



Dynamic processes of mercury over the Mediterranean region: results from the Mediterranean Atmospheric Mercury Cycle System (MAMCS) project

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Abstract

The Mediterranean Atmospheric Mercury Cycle System (MAMCS) project was performed between 1998 and 2000 and involved the collaboration of universities and research institutes from Europe, Israel and Turkey. The main goal of MAMCS was to investigate dynamic processes affecting the cycle of mercury in the Mediterranean atmosphere by combining ad hoc field measurements and modelling tasks. To study the fate of Hg in the Mediterranean Basin an updated emission inventory was compiled for Europe and the countries bordering the Mediterranean Sea. Models were developed to describe the individual atmospheric processes which influence the chemical and physical characteristics of atmospheric Hg, and these were coupled to meteorological models to examine the dispersion and deposition of Hg species in the Mediterranean Basin. One intercomparison and four two-week measurement campaigns were carried out over a three-year period. The work presented here describes the results in general terms but focuses on the areas where definite conclusions were unforthcoming and thus highlights those aspects where, in spite of advances made in the understanding of Hg cycling, further work is necessary in order to be able to predict confidently Hg and Hg compound concentration fields and deposition patterns.

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1. Introduction

It is well-known that since the industrial revolution, due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), mercury has been employed in a wide variety of applications (i.e., manufacturing, dentistry, metallurgy). As a result of its use the amount of mercury mobilised and released into the atmosphere has increased compared to pre-industrial levels. Several

advances in theoretical and experimental techniques have been made in recent years to assess spatial and temporal distributions of ambient concentrations and deposition fluxes of mercury and its compounds. Temporal and spatial scales of mercury transport in the European atmosphere and its transfer to aquatic and terrestrial receptors were found to depend primarily on the chemical and physical characteristics of the three main forms of atmospheric mercury (Petersen, et al., 1998; Pirrone et al., 2000a; Hedgecock and Pirrone, 2001). Therefore the outcome of experimental and theoretical research indicates that natural and human (anthropogenic) activities can redistribute this element

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in the atmospheric, soil and water ecosystems through a complex combination of chemical, physical and biological mechanisms.

Regional scale modelling of major atmospheric transport and removal mechanisms of elemental mercury (Hg^0), oxidised mercury (Hg^{II}) and Hg bound to particulate (Hg^{P}) have been performed within the framework of the MOE and MAMCS projects (Pirrone et al., 2000b, 2001b). Model results suggest that up to 75% of mercury in cloud and rain droplets is associated with particles in polluted areas of Europe due to adsorption on to soot particles. Modelling studies also predict that the sea salt aerosol and spray droplets play an important role in the cycling of Hg^{II} in the marine boundary layer (MBL), possibly accounting for up to 20% of the total Hg^{II} observed in coastal areas, with higher values expected for the open sea (Forlano et al., 2000; Hedgecock and Pirrone, 2001). Preliminary assessments of spatial distributions of atmospheric deposition fluxes of Hg^0 , Hg^{II} and particulate Hg over Europe have been based on the up-to-date mercury emission inventory (MEI) for anthropogenic (Pacyna et al., 2001) and natural sources (Pirrone et al., 2001b) developed for Europe, North Africa and the Middle East and performed for different seasons as discussed in Pirrone et al. (2000b).

The major goal of the MAMCS project was to examine the cycling of atmospheric mercury in order to characterise and quantify the emission, ambient concentration and deposition flux patterns in the Mediterranean region. The climatic conditions in the Mediterranean region are such that one of the major foci of the project was to investigate the role played by chemical and physical processes affecting the interaction between gas phase mercury species and the ambient aerosol and the influence this has on removal mechanisms, both wet and dry. The reason for this is that for relatively long periods during the year there is very little, if any, rainfall in the area. Under such conditions the normal mercury deposition pathway, precipitation, is unavailable, and instead deposition will be via the ambient aerosol or dry deposition of Hg^{II} from the gas phase. This fact has important implications, particularly in the marine environment where deliquesced sea salt aerosol is present, providing both a means of deposition and of oxidation of elemental mercury. This paper presents an overview of the outcome of the MAMCS project, and briefly highlights its further development and its possible implications for future EU policy (Pirrone, 2001).

2. The research strategy

The aim of the MAMCS project was to investigate the major chemical and physical mechanisms/ processes that

may influence the cycle of mercury in the Mediterranean atmosphere, its deposition fluxes to surface waters and its exchange at the air–water interface. In order to achieve these objectives the methodology applied during MAMCS was a combination of field measurements and modelling techniques. This section briefly describes the methods used to:

- estimate the emission of mercury (and its species) from natural and anthropogenic sources,
- determine the ambient concentrations of total gaseous mercury (TGM, the sum of $\text{Hg}_{(\text{g})}^0$ and $\text{Hg}_{(\text{g})}^{\text{II}}$), reactive gaseous mercury (RGM, i.e., $\text{Hg}_{(\text{g})}^{\text{II}}$) and total particulate mercury (TPM or Hg^{P}),
- model chemical and physical processes that affect the dynamics of mercury and its species in the MBL during transport, and
- model the transport and dispersion patterns of air masses over the Mediterranean Region.

2.1. Atmospheric emissions

Two complementary approaches were employed in the compilation of the inventory of European anthropogenic emissions of mercury for the reference year 1995:

- collection of emission data from countries where such data were estimated by national emission experts, and
- estimates of emissions on the basis of emission factors and statistical data on the production of industrial goods and/or the consumption of raw materials. These estimates were carried out by the authors of this paper for the countries with no national estimates.

2.1.1. Assessment of anthropogenic mercury emission data supplied by national experts

The emission data received from national authorities in 22 countries have been checked for completeness and comparability. The completeness of the data regarded primarily the inclusion of all major source categories which may emit mercury to the atmosphere. No major omissions were detected. All countries that provided emission data included all the major source categories in their reports. Emission data was categorised not only according to source type but also by the fraction of Hg^0 , Hg^{II} and Hg^{P} emitted, and also stack height.

It is very difficult to verify the data obtained from the national authorities in Europe. The following approach has been taken. Information on emissions of mercury from various sources was brought together with statistics on the production of industrial goods and/or the consumption of raw materials, and these two sets of data were used to calculate emission factors. Emission

factors calculated in this way were then compared with emission factors reported in the Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (UN ECE 1999). In the majority of cases, emission factors estimated on the basis of national emission data reported to the project were within the range of emission factors proposed in the Guidebook. This check was a proof that the estimates from various countries are comparable and thus can be accepted for further application in modelling the transport of Hg within air masses over Europe and the Mediterranean.

2.1.2. Emission estimates for countries with no national data available

Emission estimates have been performed for the countries where no national emission data were available. These estimates have been based on the statistical information on the consumption of raw materials and the production of industrial goods, available from international and national statistical yearbooks and the emission factor data. The emission factors used in the estimates were estimated on the basis of Hg content in various raw materials, and the efficiency of emission control equipment. These emission factors are presented in the final report of the MAMCS project (Pirrone et al., 2000b).

2.2. Atmospheric measurements

Within the MAMCS framework, ambient concentrations of TGM, RGM and TPM as well as mercury in precipitation were simultaneously measured at five coastal sites (see Fig. 1) during four two-week intensive measurement campaigns (see Table 1). The measurements were co-ordinated with those made during the MOE project (Wangberg et al., 2001). Prior to these campaigns an intercomparison exercise was performed in order to test the different sampling and analytical techniques used to quantify the level of TGM, RGM

and TPM in air at each partner's laboratory (Munthe et al., 2001). An overview of sampling and analytical methods used to assess TGM, RGM, TPM and mercury in precipitation is reported in Table 2. Details of these methods have been discussed in Munthe et al. (2001) and Wangberg et al. (2001).

2.3. Atmospheric mercury modelling

2.3.1. The MAMCS modelling framework

The integrated mercury modelling system developed in MAMCS is the result of the coupling of two meteorological-dispersion modelling systems with modules that account for the different chemical and physical processes affecting the mercury cycle in the atmosphere and its interactions with surface waters. Fig. 2 shows a simplified scheme of the overall structure of the integrated modelling system. In order to assure reasonable computational time (for operational mode—the simulation period is a few weeks to months) and inclusion of a detailed description of the microphysics of the troposphere (in research mode—the simulation period is a few days to up one or two weeks) the integrated modelling system is structured to use two alternative meteorological-dispersion systems, namely the Regional Atmospheric Modelling System (RAMS) (for research mode) and the SKIRON/Eta meteorological system (for operational mode).

Table 1

Time schedule of the four intensive atmospheric measurement campaigns carried out at the five MAMCS sites

Campaign	Start date	Stop date
MAMCS-1	13 November 1998	6 December 1998
MAMCS-2	15 February 1999	1 March 1999
MAMCS-3	3 May 1999	17 May 1999
MAMCS-4	19 July 1999	2 August 1999

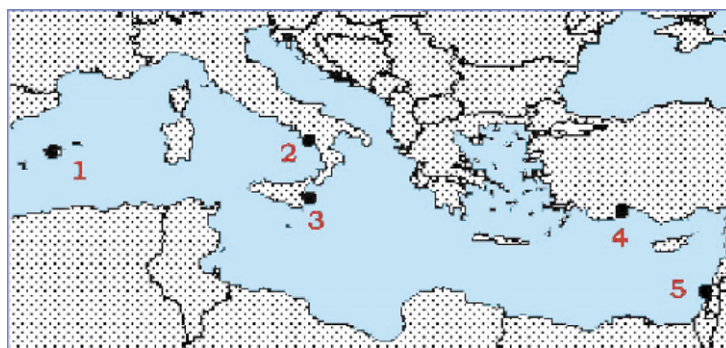


Fig. 1. The atmospheric measurement sites in MAMCS. (1) Mallorca ($39^{\circ}40'30''\text{N}$, $2^{\circ}41'36''\text{E}$), (2) Calabria ($39^{\circ}25'\text{N}$, $16^{\circ}00'\text{E}$), (3) Sicily ($36^{\circ}40'\text{N}$, $15^{\circ}10'\text{E}$), (4) Turkey ($36^{\circ}28'12''\text{N}$, $30^{\circ}20'24''\text{E}$) and (5) Israel ($32^{\circ}40'\text{N}$, $34^{\circ}56'\text{E}$).

Table 2

Sampling and analytical methods used to assess the level of total gaseous mercury (TGM), reactive gaseous mercury (RGM) and total particulate mercury (TPM) at the MAMCS sites

Mercury species	Sampling methodology	Analytical method	Reference
TGM	Tekran 2537A-Analyser (automated)	CVAFS	Tekran (1998) and Sommar et al. (1999)
TGM	Gardis (automated)	CVAAS	Wangberg et al. (2001) and Munthe et al. (2001)
TGM	Gold Traps (manual)	CVAFS (After thermal desorption)	Brosset (1987) and Bloom and Fitzgerald (1988)
TGM	Charcoal adsorbents-INAA (manual)	INAA	Wangberg et al. (2001) and Munthe et al. (2001)
RGM	Mist chamber with 0.1 M HCl (manual)	SnCl ₂ reduction, gold trap preconcentration and CVAFS detection	Stratton and Lindberg (1995)
RGM	Tubular KCl-coated denuders (manual)	CVAFS (after thermal desorption/conversion)	Wangberg et al. (2001) and Munthe et al. (2001)
RGM	Annular KCl-coated denuders coupled to Tekran 2537A Analyser (automated)	CVAFS (after thermal desorption/conversion)	Munthe et al. (1999) and Lindberg et al. (2002)
TPM	Miniature quartz fibre filters (manual)	CVAFS (After thermal desorption/conversion)	Lu et al. (1998) and Wangberg et al. (2001) and Wangberg et al. (2002)
TPM	Teflon filters (manual)	Acid digest., SnCl ₂ reduction, gold trap precon. and CVAFS detection.	Wangberg et al. (2001) and Munthe et al. (2001)
TPM	Cellulose acetate filters (manual)	Acid digest., SnCl ₂ reduction, gold trap precon. and CVAFS detection.	Wangberg et al. (2001) and Munthe et al. (2001)
TPM	Glass fibre filters (manual)	Acid digest., SnCl ₂ reduction, gold trap precon. and CVAFS detection.	Keeler et al. (1995)

RAMS was developed originally at the Colorado State University (Pielke et al., 1992) to study mesoscale and regional scale meteorological patterns and pollutant dynamics. RAMS is the core of the MAMCS modelling framework providing a detailed parameterisation of the microphysics of the troposphere and allowing special treatment of the key mechanisms that are known to occur in the MBL. The surface-layer parameterisation (soil, vegetation type, lakes and seas, etc.) may be used with different levels of complexity depending on the users requirements. RAMS is therefore a highly versatile tool and is used in air quality studies and to study a wide variety of other atmospheric phenomena. The second meteorological model is the SKIRON system, it requires less CPU time than RAMS because the treatment of cloud microphysics is simplified. The SKIRON system is based on the ETA/NCEP model (Mesinger, 1984, Janjic, 1994). It has since been developed at the University of Athens as an integrated, stand alone, weather forecasting system (Kallos et al., 1997a). It is in use in Europe and other Mediterranean countries as an operational weather forecast system. SKIRON/Eta has several capabilities that make it appropriate for regional/mesoscale simulations. One of the most important

features useful for modelling Hg processes is the viscous sub-layer module which describes fluxes from water surfaces accurately (Janjic, 1994). It also uses the Betts-Miller-Janjic cloud micro-physical scheme, which is considered to be both accurate and computationally efficient. Additional information about the use of the two modelling systems combined with the Hg process models may be found in Kallos et al. (2000, 2001a).

In order to model the dynamic processes of gaseous and particulate mercury with changing meteorological conditions over the Mediterranean Sea, a number of adhoc modules were developed and coupled to both the RAMS and SKIRON systems. These modules account for major mechanisms/processes that affect the fate of mercury in the atmosphere and include:

- particle dry deposition,
- wet scavenging by precipitation,
- gas–particle partitioning,
- chemical transformations in the gas and aqueous phases in the troposphere with particular attention to the MBL, and
- air–water exchange of Hg and its compounds.

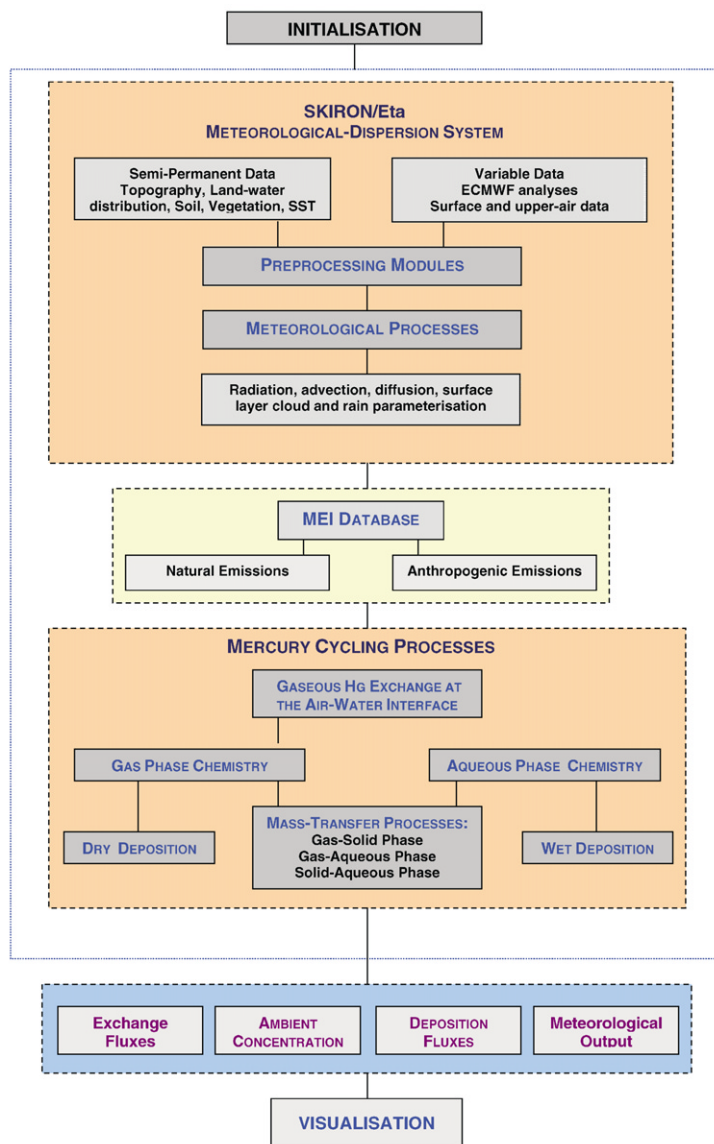


Fig. 2. Schematic of the overall MAMCS modelling framework.

The main components of the integrated mercury modelling system are discussed below, further details can be found in the cited literature.

2.3.2. Chemical and physical atmospheric processes

In spite of being relatively unreactive Hg in the atmosphere is involved in a number of phase equilibria (volatilisation and condensation, for example) and also in both gas and aqueous phase chemical processes. The deposition of Hg is the focal point for the modelling of physical and chemical processes, as it is the

calculation of the Hg flux to terrestrial and aquatic ecosystems which is of interest. Ideally the chemical form of Hg (whether elemental or oxidised) should also be obtained from the model output, as bioavailability, solubility and the chances of rapid re-emission depend very much on the chemical form of the deposited Hg. Deposition of Hg occurs via dry deposition of Hg^0 and Hg^{II} from the gas phase, in conjunction with particle deposition where Hg is physically adsorbed (reversibly or irreversibly) on atmospheric particulate matter, and of course via

scavenging by cloud and fog droplets and subsequent wet deposition.

Perhaps the best way to give an overview of the progress of process modelling during MAMCS is to describe chronologically the various steps that have led to the current versions of the process models. The solubility of Hg^{II} compounds and their very high Henry's Law constants mean that where there is regular rainfall, scavenging by water droplets is by far the most efficient atmospheric removal process. In the Mediterranean however, particularly in the summer when anticyclonic conditions often prevail, precipitation events can be few and far between. Thus it was hypothesised that deposition of Hg (elemental and oxidised) associated with particulate matter could be a major route for Hg input in the area. To test this a model describing GAS-PARTicle partitioning (GASPAR) was produced. As GASPAR was intended for use with dynamic atmospheric models, it uses a parameterised description of the ambient aerosol, using four source categories (urban, continental, marine and desert), each with three possible modal diameters. The parameterisation also includes characteristics important for Hg adsorption and chemistry such as the soot content and the chloride ion content (Pirrone et al., 2000a). The deposition velocity of particulate matter being a function of particle size, which in turn depends on the particle hygroscopicity and relative humidity, the fraction of hygroscopic material in the particle was also included in the parameterisation. The possibility of particle deliquescence indicated the need to include aqueous phase Hg chemistry and also mass transfer between both the gas and aqueous phases, but also between insoluble material contained in the particles and the aqueous phase around it (as first proposed by Pleijel and Munthe, 1995).

The first version of GASPAR therefore included gas–solid equilibria for low humidity conditions and gas–aqueous, aqueous–solid equilibria for deliquescence conditions; as well as a relatively simple description of Hg aqueous phase chemistry similar to that used by Petersen et al. (1998), which was a reduced version of the Hg chemistry in cloud droplets model by Pleijel and Munthe (1995). The aqueous phase chemistry model had been updated to include the aqueous phase oxidation of elemental mercury by HOCl and the aqueous phase reduction of oxidised mercury by HO_2 (Lin and Pehkonen, 1998). This version of GASPAR was used to investigate the dispersion and transformation of Hg emitted from a single source in the Mediterranean, and to calculate the speciated Hg deposition flux (Forlano et al., 2000). Sensitivity analysis of the chemistry module of GASPAR using the direct decoupled method (DDM) (Dunker, 1984; Pirrone et al., 2000a) revealed that the concentration of Hg^{II} associated with deliquesced

particles was extremely sensitive to the particle chloride content. This fact prompted the further evolution of the chemistry model, which was expanded to include gas and aqueous phase tropospheric photochemistry in the MBL.

The presence of Hg^{II} in the gas phase, (RGM), is important because it has a much higher dry deposition velocity than Hg^0 . Dry deposition of elemental Hg is extremely difficult to quantify depending as it does on meteorological phenomena such as temperature and wind speed, and also on the type and geomorphology of the surface in consideration. Most regional scale studies performed in the past have assumed that the gaseous flux of Hg^0 at the air–water and air–soil interfaces is zero (Pai et al., 1997). Recently, a number of flux chamber experiments, especially on water surfaces have been performed to test the validity of this assumption and to determine whether it is possible to parameterise net fluxes as a function of air and sea temperature and solar irradiation (see papers in Pirrone et al., 2001a; Ferrara et al., 2000). RGM however is known to deposit rapidly (Lindberg and Stratton, 1998), although it had been assumed that RGM was primarily the result of emissions and therefore to be found relatively close to emission sources. The first results from the MAMCS campaign sites showed that RGM concentrations in the Mediterranean (far from sources, and particularly with onshore winds) were comparable to if not greater than RGM concentrations in much more industrial northern Europe. Lower concentrations in northern Europe could be explained by a higher rainfall frequency but the origin of RGM observed over the Mediterranean Sea was unclear. The high concentration of chloride ions in sea salt aerosol modelled with GASPAR had suggested that with low atmospheric liquid water content the concentration of $\text{HgCl}_{2(\text{aq})}$ could become high enough that to maintain equilibrium with the gas phase, notwithstanding its high Henry's Law Constant, HgCl_2 could outgas from the aerosol droplets to the gas phase. Without an exhaustive description of gas and aqueous phase chemistry and photochemistry of the MBL it was not possible to be certain.

The MBL photochemistry box model developed to describe the mercury chemistry in the MBL is described in Hedgecock and Pirrone (2001). It was shown that the sea salt aerosol could indeed scavenge HgO produced by the gas-phase oxidation of Hg^0 by O_3 , and then RGM was recycled to the atmosphere as HgCl_2 . The measurement of the reaction rate constant for $\text{Hg}^0 + \text{OH}$ in the gas phase (Sommar et al., 2001), indicated that the rate of gas phase HgO production was higher, particularly in sunny conditions, than had previously been thought, and therefore that cycling of RGM occurred to a much greater extent than imagined. The MBL box model was updated with new reaction constant data and submitted to the same rigorous sensitivity analysis performed on

GASPAR (Hedgecock et al., 2003). The use of sensitivity analysis on a box model including detailed chemistry allows the reactions of major importance and the most relevant aerosol characteristics to be chosen for use in dispersion models where a large reaction data base would prove prohibitively time consuming. Thus the chemistry model normally used in the MAMCS modelling framework includes gas phase and aqueous phase oxidation pathways, and in the aqueous phase the complexation equilibria, which determine the speciation and concentration of oxidised mercury compounds. In this version of the model the concentrations of the important oxidants produced by photolytic processes is calculated using a minimum and maximum value for each grid cell and varying the concentration sinusoidally with a maximum when the sun reaches its zenith.

Wet removal processes concern soluble chemical species (Hg^{II} and its compounds, and some Hg^0) and also particulate matter scavenged from below the precipitating clouds. The total wet deposition flux is made up of two contributory factors. The first derives from the continuous transfer of both Hg^0 and Hg^{II} to cloud water, described by chemistry models. There are two limiting factors here, the rate of uptake of gas-phase elemental mercury, which is regulated by Henry's constant, and the subsequent oxidation of $\text{Hg}_{(\text{aq})}^0$ to $\text{Hg}_{(\text{aq})}^{\text{II}}$ which is governed by reaction rate constants and the initial concentrations of the oxidant species. The total flux depends on the liquid water content of the cloud and the percentage of the droplets in the cloud which reach the earth's surface. The second contribution to the total mercury flux is the physical removal of particulate matter during precipitation events. The latter case is modelled by specifying a scavenging coefficient.

Another important process in the global mercury cycle is the exchange of gaseous mercury at the air–water interface. This may occur by gas-phase diffusion to water surfaces and evasion from the top water micro-layer, or it may be provoked by the mechanical action of the wind on the water surface producing waves and thereby mechanically generating sea-water droplets which may either release or take up elemental mercury. These processes are not as yet thoroughly understood but empirical models capable of reproducing experimental data from flux chamber measurements exist, as do models to predict the size distribution of droplets produced by the action of the wind on the water surface as a function of wind speed (Pirrone et al., 2000b; Trombino et al., 2000).

3. Results and discussion

Detailed descriptions of the results of the various work packages within the MAMCS project are presented in some of the articles in this special issue and

also in a previous special issue (Pirrone et al., 2001a). Therefore the results presented here are intended to highlight what has been learnt about the directions in which Hg research should go as a result of the MAMCS project.

3.1. Meteorological patterns of the region

The Mediterranean Sea is surrounded by high peninsulas and important mountain barriers. The most important are the Alps and the Balkan Peninsula to the north, the Iberian Peninsula to the west, the Atlas Mountains to the southwest and the Asia Minor to the northeast. The gaps between these major mountainous regions act as channels for air mass transport from/to the Mediterranean. This kind of transport is considered very important for cyclogenetic activities and the air quality in the Mediterranean Region. These topographic features along with the significant variation of the physiographic characteristics are partially responsible for the development of various-scale atmospheric circulations. These locally produced atmospheric circulations are quite strong, especially during the warm period of the year (Kallos et al., 1996a, b, 1998a). The most significant of these regional to mesoscale circulations in the area are described in the UK (Meteorological Office publication "Weather in the Mediterranean," 1962).

The Mediterranean climate has some distinctive characteristics (Kallos et al., 1996a, b, 1998a, b, 2001a, b). It cannot be characterised as either maritime or continental. The cold season (end of October—beginning of March) is the rainy period. The warm season (June–September) is the dry period with almost no rain. The rest of the year consists of the transient seasons (spring and autumn) where the winter and summer-type weather patterns are interchanging. In order to assess the levels of mercury species with prevailing meteorological patterns in the region, the measurement campaigns were scheduled according to these patterns as summarised below.

- During winter, cyclogenesis in the Mediterranean takes place in preferred locations such as Cyprus (El Fandy, 1946; Kallos and Metaxas, 1980), Southern Ionian Sea, Gulf of Genoa, Gulf of Lyon, Gulf of Syrtis and Atlas Mountains (Alpert et al., 1990). This cyclogenetic activity is associated with the low-index circulation and is a result of positive vorticity advection and invasion of cold air over relatively warm waters (Metaxas, 1978; Kallos and Metaxas, 1980). These cold air masses originate from Western, Central or Eastern Europe and Scandinavia. Usually, the cold outbreak is associated either with cyclogenesis in the preferable locations aforementioned or with the rejuvenation of dissipating lows moving into

the area. Anticyclonic circulation during winter is associated with a cold core anticyclone laying over Central Europe and/or the Mediterranean. This high-pressure system has a relatively long duration (two to four weeks) and is associated with weak northerly flow in the Mediterranean.

- During the warm period of the year, the land of North Africa becomes very hot during the day while the Mediterranean waters have a moderate temperature (23–27°C). The land of South Europe also becomes hot during the day but not as hot as the land of North Africa. Because of this differential heating, the Mediterranean region and South Europe are covered by an anticyclonic system, which is relatively shallow. Large-scale subsidence is evident (Kallos et al., 1996a). There is almost no rain in the region with the exception of some convective storms. Air masses from the Mediterranean move towards North Africa (Kallos et al., 1993, 1996a, 1997a). Trade winds persist over areas like the Aegean Sea (Etesians). The Etesians are a regional-scale phenomenon with significant diurnal variation. Local thermal circulations are evident across the Mediterranean coastlines while in regions like the Iberian Peninsula more complicated phenomena such as funnelling and multiple layering occur (Millan et al., 1997). In general, during the warm period of the year the flow has a major component from the European coasts towards North Africa in a prevailing direction from N to NW (Kallos et al., 1993, 1996a, 1997a, 1998a).
- During the transient seasons, the weather type changes between summer and winter type. This change occurs rapidly during spring and slowly during autumn.

Because of these complicated flow patterns in the Mediterranean Region air pollutants released from various sources located in the surrounding areas can be transported over long distances, in a complex fashion. During the last decade, a significant effort has been devoted to study the transport phenomena in the Mediterranean Region and their implications for air quality. The European Union funded projects MECA-PIP, SECAP, T-TRAPEM (i.e., Millan et al., 1997; Kallos et al., 1997b) were focused on air pollution transport and transformation processes in the Mediterranean Region during summer. In addition, Saharan dust transport and deposition has been explored during the EDUSE project. Rodriguez et al. (2001) studied the implications of such transport in the urban environment of various Spanish cities.

3.2. Mercury emission inventory (MEI)

In 1995 total Hg emissions in Europe were estimated to be 342 tonnes. The largest emissions were estimated

for Russia (the European part of the country), contributing about 25% to European emissions, followed by Ukraine, Poland, Germany, Romania and the United Kingdom. Details of these estimates for major source categories in individual countries in Europe are available from Pacyna et al. (2001).

Combustion of coal in power plants and residential heat furnaces generates more than half of the European emissions, followed by the production of caustic soda with the use of the Hg cell process (12%). Major points of mercury emission in the mercury cell process include: by-product hydrogen stream, end box ventilation air and cell room ventilation air. This technology is now being changed to other caustic soda production technologies and further reduction of Hg emissions is expected in this connection. As much as 15% of total Hg emissions in Europe is generated during various uses of mercury, and particularly, in primary battery production, production of measurement and control instruments, and production of electrical lighting, wiring devices, and electrical switches. All of these uses of mercury are decreasing and lower emissions of Hg are expected from these sources in the future. Estimates of Hg emissions from waste incineration in Europe are relatively low (about 3%). These emissions are clearly underestimated due to the lack of reliable information on the amounts of incinerated wastes and Hg content in these wastes.

Information on the geographical location of point sources was used together with population density information as a surrogate parameter for area emission sources to obtain the spatial distribution of Hg emission in Europe. This distribution is presented in Fig. 3 on a $56 \times 56 \text{ km}^2$ grid. However, due to the lack of emission data, this figure does not include emissions from North Africa and the Middle East.

The major chemical form of mercury emitted from the anthropogenic sources in Europe to the atmosphere is Hg^0 , contributing about 205 tonnes in 1995, about 61% of the total Hg emitted. Hg^{II} contributed about 108 tonnes (about 32% of the total), and the emissions of Hg^{P} were about 25 tonnes (7% of the total). Hg^0 contributes the most to the total emissions of Hg from all source categories, except for waste disposal. In the latter case, gaseous divalent mercury is the most abundant form of Hg emitted. This is probably due to the high chlorine content in wastes which results in the formation of mercury chlorides. Details on chemical speciation of Hg emissions are available from Pacyna et al. (2001).

It should be acknowledged that more studies are needed to understand better the emission of various chemical and physical forms of Hg to the atmosphere. This information is needed for the assessment of the environmental chemistry of Hg, its transport pathways within both air masses and marine currents, cycling

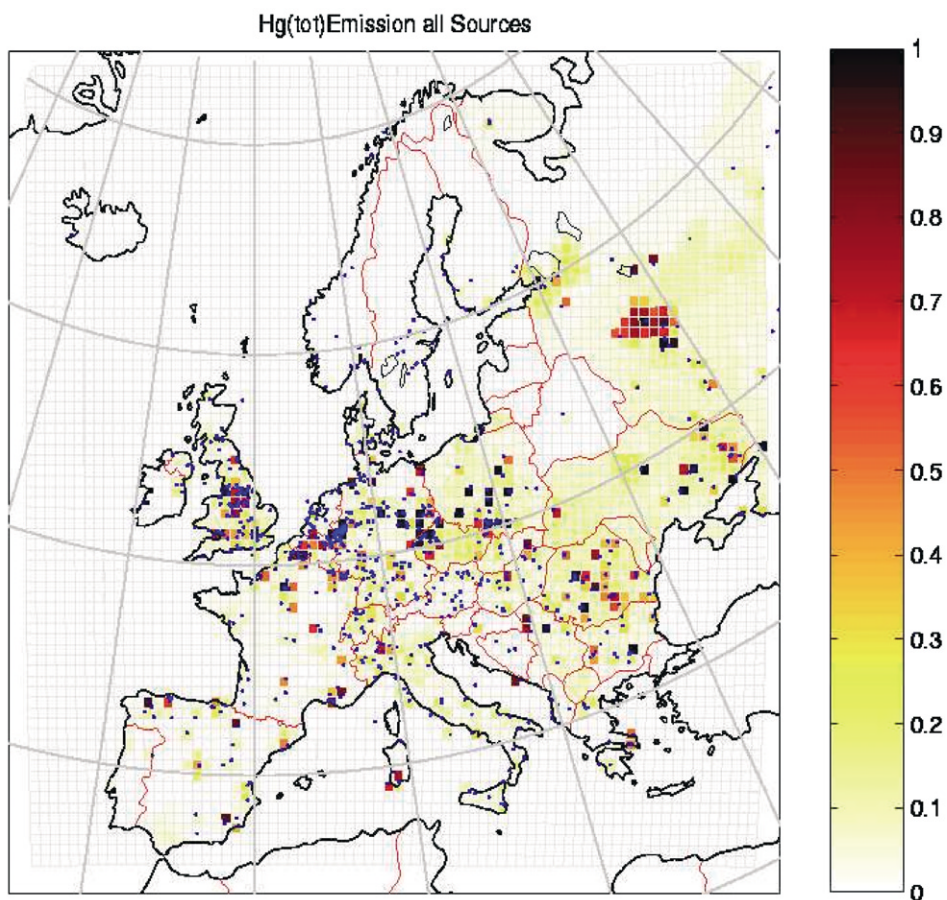


Fig. 3. Emissions of total Hg from anthropogenic sources in Europe in 1995 distributed within the EMEP grid system of 50 km × 50 km.

through different environmental compartments, and environmental and human health effects.

3.3. Integrated atmospheric measurements

During MAMCS four simultaneous two week-field campaigns were performed at five sites (see Fig. 1) located in coastal areas of the Mediterranean, one in each of the four seasons (see Table 1). The criteria adopted for selection of the sampling site locations were:

- the sites should be far from emission sources,
- linked by air mass transport,
- close to the sea shore, and
- easily accessible and close to laboratory facilities.

Three airborne mercury species, TGM, RGM and TPM were simultaneously measured at all sites using a number of different sampling and analytical techniques (see Table 2) that were evaluated in a field intercompar-

ison prior to the measurement campaigns (see Munthe et al., 2001).

Average TGM, RGM and TPM concentrations obtained during the four MAMCS campaigns, representing annual average values at the five chosen sites in the Mediterranean basin are shown in Fig. 4. At Sites 1, 4 and 5 manual gold-traps were used to determine TGM levels. A Gardis automatic TGM analyser was used at Site 3 and at Site 2 a Tekran automatic TGM analyser was employed. The RGM content of ambient air was measured using a mist chamber (MC) (Stratton and Lindberg, 1995). At Sites 2 and 3 denuders (Xiao et al., 1997) were also employed to determine RGM ambient concentrations. TGM concentrations observed at the sites in Sicily, Calabria and Israel are in good agreement with regional background concentrations observed at rural sites in Europe which are in the range of 0.8–2.3 ng m⁻³, with a mean value of 1.9±0.54, 1.4±0.34 and 1.3±0.52 ng m⁻³, respectively. Fig. 5 shows annual TGM distribution for Sites 2, 3 and 5. TGM levels observed at Palma de Mallorca (Spain) and at Anatalya

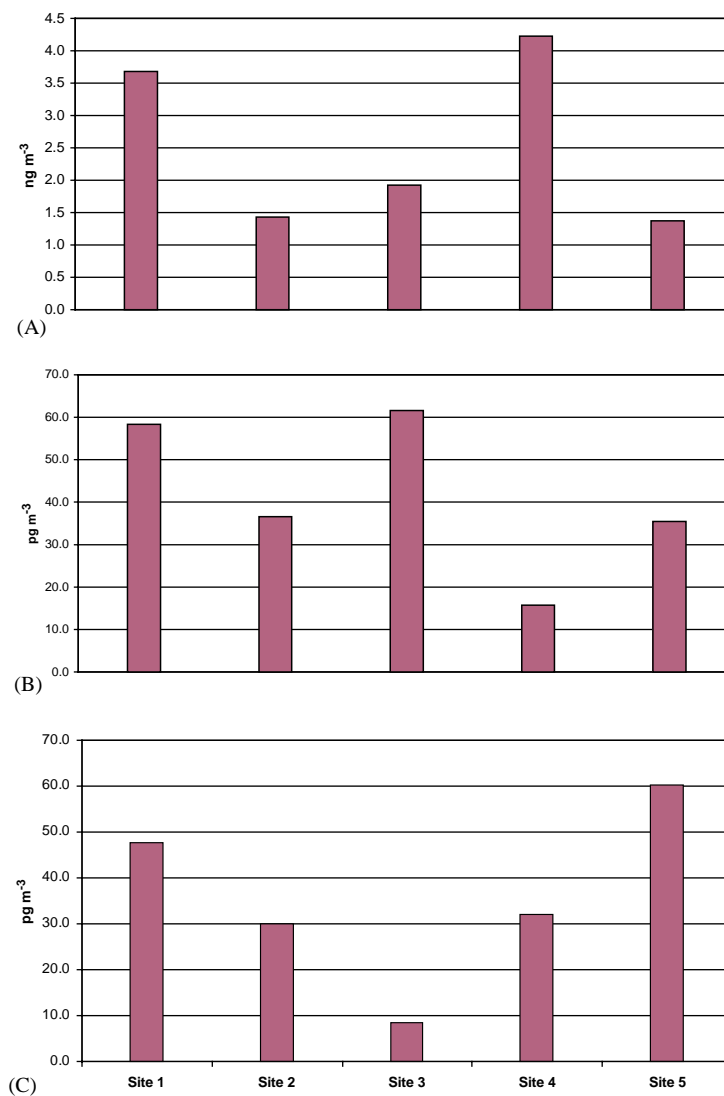


Fig. 4. Annual TGM (A), RGM (B) and TPM (C) average concentrations at MAMCS sites. Site 1 = Palma de Mallorca (Spain); Site 2 = Fuscaldo (Italy); Site 3 = Porto Palo (Italy); Site 4 = Anatolia (Turkey); Site 5 = Neve Yam (Israel).

(Turkey) sites were much higher (at Palma de Mallorca TGM concentrations were in the range of 2.4–6.19 ng m⁻³, with a mean value of 3.67 ± 0.87 ng m⁻³; at Anatolia TGM concentrations ranged from 0.86–16.48 ng m⁻³ with a mean value of 4.22 ± 4.72 ng m⁻³) suggesting the likely influence of local sources located upwind of these two sampling sites. However, it is important to point out that TGM levels in coastal areas are influenced by general atmospheric circulation which involves the transport of air pollutants from natural and anthropogenic emission sources.

The transport and the dispersion of air masses reaching the Mediterranean region have been investigated in a number of studies (Kallos et al., 1996a, 1998a)

and in MAMCS as well (Kallos et al., 2000). The results of these studies have shown that plumes (urban or industrial) located near the coast are injected almost entirely within the MBL and stay within it until they reach the southern or southeastern coast of the Mediterranean. During both the cold and warm periods of the year the general trend of the air flow is from north to south across the Mediterranean with variations in each area mainly due to differential heating between the northern and southern sides of the Mediterranean basin. Because of these flow patterns, air pollutants can be transported for long distances, especially during summer because of the lack of rain which precludes washout, affecting the air quality of areas like the North African

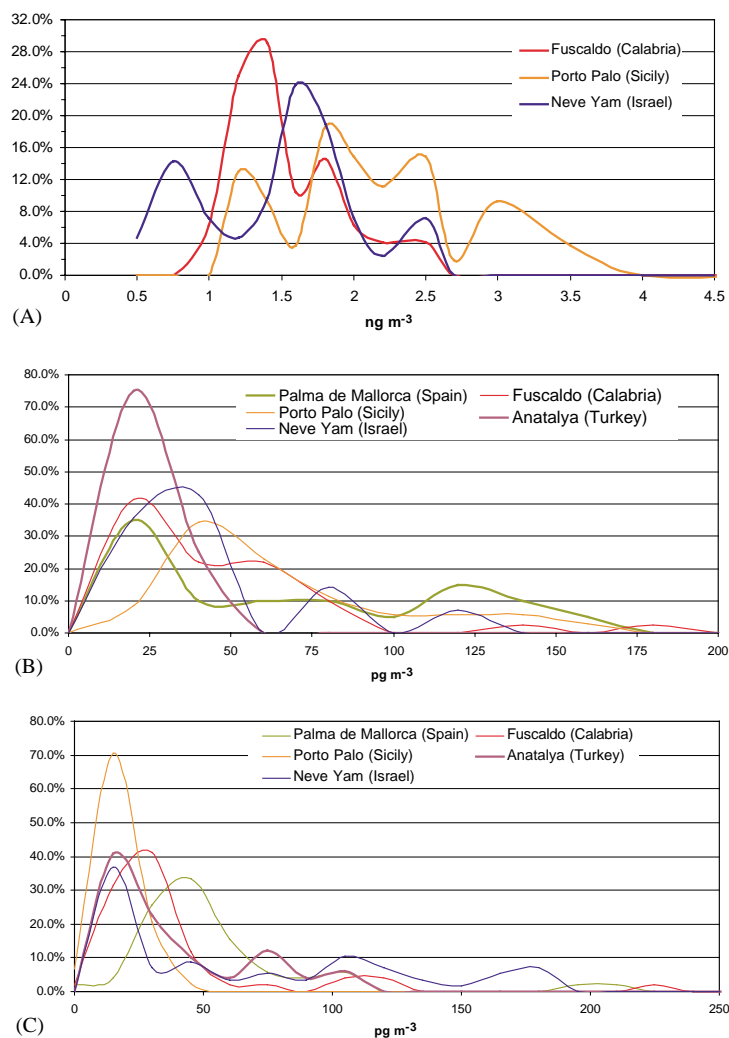


Fig. 5. Annual TGM (A), RGM (B) and TPM (C) frequency distribution at MAMCS sites during the four intensive measurement campaigns.

coast and the Middle East significantly. The higher values observed at Sites 3 and 4, in Spain and Turkey, respectively, thus could be due to influence from local sources, natural or anthropogenic, or a combination of both. A comparison between the TGM data obtained during MAMCS with that from the MED-OCEANOR project (see Sprovieri et al., 2003) suggests that Hg^0 concentrations observed over the water were higher than those observed at MAMCS sites (1, 2 and 5) and that the higher values observed during the research cruise are most likely related to elemental mercury evasion from the seawater due to chemical reduction of oxidised mercury in the top water micro-layer. Therefore, in order to assess the relative contribution of local natural sources versus anthropogenic sources it is necessary to evaluate the MAMCS data with the use of trajectory

analysis in order to assess the origin of air masses that crossed Sites 3 and 4 during the sampling periods.

With the exception of RGM concentrations measured at the Anatalya (Site-4), all measurements performed at coastal sites in the Mediterranean basin during MAMCS show higher concentrations than that over water during MED-OCEANOR. This confirms that high RGM concentrations are usually found close to emission sources, be they natural or anthropogenic, the majority of Hg compounds forming the so-called RGM are characterised by high solubility and low vapour pressure which influence the permanence of RGM in the air mass during its over-water transport and thus affects the level of RGM in the atmosphere. A preliminary trajectory analysis of air mass transport to the coastal site in Calabria (Site 2) showed that high RGM concentrations

were associated, most of the time, with air masses transported from the sea suggesting that gaseous mercury evasion from the top water micro-layer followed by the gas-phase oxidation of Hg^0 as well as by the out-gassing of HgCl_2 from aerosol particles in the MBL plays an important role in the cycling of Hg between the atmosphere and seawater. This last process is of great importance where the chloride concentration of particles is high, such as in the MBL, where sea salt aerosol predominates (Pirrone et al., 2000a; Hedgecock and Pirrone, 2001), contributing to the cycling of mercury in the marine boundary layer as a constant source of the oxidised Hg compounds (see discussion in the modelling section below).

All RGM frequency distributions for the five sampling sites show a roughly log-normal shaped form with maximum values observed around 25–35 pg m^{-3} ; also annual TPM distributions for all sites (see Fig. 5) show a more regular shaped form with maximum values around 30–40 pg m^{-3} .

A quartz glass filter trap for the sampling of TPM was used at all five sites during the campaigns. The TPM distribution is not uniform (see Fig. 5); the TPM concentrations in Sicily did not exceed 10 pg m^{-3} . This is fairly low and is comparable to remote areas above 60°N (Sprovieri and Pirrone, 2000); while higher TPM values were obtained at Neve Yam (Israel) and at Palma de Mallorca with concentrations around 70 and 50 pg m^{-3} , respectively, indicating influences from nearby sources. Results from Fuscaldo (Calabria) and Anatalya (Turkey) are relatively low with TPM concentrations around 30 pg m^{-3} . A trajectory analysis of the TPM data from Anatalya obtained during the May and July campaigns indicates that air masses entering Anatalya from the northeast and west contained high concentrations of particulate mercury. The result of the trajectory analysis was not conclusive, however. It is possible that the high TPM values observed at Anatalya are not due to one or two major sources, and the distribution may be more complex.

3.4. Atmospheric modelling

3.4.1. Chemical and physical processes in the MBL

Both measurements and modelling have improved greatly since the beginning of the MAMCS project in 1998. The presence of RGM in the MBL has by now been conclusively established and the modelling studies suggesting that this RGM derives from in situ production are very close to qualitatively reproducing diurnal variation in RGM concentrations and also variations with meteorological parameters such as relative humidity and liquid water content (LWC). Quantitative reproduction, however, which is obviously the goal of any model, is in the case of Hg not a trivial problem. The RGM concentration calculated by the photochemical

model when constrained by measured $\text{Hg}_{(\text{g})}^0$ and $\text{O}_{3(\text{g})}$ has been compared with measured data from the MED-OCEANOR project (Hedgecock et al., 2003). Two data sets were obtained, the first measurement period was during rough weather and thus there was an atmospheric LWC, using the boundary layer height as a fitting parameter the results are reasonable both qualitatively and quantitatively. The second measurement period was during much more typical and stable Mediterranean summer weather when the boundary height is around 400 m and cannot be used as a fitting parameter. The results for this period underestimate the RGM concentration by up to a factor of 2. The RGM measurements during the MAMCS project were not performed with the same sampling frequency as those in the MED-OCEANOR project as the instrumentation was not available at that time, and only 24 h averaged data is available. From this data the diurnal variation in RGM concentrations is obviously not apparent. However there is data from four different periods during the year, and it is possible to ascertain whether the photochemical model gives a consistent indication of the RGM concentration at various times of the year. Fig. 6 shows the predicted winter and summer concentrations of RGM, assuming the boundary layer is 400 m high and using an initial $\text{O}_{3(\text{g})}$ concentration of 50 ppb.

The concentrations not only very different but the pattern of the diurnal variation is different. The reason for this is that during the summer the dominant contribution to RGM comes from HgO produced by the reaction of $\text{Hg}_{(\text{g})}^0$ with $\text{OH}_{(\text{g})}$, whereas in winter when photolysis rates are slower and the daylight hours are less, OH although still important is relatively less so, and HgCl_2 produced by the reaction of $\text{Hg}_{(\text{g})}^0$ with $\text{Cl}_{2(\text{g})}$ and also by the outgassing of HgCl_2 from sea salt aerosol particles becomes the dominant contributor to RGM after day 2 of the simulation. The simulations however do not in any way reflect the concentrations of RGM measured during the winter and summer campaigns of the MAMCS project. The average RGM values measured (of all the Mediterranean measurement sites) were 31.5 ± 39.2 , 40.4 ± 43.0 , 52.3 ± 43.9 and 32.3 ± 17.8 pg m^{-3} for the November, February, May and July campaigns, respectively. Even if there is some doubt about the accuracy of the techniques used it is quite clear that the seasonal variation predicted by the model is not seen. The model therefore would appear to have two problems: it underestimates the summer RGM concentrations by a factor of two even using measured $\text{Hg}_{(\text{g})}^0$ and $\text{O}_{3(\text{g})}$ data (Hedgecock et al., 2003), and predicts a much lower winter than summer RGM concentration, which is not borne out by experiment.

Unfortunately, all the known chemistry of Hg in the atmosphere has been included in the model. There is a strong current of opinion that one or perhaps more gas-phase bromine containing radicals is involved in the

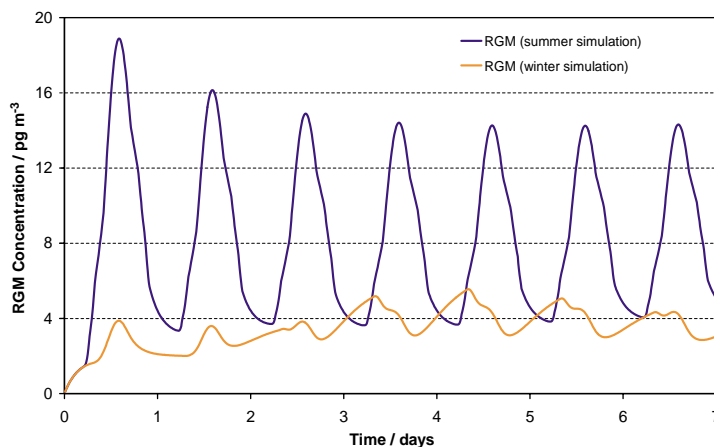


Fig. 6. The simulated concentration of RGM in the Mediterranean over 7 days from the 14th June (summer) and the 14th December (winter).

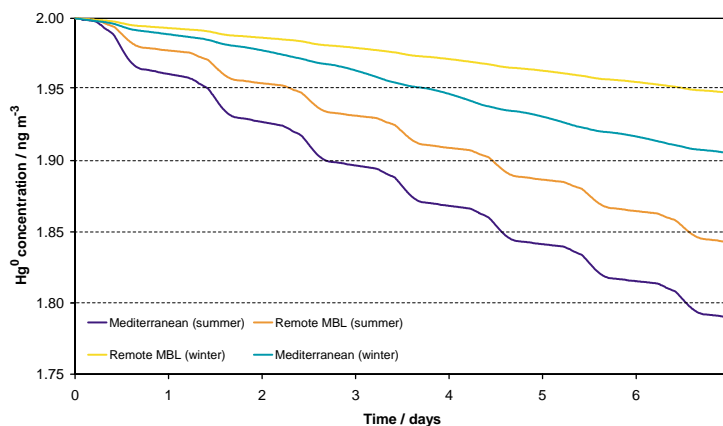


Fig. 7. The decrease of the gas phase Hg^0 concentration for four different marine scenarios, assuming there is no replenishment.

$\text{Hg}_{(\text{g})}^0$ depletion seen in the Arctic troposphere around polar dawn. If BrO were found to be an important atmospheric oxidant for Hg^0 it could explain both the problems with the model. A photolytically derived radical oxidant would increase the nighttime production rate of RGM whilst having little or no influence on the daytime rate, which is quantitatively what the model lacks, and BrO because its major loss pathway in the atmosphere is reaction with HO_2 , is actually more abundant in the MBL in the winter than in the summer, due to slower O_3 photolysis in the winter. Thus BrO would have most effect on the RGM concentration in the winter and during daytime. Given the uncertainty in the RGM production mechanism it is only possible to establish a maximum (from known chemistry) destruction rate for $\text{Hg}_{(\text{g})}^0$ in the MBL. Fig. 7 shows the results of model calculations of the $\text{Hg}_{(\text{g})}^0$ concentration for winter and summer in both the remote MBL and the

Mediterranean. The Mediterranean, because the height of the boundary layer (≈ 400 m) is lower than that of the remote MBL (≈ 1000 m), has a more rapid turnover of Hg^0 , with roughly 10% of the Hg^0 being oxidised in 7 days.

From this brief description of the modelling of the processes affecting Hg in the MBL the next steps necessary in model development, kinetics studies and campaign planning have become clear. It is extremely important that the missing oxidation reaction or reactions be identified and upper and lower limits on reaction rates established. The possible variation in RGM concentrations with height in the MBL as relative humidity and particle acidity change is a question which can be addressed both experimentally using aerial measurement campaigns and using modelling studies. Still on the subject of measurement campaigns it is now clear that without knowledge of O_3 concentrations,

relative humidity and an indication of insolation (for photolysis rates) it is well nigh impossible to distinguish between RGM produced in situ and that transported from emission sources. One last process which needs to be addressed is the general stability of the Hg^0 background concentration. The model shows that the Hg^0 concentration would diminish with distance from its source, which measurements show is not the case, in fact the Hg^0 concentration is remarkably constant on a hemispherical scale. Therefore Hg^0 is replenished by exchange with the free troposphere and/or emission from the ocean. If the only source were ocean emissions this would imply a minimum average emission rate of $0.9 \text{ ng m}^{-2} \text{ h}^{-1}$ in the remote MBL during the summer, which given the area of the earth's surface covered by oceans would make the oceans a major area source of atmospheric Hg.

3.4.2. Atmospheric transport and deposition

One of the most significant questions addressed in the MAMCS project was whether and how atmospheric mercury is transported long distances before deposition. This is important since mercury enters the aquatic and terrestrial ecosystems through the deposition processes. The previous discussion revealed that single-site measurements are not adequate for the understanding of the sources of the observed mercury concentrations. 3D numerical modelling of the mercury cycle using full-physics models is most appropriate way to understand mercury transport, transformation and deposition.

The wet and dry deposition patterns of Hg^{P} , Hg^{II} and Hg^0 adsorbed (Hg which is reversibly bound to particulate matter, unlike Hg^{P} which is irreversibly bound) are discussed in this section. The summer and winter experimental campaigns were simulated in 17 day runs. The wet and dry accumulated depositions of the three mercury species for the summer and winter simulations are presented in Figs. 8 and 9, respectively.

The solubility of Hg^{II} and the scavenging of Hg^0 adsorbed and Hg^{P} mean that scavenging by water droplets is the most efficient removal pathway of atmospheric mercury. This is clearly illustrated in the wet deposition patterns shown in Figs. 8d–f, 9d–f. The highest levels of wet deposition are predicted to be over mountainous areas, such as the Alps, the Atlas mountains, the Pyrenees, and the mountains of Greece and eastern Turkey, as expected due to the higher precipitation usually occurring there.

The dry deposition patterns of the three mercury species exhibit large differences. Divalent gas mercury is known to deposit rapidly (Lindberg and Stratton, 1998) since it has a high deposition velocity. In agreement with the literature (Schroeder and Munthe, 1998) the highest amounts of Hg^{II} are dry-deposited near the sources (Figs. 8b and 9b). The dry deposition patterns of Hg^{P} (Figs. 8c and 9c) exhibited larger values over the sea,

especially downstream in the Mediterranean basin, than over land despite the fact that all anthropogenic sources are located on land. This is due to the dependence of the deposition velocity of Hg^{P} particle size. The dominant feature is the existence of maximum values over the eastern Mediterranean implying the transport of particulate mercury from continental Europe towards the eastern Mediterranean. This is in agreement with the well-defined transport paths in the eastern Mediterranean (Kallos et al., 1996a, b, 1998a, b).

The dry deposition pattern of Hg^0 adsorbed shows a marked seasonal variation (Figs. 8a and 9a). The dry deposition patterns also vary significantly over sea and over land. Higher values are observed over the sea during the rainy season. These dry deposition patterns can be attributed firstly to the prevailing flow and turbulence conditions at the region, and secondly to the size of the particles. Relatively strong northwesterly and northerly flow was evident over Central and North Europe during the winter simulation period. The above-described atmospheric circulation favoured the increase of mercury concentration over the Mediterranean Region.

In conclusion the Mediterranean Sea region is not only affected by mercury released in its vicinity but also from air masses enriched in mercury from regions of northern and northeastern Europe. This suggests that local and remote sources must be taken into account in mercury studies in the Mediterranean. This is particularly important for particulate and elemental mercury that can be transported far from the sources before deposition.

3.5. Final remarks

The integrated approach followed within the framework of MAMCS project showed that the complexity of Hg cycling is becoming more apparent all the time. More specifically, the atmospheric processes involved in Hg transport from emission source to receptor locations is strongly influenced by the emission types and characteristics, the prevailing meteorological conditions of various scales and the photochemistry occurring within the air masses as they are transported. It is predominantly the rapidity with which Hg^0 is taken up by particles or oxidised in the gas phase and then scavenged by particles, droplets or dry deposited which influence the long range transport of Hg.

The points listed below summarise the further work which is required to be able to characterise the relationship between emissions and spatial patterns of ambient concentrations and deposition fluxes of mercury and its species with greater accuracy:

- There is a strong need to promote measurement programs to assess the level of mercury and its

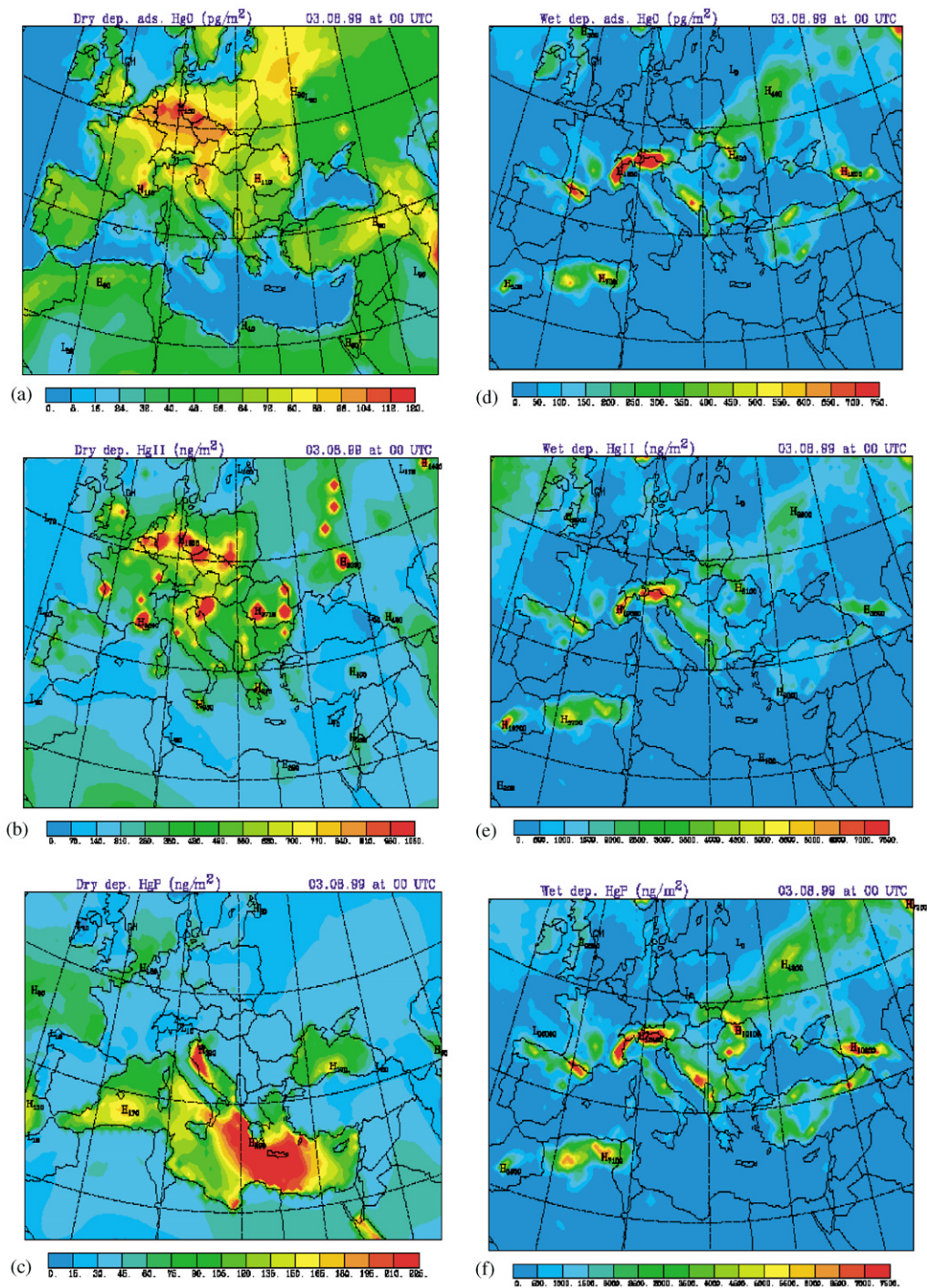


Fig. 8. Total deposition of Hg species for the time period 17 July–3 August 1999. (a) Dry deposition of adsorbed Hg⁰ (pg m⁻²), (b) dry deposition of Hg² (pg m⁻²), (c) dry deposition of Hg^P (pg m⁻²), (d) wet deposition of adsorbed Hg⁰ (pg m⁻²), (e) wet deposition of Hg² (pg m⁻²), and (f) wet deposition of Hg^P (pg m⁻²). From the MAMCS modelling framework based on SKIRON/Eta model.

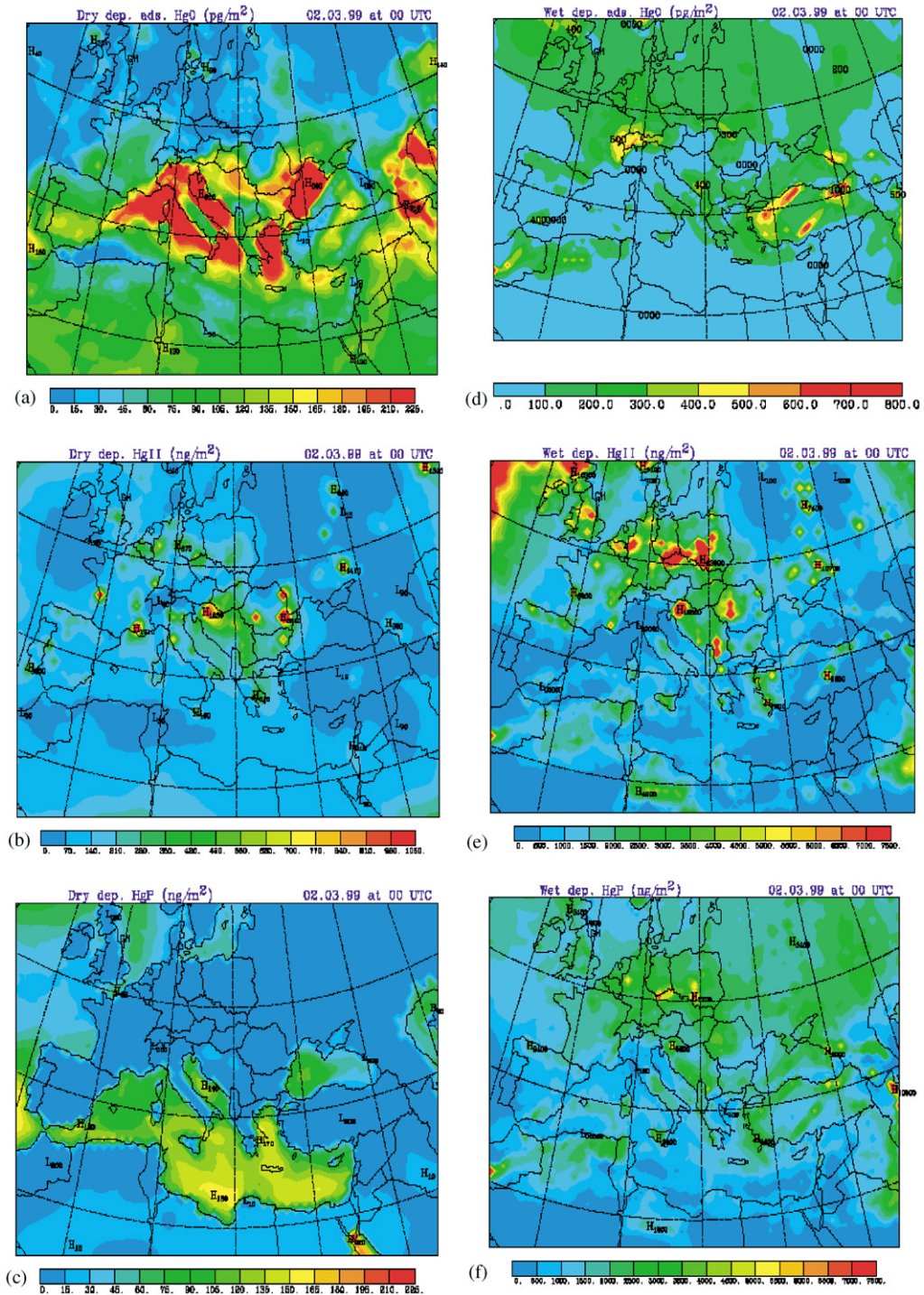


Fig. 9. Total deposition of Hg species for the time period 13 February–2 March 1999. (a) Dry deposition of adsorbed Hg⁰ (pg m⁻²), (b) dry deposition of Hg² (pg m⁻²), (c) dry deposition of Hg^P (pg m⁻²), (d) wet deposition of adsorbed Hg⁰ (pg m⁻²), (e) wet deposition of Hg² (pg m⁻²), and (f) wet deposition of Hg^P (pg m⁻²). From the MAMCS modelling framework based on SKIRON/Eta model.

compounds (Hg^0 , Hg^{II} and particulate Hg) on a European scale and at major urban, industrial and remote sites.

- In order to reduce the uncertainty associated with ambient measurements and assure data comparability at European level, there is a strong need to develop standard methods for assessing the Hg^0 , Hg^{II} and particulate Hg concentrations in ambient air.
- An improved mercury emission inventory for major anthropogenic sources, possibly on a $0.5 \times 0.5^\circ$ spatially resolved grid including North Africa and the Middle East regions along with speciation at the stack, is necessary.
- Our preliminary investigation performed in MAMCS showed that the sea salt aerosol and sea spray formation play a major role in cycling of mercury and its compounds in the MBL and thus affect its deposition to marine waters.
- The improvement of mesoscale and regional scale models are very much related on the future progress of kinetic studies to assess the interaction of gas-phase mercury and halogen containing radicals.
- A number of preliminary modelling studies performed in MAMCS and other research programmes have highlighted the need of accounting for the time-dependent vertical profile of Hg^0 concentrations at the model inflow boundaries. Meanwhile advanced hemispherical/global models would contribute to improve modelling capability by providing a better assessment of the boundary conditions on a regional scale.
- One of the major source of uncertainty in mesoscale and regional scale mercury modelling is the lack of knowledge of the mechanisms controlling the exchange fluxes of gaseous mercury at the air–water, air–soil and air–vegetation interfaces with changing meteorological conditions, geophysical parameters and the occurrence of biotic and abiotic processes in the top-water micro-layer that may affect the exchange of gaseous mercury between surface water and lower atmosphere.

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