Regional Climate Variability and its Impacts in the Mediterranean Area

Edited by

A. Mellouki and
A.R. Ravishankara

NATO Science Series

CD-ROM INCLUDED

IV. Earth and Environmental Sciences – Vol. 79

REGIONAL CLIMATE VARIABILITY AND ITS IMPACTS IN THE MEDITERRANEAN AREA

NATO Science Series

A Series presenting the results of scientific meetings supported under the NATO Science Programme.

The Series is published by IOS Press, Amsterdam, and Springer (formerly Kluwer Academic Publishers) in conjunction with the NATO Public Diplomacy Division.

Sub-Series

I. Life and Behavioural Sciences	IOS Press
II. Mathematics, Physics and Chemistry	Springer (formerly Kluwer Academic Publishers)
III. Computer and Systems Science	IOS Press
IV. Earth and Environmental Sciences	Springer (formerly Kluwer Academic Publishers)

The NATO Science Series continues the series of books published formerly as the NATO ASI Series.

The NATO Science Programme offers support for collaboration in civil science between scientists of countries of the Euro-Atlantic Partnership Council. The types of scientific meeting generally supported are “Advanced Study Institutes” and “Advanced Research Workshops”, and the NATO Science Series collects together the results of these meetings. The meetings are co-organized by scientists from NATO countries and scientists from NATO’s Partner countries – countries of the CIS and Central and Eastern Europe.

Advanced Study Institutes are high-level tutorial courses offering in-depth study of latest advances in a field.
Advanced Research Workshops are expert meetings aimed at critical assessment of a field, and identification of directions for future action.

As a consequence of the restructuring of the NATO Science Programme in 1999, the NATO Science Series was re-organized to the Four Sub-series noted above. Please consult the following web sites for information on previous volumes published in the Series.

http://www.nato.int/science
http://www.springeronline.com
http://www.iospress.nl

Series IV: Earth and Environmental Sciences – Vol. 79

REGIONAL CLIMATE VARIABILITY AND ITS IMPACTS IN THE MEDITERRANEAN AREA

edited by

A. Mellouki

ICARE, CNRS,
Orléans, France

and

A.R. Ravishankara

NOAA, R/CSD,
Boulder, CO, U.S.A.

Springer

Published in cooperation with NATO Public Diplomacy Division

Proceedings of the NATO Advanced Research Workshop on
Regional Climate Variability and its Impacts
in the Mediterranean Area
Marrakech, Morocco
1 September 2006

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-1-4020-6428-9 (PB)
ISBN 978-1-4020-6427-2 (HB)
ISBN 978-1-4020-6429-6 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

CONTENTS

CD-ROM with colour figures included.

PREFACE

A. Mellouki, A. R. Ravishankara, M. Kanakidou, K-H. Becker, L. Elmaimouni and A. Dakkina

Global change due to natural processes and anthropogenic activity as well as the natural variability of the climate system will impact all areas of the globe. However, the impact will not be uniform and different impacts of differing magnitude and nature will be felt in various regions of the globe. The Mediterranean region, like other regions of the world, will face some unique and different impacts of the climate change and variability on.

The uniqueness and difference in the Mediterranean are to be expected given some special dynamical, chemical, biological, and land characteristics of the region. Mediterranean is a landmass that surrounds a "sea," a body of saline water that does not exchange very rapidly with the rest of the oceans on Earth. It is apparent that the meteorology and chemistry in this region leads to two "distinct," but interlinked regions. In summer, two semi-permanent weather systems located at each end of the Mediterranean dominate the entire basin: at the west, the Azores anticyclone and at the east, a low pressure (monsoon) system, which extends from the middle-east to the whole of southwestern Asia. Between these two major weather systems the average air flow is diverted southward towards North Africa (close to the thermal equator in summer) via the Adriatic and Ionian seas and/or the Black sea, Agean Sea and the Levantine basin (*Millan M. et al., Photoxidant dynamics in the Mediterranean basin in summer: results from European research projects, JGR, 102, 8811-8823,1997; Barry R.G. and Chorley R.J., Atmosphere, Weather & Climate Methuen & Co Ltd, NewYork, ISBN 0-416-07142-2, 1987, pages 262-271*). Recirculation and regional patterns are more important in the west Mediterranean, basin that receives more precipitation with regard to the East basin that is drier and its seawater is more oligotrophic. The Mediterranean region has gradients in emissions of dust, hydrocarbons, and industrial pollutants (such as SO_2, NOx, and aerosols and their precursors). This is region that influenced by transport from such varied landmasses as Europe, Africa, and Asia. The nature and intensities of the emissions from Europe are vastly different from those from Africa, which in itself is diverse given the change in terrain from vegetated regions of Central Africa to deserts of North Africa.

The Mediterranean region is often exposed to multiple stresses, such as a simultaneous water shortage and air pollution. This is a consequence of its unique location and emissions. One of the common stresses in North Africa is water shortage and distribution amongst the seasons. Air pollution can often add to the water stress. Air pollution occurs due to emissions in the region as well as from those transported from other areas and can occur when there is low water availability. Multiple stresses are likely to grow in the future when human induced stress is likely to increase due to the rapid industrialization of the region.

This NATO workshop was set up to discuss these issues in general, and the influence of chemical emissions and transformation in particular. This workshop was "special" because it involved a very large number of scientists (>75%) from the region, either from North Africa or the Mediterranean Europe. This participation greatly enabled infusion of key information about the region from the people who live in the region.

Many key issues, some of which are specific to this region, were identified after presentation and discussions for 3 days. These key findings are very briefly summarized here. Details of the finding and suggestions can be found in the articles in this volume.

Earth system science involves many highly diverse phenomena that are studies as processes in biology, ocean sciences, land surface changes, and atmosphere chemistry and dynamics. These phenomena are represented in models and are usually developed and sharpened by people involved in those disciplines. However, the superposition of these phenomena leads to additional requirements of connecting the processes across the regions, disciplines, and timescales. Often, the important issues involve phenomena occurring at the interface of these areas. Development of the necessary information and simultaneously incorporating the differing areas are essential. Examples include atmospheric chemistry with biological processes and ocean chemistry with emissions and deposition. A strong sentiment was expressed by the participants for a larger emphasis on cross-discipline, interfacial, phenomena. Such a need is not unique to the Mediterranean region, but is essential for a clear understanding and predicting for this region.

Often, information on the details of an individual process is on a time and spatial scale that is very different from those with which it is coupled in the atmosphere. For example, the scale of the processes involved in the emissions of dust to the atmosphere are much shorter in time and smaller in space than the atmospheric transport and transformation of these particles. Therefore, including this information from in global climate and earth system models pose specific difficulties and challenges. Scaling up the information from the short time and space scale studies to global representation is essential and needs to be improved. Similarly, the time scales for some chemical processes can be very different than those for atmospheric processing. The range of such "scaling" of information, either as parameterizations or detailed process representation, is important in understanding various feedbacks in the climate system. As noted above, one of the specific processes of importance to the Mediterranean region is the incorporation of dust into the atmosphere.

The knowledge of the emissions into the atmosphere from various natural and human-induced sources is one of the largest uncertainties in climate studies as well as in the estimation of the impacts on regions and the globe. Inventories of the emissions are good for some sources (e.g., CO_2 from fossil fuel combustion) than for others (e.g., black carbon from biomass burning). The inventories have to include the amount, type, nature, the mix, and the temporal evolution of emissions. Such information is not currently available for most regions of the globe. This is particularly a problem for the Mediterranean region where the type, diversity, and nature of emissions are large and the time evolution of these emissions are different. Good emission inventories, in usable forms, from the Mediterranean region will be of great importance to not only the global representation but also for assessing the contribution of the Mediterranean region and impacts on this region.

Deposition from the atmosphere appears to be a process that is not well understood, quantified, and represented in models. Currently, most depositions are presented in models as very simple parameterizations. Studies aimed at understanding the processes responsible for deposition are needed. When the understanding is sufficient, it will be a good idea to include deposition as a process, rather than a parameterization. An accurate representation of deposition will be essential for quantifying feedbacks, especially in such diverse areas as impact of land cover change and ocean uptake on atmospheric composition and its changes.

It was believed by the participants that the Mediterranean region is under-sampled, much more so than many parts of the globe. The lack observations in the Mediterranean region has led to inaccuracies in calculating emissions, atmospheric composition, and transport in and out of the region. Observations of processes that are unique to this region are needed. Further, it is clear that long-term monitoring of various atmospheric parameters and chemical composition is essential for understanding the contribution of this region to the globe and for assessing the impact of change on the unique Mediterranean region.

Even though there is a lack in observations from the Mediterranean region, compared to other parts of the world, in the current period, there are a relatively large number of historic and pre-existing observations available from this region. A thorough compilation, quality checking, and interpretation of these observations would be highly beneficial to not only the Mediterranean region but also for the global climate studies.

As noted earlier, the above are not all-inclusive, but represent a few of the key issues that were noted in the workshop. For full details, the reader is referred to other articles in this volume.

The workshop was held in Hotel Kenzi-Farah in Marrakech, Morocco, from 23rd to 26th November 2006.

ACKNOWLEDGEMENTS

The NATO Science Committee is very gratefully acknowledged for providing the main financial support for the workshop. Special thanks to the Moroccan Ministry of Environment for practical information as well as financial support. Additional financial support was received from CNRS-Orléans (France), University of Agadir (Morocco) and Eurochamp Project (EU) for which they are acknowledged.

The organising committee would like to thank V. Daële, J. Pagé, R. Herbin, A. Chehbouni and A. Melouki for their help.

Financial support of the workshop was by the following organizations:

- NATO Scientific and Environmental Affairs Division, Brussels
- Centre National de la Recherche Scientifique (CNRS)
- Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE)
- University of Agadir
- EUROCHAMP Project

LIST OF CONTRIBUTORS

Arsene Cecilia
Environmental Chemical Processes Laboratory
Department of Chemistry, University of Crete
P.O.Box 2208, Voutes, GR-71003 Heraklion, Greece
carsene@chemistry.uoc.gr

Azzi Abbès
Département de Génie-Maritime, Faculté de Génie-Mécanique
Université des Sciences et de la Technologie d'Oran (USTO)
BP. 1505 El-Mnaouar, 31000, Oran, Algeria
abbes.azzi@gmail.com

Balafrej Taha
Ministère de l'Aménagement du Territoire, de l'Eau et de l'Environnement
Point Focal de la CCNUCC
Agdal Rabat, Morocco
balafrej@minenv.gov.ma

Barnes Ian
Physikalische Chemie / Fachbereich C
Bergische Universitaet Wuppertal
Gauss Strasse 20, D-42097 Wuppertal, Germany
barnes@uni-wuppertal.de

Becker Karl H.
Institute of Physical Chemistry
Department of Chemistry, University Wuppertal
Gauss-Str. 20, D-42097 Wuppertal, Germany
khbecker@uni-wuppertal.de

Bergametti Gilles
Laboratoire Inter-Universitaire des Systèmes Atmosphériques (LISA)
Faculté des Sciences et Technologie
61 avenue du Général de Gaulle, F-94010 Créteil Cedex, France
bergametti@lisa,univ-paris12.fr

Bounoua Lahouari
Biospheric Sciences Branch, Code 614.4
NASA - Goddard Space Flight Center
Greenbelt MD 20771, USA
bounoua@ltpmail.gsfc.nasa.gov

Chehbouni Ahmed
Université Cadi Ayyad, Faculté des Sciences Semlalia
BP 2390, Marrakech, Morocco
chehbouni@ucam.ac.ma

Daële Véronique
CNRS, Laboratoire de Combustion et Systèmes Réactifs (LCSR)
1C, Avenue de la recherche scientifique
F-45071 Orléans cedex 02, France
daele@cnrs-orleans.fr

Dakkina Abdelali
Centre d'Information sur l'Energie Durable et l'Environnement (CIEDE)
Ministry of Environment
Rabat, Morocco
dakina2002@yahoo.fr

Elmaimouni Lahcen
Laboratoire de Chimie Physique, département de Chimie
FSA, Agadir, Morocco
lelmaimouni@yahoo.fr

George Christian
Laboratoire d'Application de la Chimie à l'Environnement (LACE)
Domaine Scientifique de la Doua, Batiment J. Raulin
43 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France
Christian.George@univ-lyon1.fr

Hjorth Jens
Institute for Environment and Sustainability (IES)
The European Commission Joint Research Centre
TP 290, 21020 ISPRA (VA), Italy
jens.hjorth@jrc.it

Kanakidou Maria
Environmental Chemical Processes Laboratory
Department of Chemistry, University of Crete
P.O.Box 2208, Voutes, GR-71003 Heraklion, Greece
mariak@chemistry.uoc.gr

Karrouk Mohamed-Saïd
Université Hassan II Centre de Recherche de Climatologie (CEREC)
Laboratoire de Climatologie et de Télédétection (CLIMTEL)
BP 8220 Oasis, MA-20103 Casablanca, Morocco
Karrouk.MS@UnivH2M.Ac.Ma
KarroukSaid@Yahoo.Com

Kubilay Nilgün
Institute of Marine Sciences
Middle East Technical University
PO Box 28, Erdemli-Mersin, Turkey
kubilay@ims.metu.edu.t

Maione Michela
Universita' di Urbino Istituto di Scienze Chimiche
6, Piazza Rinascimento, 61029 Urbino, Italy
michela@uniurb.it
project.office@accent-network.org

Mallet Marc
Laboratoire d'Aérologie (LA), Observatoire Midi-Pyrenees
14 av Edouard Belin, F-31400 Toulouse, France
malm@aero.obs-mip.fr

Mellouki Wahid
CNRS, Laboratoire de Combustion et Systèmes Réactifs (LCSR)
1C, Avenue de la recherche scientifique
F-45071 Orléans cedex 02, France
mellouki@cnrs-orleans.fr
wmellouki@laposte.net

Mihalopoulos Nikos
Environmental Chemical Processes Laboratory
Department of Chemistry, University of Crete
P.O.Box 1470, Voutes, GR-71409 Heraklion, Greece
Mihalo@chemistry.uoc.gr

Millán Millán
Fundacion CEAM
Parque tecnologico c/4, Sector Oeste, Paterna
46980 Valencia, Spain
pilarz@ceam.es

Mohamed Mohamed A.
Atomic Energy Authority
National Centre for Nuclear Safety and Radiation Control (NCNSRC)
Material and Nuclear Fuel Cycle Dept.
3 Ahmed El-Zomer St. Nasr City, 11762, Cairo, Egypt, P.O.Box 7551
mageleel2000@yahoo.com

Mousa Ashraf
Crustal Movements Laboratory
National Research Institute of Astronomy and Geophysics
Elmarsad St., Helwan, Cairo, 11421, Egypt
ashrafkm@yahoo.com

Niedojadlo Anita
AGH University of Science and Technology
Faculty of Mining Surveying and Environmental Engineering
Department of Management and Protection of Environment
Al. Mickiewicza 30, C4, 30-059 Cracow, Poland
niedan@poczta.fm

Pilling Mike
School of Chemistry
University of Leeds
Leeds LS2 9JT, United Kingdom
M.J.Pilling@leeds.ac.uk

Prospero Joseph M.
RSMAS/MAC, University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149, USA
jprospero@rsmas.miami.edu

Ravishankara A.R. (Ravi)
Chemical Sciences Division, Earth System Research Laboratory
NOAA, R/CSD 2
325 Broadway, Boulder CO 80305, USA
A.R.Ravishankara@noaa.gov

Saliba Najat A.
IBSAR - American University of Beirut
American University of Beirut
P.O.Box 11-0236 Riad El-Solh, Beirut 1107 2020, Lebanon
ns30@aub.edu.lb

Tanimoto Hiroshi
National Institute for Environmental Studies
Asian Environment Research Group Regional Atmospheric Modeling
Section & Center for Global Environment Research
16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan
tanimoto@nies.go.jp

Wiesen Peter
Physikalische Chemie / Fachbereich C
Bergische Universitaet Wuppertal
Gauss Strasse 20, D-42097 Wuppertal, Germany
wiesen@uni-wuppertal.de

CLIMATE AND ITS VARIABILITY: GLOBAL AND REGIONAL PERSPECTIVE

LONG-RANGE TRANSPORT OF POLLUTANTS ABOVE THE EASTERN MEDITERRANEAN: IMPLICATIONS FOR AIR QUALITY AND REGIONAL CLIMATE

NIKOLAOS MIHALOPOULOS
University of Crete, Department of Chemistry, Voutes 71003, Heraklion, Greece, mihalo@chemistry.uoc.gr

Key Words: Transport parthways, Ozone, PM, aerosols, chemical composition, oxidation capacity, Eastern Mediterranean.

Abstract The present work provides an overview of the transport and transformation processes occurred above the Mediterranean with emphasis in the Eastern basin. It summarises the results from several campaigns performed since the last decade. The measurements gave evidence of a remarkably high level of air pollution from the surface to the top of the troposphere up to 15 km altitude. The strongest anthropogenic influence was observed in the lower 4 km by pollutants originating from both West- and East Europe transported by the northerly flow. The sources are industrial activity, traffic, forest fires, agricultural and domestic burning. Trajectory analysis and model results suggest also an important influence by Asian pollution plum near the tropopause from the east.

Near the surface the air pollution has several undesirable consequences. First, the European Union eight-hourly air quality standard for ozone is exceeded throughout the summer in the entire Mediterranean region. Second, the concentrations of aerosols are high as well, affecting human health. The aerosols furthermore influence the Mediterranean atmospheric energy budget by scattering and absorbing solar radiation. During summer, they reduce solar radiation absorption by the sea by about 10% and they alter the heating profile of the lower troposphere. As a consequence, evaporation and moisture transport, in particular to North Africa and the Middle East, are suppressed.

In the free troposphere, pollution is largely determined by intercontinental transport, whereas upper tropospheric pollution from Asia can reach the stratosphere. These "crossroads" carry large pollution loads over the Mediterranean, and the negative effects extend far beyond the region. Internatio-nal efforts are called for to reduce these atmospheric environmental stresses and to further investigate the links between Mediterranean and global climate change.

A. Mellouki and A.R. Ravishankara (eds.), Regional Climate Variability and its Impacts in the Mediterranean Area, 1–13.

1. Introduction

The Eastern Mediterranean is the cross road of air masses where emissions from pollution meet with natural ones. These emissions include trace gases like nitrogen oxides, carbon monoxide, volatile organic compounds, and particles. Pollution in the area results from industrial and traffic sources and domestic burning mainly from Europe, Balkans and the Black Sea. Forest fires and agricultural burning emissions are also affecting the area during the dry season. Natural emissions from the Sahara region, from the vegetation that surrounds the Mediterranean Sea and from the Mediterranean Sea itself also affect the area (Mihalopoulos et al., 1997; Lelieveld et al., 2002). Air masses transported from the Atlantic Ocean atmosphere but also from Asia (via the upper troposphere) can reach the area under favourable air flow conditions (Lelieveld et al., 2002; Kallos et al., 1998). South winds from Africa carry to the Eastern Mediterranean air masses with high loadings of Sahara dust and low levels of NO_X and O_3. This air flow is more frequently occurring during the transition periods in spring and fall.

Transport and transformation processes in the Eastern Mediterranean are the topic of intensive studies that aim to evaluate the intensity of these processes and their impact on regional air quality and visibility, climate and atmospheric composition change as well as on terrestrial and marine ecosystems.

2. Major Air Flow Patterns in the Eastern Mediterranean

During the MINOS campaign in July-August 2001, ground based, aircraft and remote sensing measurements gave evidence of a remarkably high level of air pollution from the surface to the top of the troposphere up to 15 km altitude and of the existence of 3 distinct atmospheric layers affected by different pollution sources (Figure 1).

The strongest anthropogenic influence was observed in the lower 4 km, originating from both West and East Europe transported by the northerly flow (Lelieveld et al., 2002). The sources are industrial activity, traffic, forest fires, agricultural and domestic burning (Gros et al., 2003). Biomass burning emissions in the area present large inter-annual variability, they maximized in 2000 when in July exceptionally intensive forest fires burnt a surface of more than 600 Km^2 that is about twice the annual mean burnt area over Greece the past 10 years (Latos et al., 2006). In addition to local fire events, biomass burning effluents from surrounding areas affect the area like those observed over the region north of the Black Sea during summer 2001 (Lelieveld et al., 2002).

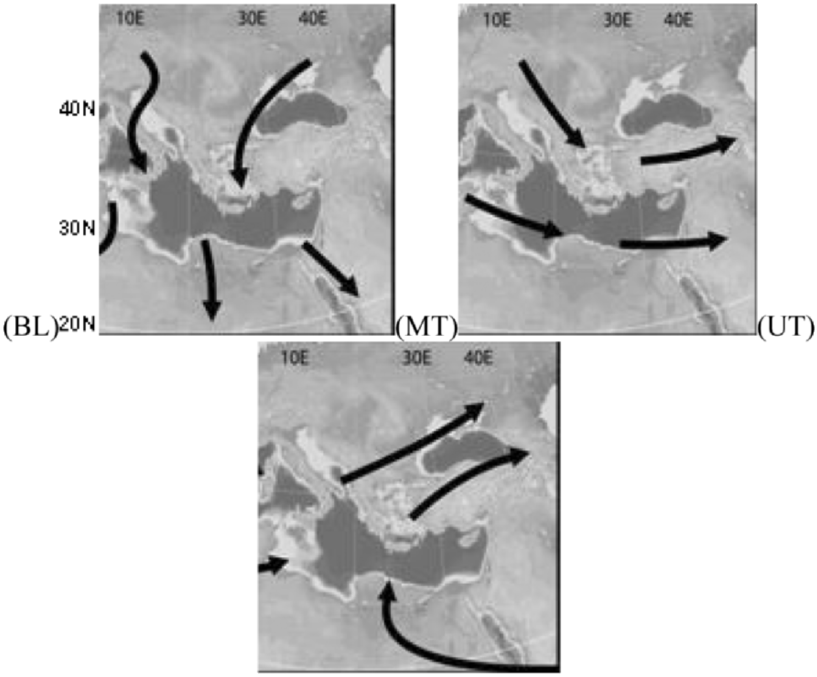

Figure 1. Major air mass flow pathways over the East Mediterranean during summer, in the boundary layer (BL), the middle troposphere (MT) and the upper troposphere (UT) – figure adopted from Lelieveld et al. (2002)

At higher altitudes, above 4 km, strong contributions from long-distance pollution transport from North America and Asia were detected during the MINOS campaign, for example, for carbon monoxide (CO) (Lawrence et al., 2002). It is quite remarkable that in summer 2001 about half of the mid-tropospheric CO over the Mediterranean originates from Asia and 25-30% from North America. These transports follow the prevailing westerly winds that are typical for the extra-tropics. Mid-troposphere is moreover substantially affected by ozone that is mixed down from the stratosphere (Roelofs et al., 2003). In addition, transport of anthropogenic O_3 and its precursor gases from the USA exerts a significant influence in the free troposphere.

In the upper troposphere, above 8 km altitude, another distinct layer was distinguished, especially over the eastern Mediterranean, associated with high levels of reactive species such as formaldehyde (Lelieveld et al., 2002). This was caused by anthropogenic emissions transported from South Asia, following convective lifting into the upper troposphere by thunderstorms in the Indian monsoon (Traub et al., 2003). Subsequently these air parcels followed the easterly tropical jet and turned north over the eastern Mediterranean in a large upper level anticyclone. The chemical “fingerprint” of biomass burning, in particular by biofuel use in India as also observed during the Indian Ocean Experiment, was evident by measurements of enhanced levels of enhanced CH_3CN, CH_3Cl and C_2H_2 (Scheeren et al., 2003).

From the upper troposphere over the eastern Mediterranean these species can even penetrate the lowermost stratosphere. Thus especially the middle troposphere in summer is influenced by stratosphere-troposphere exchange, leading to a stratospheric contribution to column O_3 in the troposphere of nearly 30%. It appears that the Mediterranean region seems to be a preferred location for cross-tropopause exchanges, partly related to direct convective penetration of the lower stratosphere over southern Europe (Fischer et al., 2002; Galani et al., 2003).

3. Tropospheric Ozone and Aerosols Over the East Mediterranean

Experimental studies over the East Mediterranean (Zerefos et al., 2002; Kourtidis et al., 2002; Kouvarakis et al., 2002a) have demonstrated that the background conditions in O_3 are high over the area and that Finokalia sampling station on the island of Crete is a site representative of the area for such monitoring. A seven year time series (1997-2004) of surface ozone at Finokalia, Crete, identified transport from the European continent as the main mechanism that controls ozone levels in the Eastern Mediterranean, especially during summer when ozone presents a maximum (July) of 58 ± 10 ppbv (Gerasopoulos et al., 2005). Because the Mediterranean background O_3 levels are so high, it is difficult to control ozone in urban and industrial areas. Radon-222 has been proved a useful tool for the verification of the continental origin of ozone. The role of local photochemistry and pollution becomes important under western flow and stagnant wind conditions.

For the whole 7-year period, a profound ozone decreasing trend was also observed with a decline of 1.6 ± 0.2 ppbv y^{-1} (Figure 2). The sharp decline of ozone during the first 5 years (i.e. 3.4 ± 0.2 ppbv y^{-1} or 5.6% per year for 1998-2002) has been succeeded by an abrupt increase in 2003 (to the 1999 ozone levels), followed by a return to the "regular" ozone declining levels in 2004. Note that summer 2003 was a rather dry and warm summer over Europe with intensive photochemical activity. The rates of O_3 decline were higher for the spring and summer concentrations. In parallel with the ozone decline, a shift of the maximum ozone concentrations from summer to spring, attributed to a continuous decrease of the summer ozone concentrations, was also observed, with the year 2002 presenting a clear spring maximum. These changes in O_3 could be related (i) to the reduction of ozone precursors occurred both in western/central and eastern European countries, (ii) to the severe weather phenomena that influenced mainly central Europe in summer 2002 (rather wet and cold summer, incessant precipitation, devastating floods in Central and East Europe) and (iii) to the induced meteorological

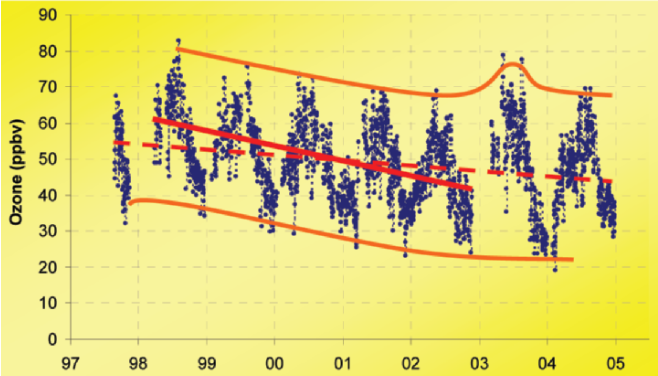

Figure 2. Observed surface O_3 levels from summer 1997 to 2004 at Finokalia monitoring station, Crete, Greece. Dashed red line indicates the trend for the whole period whereas the continuous red line indicates the 1998-2002 trend. Figure adopted from Gerasopoulos et al. (2005)

disturbance in 2002 that caused the prevalence of NW winds instead of the dominant NE flow (Gerasopoulos et al., 2005).

This dataset has been further analyzed in conjunction with simultaneously measured chemical and meteorological parameters (i) to investigate the factors that control the diurnal variability of ozone, and (ii) to evaluate the seasonally distributed ozone production/destruction rates in the area. The diurnal variability of ozone is small (~10%). The observed diurnal evolution of related chemical/physical parameters indicates that ozone morning built-up is driven by photochemistry while during summer the entrainment from the free troposphere is the dominant process in the afternoon. This was further supported by the observed similar behaviour of ozone maxima and Radon-222 minima. Ozone night time depletion has been mainly attributed to deposition and to a lesser extent to chemical reactions. On an annual basis the role of local photochemistry is found to be limited (–1 to 1.7 ppbv d^{-1}) contributing by less than 4% to the observed ozone levels. During summer the enhanced ozone destruction via deposition and chemistry are almost balanced by the chemical production and the entrainment of ozone rich air masses from the free troposphere that maximizes in summer (4-6% of the observed ozone levels). Chemical box model simulations also indicate low net chemical production in the area throughout the year that results from high chemical production and destruction terms. Especially during summer photochemical ozone depletion over the area is revealed both by model results and observations (0.5-1.0 ppbv d^{-1}) (Gerasopoulos et al., 2006a).

Observations over the East Mediterranean also show high concentrations of aerosols that can affect human health. The fine aerosol fraction (<1 µm) is mainly composed of sulfate (35-40%), organics (30-35%), ammonium

(10-15%) and black carbon (5-10%), mostly from fossil fuel and biomass combustion (Lelieveld et al., 2002; Bardouki et al., 2003).

High sulfate loadings in the area are mostly attributed to long range transport of pollution sources as also observed from space (SO_2 observations from space- Figure 3, see also in Eisinger and Burrows, 1998, Zerefos et al., 2000). Indeed, four-year aerosol observations performed by Amiridis et al. (2005) with a Raman lidar at Thessaloniki, Greece, in the framework of European Aerosol Research Lidar Network (EARLINET) indicate higher aerosol optical depth values and extinction to backscatter ratio mostly corresponding to air masses originating from the northeast Balkans and eastern Europe. Only about 20% of the non-sea-salt sulfate in the area is attribu ted to the oxidation of dimethylsulfide of marine origin (Kouvarakis and Mihalopoulos, 2002).

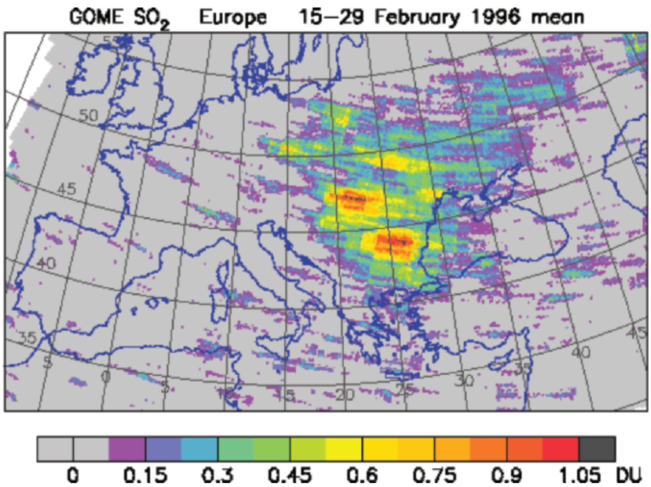

Figure 3. SO_2 column observations by GOME in 1996 (available at http://www.awi-potsdam.de/www-pot/atmo/gome/gome.html)

In addition to the particles of anthropogenic origin, significant amounts of naturally emitted airborn particles are present in the area. Large dust outbreaks from the Northern African continent are affecting the Mediterranean and to a lesser extend Central Europe (Figure 4). Dust reaches Europe either via vertically extended transport (VET) arriving over Crete simultaneously in the lower-free troposphere and inside the boundary layer, or via Free Troposphere Transport (FTT) arriving over Crete initially into the free troposphere with the heavier particles gradually being scavenged inside the boundary layer (Kalivitis et al., 2006). An analysis of southerly air masses arriving over Crete over a five year period (2000-2005), showed that both pathways present significant seasonal variations, but on an annual basis contribute almost equally to the dust transport in the area.

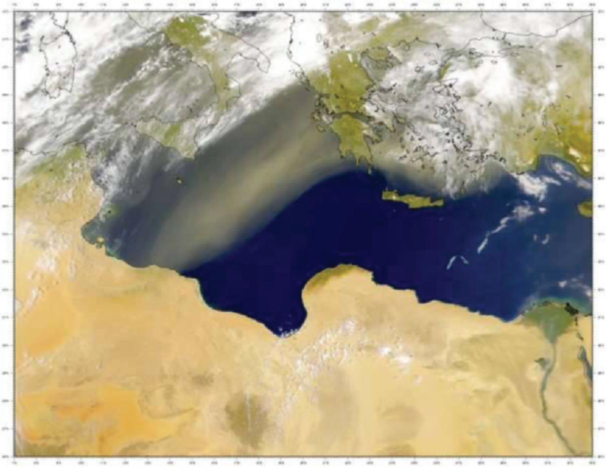

Figure 4. Observation of transport of dust over the east Mediterranean (SEAWIFS – Oct 2002)

Multiyear surface PM_{10} (airborn particles of diameter smaller than 10 um) measurements performed on Crete Island, Greece, have been analysed in conjunction with satellite (Total Ozone Mapping Spectrometer; TOMS) and ground-based remote sensing measurements (Aerosol Robotic Network; AERONET) (Kalivitis et al., 2006). They indicate that the majority of PM10 exceedences in the area seems to be related with mineral dust events that occur episodically over the Eastern Mediterranean. The EU limit of 50 μgm^{-3} is exceeded at Heraklion, one in 4 days, during winter and spring (50% due to transported dust) and half of the days during summer and fall (pollution). At Finokalia exceedences are observed in winter and spring during one in 5 days, 80-100% of which are associated with dust events. A significant covariance between PM_{10} and AOT was observed during VET indicating that aerosol optical thickness (AOT) levels from AERONET may be estimated by PM_{10} levels at the surface. During VET the Aerosol Index (AI) derived from TOMS (indicative of absorbing aerosol particles (airborne microscopic dust/smoke) was significantly correlated with surface PM_{10}, and in general AI was found to be adequate for the characterization of dust loadings over the Eastern Mediterranean on a climatological basis. The AI derived from TOMS was found to be adequate for the characterization of dust loading over the Eastern Mediterranean despite the fact that 20-30% of the dust related spikes in the PM_{10} time series that do not correspond to AI spikes. AI peaks are more frequent in spring indicating that the presence of dust can be detected to a certain extent by TOMS.

Simultaneous measurements of AOT at two distinct wavelengths, for instance 870 nm and 440 nm, can be used to distinguish the coarse (mainly natural) form the fine (mainly anthropogenic) particles contribution. AOT in the near-infrared (870 nm), is more sensitive to coarse particles, and can be used to represent the seasonality of dust and sea-salt aerosols, while AOT in the near-ultraviolet (440 nm) shows the influence of anthropogenic sources. AOT at 870 nm maximizes primarily in spring and to a lesser extend in fall, whereas an extreme dust event has been observed on 27th of January 2005. AOT (at 440 nm) additionally exhibits a plateau in summer, probably related to the accumulation of fine anthropogenic particles due to the meteorological conditions. The difference in the covariance of the AOT at these two wavelengths attributed to either local or transported pollution, maximizes in summer Figure 5. These areas are confined to summer when pollution is shown to contribute significantly to the PM_{10} levels over the area (Gerasopoulos et al., 2006b). However, it remains an open question the involvement of volatile organic compounds in the formation of secondary organic particulate matter over the area.

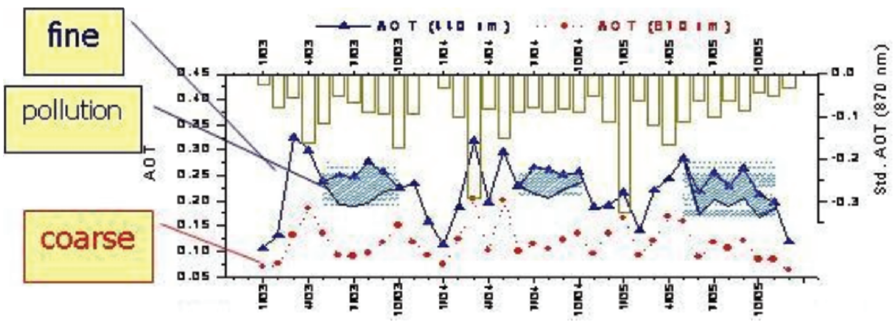

Figure 5. Monthly means of AOT at 440 and 870 nm over Crete during the period 2003-2005. Vertical bars are the standard deviation of the monthly means. The shaded areas indicate pollution aerosols (adopted from Kalivitis et al., 2006 where more explanations are provided)

4. Interactions Between Transported Pollution and Natural Emissions

A significant part of aerosols in the area is chemically formed in the atmosphere. In particular the Mediterranean atmosphere is a photochemical reactor with high levels of oxidants and particularly hydroxyl radicals that have been measured to reach mid-day maxima of approximately 2×10^7 molecules cm^{-3} (Berresheim et al., 2003). These oxidants initiate reactions that form acids including sulphuric and nitric acids. Hydroxyl radicals are efficient cleaning agents of the atmosphere and major removal pathway for persistent organics from the troposphere (Mandalakis et al., 2003; Mandalakis and Stephanou, 2002).

Nitrate radical (NO_3) measurements performed on the island of Crete for more than two years analysed together with ancillary measurements of chemical compounds and meteorological parameters show that night-time production of nitric acid (HNO_3) plus nitrate ions (NO_3^-), as initiated by NO_3 radicals, accounts for about 50-65% of the total production rate depending on season. The remainder is produced by the hydroxyl radical (OH) reaction with nitrogen dioxide during daytime. On a yearly mean basis, about 17% of the HNO_3 plus NO_3^- formation results from the reaction of NO_3 radicals with dimethylsulfide of marine origin (Figure 6). This shows important interactions between biogenic (volatile organics) and anthropogenic (nitrogen oxides and NO_3 radicals) compounds contributing to nutrient deposition to the sea (Vrekoussis et al., 2006, 2007).

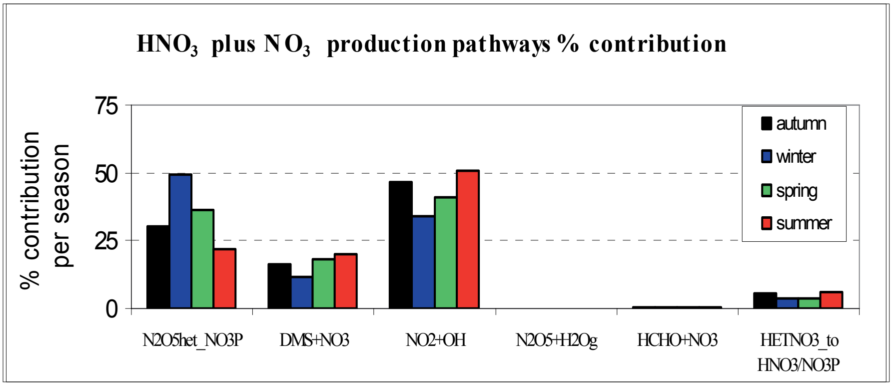

Figure 6. Percent contribution of the different pathways to the production of the sum of HNO_3 and NO_3^- (diel mean results). N2O5het_NO3p refers to the heterogeneous reaction of N_2O_5 on particles; HETNO3 refers to heterogeneous reactions of NO_3 on aerosols

5. Impacts

Near the surface the air pollution has several undesirable consequences. First, the European Union eight-hourly air quality standard for ozone (53 nmol/mol) is exceeded throughout the summer in the entire Mediterranean region. High ozone concentrations are harmful for human health and ecosystems, and they also cause agricultural crop loss.

The aerosols affect human health, visibility and furthermore influence the Mediterranean atmospheric energy budget by scattering and absorbing solar radiation (Figure 7). They reduce solar radiation absorption by the sea by about 10% and they alter the heating profile of the lower troposphere (Lelieveld et al., 2002; Markowicz et al., 2002; Vrekoussis et al., 2005). As a consequence, evaporation and moisture transport, in particular to North

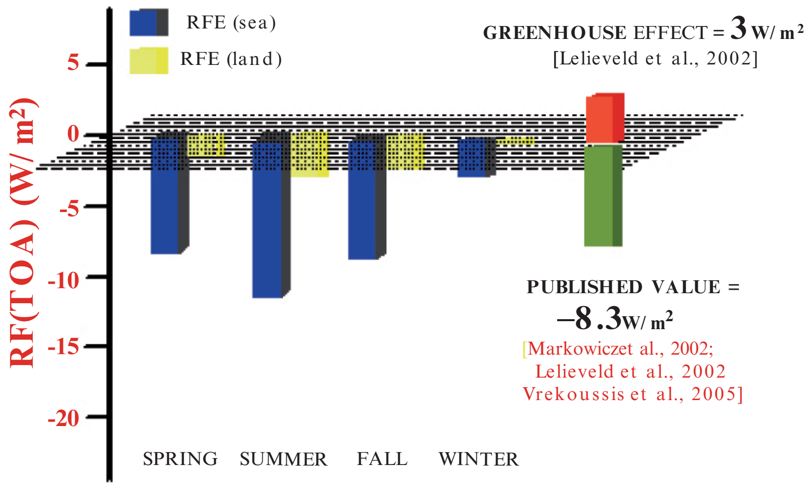

Figure 7. Radiative forcing at the Top Of the Atmosphere (RF(TOA)) induced by aerosols over sea (blue) and over land (yellow) during the 4 seasons as derived from aerosol observations and annual mean value (green) and comparison with the heating effect from the Greenhouse gases (red); figure adopted from Vrekoussis et al. (2005)

Africa and the Middle East, are suppressed. Furthermore, Rosenfeld (2000) studied satellite observations, indicating important perturbations of the cloud microstructure and convection by aerosols, probably decreasing precipitation.

The radiative forcing by aerosols (Figure 7) also influences the energy budget of the Mediterranean Sea, of which the consequences are yet poorly understood. Changing energy budget and anomalous winds are expected to influence the ocean circulation (Tragou and Lascaratos, 2003).

Therefore, aerosols may affect several components of the East Mediterranean atmosphere-ocean system including the regional water cycle. These effects by aerosols are substantial today, even though sulfate from Europe has actually decreased in the past two decades through the abatement of acidification.

Finally, during summer the persistent northerly winds carry large pollution loads from Europe that can deposit onto the Mediterranean Sea, for instance nitrate and phosphorus containing aerosols, which affect the water quality and could contribute to eutrophication (Kouvarakis et al., 2001).

6. Highlights–Conclusion Remarks

- Both observations and chemistry/transport models suggest that the troposphere of the Eastern Mediterranean is strongly polluted. Long range transport of European emissions is playing a key role in the built up of oxidants and secondary aerosols that is also enhanced by the favourable weather conditions.

- Ozone and aerosol air quality limits are often exceeded over the entire Mediterranean in particular during summer. The contribution of natural emissions to these exceedences remains to be determined.
- Middle tropospheric CO can be strongly affected by Asian and N-American pollution under favorable air circulation patterns like those observed during summer 2001.
- Ozone increase is warming the atmosphere whereas aerosols cause strong surface radiative forcing and perturbation of the water cycle in the area.
- It remains an open question how is the climate changing due to the anthropogenic forcings to the East Mediterranean environment.

7. Acknowledgments

I wish like to thank Prof. Dr. J. Lelieveld as well as all the participants of the MINOS campaign for communicating their results, my co-workers Drs. H. Bardouki, G. Kouvarakis, E. Gerasopoulos, M. Vrekoussis, and Msc N. Kalivitis, S. Pilitsidis and P. Babasakalis for the excellent collaboration and Prof. Dr. Maria Kanakidou for helpful discussions.

8. References

Aleksandropoulou, V., and Lazaridis, M. (2004) Spatial Distribution of Gaseous And Particulate Matter Emissions in Greece*, Water, Air, and Soil Pollution*, Nov 02, 2004, **153**, 15-34, 10.1023/B:WATE.0000019923. 58620.58.

Amiridis, V., Balis, D. S., Kazadzis, S., Bais, A., Giannakaki, E., Papayannis, A., and Zerefos, C. (2005) Four-year aerosol observations with a Raman lidar at Thessaloniki, Greece, in the framework of European Aerosol Research Lidar Network (EARLINET), *J. Geophys. Res*., **110**, D21203, doi:10.1029/2005JD006190.

Balis, D., Papayannis, A., Galani, E., Marenco, F., Santacesaria, V., Hamonou, E., Chazette, P., Ziomas, I., and Zerefos, C. (2000) Tropospheric LIDAR aerosol measurements and sun photometric observations at Thessaloniki, Greece, *Atmos. Environment* **34**, 925-932.

Balis, D., Amiridis, V., Kazadzis, S., Papayannis, A., Tsaknakis, G., Tzortzakis, S., Kalivitis, N., Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., Chourdakis, G., Pérez, C., Baldasano, J., and Drakakis, M. (2006) Optical characteristics of desert dust over the East Mediterranean during summer: a case study, *Annales Geophysicae*, **24**, 807-821.

Bardouki, H., Liakakou, H., Economou, C., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., and Mihalopoulos, N., (2003) Chemical composition of size resolved atmospheric aerosols in the Eastern Mediterranean during summer and winter. *Atmospheric Environment* **37**, 195-208.

Berresheim, H., Plass-Dulmer, C., Elste, T., Mihalopoulos, N., and Rohrer, F. (2003) OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, *Atmos. Chem. Phys*., **3**, 639-649.

Eisinger M., and Burrows, J. P. (1998) *Tropospheric Sulfur Dioxide observed by the ERS-2 GOME Instrument*, Geophys. Res. Letters, **25** (22), 4177-4180.