arriving at 700 and 500 hPa start from lower levels, representing cyclonic motion. At the synoptic scale, the upper level trajectories show significant upward motion and in contrast, the lower level trajectories show notable downward motion.



(a) (b)

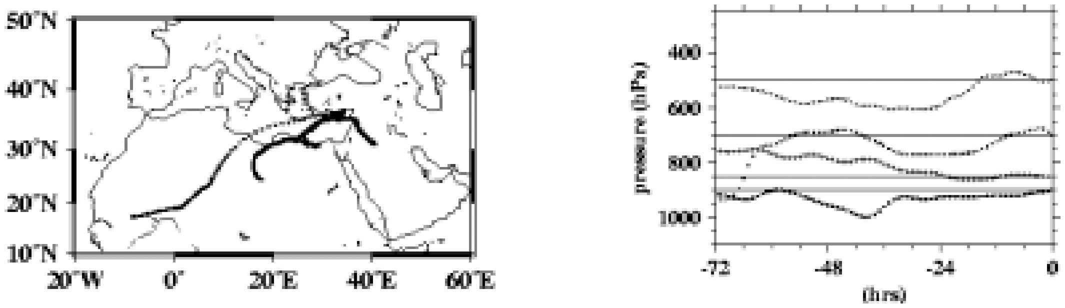
(c) (d)

Figure 6. Air-mass back trajectories arriving at Erdemli. Vertical motions along trajectories are given at the lower panel. (a,c) Trajectories arriving at 900 hPa level. (b,d) Trajectories arriving at 700 and 500 hPa levels.

It is thus suggested that desert dust transport to the Mediterranean region is characterised by a frontal system in agreement with the previous works of Martin *et al*. (1990) and Kubilay *et al*. (2000). This frontal process induces strong vertical mixing and thus rainfall in the frontal zone, which allows the observation of dust at ground level despite its mean transport at higher levels.

Throughout the sampling period of which we presented aerosol Al concentrations, for a total of 164 samples collected at Erdemli within the months of March, April and May, sixty four of these samples have a median Al concentration of 1412 ng m^{-3} (similar to the summer months' median Al concentrations where there is almost no rainfall) whereas their arithmetic average is about two times of the median (3422 ng m^{-3}). The remaining 100 samples have a median value of 300 ng m^{-3} and arithmetic mean of 325 ng m^{-3} which is similar to the mean Al concentration of the winter months where the most important process controlling the Al concentrations is rainfall.

The use of satellite data, transport modelling and three-dimensional air mass trajectories gives a more precise description of the long-range dust transport. Accordingly, the dust event observed on 14 April 1998 which had Al concentration of 7554 ng m^{-3} was analysed based on satellite picture (in the visual spectrum), numerical model outputs (synoptic charts and mineral dust transport) and 3-days air mass back trajectories (Figs. 7 and 8).



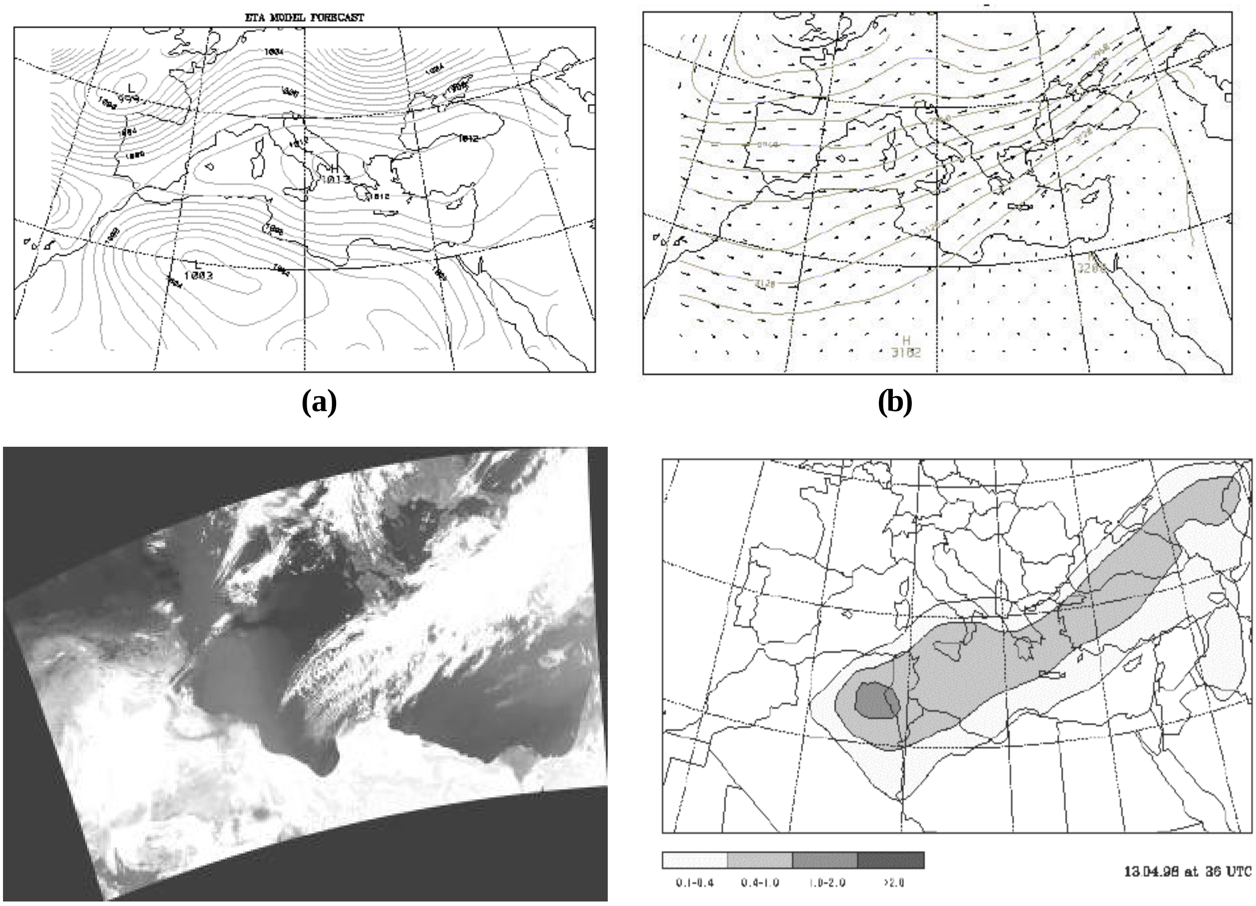
(a)

(b)

Figure 7. Three dimensional three days backward trajectories arriving at Erdemli, at 900, 850, 700 and 500 hPa levels on 14 April 1998. The pressure profiles are shown at the right hand side of the figure.

The computed air-mass trajectories arriving at Erdemli (Figure 7) on 14 April suggest that the origin of the high Al concentration observed was mineral dust originated from the North African desert. The 900-hPa air mass arrived from the Middle East, while trajectories ending at 850, 700 and 500 hPa indicated the Saharan origin. The vertical components especially at 700 hPa reveal significant upward motion allowing dust to ascend and to be transported over long distances. In the NOAA –AVHRR image, dust in the central and eastern Mediterranean appeared as a greyish white area somewhat resembling clouds, but with softer boundaries hidden by the clouds (Figure 8c). In order to understand the generation and transport of dust storms over the Mediterranean Sea, an analysis of the synoptical conditions leading to anomalous Al concentrations at the ground level is necessary. This dust intrusion is caused by the presence of a deep barometric low pressure (1003 hPa) (Figure 8a) on the lee side of Atlas Mountains, which is a typical example of the dust carrying Sharav cyclones of the spring season, as described by Alpert and Ziv (1989). The airflow pattern at 700 hPa was suitable to the transport of the trough (Sharav cyclone) from north Africa to the northeastward direction (Figure 8b). The observed (Figure 8c) and predicted (Figure 8d) dust loading generally coincide with each other.

The analysis of the selected case shows that by combining the observations and modelling it may be possible to obtain more insight into the features of dust transport events. The trajectory model addresses general flow features responsible for the long-range mineral dust transport. The three dimensional Eulerian modelling offers more detailed description of the atmospheric dust cycle. The ETA dust model yielded reasonably successful simulation of the major features of the event. The availability of the satellite observations and ground-truth measurements are of crucial importance for further refinement and tuning of the models.



(a) **(b)**

(c) **(d)**

Figure 8. The numerical model outputs and satellite pictures belonging to mineral dust transport observed at Erdemli on 14 April 1998. (a) The pressure pattern at the surface, (b) Winds and geopotential heights at 700 hPa, (c) NOAA-AVHRR vis image, (d) Vertically integrated model dust concentration (g m^{-2}).

3. 5 Aerosol Trace Metal Seawater Soulibility studies in the Eastern Mediterranean

Up to this section, the total trace metal concentrations for the sampling site were discussed. The total concentrations, which are normally quoted in the literature, do not however give an indication with regard to the bioavalibility and toxicity of metals in the marine system. To estimate the net atmospheric trace metal flux to the Mediterranean Sea, the solubility of the trace metals in both rainwater and when deposited at the sea surface need to be considered.

The percentage of the total fraction of the aerosol associated with Cu, Pb, Zn , Ni and Co which was soluble in seawater was determined in two contrasting samples: one sample representing a “Saharan” type aerosol population and one representing a “European” type aerosol population. Because of experimental problems it was not possible to determine solubility values for Co in the “Saharan” population. The seawater solubilities observed are compared with recent determinations carried out by Medway *et al.*, 2000 (in preparation) on a set of aerosol samples collected off the coast of North Israel (Haifa), (Table 3). In addition a comparison was made between other European maritime aerosol populations. The presented values indicate a similar trends in the seawater solubilities to those determined previously for the Eastern Mediterranean with a greater seawater solubility for trace matals present in aerosol populations representative of the “European” type compared with that observed in the “Saharan” type aerosol population. However it was apparent for the two contrasting samples analysed from Erdemli where a greater differential elemental seawater solubility was detected (e.g. for Zn % seawater solubilities ranged from 43% to 84%) than those detected at the Haifa sampling site. For the current location a greater number of aerosol samples will be characterised for their seawater solubilities. This is required before the atmospheric inputs of soluble trace metals may be evaluated with a sufficient degree of confidence.

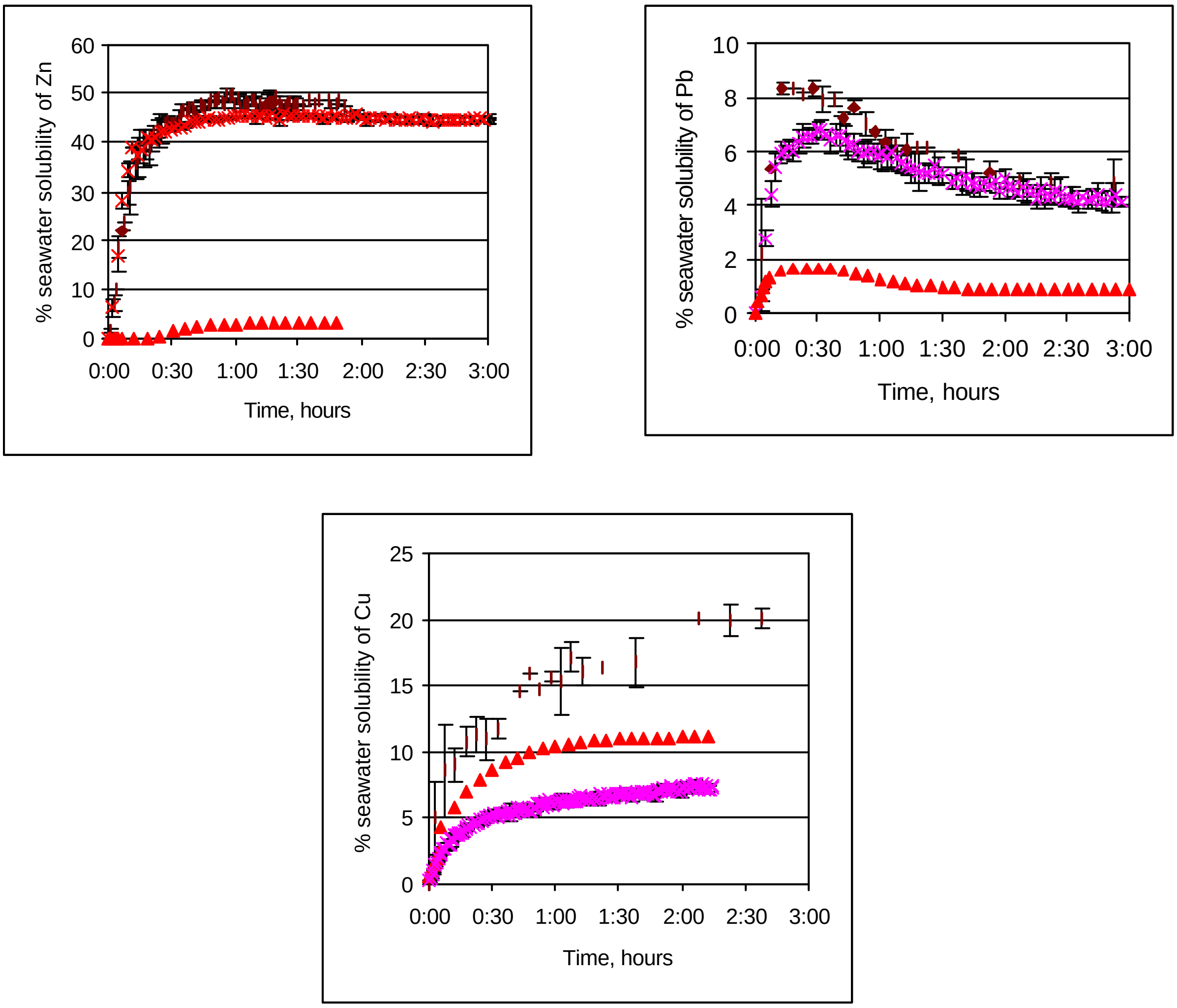
Table 3. Seawater solubility (%) of the Eastern Mediterranean aerosol (%) and of other aerosol populations

	Eastern Med. – Haifa		Eastern Med. – Erdemli		Literature data		
	Crustal aerosol	Urban aerosol	Saharan aerosol	European aerosol	W. African coast^a	North Sea^b	Irish Sea^c
Co	32 ± 14	39 ± 19	-	35		53	32
Cu	25 ± 10	32 ± 16	2	90	<1-3	38	58
Ni	46 ± 9	39 ± 12	4	18		41	38
Pb	45 ± 5	63 ± 22	29	39	<1 - 1.5	16	37
Zn	41 ± 14	67 ± 16	43	84	<1	41	

^{a}Chester *et al*. (1993); ^{b}Kersten *et al*. (1991) and ^{c}Fones (1996)

While defining aerosol trace metal seawater solubilities in contrasting aerosol populations, for the development of predictive atmospheric input models, it is necessary to define and understand the factors which influence the **extent** and **kinetics** of trace metal dissolution. These are currently being investigated using a stripping voltametric flow through system.

One of the advantges of ACSV is its ability to detect the operationally defined speciation of dissolved trace metals. This is undertaken for the “urban” aerosol material by measuring the trace metal concentrations before and after UV irradiation for a period of three hours. When the sample was analysed before UV irradiation it yielded the ACSV $_{\text{labile}}$ fraction. After UV irradiation of the seawater the dissolved organic material is oxidised and any organically complexed metal will be available for analysis yielding the total ACSV dissolved fraction. The system allows high temporal (1 measurement per minute) resolution direct sweater trace metal measurements, enabling the release of trace metals from end member bulk aerosol particulate to be monitored once added to seawater. Examples of the kinetic characteristics for Zn, Cu and Pb seawater dissolution (total dissolved, the electrochemical “labile” and “non-labile” fractions) from initial experiments carried out with “urban” aerosol material are highlighted on Figure 9. Factors effecting the extent and kinetics of dissolution such as (i) seawater temperature, (ii) particle concentrations, and (iii) proportions of contrasting aerosol types are currently being considered and these studies will continue in the next year as a collaborative study. The “Saharan” bulk aerosol material collected at Erdemli will undergo similar experiments to serve as **a crustal end member** comparative aerosol population.



”Labile” fraction ❄, total dissolved ◆, ”non-labile” fraction ▲

Figure 9. Kinetics of Zn, Pb and Cu dissolution in UV irradiated sterile seawater (25°C, 50 mg l^{-1} particulate concentration).

Such a process may play an important role in influencing the trace metal marine biogeochemical cycling. The results would suggest two contrasting behaviours of the metal dissolved fractions: (i) the ACSV $_{\text{labile}}$ metal remains in solution and (ii) the ACSV $_{\text{non-labile}}$ metal fraction being surface active undergoes adsorption onto particle surfaces. This contrasting behaviour will have implications on their marine pathways, with the former having longer oceanic residence times and undergoing successive recycling in surface marine waters.

4. CONCLUDING REMARKS

The present day temporal and geographic variations in the open ocean chemistry and regional climate for the Mediterranean basin are, so far, largely due to natural oceanic processes rather than human activities. But for early detection, prediction and potential mitigation of human impacts it is however essential to distinguish these human influences from the natural background variations, that is only possible if natural variability is thoroughly characterised and understood in terms of the governing processes. It is presently difficult to identify any impact of inputs of anthropogenic nitrogen and metals to the open ocean via the atmosphere, although such inputs are known to occur and could potentially affect primary productivity. For example, dust deposition onto the nutrient limited basin (2.3. 10^6 km^2) is one of the greatest in the contemporary ocean (20-

50 10^6 tons yr $^{-1}$). There have been several hypothesis suggesting that this large input is responsible for biogeochemical effects, although no concerted scientific program aimed at directly elucidating these effects has yet been set up (Guerzoni *et al*., 1999 and references therein).

The deposition of Sahara dust on the Mediterranean basin is believed to locally supply nutrients and to increase the production of the pelagic system (Herut *et al*., 199a; Bergametti *et al*., 1992; Ridame and Guieu, 2000; Saydam, 1996; Saydam and Polat, 1999). Despite its importance for climate change (via biogeochmical cycles) this phenomena is very contraversial within the scientific community. Eastern Mediterranean is a suitable site to try to evidence that since it experinces strong dust transport and it is oligotrophic. Both phosphate and iron inputs are candidates to explain the fertilization impact of dust in this region.

One of the major difficulties faced in determining phytoplankton-dust connection and linkages has been the lack of long term records of atmospheric aerosols on a regional scale. Even though a few ground-based stations do exist, a network of stations that span the open Mediterranean basin is not available and does not seem practical. The remedy to this problem may be the satellite based measurements. Earth-observing satellites, particularly ocean-color sensors, can provide a platform for sensors to acquire related synoptic information as well as long-term records of atmospheric aerosols. Thus satellite measurements of regional aerosol loading can help us to understand the role of the oceans in climate patterns. The first necessary step is to try to study the relationship between phytoplankton growth and mineral aerosols via satellite with the ability to measure both parameters (dust and chlorophyll) at relevant scales on a regional basis. Such a study is planning to be performed at the Institute of Marine Sicences. The overall objective is to develop and implement a system for routine monitoring and prediction of the Saharan dust transport and impact of desert dust in the Eastern Mediterranean region, based on a numerical weather prediction model enhanced by a module for the simulation of the dust uptake, transport and wet deposition together with satellite observation of dust and chlorohyll.

Acknowledgments: Substantial parts of the study were funded by the Turkish Scientific and Technical Research Council (TUBITAK) through the DEBAG-79/6 and YDABCAG 462/6 projects. The authors are grateful for support for this work under the following grants and contracts: METU Research Fund Project (AFP-98-06-01-01). and special service aggreement with WMO.

References

Alpert, P. and Ziv, B., 1989. The Sharav cyclone: observations and some theoritical considerations.
J. Geophys. Res., 94: 18495-18514.

Bergametti, G., Dutot, A. L., Buat-Menard, P., Losno, R. and Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the north-western Mediterranean. Tellus, 41B: 353-361.

Bergametti, G., Remoudaki, E., Losno, R., Steiner, E., Chatenet, B. and Buat-Menard, P., 1992. Source, transport and deposition of atmospheric phosphorus over the Northwestern Mediterranean.
J. Atmos. Chem., 14: 501-513.

Brody, L. R. and Nestor, M. J. R., 1980. Handbook for Forecasters in the Mediterranean, Part 2. Regional forecasting aids for the Mediterranean Basin. Naval Environmental Prediction Research Facility (Technical Report TR 80-10), pp. VII-1; VII-13. Monterey, California.

Chester, R., Nimmo, M., Murphy, K. J. T. and Nicolas, E., 1990. Atmospheric trace metals transported to the western Mediterranean: data from a station on Cap Ferrat. In *Water Pollution*

Research Reports, vol.20 (edited by Martin J. M. and Barth H.), pp. 597-612. Commission of the European Communities.

Chester, R., Nimmo, M., Alarcon, M. and Corcaron, P., 1991. The chemical character of the north western Mediterranean aerosol. In *Water Pollution Research Reports*, vol.28 (edited by Martin J. M. and Barth H.), pp. 495-504. Commission of the European Communities.

Chester, R., Murphy, K.J.T., Lin, F.J., Berry, A.S., Bradshaw, G.A. and Corcoran, P.A. (1993) Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the 'dry' deposition mode. Mar. Chem. ,42**,** 107-126.

Chester, R., Mimmo, M. and Keyse, S., 1996. The influence of Saharan and Middle Eastern desert derived dust on the trace metal composition of Mediterranean aerosols and rainwaters: an overview. In *The impact of desert dust across the Mediterranean*, (edited by S. Guerzoni and R. Chester), pp. 253-274, Kluwer, Dordrecht.

Chester, R., Nimmo, M., Fones, G. R., Keyse, S. and Zhang, Z., 2000. Trace metal chemistry of particulate aerosols from the UK mainland coastal rim of the NE Irish sea. Atmospheric Environment, 34: 949-958.

Dayan, U., J. L. Heffter and J. M. Miller, 1996. Seasonal distribution of the boundary layer depths over the Mediterranean basin. In: *The Impact of Desert Dust Across the Mediterranean* (eds. S. Duerzoni and R. Chester), pp 103-112. Kluwer Academic Publishers, the Netherlands.

Duce, R.A., Liss, P.S., Merill, J.T., Atlas, E.L., Buat-Menart, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R. and Zhou, M., 1991. The atmospheric input of trace species to the world ocean. Global Biogeochemical Cycles, 5: 193-259.

Fones, G.R. (1996) Atmospheric deposition of trace metals to urban and coastal environments. PhD thesis, University of Lancaster, pp.1-364.

Guerzoni, S., Molinaroli, E. and Chester, R., 1997. Saharan dust inputs to the western Mediterranean Sea: depositional patterns, geochemistry and sedimentological implications. Deep-Sea Research II, 44: 631-654.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M-D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Saydam, C., Soudine, A. and Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, Progress in Oceanography, 44: 147-190.

Guieu, C., Martin, J. M., Thomas, A. J. and Elbaz-Polichet, F., 1991a. Atmospheric versus river inputs of metals to the Gulf of Lions; total concentrations, partitioning and fluxes. Mar. Pollut. Bull., 22: 176-183.

Guieu, C., 1991b. Apports atmospheriques a la Mediterranee nord-occidentale. These de doctorat de l’Universite de Paris, pp. 225.

Guieu, C., Chester, R., Nimmo, M., Martin, J.M., Guerzoni, S., Nicolas, E., Mateu, J. and Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the north-western Mediterranean. Deep-Sea Research II, 44: 655-674.

Güllü, G. H., Ölmez, Ý., Aygun, S. and Tuncel, G., 1998. Atmospheric concentrations of trace elements over the eastern Mediterranean Sea: factors affecting temporal variability. J. Geophys. Res., 103: 21943-21954.

Harris, J. M. and J. D. W. Kahl, 1990. A descriptive atmospheric transport climatology for the Mauna Loa observatory, using clustered trajectories. J. Geophys. Res., 95: 13651-13667.

Herut, B., Krom, M. D., Pan, G. and Mortimer, R., 1999a. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: sources, fluxes, and possible impact. Limnol. Oceanogr., 44: 1683-1692.

Herut, B., Zohary, T., Robarts, R. D. and Kress, N., 1999b. Adsorption of dissolved phosphate onto loess particles in surface and deep Eastern Mediterranean water**.** Marine Chemistry, 64: 253-265.

Herut, B., Nimmo, M., Medway, A., Chester, R. and Krom, M. Dry atmospheric inputs of trace metals along the Mediterranean coast of Israel (SE Mediterranean): Sources and fluxes. Atmos. Environ. (*in press*)

Jickells, T., 1995. Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. Marine Chemistry, 48: 199-214.

Jickells, T. D., 1999. The inputs of dust derived elements to the Sargasso Sea; a synthesis. Marine Chemistry, 68: 5-14.

Rahn, K. A., 1976. The chemical composition of the atmospheric aerosols. Technical Report. Graduate School of Oceanography, University of Rhode Island, Kingston, R. I., 265 pp.

Ridame, C., Guieu, C. and Loye-Pilot, M-D., 1999. Trend in total atmospheric deposition fluxes of aluminium, iron and trace metals in the north-western Mediterranean, over the past decade (1985-1997), Journal of Geophysical Research, 104: 30127-30138.

Ridame, C.and Guieu, C., 2000. Saharan Source of dissolved phosphorus to the Mediterranean, 2000 Ocean Science Meeting, Jan 24-28, San Antonio, Texas, EOS, 80, N°49.

UNEP/MAP, 1996. State of the marine and coastal environment in the Mediterranean region. MAP Technical Reports Series, No 100, UNEP, Athens, 142 pp.

Karakaº, D., 1999. Determination of the European contribution on the aerosol composition in the Black Sea basin and investigation of transport mechanisms. Ph.D. Dissertation, pp.175, The Department of Chemistry-METU, Ankara-Turkey.

Karakoc, F., 1995. Comparision of atmospheric trace element distributions over the Black Sea, Marmara Sea and Mediterranean Sea regions. Ma. Sc. Thesis, pp.130, Institute of Marine Sciences-METU, Erdemli-Turkey.

Kersten, M., Kriews, M. and Forstner, U. (1991) Partitioning of trace metals released from polluted marine aerosols in coastal seawater. *Marine Chemistry* 36, 165-182.

Krom, M.D., Kress N., Brenner, S. and Gordon, L.I., 1991. Phosphorus limitation of primary productivity in the eastern Mediterranean Sea. Limnology and Oceanography, 36:424-432.

Kubilay, N. N., Yemenicioðlu, S. and Saydam, A. C., 1994. Trace metal characterisation of airborne particles from the Northeastern Mediterranean. Fresenius Environ. Bull., 3: 444-448.

Kubilay, N. N. and Saydam, A. C., 1995. Trace elements in atmospheric particulates over the eastern Mediterranean; Concentrations, sources and temporal variability. Atmos. Environ., 29: 2289-2300.

Kubilay, N.N., Yemenicioðlu, S. and Saydam, A.C., 1995. Airborne material collections and their chemical composition over the Black Sea. Mar. Poll. Bull., 30: 475-483.

Kubilay, N. N., 1996. The Composition of Atmospheric Aerosol Over The Eastern Mediterranean; The coupling of geochemical and meteorological parameters. Ph.D. Dissertation, pp.219, Institute of Marine Sciences, METU, Erdemli-Turkey.

Kubilay, N., S. Nickovic, C. Moulin and F. Dulac, 2000. An illustration of the transport of mineral dust onto the eastern Mediterranean. Atmos. Environ., 34/8: 1293-1303.

Martin, D., Bergametti, G., Strauss, B., 1990. On the use of the synoptic vertical velocity in trajectory model: validation by geochemical tracers. Atmos. Envr. 24A: 2059-2069.

Martin, J.M., Elbaz-Poulichet, F., Guieu, C., Loye-Pilot M-D. and G., Han, 1989. River versus atmospheric input of material to the Mediterranean Sea: An overview, Marine Chemistry, 28: 159-182.

Mc Grath, R., 1989. Trajectory models and their use in the Irish Meteorological service. Internal Memorandum No. 112/89. Irish Meteorological Service, Glasnevin Hill, Dublin, pp. 12.

Mesinger, F., Janjic, Z. I., Nickovic, S., Gavrilov, D., Deaven, G. G., 1988. The step-mountain coordinate: model description and performance for cases of alpine lee cyclogenesis and for a case of Appalachian redevelopment. Monthly Weather Review, 116: 1493-1518.

Migon, C. and Sandroni, V., 1999. Phosphorus in rainwater: Partitioning inputs and impact on the surface coastal ocean. Limnol. Oceanogr., 44: 1160-1165.

Moulin, C., E. Lambert, U. Dayan, V. Masson, M. Ramonet, P. Bousquet, M. Legrand, Y. J. Balkanski, W. Guelle, B. Marticorena, G. Bergametti and F. Dulac, 1998: Satellite climatology of African dust transport in the Mediterranean atmosphere. J. Geophys. Res. 103: 13137-13144.

Nickovic, S. and Dobricic, S., 1996. A model for long-range transport of desert dust. Monthly Weather Review, 124: 2537-2544.

Nickovic, S., Jovic, D., Kakaliagou, O. and Kallos, G., 1997. Production and long-range transport of desert dust in the Mediterranean region: Eta model simulations, 22nd NATO/CCMS International Technical Meeting and its Aplication. 2-6 June 1997, Clermont-Ferrand, France.

Özsoy, E., Kubilay, N., Nickovic, S. and Saydam, C., 1998. A hemispheric dust storm in April 1994 – observations, modelling and analyses. 23 rd NATO/CCMS International Technical Meeting on Air Pollution Modelling and its Application. September 28 – October 2, 1998, Bulgaria.

Saydam, A. C., 1996. Can we predict harmful algae blooms. Harmful Algae News, 15, 5-6.

Saydam, A. C and Polat, I., 1999. The impact of Saharan dust on the occurence of algae bloom. Proceeding of EUROTRAC Symposium'98. Eds: Borrell, P. M. and Borrell, P.WIT press, Southampton. pp:656-663.

UNEP/WMO, 1992. Airborne Pollution of the Mediterranean Sea. Report and Proceedings of the second WMO/UNEP workshop. MAP Technical Reports Series No. 64.

Wedepohl, K. H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta, 59: 1217-1232.

LIST OF MAP TECHNICAL REPORTS

Please note that you can access many of the MTS Reports on the MAP Web Site at www.unepmap.org

(*)Not currently available in hard copy.

MTS 1. (*) UNEP/IOC/WMO: **Baseline studies and monitoring of oil and petroleum hydrocarbons in marine waters (MED POL I).** MAP Technical Reports Series No. 1. UNEP, Athens, 1986 (96 pgs.) (Parts in English, French or Spanish only). PNUE/COI/OMM: **Etudes de base et surveillance continue du pétrole et des hydrocarbures contenus dans les eaux de la mer (MED POL I).** MAP Technical Reports Series No. 1. UNEP, Athens, 1986 (96 pgs.) (parties en anglais, français ou espagnol seulement).

MTS 2. (*) UNEP/FAO: **Baseline studies and monitoring of metals, particularly mercury and cadmium, in marine organisms (MED POL II).** MAP Technical Reports Series No. 2. UNEP, Athens, 1986 (220 pgs.) (Parts in English, French or Spanish only). PNUE/FAO: **Etudes de base et surveillance continue des métaux, notamment du mercure et du cadmium, dans les organismes marins (MED POL II).** MAP Technical Reports Series No. 2. UNEP, Athens, 1986 (220 pgs.) (Parties en anglais, français ou espagnol seulement).

MTS 3. (*) UNEP/FAO: **Baseline studies and monitoring of DDT, PCBs and other chlorinated hydrocarbons in marine organisms (MED POL III).** MAP Technical Reports Series No. 3. UNEP, Athens, 1986 (128 pgs.) (Parts in English, French or Spanish only). PNUE/FAO: **Etudes de base et surveillance continue du DDT, des PCB et des autres hydrocarbures chlorés contenus dans les organismes marins (MED POL III).** MAP Technical Reports Series No. 3. UNEP, Athens, 1986 (128 pgs.) (Parties en anglais, français ou espagnol seulement).

MTS 4. (*) UNEP/FAO: **Research on the effects of pollutants on marine organisms and their populations (MED POL IV).** MAP Technical Reports Series No. 4. UNEP, Athens, 1986 (118 pgs.) (Parts in English, French or Spanish only). PNUE/FAO: **Recherche sur les effets des pollutants sur les organismes marins et leurs peuplements (MED POL IV).** MAP Technical Reports Series No. 4. UNEP, Athens, 1986 (118 pgs.) (Parties en anglais, français ou espagnol seulement).

MTS 5. (*) UNEP/FAO: **Research on the effects of pollutants on marine communities and ecosystems (MED POL V).** MAP Technical Reports Series No. 5. UNEP, Athens, 1986 (146 pgs.) (Parts in English or French only). PNUE/FAO: **Recherche sur les effets des pollutants sur les communautés et écosystèmes marins (MED POL V).** MAP Technical Reports Series No. 5. UNEP, Athens, 1986 (146 pgs.) (Parties en anglais ou français seulement).

MTS 6. (*) UNEP/IOC: **Problems of coastal transport of pollutants (MED POL VI).** MAP Technical Reports Series No. 6. UNEP, Athens, 1986 (100 pgs.) (English).

MTS 7. (*) UNEP/WHO: **Coastal water quality control (MED POL VII).** MAP Technical Reports Series No. 7. UNEP, Athens, 1986 (426 pgs.) (Parts in English or French only). PNUE/OMS: **Contrôle de la qualité des eaux côtières (MED POL VII).** MAP Technical Reports Series No. 7. UNEP, Athens, 1986 (426 pgs.) (Parties en anglais ou français seulement).

MTS 8. (*) UNEP/IAEA/IOC: **Biogeochemical studies of selected pollutants in the open waters of the Mediterranean (MED POL VIII).** MAP Technical Reports Series No. 8. UNEP, Athens, 1986 (42 pgs.) (parts in English or French only). PNUE/AIEA/COI: **Etudes biogéochimiques de certains pollutants au large de la Méditerranée (MED POL VIII).** MAP Technical Reports Series No. 8. UNEP, Athens, 1986 (42 pgs.) (parties en anglais ou français seulement).

MTS 8. Add. (*)UNEP: **Biogeochemical studies of selected pollutants in the open waters of the Mediterranean MED POL VIII). Addendum, Greek Oceanographic Cruise 1980.** MAP Technical Reports Series No. 8, Addendum. UNEP, Athens, 1986 (66 pgs.) (English).

MTS 9. (*) UNEP: **Co-ordinated Mediterranean pollution monitoring and research programme (MED POL - PHASE I). Final report, 1975-1980.** MAP Technical Reports Series No. 9. UNEP, Athens, 1986 (276 pgs.) (English).

MTS 10. (*) UNEP: **Research on the toxicity, persistence, bioaccumulation, carcinogenicity and mutagenicity of selected substances (Activity G). Final reports on projects dealing with toxicity (1983-85).** MAP Technical Reports Series No. 10. UNEP, Athens, 1987 (118 pgs.) (English).

MTS 11. (*) UNEP: **Rehabilitation and reconstruction of Mediterranean historic settlements. Documents produced in the first stage of the Priority Action (1984-1985).** MAP Technical Reports Series No. 11. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1986 (158 pgs.) (parts in English or French only). PNUE: **Réhabilitation et reconstruction des établissements historiques méditerranéens. Textes rédigés au cours de la première phase de l'action prioritaire (1984-1985).** MAP Technical Reports Series No. 11. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1986 (158 pgs.) (parties en anglais ou français seulement).

MTS 12. (*) UNEP: **Water resources development of small Mediterranean islands and isolated coastal areas. Documents produced in the first stage of the Priority Action (1984-1985).** MAP Technical Reports Series No. 12. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (162 pgs.) (parts in English or French only). PNUE: **Développement des ressources en eau des petites îles et des zones côtières isolées méditerranéennes. Textes rédigés au cours de la première phase de l'action prioritaire (1984-1985).** MAP Technical Reports Series No. 12. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (162 pgs.) (parties en anglais ou français seulement).

MTS 13. (*) UNEP: **Specific topics related to water resources development of large Mediterranean islands. Documents produced in the second phase of the Priority Action (1985-1986).** MAP Technical Reports Series No. 13. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (162 pgs.) (parts in English or French only). PNUE: **Thèmes spécifiques concernant le développement des ressources en eau des grandes îles méditerranéennes. Textes rédigés au cours de la deuxième phase de l'action prioritaire (1985-1986).** MAP Technical Reports Series No. 13. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (162 pgs.) (parties en anglais ou français seulement).

MTS 14. (*) UNEP: **Experience of Mediterranean historic towns in the integrated process of rehabilitation of urban and architectural heritage. Documents produced in the second phase of the Priority Action (1986).** MAP Technical Reports Series No. 14. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (500 pgs.) (parts in English or French only). PNUE: MAP Technical Reports Series No. 14. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (500 pgs.) (parties en anglais ou français seulement).

MTS 15. (*) UNEP: **Environmental aspects of aquaculture development in the Mediterranean region. Documents produced in the period 1985-1987.** MAP Technical Reports Series No. 15. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (101 pgs.) (English).

MTS 16. (*) UNEP: **Promotion of soil protection as an essential component of environmental protection in Mediterranean coastal zones. Selected documents (1985-1987).** MAP Technical Reports Series No. 16. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (424 pgs.) (parts in English or French only). PNUE: **Promotion de la protection des sols comme élément essentiel de la protection de l'environnement dans les zones côtières méditerranéennes. Documents sélectionnés (1985-1987).** MAP Technical Reports Series No. 16. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (424 pgs.) (parties en anglais ou français seulement).

MTS 17. (*) UNEP: **Seismic risk reduction in the Mediterranean region. Selected studies and documents (1985-1987).** MAP Technical Reports Series No. 17. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (247 pgs.) (parts in English or French only). PNUE: **Réduction des risques sismiques dans la région méditerranéenne. Documents et études sélectionnés (1985-1987).** MAP Technical Reports Series No. 17. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1987 (247 pgs.) (parties en anglais ou français seulement).

MTS 18. (*) UNEP/FAO/WHO: **Assessment of the state of pollution of the Mediterranean Sea by mercury and mercury compounds.** MAP Technical Reports Series No. 18. UNEP, Athens, 1987 (354 pgs.) (English and French). PNUE/FAO/OMS: **Evaluation de l'état de la pollution de la mer Méditerranée par le mercure et les composés mercuriels.** MAP Technical Reports Series No. 18. UNEP, Athens, 1987 (354 pgs.).

MTS 19. (*) UNEP/IOC: **Assessment of the state of pollution of the Mediterranean Sea by petroleum hydrocarbons.** MAP Technical Reports Series No. 19. UNEP, Athens, 1988 (130 pgs.) (English and French). PNUE/COI: **Evaluation de l'état de la pollution de la mer Méditerranée par les hydrocarbures de pétrole.** MAP Technical Reports Series No. 19. UNEP, Athens, 1988 (130 pgs.).

MTS 20. (*) UNEP/WHO: **Epidemiological studies related to environmental quality criteria for bathing waters, shellfish-growing waters and edible marine organisms (Activity D). Final report on project on relationship between microbial quality of coastal seawater and health effects (1983-86).** MAP Technical Reports Series No. 20. UNEP, Athens, 1988 (156 pgs.) (English).

MTS 21. UNEP/UNESCO/FAO: **Eutrophication in the Mediterranean Sea: Receiving capacity and monitoring of long-term effects.** MAP Technical Reports Series No. 21. UNEP, Athens, 1988 (200 pgs.) (parts in English or French only). PNUE/UNESCO/FAO: **Eutrophisation dans la mer Méditerranée: capacité réceptrice et surveillance continue des effets à long terme.** MAP Technical Reports Series No. 21. UNEP, Athens, 1988 (200 pgs.) (parties en anglais ou français seulement).

MTS 22. UNEP/FAO: **Study of ecosystem modifications in areas influenced by pollutants (Activity I).** MAP Technical Reports Series No. 22. UNEP, Athens, 1988 (146 pgs.) (parts in English or French only). PNUE/FAO: **Etude des modifications de l'écosystème dans les zones soumises à l'influence des pollutants (Activité I).** MAP Technical Reports Series No. 22. UNEP, Athens, 1988 (146 pgs.) (parties en anglais ou français seulement).

MTS 23. UNEP: **National monitoring programme of Yugoslavia, Report for 1983-1986.** MAP Technical Reports Series No. 23. UNEP, Athens, 1988 (223 pgs.) (English).

MTS 24. UNEP/FAO: **Toxicity, persistence and bioaccumulation of selected substances to marine organisms (Activity G).** MAP Technical Reports Series No. 24. UNEP, Athens, 1988 (122 pgs.) (parts in English or French only). PNUE/FAO: **Toxicité, persistance et bioaccumulation de certaines substances vis-à-vis des organismes marins (Activité G).** MAP Technical Reports Series No. 24. UNEP, Athens, 1988 (122 pgs.) (parties en anglais ou français seulement).

MTS 25. UNEP: **The Mediterranean Action Plan in a functional perspective: A quest for law and policy.** MAP Technical Reports Series No. 25. UNEP, Athens, 1988 (105 pgs.) (English).

MTS 26. UNEP/IUCN: **Directory of marine and coastal protected areas in the Mediterranean Region. Part I - Sites of biological and ecological value.** MAP Technical Reports Series No. 26. UNEP, Athens, 1989 (196 pgs.) (English).

MTS 27. UNEP: **Implications of expected climate changes in the Mediterranean Region: An overview.** MAP Technical Reports Series No. 27. UNEP, Athens, 1989 (52 pgs.) (English).

MTS 28. UNEP: **State of the Mediterranean marine environment.** MAP Technical Reports Series No. 28. UNEP, Athens, 1989 (225 pgs.) (English).

MTS 29. UNEP: **Bibliography on effects of climatic change and related topics.** MAP Technical Reports Series No. 29. UNEP, Athens, 1989 (143 pgs.) (English).

MTS 30. UNEP: **Meteorological and climatological data from surface and upper measurements for the assessment of atmospheric transport and deposition of pollutants in the Mediterranean Basin: A review.** MAP Technical Reports Series No. 30. UNEP, Athens, 1989 (137 pgs.) (English).

MTS 31. 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 (247 pgs.) (parts in English or French only). 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 (247 pgs.) (parties en anglais ou français seulement).

MTS 32. UNEP/FAO: **Biogeochemical cycles of specific pollutants (Activity K).** MAP Technical Reports Series No. 32. UNEP, Athens, 1989 (139 pgs.) (parts in English or French only). PNUE/FAO: **Cycles biogéochimiques de polluants spécifiques (Activité K).** MAP Technical Reports Series No. 32. UNEP, Athens, 1989 (139 pgs.) (parties en anglais ou français seulement).

MTS 33. UNEP/FAO/WHO/IAEA: **Assessment of organotin compounds as marine pollutants in the Mediterranean.** MAP Technical Reports Series No. 33. UNEP, Athens, 1989 (185 pgs.) (English and French). PNUE/FAO/OMS/AIEA: **Evaluation des composés organostanniques en tant que polluants du milieu marin en Méditerranée.** MAP Technical Reports Series No. 33. UNEP, Athens, 1989 (185 pgs.).

MTS 34. UNEP/FAO/WHO: **Assessment of the state of pollution of the Mediterranean Sea by cadmium and cadmium compounds.** MAP Technical Reports Series No. 34. UNEP, Athens, 1989 (175 pgs.) (English and French). PNUE/FAO/OMS: **Evaluation de l'état de la pollution de la mer Méditerranée par le cadmium et les composés de cadmium.** MAP Technical Reports Seri es No. 34. UNEP, Athens, 1989 (175 pgs.).

MTS 35. UNEP: **Bibliography on marine pollution by organotin compounds.** MAP Technical Reports Series No. 35. UNEP, Athens, 1989 (92 pgs.) (English).

MTS 36. PNUE/UICN: **Répertoire des aires marines et côtières protégées de la Méditerranée. Première partie- Sites d'importance biologique et écologique.** MAP Technical Reports Series No. 36. UNEP, Athens, 1990 (198 pgs.) (français seulement).

MTS 37. UNEP/FAO: **Final reports on research projects dealing with eutrophication and plankton blooms (Activity H).** MAP Technical Reports Series No. 37. UNEP, Athens, 1990 (74 pgs.) (parts in English or French only). PNUE/FAO: **Rapports finaux sur les projets de recherché consacrés à l'eutrophisation et aux efflorescences de plancton (Activité H).** MAP Technical Reports Series No. 37. UNEP, Athens, 1990 (74 pgs.) (parties en anglais ou français seulement).

MTS 38. UNEP: **Common measures adopted by the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against pollution.** MAP Technical Reports Series No. 38. UNEP, Athens, 1990 (100 pgs.) (English, French, Spanish and Arabic). PNUE: **Mesures communes adoptées par les Parties Contractantes à la Convention pour la protection de la mer Méditerranée contre la pollution.** MAP Technical Reports Series No. 38. UNEP, Athens, 1990 (100 pgs.). PNUE: **Medidas comunes adoptadas por las Partes Contratantes en el convenio para la Proteccion del Mar Mediterraneo contra la Contaminacion.** MAP Technical Reports Series No. 38, UNEP, Athens, 1990 (100 pgs.).

MTS 39. UNEP/FAO/WHO/IAEA: **Assessment of the state of pollution of the Mediterranean Sea by organohalogen compounds.** MAP Technical Reports Series No. 39. UNEP, Athens, 1990 (224 pgs.) (English and French). PNUE/FAO/OMS/AIEA: **Evaluation de l'état de la pollution par les composés organohalogénés.** MAP Technical Reports Series No. 39. UNEP, Athens, 1990 (224 pgs.).

MTS 40. UNEP/FAO: **Final reports on research projects (Activities H, I and J).** MAP Technical Reports Series No. 40. UNEP, Athens, 1990 (125 pgs.) (English and French). PNUE/FAO: **Rapports finaux sur les projets de recherche (Activités H, I et J).** MAP Technical Reports Series No. 40. UNEP, Athens, 1990 (125 pgs.).

MTS 41. UNEP: **Wastewater reuse for irrigation in the Mediterranean region.** MAP Technical Reports Series No. 41. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1990 (330 pgs.) (English and French). PNUE: **Réutilisation agricole des eaux usées dans la région méditerranéenne.** MAP Technical Reports Series No. 41. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1990 (330 pgs).

MTS 42. UNEP/IUCN: **Report on the status of Mediterranean marine turtles.** MAP Technical Reports Series No. 42. UNEP, Athens, 1990 (204 pgs.) (English and French). PNUE/UICN: **Rapport sur le statut des tortues marines de Méditerranée.** MAP Technical Reports Series No. 42. UNEP, Athens, 1990 (204 pgs.).

MTS 43. PNUE/UICN/GIS **Posidonie: Livre rouge "Gérard Vuignier" des végétaux, peuplements et paysages marins menacés de Méditerranée.** MAP Technical Reports Series No. 43. UNEP, Athens, 1990 (250 pgs.) (français seulement).

MTS 44. UNEP: **Bibliography on aquatic pollution by organophosphorus compounds.** MAP Technical Reports Series No. 44. UNEP, Athens, 1990 (98 pgs.) (English).

MTS 45. UNEP/IAEA: **Transport of pollutants by sedimentation: Collected papers from the first Mediterranean Workshop (Villefranche-sur-Mer, France, 10-12 December 1987).** MAP Technical Reports Series No. 45. UNEP, Athens, 1990 (302 pgs.) (English).

MTS 46. UNEP/WHO: **Epidemiological studies related to environmental quality criteria for bathing waters, shellfish-growing waters and edible marine organisms (Activity D). Final report on project on relationship between microbial quality of coastal seawater and rotarus-induced gastro-enteritis among bathers (1986-88).** MAP Technical Reports Series No.46. UNEP, Athens, 1991 (64 pgs.) (English).

MTS 47. UNEP: **Jellyfish blooms in the Mediterranean. Proceedings of the II workshop on jellyfish in the Mediterranean Sea.** MAP Technical Reports Series No.47. UNEP, Athens, 1991 (320 pgs.) (parts in English or French only). PNUE: **Les proliferation's de medusas en Méditerannée. Actes des IIèmes journées d'étude sur les méduses en mer Méditerranée.** MAP Technical Reports Series No.47. UNEP, Athens, 1991 (320 pgs.) (parties en anglais ou français seulement).

MTS 48. UNEP/FAO: **Final reports on research projects (Activity G).** MAP Technical Reports Series No. 48. UNEP, Athens, 1991 (126 pgs.) (parts in English or French only). PNUE/FAO: **Rapports finaux sur les projets de recherche (Activité G).** MAP Technical Reports Series No. 48. UNEP, Athens, 1991 (126 pgs.) (parties en anglais ou français seulement).

MTS 49. UNEP/WHO: **Biogeochemical cycles of specific pollutants. Survival of pathogens. Final reports on research projects (Activity K).** MAP Technical Reports Series No. 49. UNEP, Athens, 1991 (71 pgs.) (parts in English or French only). PNUE/OMS: **Cycles biogéochimiques de polluants spécifiques. Survie des Pathogènes. Rapports finaux sur les projets de recherche (activité K).** MAP Technical Reports Series No. 49. UNEP, Athens, 1991 (71 pgs.) (parties en anglais ou français seulement).

MTS 50. UNEP: **Bibliography on marine litter.** MAP Technical Reports Series No. 50. UNEP, Athens, 1991 (62 pgs.) (English).

MTS 51. UNEP/FAO: **Final reports on research projects dealing with mercury, toxicity and analytical techniques.** MAP Technical Reports Series No. 51. UNEP, Athens, 1991 (166 pgs.) (parts in English or French only). PNUE/FAO: **Rapports finaux sur les projets de recherche traitant du mercure, de la toxicité et des techniques analytiques.** MAP Technical Reports Series No. 51. UNEP, Athens, 1991 (166 pgs.) (parties en anglais ou français seulement).

MTS 52. UNEP/FAO: **Final reports on research projects dealing with bioaccumulation and toxicity of chemical pollutants.** MAP Technical Reports Series No. 52. UNEP, Athens, 1991 (86 pgs.) (parts in English or French only). PNUE/FAO: **Rapports finaux sur les projets de recherche traitant de la bioaccumulation et de la toxicité des polluants chimiques.** MAP Technical Reports Series No. 52. UNEP, Athens, 1991 (86 pgs.) (parties en anglais ou français seulement).

MTS 53. UNEP/WHO: **Epidemiological studies related to environmental quality criteria for bathing waters, shellfish-growing waters and edible marine organisms (Activity D). Final report on epidemiological study on bathers from selected beaches in Malaga, Spain (1988-1989).** MAP Technical Reports Series No. 53. UNEP, Athens, 1991 (127 pgs.) (English).

MTS 54. UNEP/WHO: **Development and testing of sampling and analytical techniques for monitoring of marine pollutants (Activity A): Final reports on selected microbiological projects.** MAP Technical Reports Series No. 54. UNEP, Athens, 1991 (83 pgs.) (English).

MTS 55. UNEP/WHO: **Biogeochemical cycles of specific pollutants (Activity K): Final report on project on survival of pathogenic organisms in seawater.** MAP Technical Reports Series No. 55. UNEP, Athens, 1991 (95 pgs.) (English).

MTS 56. UNEP/IOC/FAO: **Assessment of the state of pollution of the Mediterranean Sea by persistent synthetic materials which may float, sink or remain in suspension.** MAP Technical Reports Series No. 56. UNEP, Athens, 1991 (113 pgs.) (English and French). PNUE/COI/FAO: **Evaluation de l'état de la pollution de la mer Méditerranée par les matières synthétiques persistantes qui peuvent flotter, couler ou rester en suspension.** MAP Technical Reports Series No. 56. UNEP, Athens, 1991 (113 pgs).

MTS 57. UNEP/WHO: **Research on the toxicity, persistence, bioaccumulation, carcinogenicity and mutagenicity of selected substances (Activity G): Final reports on projects dealing with carcinogenicity and mutagenicity.** MAP Technical Reports Series No. 57. UNEP, Athens, 1991 (59 pgs.) (English).

MTS 58. UNEP/FAO/WHO/IAEA: **Assessment of the state of pollution of the Mediterranean Sea by organophosphorus compounds.** MAP Technical Reports Series No. 58. UNEP, Athens, 1991 (122 pgs.) (English and French). PNUE/FAO/OMS/AIEA: **Evaluation de l'état de la pollution de la mer Méditerranée par les composés organophosphorés.** MAP Technical Reports Series No. 58. UNEP, Athens, 1991 (122 pgs.).

MTS 59. UNEP/FAO/IAEA: **Proceedings of the FAO/UNEP/IAEA Consultation Meeting on the Accumulation and Transformation of Chemical contaminants by Biotic and Abiotic Processes in the Marine Environment (La Spezia, Italy, 24-28 September 1990), edited by G.P. Gabrielides.** MAP Technical Reports Series No. 59. UNEP, Athens, 1991 (392 pgs.) (English).

MTS 60. UNEP/WHO: **Development and testing of sampling and analytical techniques for monitoring of marine pollutants (Activity A): Final reports on selected microbiological projects (1987-1990).** MAP Technical Reports Series No. 60. UNEP, Athens, 1991 (76 pgs.) (parts in English or French only). PNUE/OMS: **Mise au point et essai des techniques d'échantillonnage et d'analyse pour la surveillance continue des polluants marins (Activité A): Rapports finaux sur certains projets de nature microbiologique (1987-1990).** MAP Technical Reports Series No. 60. UNEP, Athens, 1991 (76 pgs.) (parties en anglais ou français seulement).

MTS 61. UNEP: **Integrated Planning and Management of the Mediterranean Coastal Zones. Documents produced in the first and second stage of the Priority Action (1985-1986).** MAP Technical Reports Series No. 61. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1991 (437 pgs.) (parts in English or French only). PNUE: **Planification intégrée et gestion des zones côtières méditerranéennes. Textes rédigés au cours de la première et de la deuxième phase de l'action prioritaire (1985-1986).** MAP Technical Reports Series No. 61. UNEP, Priority Actions Programme, Regional Activity Centre, Split, 1991 (437 pgs.) (parties en anglais ou français seulement).

MTS 62. UNEP/IAEA: **Assessment of the State of Pollution of the Mediterranean Sea by Radioactive Substances.** MAP Technical Reports Series No. 62, UNEP, Athens, 1992 (133 pgs.) (English and French). PNUE/AIEA: **Evaluation de l'état de la pollution de la mer Méditerranée par les substances radioactives.** MAP Technical Reports Series No. 62, UNEP, Athens, 1992 (133 pgs.).

MTS 63. PNUE/OMS: **Cycles biogéochimiques de polluants spécifiques (Activité K) - Survie des pathogènes - Rapports finaux sur les projets de recherche (1989-1991).** MAP Technical Reports Series No. 63. UNEP, Athens, 1992 (86 pgs.) (français seulement).

MTS 64. UNEP/WMO: **Airborne Pollution of the Mediterranean Sea. Report and Proceedings of the Second WMO/UNEP Workshop.** MAP Technical Reports Series No. 64. UNEP, Athens, 1992 (246 pgs.) (English).

MTS 65. UNEP: **Directory of Mediterranean Marine Environmental Centres.** MAP Technical Reports Series No. 65, UNEP, Athens, 1992 (351 pgs.) (English and French). PNUE: **Répertoire des centres relatifs au milieu marin en Méditerranée.** MAP Technical Reports Series No. 65. UNEP, Athens, 1992 (351 pgs.).

MTS 66. UNEP/CRU: **Regional Changes in Climate in the Mediterranean Basin Due to Global Greenhouse Gas Warming.** MAP Technical Reports Series No. 66. UNEP, Athens, 1992 (172 pgs.) (English).

MTS 67. UNEP/IOC: **Applicability of Remote Sensing for Survey of Water Quality Parameters in the Mediterranean. Final Report of the Research Project.** MAP Technical Reports Series No. 67. UNEP, Athens, 1992 (142 pgs.) (English).

MTS 68. UNEP/FAO/IOC: **Evaluation of the Training Workshops on the Statistical Treatment and Interpretation of Marine Community Data.** MAP Technical Reports Series No. 68. UNEP, Athens, 1992 (221 pgs.) (English).

MTS 69. UNEP/FAO/IOC: **Proceedings of the FAO/UNEP/IOC Workshop on the Biological Effects of Pollutants on Marine Organisms (Malta, 10-14 September 1991), edited by G.P. Gabrielides.** MAP Technical Reports Series No. 69. UNEP, Athens, 1992 (287 pgs.) (English).

MTS 70. UNEP/IAEA/IOC/FAO: **Organohalogen Compounds in the Marine Environment: A Review.** MAP Technical Reports Series No. 70. UNEP, Athens, 1992 (49 pgs.) (English).

MTS 71. UNEP/FAO/IOC: **Selected techniques for monitoring biological effects of pollutants in marine organisms.** MAP Technical Reports Series No. 71. UNEP, Athens, 1993 (189 pgs.) (English).

MTS 72. UNEP: **Costs and Benefits of Measures for the Reduction of Degradation of the Environment from Land-based Sources of Pollution in Coastal Areas. A - Case Study of the Bay of Izmir. B - Case Study of the Island of Rhodes.** MAP Technical Reports Series No. 72. UNEP, Athens, 1993 (64 pgs.) (English).

MTS 73. UNEP/FAO: **Final Reports on Research Projects Dealing with the Effects of Pollutants on Marine Communities and Organisms.** MAP Technical Reports Series No. 73. UNEP, Athens, 1993 (186 pgs.) (English and French). PNUE/FAO: **Rapports finaux sur les projets de recherche traitant des effets de polluants sur les communautés et les organismes marins.** MAP Technical Reports Series No. 73. UNEP, Athens, 1993 (186 pgs.).

MTS 74. UNEP/FIS: **Report of the Training Workshop on Aspects of Marine Documentation in the Mediterranean.** MAP Technical Reports Series No. 74. UNEP, Athens, 1993 (38 pgs.) (English).

MTS 75. UNEP/WHO: **Development and Testing of Sampling and Analytical Techniques for Monitoring of Marine Pollutants (Activity A).** MAP Technical Reports Series No. 75. UNEP, Athens, 1993 (90 pgs.) (English).

MTS 76. UNEP/WHO: **Biogeochemical Cycles of Specific Pollutants (Activity K): Survival of Pathogens.** MAP Technical Reports Series No. 76. UNEP, Athens, 1993 (68 pgs.) (English and French). PNUE/OMS: **Cycles biogéochimiques de polluants spécifiques (Activité K): Survie des pathogènes.** MAP Technical Reports Series No. 76. UNEP, Athens, 1993 (68 pgs.).

MTS 77. UNEP/FAO/IAEA: **Designing of monitoring programmes and management of data concerning chemical contaminants in marine organisms.** MAP Technical Reports Series No. 77. UNEP, Athens, 1993 (236 pgs.) (English).

MTS 78. UNEP/FAO: **Final reports on research projects dealing with eutrophication problems.** MAP Technical Reports Series No. 78. UNEP, Athens, 1994 (139 pgs.) (English).

MTS 79. UNEP/FAO: **Final reports on research projects dealing with toxicity of pollutants on marine organisms.** MAP Technical Reports Series No. 79. UNEP, Athens, 1994 (135 pgs.) (parts in English or French only). PNUE/FAO: **Rapports finaux sur les projets de recherche traitant de la toxicité des polluants sur les organismes marins.** MAP Technical Reports Series No. 79. UNEP, Athens, 1994 (135 pgs.) (parties en anglais ou français seulement).

MTS 80. UNEP/FAO: **Final reports on research projects dealing with the effects of pollutants on marine organisms and communities.** MAP Technical Reports Series No. 80. UNEP, Athens, 1994 (123 pgs.) (English).

MTS 81. UNEP/IAEA: **Data quality review for MED POL: Nineteen years of progress.** MAP Technical Reports Series No. 81. UNEP, Athens, 1994 (79 pgs.) (English).

MTS 82. UNEP/IUCN: **Technical report on the State of Cetaceans in the Mediterranean.** MAP Technical Reports Series No. 82. UNEP, Regional Activity Centre for Specially Protected Areas, Tunis, 1994 (37 pgs.) (English).

MTS 83. PNUE/UICN: **Les aires protégées en Méditerranée. Essai d'étude analytique de la législation pertinente.** MAP Technical Reports Series No. 83. PNUE, Centre d'activités régionales pour les aires spécialement protégées, Tunis, 1994 (55 pgs) (français seulement).

MTS 84. UNEP: **Integrated Management Study for the Area of Izmir.** MAP Technical Reports Series No. 84. UNEP, Regional Activity Centre for Priority Actions Programme, Split, 1994 (130 pgs.) (English).

MTS 85. UNEP/WMO: **Assessment of Airborne Pollution of the Mediterranean Sea by Sulphur and Nitrogen Compounds and Heavy Metals in 1991.** MAP Technical Report Series No. 85. Athens, 1994 (304 pgs.) (English).

MTS 86. UNEP: **Monitoring Programme of the Eastern Adriatic Coastal Area - Report for 1983-1991.** MAP Technical Report Series No. 86. Athens, 1994 (311 pgs.) (English).

MTS 87. UNEP/WHO: **Identification of microbiological components and measurement development and testing of methodologies of specified contaminants (Area I) - Final reports on selected microbiological projects.** MAP Technical Reports Series No. 87. UNEP, Athens, 1994 (136 pgs.) (English).

MTS 88. UNEP: **Proceedings of the Seminar on Mediterranean Prospective.** MAP Technical Reports Series No. 88. UNEP, Blue Plan Regional Activity Centre, Sophia Antipolis, 1994 (176 pgs.) (parts in English or French only). PNUE: **Actes du Séminaire débat sur la prospective méditerranéenne.** MAP Technical Reports Series No. 88. UNEP, Blue Plan Regional Activity Centre, Sophia Antipolis, 1994 (176 pgs.) (parties en anglais ou français seulement).

MTS 89. UNEP: **Iskenderun Bay Project. Volume I. Environmental Management within the Context of Environment-Development.** MAP Technical Reports Series No. 89. UNEP, Blue Plan Regional Activity Centre, Sophia Antipolis, 1994 (144 pgs.) (English).

MTS 90. UNEP: **Iskenderun Bay Project. Volume II. Systemic and Prospective Analysis.** MAP Technical Report Series No. 90. Sophia Antipolis, 1994 (142 pgs.) (parts in English or French only). PNUE: **Projet de la Baie d'Iskenderun. Volume II. Analyse systémique et prospective.** MAP Technical Reports Series No. 90. UNEP, Sophia Antipolis, 1994 (142 pgs.) (parties en anglais ou français seulement).

MTS 91. PNUE: **Une contribution de l'écologie à la prospective. Problèmes et acquis.** MAP Technical Reports Series No. 91. Sophia Antipolis, 1994 (162 pgs.) (français seulement).

MTS 92. UNEP/WHO: **Assessment of the State of Pollution in the Mediterranean Sea by Carcinogenic, Mutagenic and Teratogenic Substances.** MAP Technical Reports Series No. 92. UNEP, Athens, 1995 (238 pgs.) (English).

MTS 93. UNEP/WHO: **Epidemiological studies related to the environmental quality criteria for bathing waters, shellfish-growing waters and edible marine organisms.** MAP Technical Reports Series No. 93. UNEP, Athens, 1995 (118 pgs.) (English).

MTS 94. UNEP: **Proceedings of the Workshop on Application of Integrated Approach to Development, Management and Use of Water Resources.** MAP Technical Reports Series No. 94. UNEP, Athens, 1995 (214 pgs.) (parts in English or French only). PNUE: **Actes de l'Atelier sur l'application d'une approche intégrée au développement, à la gestion et à l'utilisation des ressources en eau.** MAP Technical Reports Series No. 94. UNEP, Athens, 1995 (214 pgs.) (parties en anglais ou français seulement).

MTS 95. UNEP: **Common measures for the control of pollution adopted by the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution.** MAP Technical Reports Series No 95. UNEP, Athens, 1995 (69 pgs.) (English and French). PNUE: **Mesures communes de lutte contre la pollution adoptées par les Parties contractantes à la Convention pour la protection de la mer Méditerranée contre la pollution.** MAP Technical Reports Series No. 95. UNEP, Athens, 1995 (69 pgs.).

MTS 96. UNEP/FAO: **Final reports of research projects on effects (Research Area III) - Pollution effects on plankton composition and spatial distribution, near the sewage outfall of Athens (Saronikos Gulf, Greece).** MAP Technical Reports Series No. 96. UNEP, Athens, 1996 (121 pgs.) (English).

MTS 97. UNEP/FAO: **Final reports of research projects on effects (Research Area III) - Pollution effects on marine communities.** MAP Technical Reports Series No. 97. UNEP, Athens, 1996 (141 pgs .) (English and French). PNUE/FAO: **Rapports finaux des projets de recherche sur les effets (Domaine de recherche III) -Effets de la pollution sur les communautés marines.** MAP Technical Reports Series No. 97. UNEP, Athens, 1996 (141 pgs.).

MTS 98. UNEP: **Implications of Climate Change for the Albanian Coast.** MAP Technical Reports Series No. 98. UNEP, Athens, 1996 (179 pgs.) (English).

MTS 99. UNEP: **Implications of Climate Change for the Sfax Coastal Area (Tunisia).** MAP Technical Reports Series No. 99. UNEP, Athens, 1996 (326 pgs.) (English and French). PNUE: **Implications des changements climatiques sur la zone côtière de Sfax.** MAP Technical Reports Series No. 99. UNEP, Athens, 1996 (326 pgs.).

MTS 100. UNEP: **State of the Marine and Coastal Environment in the Mediterranean Region.** MAP Technical Reports Series No. 100. UNEP, Athens, 1996 (142 pgs.) (English).

MTS 101. PNUE: **Etat du milieu marin et du littoral de la région méditerranéenne.** MAP Technical Reports Series No. 101. UNEP, Athens, 1996 (148 pgs.) (français seulement).

MTS 102. UNEP: **Implications of Climate Change for the Coastal Area of Fuka-Matrouh (Egypt).** MAP Technical Reports Series No. 102. UNEP, Athens, 1996 (238 pgs.) (English).

MTS 103. UNEP/FAO: **Final reports on research projects dealing with biological effects (Research Area III).** MAP Technical Reports Series No. 103. UNEP, Athens, 1996 (128 pgs.) (English and French). PNUE/FAO: **Rapports finaux sur les projets de recherche relatifs aux effets biologiques (Domaine de Recherche III).** MAP Technical Reports Series No. 103. UNEP, Athens, 1996 (128 pgs.).

MTS 104. UNEP/FAO: **Final reports on research projects dealing with eutrophication and heavy metal accumulation.** MAP Technical Reports Series No. 104. UNEP, Athens, 1996 (156 pgs.) (English and French). PNUE/FAO: **Rapports finaux sur les projets de recherche relatifs à l'eutrophisation et à l'accumulation des métaux lourds.** MAP Technical Reports Series No. 104. UNEP, Athens, 1996 (156 pgs.).

MTS 105. UNEP/FAO/WHO: **Assessment of the state of pollution of the Mediterranean sea by zinc, copper and their compounds.** MAP Technical Reports Series No. 105. UNEP, Athens, 1996 (288 pgs.) (English and French). PNUE/FAO/OMS: **Evaluation de l'état de la pollution de la mer Méditerranée par le zinc, le cuivre et leurs composés.** MAP Technical Reports Series No. 105. UNEP, Athens, 1996 (288 pgs.).

MTS 106. UNEP/FAO/WHO: **Assessment of the state of eutrophication in the Mediterranean sea.** MAP Technical Reports Series No. 106. UNEP, Athens, 1996 (456 pgs.) (English and French). PNUE/FAO/OMS: **Evaluation de l'état de l'eutrophisation en mer Méditerranée.** MAP Technical Reports Series No. 106. UNEP, Athens, 1996 (456 pgs.).

MTS 107. UNEP/WHO: **Guidelines for authorization for the discharge of liquid wastes into the Mediterranean Sea.** MAP Technical Reports Series No. 107. UNEP, Athens, 1996 (200 pgs.) (English and French). PNUE/OMS: **Lignes directrices concernant les autorisations de rejet de déchets liquides en mer Méditerranée.** MAP Technical Reports Series No. 107. UNEP, Athens, 1996 (200 pgs.).

MTS 108. UNEP/WHO: **Assessment of the state of microbiological pollution of the Mediterranean Sea.** MAP Technical Reports Series No. 108. UNEP, Athens, 1996 (270 pgs.) (English and French). PNUE/OMS: **Evaluation de l'état de la pollution microbiologique de la mer Méditerranée.** MAP Technical Reports Series No. 108. UNEP, Athens, 1996 (270 pgs.).

MTS 109. UNEP/WHO: **Survey of pollutants from land-based sources in the Mediterranean.** MAP Technical Reports Series No. 109. UNEP, Athens, 1996 (188 pgs.) (English and French). PNUE/OMS: **Evaluation de l'enquête sur les polluants d'origine tellurique en Méditerranée (MED X BIS).** MAP Technical Reports Series No. 109. UNEP, Athens, 1996 (188 pgs.).

MTS 110. UNEP/WHO: **Assessment of the state of pollution of the Mediterranean Sea by anionic detergents.** MAP Technical Reports Series No. 110. UNEP, Athens, 1996 (260 pgs.) (English and French). PNUE/OMS: **Evaluation de l'état de la pollution de la mer Méditerranée par les détergents anioniques.** MAP Technical Reports Series No. 110. UNEP, Athens, 1996 (260 pgs.).

MTS 111. UNEP/WHO: **Guidelines for treatment of effluents prior to discharge into the Mediterranean Sea.** MAP Technical Reports Series No. 111. UNEP, Athens, 1996 (247 pgs.) (English).

MTS 112. UNEP/WHO: **Guidelines for submarine outfall structures for Mediterranean small and medium-sized coastal communities.** MAP Technical Reports Series No. 112. UNEP, Athens, 1996 (98 pgs.) (English and French). PNUE/OMS: **Lignes directrices pour les émissaires de collectivités côtières de petite et moyenne taille en Méditerranée.** MAP Technical Reports Series No. 112. UNEP, Athens, 1996 (98 pgs.).

MTS 113. UNEP/IOC: **Final reports of research projects on transport and dispersion (Research Area II) - Modelling of eutrophication and algal blooms in the Thermaikos Gulf (Greece) and along the Emilia Romagna Coast (Italy).** MAP Technical Reports Series No. 113. UNEP, Athens, 1996 (118 pgs.) (English).

MTS 114. UNEP: **Workshop on policies for sustainable development of Mediterranean coastal areas, Santorini island, 26-27 April 1996. Presentation by a group of experts.** MAP Technical Reports Series No. 114. UNEP, Athens, 1996 (184 pgs.) (Parts in English or French only). PNUE: **Journées d'étude sur les politiques de développement durable des zones côtières méditerranéennes, Ile de Santorin, 26-27 avril 1996. Communications par un groupe d'experts.** MAP Technical Reports Series No. 114. UNEP, Athens, 1996 (184 pgs.) (Parties en anglais ou français seulement).

MTS 115. UNEP/BP **Methodes et outils pour les etudes systemiques et prospectives en Méditerranée, PB/RAC, Sophia Antipolis, 1996.** MAP Technical Reports Series No. 115. UNEP/BP, Athens, 1996 (117 pgs.) (français seulement).

MTS 116. UNEP/IAEA: **Data Quality Review for MED POL (1994-1995), Evaluation of the analytical performance of MED POL laboratories during 1994-1995 in IAEA/UNEP laboratory performance studies for the determination of trace elements and trace organic contaminants in marine biological and sediment samples.** MAP Technical Reports Series No. 116. UNEP, Athens, 1997 (126 pgs.) (English).

MTS 117. UNEP: **La Convention de Barcelone pour la protection de la mer Méditerranée contre la pollution et le développement durable.** MAP Technical Reports Series No. 117. UNEP, Athens, 1997 (97 pgs.) (Français seulement).

MTS 118. UNEP/WMO: **The Input of Anthropogenic Airborne Nitrogen to the Mediterranean Sea through its Watershed.** MAP Technical Reports Series No. 118. UNEP, Athens, 1997 (95 pgs.) (English).

MTS 119. UNEP: **Strategic Action Programme to Address Pollution from Land-Based Activities.** MAP Technical Reports Series No. 119. UNEP, Athens, 1998, (178 pgs) (English and French) PNUE: **Programme d'Actions Stratégiques visant à combattre la pollution due à des activités menées à terre.** MAP Technical Reports Series No. 119. PNUE Athens 1998, (178 pgs) (Francais et anglais)

MTS 120. UNEP: **MED POL Phase III. Programme for the Assessment and Control of Pollution in the Mediterranean Region (1996-2005).** MAP Technical Reports Series No. 120. UNEP, Athens, 1998, (120 pgs).

MTS 121. PNUE: **MED POL Phase III. Programme d'évaluation et de maîtrise de la pollution dans la région Méditerranéenne (1996-2005).** MAP Technical Reports Series No. 121. Athens 1998, (123 pgs).
(In publication)

MTS 122. UNEP/WMO: **Atmospheric Input of Mercury to the Mediterranean Sea.** MAP Technical Reports Series No. 122. Athens, 1998, (78 pages).

MTS 123. UNEP/WMO: **MED POL Manual on Sampling and Analysis of Aerosols and Precipitation for Major Ions and Trace Elements.** MAP Technical Reports Series No. 123. UNEP, Athens, 1998, (166 pgs.).

MTS 124. UNEP/WHO: **Identification of Priority Hot Spots and Sensitive Areas in the Mediterranean.** MAP Technical Reports Series No. 124. UNEP, Athens, 1999. (102 pgs.). PNUE/OMS: **Identification des "Points Chauds" et "Zones Sensibles" de polution prioritaire en Méditerranée.** MAP Technical Reports Series No. 124. UNEP, Athens, 1999 (102 pgs.).

MTS 125. UNEP: **Proceedings of the Workshop on Invasive *Caulerpa* Species in the Mediterranean,** Heraklion, Crete, Greece, 18-20 March 1998. MAP Technical Reports Series No. 125, UNEP, Athens 1999. (317 pgs). (English and French). PNUE: **Actes de l'atelier sur les especes *Caulerpa* invasives en Méditerranée,** Heraklion, Crète, Grèce, 18-20 mars 1998. No. 125 de la série des rapports techniques du PAM, PNUE, Athènes, 1999. (317 pgs). (Anglais et francais).

MTS 126. UNEP/MCSD/Blue Plan: **Report of the Workshop on Tourism and Sustainable Development in the Mediterranean,** Antalya, Turkey, 17-19 September 1998. MAP Technical Reports Series No. 126, UNEP, Athens 1999. (English and French). PNUE/CMDD/Plan Bleu: **Rapport de l'atelier sur le tourisme et le développement durable en Méditerranée**, Antalya, Turquie, 17-19 septembre 1998. No. 126 de la série des rapports techniques du PAM, PNUE, Athènes, 1999. (Anglais et francais).

MTS 127. UNEP: **Minutes of the Seminar, Territorial Prospective in the Mediterranean and the Approach by Actors,** Sophia Antipolis, France, 7-9 November 1996. MTS No. 127, UNEP, Athens 2000. (French only). PNUE: **Actes du séminaire, La prospective territoriale en Méditerranée et l'approche par acteurs,** Sophia Antipolis, 7-9 novembre 1996. No. 127 de la série des rapports techniques du PAM, PNUE, Athènes, 2000. (In French with English introduction and 1 paper).

MTS 128. UNEP/MED POL/WHO: **Municipal Wastewater Treatment Plants in Mediterranean Coastal Cities.** MTS no. 128, UNEP, Athens 2000 (English and French).
PNUE/MED POL/OMS**: Les Stations d'épuration des eaux usées municipales dans les villes cotières de la Méditerranée.** No. 128 de la série des rapports techniques du PAM, PNUE, Athènes, 2000. (Anglais et français).

MTS 129. UNEP/MED POL: **Guidelines for the Management of Dredged Material.** MAP Technical Reports Series No. 129, UNEP, Athens 2000. (English, French, Spanish and Arabic).
PNUE/MED POL: **Lignes Directrices pour la gestion des matériaux de dragage.** No. 129 de la série des rapports techniques du PAM, PNUE, Athènes 2000. (161 pgs.). (Anglais, français, espagnol et arabe).

MTS 130. UNEP/MAP/WMO: **Atmospheric Input of Persistent Organic Pollutants to the Mediterranean Sea.** MAP Technical Reports Series No. 130, UNEP/MAP, Athens, 2001. (English).

MTS 131. UNEP/MAP: **MAP CAMP Project "Fuka-Matrouh", Egypt: Final Integrated Report and Selected Documents**. MAP Technical Reports Series No. 131, (2 Vols.), UNEP/MAP, Athens, 2001. (English).

MTS 132. UNEP/MAP/WHO: **Remedial Actions for Pollution Mitigation and Rehabilitation in Cases of Non-compliance with Established Criteria.** MAP Technical Reports Series No. 132, UNEP/MAP, Athens 2001. (English).