İSTANBUL TECHNICAL UNIVERSITY ★ EURASIA INSTITUTE OF EARTH SCIENCES

**LONG-RANGE AEROSOL TRANSPORT FROM
EUROPE TO ISTANBUL, TURKEY**

**Ph.D. Thesis by
Tayfun KINDAP, M.Sc.**

Department : Climate and Marine Sciences

Programme: Earth System Science

MARCH 2005

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Supervisor : Prof. Dr. Mehmet KARACA

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ AVRASYA YER BİLİMLERİ ENSTİTÜSÜ

**AVRUPA KAYNAKLI AEROSOLLERİN ÜLKEMİZE
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**DOKTORA TEZİ
Y. Müh. Tayfun KINDAP**

Tez Danışmanı: Prof.Dr. Mehmet KARACA

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Istanbul
January 5, 2005

FOREWORD

Northern and western parts of Turkey frequently experience air pollution episodes. Transport of air pollutants from Europe to these regions has not been studied sufficiently. This study aims to identify and analyze the contribution of long range aerosol transport to air pollution in the city of Istanbul, Turkey. At the end of this study, a significant impact of Eastern European emissions to PM10 concentrations in Istanbul has been demonstrated clearly. It is worth to not that a study of this magnitude had never been carried out before for Turkey. Besides studying qualitative and quantitative of long range PM10 transport from Europe to Turkey, this study gave a chance to see the deficiency of air quality modeling and management in Turkey. Difficulties and absences which were faced during the study provided a comprehensive overview of air quality in Turkey.

January, 2005
Istanbul

Tayfun KINDAP

TABLE OF CONTENTS

TITLE PAGE	ii
ACKNOWLEDGMENTS	iii
FOREWORD	v
TABLE OF CONTENTS	vi
ABBREVIATION	viii
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF SYMBOLS	xv
ABSTRACT	xvi
ÖZET	xx
1. INTRODUCTION	1
2. LITERATURE REVIEW	9
3. METEOROLOGICAL MODELING	35
3.1. Modeling System	36
3.1.1. Terrain	36
3.1.2. Regrid	37
3.1.3. Objective Analysis (Little_r)	38
3.1.4. Setting the Initial and Boundary Conditions (Interpf)	38
3.1.5. MM5	38
4. EMISSION MODELING	40
4.1. Atmospheric Emission Inventory Methodology	41
4.2. Modeling System	46
4.2.1. Antropogenic Emission Processes	48
4.2.2. Biogenic Emission Processes	49
5. CHEMISTRY AND TRANSPORT MODELING	50
5.1. Modeling System	51
5.1.1. The Initial Concentration and Boundary Condition Processors	53
5.1.2. Photolysis Rates for CMAQ (JPROG)	53
5.1.3. Meteorology-Chemistry Interface Processor (MCIP)	54
5.1.4. Emissions	55
5.1.5. Chemistry	55
6. CASE STUDY	57
6.1. Pollution Episodes	58
6.2. Overview of the Air Quality Modeling System	60
6.2.1. Meteorological Model Setup	60

6.2.2. Emission Model Setup	64	
6.2.2.1. Modeling of Anthropogenic Sources	64	
6.2.2.1.1. Import Gridded Anthropogenic Inventory Data	65	
6.2.2.1.2. Speciation	70	
6.2.2.1.3. Temporal Allocation	71	
6.2.2.1.4. Vertical Layer Distribution	73	
6.2.2.2. Modeling of Biogenic Sources	74	
6.2.2.2.1. Imported Land-Use Data	79	
6.2.2.2.2. Meteorology (T & PAR)	80	
6.2.2.2.3. Estimation of Hourly Data	80	
6.2.2.2.4. Speciation	88	
6.2.2.3. Other Natural Sources	89	
6.2.2.4. Merge	94	
6.2.3. Chemistry Transport Model Setup	95	
7. RESULTS		97
7.1. Meteorological Model		97
7.1.1. Model Performance	98	
7.1.2. Backward Trajectories Results	103	
7.1.3. Tracer Simulation Results	103	
7.2. Emission Model		112
7.2.1. Anthropogenic Model	112	
7.2.2. Biogenic Model	117	
7.2.3. Model Performance	117	
7.3. Chemistry Transport Model		122
7.3.1. Model Performance	122	
7.3.2. Sensitivity Analysis (Brute Force)	126	
8. CONCLUSIONS AND FUTURE STUDIES		133
REFERENCES		138
APPENDICES		162
CURRICULUM VITAE		183

ABBREVIATIONS

ADOM	: The Acid Deposition and Oxidant Model
ADEME	: Agence de l'Environnement et de la Maîtrise de l'Energie
AEP	: The Anthropogenic Emissions Process
AGRICE	: Agriculture pour la Chimie et l'Energie
ALD2	: Acetaldehyde
ATDL	: Atmospheric Turbulence and Diffusion Laboratory
AQM	: Air Quality Model
BCON	: Boundary Condition Processors
BEIS	: The Biogenic Emission Inventory System
BEMA	: The Biogenic Emissions in the Mediterranean Area
BS	: Black Smoke
BVOC	: Biogenic Volatile Organic Compound
CALGRID	: The California Grid Model
CALMET	: CALMET
CB4	: The Carbon Bond-IV photochemical mechanism
CB4_AE_AQ	: The CB4 gas-phase mechanism with AErosol and AQueous Chemistry
CCTM	: The CMAQ Chemistry Transfer Model
CLRTAP	: Convention on Long-Range Transboundary Air Pollution
CMAQ	: The Community Multiscale Air Quality Modeling System
CNTL	: Control
CO	: Carbon Monoxide
CO2	: Carbon Dioxide
CORINAIR	: CO-ordination d'Information Environnementale
DEHM	: The Danish Eulerian Hemispheric Model
DEM	: Digital Elevation Models
ECF	: Environmental Correction Factors
ECODEV	: Recherche Interdisciplinaire sur les Technologies pour Ecodéveloppement
EEM	: EURAD Emission Model
EFTA	: European Free Trade Association
EME	: The Emission Modeling for Europe
EMEP	: The European Monitoring and Evaluation Program
EMEP/CCC	: Chemical Co-ordinating Centre of EMEP
EMIMA	: Global Emission Modeling
EMIMO	: EMission MOdel
ESCOMPTE	: Realisation of Field Exp. to Const. Models of Atm. Poll.and Emis. Trans.
ETH	: Ethene

EU	: The European Union
EURAD	: The European Air Pollution Dispersion Model
EURAD-CTM	: EURAD Chemistry Transport Model
FCCC	: The Framework Climate Change Convention
FORM	: Formaldehyde
GDAS	: Global Data Assimilation System
GENEMIS	: The Generation and Evaluation of Emission Data
GIS	: Geographic Information System
GLOREAM	: GLObal and REgional Atmospheric Modeling
HIRLAM	: Danish Meteorological Institute. The operational DMI-HIRLAM system
ICON	: The Initial Concentration
IER	: Institut für Energiewirtschaft und Rationelle Energieanwendung
IIASA	: International Institute for Applied Systems Analysis
IPCC	: Intergovernmental Panel on Climate Change
I/O API	: Input/Output Applications Programming Interface
ISOP	: Isoprene
JPROG	: Photolysis Rates for CMAQ
LAI	: Leaf Area Index
LRTAP	: The Long Range Trans-boundary Air Pollution
MATCH	: Multi-scale Atmospheric Transport and Chemistry Model
MATCH-MPIC	: Model of Atm. Trans.and Chem., Max Planck Ins.for Chem.Version 3.0
MCIP	: Meteorology Chemistry Interface
MCNC	: Microelectronics Center of North Carolina
MCNC-SMOKE	: Microelectronics Center of North Carolina Sparse Matrix Ope. Ker. Emis.
MINOS	: The Mediterranean INTensive Oxidant Study
MM5	: Mesoscale Meteorological Model
MONO	: Monoterpenes
MRF	: The Medium Range Forecast
MSA	: Methanesulphonate
N₂O	: Nitrous Oxide
NAO	: The North Atlantic Oscillation
NCAR	: National Center for Atmospheric Research
NCEP	: The National Centers for Environmental Prediction
NE-OPS	: The Northeast-Oxidant and Particle Study
NH₃	: Ammonia
NMVOC	: Non Methane Volatile Organic Compounds
NO	: Nitric Oxide
NO₃	: Nitrate Radical
NOAA	: National Oceanic and Atmospheric Research
NO_x	: Nitrogen Oxides
NR	: Non-Reactive carbon atoms
O₃	: Ozone
OH	: Hydroxyl Radical
OLE	: Olefin

OVOC	: Other Volatile Organic Compounds
PAR	: Paraffin
PBL	: Planetary Boundary Layer
PM	: Particulate Matter
PORG	: The United Kingdom Photochemical Oxidants Review Group
PRQA	: Regional Planning for Air Quality Management in Alsace
PEGASUS	: PNNL Eulerian Gas and Aerosols Scalability Unified System
PELCOM	: Pan-European Land Use and Land Cover Monitoring
PNNL	: The Pacific Northwest National Laboratory
QA/QC	: Quality Assurance/Quality Check
RADM	: The Regional Acid Deposition Model
RAINS	: Regional Air Pollution Information and Simulation
RELMAP	: The Regional Lagrangian Modeling of Air Pollution model
ROM	: The Regional Oxidant Model
RRTM	: The Rapid Radiative Transfer Model
SATURN	: Studying Atmospheric Pollution in Urban Areas
SCAQS	: The Southern California Air Quality Study
SMOKE	: Sparse Matrix Operator Kernel Emissions
SO₂	: Sulfur Dioxide
SO₄₂₋	: Sulfate
SOA	: The Secondary Organic Aerosol
SO_x	: Sulphur Oxides
STEM	: The Sulfur Transport and Emissions Model
TAPOM	: The Transport and Air Pollution Model
TFS	: The German Tropospheric Research Program
TNO	: Netherlands Organization for Applied Scientific Research
TOL	: Toluene
TSP	: Total Suspended Particulate
UAM	: Urban Airshed Model
UNECE	: United Nations Economic Commission for Europe
USEPA	: The U. S. Environmental Protection Agency
USGS	: The U.S. Geological Survey
WHO	: The World Health Organization
XYL	: Xylene
VI	: Vegetations Index

LIST OF TABLES

	<u>Page No</u>
Table 1.1. Comparison of ambient particle fractions adapted from Wilson and Suh (1997)	2
Table 1.2. General descriptions of PM emissions and source types adapted from NARSTO (2004)	4
Table 6.1. Sectors of Anthropogenic Emissions	66
Table 6.2. Specified anthropogenic emissions for each sector	72
Table 6.3. Vertical Distribution of Anthropogenic Emissions: Percentage of each sector allocated to the vertical layers of the air quality model (given as heights of layers, in meters)	73
Table 6.4. Estimated Global Annual Biogenic VOC Emissions (Tgyr^{-1}) from Guenther (1999)	77
Table 6.5. Description of 24-category (USGS) land-use categories	81
Table 6.6. Default foliar biomass densities (adapted from Veldt, 1989)	86
Table 6.7. Leaf biomass, winter biomass factor and flux values according to BEISS	87
Table 6.8. Winter biomass factor and flux values according to European Forest features	88
Table 6.9. Specified biogenic emissions for vegetation sector	89
Table 7.1. Istanbul PM10 response to 50% change in all emissions after 5-day simulations. Brute force sensitivity analyses results give quantitative information about each country or regional base responses to Istanbul	127

LIST OF FIGURES

	<u>Page No</u>
Figure 1.1 : Illustrative transport scales for PM and other atmospheric pollutants adapted from NARSTO (2004)	3
Figure 1.2 : General model data flow chart for the modeling system	8
Figure 3.1 : The MM5 modeling system flow chart	37
Figure 3.2 : Observation Stations located in related domain	39
Figure 4.1 : The EME modeling system flow chart	49
Figure 5.1 : Inputs and outputs of CMAQ photochemical air quality model and related modeling tools, and the model interactions	52
Figure 6.1 : Time series of aerosol mass concentration (PM10) measured on the Besiktas, Sarachane and Alibeykoy observation stations in Istanbul during the January, 2002.....	59
Figure 6.2 : Time series of measured PM10 concentration at Umraniye, Uskudat, Besiktas, and Sarachane observation stations in Istanbul from 00 UTC 5 to 00 UTC 12 January, 2002	60
Figure 6.3 : Temporal revolution of simulated wind vectors at 900 mb on (a) 8th of January, 2002, 00.00 UTC and (b) 10th of January, 2002, 00.00 UTC	61
Figure 6.4 : General model data flow chart for the modeling system	61
Figure 6.5 : MM5 –TERRAIN model domain cover area	62
Figure 6.6 : MM5-TERRAIN dominant vegetation/land-use maps. Colors indicate each land use type	63
Figure 6.7 : The Flowchart of Anthropogenic Emission Data Processes (AEP)	65
Figure 6.8 : Biogenic Emission Data Processes	80
Figure 6.9 : Effect of light on isoprene emission rate from (a) aspen leaf and (b) velvet bean leaf (adapted from Monson et al., 1992; and Fall, 1999)	85
Figure 6.10 : Effect of willow leaf temperature on isoprene emissions rate (adapted from Fall and Wildermuth, 1998; and Fall, 1999)	85
Figure 6.11 : CMAQ model domains	95
Figure 6.12 : Vertical structure of CMAQ model. The troposphere is represented in the model by 20 σ layers. Sigma values for the boundaries of each level are shown on the left hand side of the figure. The corresponding height above the ground, computed for a standard atmosphere, is given on the right-hand side	96
Figure 7.1 : (a) and (b) are observed (dashed lines) and 168-h MM5 simulated (solid lines) 10-m winds (a full barb equals 10 knots and half a barb equals 5 knots) for Gokceada and Malkara	

	meteorology stations, respectively. (c), Gokceada, and (d), Malkara, are the same information but for 2-m temperature (°C)..	98
Figure 7.2	: Observed (dashed lines) and 168-h MM5 simulated (solid lines) 10-m winds (a full barb equals 10 knots and half a barb equals 5 knots) and 2-m temperature (oC) for Kirecburnu meteorology station	99
Figure 7.3	: The study area comprising Gokceada, Malkara and Kirecburnu meteorological stations	100
Figure 7.4	: ECMWF analysis (a-c-e) and MM5 model (b-d-f) simulation sea level pressure maps	101
Figure 7.5	: MM5 model simulated sea level pressure, 850 mb temperature and horizontal wind vector in panel (a) and ECMWF analysis panel (b). MM5 model simulated 500 mb geopotential height and horizontal wind vector in panel (c) and ECMWF analysis in panel (d)	102
Figure 7.6	: Two sets of model-generated backward trajectories calculated over (a) a 36-hour period and (b) a 21-hour period respectively ...	103
Figure 7.7	: Simulated tracers and wind vectors at the 980 mb surface after (a) 12-h and (b) 48-h simulations. The tracers were released at the initial time of 0000 UTC January 5, 2001 from five different cities. (c) and (d) show the same fields as those in (a) and (b), respectively, except that (c) is 18-h instead of 12-h simulation and the initial time is at 1200 UTC January 7 2001	105
Figure 7.8	: 24 h forecast from EXP1, showing sea level pressure (shaded; hPa), 1.5-km potential temperature (solid lines; K), and 950-mb wind vectors at 00 UTC 6 January, 2002. Large dot indicates the location of Istanbul	107
Figure 7.9	: Simulated tracers and wind vectors at the 100 m height at (a) 48-h simulation from EXP1 and (b) 54-h simulation from EXP2. Tracers from Bucharest (dashed lines; 0.05 unit of interval) and Plovidiv (solid lines; 0.1 unit of interval) are released during the 2nd day and from Silesia and Krakow (shaded) are released during the first 2 daysBiogenic Emission Data Processes	108
Figure 7.10	: Vertical cross-sections of simulated tracers below 3 km along the lines AB and CD in Figs. 7.9a and 7.9b for (a) EXP1 and (b) EXP2, respectively	109
Figure 7.11	: Total accumulated rainfalls (mm) at 00 UTC 7 January, 2002 from EXP1	110
Figure 7.12	: PM10 and PM2.5 emission distribution map based on the polar stereographic projection	115
Figure 7.13	: PM10 and PM2.5 emission distribution map which is converted to the Lambert Conformal projection from the Polar Stereographic Projection	116
Figure 7.14	: Gridded EME emission output data (Example)	118
Figure 7.15	: Gridded EME emission output data. Examples for NH3 (a), NOx (b), SOx (c) and CO (d)	119
Figure 7.16	: Isoprene emission distribution map according to biogenic	

	emission modeling (Example)	120
Figure 7.17	: Time series of PM10 (g/s) at Istanbul Grid: 76-35 according to the emission model	121
Figure 7.18	: Time evaluation of PM10 concentration from observation (plain line) and model simulated result from base case at Besiktas (line with open circle) and Sarachane (line with filled triangle) stations in Istanbul	122
Figure 7.19	: Origins and types of uncertainty present in Photochemical Air Quality Simulation	124
Figure 7.20	: PM10 emission distribution maps for (a) January 5, 2002 20:00 (b) January 6, 2002 20:00 (c) January 7, 2002 20:00 (d) January 8, 2002 20:00 (e) January 9, 2002 20:00 (f) January 10, 2002 20:00 according to CMAQ model results	125
Figure 7.21	: Time evolution of PM10 concentration in Istanbul, Turkey during simulation period. (a) to (e) are experiments with an increase of 50% anthropogenic emissions for Romania, Bulgaria, Poland, Ukraine, and Russia, respectively. The light gray area indicates the PM10 result from the base case and dark gray indicates the discrepancy of each experiment from the base case..	129
Figure 7.22	: Total emission values in a country base. According to EMEP data base; CO, NH3, NOx, SOx, NMVOC and PM10 pollutants has been considered	130
Figure 7.23	: Time evolution of PM10 concentration in Istanbul, Turkey during simulation period. (a) to (b) are experiments with an increase of 50% anthropogenic emissions for Regional and Regional + Turkey respectively. The light gray area indicates the PM10 result from the base case and dark gray indicates the discrepancy of each experiment from the base case	133

LIST OF SYMBOLS

ε	: The average emission potential ($\mu\text{g g}^{-1} \text{h}^{-1}$) for any particular species
D	: The foliar biomass density (g dry weight foliage m^{-2})
γ	: A unit-less environmental correction factor representing the effects of short-term (e.g. hourly) temperature and solar radiation changes on emissions
T	: Temperature
T_s	: Soil temperature
C_L	: Light dependent factor
C_T	: Temperature Dependant Factor
R	: The gas constant

LONG-RANGE AEROSOL TRANSPORT FROM EUROPE TO ISTANBUL, TURKEY

ABSTRACT

It is a fact that airborne particles bring about more health problems and more visibility degradation than do gases. Especially, obvious connection between high levels of particles pollution and day-to-day excessive mortality attract attention of researchers. At this point, urban areas where extremely high levels of particulate matter (PM) are observed might be given priority to be investigated immediately. Although urban areas are responsible, to some extent, for their own poor air quality, long-distance man-made sources could significantly contribute to urban pollution. As a result of this, long-range aerosol transport can be just as important as the local sources. Considering the importance of long range transport, understanding its significance is critical before taking any action or making any policy on air quality.

Long-range transport of air pollutants has generally been studied in Europe under the framework of the European Monitoring and Evaluation Program (EMEP). As the results of these studies show, long-range trans-boundary transport is responsible for a significant fraction of the particulate pollution in European cities as well as in rural areas (EMEP-WMO, 1999). Anthropogenic sources are dominant in Europe because of the urbanization of many countries and the large number of vehicle and combustion sources (industrial and residential). The industrial activity, the high volumes of traffic and the urbanization of the Continent of Europe had as a result the anthropogenic sources of PM to be predominant, mainly in urban areas (EMEP/CCC-Report, 1999). Recently there has been extensive research and several regulations have been issued on PM focused air pollution mainly because of severe public health risks for susceptible members of the population, as well as visibility reduction and damages to sensitive ecosystems in Europe. These studies have indicated a significant association between the long-range

component of PM and a wide range of health damaging effects (EMEP/CCC-Report, 1999).

Compositions, morphology, physical and thermodynamic properties of aerosols vary between geographical places and seasons (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998; Alpert and Hopke, 1981). The studies have shown that in Northwestern Europe, PM₁₀ concentrations between urban and non-urban areas do not exceed 20% (e.g. Van Der Zee et al., 1998). Furthermore, a number of studies on wintertime concentrations of PM₁₀ and black smoke in 14 urban and 14 non-urban locations in Europe indicate a relatively small difference between urban and rural sites (Hoek et al., 1997). Similar observations on the regional character of PM are reported also in United States (EPA, 1996). This can be attributed to high emissions from a dense population area, the small weather variability between the measurement sites and the importance of long-range transport of air pollutants.

Long-range transport of PM has also been studied intensively in Southern Scandinavia (Pakkanen et al., 1996; Lannefors et al., 1983; Amundsen et al., 1992). Air masses originating from the British Isles, Central and Eastern Europe were mainly responsible for the long range transport of pollution such as sulphur. Other studies show that long-range CO transport from both Western and Eastern Europe, mostly from fossil fuel use, contributes 60 to 80% of the boundary-layer CO over the Mediterranean (J. Lelieveld et al. 2002). Hacısalıhoğlu et al. (1992) showed that during a field experiment near the Black Sea, 70% of the mean concentrations of various pollutants have originated from Western and Central Europe. Sciare et al. (2003) found major aerosol contribution of Central Europe to the Mediterranean region which was confirmed in terms of anthropogenic emissions.

Sometimes unexpected poor air conditions are observed in the west and northwest of Turkey, and the high pollutants over western Turkey are suspected to be transported from other countries. Because of the wide range of sources of particulate pollution, it is very difficult to determine the origins of particulate pollution episodes for northern and western Turkey. It has become clear in recent years that the most severe particulate matter episodes are accompanied by westerly winds. The possible flow on the east of the

Carpathian Mountains is channeled over the Black Sea, the Marmara Sea, and the Aegean Sea. Under this situation, Istanbul, which is located in the northwest of Turkey, is open to be exposed to long-range air pollution originating from European countries. For example, extremely poor air quality was observed between January 5 and January 12, 2002 in Istanbul. According to the observations from monitoring sites which are operated by the Istanbul Metropolitan Municipality, the peaks of 24-h PM₁₀ (Particulate Matter with aerodynamic diameter less than 10 μ m) level exceeded the World Health Organization (WHO) standard of 60 μ g/m³ and U.S. Environmental Protection Agency (EPA) standard of 150 μ g/m³ (24-hour average). Peaks of hourly PM₁₀ concentrations were measured in excess of 300 μ g/m³ and could be up to 780 μ g/m³ along several different locations in Istanbul during this episode. Pollutant concentrations increase considerably during this period, indicating that the long-range transport plays an essential role over ambient PM levels of Istanbul. Concentrations of PM in Turkey are, to some extent, determined by the prevailing westerly winds over the Europe.

The objective of this paper is to visualize the long-range aerosol transport and reveal some quantitative information in terms of source/receptor relationships between emission throughout Europe and Turkey. Unfortunately, the existing PM₁₀ observations are limited and they are only for the city of Istanbul. Nevertheless, when we consider the present knowledge about the long-range aerosol transport for Turkey, which is very limited, this study will fill the gap in this area and we will gain a more comprehensive point of view.

The assessment of Istanbul PM₁₀ response to emissions from European countries has been performed using atmospheric models. The modeling system includes meteorological forecasting, emission modeling, and air quality modeling. The long-range air quality simulation of the specific episode has been performed over Europe with a horizontal resolution of 50 km. We use MM5V3 (The Fifth-Generation NCAR/Penn State Mesoscale Model) to provide meteorological fields to CMAQ (U.S/EPA Community Multi-scale Air Quality Modeling System). In addition, EME (Emission Modeling for Europe) has been developed to process the EMEP emission inventory data to provide hourly input emission data. The study discussed in this paper combined the new emission processor, EME with the CMAQ chemistry/transport model to investigate

a winter episode between January 5 and January 12, 2002 in Europe. A base case and several emission scenarios are modeled to test the sensitivity of the CMAQ results to the emission change.

It is noted that the availability of data on particulate mass and on the chemical composition of particles over Europe is still very limited. It is apparent from the current measurements and previous studies that more precise and quality controlled measurements are needed to obtain a comprehensive picture of geographical and seasonal characteristics of particulate matter in Europe. Additional data with more detailed physical and chemical characterization of ambient aerosols is necessary in understanding their dynamics at urban and rural locations in Europe. (Trans-boundary Particulate Matter in Europe: Status Report 2001). Furthermore, measurements of particulate matter in Turkey did not exist until recently and their possible influence by long-range aerosol transport from Europe has not been discussed in literature.

In addition, the MM5 on-line tracer model (MM5T) and backward trajectory were studied qualitatively for high-pollution events that occurred in Istanbul. The simulated tracer evolution provided qualitative proof that transport of PM₁₀ emitted from Eastern Europe could have contributed to the high-pollutant events in Istanbul. The model suggests that PM₁₀ transport to Istanbul took from hours to a few days for different locations in the related area during these events. Furthermore, trajectories studies showed that the major pollution transport routes occurred in Eastern Europe. Results obtained from this tracer and backward trajectory studies are very reasonable and qualitatively support the hypothesis that the long-range transport from the north and northwest played an important role in both high PM₁₀ events in Istanbul. They are a very preliminary, qualitative study for understanding the causes of these high pollution events.

The objective of this study is to visualize long-range aerosol transport and reveal some quantitative information in terms of source/receptor relationships between Turkey and throughout European emissions. Unfortunately, the existing PM₁₀ observations left us no choice but compare only the city of Istanbul. Nevertheless, when we consider the present knowledge about the long-range aerosol transport for Istanbul, which is very

limited, this study will fill the gap in this area and we will gain a comprehensive point of view.

AVRUPA KAYNAKLI AEROSOLLERİN TÜRKİYE' YE TAŞINIMI

ÖZET

Atmosferde uçuşan partiküllerin, gazlara nazaran daha fazla sağlık problemleri oluşturduğu ve görüş uzaklığını daha fazla azalttığı bir gerçektir. Özellikle yüksek hava kirliliği seviyeleri ve takip eden günlerde artan insan ölümleri arasındaki açık ilişki, araştırmacıların ilgisini de çekmektedir. Bu noktada, şehirlerde son derece yüksek seviyelerde olduğu gözlenen partikül maddelerin acilen araştırılması için gerekli önceliğin verilmesi iyi olacaktır. Yerleşim alanlarındaki, düşük hava kalitesinin sorumluluğu, kendi kirleticiler kaynakları olarak bir yere kadar düşünülse de, uzun mesafeli insan kaynaklı kirleticilerin taşınımı da şehir kirliliğine önemli katkılar yapabilmektedir. O halde, uzun mesafeli taşınım, lokal kaynaklar kadar önemli olabilmektedir. Uzun mesafeli taşınımın önemini dikkate alarak, hava kalitesi ile ilgili olarak yapılacak herhangi bir uygulama veya yaptırımdan önce bunların anlaşılması ve hesaba katılması gerekmektedir.

Avrupa için hava kirleticilerinin uzun mesafeli taşınımı genellikle EMEP (The European Monitoring and Evaluation Program) çerçevesi içerisinde çalışılmıştır. Bu çalışmaların sonucunda, Avrupa şehirlerindeki önemli miktarlardaki partikül maddelerinden, uzun mesafeli taşınımın sebep olduğu anlaşılmıştır (EMEP-WMO, 1999). Bir çok Avrupa ülkesindeki şehirleşme ve büyük miktarlardaki araç ve endüstri kaynakları nedeniyle antropojenik kaynaklar Avrupa'da belirgin bir şekilde baskın durumdadır. Avrupa kıtasında, endüstriyel aktiviteler ve büyük hacimlerde trafik ve şehirleşme özellikle şehirlerde insan kaynaklı partikül maddenin yaygın olmasına neden olmaktadır (EMEP/CCC-Report, 1999). Son yıllarda, Avrupa'da, görüş kalitesinin azalması ve hassas ekolojik sistemlerin zarar görmesi ile ilgili çalışmaların yanısıra, özellikle hava kirliliğine kolay hedef olabilecek gruplar için (çocuklar ve yaşlılar gibi) çok ciddi boyutlarda toplum sağlığını tehdit riski nedeniyle, partikül madde

alışmalarına yoğunluk verecek şekilde hava kirlilięi ile ilgili bir ok araştırma ve dzenleme ortaya konulmuştur. Bu alışmalar, uzun mesafeli partikl madde taşınımı ve bunun yaygın bir şekilde grlen insan saęlıęına zararlı etkileri arasında nemli bir iliştikiyi ortaya koymaktadır (EMEP/CCC-Report, 1999).

Aerosollerin kompozisyonu, şekli, fiziksel ve termo-dinamik zellikleri, coęrafi konumlarına ve mevsimlere gre deęişimler gstermektedir (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998; Alpert and Hopke, 1981). Kuzeybatı Avrupa’ da yapılan bir alışma, şehir ve şehirleşmenin olmadığı yerler arasında PM10 konsantrasyonlarının %20 lerden daha fazla olmadığını gstermektedir (e.g. Van Der Zee et al., 1998). Buna ek olarak, Avrupa’ da 14 şehir ve 14 kırsal alan iin yapılan alışmalar, PM10 ve siyah dumanın kış konsantrasyonları iin şehir ve kırsal alanlar arasında nispeten kk farklar olduğunu işaret etmiştir (Hoek et al., 1997). PM’ in blgesel karakterde benzer gzlemleri, Amerika Birleşik Devletleri iin de rapor edilmiştir (EPA, 1996). Bu durum, nfusun yoğun olduğu yerlerden kaynaklanan yksek emisyonlar, lm yapılan yerlerdeki kk hava deęişkenlięi ve kirleticilerin uzun mesafeli taşınımları olarak açıklanabilir.

PM’ in uzun mesafeli taşınımları ile ilgili yoğun alışmalara Gney İskandinavya’ da rastlamak mmkndr (Pakkanen et al., 1996; Lannefors et al., 1983; Amundsen et al., 1992). Britanya’ ya ait adalar kaynaklı hava kmeleri Orta ve Doęu Avrupa’ daki uzun mesafeli kirleticilerin sebebidir (Kkrt gibi). Dięer başka alışmalar ise, Batı ve Doęu Avrupa’ dan genellikle katı yakıtların kullanılmasından ortaya ıkan karbonmonoksit’ in (CO) uzun mesafeli taşınımının Akdeniz blgesi zerinde sınır tabaka ierisindeki CO deęerlerine %60-80 civarında katkıda bulunduęunu gstermektedir (J. Lelieveld et al. 2002). Hacısalıhoęlu ve dięerlerinin (1992) Karadeniz yakınlarında yaptıkları saha lmleri, eşitli kirleticilerin ortalama konsantrasyonlarının %70’ nin Batı ve Orta Avrupa kkenli olduğunu ortaya koymaktadır. Sciare ve dięerleri (2003) ise Orta Avrupa’nın Akdeniz blgesine, antropojenik kaynaklar aısından, ciddi aerosol katkısında bulunduęunu ispatlamıştır.

lkemizin batı ve kuzeybatı kısımlarında da bazen beklenmedik dşk hava kalitesi gzlemlenmektedir ve batı Trkiye zerindeki bu yksek kirlilięin nedeni olarak dięer

lkelerden Őphenilmektedir. Partikl kirlilięi kaynaklarının ok geniŐ spektrumda olması nedeniyle, kuzey ve batı Trkiye zerindeki partikl kirlilik olaylarının kaynaklarını belirlemek olduka zordur. Batılı rzgarların eŐlik ettięi ok fazla sayıda partikl madde gzlemleri son yıllarda aıka ortaya ıkmıŐtır. Doęu Karpatlar zerindeki olası akım, Karadeniz, Marmara ve Ege Denizleri zerine doęru yn alacaktır. Bu durumda, Trkiye' nin kuzeybatısında yer alan İstanbul, Avrupa lkeleri kaynaklı uzun mesafeli hava kirlilięine maruz kalacaktır. rneęin, Ocak 5 ile 12, 2002 tarihleri arasında, İstanbul' da son derece dŐk hava kalitesi gzlemlenmiŐtir. İstanbul Byk Őehir Belediyesi tarafından yapılan gzlemlere gre 24 saatlik PM10 (Aerodinamik apı 10 mikro metreden az partikl madde) seviyesi Dnya Saęlık TeŐkilatı (WHO) 'nın 24 saatlik en st standart deęeri ($60\mu\text{g}/\text{m}^3$) ve Amerika BirleŐik Devletleri evre Koruma TeŐkilatı (USEPA)' nin 24 saatlik en st standart deęeri ($150\mu\text{g}/\text{m}^3$), İstanbul iin geilmektedir. Saatlik en yksek deęerlerin, $300\mu\text{g}/\text{m}^3$ ten daha fazla olduęu ve hatta $780\mu\text{g}/\text{m}^3$ e kadar ıktıęı epizot boyunca İstanbul' daki bir ok lm istasyonunda kaydedilmiŐtir. Kirletici konsantrasyonları, İstanbul zerindeki PM seviyelerinde, uzun mesafeli bir taŐınının nemli rol oynadıęını iŐaret ederek aynı tarihler boyunca dikkat ekecek bir Őekilde artmıŐtır. Trkiye' deki PM konsantrasyonları bir dereceye kadar Avrupa zerindeki hakim batılı rzgarlar ile belirlenmektedir.

Avrupa lkelerine baęlı olarak İstanbul PM10 deęiŐiminin deęerlendirilmesi bir dizi atmosferik modellerle ortaya konulmuŐtur. Tm model sistemi meteorolojik tahmin modeli, emisyon modeli ve hava kirlilięi modelinden oluŐmaktadır. Uzun mesafeli hava kalitesi simlasyonları belirli bir tarih iin tm Avrupa kıtasını kapsayacak Őekilde 50 km. lik yatay znrlkte uygulanmıŐtır. Meteorolojik deęerleri elde etmek iin, NCAR (National Center of Atmospheric Research) ve Penn State niversitesi'nin birlikte hazırladıęı MM5 meteorolojik model kullanılmıŐ ve bu deęerler CMAQ (Community Multiscale Air Quality Modeling System) hava kalitesi modelinde kullanılmıŐtır. Bunlara ek olarak, EMEP'e (European Monitoring and Evaluation Program) ait emisyon envanterinden saatlik emisyon deęerlerini elde edebilmek amacı ile, EME (Emission Modeling for Europe) emisyon modeli geliŐtirilmiŐtir. Bu yeni geliŐtirilen emisyon model yntemi ve CMAQ kimyasal/taŐınım modeli ile birlikte tm

Avrupa’da kış dönemi için Ocak 5 ve Ocak 12 2002 periyodunu kapsayacak şekilde araştırmalar yapılmıştır. CMAQ modelin emisyon değişimine duyarlılığı bir temel çalışma ve farklı emisyon senaryoları modellenerek test edilmiştir.

Avrupa üzerindeki partikül kütle ve kimyasal kompozisyonlarla ilgili mevcut veri oldukça sınırlıdır. Avrupa’ daki partiküler maddenin, kapsamlı bir coğrafi ve mevsimsel karakteristik resmini elde edebilmek için, yapılmakta olan ölçümler ve önceki çalışmalar daha doğru ve yüksek kalitede kontrol edilmiş ölçümlere ihtiyaç olduğunu açıkça göstermektedir. PM’ nin Avrupa’ daki şehir ve kırsal alanlardaki dinamiğini anlamak için, fiziksel ve kimyasal özelliklerini içeren daha detaylı bir veri gerekmektedir (Trans-boundary Particulate Matter in Europe: Status Report 2001). Bütün bunlara ek olarak, Türkiye’ de partikül madde ölçümleri son zamanlara kadar yapılmamaktaydı ve Avrupa’ dan olası uzun mesafeli aerosol taşınımının etkisi literatürde şu ana kadar da tartışılmamıştı.

Ayrıca, MM5T (MM5 on-line Tracer Model) yayılım (tracer) ve geriye doğru yapılan izleme (backward trajectory) çalışmalarıyla da İstanbul’da olan yüksek kirlilik olayları nicelik çalışmalarının yanısıra niteliksel olarak da araştırılmıştır. Simüle edilen MM5T model sonuçları, Doğu Avrupa’dan yayılan PM10 emisyonlarının taşınımını ve İstanbul’daki yüksek kirlilik değerlerine olası katkılarını niteliksel olarak açıkça ortaya koymuştur. Model, araştırılan tarihler için, ilgili alandaki farklı noktalardaki PM10 emisyonlarının İstanbul’a taşınımının birkaç saat ile birkaç gün arasında olduğunu ileri sürmektedir. Buna ek olarak, backward-trajectory çalışmaları açıkça göstermiştir ki, bu taşınımın esas rotası Doğu Avrupa yolu ile olmaktadır. Tracer ve trajectory çalışmalarından elde edilen sonuçlar oldukça makul ve niteliksel olarak hipotezi destekleyerek, sınırlar arası kirlenici taşınımının İstanbul’un yüksek PM10 konsantrasyonlarında önemli rol oynayabileceğini göstermektedir. Bu çalışmalar, yüksek hava kirliliği olaylarını açıklayabilmek ve anlayabilmek için nicelik çalışmalardan önce yapılan niteliksel yaklaşımlardır.

Bu çalışmanın amacı kaynak/alıcı ilişkisi açısından Avrupa’dan Türkiye’ye olan uzun mesafeli aerosol taşınımını hem niteliksel hem de niceliksel olarak kanıtlamak ve ortaya koymaktır. Fakat Türkiye’de sadece İstanbul için yapılan partikül madde (PM10)

ölçümleri bize gerekli karşılaştırmayı yapabilecek imkanı vermektedir. Herşeye rağmen, uzun mesafeli aerosol taşınımı ile ilgili hemen hemen hiçbir bilgiye sahip olmadığımızı düşünecek olursak, bu çalışma bu alandaki boşluğu doldurmakla birlikte, bizlere geniş bir bakış açısı da kazandıracaktır.

1. INTRODUCTION

Air Quality modeling is becoming a very important issue for urban, regional and national authorities in Europe and also other continents. Gases or particular matters emitted into the atmosphere by human and natural activities cause many current and potential environmental problems, including acidification, air quality degradation, climate change, damage and soiling of buildings and other structures, stratospheric ozone depletion, human and ecosystem exposure to hazardous substances. It is essential to have quantitative information on these emissions and their sources in order to define environmental priorities and identify the activities and actors responsible for the problems.

It is a fact that airborne particles bring about more health problems and more visibility degradation than do gases. Above all, an obvious connection between high levels of particle pollution and day-to-day excessive mortality rate attract the attention of researchers. At this point, urban areas, where extremely high levels of particulate matter (PM) are observed, might be given priority to be investigated immediately. Although urban areas themselves create poor air quality ambience by themselves, long-distance man-made sources could significantly contribute to urban pollution. As a result of this, long-range aerosol transport has gained an outstanding importance in addition to local sources. Considering the importance of long range transport, its' evaluation is inevitable before taking any decision or making any policy of air quality.

Individual particles are characterized by their sizes, shapes and chemical composition. They can be solid or liquid, spherical or irregularly shaped, and can contain internal mixtures of species and phases. PM is typically composed of a complex mixture of chemicals, which is strongly dependent on source characteristics.

As indicated in Table 1.1, PM composition varies between the fine and coarse fractions. The fine fraction is characterized by constituents such as sulfate, nitrate, ammonium, metals, elemental carbon, and hundreds of different organic carbon compounds. The

coarse fraction is characterized by materials typical of the earth's crust (primarily fugitive dust and construction sources) and grinding processes (metals).

Table 1.1: Comparison of ambient particle fractions adapted from Wilson and Suh (1997).

	Fine ($\leq 2.5 \mu\text{m}$)		Coarse ($2.5 - 10 \mu\text{m}$)
	Ultrafine ($< 0.1 \mu\text{m}$)	Accumulation ($0.1 - 2.5 \mu\text{m}$)	
Formed from:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, and abrasion of surfaces) Evaporation of sprays Suspension of dusts Reactions of gases in or on particles
Composed of:	Sulfates Black carbon Metal compounds Low-volatility organic compounds	Sulfate, SO_4^{2-} Nitrate, NO_3^- Ammonium, NH_4^+ Hydrogen ion, H^+ Black carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc. Particle-bound water	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates and chlorides from HNO_3 and HCl Oxides of crustal elements (Si, Al, Ti, and Fe) CaCO_3 , NaCl , and sea salt Pollen, mold, and fungal spores Plant and animal fragments Tire, brake pad, and road wear debris
Typical Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Important Removal processes:	Growth into accumulation mode Wet and dry deposition	Wet and dry deposition	Wet and dry deposition
Typical Travel distance:	< 1 to 10s of km	100s to 1000s of km	< 1 to 10s of km (100s to 1000s in dust storms)

Particles directly emitted to the atmosphere are termed primary particles. Such particles can be coarse or fine. Secondary PM results from the condensation/deposition of gaseous precursors to the particulate phase. Although direct nucleation from the gas phase definitely is a contributing factor, most secondary material accumulates on pre-existing particles in the 0.1 to 1.0 μm range and typically accounts for significant fractions of the PM_{2.5} mass.

PM can be classified into four modes, which reflect particle origins. These include the coarse mode (particle diameter larger than $\sim 2\ \mu\text{m}$), the accumulation mode (0.1 to $2\ \mu\text{m}$), the Aitken mode (10 to 100 nm) and the nucleation mode ($<10\ \text{nm}$). Coarse-mode particles are lost rapidly by sedimentation, and ultrafine particles grow and coagulate, typically migrating into the Aitken mode as a result.

PM mass concentrations vary significantly on both temporal and spatial scales. The highest PM loadings, excluding dust storms and fires, are often found in major urban centers and small industrial areas where local sources strongly influence air quality. Long-range transport of PM and precursor gases has been documented for ground-level ozone and its precursors, as well as nitrate and sulfate compounds on regional, continental, and trans-oceanic scales. Figure 1.1 illustrates the potential for PM to be issue at all spatial scales depending on the relative contributions of precursor gases and primary particles.

Figure 1.1: Illustrative transport scales for PM and other atmospheric pollutants adapted from NARSTO (2004).

PM varies both geographically and seasonally. Table 1.2 summarizes the major source contributions to primary and secondary PM. Varying source contributions and meteorological influences drive a large dynamic range of seasonal and diurnal variation in PM mass concentration and composition. Origins of PM could be both anthropogenic and natural sources. Anthropogenic emissions can readily be identified with industrial sources, commercial operations, power plants, residential dwellings, and transportation. Natural emissions result from volcanic eruptions, wind blown sea spray, dust storms from remote arid areas, and forest or brush fires initiated by lightning strikes. Other natural emissions include sulfur gases from terrestrial and marine sources, nitrogen oxides from soil respiration and lightning strikes, and organic vapors from vegetation.

Table 1.2: General descriptions of PM emissions and source types adapted from NARSTO (2004).

Emissions		General Source Types
Primary	Crustal / Soil Dust / Road Dust	Paved / unpaved roads, vehicle tire and brake wear, construction, agricultural and forestry operations, high wind events and fires.
	Salt (NaCl)	Oceans, road salt and salt pans / dry lake beds.
	Biogenic material	Pollen, spores and plant waxes.
	Metals	Industrial processes and transportation
	Black carbon	Fossil fuel combustion (especially diesel engines).
	Semi-volatile organic compounds (direct condensation of organic vapors at ambient conditions) and non-volatile organic compounds.	Contemporary and fossil fuel combustion, surface coatings and solvents, cooking, and industrial processes. Forest fires and biomass burning.
Secondary	Semi- and volatile organic compounds (forming secondary organic aerosols)	
	Sulfur dioxide (forming sulfate particles)	Electrical utilities, transportation, mining and smelting, and industrial processes.
	Ammonia (contributing to formation of ammonium sulfate and ammonium nitrate)	Agriculture and animal husbandry, with minimal contributions from transportation and industrial processes.
	Nitrogen oxides (forming ammonium nitrate with ammonia)	All types of fossil fuel combustion, and to minor degree microbial processes in soils.

Long-range transport of air pollutants has generally been studied in Europe under the framework of the European Monitoring and Evaluation Program (EMEP). As a result of

these studies, long-range trans-boundary transport is responsible for a significant fraction of the particulate pollution in European cities as well as in rural areas (Baltensperger, 1999). Anthropogenic sources are dominant in Europe because of the urbanization of many countries and the large number of vehicle and combustion sources (industrial and residential). The industrial activities, high volumes of traffic and urbanization of the Continent of Europe had, as a result, the anthropogenic sources of PM to be predominant, mainly in urban areas (EMEP/CCC-Report, 1999). Recently, there has been an extensive research and several regulations have been issued on PM focused air pollution mainly because of severe public health risks for susceptible members of the population, more visibility reduction and damages to sensitive ecosystems in Europe. These studies have indicated a significant association between the long-range component of PM and a wide range of health damaging effects (EMEP/CCC-Report, 1999).

Compositions, morphology, physical and thermodynamic properties of aerosols vary between geographical places and seasons (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998; Alpert and Hopke, 1981). Some studies have shown that in Northwestern Europe, aerosol concentrations between urban and non-urban areas do not exceed 20% (e.g. Van Der Zee et al., 1998). Furthermore, a number of studies on wintertime concentrations of PM₁₀ and black smoke in 14 urban and 14 non-urban locations in Europe indicate a relatively small difference (on average 22% for PM₁₀ and 43% for black smoke) (Hoek et al., 1997). Similar observations on the regional character of PM are reported also in United States (EPA, 1996a). These results have indicated that there was a long-range transport of air pollutants. Long-range transport of PM has also been studied intensively in Southern Scandinavia (Pakkanen et al., 1996; Lannefors et al., 1983; Amundsen et al., 1992). Air masses originating from the British Isles, Central and Eastern Europe were mainly responsible for the long range transport of pollutions. Other studies show that long-range CO transport from both Western and Eastern Europe, mostly from fossil fuel use, contributes 60 to 80%, to the boundary-layer CO over the Mediterranean (J. Lelieveld et al. 2002). Hacısalihoglu et al. (1992) showed that during a field experiment near the Black Sea, 70% of the mean concentrations of various pollutants have originated from Western and Central Europe. Sciare (2003) and his

colleagues obtained the major contribution of aerosols of Central Europe to the Mediterranean region which was confirmed in terms of anthropogenic emissions. In addition Al-Momani (1997) and his colleagues demonstrated some indications of long-range transport from Europe to Eastern Mediterranean.

Sometimes, unexpected poor air conditions are observed in the West and North-west of Turkey, and the high pollutants over Western Turkey are suspected to be transported from other countries. Because of the wide range of sources which are composed of particulate pollution, it is very difficult to classify particulate pollution episodes for Northern and Western Turkey. It has become clear in recent years that the most severe PM episodes are accompanied by westerly winds. The possible flow on the east of the Carpathian Mountains is channeled over the Black Sea, the Marmara Sea, and the Aegean Sea. Under this situation, Istanbul, which is located in the North-west of Turkey, is open to be exposed to long range air pollution originating from European countries. According to the observations from monitoring sites which are operated by the Istanbul Metropolitan Municipality, the peaks of 24-h PM₁₀ (Particulate Matter less than 10 μ m) level exceeded the World Health Organization (WHO) standard of 60 μ g/m³ and U.S Environmental Protection Agency (EPA) standard of 150 μ g/m³ (24-hour average). Peaks of hourly PM₁₀ concentrations were measured in excess of 300 μ g/m³ and could be up to 780 μ g/m³ along several different locations in Istanbul. Pollutant concentrations increase considerably during this period, indicating that the long-range transport plays an essential role over the ambience of Istanbul. Concentrations of PM in Turkey are, to some extent, determined by the prevailing westerly winds over Europe.

The objective of this thesis is to visualize long-range aerosol transport and reveal some quantitative information in terms of source/receptor relationships between Turkey and throughout European emissions. Unfortunately, the existing PM₁₀ observations left us no choice but compare only the city of Istanbul. Nevertheless, when we consider the present knowledge about the long-range aerosol transport for Istanbul, which is very limited, this study will fill the gap in this area and we will gain a comprehensive point of view.

It is noted that the availability of data on particulate mass and on the chemical composition of particles over Europe is still very limited. It is apparent from the current measurements and previous studies that more precise and quality controlled measurements are needed to obtain a comprehensive picture of geographical and seasonal characteristics of PM in Europe. Additional data with more detailed physical and chemical characterization of ambient aerosols is a necessary aspect in understanding their dynamics at urban and rural locations in Europe (EMEP: Status Report 2001). Furthermore, measurements of PM have recently been started in Turkey and their possible long-range transport from Europe is very scarce in literature.

In a nut shell, it is essential to know not only the ambient pollutant concentrations that would result from certain situations, but also the extent to which percentages would be responsible for long range transport. Probably, this question of atmospheric sensitivity corresponds to a “brute force sensitivity” method. An air quality model is run once under base case conditions, and the results of ambient pollutant concentrations are compared with the results of country-base or regional-base emission perturbation model runs. Therefore this study might provide some significant information which is useful for several purposes. The origin of PM which is essential information in the design of emission reduction strategies is a driving force for the study of long-range aerosol transport. Furthermore, prevailing westerly winds which are the reason of the unexpected poor air quality over Istanbul also motivated us to determine the sources and quantity of contribution of this common long-range pollutant transport. If ongoing long-range sources are confirmed, working within the international framework for increase of air quality could put an efficient plan into practice.

The assessment of Istanbul PM₁₀ response to European countries has been performed by atmospheric models. The whole forecast system includes meteorological forecasting, emission modeling, and air quality modeling (Fig. 1.2). Long-range air quality simulation with respect to the specific episode has been performed for the European scale with a horizontal resolution of 50 km. The Fifth-Generation NCAR / Penn State Message Model (MM5; Grell et al. 1994) was used to provide meteorological fields to the Community Multiscale Air Quality Modeling System (CMAQ; Byun and Ching, 1999). In addition, the Emission Modeling for Europe (EME) has been developed to

process the emission inventory data of the European Monitoring and Evaluation Program (EMEP) to provide hourly input emission data. The study discussed in this thesis combined the new emission processor, the EME with the CMAQ chemistry/transport model to investigate a winter episode between January 5 and January 12, 2002 in Europe. A base case and several emission scenarios are modeled to test the sensitivity of the CMAQ results to the emission change.

Figure 1.2: General model data flow chart for the modeling system.

In light of the rapid development of atmospheric modeling, accurate simulations of the transport, diffusion, dry and wet deposition, and chemical transformations for gases and particulate matter are largely dependant on quality of meteorological and emission inventory data sets. Appropriate spatial and temporal evolution of the meteorological

fields and emission inventories could be the first and most important step to get correct results of air quality.

The meteorological model, the emission model and the air quality model are briefly introduced in the following paragraphs. In addition, the important studies and different application for each model system which is given from the previous efforts to current approaches can also be seen.

2. LITERATURE REVIEW

Meteorological models are used to simulate and forecast short-range meteorological conditions. In addition, operational use of weather prediction models has become widespread in recent years (Mass and Kuo, 1998). Moreover, prognostic meteorological models have been used to provide the meteorological inputs for air quality modeling studies (Pielke and Uliasz, 1998).

Alapaty et al. (1995) investigated the sensitivity of the US EPA Regional Oxidant Model (ROM) for different meteorological (prognostic MM4 and diagnostic model) inputs over Eastern U.S. The comparison of predicted concentrations of chemical species indicated higher values (1–5 ppb for NO_x and 1–25 ppb for reactive organic gases) when the prognostic model outputs were used.

Kumar and Russell (1996) investigated the impact of prognostic (MM4) and diagnostic meteorological inputs on photochemical air quality modeling performance for Southern California region during the Southern California Air Quality Study (SCAQS) period (27–29 August 1987). The results indicated that the temperature and mixing heights derived from the prognostic models agreed better with observations as compared to velocity data. However, the results obtained from the photochemical models were similar for both inputs except that a lower ozone peak was predicted using the prognostic meteorological inputs.

The necessity of correct description of the wind and turbulence fields used in air quality assessment models should be obvious (e.g., Svensson, 1996a; Berkowitz and Fast, 1996; Liu and Carroll, 1996). Otherwise, it was not possible to represent the transport, deposition, and dispersion of a chemical species and their concentration fields and chemical reactions accurately. Sistla et al. (1996), for example, showed the influence of meteorological uncertainties with respect to ozone control strategies. Al-Wali and Samson (1996) illustrated the sensitivity of the Urban Airshed Model to the placement

of boundary layer measurements with respect to the location of emissions. Svensson (1996a-b) demonstrated that relative errors in meteorological variables simulated in chemical rate constants.

Pielke and Uliasz (1998) emphasized the importance of understanding how errors in the meteorological fields affect the results and conclusions from the air quality model. The importance of meteorological variability and uncertainty was described and discussed in the context of dispersion and chemistry of air pollution. They considered the importance of the spatial effects and temporal effects in terms of models. In the study, examples of uncertainty were given due to spatial resolution, model type and average time of the meteorological model-simulated fields. Their conclusion was not good to take full advantage of meteorological model-generated wind and turbulence fields.

Langner and his colleagues using the MATCH (Multi-scale Atmospheric Transport and Chemistry Model, 1996) model researched the parameterization of wet and dry deposition and compared them with the EMEP data. They also used the MM5 model to get 3D meteorological data. The EMEP and the MATCH results were found similar for deposition of sulfur to Sweden.

The Norwegian Meteorological Institute has implemented the MM5 modeling system and it ran operationally with a 1 km resolution for the city of Oslo, Norway in order to produce high resolution meteorological data as input to an urban air pollution model during the winter season 1999/2000 (Berge et al., 2000). 22 days with calm winds during the winter of 1999/2000 were chosen to evaluate the prognosis of MM5 against screen level observations of wind, temperature and humidity and the ability of MM5 to improve the hydrostatic model (HIRLAM10) prognosis that was used as initial and boundary conditions. In order to investigate the gain by using higher resolution non-hydrostatic models, results during days with low winds and stable stratification are evaluated. Comparisons of 24 to 48 hour forecasts of wind, temperature and relative humidity for a 10 km resolution hydrostatic model (HIRLAM10) and 1 km forecasts with MM5 based on 24 hour forecasts from HIRLAM10 have been conducted. The finer resolution MM5 runs compared better for wind and relative humidity both with respect to bias and non-systematic errors.

Barna et al. (2000) ventured to utilize the MM5 output as an initial guess wind field for CALMET (The California Meteorological model/photochemical model) to create the meteorological fields for July 1996 in the Cascadia region. The predicted ozone concentration by the California Grid Model (CALGRID) agreed well with observations at the monitors located along the Interstate Highway No. 5 corridor.

Barna and Lamb (2000) also carried out three air quality simulations using CALGRID for an ozone episode which occurred in the Cascadia region of the Pacific Northwest during 11–14 July 1996. These simulations individually utilized the wind field obtained from the MM5 model without observational nudging, MM5 model output without observational nudging as an initial-guess field for CALMET and finally the MM5 model output with observational nudging. The results indicated that ozone predictions significantly improved when the MM5 output with observational nudging was used in comparison with the other two simulations.

John W. Nielsen-Gammon produced MM5 simulations of the August-September 2000 ozone episode in the Houston-Galveston area (2002). This episode was supported by special meteorological observations including three radiosonde launch site, six wind profiles, a Doppler Lidar, four instrumented aircraft, and special surface flux measurements. As a result, the MM5 successfully simulated the diurnal heating cycle. During the second half of the ozone episode, when a low-level jet was present, the MM5 gave a poor performance. But it was not surprising, since low-level jet was produced by a complex interaction between the diurnal variations of heating and turbulence.

Nelson L. Seaman (2000) studied meteorological modeling for the air quality assessments. Based on this review of current state-of-the-science models and projected demands for meteorological information for future air-quality assessments, the following major conclusions were made: (1) For most purposes, data-assimilating dynamical models are currently the best method available for generating reasonably accurate and dynamically consistent meteorological fields required for air quality applications. (2) The rapid expansion of remote sensing technology provides an outstanding opportunity to reduce errors in meteorological fields, but research is needed to learn how to best use these data in analysis and assimilation techniques. (3) As better land-surface schemes are

introduced into meteorological models, considerable benefit may be gained by better coupling with emission models, perhaps leading to fully integrated meteorological emission modeling systems. (4) Rapid growth in computer technology has made it feasible to run multi-day regional meteorological model simulations having very fine grid resolutions. To take full advantage of this new technology, however, more research is needed to develop scale-appropriate physical parameterizations (land/surface fluxes, soil hydrology, boundary layer fluxes, deep convection, shallow clouds). (5) Mandated limits on long-term exposure to pollutants will require greater emphasis on long-range transport. This necessitates the re-evaluation of mesoscale models for inter-regional transport problems, particularly in episodes of poor air quality associated with weak dynamical forcing and convection. (6) Better coupling and interfacing of meteorological models and AQMs is a significant need, and preliminary efforts are being made to reduce errors due to model incompatibilities. Eventually, this should lead to fully integrated models that perform both meteorology and chemistry processing.

Philippe Thunis researched the influence of the scale on modeled ground level O₃ concentrations for Europe in 2001. In the study, meteorological data requested to drive the TAPOM (Transport and Air Pollution Model) air quality model were simulated by the mesoscale non-hydrostatic model MM5. The comparison of air quality results obtained with different resolution meteorological datasets showed a similar pattern for the pollution plume although differences in resolution ranged from 1.5 to 50 km. Even a very coarse resolution of 50 km was able to capture the main features of the atmospheric circulations in the Milan region. On the other hand, the variability of O₃ levels as simulated with the different meteorological resolutions was shown to be significant and at least as important as the variability associated with the resolution of the air pollution model itself. In the area of Genova, where sharp changes in land-use were present (coastline), the impact of the spatial resolution of meteorology was shown to produce large errors in O₃ concentrations. Although these conclusions are valid only for the specific area of Milan and only for May 13th, 1998, one can expect a similar behaviour in other conditions (P. Thunis, 2001).

Arellano and co-workers carried out observational evaluation of PBL (Planetary Boundary Layer) parameterization modeled by MM5 (2001). In this study, PBL

schemes implemented in the mesoscale model MM5 were evaluated with the observational data set, because they emphasized that mesoscale models were currently used to simulate and forecast short-range meteorological and air pollution problems. As a result, the convective boundary layer modeled by MM5 strongly depends on the selected PBL scheme.

Mass et al. (2002) studied the effects of increasing horizontal resolution on the forecast skill by examining the results of two years of the University of Washington Real-Time MM5 Modeling and Verification System over the Pacific Northwest. They found that decreasing grid spacing did improve the reliability of the results, but does not necessarily improve significantly the skill accuracy of the forecasts.

Fast et al. (2002) studied the relative role of local and regional scale processes on ozone in Philadelphia for the period of 15 July – 4 August, 1999 by utilizing a coupled meteorological and chemical modeling system, the Pacific Northwest National Laboratory (PNNL) Eulerian Gas and Aerosols Scalability Unified System (PEGASUS). The results indicated little model bias in the simulated wind speed as compared to the wind profilers, but the simulated wind directions were more westerly by about 15°.

Concern for the potential economic cost from severe storms to the European Community has provided justification for increasing research and field studies with hopes of improving the ability to forecast these extreme events. To take this situation as a goal, Peter S. Dailey and John Keller made an approach and verification for extreme wind events by using the MM5 model (2002). The model was initialized and bounded by the NCAR/NCEP (The National Center of Atmospheric Research / National Centers for Environmental Predictions) reanalysis data from 1958 to 1998 for each 36 hour-period that included at least one winter season mid-latitude cyclone passing over Europe. The MM5 model domain included two grids, 90 km and 30 km, respectively. Four-dimensional data assimilation (analysis nudging) was used to nudge the wind field to the reanalysis data. At the end of the research, they proved that MM5 is capable of producing a realistic wind climate for European winter storms.

The PSU/NCAR (The Pennsylvania State University / The National Center of Atmospheric Research) model version 3.2 was configured using 4 nested domains with 1

way nesting interaction and with horizontal resolution of 54, 18, 6 and 2 km to statistical evaluation of surface winds and temperatures over Israel by D. Rostkier-Edelstein et al. (2003). Their evaluation showed that in some cases correct prediction of temperatures did not guarantee correct wind prediction. For example, at some stations, the model succeeded to predict the temperature correctly, but failed to predict the correct wind speeds. The study showed that the performance of the model was different according to the characteristics of the terrain.

In the troposphere, the long-range transport of pollutants into the Arctic was researched by Jesper H. Christensen et al. (National Environmental Research Institute Department of Atmospheric Environment Denmark, 2003). They used long-range transport modeling DEHM (The Danish Eulerian Hemispheric Model). The model system has two meteorological versions: Analyses version coupled with the MM5 and the ECMWF data and, forecast version coupled with Eta and NCEP data. The MM5 model was run with one nest for a period of 10 years 1993-2002 (150 km and 50 km resolution). The results for a 10 year period from 1993 to 2002 were compared with measurements from both EMEP data and Danish stations. The comparison showed good performance.

Anantharaman C. and co-workers evaluated the performance of a computationally efficient the MM5/CALMET (The California Meteorological model/photochemical model) system for developing wind field inputs to air quality models (2003). Wind fields derived from this system were compared with the wind profiler observations from the Northeast-Oxidant and Particle Study (NE-OPS) field campaign over Philadelphia, undertaken during one of the summer ozone episodes in 1999 (23–24 July 1999). The MM5 simulations were performed on a nested grid (36, 12 and 4 km horizontal resolution) with 14 layers in the vertical direction for the period 21 July 1999; 00 UTC to 25 July 1999; 05 UTC. The CALMET meteorological model was applied to 14 layers in the vertical direction, a horizontal resolution of 4 km and a domain which included New Jersey and the Philadelphia region and was employed in two modes. In the first mode, the MM5 model wind and mixing height output results (for 36, 12 and 4 km horizontal resolution) were ingested every hour into the CALMET diagnostic meteorological model along with an objective analysis procedure using all available observations. In the second mode, no the MM5 results were utilized and the CALMET

employed the objective analysis procedure. All the above simulations were compared with the wind profiler data collected during the NE-OPS program. The results of this study indicated that utilizing the coarsest prognostic meteorological model output in a diagnostic model provided an attractive option for generating accurate meteorological inputs for air quality modeling studies, especially for long-term simulations of periods lasting from several weeks to a year.

Accurate simulations of the transport, diffusion, dry and wet deposition and chemical transformations for airborne chemical species, aerosols and particulate matter are largely dependant on data sets than can properly resolve the spatial and temporal evolution of the meteorological fields on a wide range of scales. In recent years, the use of three-dimensional high frequency mesoscale data sets derived from the MM5 to drive air quality simulation models has been growing. The MM5 model proved to be a powerful tool for developing three-dimensional high-resolution meteorological fields for air quality assessments (Kalusmann, et al., 2003).

Researchers have recently put forth several studies to improve methods, models and emission factors for the generation of emission data to be used in the atmospheric models. Furthermore, the assessment of the accuracy of emission data has been performed for each study. Details of these studies can be seen in the following paragraphs.

An emission inventory for NH_3 was constructed for the Danish county of Vejle (area about 3000 km^2) with a spatial resolution of 100x100 m^2 (Asman et al., 1999). Also a newly developed atmospheric transport and deposition model for the total nitrogen deposition was calculated for the same area taking into account all Danish and foreign NH_3 and NO_x emissions. The aim of the research was to model the emission of ammonia from agricultural sources and its diurnal and seasonal variation. At the end of the study, they were able to generate emission inventory of ammonia for Denmark.

José M. Baldasano, Cecilia Soriano and Isabel Toll (Universitat Politècnica de Catalunya (UPC), Laboratory of Environmental Modeling- ETSEIB) prepared an emission inventory (1999). The result of the study was a highly disaggregated emission inventory for the Barcelona-Catalonia area, including both biogenic and anthropogenic

emissions. These emissions were used as input in the coupled meteorological/photochemical modeling system to predict concentrations of pollutants over the Barcelona Geographical Area.

Another research was implemented by R. Friedrich, B. Wickert, U. Schwarz and S. Reis to calculate multi-scale high resolution emission data for Germany and Europe. The aim of the research was the improvement and further development of methods to calculate data on anthropogenic emissions of air pollutants with high a spatial and temporal resolution. For Germany and Europe, air pollutants NO_x, CO and VOC (in a detailed speciation) were covered. Emission data calculated with these models were used as input in the German tropospheric research program (TFS) for numeric simulations of atmospheric processes. The main conclusions were that emission data sets and their fast and flexible calculation remain to be vital for all modeling and evaluation issues being conducted within the Generation and Evaluation of Emission Data (GENEMIS) program. By improving the software and approaches for this calculation, it was possible to provide data sets with up to several greater Berlin areas of data within an acceptable time frame.

Within the scope of EUROTRAC/GENEMIS (A EUREKA Environmental Project/ The Generation and Evaluation of Emission Data), the study of Turkish emission inventory covered by the Aegean Region was implied by Aysen Muezzinoglu et al (1999). Inventories for these regions included the largest point sources (industries), domestic heating and traffic sectors. All emissions calculated with respect to four pollutant types (SO_x, NO_x, MVOC and CO) were evaluated in three pollutant source categories of point, area and line sources.

The group of Ponche et al. worked on the improvement of the methodology of emission inventories and emission scenarios for air quality management. In the ESCOMPTE programme (realisation of field experiments to constraint models of atmospheric pollution and emission transport), and with the support of the ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie), improvements of emission inventory methodology consistent with the European emission databases have been started to facilitate emission database settlement for all regions in France. In the frame of the

French ECODEV (Recherche Interdisciplinaire sur les Technologies pour l'Ecodéveloppement) - AGRICE (Agriculture pour la Chimie et l'Energie) programme and the PRQA Alsace (Regional Planning for Air Quality Management in Alsace), some scenarios have been elaborated to study respectively the impacts of some reformulated and oxygenated fuel car blends on the air quality and the impact of future European regulations (2015) at the regional scale.

Another study carried out in the related area was a new emission model EMIMO (EMISSION MOdel) based on the V2.0 version of EMIMA (Global Emission Modeling; San José et al. 1996) for general applications applied over the Bilbao and Madrid (Spain) domains. The IER (Institut für Energiewirtschaft und Rationelle Energieanwendung - Stuttgart, Germany) emission model (Schwarz and Friedrich) was also used to compare the emission data with both data bases. Both models followed the CORINAIR emission methodology. The results showed the importance of GIS data for final emission inventories. The ARC/INFO E00 maps from the Digital Chart of the World (1 km spatial resolution) and the DXF (100 m spatial resolution for only the Municipality of Bilbao) maps from the Municipality of Bilbao had been used to compare the emission data. The results showed that the DCW managed to obtain better comparisons with the IER emission data base than the DXF Municipality Maps which highlight the importance of having a homogeneous spatial distribution of geographical data.

The Technical University of Madrid (UPM) is currently studying the different alternatives to reduce air pollution in Spain. The policy design and decision-making for improving air quality are based on emission projections up to the year 2020 under several scenarios. The US/EPA CMAQ modeling system has been selected and therefore the SMOKE emission inventory information has been used to generate model-ready emission data. In spite of having a very flexible design, both modeling systems (CMAQ and SMOKE) have been developed, taking into account the inventory formats and particular conditions of the United States. This poses an obstacle for its application to other countries. Therefore, Borge and his colleagues developed a specific methodology for the Spanish case (2002). Their study showed the initial efforts to achieve a high quality emission data set suitable for modeling from the Spanish Emission Inventory.

Land-use, topographic information and elevation data are very important input parameters for modeling anthropogenic and biogenic emissions. Several land-use data sets have been provided to the users within the GENEMIS (Generation and Evaluation of Emission Data), GLOREAM (GLObal and REgional Atmospheric Modeling) and SATURN (Studying Atmospheric Pollution in Urban Areas) subprojects. They include data at general categories as well as data at plant species-specific level. Gerhard Smiatek (Fraunhofer Institute for Atmospheric Environmental Research – Germany) provided appropriate land-use data for modeling anthropogenic and biogenic emissions by using data from existing sources and data from remote sensing (1999). In addition, how the biomass and leaf area index could be derived from remote sensing imagery was studied. The third task was to provide information on typical seasonal changes of vegetation. This data was needed to improve the accuracy of the modeling of biogenic emissions. At the end of the research, more than 44 different land-use data sets with 14 different nomenclatures, 30 data sets with vegetations index (VI) and leaf area index (LAI) data, 15 digital elevation models (DEM) were processed. More than 130 plant species names, 33 chemical compounds as well as 668 emission factors for biogenic VOC, 3600 records of information on forest area with 6 different nomenclatures and more than 400 regions were integrated into the relational data base.

Tolga Elbir and Aysen Muezzinoglu (2004) presented the air pollutant emission inventory of primary pollutants for Izmir, which is a highly industrialized area situated in the western part of Turkey. A proper emission inventory is very important for planning pollution control programs, particularly in coastal sites like Izmir, where environmental quality is of growing concern owing to their typical meteorological conditions. The sources were broadly classified as point, line and area sources in a systematic way. The data on activity levels of industries, fuel consumption in vehicles and domestic activities along with the respective emission factors were used for estimating the emissions for the year 2000. Their results showed that industry is the most polluting sector for sulfur dioxide (SO₂) in the study area contributing about 88% of total emissions. On the other hand, domestic heating is the most polluting sector contributing about 56% of total PM emissions, while traffic has the highest portion for NO_x emissions. Especially, emissions from industries located outside the metropolitan

city center are much higher in amount. Industries located around Izmir metropolitan center contribute to the industrial SO₂ emissions by 93%, PM emissions by 59% and NO_x emissions by 80% of the total.

On a global scale, European biogenic emissions are not significant, a consequence of the climate and size (7% of global land area) of Europe and of the destruction of natural ecosystems since prehistoric times. However, for the evaluation of the local budgets and for the photochemical oxidant modeling, natural/biogenic emissions can play an important role (David Simpson et al., 1999). As a result, besides studying anthropogenic emissions, biogenic emissions should be researched as well.

As part of the work of the UNECE (United Nations Economic Commission for Europe) Task Force on Emission Inventories, a so called “Nature Panel” was set up to write a chapter for the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (McInnes, 1996) dealing with emissions from biogenic and natural sources. This Guidebook has been used by many European countries in reporting their national emissions to UN-ECE and the European Union.

As part of the work of the Economic Commission for Europe of the United Nations Task Force on Emission Inventories, a new set of guidelines has been developed for assessing the emissions of sulphur, nitrogen oxides, NH₃, CH₄, and nonmethane volatile organic compounds (NMVOC) from biogenic and other natural sources in Europe by David Simpson (1999). This study is the most comprehensive work about biogenic of Europe. This research described the sources and gave important recommended methodologies for estimating emissions. In terms of relative contribution to total European emissions for different pollutants, NMVOC from forests and vegetation are clearly the most important emission sources (David Simpson, 1999). Total emissions from nature derived in this study amount to ~1.1 Tg S yr⁻¹, 6–8 Tg CH₄ yr⁻¹, 70 Gg NH₃ (as N) yr⁻¹, and 13 Tg NMVOC yr⁻¹. Estimates of biogenic NO_x emissions covered a wide range, from 140 to 1500 Gg NO_x (as N) yr⁻¹. CH₄ from wetlands and sulphur from volcanoes were also significant emissions in the European budgets. The most important contributor in this regard was found to be from forest VOC emissions.

In another study for Europe; Wilfried Winiwarter, Florian Kressler and Klaus Steinnocher, prepared emissions from forests using PELCOM (Pan-European Land Use and Land Cover Monitoring) land-cover data in 2001. The PELCOM land-cover data were used to improve existing information about emissions of terpenes and isoprenes from forests. The application covered both the European scale and the test area of Austria. The results derived from PELCOM were compared with an alternate set of European data. This comparison helped to identify inconsistencies in underlying statistical data which had previously been used for emission assessment. Also, a number of other sensitive parameters were identified and attributed to specific countries. Improved emission information would specifically require better knowledge on the composition and the emissions from poplar forests in Russia, and on the tree species composition of the Mediterranean forests. While meteorological information was available at low resolution only, the available information is sufficient to feed into photochemical models which provide their own sets of temperature and radiation in the course of a model run.

The Mediterranean area is a region with high photochemical activity. The region is especially rich in aromatic plants emitting a lot of BVOCs, but the source strength is almost unknown. The BEMA- project on Biogenic Emissions in the Mediterranean Area has been initiated by the Joint Research Centre of the European Commission in collaboration with 12 European laboratories and is partially funded by the Environment and Climate Programme. The overall BEMA goal is to characterize the type and amount of VOC emissions from vegetation in the Mediterranean area and to assess their potential role in atmospheric chemistry and ozone formation (Versino, 1997). Within the general BEMA working concept, the goal of the Castelporziano study (An Overview of The Castelporziano Experiments, G. Seufert, 1997) as the initial BEMA field experiment was to develop the basic process understanding to parameterize biogenic emissions at the leaf and canopy levels; mesoscale transport and chemical transformation were treated only as preparatory activities for the more complete studies in BEMA. The core activities of the BEMA were field measuring campaigns on test sites representative of the Mediterranean vegetation cover in Italy, southern France and Spain. The starting action was a series of campaigns at the Castelporziano test site near Rome.

Confirming the basic finding of the Castelporziano study, the monoterpenes made an important contribution to overall emissions and should not be omitted when considering the role of BVOCs in air chemistry.

The standardized emission factors observed in the study were very different from the values of 1.2 and 16 $\mu\text{g Cg}^{-1}\text{h}^{-1}$ assigned to monoterpene and isoprene emissions, respectively, and also from Mediterranean ecosystems (Guenther et al., 1995), as well as from the isoprene emission rates of 4 $\mu\text{g Cg}^{-1}\text{h}^{-1}$ assigned to Mediterranean oaks by Simpson et al. (1995). Evergreen oak species like *Q. ilex* emitted monoterpenes in the range of 15 $\mu\text{g Cg}^{-1}\text{h}^{-1}$. Isoprene emissions from deciduous oaks like *Q. pubescens* and *Q. fiainetto* were in the range of 85 $\mu\text{g Cg}^{-1}\text{h}^{-1}$, whereas the deciduous oak *Q. cerris* and the evergreen oak *Q. suber* did not show any measurable emissions during early summer. Therefore, a first attempt to assigning more realistic emission rates to Mediterranean oak woods could be about 50 $\mu\text{g Cg}^{-1}\text{h}^{-1}$ isoprene for deciduous oak forests, and 15 $\mu\text{g Cg}^{-1}\text{h}^{-1}$ monoterpenes for evergreen oak woods.

Biogenic emission of isoprene and monoterpenes were modeled in order to study their impact on regional atmospheric chemistry and pollution in France by Solmon et al. (2004). First, an emission potential inventory was developed using a fine scale land use database, forest composition statistics, biometric data and species emission factors. The temporal evolution of biogenic fluxes with meteorological conditions was calculated online in the MesoNH-C meso-scale atmospheric chemistry model. Leaf-level algorithms were integrated at the ecosystem scale using sub-grid prognostic surface temperature and canopy shading effects. Uncertainties associated with these estimations were discussed with respect to different spatial scales. In the second part of the paper, these developments were used to study biogenic emission impacts on regional ozone formation.

The results of biogenic fluxes led to an increase in simulated surface ozone concentrations, reaching 18–30% in the Paris plume and about 20–30% in some rural areas. Authors claimed that this impact was mainly due to large biogenic fluxes as well as to the chemical conditions prevailing in the anthropogenic plumes reaching biogenic sources.

A modeling study was performed to understand and quantify the influence of biogenic volatile organic compound (BVOC) emissions on the formation of tropospheric ozone in the Burriana area (north of Valencia) on the east coast of Spain by Thunis and Cuvelier (1999). The mesoscale modelling system consisted of the meteorology/transport module and the chemical reaction mechanism. The results of the model simulations were validated and compared with the data collected during the biogenic emissions over the Mediterranean area. In addition, the impact of biogenic emissions was investigated on peak ozone values by performing simulations with and without biogenic emissions, while keeping anthropogenic emissions constant. The results indicated that the maximum impact of biogenic emissions on ozone formation represents at the most 10 ppb, while maximum ozone values are of the order of 100 ppb. By performing different emission reduction scenarios, BVOC impacts were found to be sensitive mainly to NO_x, and not to AVOC.

The first detailed inventory for non-methane hydrocarbon emissions from vegetation over Greece was studied by Simeonidis et al. (1999). The emission inventory, based on a Geographic Information System (GIS), was prepared in 5 km spatial resolution and 1 hour time resolution. The CORINAIR methodology was applied for the calculation of emission rates. The results indicated that total annual BVOC emissions in Greece are of comparable magnitude to the anthropogenic NMHC emissions.

Although some advanced methods have been used and a lot of researchers have focused on the topic, both of the emission inventories (Anthropogenic and Biogenic) bear still uncertainties. Furthermore, to get hourly data which is needed for air quality models, some processes must be performed on any given emission inventory which mean additional uncertainties in terms of emissions.

Comprehensive air quality models (AQMs) have been developed during recent decades to simulate the transport, chemical transformation and deposition of air pollutants on the regional scale. The first applications of AQMs have been performed for episodes, e.g. for the investigation of photo-oxidant formation or acid rain. In recent years the formation of secondary particles from gaseous precursors and particle dynamics has been added to the physical and chemical processes handled in AQMs (Binkowski and

Shankar, 1995; Ackermann et al., 1998; Binkowski, 1999; Schell et al., 2002, Riemer et al., 2003).

The extensive research shows that any comprehensive modeling study of air quality over Istanbul or Turkey hasn't been performed properly up to now. Solving air quality problems has generally been a diagnostic approach instead of a prognostic one.

A modified version of the ATDL (Atmospheric Turbulence and Diffusion Laboratory) urban dispersion model was applied to estimate annual SO₂ and suspended particulate concentrations in the Golden Horn region of Istanbul (Erturk, 1986). The emissions were categorised as area sources (residential and commercial districts or small industries) and point sources (power plants and large industries). The area sources were distributed into a 3 km square grid pattern. The concentrations predicted from the model were compared with the observed concentrations. The results were found to be very reasonable. The model was used to estimate the effect of various control strategies on the reduction of SO₂ and suspended particulate levels, and the comparisons of these strategies were discussed.

UAM-V (Urban Airshed Model) modeling system was used to determine surface ozone over Istanbul in Ph.D. thesis (Anteplioglu, 2000). In the study, meteorological variables were obtained from a mesoscale prognostic meteorological model. Emissions responsible for ozone formation over the region were assumed to be originated from highway vehicles only. EPA Mobile5 modeling system was utilized for emission factors and other requirements.

Combined SO₂ and total suspended particulate (TSP) concentrations from different locations in Istanbul province were used to investigate intense air pollution episodes from 1985 through 1991 (Incecik, 1996). Occurrence of intense episodes was found only after November 1989. These episodes were associated mainly with high-pressure systems, inversions and low wind speeds. The European side of the Bosphorus was found to be more polluted than the Asian side, probably because of weaker dispersion and the greater use of poor-quality fuels.

In a research (Memmesheimer et al., 2004), the results of a long-term run carried out with the European Air Pollution Dispersion Model (EURAD, Jakobs et al., 2002a,b)

were discussed with special emphasis on atmospheric particulate matter over Europe. Strongly polluted areas like North-Rhine-Westphalia had been considered in detail using nesting techniques. The results of the annual model run for the year 1997 had been analyzed with respect to the requirements of the EU directives on air quality for PM₁₀ and other air pollutants, compared with observations. PM₁₀ evidently was strongly influenced by transport whereas NO_x was controlled mainly by local sources.

A chain of global to mesoscale models focussing on Europe, Germany and Berlin-Brandenburg was applied by Langmann et al. (2003) for the investigation of the effect of long-range transport of pollution on surface air composition during a summer smog episode at the end of July 1994. The evaluation of model results with near-surface observations of ozone reveals a more realistic reproduction of the variability of simulated ozone mixing ratios with increasing horizontal resolution. Ozone mixing ratios simulated by the mesoscale models in the PBL and the free troposphere are considerably closer to observed levels when initial and lateral boundary conditions are taken from the global model simulation. However, the observed unusually high mixing ratios of ozone in the free troposphere are still underestimated in these model simulations. Also, when reducing anthropogenic emissions by 25 % (corresponding approximately to the emission reduction in Germany between 1994 and 2000) in a European-wide model simulation, a modification of 5-10 ppbv in maximum near-surface ozone over Central Europe was received again, a decrease in this case. From these results it was concluded that intercontinental transport of pollution can complicate the results of local efforts to reduce critical exposure levels of ozone during summer smog conditions. European pollution might also be reduced by decreasing emissions elsewhere due to the decreasing contribution to the long-range transport of pollution. Other aspects that affect the long-range transport of pollution and its impact on European pollution levels are modifications in large scale dynamics. For example, Li et al. (2002) found a high correlation ($r = 0.57$) between the North Atlantic Oscillation (NAO) index and 'North American ozone' at Mace Head, a remote site at the Atlantic coast of Ireland for the period 1993 – 1997. A decline in the NAO index would reduce transatlantic transport of American pollution to Europe. Although in the study of Osborn et al. (1999) a significant decline in the NAO index is predicted using a general circulation model with

anthropogenic forcing from greenhouse gases and sulphate aerosols, a new manuscript in preparation by Osborn (2004) using a pattern-based measure of the NAO concludes the opposite – namely a weak increase in the NAO. This revised result concerning NAO could lead to an increase of transatlantic transport of American pollution to Europe emphasising that global restrictions of anthropogenic CO, VOC and NO_x emissions are necessary to reduce and control the formation of photooxidants.

A real-time forecast system for atmospheric pollutants has been used based on the EURAD Model (European Air Pollution Dispersion Model) for Europe, Central Europe and the German State of Northrhine-Westfalia. The whole forecast system includes the meteorological forecast (MM5) and an updated emission data base for the above mentioned regions. The results of the forecasts on the different regions have been published and are updated every day on the EURAD homepage. For about 15 years, the EURAD model was developed and improved for applications within numerous case studies on the regional scale in Europe (e.g. Jakobs et al., 1995; Ebel et al., 1997). The main purpose of the predictions was to answer the following questions: How reliable are the predictions and how can they be improved ?

A simple model of atmospheric transport and an emissions inventory prepared by Netherlands Organization for Applied Scientific Research (TNO) were used to estimate the contribution of primary particulate material to PM₁₀ and PM_{2.5} concentration across Europe. The resulting population exposure was compared with that of secondary particulates, and it was noted that both primary and secondary contributions would be significantly reduced with the implementation of new protocols under the Convention on Long-Range Transboundary Air Pollution (CLRTAP). Since concentrations of primary PM₁₀ could become elevated in episodic situations, when long-range transport of particulate could, on its own, exceed 24 h average targets of 50 µg m⁻³ over large areas of Europe, such reduction was important for achievement of current air quality standards to control exposure to atmospheric particulate PM₁₀. These results presented only a preliminary step. A sophisticated atmospheric modeling and more refined emission inventories were recommended.

Between November 1995 and October 1996, particulate matter concentrations (PM₁₀ and PM_{2.5}) were measured in 25 study areas in six Central and Eastern European countries: Bulgaria, The Czech Republic, Hungary, Poland, Romania and The Slovak Republic (Houthuijs et al., 2001). To assess annual mean concentration levels, 24-h averaged concentrations were measured every sixth day on a fixed urban background site using Harvard impactors with a 2.5 and 10 mm cut-point. The concentration of the coarse fraction of PM₁₀ was calculated as the difference between the PM₁₀ and the PM_{2.5} concentration. Spatial variation within study areas was assessed by additional sampling on one or two urban background sites within each study area for two periods of one month. QA/QC procedures were implemented to ensure comparability of results between study areas. A two to threefold concentration range was found between study areas, ranging from an annual mean of 41 to 98 µg m⁻³ for PM₁₀, from 29 to 68 µg m⁻³ for PM_{2.5} and from 12 to 40 µg m⁻³ for PM_{10-2.5}. The lowest concentrations were found in The Slovak Republic, the highest concentrations in Bulgaria and Poland. The variation in PM₁₀ and PM_{2.5} concentrations between study areas was about 4 times greater than the spatial variation within study areas suggesting that measurements at a single sampling site sufficiently characterise the exposure of the population in the study areas. PM₁₀ concentrations increased considerably during the heating season, ranging from an average increase of 18 µg m⁻³ in The Slovak Republic to 45 µg m⁻³ in Poland. The increase of PM₁₀ was mainly driven by increases in PM_{2.5}; PM_{10-2.5} concentrations changed only marginally or even decreased. Overall, the results indicated high levels of particulate air pollution in Central and Eastern Europe with large changes between seasons, likely caused by local heating.

The Met Office's Lagrangian dispersion model ran over a regional scale for 1996 to predict both nitrate and sulphate aerosol (Redington and Derwent, 2002). Import to the UK from Europe has been quantified. The model validated by comparison with available measurement data and results from the EMEP Eulerian model. Results were presented in the form of daily time series of aerosol at two rural sites and one urban site. Annual average maps of sulphur dioxide, nitrogen dioxide, sulphate aerosol, nitrate aerosol and nitric acid were presented and were found to exhibit a reasonable agreement with the exception of sulphur dioxide which over-predicts substantially. The model results

indicated the maximum contribution to secondary inorganic aerosol in the UK was in the southeast, where the annual average contribution was $14 \mu\text{g (PM}_{10}\text{) m}^{-3}$ based on 1996 data. On average, 30% of UK aerosol was imported from Europe in the summer and 25% in winter months.

During the winters of 1992/1993, 1993/1994 and 1994/1995 a monitoring study was performed in three urban and three non-urban areas in the Netherlands by Saskia C. Van Der Zee et al. (1998). PM₁₀, black smoke (BS), sulfate, nitrate, ammonium (non-organic secondary aerosols) and aerosol acidity were measured on a daily basis in both the urban and non-urban areas. The elemental composition of PM₁₀ was analyzed. PM₁₀ and BS concentrations were on average 13% and 19% higher in the urban areas than in the non-urban areas. PM_{2.5} concentrations were similar in the urban and non-urban areas. The small contrast in particle concentrations between urban and non-urban areas in the Netherlands was explained as a result of the small size of the country, the high population density, the lack of small-scale geographical and meteorological differences, and the importance of long-range transport of air pollutants. It was found that urban and non-urban differences depended strongly on wind direction. Easterly winds resulting in an influx of air masses from Central and Eastern Europe were associated with high concentrations and minimal urban-non-urban differences. Winds from the sea resulted in low concentrations but larger relative differences between urban and non-urban areas.

In the framework of the PEACE study, Hoek and his colleagues measured particles less than $10\mu\text{m}$ (PM₁₀) and black smoke (BS) in ambient at 28 sites in ten countries in Europe (1997). For about two months in the winter of 1993/94, 24-h average measurements were conducted. Each center studied both an urban and a more rural site. The difference of particle concentrations across countries appeared to be considerably larger than the difference between the urban and rural locations within countries. The median PM₁₀ concentration ranged from $11\mu\text{gm}^{-3}$ at three rural Scandinavian sites to $92\mu\text{gm}^{-3}$ in Athens, Greece. The median BS concentration ranged from $3\mu\text{gm}^{-3}$ in Umea, Sweden to $99\mu\text{gm}^{-3}$ in Athens, Greece. The most striking difference across countries was the low particle concentration found at the eight Scandinavian locations. PM₁₀ and BS concentrations in the urban areas were on average 22% and 43% higher than the

corresponding rural area concentrations, respectively. The correlation between the particle concentration measured at the urban and the more rural site exceeded 0.70 at almost all sites. PM₁₀ concentrations from all Western and Central European locations were significantly correlated. Low or no correlation was found between these locations and the South-European and Scandinavian locations. PM₁₀ and BS measured at the same site were highly correlated at most sites. However, the median PM₁₀/BS ratio ranged from 0.67 to 3.67 across sites. PM₁₀/BS ratios were close to unity for Athens, the Central European sites and Oslo. There was a tendency of lower PM₁₀/BS ratios in the urban area, consistent with the contribution of (diesel) motor vehicle emissions.

The study of Salisbury et al. (2003) presented measurements of acetonitrile, benzene, toluene, methanol and acetone made using the proton-transfer-reaction mass spectrometry (PTR-MS) technique at the Finokalia ground station in Crete during the Mediterranean INTensive Oxidant Study (MINOS) in July–August 2001. Three periods during the campaign with broadly consistent back trajectories were examined in detail. First, air was advected from Eastern Europe without significant biomass burning influence. In the second period, the sampled air masses originated in Western Europe, and were advected approximately east-south-east, before turning southwest over the Black Sea and north-western Turkey. The third well-defined period included air masses advected from Eastern Europe passing east and south of/over the Sea of Azov, and showed significant influence by biomass burning, confirmed by satellite pictures. The mean toluene-benzene ratios observed in the three campaign periods described were 0.35, 0.37 and 0.22, respectively; the use of this quantity to determine air mass age was discussed. Methanol and acetone were generally well-correlated both with each other and with carbon monoxide throughout the campaign. Comparison of the acetone and methanol measurements with the MATCH-MPIC model (Model of Atmospheric Transport and Chemistry, Max Planck Institute for Chemistry version 3.0) showed that the model underestimated both species by a factor of 4, on average. The correlations between acetone, methanol and CO implied that the relatively high levels of methanol observed during MINOS were largely due to direct biogenic emissions, and also that biogenic sources of acetone were highly significant during MINOS (~35%). This in turn

suggests that the model deficit in both species may be due, at least in part, to missing biogenic emissions.

Aerosol modeling is a challenging scientific problem aimed at improving current knowledge in the many complex processes involved in multiphase chemistry and transport. Correct simulations of aerosols are also required in order to elaborate particle emission reduction strategies. As a result, the CHIMERE chemistry transport model (Schmidt et al. 2001) has been improved to account for particle transport, formation and deposition at the European scale. The aerosol model has accounted both for inorganic and organic species of primary or secondary origin. Secondary organic aerosols from biogenic and anthropogenic gas precursors have been partitioned into gas and particulate phases through a temperature dependent partition coefficient. The modeling approach was presented in the study (Bessagnet et al., 2004) with preliminary simulation results over Europe. Comparisons with available data at background stations gave acceptable results on PM₁₀, with correlation coefficients usually exceeding 0.5 and normalized errors in the 30–80% range in many regions. However, results on sulfate, nitrate and ammonium species displayed less correct error statistics. Comparisons on sulfate concentrations gave normalized errors in the range 30–80% in summer and less correct in winter. Temporal correlation coefficients usually ranged from 0.30 to 0.70. Nitrate concentrations were better simulated during winter than during summer. Difficulties in simulating heterogeneous and aqueous phase processes could explain model deficiencies. Moreover, temperature dependence of gas/particle partitioning processes for nitrate, ammonium and secondary organic species could mainly explain the seasonal variability of biases. Model deficiencies were observed in Southern countries, certainly due to natural dust emissions and resuspended particles. Finally, sea salts seemed to have a quite significant influence on error statistics in coastal areas.

The concentration of different species in the atmospheric aerosol is influenced significantly by human activities, so the study of the source origin of elements in aerosol particles is of crucial importance for environmental management on an urban scale. As a result, receptor modeling applied in the study (Bozo et al., 2002) provides quantitative estimates of the impacts of sources on ambient air. In contrast to dispersion modeling, only minimal meteorology and emission inventory information were applied. Based on

ADMS dispersion model computations (Singles and Carruthers, 1999) spatial distribution of PM₁₀ was also estimated for Budapest to get a general picture on the particle pollution level at different locations in Budapest. It was concluded based on multiyear sampling and measurements that waste incineration provided the most significant contribution to the toxic metal load in Budapest (65-70%). The relative contribution of traffic sources was between 11-17%. Coal burning had no significant importance in Budapest regarding the contribution to the receptor profile. This could be explained by the fact that coal consumption was significantly reduced in Budapest during the past decades since it was replaced by natural gas at most of the industrial, residential and energy sources. In co-operation with The National Oceanic and Atmospheric Research (NOAA), three dimensional backward trajectories were also computed so as to estimate the origin of air masses on different days. It was found that episodes with relatively high concentrations of Ni and V measured in Budapest were accompanied by south winds indicating the effects of an oil refinery located 25 km South of Budapest.

Regional and local air quality models have become an important tool for environmental research and application to environmental assessment and policy questions. On one hand it is important to use air quality models as a tool to understand the simulations carried out with them, and on the other hand, evaluated, highly improved models should be used to forecast atmospheric pollutants in an operational state. The European Air Pollution Dispersion Model (EURAD) has been used to evaluate air quality problem for Europe. Since summer 2001 a real-time forecast system based on the EURAD Model has been tested and established to predict the main atmospheric pollutants on different scales in Europe. The EURAD forecast system consists mainly of the mesoscale meteorological model MM5 (PennState/NCAR mesoscale model Version 5), the emission Processor EURAD Emission Model (EEM) and the EURAD Chemistry Transport Model (EURAD-CTM). The EURAD forecast system consists mainly of the mesoscale meteorological model MM5 (PennState/NCAR mesoscale model Version 5), the emission Processor EEM (EURAD Emission Model) and the EURAD Chemistry Transport Model (EURAD-CTM). For about 15 years the EURAD model was developed and improved for applications within numerous case studies on the regional

scale in Europe (e.g. Jakobs et al., 1995; Ebel et al., 1997). Every day, an extensive amount of data is produced by the EURAD forecast system. This includes the meteorological prediction variables and the concentrations of the atmospheric constituents at all model levels, as well. In order to compare later especially the concentrations of air pollutants, the main effort was made to visualize the near surface concentrations of the main air pollutants O₃, NO₂, SO₂, CO and PM₁₀ for the entirety of Europe. For assessment studies, the ranges for the concentration thresholds were selected according to the EU directives (Jakobs et al. 2002).

The RAINS (Regional Air Pollution INformation and Simulation) model has been developed by IIASA (International Institute for Applied Systems Analysis, Laxenburg, Austria) as a tool for the integrated assessment of alternative strategies to reduce atmospheric pollution in Europe (Schöpp et al., 1999). The current version of this model describes the pathways of emissions of sulphur dioxide, volatile organic compounds (VOC), nitrogen oxides, ammonia and particulate matter and explores health and ecosystems' impacts of particulate pollution, acidification, eutrophication and tropospheric ozone. This model has a strong political importance. It has been used several times since the beginning of the 1990s as a basis for the definition of European emission reduction strategies. Klimont and his colleagues (2002) used RAINS model to evaluate particulate matter in the European Union (EU) and the non-EU countries. The model assumptions need further verification but its results already compare fairly well with published national and international inventories.

Vertical profiles, horizontal profiles and size distribution of airborne particulate matter were measured near major roads in Macao using DustTrak and TEOM monitors (Wu et al., 2002). A significant decrease in the concentrations of PM₁₀, PM_{2.5} and PM₁, as the height above the ground increases from 2 to 79m, was found. At the height of 79 m, the concentrations of PM₁₀, PM_{2.5} and PM₁, decrease to about 60%, 62% and 80% of the maximum occurrence at 2m above the ground, respectively. However, the horizontal profiles near another major road revealed there was no significant trend of decrease in concentrations of particulate matter as the distance from the road increases. Over the total measured distance (0–228 m), the maximum decreases of PM₁₀, PM_{2.5} and PM₁ are only 7%, 9% and 10%, of the maximum occurrence at 2m from the road,

respectively. The daytime averaged PM_{2.5} and PM₁ contribute 66–67% and 51–60%, respectively, of the total PM₁₀ mass after the particle readings by DustTrak were recalibrated by TEOM. It showed that fine particles and submicrometer particles contributed a major part of PM₁₀ at the roadside in Macao, which is most likely attributed to the combinations of local sources including exhausted particulate matter from vehicles and re-suspended fine dust, and secondary particles (sulfate, nitrate and ammonium) of regional scales.

Field data were used to evaluate the vertical distribution of suspended particulates at different height levels in an urban area of Hong Kong (Chan et al., 2000). Four buildings in different street configurations and street environments were selected. According to the street configurations, they were classified into two groups: street-canyon and open-street. In the street canyon, TSP and PM₁₀ concentration varied with height exponentially. However, the rate of TSP, PM₁₀ and PM_{2.5} decrease with distance from the ground floor was in decreasing order of TSP, PM₁₀ and PM_{2.5}. The particulate matter dispersion in street canyon was affected by the prevailing wind direction and the street configuration in particular the height-to-width ratio. In open streets, the vertical concentration depended on the vertical mixing, local dilution and other external factors such as sea breeze, as well as the proximity of trunk road and construction activity.

On the basis of the recently estimated emission inventory for East Asia with a resolution of $1 \times 1^\circ$, the transport and chemical transformation of sulfur compounds over East Asia during the period of 22 February through 4 May 2001 was investigated by using the CMAQ modeling system with meteorological fields calculated by the regional atmospheric modeling system (Zhang et al., 2004). For evaluating the model performance, simulated concentrations of sulfur dioxide (SO₂) and aerosol sulfate (SO₄²⁻) were compared with the observations on the ground level at four remote sites in Japan and on board aircraft and vessel during the transport and chemical evolution over the Pacific and Asian Pacific regional aerosol characterization experiment field campaigns. Analysis of model results shows that emission was the dominant term in regulating the SO₂ spatial distribution, while conversion of SO₂ to SO₄²⁻ in the gas phase and the aqueous phase and wet removal were the primary factors that controlled SO₄²⁻ amounts. The gas phase and the aqueous phase have the same importance in oxidizing SO₂, and

about 42% sulfur compounds (~25% in SO₂) emitted in the model domain was transported out, while about 57% (~35% by wet removal processes) was deposited in the domain during period of study.

The MM5-CMAQ model was used to assess the causes of weekday/weekend O₃ differences in the north-eastern Iberian Peninsula during an episode of photochemical pollution covering the whole Western Mediterranean Basin (Jimenez et al., 2004). The response of both ambient and simulated O₃ concentrations to day-of-week varied by location. Rural locations, dominated by medium-long range transport, depict similar O₃ concentrations. Both discrete and categorical model evaluations were shown in order to test the accuracy of the model for representing weekdays/weekends differences within the air basin. This study helped identify the major causes of the weekend effect in the considered domain, as the change in mass and time of precursor's emissions, and might be a useful tool to reduce ambient O₃ levels.

All in all, a general review of literature has been presented above for meteorology, emission and air quality studies. Although limited research could be found over Turkey, sufficient studies covering Europe were available. All these applications and researches put forward an opinion of the novelties and current situations of studies. In addition, they help compare the level of studies on atmospheric modeling between Turkey and other countries of the world.

3. METEOROLOGICAL MODELING

Meteorology is well-known to be an essential factor contributing to air quality. It contains many atmospheric processes that control or strongly influence the change in emissions, chemical species and particulate matter. These processes include horizontal and vertical transport, turbulent mixing, convection and both dry and wet deposition to the surface. By and large, meteorological models have similar modules in concept. They solve the equations of atmospheric motion over a three-dimensional grid, and use parameterization to calculate fluxes at the boundaries and estimate sub-grid scale processes such as cloud. In many studies, researchers have demonstrated accurately phenomenal events over Europe or also other different areas by using one meteorological model, or another. On the other hand, meteorological models produce input data to air quality models. The principal meteorological state variables needed for air quality models have to be obtained correctly. They are horizontal and vertical wind components, temperature, water vapor mixing ratio, cloud fraction and liquid water content, precipitation, solar actinic flux, sea level pressure, boundary layer depth, turbulence intensity (turbulent kinetic energy or vertical diffusion coefficient), and surface fluxes for heat, moisture and momentum. Furthermore, models have been designed to simulate biogenic emissions. They are highly sensitive to the accuracy of meteorological inputs, especially the temperature in the plant canopy and photosynthetic active radiation. At this point, air-quality models may contain significant uncertainties which adversely affect model simulations because of the meteorological input data.

The application of a meteorological model to air quality assessments is the first step of the entire research. Accuracy of air quality prediction largely depends on meteorological data sets. Although all of the models have broadly similar characteristics, the MM5 currently are the most thoroughly tested models for air-quality studies (Seaman N. L., 2000). In this study, taking into consideration the importance of meteorological fields for air quality models, Fifth-Generation Pennsylvania State University (PSU) / National

Center for Atmospheric Research (NCAR) Mesoscale Model (MM5) has been used purposefully to obtain atmospheric variables. The PSU/NCAR mesoscale modeling system consists of a mesoscale model and several auxiliary programs. These auxiliary programs are performed for the pre-processing and post-processing applications. MM5 model is a fifth-generation mesoscale meteorological model originally developed at Pennsylvania State University (Grell, Dudhia and Stauffer, 1994). It is a popular and powerful model that assists to improve forecast of weather (UCAR, 2002). The non-hydrostatic MM5 model (Dudhia, 1993; Grell et al., 1994) is a three-dimensional prognostic model which has been used widely in regional air quality model applications (e.g., Russell and Dennis, 2000; Seaman et al., 1995; Seaman and Stauffer, 1996; Tesche et al., 1998b, 1998c; 2002). The basic model has been under continuous improvement and testing for more than 20 years (e.g., Anthes and Warner, 1978; Anthes et al., 1987) and has been used world-wide by hundreds of scientists for a variety of meteorological studies including air quality research.

3.1 Modeling System

Before running the meteorological model, several pre-processing programs must be run to set up the domain for the simulation and to generate a set of initial and boundary conditions for the model. Flow-charts of the complete modeling system are depicted in the schematic diagrams in Fig. 3.1.

3.1.1 Terrain

This program, TERRAIN, makes use of high-resolution global terrain and land use data sets to create static files for the domain. The static files currently include values for each grid point for terrain height and land use specification (e.g., deciduous forest, desert, water). This is essential for an accurate run. It also defines the model domain and map projection that locates the area the model will simulate. Various types of terrain affect atmospheric circulation patterns. Therefore, the type of terrain and vegetation cover must be specified and accurately defined within the chosen domain for the simulation to produce accurate results (Guo and Chen, 1994).

The REGRID and the RAWINS (or the LITTLE_R) are the auxiliary programs of the modeling system and they together accede to all of the meteorological data used as input to the mesoscale model.

Figure 3.1: The MM5 modeling system flow chart.

3.1.2 Regrid

After the simulation domain had been established, the program REGRID was run to process the meteorological background fields. REGRID generated first-guess fields for the model simulation by horizontally interpolating a larger-scale data set (global or regional coverage) to the simulation domain. REGRID interpolated the background fields to the simulation domain throughout the simulation period; these files were used ultimately to generate lateral boundary conditions for the coarse-domain simulations.

In brief, the main purpose of the program REGRID was to interpolate coarse-resolution global or hemispheric meteorological analyses horizontally to the mesoscale grid. The input analyses were obtained from the NCEP (The National Centers for Environmental

Prediction) database. This data set is a global analysis beginning in 1948 using a single analysis system for the entire dataset. Analyses are available every six hours. Data are archived on a 2.5 x 2.5 degree lat/lon grid and a gaussian grid (~1.9 degrees lat, 2.5 degrees lon).

3.1.3 Objective Analysis (Little_r)

The goal of objective analysis in meteorological modeling is to improve meteorological analyses (the first guess) on the mesoscale grid by incorporating information from observations. In this study, an objective analysis was performed with the program LITTLE_R to improve interpolated analysis later used as an input to the INTERPF program. Also, quality control checks were performed for some atmospheric variations.

All of the observation stations located in the related domain can be seen in Figure 3.2. There are lots of points for observations. As a result of this, their positive effects couldn't be undervalued in terms of improved analysis data. The analyses from LITTLE_R were interpolated to the MM5's staggered grid configuration and from their native vertical coordinate (pressure) to the MM5's vertical coordinate (a terrain-following, pressure-based sigma coordinate) by the INTERPF module.

3.1.4 Setting the Initial and Boundary Conditions (Interpf)

The INTERP program sets the initial and boundary conditions for the meteorology simulation. In the program, the analyses from one time were interpolated to provide MM5's initial conditions, while analyses from all running times were interpolated to get MM5's lateral boundary conditions. This was the final step before the actual MM5 model could be run.

3.1.5 MM5

This is the numerical weather prediction part of the modeling system. MM5 can be used for a broad spectrum of theoretical and real-time studies, including applications of both predictive simulation and four-dimensional data assimilation to monsoons, hurricanes, and cyclones. On the smaller meso-beta and meso-gamma scales (2-200 km), MM5 can

be used for studies involving mesoscale convective systems, fronts, land-sea breezes, mountain-valley circulations, and urban heat islands.

MM5 is based on primitive physical equations of momentum, thermodynamics, and moisture. The state variables are temperature, specific humidity, grid-relative wind components, and pressure. Several model physics options in MM5 are put together including radiation, convective parameterization, planetary boundary layer processes, surface layer processes and resolvable-scale microphysics schemes.

Figure 3.2: Observation Stations located in related domain.

4. EMISSION MODELING

Gases or particular matters are emitted into the atmosphere by human and natural activities. They cause many current and potential environmental problems, including acidification, air quality degradation, global climate change, damage and soiling of buildings and other structures, stratospheric ozone depletion, human and ecosystem exposure to hazardous substances. The quantitative information of the emissions and their sources is essential with regards to determine and solve the problems. This information is required to inform the policy makers and the public. In addition, reliable quantitative knowledge is necessary to define environmental priorities, identify the activities and actors responsible for the problems, evaluate the potential environmental impacts and implications of different strategies and plans, and assess the environmental costs and benefits of different policies. The most important aspect may even be detailed information about emissions needed to improve the public health.

It is increasingly important to provide accurate, detailed, and consistent emission information to support air quality planning and atmospheric modeling requirements. There are many types of sources of atmospheric emissions and many examples (often millions) of each type, for example: power plants, refineries, incinerators, factories, domestic households, cars and other vehicles, animals and humans, fossil fuel extraction and production sites, offices and public buildings, trees and other vegetation, distribution pipelines, fertilized land, land with biological decay. It is impossible to measure emissions from all of the individual examples of these sources or, in the short term, from all the different source types. In practice, atmospheric emissions are estimated on the basis of measurements which are made at selected or representative samples of the main sources and source types.

The basic model for an emission estimate is the product of (at least) two variables, for example; an activity statistic and a typical average emission factor for the activity. Emission estimates are collected together into inventories or databases which usually

also contain supporting knowledge about the data, for example: the locations of the sources of emissions; emission measurements where available; emission factors; capacity, production or activity rates in the various source sectors; operating conditions; methods of measurement or estimations, etc. Emission inventories may contain data on three types of sources, namely point, area and line. However, in some inventories all of the data may be on area basis - region, country, sub region etc. Point source emission estimates are provided on an individual plant or emission outlet (usually large) generally in conjunction with data on location, capacity or throughput, operating conditions etc. Area sources smaller or more diffused sources of pollution are provided on an area basis either for administrative areas, such as counties, regions etc, or for regular grids (for example EMEP 50x50 km grid). Line sources in some inventories, vehicle emissions from road transport, railways, inland navigation, shipping or aviation are provided for sections along the line of the roads, railway-tracks, sea-lanes etc.

4.1 Atmospheric Emission Inventory Methodology

The most important and necessary step is the preparation of an emission inventory in view of the evaluation of the air quality problems. It provides emission data for the chemistry-transport calculation with a model. Actually, an emission inventory provides impact of emissions of man-made or natural sources on the chemistry of the atmosphere and ecosystem in terms of a general look. It acts as an interface between emission data and a chemistry model. An atmospheric emission inventory should be defined as a collection of data presenting an emission of a pollutant and related parameters including:

- chemical identity (characterizes the chemical properties of the pollutant)
- activity or technology (characterizes the cause of the emission and relates it to activity)
- location (describes both the location on the map and the height of the release)
- time dependence (emission inventories store as annual totals).

Current emission inventories are not only used as an input to air quality models, but also as the basis for emission-control-related agreements, laws, or arrangements. Natural

emissions are often accorded by special treatment in models and are usually exempted from emission reduction strategies. However, anthropogenic emissions have altered the behavior of ecosystems in a way that makes it difficult to attribute the emissions entirely to man or nature. But recent studies show that especially biogenic emissions should be considered because of the impact of atmospheric chemistry. The discrimination between natural and anthropogenic emissions is also needed in areas other than air pollution.

Emission inventory preparation is a critical stage in air quality modeling and probably there is a great lack of quality input information. Practical efforts in assessing emissions have led to a number of comprehensive inventory activities. There have been several major international initiatives over the past 10 years. These efforts have helped to develop the emission inventory methodology. These include The Organization for Economic Co-operation and Development (OECD) Control of Major Air Pollutants (MAP) Project, The DGXI Inventory (Commission of The European Communities Environment, Nuclear Safety and Civil Protection - Agency Task Force DG XI), The US-EPA (Environmental Protection Agency), The CORINE (CO-oRdination d'Information Environnementale) Program and subsequent work by the EEA (European Environment Agency) Task Force, The Co-operative Program for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) and The IPCC/OECD Greenhouse Gas Emissions Program. Detailed information about European emission inventories can be seen in the following paragraphs.

CORINE and the EEA Task Force

European Council Decision (85/338/EEC, OJ, 1985) established a work program concerning an "experimental project for gathering, coordinating and ensuring the consistency of information on the state of the environment and natural resources in the Community". The work program was given the name CORINE (CO-oRdination d'Information Environnementale) and includes a project to gather and organize information on emissions into the air relevant to acid deposition (CORINAIR). This project was started in 1986 by the 12 Member States of the Community. The CORINAIR 1985 Inventory covered three pollutants - SO₂, NO_x, and VOC (total volatile organic compounds) - and recognized eight main source sectors: combustion

(including power plants but excluding other industries), oil refineries, industrial combustion, processes, solvent evaporation, road transportation, nature and miscellaneous others.

The project has also developed a source sector nomenclature for emission source sectors, sub-sectors and activities, a default Emission Factor Handbook and a computer software package. The CORINAIR 1985 Inventory was developed in collaboration with the Member States, Eurostat (Statistical Office of the European Union), OECD (Organisation for Economic Co-operation and Development) and UNECE/EMEP (United Nations Economic Commission for Europe/Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe). The Inventory was completed in 1990 and the results have been published (Eurostat, 1991; CEC, 1995).

However, the European Environment Agency decided to produce an update of CORINAIR for 1990 in 1991 (CORINAIR 1990). This update has been performed in co-operation with EMEP and IPCC (Intergovernmental Panel on Climate Change) -OECD to assist in the preparation of inventories required under the Long Range Trans-boundary Air Pollution (LRTAP) Convention and the Framework Climate Change Convention (FCCC) respectively.

The CORINAIR90 system was made available to the 12 member states of the European Community in 1990 (Belgium, Denmark, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain and United Kingdom), 5 EFTA (European Free Trade Association) countries (Austria, Finland, Norway, Sweden and Switzerland), 3 Baltic States (Estonia, Latvia and Lithuania), and 9 Central and Eastern European countries (Albania, Bulgaria, Croatia, Czech Republic, Hungary, Poland, Romania, Slovakia, Slovenia and Russia). This collaboration produced a more sophisticated nomenclature, a greater number of pollutants (Sulphur dioxide; oxides of nitrogen; non-methane volatile organic compounds; ammonia; carbon monoxide; methane; nitrous oxide and carbon dioxide), extended sources and extended countries.

The CORINAIR 1990 Inventory covers 11 main source sectors (as agreed with EMEP):

- Public power, cogeneration and district heating plants

- Commercial, institutional and residential combustion plants
- Industrial combustion
- Production processes
- Extraction and distribution of fossil fuels
- Solvent use
- Road transport
- Other mobile sources and machinery
- Waste treatment and disposal
- Agriculture
- Nature.

The Goal of CORINAIR90 is to provide a complete, consistent and transparent air pollutant emission inventory for Europe in 1990 within a reasonable time scale to enable widespread use of the inventory for policy, research and other purposes. Completeness covers two aspects: the CORINAIR90 system is available to almost all countries of Europe and the SNAP90 nomenclature has been designed to provide a comprehensive list of activities generating emissions of the eight pollutants to be quantified. Consistency will be provided by the systematic application of the CORINAIR methodology to provide emission estimates. Transparency will be achieved through the provision within the inventory of activity statistics/data and emission factors used to calculate emissions and through the supply of full references to the sources of these data.

EMEP

The Cooperative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) formed by a Protocol under the Long Range Transboundary Air Pollution Convention has arranged a series of workshops on Emission Inventory Techniques to develop guidelines for estimation and reporting of emission data for SO_x, NO_x, NMVOCs, CH₄, NH₃ and CO.

These guidelines included a recommendation that emission data should be reported as totals and at least for the 11 major source categories agreed with the CORINAIR project and other experts for the CORINAIR 1990 Inventory. The proposed task force was set up under the EMEP Steering Body with leadership from the United Kingdom and support from Germany and the European Community (including the European Environment Agency).

The inventorying of anthropogenic emissions in Europe has attained a high standard of consistency and detail within the last few years. This has largely been achieved through the use of a joint nomenclature agreed between the EMEP and CORINAIR programs and the joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (McInnes, 1996). This Guidebook, the European equivalent of America's AP42 document (U.S. Environmental Protection Agency, 1997), aims to provide an up-to-date and comprehensive summary of emission inventory methodology and emission factors for each of the pollutants and sources to be quantified. Unfortunately, the first edition of this guidebook was restricted to anthropogenic emissions; biogenic emissions were only considered for agricultural activities, especially for NH_3 .

Emissions from natural sources take part in the background chemistry of the atmosphere. As a result, it is worthy to study them. In order to assess biogenic emissions, certain input information is needed. Temperature and radiation directly affects the emission behavior. These parameters can be combined through environmental correction factors. In addition, detailed information about the distribution and the density of plants, including specific species, is required. In this study, land-cover information of the meteorological model (global forest and vegetation coverage-USGS) was used. All Europe has been investigated.

It is a well-known fact that any emission inventory has an impact on the accuracy of the results of any air quality model. In this study, anthropogenic and natural-biogenic sources were handled separately. The database of the EMEP annual emissions (2001) has been used for the anthropogenic sources. This database has provided emissions for 10 anthropogenic source sectors. Since biogenic emissions are still not available in EMEP gridded emissions database, a separate methodology has been utilized for the

biogenic emissions. This method is broadly similar to in the Biogenic Emissions Inventory System (BEIS3 model).

The emission inventories are calculated in a yearly basis. However, any air quality model requires hourly emission data. Therefore, some processes have to be applied for an emission inventory to obtain model-ready input data. For temporal processing, specific temporal profiles should be generated to convert the inventory information on annual basis to values from day and hour-specific emission data sets. The speciation profile is needed to adapt the pollutants to an air quality model. Finally, the spatial processing operation or gridding is a key issue in the transformation of inventory emissions to gridded emissions useful for an air quality model.

Any emission inventory preparation for modeling is a critical step on the air quality modeling. Although there are some powerful models to evaluate concentrations of air pollutants, the reliable emission input is as important as using a good model. For this reason, emission inventories and their processes have been studied by several groups and associations.

4.2 Modeling System

Emission models, one of main components of an air quality modeling system, with meteorology, chemistry and transport, are used to make input files ready for air quality prediction. Emission processing, defined as the creation of spatially and temporally resolved emissions from raw data is a crucial part of the air quality modeling. The European Emission Modeling (EME) have been developed by using the SMOKE (Sparse Matrix Operation Kernel Emissions) model developed by North Carolina Supercomputing Center (NCSC) and BEIS3 (The Biogenic Emissions Inventory System version 3) systems.

SMOKE is used to convert the source-level emissions (tons per year per county per source) to gridded, speciated, and temporally processed emissions (tons per hour per grid cell per source). This conversion consists of multiplying emissions of various sources by several factors in steps called temporalization, speciation, and gridding. At each step, the processing model uses profile tables and cross-reference tables to convert

or modify the emission resolution. The profile tables contain the factors for converting emissions from county wide, yearly emissions to hourly emissions with finer spatial resolution. Cross-reference tables are used to assign the profiles to each source (Houyoux et al., 1999; 2000). In the temporalization step, SMOKE creates an hourly pollutant emissions inventory by applying the monthly, weekly, and diurnal profiles based on the source characteristics, using the cross-reference table to match the profile to the source type. In the speciation step, it creates a speciation matrix containing conversion factors, used to convert Volatile Organic Compound (VOC) concentrations to the concentrations of specific organic compounds. There are nine specific organic compounds for the Carbon-Bond IV (CB4) chemical mechanism. The CB4 mechanism is one of many mechanisms developed to represent chemical interactions among atmospheric constituents. This lumped structure mechanism creates a balance between computing efficiency, which favors compressed chemical mechanisms, and accuracy, which demands explicit treatment of chemical reactions, and favors large chemical mechanisms. The nine organic compounds for the partitioning of VOC are ethene (ETH), isoprene (ISOP), formaldehyde (FORM), paraffin (PAR) representing single carbon bonds, olefin (OLE) representing double-bonded carbon atoms, toluene (TOL) representing 7-carbon ring structures, xylene (XYL) representing 8-carbon ring structures, acetaldehyde (ALD2) representing carbonyl group and adjacent carbon atoms in acetaldehyde and higher molecular weight aldehydes, and non-reactive (NR) carbon atoms (Jacobson, 1999). In the gridding or spatial allocation step, SMOKE uses a gridding surrogate to create a matrix containing conversion factors, used to transform county level aggregate emissions to emissions in each grid cell. A gridding surrogate is a dataset developed from geographic information (e.g. population or land use) at a finer spatial resolution than the initial emissions data, and it is used to spatially allocate the emissions to the grid cells (Choi et al., 2001).

The BEIS3 model uses spatially and temporally resolved meteorological data including temperatures, solar radiation and surface pressures; spatially resolved, species-specific vegetation; species-specific biogenic emissions factors (including a winter adjustment); species-specific leaf area indices and chemical speciation profiles. Emission factors in BEIS consist of isoprene, monoterpene, nitrogen oxide and other VOC factors for all

land use types. The emissions factors are the flux-rate that each species emits under standard environmental conditions (i.e. 30°C and 1000 $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ PAR for isoprene and 30°C for monoterpenes, other VOCs, and NO). This emission factors file also includes a winter adjustment factor and a leaf area index (LAI) for each land use type. LAI is defined as the total one-sided, or one half of the total all-sided, green leaf area per unit ground surface area (Chen et al., 1992). In BEIS3, LAI is used to adjust the isoprene emissions for the effects of PAR penetrating through the leaf canopy. The modeling system is a two-step process. In step one, the landuse data and emissions factors file are input into the program. The program estimates normalized emissions (at 30°C and 1000 $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ PAR environmental conditions) by multiplying the emissions factor by the appropriate land use for each grid cell. In the next step, the input data for this program consist of the meteorological data, speciation profiles, and the normalized emissions generated after the execution of the program. The speciation profiles are used to allocate other VOC and monoterpene emissions to species recognized by the chemistry mechanism in the desired air quality model.

It has been developed the EME model to process the emission inventory according to the SMOKE and BEIS3 models. This system includes mainly speciation, temporal allocation and gridded processes for both sources of anthropogenic and biogenic emissions (Figure 4.1).

4.2.1 Anthropogenic Emission Processes

The anthropogenic emission processes (AEP) were performed for the EMEP emission inventory data. This inventory provides emissions for 10 anthropogenic source sectors. For temporal processing, specific temporal profiles are used to convert the inventory information on annual basis to values from day and hour-specific emissions data sets. The spatial processing operation or gridding is a key issue in the transformation of inventory emissions to gridded emissions useful for the air quality model. Raw emission inventories, in general, provide data for total VOCs, SO_x and NO_x. In order to be able to input data to air quality model, these raw values need to be speciated.

Figure 4.1: The EME modeling system flow chart.

4.2.2 Biogenic Emission Processes

Biogenic emission data are still not available in EMEP gridded emission database. For this reason, an inventory of biogenic emissions was prepared for the related area. In this study, isoprene, monoterpene, OVOC (NR, OLE, PAR, ALD2, TERPB) and NO emissions have been dealt with from all types of forests, vegetation and land use. This method is broadly similar to the one used in the Biogenic Emissions Inventory System (BEIS3 model). The biogenic emission processes were performed for the biogenic sources including land use data import, estimation of hourly emission and speciation.

5. CHEMISTRY AND TRANSPORT MODELING

Air quality modeling is a popular and efficient method to evaluate the ambient air quality over city or regional area. Actually, it has complex tools which are used for different purposes such as pure environmental research, air quality management, economical effects, impact of long-range transport and future scenario analysis.

The development of comprehensive air quality models started in the late seventies. The Urban Airshed Model (UAM) (Morris and Myers, 1990) followed by the Regional Oxidant Model (ROM) (Lamb, 1983a, 1983b) provided Eulerian-based models for ozone, the former on urban and the latter on regional scale. Attention to acid deposition issues were addressed in the eighties with the development and evaluation of regional acid deposition models such as the Regional Acid Deposition Model (RADM) (Chang et al., 1987; Chang et al., 1990), the Acid Deposition and Oxidant Model (ADOM) (Venkatram et al., 1998), and the Sulfur Transport and Emissions Model (STEM) (Carmichael and Peters, 1984a, 1984b; Carmichael et al., 1991). Other major modeling systems included the Regional Lagrangian Modeling of Air Pollution model (RELMAP) (Eder et al., 1986), a Lagrangian framework system, and semi empirical and statistical models. The style of models of this period was designed to address specific air pollution issues such as ozone or acid deposition. Dealing with other issues, such as particulate matter or toxics, was very limited. As a result, these models were useless and limited to handle more complex implementations and pollutants. In the early nineties, a wide range of additional pollutants was identified including visibility, fine and coarse particles, indirect exposure to toxic pollutants such as heavy metals, semi-volatile organic species, and nutrient deposition to water bodies.

With development of computational capabilities at the start of the nineties, the opportunity arose for a strategic review of modeling approaches leading to the design of a system that would both meet and keep pace with the increasing requirements on air quality modeling. The scope of such a system must be able to process great and diverse

information from complicated emission mixtures and complex distributions of sources. It should model the complexities of atmospheric processes (such as transport and transformation) on a large range of time scales covering minutes to days and weeks. In addition, it has to be flexible spatial scales ranging from local to continental scales.

To meet both the challenges and the need to address the complex relationships between pollutants, the USEPA started the Models-3 project and developed the Community Multiscale Air Quality (CMAQ) system, an advanced air quality modeling system that addressed air quality from this one atmosphere-multi-pollutant perspective. Based on its conceptual design, the high performance computational Models-3 framework serves to manage and orchestrate air quality simulations, using the CMAQ modeling system. The Models-3 framework is an advanced computational platform that provides a sophisticated and powerful modeling environment for science and regulatory communities.

5.1 Modeling System

Air quality simulation models are important tools for regulatory, policy, and environmental research communities. The CMAQ modeling system is a powerful third generation air quality modeling and can address tropospheric ozone, acid deposition, visibility, fine particulate and other air pollutant issues in the context of one atmosphere perspective where complex interactions between atmospheric pollutants and regional and urban scales are confronted.

The primary goals for the Models-3/Community Multiscale Air Quality (CMAQ) modeling system are to improve the environmental management community's ability to evaluate the impact of air quality management practices for multiple pollutants at multiple scales and the scientist's ability to better probe, understand, and simulate chemical and physical interactions in the atmosphere.

The CMAQ modeling system includes auxiliary programs and interface processors to incorporate the outputs of the meteorology and emission processors and to prepare the pre-required input information for initial and boundary conditions and photolysis rates to the CMAQ Chemistry Transfer Model (CCTM). Figure 5-1 illustrates the relationship

and purpose of each of the CMAQ processors (and requisite interfaces) and their relation to the chemical transport modeling system. The arrows show the flow of data through the modeling system. Each of these processors is described briefly below:

Figure 5.1: Inputs and outputs of CMAQ photochemical air quality model and related modeling tools, and the model interactions.

5.1.1 The Initial Concentration and Boundary Condition Processors (ICON-BCON)

This part describes the two processors in the Community Multiscale Air Quality (CMAQ) modeling system that generate the initial concentrations and boundary conditions that are required by the CMAQ Chemical Transport Model (CCTM).

For initial concentrations (ICs), the CCTM requires that the concentrations of all model species within each grid cell in the modeling domain be specified for the start of the simulation. Concentrations of all model species at the boundaries of the modeling domain throughout the simulation are required as boundary conditions (BCs) to the CCTM.

The ICON and BCON processors generate ICs and BCs for individual model species, which include gas-phase mechanism species, aerosols, nonreactive species and tracer species. The ICON processor generates species concentrations for every cell in the modeling domain, whereas the BCON processor generates species concentrations for the cells immediately surrounding the modeling domain. The ICON and BCON processors generate IC and BC files from one of three input sources. The first is a time invariant set of vertical concentration profiles. The second source of input data consists of existing Models-3 IO/API 3-dimensional concentration files, normally generated by the CCTM. The final source of IC and BC data involves the generation of special tracer species concentrations used to test numerical transport algorithms. In this study, a time invariant set of vertical concentration files prepared as profiles were used. Appendix3 contains a listing of the CMAQ predefined IC profile file and the corresponding predefined BC profile file.

5.1.2 Photolysis Rates for CMAQ (JPROG)

Many chemical reactions in the atmosphere are initiated by the photo dissociation of numerous trace gases. These reactions are responsible for most of the smog build-up detrimental to humans, animals, plant life and materials. In order to accurately model

and predict the effects of air pollution, good photo dissociation reaction rate (or photolysis rate) estimates must be made.

Photodissociation is the conversion of solar radiation into chemical energy to activate and dissociate chemical species. Examples of species that photodissociate include many important trace constituents of the troposphere such as NO₂, O₃, HCHO, CH₃CHO, HONO, the NO₃ radical, and H₂O₂. The simulation accuracy of the entire chemical system is highly dependent upon the accuracy of photolysis rates, which are the primary sources of radicals in the troposphere.

Preprocessor JPROC calculates a table of clear-sky photolysis rates (or J-values) for a specific date. The table is dimensioned by latitude, altitude, and time. The current approach taken for setting photolysis rates in the Models-3/CMAQ framework follows that of the Regional Acid Deposition Model (RADM) (Chang et al., 1987). Appendix 2 (Table2.2) lists the photolysis reactions for the RADM2 mechanism. It includes two stages of processing:

- (1) a table of clear-sky photolysis rates is calculated for specified heights, latitudes, and hours from local noon; and
- (2) photolysis rates are interpolated from the table within the CMAQ Chemistry Transport Model (CCTM) based on grid cell location and the model time, and are corrected for cloud cover.

This approach is computationally efficient and has been shown by Madronich (1987) to give clear-sky photolysis rates within the uncertainty of the surface-based measurements.

5.1.3 Meteorology-Chemistry Interface Processor (MCIP)

The Meteorology-Chemistry Interface Processor (MCIP) links meteorological models such as MM5 with the Chemical Transport Model (CTM) of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system to provide a complete set of meteorological data needed for air quality simulations. Because most meteorological models are not built for air quality modeling purpose, MCIP deals with issues related to

data format translation, conversion of units of parameters, diagnostic estimations of parameters not provided, extraction of data for appropriate window domains, and reconstruction of meteorological data on different grid and layer structures.

MCIP is a key processor linking meteorological models to the CMAQ modeling system. Its major roles are:

1. To read meteorological data from a meteorological model and convert them in Models-3 I/O API format.
2. To provide all the necessary meteorological parameters for air quality simulations. When necessary, PBL parameters and other derived quantities are computed using gridded meteorology data and high-resolution fractional land use information (Appendix5).
3. To support multiscale generalized coordinate implementation of the CCTM.

5.1.4 Emissions

The emission input required by EMEP model consists of gridded annual national emissions of sulphur oxides ($\text{SO}_x = \text{SO}_2 + \text{SULF}$), nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), ammonia (NH_3), non-methane volatile organic compounds (NMVOC), carbon monoxide (CO), and particulates (PM_{2.5}, PM₁₀). These emissions are provided for 10 anthropogenic source sectors. Contrary to anthropogenic emissions, biogenic emission data are still not available in EMEP gridded emission database. For this reason, a separate methodology was used for biogenic emissions. This method is broadly similar to the one used in the Biogenic Emissions Inventory System (BEIS3 model). Other details which are related to preparation of emission data have already been explained in the previous section of the emission modeling. In addition, detailed information related to aerosol can be seen in the Appendix4.

5.1.5 Chemistry

Photochemical reaction mechanisms are formulated to depict the complex chemical interactions controlling the atmospheric concentrations of natural and anthropogenic

compounds. Several different representations of the chemistry within any mechanism have stimulated an attempt to provide simplified, yet accurate, descriptions of tropospheric chemical systems to be used in air quality simulation models. By generalizing the common chemistry of similarly reacting hydrocarbon groups with a few surrogate species, it is possible to make the organic chemistry more manageable, while still achieving a reasonably accurate representation of the chemical system (Gery et al., 1989).

All important chemical transformations relevant to the problem being studied must be included to make accurate predictions of ambient pollutant concentrations. This approach has been adopted in the Chemical Transport Model (CTM) that is part of the Community Multiscale Air Quality (CMAQ) modeling system (CCTM).

Interactions in the gas-phase are represented in air quality models by means of chemical mechanisms. In this study the CB4 (Gery et al., 1989) chemical mechanisms were chosen. The CMAQ implementation of the basic CB4 mechanism includes 36 species and 93 reactions, including 11 photolytic reactions. The CB4 mechanism described by Gery et al. (1989) has undergone several changes since its publication. All of these changes have been incorporated in the CMAQ version. CB4 gas-phase chemical mechanism has been linked to aqueous chemistry and to aerosol formation processes. Since these linkages required some modifications to the original gas-phase mechanisms, different versions of the same mechanism were created for modeling gas-phase chemistry alone or for modeling gas-phase chemistry with or without aerosols and/or aqueous chemistry. Mechanisms that have been modified to account for aerosol production have their names appended with “_AE”, mechanisms modified for aqueous chemistry are appended with “_AQ”, and mechanisms modified for both are appended with “_AE_AQ”. Thus, CB4_AE_AQ refers to the CB4 gas-phase mechanism that has been modified to include linkages to both aerosols and aqueous chemistry. Complete listings of all mechanisms currently available in the CMAQ system are included in Appendix 2.

6. CASE STUDY

In Europe, anthropogenic sources are dominant because of the urbanization of many countries and the large number of vehicle and combustion sources (industrial and residential) (EMEP/CCC-Report 8/99, 1998). Natural sources of primary aerosols in Europe include sea spray, fugitive dust (e.g. soil re-suspension by the wind), long-range transport of the Sahara dust, volcanic and biogenic emissions. However, the majority of monitoring data is from urban networks in some parts of Europe and there is no systematic monitoring program with representative rural sites in most countries. In addition, many research studies have been performed in northwestern Europe, where aerosol concentrations between urban and non-urban areas do not exceed 20% (e.g. Van Der Zee et al., 1998). This can be attributed to high emissions from a dense population area, the small weather variability between the measurement sites and the importance of long-range transport of air pollutants. The absence of comprehensive transport of pollutants and the deficiency of observations of pollutants over the Eastern Europe do not give any permission to extensive evaluation about the pollutants.

In addition, particulate matter (PM) in the atmosphere has been a great concern in recent years, affecting human health, visibility (regional haze), and climate change. PM consists of mixtures of hundreds of components over a wide size distribution resulting from various physical and chemical processes that make a difficult pollutant to model. PM modeling evaluation is currently difficult, due to the lack of adequate data for comparison.

Airborne particulate matter is a complex mixture of many different chemical species originating from a variety of sources. Compositions, morphology, physical and thermodynamic properties of PM vary in different geographical places and have a seasonal variability (Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1998; EPA, 1996; Alpert and Hopke, 1981). Sources of PM can be either primary or secondary in nature. Primary particles can be furthermore divided as anthropogenic or natural

depending on their origin. Secondary formed particles in the atmosphere are from both natural and anthropogenic origin and are originating from chemical transformations of gaseous precursors such as sulphur dioxide, nitrogen oxides and VOCs. Recent research studies highlight also the importance of biogenic hydrocarbons (such as terpenes) to the formation of organic aerosols (Hoffman et al., 1998; Kavouras et al., 1998).

Long-range transport of gaseous air pollutants has been studied extensively in Europe the last decades under the framework of the European Monitoring and Evaluation Program (EMEP) (EMEP-WHO, 1997; Eliassen and Saltbones, 1983; Tarasson and Tsyro, 1998; Pacyna et al., 1991) and several national and international efforts (Berdowski et al., 1998; EPA, 1996a,b; EU, 1996, 1997; Quality of Urban Air Review Group, 1996; EMEP/CCC-Report 8/99, 1998). Emissions of pollutant rise up in the air due to buoyancy effects, carry downwind, and disperse horizontally and vertical due to turbulence field and prevailing meteorological patterns. The last years there is an extensive research focus on particulate matter (PM) (EPA, 1996; EU, 1996, 1997; EMEP-WHO, 1997, WHO, 1996) mainly because of serious public health risks for susceptible members of the population and risks to sensitive ecosystems. The transport of PM in the atmosphere is similar to that of gaseous pollutants for the fine particle fraction but deviates at larger sizes (coarse particles) due to deposition processes. Therefore, the long-range transport of PM contributes significantly in the background particle mass and number size distribution. However, there is still considerable debate among the scientific community regarding the vertical exchange processes involved and the spatial and temporal scales of atmospheric particle transport.

6.1 Pollution Episodes

Istanbul is the largest urban center in the North-West of Turkey, with more than 12 million inhabitants in the metropolitan area. It has become clear in recent years that the most severe particulate matter episodes are accompanied by westerly and northwesterly winds (Tayanç, et al., 1997). Figure 6.1 shows hourly PM₁₀ concentration in Istanbul throughout January 2002 and Figure 6.2 shows possible transport may have contributed to two high pollution events that occurred in Istanbul, Turkey on 7-8 and 10-11 January 2002. During that month, the most severe air pollution episode in Istanbul occurred on

10 January (216 to 240 hr in Fig. 6.1); the PM10 monthly averaged value reached $70\mu\text{g m}^{-3}$ and local hourly concentrations were up to $780\mu\text{g m}^{-3}$.

Figure 6.1: Time series of aerosol mass concentration (PM10) measured on the Besiktas, Sarachane and Alibeykoy observation stations in Istanbul during the January, 2002.

During these events, the atmospheric circulation over central Europe was dominated by a cold-core surface anti-cyclone, a climatologically favored feature during the cold season (Kallos et al. 1998). Air trajectories associated with this anti-cyclone were capable of transporting high concentrations of PM10 (particles with diameter $< 10\mu\text{m}$) over long distances to Istanbul. Therefore, we hypothesize that PM10 transported from other highly polluted cities in Europe are partially responsible for these two pollution events in Istanbul.

It is suspected that those peak levels of pollution in Istanbul were a combination of transported pollution and local emissions. From 5th to 12th of January, strong westerly and northwesterly winds were observed (Fig.6.3) and might have brought particulate pollution from Europe to Istanbul. In Fig. 6.3a, strong 900-mb westerly winds occurred over Northern Europe and then turned into northerly before reaching Turkey at 00:00 UTC 8th of January, 2002. A similar pattern, but smoother flow was observed at 00:00 UTC 10th of January, 2002 (Fig.6.3b). These winds have a great potential to carry pollutants from northern and northwestern Europe to Turkey.

Figure 6.2: Time series of measured PM10 concentration at Umraniye, Uskudar, Besiktas, and Sarachane observation stations in Istanbul from 00 UTC 5 to 00 UTC 12 January, 2002.

6.2 Overview of the Air Quality Modeling System

A regional-scale air quality modeling system is adopted in this study, and it consists of three main components: a meteorological model, an emission inventory processor, and a chemistry/transport model (Fig. 6.4). The meteorological model is the Fifth-Generation NCAR / Penn State Mesoscale Model (MM5; Grell et al. 1994). The emission processing module is the Emission Modeling for Europe (EME) which is a newly developed module. The chemistry/transport model is the US/EPA Community Multiscale Air Quality Modeling System (CMAQ; Byun and Ching, 1999). The meteorological model and the emission model have already explained the preceding chapters. The air quality model is briefly introduced in the following sections.

6.2.1 Meteorological Model Setup

In this study, it took great pains to set up domain configuration. Actually, since the emission inventory was prepared in a 50 km. resolution for Europe, the domain resolution of the meteorological model had to be set up at the same resolution. However, land use data resolution was chosen 9 km. to capture more details, especially vegetation types of the area. According to the emission inventory, which covers all Europe, a single domain with a horizontal resolution of 50 km was used, and there were 137, 116, 37 grid intervals in the East-west, North-south, and vertical directions, respectively.

Figure 6.3: Temporal revolution of simulated wind vectors at 900 mb on (a) 8th of January, 2002, 00.00 UTC and (b) 10th of January, 2002, 00.00 UTC.

Although these numbers of grids were bigger than those of emissions inventory, extra grids were cut in the meteorology-chemistry interface processor (MCIP) of the Model-3 air quality model.

Figure 6.4: General model data flow chart for the modeling system.

The established domain can be seen in Figure 6.5 as a result of TERRAIN pre-processor module. On the other hand, land-use data are critical for the calculation of biogenic emissions. To get a correct biogenic emission data, the accurate vegetation cover is essential. In this study, global 25-category from U.S. Geological Survey (USGS) data was used. The dominant vegetation and land use type can be seen in Figure 6.6. In addition, to use calculation of biogenic emissions, vegetation fraction data were prepared in the TERRAIN program. This data information can also be seen in Appendix 1.

Figure 6.5: MM5 –TERRAIN model domain cover area.

The model configuration of each physical option includes only coarse domain with 50 km. horizontal grid spacing. The model runs for specific days at 0000 UTC and lasting 10,080 hours (7 days). For the radiation scheme, RRTM (Rapid Radiative Transfer Model) long wave scheme was used. This longwave scheme is a new highly accurate and efficient method (Mlawer et al. 1997). It is the Rapid Radiative Transfer Model and uses a correlated-k model to represent the effects of the detailed absorption spectrum taking into account water vapor, carbon dioxide and ozone.

The Kain-Fritsch - II convective parameterization scheme was performed in this research. It has a sophisticated cloud-mixing scheme to determine entrainment/detrainment, and removing all available buoyant energy in the relaxation time (Kain and Fritsch, 1990). Contrary to the first Kain-Fritsch scheme (Kain and Fritsch., 1993), it includes shallow convection.

Figure 6.6: MM5-TERRAIN dominant vegetation/land-use map. Colors indicate each land use type.

Seven planetary boundary layer (PBL) parameterization schemes are available in MM5. The Medium Range Forecast (MRF) model scheme suitable for high-resolution planetary boundary layer was used in this study. It is based on a Troen-Mahrt (1986) representation of the counter-gradient term and a first order eddy diffusivity profile in the well-mixed PBL (Hong and Pan, 1996). This scheme has been taken from the National Centers for Environmental Prediction's (NCEP's) MRF model

There are six resolvable-scale microphysics schemes in MM5. The Simple Ice scheme was performed in this study. This scheme does not have super-cooled water, and snow is immediately melted below the freezing level (Dudhia, 1989).

6.2.2 Emission Model Setup

Advanced air quality models require input of gridded-emissions for each pollutant. These pollutants include sulfur oxides, nitrogen oxides, ammonia, non-methane volatile organic compounds, carbon monoxide, and particulate matter. The characterization of emissions must be an hourly format and they need to be speciated especially for VOCs to be used in any air quality model. Any plume rise estimates should also be completed before using them in the air quality model.

Emission inventories are typically obtained by combining the rate of emissions from various sources with the number of each type of source and the time when the emissions occur. Inventories are compiled in various formats. More commonly, emission inventories are collected by species, showing the various sources that contribute to the total emission of each.

Emission inventory preparation is a critical stage in air quality modeling and there is a great lack of quality input information for the domain which covers the entirety of Europe. Furthermore, there is no auxiliary-model to produce input data from emission inventory into the air quality model.

In this study, anthropogenic and natural-biogenic sources were handled separately. The methodology used for both anthropogenic and biogenic sources will be explained in the following section.

6.2.2.1 Modeling of Anthropogenic Sources

There aren't any regions on the earth's surface that have not been significantly affected by anthropogenic emissions. Important contributions of anthropogenic emissions to the chemistry are often observed (e.g., Parrish et al., 1993; Dickerson et al., 1995) even over the central Atlantic and Pacific Oceans. As a result, anthropogenic emissions should be evaluated in a comprehensive manner.

An algorithm in FORTRAN code was developed in order to process emission database, so that it could be used in the air quality model as an input. Figure 6.7 gives a schematic diagram of the sections of the Anthropogenic Emissions Process (AEP) algorithm. The

main sections of this process include: gridded data import, temporalization; speciation; and vertical distribution.

Figure 6.7: The Flowchart of Anthropogenic Emission Data Processes (AEP).

6.2.2.1.1 Import Gridded Anthropogenic Inventory Data (CORINAIR/EMEP)

In this study, gridded annual emission data which were obtained from EMEP (Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) database have been used for anthropogenic sources. This database provides emissions for 10 (EMEP) anthropogenic source sectors. A list of these source categories are given in Table 6.1.

Table 6.1: Sectors of Anthropogenic Emissions

Sector No	Anthropogenic Sources
1	Combustion in energy and transformation industries
2	Non-industrial combustion plants
3	Combustion in manufacturing industry
4	Production processes
5	Extraction and distribution of fossil fuels and geothermal energy
6	Solvents and other product use
7	Road transport
8	Other mobile sources and machinery
9	Waste treatment and disposal
10	Agriculture

Combustion in energy and transformation industries

Combustion in energy and transformation industries are taken into account as point sources or area sources depend on their capacities. Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon dioxide (CO₂) and heavy metals. Emissions of volatile organic compounds (non-methane VOC and methane), nitrous oxide (N₂O), carbon monoxide (CO) and ammonia (NH₃) are also released through the stack.

Non-industrial combustion plants

Non-industrial combustion plants cover commercial and institutional plants, residential plants and plants in agriculture, forestry & aquaculture. A specific methodology for these activities has not been prepared by CORINAIR/EMEP, because the contribution to

the total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

Combustion in manufacturing industry

Combustion in manufacturing industry covers emissions released from that of combustion for furnaces with and without contact with different type of metals. Relevant pollutants are sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO₂), nitrous oxide (N₂O) and heavy metals. Approximately, combustion in the manufacturing industry is responsible for 25% SO₂, 24% CO₂, 14% NO₂ and 12% CO of the all sectors.

Production processes

Production processes include processes in petroleum industries; iron & steel industries & collieries, non-ferrous metal industries, inorganic chemical industries, wood, paper pulp, food, drink and other industries; production of halocarbons and sulphur hexafluoride. This sector covers emissions of SO_x (3% of all sectors), NO_x (2% of all sectors), CO (5% of all sectors), CO₂ (4% of all sectors), NMVOC (6% of all sectors), N₂O (19% of all sectors), NH₃ (3% of all sectors), PM and heavy metals.

Extraction and distribution of fossil fuels and geothermal energy

Extraction and distribution of fossil fuels and geothermal energy include processes in extraction and the first treatment of solid/liquid/gas fossil fuels; liquid/gasoline fuel distribution; gas distribution networks and geothermal energy extraction. This sector covers emissions of NO_x, CO₂, VOC, NMVOC and CH₄. When we compare the sector of extraction and distribution of fossil fuels with all sectors; its main contribution is 23 % CH₄, 6% NMVOC and 1% CO₂.

Use of solvents and other products

Solvent use is a major contributor to NMVOC emissions. On a European scale its contribution is roughly a quarter of the total anthropogenic NMVOC emission. The contribution of the sector to anthropogenic NMVOC emissions varies between 15% and 30%. Also, solvent use contributes to the emissions of some heavy metals (Cd, Cu, Pb and Zn), CO, PM, SO_x and NO_x

Most solvents are part of a final product, e.g. paint, and will sooner or later evaporate. This evaporation of solvents is a major source of NMVOC emission in any country, thus inventorying of this source is of great importance. The use of solvents, like that of other products, has three stages in which emissions occur: during production, during actual use and during disposal.

The NMVOC emission from solvent use is calculated based on per capita data for several source categories. The categories most used for this purpose are: paint, all applications; industrial degreasing; dry cleaning; glues & adhesives; graphic arts (ink); chemical industry (e.g. pharmaceuticals); household products (e.g. toiletries); rubber and plastics industry; vegetable oil extraction; leather industry; pesticides and other solvent uses.

Road Transport

Road Transport includes the emissions produced by the exhaust systems of road vehicles. It does not cover non-exhaust emissions such as fuel evaporation and component attrition. The vehicle category splits into base parts when we consider the report emissions from road transport to international bodies. However, from a technical point of view, it does not provide the level of detail considered necessary to collect emissions from road vehicles in a systematic way. This is because road vehicle power trains make use of a great range of fuels, engine technologies and after treatment devices. Thus, a more detailed vehicle category split is necessary and has been developed.

Pollutants covered include all major emission contributions from road transportation: Ozone precursors (CO, NO_x, and NMVOC), greenhouse gases (CO₂, CH₄, and N₂O),

acidifying substances (NH₃, SO₂), particulate matter (PM), carcinogenic species (PAHs & POPs), toxic substances (dioxins and furans) and heavy metals. In detail, the sector covers exhaust emissions of CO, NO_x, NMVOC, CH₄, CO₂, N₂O, NH₃, SO_x, diesel exhaust particulates (PM), PAHs and POPs, Dioxins and Furans and heavy metals contained in the fuel (Lead, Cadmium, Copper, Chromium, Nickel, Selenium and Zinc). A detailed NMVOC split is also included to distinguish hydrocarbon emissions as alkanes, alkenes, alkynes, aldehydes, ketones and aromatics.

Road transport poses significant environmental pressures. Until lately, air quality was the major issue of concern for road transport emissions but significant technological improvements have effectively alleviated the risks. Today, greenhouse gases (and energy consumption) from road vehicles arise as the main concern for sustainable road transport development. Available data show that in 1999, road transport contributed to about 24% of total CO₂ emissions in EU and 47% of total NO_x emissions. However, the trends in those two pollutants are opposite, with ~15% increase and ~20% decrease of CO₂ and NO_x in 1999 respectively, compared to 1990 levels. Other Mobile Sources and Machinery includes military, railways, inland waterways, agriculture, forestry, industry, household and gardening, other off-road, shipping activities and air traffic. These sectors cover emissions of NO_x, NMVOC, CH₄, CO, CO₂, NH₃, N₂O, PM, SO_x and some heavy metals.

Other mobile sources and machinery

On a European scale, SO₂ and NO_x emissions from national shipping can be important with respect to total national emissions. However, emissions from national shipping generally only represent a few percent of the emissions from shipping operating internationally. Globally, shipping is estimated to be responsible for around 5-12 % and 3-4% respectively of anthropogenic NO_x and SO₂ emissions (extrapolations from Marintek, 1990 and Lloyd's Register, 1995). Estimated total NO_x attributable to shipping in the Northeastern Atlantic is approximately equivalent to the national total for France and Denmark combined, and slightly greater than the emissions attributed to road transport in Germany in 1990. Total SO₂ emissions are estimated to be equivalent to the total emission from France and half that emitted by UK power stations in 1990.

Shipping- generated exhaust emissions of hydrocarbons (VOC) and CO are relatively insignificant in comparison to national land based sources (Lloyd's Register, 1995). The total contribution of aircraft emissions to total global anthropogenic CO₂ emissions is considered to be about 2% (IPCC, 1999). This relatively small contribution to global emissions should be seen in relation to the fact that most aircraft emissions are injected almost directly into the upper free troposphere and lower stratosphere. IPCC has estimated that the contribution to radiative forcing is about 3.5 %. The importance of this source is growing as the volume of air traffic is steadily increasing.

Waste Treatment and Disposal

Waste treatment and disposal includes waste incineration, solid waste disposal on land, open burning of agricultural wastes, cremation and other waste treatment. The relative proportion of emissions contributed by the sector varies between pollutants. The emissions of compounds such as non methane volatile organic compounds (NMVOCs), NO_x, CO₂ and N₂O are unlikely to contribute significantly to total emissions. However, waste treatment and disposal have been a major source of emissions of CH₄ (19%) and CO (6%).

Agriculture

Agriculture is a branch of industry which cultivates land and keeps animals in order to produce food, fodder or raw materials used for industrial processes, and comprises arable agriculture, animal agriculture, horticulture, viniculture, etc., with a wide range of intensities. In principle, a sharp distinction between agriculture and natural systems is impossible, as even these systems are used intentionally for food, fodder or animal production and – at least in Europe – are almost everywhere subject to management measures.

6.2.2.1.2 Speciation

Raw emission inventories, in general, provide data for total VOCs, SO_x and NO_x. In order to be able to input data to air quality model, these raw values need to be speciated.

For example, total VOCs should be divided into individual organic compounds (e.g., PAR, OLE, ALD etc). For this purpose, we used the source sector specific VOC speciation profile obtained from the United Kingdom speciation given in PORG (Third Report of the United Kingdom Photochemical Oxidants Review Group-1993).

According to CORINAIR/EMEP and EPA-Emission Inventories, speciation of SO_x, NO_x emissions are specified 97% SO₂ - 3% sulfate and 95% NO - 5% NO₂ for each source-sector, respectively. Table 6.2 presents sector specific speciation factor used in this study.

6.2.2.1.3 Temporal Allocation

EMEP gridded data provides annual emissions, whereas air quality models require hourly values. In order to allocate emissions data temporally, temporal allocation factors need to be utilized. In this study, the methodology used in Microelectronics Center of North Carolina Sparse Matrix Operator Kernel Emissions (MCNC-SMOKE) model was followed. In this method, temporal allocation factors for monthly, weekly, weekdays-weekend diurnal variations are determined. Then, annual emission data are multiplied with these factors. It should be noted that, temporal factors are source sector specific. It is possible that there might be differences between European and American source sectors in terms of temporal allocation. Temporal allocation factors for the U.S were used, since no publicly available data for European sectors were found.

Table 6.2: Specified anthropogenic emissions for each sector.

Sector	PM10	PM2.5	PMc	NO	NO2	CO	NH3	SO2	SULF	PAR	ETN	OLE	XYLENE	HCHO	ALD
1	1	1	1	0.95	0.05	1	1	0.97	0.03	0.53	0.17	0.23	0.03	0.02	0.02
2	1	1	1	0.95	0.05	1	1	0.97	0.03	0.53	0.17	0.23	0.03	0.02	0.02
3	1	1	1	0.95	0.05	1	1	0.97	0.03	0.53	0.17	0.23	0.03	0.02	0.02
4	1	1	1	0.95	0.05	1	1	0.97	0.03	0.02	0.03	0.94	0.01	0.00	0.00
5	1	1	1	0.95	0.05	1	1	0.97	0.03	0.86	0.02	0.09	0.02	0.00	0.00
6	1	1	1	0.95	0.05	1	1	0.97	0.03	0.49	0.00	0.15	0.34	0.00	0.02
7	1	1	1	0.95	0.05	1	1	0.97	0.03	0.39	0.08	0.11	0.39	0.02	0.01
8	1	1	1	0.95	0.05	1	1	0.97	0.03	0.30	0.13	0.33	0.13	0.07	0.03
9	1	1	1	0.95	0.05	1	1	0.97	0.03	0.97	0.00	0.00	0.00	0.03	0.00
10	1	1	1	0.95	0.05	1	1	0.97	0.03	0.53	0.17	0.23	0.03	0.02	0.02

6.2.2.1.4 Vertical Layer Distribution

Another important aspect of emission modeling is vertical distribution. This is especially critical for sources that emit to higher layers than the surface. For example, power plant emissions directly go to layers that are higher than the 4th layer in general.

Table 6.3: Vertical Distribution of Anthropogenic Emissions: Percentage of each sector allocated to the vertical layers of the air quality model (given as heights of layers, in meters).

No	Sources	Height of Emission Layer (m)					
		0– 92	92– 184	184– 324	324– 522	522– 781	781– 1106
1	Combustion in energy and transformation industries	0	0	8	46	29	17
2	Non-industrial combustion plants	50	50				
3	Combustion in manufacturing industry	0	4	19	41	30	6
4	Production processes	90	10				
5	Extraction and distribution of fossil fuels and geothermal energy	90	10				
6	Use of solvents and other products	100					
7	Road transport	100					
8	Other mobile sources and machinery	100					
9	Waste treatment and disposal	10	15	40	35		
10	Agriculture	100					

(Calculations by S. Vidić, Croatian Meteorological Institute)

In this study, vertical distribution from EMEP study was utilized. Emissions were distributed vertically according to a default distribution based upon the sector codes, as shown in Table 6.3. These distributions have been based upon plume-rise calculations performed for different types of emission sources which are believed to be typical for

different emission categories, under a range of stability conditions (Calculations by S. Vidić, Croatian Met. Ins.).

6.2.2.2 Modeling of Biogenic Sources

It is well-known that the uncertainties in determination of biogenic and natural emissions are very large (some authors claim that these emissions are underestimated in certain areas of the world by up to ten times). On the other hand, anthropogenic emissions in some areas of the world have been reduced considerably during the last two decades (this is especially true for Europe- Geernaert et al, 2004). This fact shows clearly that the importance of biogenic and natural emissions are increasing, because the ratio of biogenic emissions to total emissions, where the total emissions are equal to the sum of biogenic and anthropogenic emissions, is increasing. Therefore, it is necessary to study carefully variations of biogenic and natural emissions.

For the biogenic and natural emission calculation, the following sources should be included: (1) Forest (foliar emissions), even if heavily managed, (2) natural grassland and other low vegetation, including lands used for grazing, (3) forest fires, (4) soils, (5) wetlands, (6) waters, (7) wild animals and humans, (8) lightning, (9) volcanoes, and (10) gas seeps.

According to the CORINAIR-1990 inventory, natural grassland accounts for 0.6% of European NMVOC emission, 0.4% of CH₄ emissions, 2.9% of N₂O emissions and 0.3% of NH₃ emissions. On a global scale, biomass burning in all its forms is estimated to make very significant contributions to greenhouse gases (Andreae et al., 1988, Andreae, 1991). However, most of this burning is human-initiated, and takes place in the tropics. Although the magnitude of emissions from soils may be perturbed and controlled by human activities, the actual processes are considered natural. Micro-organisms in soil produced NO_x emissions. The magnitude of soil NO_x emissions may be small in overall comparison to anthropogenic NO_x emissions. However, there is considerable uncertainty in the estimates. Naturally saturated soils, either permanently or seasonally flooded with fresh water, produces methane and sulphur. Wetlands are estimated to produce about 20% of the annual global methane emissions. Sulfur gases emitted from

wetlands and soils are estimated to be less than 2% of the total sulfur budget. The contribution of water to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant. Emissions of wild animals and humans are mainly methane and ammonia. Some NMVOC emissions are also possible, but probably small and also the information available is very sparse. Lightning causes the production of NO_x in the atmosphere. For the U.S., 40% of the yearly lightning-generated NO is estimated to be produced during the summer months. While lightning exhibits different characteristics depending on whether it is cloud-to-ground, cloud-to-cloud or within-cloud, emission estimation techniques have not been resolved to this level of detail. The emissions from volcanoes show great regional and temporal variation. Volcanic activity tends to be highly variable. Most important emissions are SO₂ and CO₂, but also H₂S. Due to the irregular emission patterns, only rough estimations are possible for gas seep. A compilation of reports on gas seepages indicates that they may be between 2-13 % of global annual CH₄ emissions per year (Hovland et al., 1993). According to CORINAIR-90, forests (deciduous and coniferous) contributed 19% of total European NMVOC emissions, 4.4% of CH₄ emissions, 14.3% of N₂O emissions and 0.8% of NH₃ emissions. Forest foliage is primarily a source of VOC, and they are distinguished between isoprene, monoterpenes, and 'other VOC'. The most important contributor in this regard is undoubtedly forest VOC emissions.

In terms of relative contribution to total European emissions for different pollutants, NMVOC from forests and vegetation are clearly the most important emission sources (Simpson et al., 1998). Several thousand different biogenic non-methane volatile organic compounds (NMVOCs) have been identified (e.g., Isidorov et al., 1985; Graedel et al., 1986; Puxbaum, 1997; Fall, 1999). Plants are the largest biogenic sources of non-methane volatile organic compounds. In the atmosphere, NMVOCs are very reactive and play significant roles in many aspect of atmospheric chemistry. They are a key component of the photochemical processes that form ozone and other secondary products including organic acids, organic nitrates, aerosols etc. in the troposphere (Kasting and Singh, 1986; Trainer et al., 1987; Chameides et al., 1988; Fehsenfeld et al., 1992; Andreae et al., 1997). Today, it is a well-known that they are highly reactive towards hydroxyl and nitrate radicals and ozone and in the presence of nitrogen oxides

they contribute to ozone and aerosol formation. The most well-known are isoprene and the monoterpenes emitted by terrestrial plants. The hydrocarbons isoprene and several monoterpenes (α-pinene, β-pinene, limonene, etc.) are generally considered the most important compounds for regional ozone formation in Europe (Simpson, 1995; Stockwell et al., 1997).

Some of the VOCs from biogenic sources, such as monoterpenes, can be oxidized by hydroxyl radicals (OH), nitrate radicals (NO₃) and ozone (O₃), and directly take part in the secondary organic aerosol (SOA) formation processes. Others can indirectly affect SOA formation in the air (Kulmala et al., 1998, Griffin et al., 1999). Nitric oxide (NO), resulting from nitrifying bacteria activities in the upper few centimeters of soil, is another chemical that can affect the atmospheric chemistry. In addition to anthropogenic sources, emissions from biogenic sources can contribute to PM pollution.

Although the importance of isoprene at urban, regional, and global scales of atmospheric chemistry is well established (Fehsenfeld et al., 1992; Guenther et al., 1995; Cowling et al., 1998; Guenther et al., 2000; Fuentes et al., 2000), in many cases, an accurate representation of isoprene and other biogenic hydrocarbons is very limited. In rural areas, isoprene is almost always the dominant reactive hydrocarbon. In order to understand the chemistry of rural atmospheres, it is essential that the emissions of isoprene be well characterized.

Table 6.4 shows one estimate of the annual global emissions of isoprene, other monoterpenes, and VOCs as well as methane (Guenther, 1999). Emissions of isoprene are believed to be about four times those of the other monoterpenes and about equal to all other VOCs.

Forests are the main sources of biogenic NMVOC. Globally, emissions from forests are estimated to contribute ~820 Tgyr⁻¹ to a total biogenic emission of 1150 Tg yr⁻¹ (Guenther et al., 1995). Global anthropogenic NMVOC emissions amount to only 10% of this, ~100 Tgyr⁻¹ (Muller, 1992; Piccot et al., 1992). In contrast, European anthropogenic and biogenic NMVOC have comparable magnitudes; biogenic NMVOC emissions are estimated at ~14 Tgyr⁻¹ (David Simpson et al., 1999), compared to man-made emissions of around 24 Tgyr⁻¹. On average, ~33% of Europe's land area consists

of forests, 43% is used for agriculture, with the remaining 24% consisting of rocks, tundra, wetlands, etc. (Van de Velde, 1994). Some countries, such as the United Kingdom, are seen to be almost devoid of forests; whereas Sweden and Finland are extensively covered (the United Kingdom has 10% forest cover, while Finland has 76%). Although European forest emissions are only a small part of the global total, they are, even on an annual basis, significant in the European NMVOC inventory (David Simpson et al., 1999). Further, these emissions are strongly dependent on seasons, temperature and light intensity (e.g., Guenther, 1997; Schnitzler et al., 1997) so that in many countries of Europe they may exceed anthropogenic NMVOC emissions during warm summer days, often those days most conducive to ozone formation.

Table 6.4: Estimated Global Annual Biogenic VOC Emissions (Tg yr^{-1}) from Guenther (1999).

Source	Isoprene	Monoterpenes	Other VOCs
Canopy foliage	460	115	500
Terrestrial ground cover and soils	40	13	50
Flowers	0	2	2
Ocean and freshwater	1	<0.001	10
Animals, humans, and insects	0.003	<0.001	0.003
Anthropogenic (including biomass burning)	0.01	1	93
Total	~500	~130	~650

There are several reasons for preparing an inventory of emissions from nature. The first one is that emissions from natural sources take part in the background chemistry of the atmosphere and are thus worthy of studying in themselves. Additionally, emissions from nature can interact with man-made emissions with deleterious effects, a notable example being ozone formation brought about by the mixing of NO_x -rich plumes from urban areas with VOC emissions from surrounding forests (e.g., Chameides, 1998). In other continents, globally biogenic emissions clearly outweigh anthropogenic ones. However, even in Europe, biogenic and natural emissions can be important, especially within

individual countries. Almost every piece of land in Europe is affected by man's activities to some degree, either by direct intervention such as forestry practices or indirectly through changes brought about by acid deposition. The importance and difficulties of this question is tackled by Winiwarter et al. (1999) who attempted to give a natural scientist's view of possible boundaries between natural and anthropogenic emissions.

Biogenic emissions are an important preliminary study for photochemical models that are used to simulate air quality. Biogenic emission inventories are currently developed. They use species-specific standard emission factors and various correction terms to account for differences in environmental conditions. In order to assess biogenic emissions, certain input information is needed. First of all, these concerns are temperature and radiation, which are directly affecting the emission behavior. These parameters can be combined through environmental correction factors (ECF). Next, detailed information about the distribution and the density of plants, including specific species, is required. Recently, researchers are currently developing real-time air quality forecasting systems in which biogenic emission inventories will be important (Vaughan et al., 2004).

Currently isoprene and other biogenic hydrocarbons are incorporated into atmospheric models using a variety of methods that are all quite similar to the Biogenic Emission Inventory System (BEIS) developed by Lamb et al. (1993), revised by Geron et al. (1994) and, more recently, significantly expanded and updated as GLOBEIS by Guenther et al. (2000) (also Greenberg et al., 1999). The BEIS models generate hourly emission estimates of biogenic VOCs.

Previous efforts to estimate biogenic NMVOC emissions for Europe have been faced with very limited databases of vegetation distributions and biogenic NMVOC emission rate factors (Simpson et al., 1995). The large uncertainties associated with these emission rates are mainly due to ill-defined land use classifications, emission factors, and emission algorithms. Recent investigations in Europe have resulted in an improved understanding of biogenic NMVOC emissions from parts of the Mediterranean area (Seufert et al., 1997), although many species and areas still need to be studied.

Biogenic emissions data are still not available in EMEP gridded emissions database. For this reason, a separate methodology was utilized for biogenics. In this study, it has been dealt with, isoprene, monoterpene, OVOC (NR, OLE, PAR, ALD2, and TERPB) and NO emissions from all types of forests, vegetation and landuse. This method is broadly similar to the one used in the Biogenic Emissions Inventory System (BEIS3 model). The Biogenic Emissions Inventory System version 3 (BEIS-3) is a system that produces hourly biogenic emission estimates to be used in photochemical modeling. First, biogenic emission potential inventory was developed using a USGS land-use (5 min) database, forest composition statistics, biometric data and species emission factors. The methodology utilized for biogenic sources includes land use data import, estimation of hourly emission and speciation. Figure 6.8 presents a schematic diagram of these processes.

6.2.2.2.1 Imported Land-Use Data (MM5-TERRAIN)

In this study, gridded hourly emissions data which were obtained from the TERRAIN module of MM5 have been used for biogenic sources. This database provides emissions for biogenic source sector. As a result, land use data is the most important part of the calculation of biogenic emissions. In this study, a 24-category, global coverage with the resolution of 5 minutes, USGS landuse/vegetation data has been used (Table 6.5). This dataset includes 24 different categories for land-use and is based upon U.S. Geological Survey (USGS) criteria. Emission factors as well as correction factors for estimating total emissions are based upon previous publications (David Simpson, et al. 1999).

Most emissions in Europe come from the combustion and processing of fossil fuels rather than from biogenic or other natural sources. Europe is unique in this respect; in other continents, globally biogenic emissions clearly outweigh the anthropogenic ones.

However, even in Europe, biogenic and natural emissions can be important, especially within individual countries. When we considered the importance of the biogenic data for Europe, 9 km. resolution land-use data obtained from MM5-TERRAIN model were used.

Figure 6. 8: Biogenic Emission Data Processes.

6.2.2.2.2 Meteorology (T & PAR)

To calculate biogenic emissions, temperature and photosynthesis active radiation data are needed. These data can be obtained from any meteorological model. In this study, the MM5 meteorological model results (hourly data) were used in every step affecting the biogenic emissions during the day. More details can be seen in the following sections.

6.2.2.2.3 Estimation of Hourly Data

Light and temperature controls on emissions

In order to assess biogenic emissions, certain input information is needed. First of all, they take into consideration temperature and radiation, which directly affect emission

behavior. These parameters can be combined through environmental correction factors. Also, detailed information about the distribution and density of plants, including specific species is required.

Table 6.5: Description of 24-category (USGS) land-use categories.

Vegetation Identification	Vegetation Description	Vegetation Identification	Vegetation Description
1	Urban	13	Evergrn. Braodlf.
2	Drylnd Crop. Past.	14	Evergrn. Needlf.
3	Irrg. Crop. Past.	15	Mixed Forest
4	Mix. Dry/Irrg.C.P.	16	Water Bodies
5	Crop./Grs. Mosaic	17	Herb. Wetland
6	Crop./Wood Mosc	18	Wooded wetland
7	Grassland	19	Bar. Sparse Veg.
8	Shrubland	20	Herb. Tundra
9	Mix Shrb./Grs.	21	Wooden Tundra
10	Savanna	22	Mixed Tundra
11	Decids. Broadlf.	23	Bare Grnd. Tundra
12	Decids. Needlf.	24	Snow or Ice

Forest and Other Vegetation

All types of foliar forest emissions have been considered for this study including deciduous, coniferous and mixed forests. Forest foliage is primarily a source of VOC, and isoprene (ISO), monoterpenes (MONO), and other VOC (OVOC). According to CORINAIR-90, forests (deciduous and coniferous) contributed 19% of total European NMVOC emissions, 4.4% of CH₄ emissions, 14.3% of N₂O emissions and 0.8% of NH₃ emissions.

Biogenic emissions consist of a wide variety of species. Attention has mainly been focused on isoprene and the class of monoterpene compounds (alpha-pinene, beta-pinene, limonene, etc.). The remaining other VOC (OVOC) species consist of a large

number of species including hydrocarbons and oxygenated compounds (alcohols, aldehydes, etc.), and have proven difficult to quantify in atmospheric samples.

An algorithm for assessing emissions of isoprene and monoterpene from leaves has been described by Guenther et al. (1993). The algorithm is based on considerations of the biological activities, the formation and the emission of the compounds. Formation is an occurrence brought about a constant increase in temperature and light, in spite of the fact that, above a certain temperature (approx. 35°C), they have an inclination to go down. In the case of isoprene, the formation leads to direct emissions. Monoterpene, in contrast, can be stored in the plant. Emissions, then, are just a function of temperature. In addition, there are emissions of oxygenated compounds, which are believed to occur with a similar mechanism as monoterpene emissions.

The emission rates of trees have been determined at a variety of temperatures and light conditions, and consequently emission potentials at standard temperature and light (30°C, photosynthetically active radiation 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$) have been derived. These emission potentials vary considerably, sometimes even between different species of the same botanical genus (esp. oaks). Most recently, also a component of direct emissions (light sensitive) of monoterpenes has been discovered (Steinbrecher et al., 1997). This emission flux is to be determined in analogy to isoprene.

Standard emission potentials for a number of tree species for all four types of emissions (isoprene and monoterpene, light and temperature sensitive, as well as monoterpene and OVOC.s, just temperature sensitive) have been tabulated by Simpson et al. (1999). The authors performed quite an extensive review, not only to obtain information on many different tree species, but also to compile the data sources which are most useful. In order to obtain per area emissions, emission potentials are given per dry leaf mass, per the conversion factor for the forest area and per the foliar biomass density. Note that this is basically equivalent to a leaf area index (LAI) which is used when emission potentials are given per leaf area (e.g. Lamb et. al.1993). Foliar biomass density has also been tabulated by Simpson et al. (1999).

For all types of vegetation, an appropriate system describing the emission flux on an hourly basis is that of Guenther et al. (1996):

$$\text{Flux } (\mu\text{g m}^{-2} \text{ yr}^{-1}) = \int \varepsilon \cdot D \cdot \gamma \, dt \quad (1)$$

where ε is the average emission potential ($\mu\text{g g}^{-1} \text{ h}^{-1}$) for any particular species, "D" is the foliar biomass density ($\text{g dry weight foliage m}^{-2}$), and γ is a unit-less environmental correction factor representing the effects of short-term (e.g. hourly) temperature and solar radiation changes on emissions.

Biogenic emissions of isoprene and monoterpenes were calculated in the model as a function of temperature and solar radiation, using the land-use datasets described in this chapter (Imported Land-Use Data). Calculations were performed at every model time step, using surface temperature (T) and photosynthetically active radiation (PAR).

Guenther et al. (1991, 1993) showed that, with a very good approximation, the short-term (hourly) variations in emissions of isoprene could be described by the product of a light dependent factor, C_L and a temperature dependant factor, C_T . Thus, the so-called ISOG algorithm is:

$$\gamma_{\text{iso}} = C_L \cdot C_T \quad (2)$$

The light factor, C_L is given by:

$$C_{L_{\text{iso}}} = \frac{\alpha c_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \quad (3)$$

where α ($= 0.0027$) and c_{L1} ($= 1.066$) are empirical constants, and L is the PAR flux ($\mu\text{mol photons (400-700nm) m}^{-2} \text{ s}^{-1}$). Temperature dependence $C_{T_{\text{iso}}}$ is described by:

$$C_{T_{\text{iso}}} = \frac{\exp(C_{T1}(T - T_s) / RT_s T)}{1 + \exp(C_{T2}(T - T_M) / RT_s T)} \quad (4)$$

where R is the gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and C_{T1} ($= 95000 \text{ J mol}^{-1}$), C_{T2} ($= 30000 \text{ J mol}^{-1}$), and T_M ($= 314 \text{ K}$) are empirical coefficients based upon measurements of three plant species: eucalyptus, aspen, and velvet bean, but which seem to be valid for a variety of different plant species (Guenther et al. 1993, Guenther 1997). T_s ($= 303 \text{ K}$) is the standard temperature.

The environmental correction factor for monoterpene emissions from most plants are parameterized using the following equation (Guenther et al. 1993):

$$\gamma_{mts} = \exp(\beta \cdot (T - T_s)) \quad (5a)$$

where β ($= 0.09 \text{ K}^{-1}$) is an empirical coefficient based on non-linear regression analysis of numerous measurements present in the literature. This type of emission is associated with vaporization of terpenes from stores within the plant tissue, and this algorithm is referred to here as MTS.

Recently it has been shown that some evergreen oaks, and also Norway spruce, show a light-dependency of monoterpene emissions. At least for *Quercus ilex* this dependency seems to be well-described by the Guenther isoprene algorithms (Kesselmeier et al., 1996, Seufert et al., 1997). Denoting this behaviour by MTL, we have:

$$\gamma_{mtl} = \gamma_{iso} \quad (5b)$$

These emission algorithms represent the current knowledge of terpenoid emission by plants. This variation is mainly due to the differences in the emissions from branch to branch and from tree to tree, variation with season, nutrient condition of the plant, stress and experimental errors.

The relationship between environmental conditions and emission of OVOC is even less understood than isoprene and monoterpenes. Emissions of some of these compounds, including a group of C_6 unsaturated, are strongly influenced by external factors other than light and temperature, such as plant wounding by microbes, insects or mechanical stress. Given the lack of other information regarding the factors controlling oxygenated hydrocarbon emission, the use of equation (5) for parameterization of oxygenated hydrocarbon emission is recommended (Guenther et al, 1994, Geron et al., 1994, Konig et al. 1995). i.e.:

$$\gamma_{OVOC} = \gamma_{mts} \quad (6)$$

These light and temperature dependencies are illustrated in the following figures:

Isoprene production by plants is very sensitive to light as well as temperature (e.g., Sanadze and Kalandadze, 1966; Tingey et al., 1979). Figure 6.9 (a) shows the production of isoprene from an aspen leaf when light in the photosynthetically active range is turned on and off (Monson et al., 1989; Fall, 1999)

Figure 6.9 Effect of light on isoprene emission rate from (a) aspen leaf and (b) velvet bean leaf (adapted from Monson et al., 1992; and Fall, 1999).

When the light is switched on, isoprene emissions rise and when it is turned off, fall even more rapidly. Figure 6.9 (b) shows the emissions as a function of this light intensity; the emissions rise rapidly and approach (but do not reach) a plateau (Monson et al., 1992; Fall, 1999).

Figure 6.10: Effect of willow leaf temperature on isoprene emissions rate (adapted from Fall and Wildermuth, 1998; and Fall, 1999).

Finally, Figure 6.10 shows the effect of temperature on the isoprene emission rate; emissions rise to a temperature of ~ 35-45 °C and then rapidly fall (e.g., Monson et al., 1992; Sharkey and Singaas, 1995; Fall and Wildermuth, 1998; Fall, 1999).

For a good inventory, it is the most important to specify the correct foliar biomass density to accompany any given area of vegetation. This is because "area" is an ill-defined quantity in many instances, e.g. 1 km² of wooded area may include very dense

forest with an average foliar biomass density of, say, 1400 gm^{-2} , or it may contain scattered trees with only 100 gm^{-2} .

It can be seen from table 6.6 that different types of forest have different foliar biomass density. Furthermore, every region has specific density values although they have same type of trees. Taking this situation into consideration, generally European forest type values were used as much as possible in this study.

Table 6.6: Default foliar biomass densities (adapted from Veldt, 1989).

Forest Type		Foliar Biomass Density, D (gm^{-2})
Broadleaf		
Deciduous Oaks		320
Default deciduous broadleaved		300
Evergreen broadleaved		500
Conifers		
Norway spruce (<i>Picea abies</i>)	> 60° N lat.	800
	55- 60° lat.	1400
	< 55° N lat.	1600
Other spruce		1400
Scots pine	> 60° N lat.	500
	< 60° N lat.	700
Other coniferous		1000

As mentioned before, Biogenic Emissions Inventory System (BEISS) has been taken as a base for biogenic emissions. According to this system, all vegetation leaf biomass, winter biomass factor and flux values can be seen in the following tables:

Although this table gives all types of forest information, it has taken into consideration European forests. A new table (Table 6.8) has been created for forests in this study. As a result of this, it could get more correct emission data for European forests.

Emission potentials (ϵ) are required separately for isoprene, monoterpenes and OVOC. Further, for monoterpenes, two classes of behaviour are distinguished. For most trees, emissions are temperature-only dependant, controlled by the γ -mts environmental factor (equation 5a). For evergreen oaks, the MTL algorithm is used (equation. 5b)

Table6.7: Leaf biomass, winter biomass factor and flux values according to BEISS

Land Use Type	Dry Leaf biomass (gm ⁻²)	Winter biomass factor	Normalized emission fluxes for			
			ISOP	MONO	OVOC	NO
USGS_urban	100	0.5	10	20	183	6
USGS_drycop	300	0.5	28	11	332	34
USGS_irrcrop	500	0.5	28	50	548	34
USGS_cropgrass	400	0.5	28	28	440	34
USGS_cropwdlnd	400	0.5	2650	80	582	21
USGS_grassland	300	0.5	49	21	332	27
USGS_shrubland	400	0.5	600	250	447	2
USGS_shrubgrass	350	0.5	325	136	390	15
USGS_savanna	100	0.5	1765	60	108	27
USGS_deciforest	300	0.5	8232	90	324	2
USGS_evbrdleaf	500	1	7941	250	540	2
USGS_coniferfor	550	1	11383	1375	1346	2
USGS_mxforest	450	0.5	7729	225	563	2
USGS_water	0	0	0	0	0	0
USGS_wetwoods	400	0.5	5816	320	432	2
USGS_sprsbaren	50	0.5	0	3	60	0
USGS_woodtundra	200	0.5	3360	200	216	2
USGS_mxtundra	150	0.5	1680	15	164	5
USGS_snowice	0	0	0	0	0	0

Emission potentials for a wide variety of species have recently been compiled by Guenther et al. (1994, 1997), Geron et al.(1994) for American woodlands, and by Steinbrecher (1997) and Seufert et al. (1997) for European species. Very little reliable experimental data on the emissions of OVOCs is available, and consequently Guenther et al. (1994) recommended the use of a uniform emission rate of 1.5 $\mu\text{g g}^{-1} \text{h}^{-1}$ for all tree species, recognizing that this was a first order approximation to a ten-fold range (0.5-5 $\mu\text{g g}^{-1} \text{h}^{-1}$). The data of Konig et al.(1995) fall within this range, and so until further European data are available, 1.5 $\mu\text{g g}^{-1} \text{h}^{-1}$ also seems to be a reasonable choice for preliminary, first-order estimates of OVOC emissions in Europe.

Table 6.8: Winter biomass factor and flux values according to European Forest features.

Land Use Type	Winter Biomass Factor	ISOP (D. ϵ)	MONO (D. ϵ)	OVOC (D. ϵ)	NO (D. ϵ)
Deciduous Broadleaf	0.5	8232	90	324	2
Deciduous Needleleaf	0.5	8232	90	324	2
Evergreen Broadleaf	1	7941	250	540	2
Evergreen Needleleaf	1	16557	2000	1958	2.9
Mixed Forest	0.5	7729	225	563	2

Isoprene and monoterpene emission potentials are taken from Guenther et al., 1994, 1997, or Geron et al., 1994, except where European measurements can provide a basis, as indicated by additional refs. For terpenes ϵ -mtl denote emissions controlled by light and temperature (using γ -mtl), whereas ϵ -mts denote emissions controlled by temperature only. All isoprene rates are branch-level, often derived from leaf-level U.S. estimates divided by 1.75.

6.2.2.2.4 Speciation

Emission potentials (γ) for forests have been given separately for isoprene, terpenes, and OVOC, and this division represents the most important level of speciation. However, there are many species represented within the class of terpenes and OVOC covering a wide range of chemical behavior. This section attempts some guidance as to the likely breakdowns among the monoterpene and OVOC classes. Nitric oxide (NO) is considered to be the predominant NO_x compound emitted from soils. As for forest NMVOC emissions, biogenic emissions from grasslands consist of a wide variety of species, including isoprene, monoterpenes, (alpha-pinene, beta-pinene, limonene, etc.), and 'other' VOC. The 'other' VOC (OVOC) species consist of a large number of oxygenated compounds (alcohols, aldehydes, etc.), and have proven difficult to quantify in atmospheric samples.

In this study, BEIS (Biogenic Emissions Inventory System) was taken as a model for biogenic speciation (Table 6.9). First developed in 1988, BEIS estimates volatile organic compound (VOC) emissions from vegetation and nitric oxide (NO) emissions from soils. According to BEIS3, speciation of OVOC emissions are specified NR (non reactive), OLE and PAR for vegetation source-sector and monoterpenes are specified ALD2, OLE, PAR and TERPB for vegetation.

Table 6.9: Specified biogenic emissions for vegetation sector.

Forest and other Vegetation	ISOP	NO	NR	OLE	PAR	ALD2	TERPB
ISOP	1		-	-	-	-	-
NO	-	1	-	-	-	-	-
OVOC	-		0.5	0.5	8.5	-	-
MONO	-		-	0.5	6.0	1.5	1.0

6.2.2.3 Other Natural Sources

In addition to forest, natural and biogenic emission sources cover other sectors, as well.

All types of grasslands and other types of vegetation (natural, semi-natural and in some cases cultivated) do not fit easily into the forest classification. This includes especially the Mediterranean maquis/garrique and other low scrub-type vegetation, heathland, tundra, etc. for Europe. Most of the grasslands in mid- and northern Europe are agriculturally used for either harvesting hay (meadows) or for grazing (pastures). Natural grasslands can be found in Alpine regions above the timberline (alpine Tundra), at lower elevation northwards of the timberline (boreal Tundra), in dry climatic regions with poor soil (Steppe), on saltfloors and on moorland. Low vegetation (< 5 m height), apart from grassland, is widespread across Europe. For example, in many parts of Europe moorland and heathland cover large areas, with *Erica* sp, *Ulex* sp., *Calluna* sp., *Pteridium* sp., and similar species being common. According to the CORINAIR-1990 inventory, natural grassland accounts for 0.6% of European NMVOC emission, 0.4% of CH₄ emissions, 2.9% of N₂O emissions and 0.3% of NH₃ emissions. However emission

rates for NMVOC need to be substantially revised. Simpson et al., 1998, using the recommended defaults in this chapter estimate that pastures and meadows may contribute nearly 1 Mt to European NMVOC emissions (ca. 4%) and crops also ca. 1 Mt. Uncertainties are still very large and in some other areas emissions might be appreciable, e.g. the NH_3 emission from pastures (due to animal droppings) and meadows (in particular when fertilised with manure). The area coverage of grasslands in Europe is second highest after forests; however the biomass density of grasslands is often lower than the foliar biomass density of forests (CORINAIR, 2004). Emissions of NMVOC from plants are usually divided into isoprene, monoterpene, and OVOC (other VOC) emissions for inventory purposes. In general isoprene and monoterpene emissions are the most photochemically reactive and hence of most interest for ozone studies. However, for grasslands the major emission probably consists of OVOC. The equations which is using for forest can be used for grasslands and other type of vegetation.

Although the magnitude of emissions from soils may be perturbed and controlled by human activities, the actual processes are considered natural. NO_x emissions, mainly in the form of nitric oxide (NO) are produced by micro-organisms in soil. Emissions of NO_x from soils are estimated to be as much as 16% of the global budget of NO_x in the troposphere (Logan, 1983). The contribution of soil NO emissions from agricultural lands has previously been estimated to be 15% of the total European NO_x emissions inventory (Simpson et al., 1995), but emissions from non-agricultural areas are certainly much smaller than this. Given the lack of evaluation of any paramaterisations in Europe, a detailed methodology is probably not worthwhile for estimates of annual emissions. However, in case hourly changes in emissions are required (e.g. for modelling) the following methodology is proposed. Unfortunately, the simple and detailed methodologies are not consistent - they produce quite different annual estimates. This methodology is taken from Novak and Pierce (1993) and is known commonly as the second-version of the Biogenic Emissions Inventory System (BEIS-2). BEIS-2 can estimate NO emissions for forests, agricultural crops, urban trees, and grasslands. BEIS-2 calculates a range of emission flux rates based on land use types and soil temperature. The basis of the BEIS-2 calculation for soil NO emissions originate with the following equation (Williams et al., 1992):

$$F_{NO} = A \times \exp(0.071 \times T_s) \quad (7)$$

where

F_{NO} = NO flux, ($\text{ng N m}^{-2} \text{ s}^{-1}$)

T_s = Soil temperature, degrees Celsius

A = Experimentally derived constant for the land use types of grasslands and pasture, forests and wetlands.

A large number of emission factors based on field measurement data are given in the literature. Williams et al. (1992), Yienger and Levy (1995) and Skiba et al. (1997) provide excellent reviews on these data. Emission factors are given as a function of land use and other environmental conditions, such as temperature, soil moisture, and soil nitrate levels. The variation in these measurements is considerable, resulting in a wide range of uncertainty in current emission factors. In view of the poor coverage of data across Europe, especially in Mediterranean areas, a big uncertainty seems reasonable. Additional field studies comparing atmospheric measurements of NO_x fluxes with soil emissions derived from chamber measurements are needed to reduce this uncertainty.

On a global scale biomass burning in all its forms is estimated to make very significant contributions to greenhouse gases (Andreae et al., 1988, Andreae, 1991). However, most of this burning is human-initiated, and takes place in the tropics. Of an estimated 3550 Tg CO₂ (as C) formed yearly from biomass burning, only 117 Tg C is ascribed to fires in the temperate and boreal regions, and only a small fraction of these take place in Europe (Levine, 1994). Considering the European continent as a whole, the vast majority of these fires occur in the Eurasian part of Russia, where recent estimate suggest annual areas burnt of between 2-7 million ha (Conard and Davidenko, 1996). According to the CORINAIR-1990 inventory, forest fires account for 0.2% of European NO_x emissions, 0.5% of NMVOC emission, 0.2% of CH₄ emissions, 1.9% of CO emissions, 1.2% of N₂O emissions and 0.1% of NH₃ emissions. On the whole forest fires appear to contribute only a small percentage of emissions. However, uncertainties are very large and in some areas emissions might make appreciable contributions to ground level concentration, especially as fires occur over short periods of the time. On a global scale biomass burning is a very significant source of CO₂ and a number of other gases to the

atmosphere. However, most burning takes place in the tropical and subtropical regions, so emissions from European fires have received very little attention. The major products of biomass burning are CO₂ and water vapour. However a large number of particulates and trace gases are produced, including the products of incomplete combustion (CO, NMHCs) and nitrogen and sulphur species. These arise partly from nitrogen and sulphur contained in the vegetation and organic matter in the surface soils. Additionally, emissions can arise from the re-volatilisation of substances which have been deposited (Hegg et al., 1987, 1990). Some emissions are not considered further here as they have little relevance for tropospheric chemistry, but they are worth mentioning for their stratospheric impacts. These include H₂, COS and to a lesser extent CH₃Cl (Crutzen et al., 1979, Andreae, 1991). Many other trace emissions have been measured, but which seem to contribute little to total emissions, e.g. methanesulphonate (MSA), aldehydes, organic acids (Andreae et al., 1988).

Emissions are obtained in a two-step process:

- (i) Estimate the emissions of carbon from the burned land.
- (ii) Estimate the emissions of other trace gases using emission ratios with respect to carbon.

The basic calculation of the mass of carbon emitted, M(C), follows the methodology of Seiler

and Crutzen (1980):

$$M(C) = 0.45 \times A \times B \times \alpha \times \beta \quad (8)$$

Where

0.45 is the average fraction of carbon in fuel wood

"A" is the area burnt (m²)

"B" is the average total biomass of fuel material per unit area (kg/m²),

"α" is the fraction of the above average above-ground biomass relative to the total average biomass B,

"β" is the burning efficiency (fraction burnt) of the above-ground biomass.

Andreae (1991) suggests that the emissions of CO₂ are uncertain by about 50%. Volcanoes with geothermal activities, both eruptive and non-eruptive are important in Italy (Etna, Stromboli and Vulcano) and in Iceland (Kverkfjöll). Heated magma under pressure contains gases like sulfur dioxide, carbon dioxide, hydrogen sulfide, mercury and chlorine. These gases may be released when magma gets close to the surface and the pressure may be discharged. For Italy, the SO₂ emissions from Mount Etna have been estimated to amount to 1.5±0.3 Mt per year, while globally for all non-eruptive volcanoes 9 Mt have been reported. These volcanoes are considered to be responsible for nearly all of the continuous emissions. However, large atmospheric injections also occur from sporadic eruptions both for CO₂ and SO₂. Because of the irregular pattern of such emissions, this was not included in the emission totals.

Lightning and corona discharge during thunderstorm events cause atmospheric chemical reactions to take place at high voltages and high temperatures. These reactions cause the production of NO_x in the atmosphere. Such production processes are, strictly speaking, not real emissions as the compounds involved (primarily N₂ and O₂) are not injected into the atmosphere, but are present anyway. However, as these processes can not adequately be described by conventional atmospheric models on one hand, and their impact is eventually identical to those from (anthropogenic) emissions on the other hand, they are easy to be compared on the emission level and thus are frequently treated as such. Global NO_x production by lightning has been estimated in the range of 3-5 TgN/yr. For the U.S., 40% of the yearly lightning-generated NO is estimated to be produced during the summer months. Other estimates indicate that the lightning NO comprises only 3% of the total NO_x emissions budget, with a maximum contribution of 24% at the maximum hour with respect to anthropogenic emissions at a definite period in summer for the U.S. North-East. Because of the lack of detailed data for Europe, lightning was not included in the emission totals.

A specific methodology for water activities has not been prepared, because the contribution to total national emissions is thought to be currently insignificant, i.e. less than 1% of national emissions of any pollutant.

Gas seeps from natural gas reservoirs can not easily be distinguished from gas being developed from organic material buried in the sediment. However, differentiation should be made from methane production in soils. Due to the irregular emission patterns, only rough estimations are possible. A compilation of reports on gas seepages indicates that globally emissions may be between 8 and 65 Tg CH₄ per year (approx. 2-13 % of global annual CH₄ emissions – EMEP/CORINAIR). Because of the irregular emission patterns and small contribution, gas seep was not included in the emissions total.

For the UK, ammonia emissions from humans (excluding pets) have been estimated at 0.7 % of total ammonia emissions, and animals in nature (deer and birds) at 0.2 %. Global emissions of ammonia were estimated at 4.8 % for humans, and at 0.2 % for the latter. Estimates for methane are not available for Europe, but using global estimates or the emission factors provided below, the contribution of emissions appears to be smaller than 1% of the total (EMEP/CORINAIR). Because of the lack of detailed data for Europe, the small contribution of animals was not included in the emission totals.

Wetlands are estimated to produce about 20% of the annual global methane emissions. Recent global estimates have been 100 - 110 Tg (1012 g) per year, with a range of about 50 - 150 Tg CH₄ emitted per year. These estimates were reviewed by Matthews (1987, 1989 and 1993). Biogenic sulfur gases emitted from wetlands and soils are estimated to be less than 2% of the total sulfur budget; 5-12 Tg S per year out of a total of 310 Tg. Less than 10% of the world's soils are in brackish marsh, so sulfur emissions from saline marshes are on the order of 1-2 Tg; insignificant compared to anthropogenic sources (Warneck, 1988; Andreae, 1984-85-86-90-97). Wetlands, too, were not included in the emission total.

6.2.2.4 Merge

Any air quality model requires an hourly emission data. In the emission modeling chapter, it has been explained how to prepare anthropogenic and biogenic emissions data. On the other hand, the CMAQ air quality model needs the whole of emission data. As a result, these anthropogenic and biogenic data were merged to form the entire data.

While different pollutants kept their values, the same pollutants were written as a total one. Naturally, both data maintained all their characteristics.

6.2.3 Chemistry Transport Model

The transport and chemical evolution of PM₁₀ over Europe were investigated by use of the Models-3 Community Multi-scale Air Quality (CMAQ) modeling system (Byun and Ching, 1999). CMAQ is an Eulerian-type model developed in the US Environmental Protection Agency to address tropospheric ozone, acid deposition, visibility, particulate matter and other pollutant issues in the context of one atmosphere perspective where complex interactions between atmospheric pollutants and regional and urban scales are confronted.

The CMAQ horizontal grid size was also set to 50 km with 132 cells along the east-west direction and 111 cells in the north-south direction covering all of Europe (Figure 6.11).

Figure 6.11: CMAQ model domain.

There were 20 layers in the vertical direction with all layers being identical to the setup of MM5 simulations (Figure 6.12). Because of the insufficient observational data, the initial and boundary conditions were set to background concentrations starting from

00:00 UTC January 5, 2002 for the entire simulation. The three-dimensional meteorological fields needed by CMAQ were provided by the MM5. For CMAQ, hourly anthropogenic and biogenic emissions were obtained from the EME.

The model used the same horizontal as and less vertical grid than the meteorological data. Lambert-conformal projection was used according to output of emission modeling. CB4 chemical mechanism was chosen to simulate pollutant evaluation. Vertical resolution consists of 20 σ -layers (up to 100 hPa), 10 of them in the planetary boundary layer.

In brief, CMAQ takes terrain, land use, emissions, meteorology and other information as its inputs and produces ambient concentrations various pollutants.

Figure 6.12: Vertical structure of CMAQ model. The troposphere is represented in the model by 20 σ layers. Sigma values for the boundaries of each level are shown on the left hand side of the figure. The corresponding height above the ground, computed for a standard atmosphere, is given on the right-hand side.

7. RESULTS

7.1 Meteorological Model

The MM5 is a mesoscale atmospheric model and has been widely used to generate meteorological data for calculations in air pollution models recently. Here, a single domain with a horizontal resolution of 50 km was used, and there were 137, 116, 37 grid intervals in the east-west, north-south, and vertical directions, respectively. The physics options of the chosen model were the RRTM (Rapid Radiative Transfer Model) radiation scheme (Mlawer et al. 1997), Kain-Fritsch cumulus parameterization (Kain 2004), the MRF boundary layer parameterization (Hong and Pan 1996), and the Simple Ice microphysics scheme (Dudhia 1989). The National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) data (with 2.5 degree by 2.5 degree resolution) were used for MM5 boundary and initial conditions. The model integrated 7 days starting from 00:00 UTC January 5 2002. To reduce the error due to time interpolation in the air quality model (i.e., CMAQ in this study), high frequent hourly data were produced to be used in the air quality model. This basic run was called CNTL (control) run.

In addition to the local emissions, the transport of pollutants from other European cities to Istanbul and its vicinity is suspected to have caused some high pollution episodes. To help us understand the transport of pollutants, we used MM5 results from the CNTL run to calculate backward trajectories. The air trajectories originated in Istanbul were tracked backward starting from the times when peak values of PM10 had occurred in Istanbul (i.e., 0000 UTC January 8 and 0000 UTC January 10, 2002). Furthermore, the MM5 on-line tracer model was used to independently study the possible transport of pollutants from other Metropolitans in Europe to Turkey. The air from different cities at the particular time were flagged (i.e., different tracers) and their propagations were tracked.

7.1.1 Model Performance

For an off-line air quality study, any air quality model makes use of meteorological data, such as winds, moisture, and temperature, to calculate chemistry transport, mixing, and reactions. Therefore, the accuracy of meteorological model outputs strongly affects the performance of air quality simulations and should be evaluated. Figure 7.1 shows observed and MM5 168-h simulated 10-m winds and 2-m temperatures (oC) at Gokceada and Malkara meteorological stations, which were located in the north-west of Turkey (The Marmara Region) and near eastern European countries. Comparison shows that simulated winds were quite comparable with observations at Gokceada station during the simulation period except for day 3 (January 7th) when winds were relatively calm.

Figure 7.1: (a) and (b) are observed (dashed lines) and 168-h MM5 simulated (solid lines) 10-m winds (a full barb equals 10 knots and half a barb equals 5 knots) for Gokceada and Malkara meteorology stations, respectively. (c), Gokceada, and (d), Malkara, are the same information but for 2-m temperature ($^{\circ}\text{C}$).

As for Malkara, there was a discrepancy of 300-600 between the simulated and observed winds, and again the results were more different from the observed values on the 3rd day of the simulation. Comparison of 2m temperature shows more consistent results. MM5 is able to catch the trend of temperature changes, including diurnal cycles, except for the 3rd day simulation. In general, model simulated results at Gokceada station are better

simulated than at Malkara. Since the largest MM5 simulated error is on the 3rd day when winds were relatively calm, the error concerning to this day may still be acceptable compared to errors from other days when winds were relatively strong and accurate.

Figure 7.2: Observed (dashed lines) and 168-h MM5 simulated (solid lines) 10-m winds (a full barb equals 10 knots and half a barb equals 5 knots) and 2-m temperature (°C) for Kirecburnu meteorology station.

Because of the urbanization, some stations (e.g. Kirecburnu) which are located in the urban area of Istanbul are surrounded by roads, buildings or several unexpected, significant changes. As a result of this, comparison of observations of these kinds of stations with simulations may not give a good conclusion. The stations not affected by urbanization might be more reliable.

ECMWF analyzed sea level pressure (mb) as shown in Figure 7.4 (a) can be used to compare the spatial distribution and magnitude of the simulation (b) in the same figure. After the 96-120 and 144 hour-simulations, comparing ECMWF analysis plots (Figure 7.4 a-c-e) with the simulation results (Figure 7.4 b-d-f) at 00 UTC January 9-10-11, 2002; the model is able to simulate correct sea level pressure spread and values at any simulation time.

Figure 7.3: The study area comprising Gokceada, Malkara and Kirecburnu meteorological stations.

Figure 7.5 shows model simulation results and ECMWF reanalysis at 12:00 UTC January 10, 2002. Compared with ECMWF reanalysis, MM5 reasonably reproduces horizontal distribution of the sea level pressure, temperature and winds at 850mb, and geopotential heights and horizontal winds at 500 mb. However, there are some minor discrepancies. Model-simulated 850mb temperature is lightly warmer (cooler) than ECMWF reanalysis over central Europe (over ocean of the west coastal Europe). The simulated 500 mb cyclonic circulations over northeast Europe is weaker than the analysis.

(a)

(b)

(c)

(d)

(e)

(f)

Figure7.4: ECMWF analysis (a-c-e) and MM5 model (b-d-f) simulation sea level pressure maps.

Although the model didn't use a high resolution due to the resolution of emission inventory, meteorological model is capable of producing realistic meteorological data which is essential to the air quality model for European domain.

Figure 7.5: MM5 model simulated sea level pressure, 850 mb temperature and horizontal wind vector in panel (a) and ECMWF analysis panel (b). MM5 model simulated 500 mb geopotential height and horizontal wind vector in panel (c) and ECMWF analysis in panel (d).

7.1.2 Backward Trajectories Simulation Results

Figure 7.6 (a) shows 36-h backward trajectories from Istanbul for the first pollution peak from 00:00 UTC January 8 to 12:00 UTC January 6 and Figure 7.6 (b) shows 21-h backward trajectories from the same city for the second peak from 00:00 UTC January 10 to 03:00 UTC January 9, 2002. A quantitative indication of long range transport from western, northwestern, and northern sides of Europe to Turkey is possible. Due to low level prevailing winds, the results obtained from backward trajectory are very reasonable and quantitatively support our hypothesis that the long range transport from North and Northwest side of Turkey may play an important role in the high pollution episodes in Istanbul, in January 2002. A quantitative study can be carried out using an air pollution model and is discussed in this study as well.

Figure 7.6: Two sets of model-generated backward trajectories calculated over (a) a 36-hour period and (b) a 21-hour period respectively.

7.1.3 Tracer Simulation Results

Based on the Fifth-Generation NCAR / Penn State Mesoscale Model (MM5; Grell et al. 1994) V3.6, an on-line tracer model (MM5T) has been developed and used here. Tracers in MM5T were carried in a 4D array and the transport of tracers due to advection, MRF (Medium Range Forecast) boundary layer mixing (Hong and Pan 1996), and Kain-Fritsch cumulus convection (Kain 2004) were taken into account (no deposition or chemical reaction). Other chosen physics options were the RRTM (Rapid Radiative

Transfer Model) radiation scheme (Mlawer et al. 1997) and simple ice microphysics scheme (Dudhia 1989). With this configuration, tracer evolution was treated essentially the same as that of any other scalar in the model. This on-line approach avoids temporal interpolation errors that can inherently limit the accuracy of more commonly used off-line calculations of pollutant transport and diffusion. The National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) data (with 2.5° latitude/longitude resolution) were used for MM5T boundary and initial conditions. To mimic emission characteristics, tracers were released at the lowest model level from selected cities at time-varying rates. The selected cities were Warsaw in Poland; Kiev in Ukraine; Moscow in Russia; Athens in Greece; and Bucharest in Romania. These cities were chosen because they are potentially significant local sources of pollutants and they are positioned upstream of Istanbul on the dates in question.

Figure 7.7 shows the tracer simulation results at the lower atmosphere where the main interest layer for air pollution is. For the first simulation period (00:00 UTC January 5 to 00:00 UTC January 7), the tracer released from Bucharest, arrived the north-west side of Turkey after a 12-h simulation (Fig. 7.7a). Other tracers also propagated toward to Turkey and the region nearby. On the 7th of January, 48 hours later, tracers which originated from Kiev and Moscow reached over Turkey (Fig. 7.7b). It is also interesting to see that air from Athens did not pass over Turkey even though its geophysical location was very close, because the city was located downwind in this case.

For the second simulation period (12:00 UTC January 7 to 12:00 January 9, 2002), tracer pumped from Bucharest arrived in north-west side of Turkey after an 18-h simulation (Fig. 7.7c). Similar to the first case, tracers from Kiev, Warsaw, and Moscow reached over Istanbul after a 48-h simulation (Fig. 7.7d).

In addition, to prove our hypothesis, another on-line tracer model at a different resolution was simulated to generate qualitative evidence of PM₁₀ transport during pollution events. A single domain with grid-spacing of 30 km was configured, and it covered the entire European continent and nearby seas and countries. There were 176 x 227 x 38 grids in the east-west, north-south, and vertical directions, respectively. Physics options were the same as former tracer simulation.

Figure 7.7: Simulated tracers and wind vectors at the 980 mb surface after (a) 12-h and (b) 48-h simulations. The tracers were released at the initial time of 0000 UTC January 5, 2001 from five different cities. (c) and (d) show the same fields as those in (a) and (b), respectively, except that (c) is 18-h instead of 12-h simulation and the initial time is at 1200 UTC January 7 2001.

Two tracer simulations which were conducted, EXP1 and EXP2, corresponded to the two peak events of PM₁₀ concentration in Istanbul, 7-8 and 10-11 January 2002. Model integration ran from 00:00 UTC 5 to 00:00 UTC 8 January for EXP1 and from 00:00 UTC 8 to 00:00 UTC 11 January for EXP2. The National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) data (with 2.5°

latitude/longitude resolution) were used for MM5T boundary and initial conditions. To mimic emission characteristics, tracers were released at the lowest model level from selected cities at time-varying rates. The selected cities were Warsaw, Silesia, and Krakow in Poland; Kiev in Ukraine; Moscow in Russia; Sofia and Plovdiv in Bulgaria; and Bucharest in Romania. These cities were chosen because they are potentially significant local sources of pollutants and they were positioned upstream of Istanbul on the dates in question. Several characteristics of the simulated tracer emissions are important to note. Emission was specified to vary over a daily cycle according to a half sine curve, with a maximum about 0.1 units s^{-1} at 5 p.m. and a minimum of 0 units s^{-1} at 5 a.m. local time. The area of emission in each city had a radius of 100 km. To further understand the transport characteristics, tracers from the same city but on different days (i.e., 00:00 UTC to 00:00 UTC next day) were tracked separately.

After 24 hours of integration in EXP1, a broad scale circulation pattern that favors pollutant transport into Turkey was quite evident (Fig. 7.8). Specifically, a surface high-pressure center was positioned over central Europe while a surface low was located over western Russia. The pressure gradient between these two centers induced a strong boundary-layer flow into Turkey from the north-northwest, creating a mechanism for the transport of PM₁₀ from upstream cities to Istanbul.

Figure 7.8: 24 h forecast from EXP1, showing sea level pressure (shaded; hPa), 1.5-km potential temperature (solid lines; K), and 950-mb wind vectors at 00 UTC 6 January, 2002. Large dot indicates the location of Istanbul.

For the first simulation period (00:00 UTC January 5 to 00:00 UTC January 8), the tracer released from Bucharest on the first day (not shown) had little impact due to heavy precipitation in Istanbul during the first one and half days. But tracer released in Bucharest on the second day first reached over Istanbul at 18:00 UTC 6 January (about 18-h transport time) and gave the maximum pollution impact on the city at 00:00 UTC 7 (dashed lines in Fig. 7.9a). Tracer released from Plovdiv, Bulgaria on the first day moved southward and did not pass over Istanbul, while the edges of the plumes released in Plovdiv on the second and third days skirt Istanbul and contributed relatively small concentrations of PM10 to the city.

Silesia and Krakow in Poland are relatively far away from Istanbul, yet tracers released from both cities on the first day reached over Istanbul after about 42 h of transport (by 18:00 UTC 6 January). Silesia and Krakow tracers from the second day reached over the city as well, arriving around at 12:00 UTC 7 with a higher concentration than the first day's plume. In our simulation, tracers released from other selected cities, such as Kiev, Sofia, and Warsaw, did not reach over Istanbul due to directions of low-level winds.

Simulated tracer transport from various source cities can be seen in Figure 7.9.

Figure 7.9: Simulated tracers and wind vectors at the 100 m height at (a) 48-h simulation from EXP1 and (b) 54-h simulation from EXP2. Tracers from Bucharest (dashed lines; 0.05 unit of interval) and Plovdiv (solid lines; 0.1 unit of interval) are released during the 2nd day and from Silesia and Krakow (shaded) are released during the first 2 days.

In addition to the wind fields, PM10 concentration is strongly affected by the degree of vertical mixing, especially at the top of the planetary boundary layer. During the first simulation period, a surface cold front passed through the region, leaving in its wake an exceptionally strong stable layer at the top of the boundary layer. This stable layer suppressed vertical mixing, apparently allowing PM10 to remain concentrated at low levels. A vertical cross section from EXP1 shows that MM5T simulated this effect well (Fig. 7.10). The tracer plumes released from Bucharest, Plovdiv, Silesia, and Krakow all remained concentrated below 1.5 km during the entire simulation period as they propagated downstream toward Istanbul.

Figure 7.10: Vertical cross-sections of simulated tracers below 3 km along the lines AB and CD in Figs. 7.9a and 7.9b for (a) EXP1 and (b) EXP2, respectively. The contours indicate vertical distribution of temperature (K).

Another important influence on PM₁₀ concentrations is precipitation. Scavenging by precipitation has not been included in current MM5T tracer calculations. However, results from the horizontal distribution of 48-h accumulated rainfall (Fig. 7.11) show that very little precipitation was produced over the relevant tracer paths. Although there was relatively high simulated rainfall over the Istanbul region during the simulation, this precipitation occurred during the first 1.5 days, prior to the high-pollution event. Thus, had a precipitation scavenging process existed in the model, it may have reduced locally generated tracer concentrations near Istanbul, but it would likely not have had a significant impact on the local concentrations of remotely generated tracers at the end of the period.

For the second simulation period (00:00 UTC January 8 to 00:00 January 11), the meteorological scenario was very similar to the first. For example, a surface front passed through the region, leaving in its wake a strong stable layer at the top of the boundary layer and broad scale north-northwesterly flow at low levels. Furthermore, the evolution of tracers predicted by MM5T was also similar (Figs. 7.9b and 7.10b). However, tracers took slightly longer to propagate to Istanbul in this second period.

Figure 7.11: Total accumulated rainfall (mm) at 00 UTC 7 January, 2002 from EXP1.

The model simulated a surface high-pressure system over central Europe and a surface low over Western Russia, with a substantial pressure gradient between these two systems. This gradient induced strong north-northwesterly low-level flow, capable of transporting upstream pollutants towards Istanbul. Moreover, the model reproduced a strong frontal inversion over the path of tracer transport, a feature that suppressed mixing at the top of the planetary boundary layer and effectively trapped low-level pollutants near the ground. These weather conditions created a favorable environment for limited dilution and long-range transport of PM₁₀.

The simulated tracer evolution provided qualitative proof that transport of PM₁₀ emitted from Bucharest in Romania, Plovdiv in Bulgaria, and Silesia and Krakow in Poland could have contributed to the high-pollutant events on 7-8 and 10-11 January 2002 in Istanbul. Our model suggests that PM₁₀ transport to Istanbul took about one day from Bucharest and Plovdiv and about two days from Silesia and Krakow during these events.

Results obtained from this tracer study are very reasonable and qualitatively support the hypothesis that the long-range transport from the north and northwest played an important role in both high PM₁₀ events in Istanbul in January 2002. This is a very preliminary, qualitative study for understanding the causes of these two high pollution

events. A quantitative study of pollution contributed from local emission and long-range transports for both pollution events is underway, using an air pollution model.

The most important findings might be summarized as follows:

I – The evaluation shows that the wind and temperature fields of simulation demonstrated nearly identical results when they were compared with observations. On the contrary, similar results could not be seen in some stations because of the urbanization effects. All in all, the evaluation ensures that accurate prediction of temperatures and wind speeds and directions obtained from the meteorological model for the related area.

II – The comparison of the simulation with NCEP analysis data gave proper sea level distribution and magnitude. The overall result proved that there are no significant differences between the analysis and simulations.

III – On the other hand, besides the sea level pressure comparison, upper level geopotential heights, temperatures and horizontal winds of simulation results did not give any remarkable differences with the analysis.

IV – The studies of backward trajectory and tracer gave some indications that may lead to a discovery of the intensity and direction of long range aerosol transport.

In a nut shell, although the model did not have a fine grid resolution which was related to emission inventory, the meteorological model was capable of producing realistic input fields for the air quality model. It is a fact that, this detailed study on the accuracy of the meteorological model has provided an upper limit to the capability of the air quality model. The model performance presents a reasonable and satisfactory conclusion as regards to obtaining healthy results from the inputs in the following steps of the atmospheric modeling dealt with in this study.

7.2 Emission Model

Emission modeling is the most complicated and the most challenging task of the air quality modeling system. It involves a large number of model specific inputs and a wide variety of pre-processors. These inputs have to be prepared correctly and these pre-processors must be run properly. Besides dealing with anthropogenic and natural sources separately, each source must be taken into consideration with different sub-sources. Accurate representation of characteristics of the sub-sources might ensure the reliable evaluation of air pollutants and their origins.

Comprehensive air quality models require the input of speciated emission values for each grid box over the entire domain at each model time step. Currently, one of the best available emission datasets is the 2001 EMEP/CORINAIR (McInnes, 1996) inventory, where the data are available as annual Europe-countrywide averages. Therefore, the available data must be processed to produce the input required by the air quality model, normally as hourly averaged gridded values. As a result, the emission processing module EME (Emission Modeling for Europe) was developed for this purpose. Two emission categories, anthropogenic and biogenic, were included in these regional scale simulations.

7.2.1 Anthropogenic Model

The European continental anthropogenic emission inventory based on the Europe emission trend 2001 from the EMEP database was used in this study. This database provides emissions for 10 EMEP anthropogenic source sectors. It includes total annual anthropogenic emissions of SO_x, NO_x, NH₃, VOCs (Volatile Organic Compounds) and particulate matter. It should be noted that, at present, a major part of the EMEP/CORINAIR Emissions Inventory has been filled with expert information from the main source categories, namely energy, transport, agriculture, production processes etc.

For modelling purposes, Germany is divided into Former Federal Republic of Germany and Former German Democratic Republic, while The Russian Federation is divided into

Kaliningrad, Kola/Karelia, Rest of the Russian Federation and St. Petersburg/Novgorod-Pskov. Ships emissions are kept constant for all years due to lack of expert estimates. As mentioned earlier, the emission data are based on officially reported emissions to the extent possible, but some of the officially reported data have been corrected and gaps have been filled. The following steps were used to process the anthropogenic emission inventory:

Speciation

Raw emission inventories, in general, provide data for total VOCs, SO_x and NO_x. In order to be used as input in air quality models, these raw values need to be speciated. According to CORINAIR/EMEP and EPA-Emission Inventories, speciation of SO_x, NO_x emissions are specified for each source-sector, respectively. We used the source sector specific VOC speciation profile obtained from the United Kingdom speciation given in PORG (Third Report of the United Kingdom Photochemical Oxidants Review Group-1993).

Temporal Allocation

EMEP gridded data provides annual emissions, whereas air quality models require hourly values. In order to allocate emissions data temporally, temporal allocation factors need to be used. In this study, the methodology used in MCNC (Microelectronics Center of North Carolina) SMOKE (Sparse Matrix Operator Kernel Emissions) model was followed. In this method temporal allocation factors for monthly, weekly, weekdays-weekend diurnal variations were determined. Then, annual emission data were multiplied with these factors. It should be noted that, temporal factors were source sector specific. Temporal allocation factors in the US were used here since no publicly available data for European sectors were found. It is possible that there might be differences between European and American source sectors in terms of temporal allocation.

Vertical Distribution

In this study, a vertical distribution from EMEP study was used. Emissions were distributed vertically according to a default distribution based upon the sector codes. These distributions have been based upon plume-rise calculations performed for emission sources considered to be typical for different emission categories, under a range of stability conditions (Calculations by S. Vidic, Croatian Meteorological Institute pers. comm. - EMEP Status Report 2003).

Figure 7.12 shows the PM10 and PM2.5 emissions after emission modeling performed to yearly EMEP/CORINAIR emission inventory data. Actually, emission inventory data were prepared being based on the Polar Stereographic projection. As a result, emission modeling was run with this projection for the first step.

EMEP PM2_5

Figure 7.12: PM10 and PM2.5 emission distribution map based on the polar stereographic projection.

Polar Stereographic map projections may have possible problems with meteorology chemistry interface (MCIP) program used to prepare meteorological data for the air quality model and also for plotting. As a result of this, anthropogenic emission modeling results were converted to Lambert Conformal Map Projection System. These conversion results can be seen in figure 7.13 in terms of PM10 and PM2.5 emissions.

PM10

PM2_5

Figure 7.13: PM10 and PM2.5 emission distribution map which is converted to the Lambert Conformal projection from the Polar Stereographic Projection.

7.2.2 Biogenic Model

Emissions from biogenic sources can add to the background chemistry of the atmosphere. Thus, it is necessary to consider them in emission modeling processes. In Europe, biogenic and natural emissions can be important. For example, European forest emissions are only a small part of the global total, but even on an annual basis they are significant in the European NMVOC (Non- Methane Volatile Organic Compound) inventory (David Simpson et al., 1999). In this study, NMVOC emissions were considered for all of the European Forests. Biogenic emission data are not available currently in EMEP gridded emissions database and information of natural emissions in Europe is relatively poor. In order to assess biogenic emissions, certain input information is needed. Among the most important parameters are temperature and radiation, which directly affect the emission behavior. In addition, detailed information about the distribution and the density of plants, including specific species, is required. For these reasons, a separate methodology was carried out here for biogenic emissions. This method is similar to that in the Biogenic Emissions Inventory System (BEIS3 model), and includes land use data import and estimation of hourly emission taking into account the meteorological data (e.g., temperature and solar radiation) and speciation. For the processing of biogenic emissions, the biogenic land use files for EME were obtained from MM5 land use data for Europe. These data were provided by the U.S. Geological Survey (USGS) including 24 different categories for land-use and vegetation. Methodology developed by Guenther (1996) was used for calculation of biogenic emissions. We applied the latest algorithms and derived the differences and potential improvements in relation to Simpson et al. (1999).

7.2.3 Model Performance

With 2001 data as base year, hourly emissions were computed for anthropogenic and biogenic emissions of the European domain.

Input emission data for anthropogenic source categories of Europe with 2001 data as base year emissions were computed. Figure 7.14 shows hourly, gridded PM₁₀ emission data, which are produced by EME, at ground level at 20:00 UTC January 10, 2002. For

emission data Quality Assurance/Quality Check (QA/QC) methods were also conducted. For this distribution, after the coarse calculation, Romania has 190 Gg PM10 and Ukraine has 452 Gg PM10 yearly totals. From the EMEP data base, yearly total PM10 emissions give 186 Gg for Romania and 462 Gg for Ukraine. The comparison gives reasonable results in terms of emission modeling (EME). A similar comparative approach was performed for other pollutants.

PM10

Figure 7.14: Gridded EME emission output data (Example)

On the other hand, being different from the particulate matter, gas emissions were also compared with the emission modeling results in terms of national totals. For example, while NH_3 emission yearly total model is about 340 Gg for Ukraine, this value is 378 Gg in EMEP database. As for NO_x and SO_x emissions, while the model approximately gives 720 Gg and 1860 Gg for Turkey respectively, EMEP database gives 951 Gg and 2112 Gg respectively. In terms of NMVOC, model results are also satisfactory. For

example, while EMEP database gives 1463 Gg NMVOC for Italy, the model produces 1424 Gg NMVOC total yearly value for Italy. Samples of results of the emission model can be seen in the following figures:

Figure 7.15: Gridded EME emission output data. Examples for NH₃ (a), NO_x (b), SO_x (c) and CO (d).

Biogenic emissions were estimated using a methodology that takes into account forest and vegetation data (land-use distribution and biomass factors). Furthermore, meteorological conditions (surface air temperature and solar radiation) together with emissions factors for native regions especially Mediterranean species and Norway spruces were considered. Calculated BVOC emissions were distinguished as isoprene,

monoterpene and other BVOCs. An example of isoprene distribution of the model result can be seen in the following figure.

Figure 7.16: Isoprene emission distribution map according to biogenic emission modeling (Example).

It is well known that the uncertainties in the determination of the biogenic emissions are very large. In our particular study, the space domain is the whole of Europe with parts of Asia, Africa and the Atlantic Ocean with a resolution of 5 minutes. Although the emission model includes some processes (temporal allocation, vertical distribution), results show that EME gives reasonable hourly emission data. Turkey has approximately 220 Mg Isoprene and France has 467 Mg isoprene yearly totals. Estimated isoprene emissions have given 213 Mg for Turkey and 480 Mg for France by Simpson (1995).

In addition, as a result of the emission model, the time series of PM₁₀ at Istanbul Grid: 76-35 for 3 days can be seen in figure 7.17 with an accompanying example of the emission model result.

Figure 7.17: Time series of PM10 (g/s) at Istanbul Grid: 76-35 according to the emission model.

7.3 Chemistry Transport Model

In order to validate the model, sufficient measurement data both in terms of site density, data quality and pre-determined chemical/physical parameters, are needed. Even though a new monitoring strategy for PM has recently been developed, the EMEP monitoring program provides insufficient data.

7.3.1 Model Performance

Model simulated PM10 concentrations are compared with those measured at two stations in Istanbul (Fig. 7.18). Discrepancies are likely to arise from horizontal and vertical coarse grid resolution and uncertainties in emission data. However, it should be noted that the CMAQ correctly reproduces the temporal pattern of PM10 values observed in Istanbul.

Figure 7.18: Time evaluation of PM10 concentration from observation (plain line) and model simulated result from base case at Besiktas (line with open circle) and Sarachane (line with filled triangle) stations in Istanbul.

The first model layer above the ground surface is 92m which is related to EMEP study and the horizontal resolution is 50 km. This coarse resolution can dilute the concentration of pollutants. In addition, the discrepancies can come from the EMEP emission data. The annual emission inventory data are based on data reported from

the European countries, and these data are estimated with experts' estimates if data are incomplete or inconsistent. This manual interpretation may introduce some errors. Furthermore, natural emissions are not available in EMEP database. These are possible reasons why the model concentration of PM₁₀ is much lower than observations. Note that the major error sources for the Unified EMEP model are volatile species, water, and, perhaps most importantly, an insufficient characterization of elemental and organic carbon (EMEP Status Report, 4/2003). This kind of speciation for PM₁₀ is still not available in EMEP dataset.

For the most part, CMAQ correctly reproduces the pattern of distributions of observed PM₁₀ values for Istanbul. The discrepancies between observations and model results are due to the reasons mentioned earlier. Furthermore, comparing 50 km grid averaged values with point observations can give quite different results. However, the model is able to catch the high-polluted air conditions which are observed January 7 and January 10 over Istanbul.

Similar large differences are seen between observations and modeled PM₁₀ from the Unified EMEP Eulerian Model in Spain and Italy. Important factors to consider are inadequate emission data (particularly important for primary PM from anthropogenic sources and for natural emission sources) as well as inadequate monitoring data for validation (Trans-boundary Particulate Matter in Europe: Status Report 2001).

In addition, the use of 2001 emission data (instead of 2002 data, which are not available) in combination with a January 2002 meteorological episode resulted in added uncertainty when comparing the CMAQ model results to pollutant monitoring data.

Origins and types of the uncertainty of the air quality modeling can be seen in the Figure 7.19 Insufficient data, inadequate qualified models and observation errors may probably give significant differences between models and measurements.

Figure 7.19: Origins and types of uncertainty present in Photochemical Air Quality Simulation.

As mentioned before, the chemistry transport model correctly reproduces the temporal pattern of PM₁₀ values according to the observations in Istanbul. In addition, an increasing day-to-day trend of PM₁₀ over Istanbul and its vicinity can be seen in figure 7.20 according to results of the CMAQ model.

Figure 7.20: PM10 emission distribution maps for (a) January 5, 2002 20:00 (b) January 6, 2002 20:00 (c) January 7, 2002 20:00 (d) January 8, 2002 20:00 (e) January 9, 2002 20:00 (f) January 10, 2002 20:00 according to CMAQ model results.

In figure 7.18, observations of PM10 values show poor air quality levels for 7th and 10th of January in Istanbul. Figure 7.20 also shows similarly high PM10 levels for the same days over Istanbul. All the above plots of the simulated chemistry-transport model demonstrated the excessive day-to-day PM10 levels over the northwest of Turkey with possible long-range transport from Europe to Turkey under westerly and northwesterly prevailing winds.

7.3.2 Sensitivity Analysis (Brute Force)

Model results have been compared to observations and analyzed with respect to the effect of different source-areas to Turkey and regions nearby. It is a fact that existing PM10 observations give us no choice but compare only data from Istanbul. Any differences between the model and observation statistics have given direct information about the quantity of transport and local processes. The backward trajectory was used to qualitatively prove the possible sources of PM10 transported to Turkey. To further quantitatively examine the PM10 response to local and transported emissions, we have rerun CMAQ with perturbed anthropogenic emission data. An increase of 50% of anthropogenic emissions is conducted to see the contribution of transport. Another increase of 50% of anthropogenic emissions for several countries including Turkey has been examined and its difference from the previous one could approximately tell the response of Istanbul PM10 emissions. The change of anthropogenic emissions for individual countries has also been carried out (Romania, Bulgaria, Poland, Ukraine and Russia) so that we could further understand the transport from individual countries.

Brute force (Table 7.1) shows the difference in PM10 concentrations between two model runs with different emission inputs. In order to analyze the response of Istanbul PM10 to the emissions of the European countries in the CMAQ model, a base case and several emission scenarios were modeled to test the sensitivity of the CMAQ results to the emission change. Two different approach runs have been presented. One includes the country-based change emissions; the other covers the regional-based change emissions.

Table 7.1: Istanbul PM10 response to 50% change in all emissions after 5-day simulations. Brute force sensitivity analyses results give quantitative information about each country or regional base responses to Istanbul.

Country	Istanbul PM10 Response to 50% Increase		Istanbul PM10 Response to 50% Decrease	
	Ave	Max	Ave	Max
Bulgaria	2%	7%	2%	8%
Romania	4%	13%	4%	13%
Poland	1.5%	7%	1.6%	9%
Ukraine	1.5%	8%	1.8%	10%
Russia	0.5%	8%	0.5%	7%
Regional*	12%	24%	9%	26%
Regional* and Turkey	45%	50%	46%	50%

*Regional approach covers Bulgaria, Romania, Poland, Ukraine, Russia, Hungary, Slovakia, Moldova, Belarus, Lithuania, Latvia and Estonia.

Taking into consideration only anthropogenic emissions, the model was performed for the whole of Europe. The uncertainties in the evaluation of biogenic emissions are quite big. The large uncertainties in the assessment of the amount of the biogenic emissions create bigger and bigger difficulties in the evaluation of different scenarios. As a result, the approach covered only the change in anthropogenic emissions during the simulation period.

All the studies show that the most continuous and major responses of the PM10 to Istanbul occurred in Romania-origin emissions during the period (Figure 7.21-a). The response of Istanbul PM10 to increasing emissions from Romania can be seen in the same figure. Dark gray background color shows differences between base-case (no change in emissions) and 50% increased emissions of Romania in terms of the city of Istanbul. During the simulation period, increased emissions from Romania augmented the PM10 concentrations in Istanbul by sometimes 13 percent. The country average occurred 4 percent for all simulations. As for 50% reduction scenario, the same results have been observed (Table 7.1).

The revised emissions of Bulgaria were also observed to create a continuous response in Istanbul PM10 (Figure 7.21-b). The maximum response of emissions of

Bulgaria to Istanbul PM10 in 50% increase scenario was observed to increase by 7 percent. The country average response of Istanbul PM10 was 2% for all simulations. Similar results can be seen in Figure 7.21 (c) for Poland, but not as much as Romania. During the simulation period, the revised emission change of Poland by 50% could give maximum 7 percent increase and 9 percent decrease to Istanbul PM10 emission. Another Eastern European country, Ukraine, has also been researched (Figure 7.21-d). The same increase and reduction scenarios were performed for Ukraine emissions. Maximum impact was observed to be 8% increase and 10% decrease respectively. While the average impact of increased Ukraine emissions to PM10 Istanbul emission occurred 1.5 %, 1.8 % decrease was observed for the reduction scenario. In contrast to Romania, Bulgaria and Poland, the continuity of response of Ukraine emissions were very limited and occurred in absolutely different time periods.

Russia has the biggest emission potential in Europe. It has approximately 1129Gg PM10 annual total (EMEP). This value is bigger than total PM10 emissions of Bulgaria, Romania, Poland and Ukraine (Figure 7.22). However, according to brute-force sensitivity, the impact of emission of Russia to the PM10 concentration of Istanbul did not exceed plus or minus 8%. Furthermore, these effects could be observed in the late hours of January 8 in a short period (Figure 7.21-e). This result had been expected after the backward trajectory studies were performed.

Figure 7.21: Time evolution of PM10 concentration in Istanbul, Turkey during simulation period. (a) to (e) are experiments with an increase of 50% anthropogenic emissions for Romania, Bulgaria, Poland, Ukraine, and Russia, respectively. The light gray area indicates the PM10 result from the base case and dark gray indicates the discrepancy of each experiment from the base case.

Both observations and results of base-case CMAQ model have demonstrated two different poor air quality ambiances over Istanbul. The first one was observed on January 7 and second one was observed on January 10. During the first high polluting period over Istanbul, brute-force runs gave a response of 2% to Ukraine, 4% to Bulgaria, 7% to Poland and 10% to Romania in terms of PM10. As for the second high polluting period over Istanbul, simulations gave 1% response to Ukraine and Russia, 3% to Poland, 7% to Bulgaria and 13% to Romania in terms of PM10.

Figure 7.22: Total emission values in a country base. According to EMEP data base; CO, NH₃, NO_x, SO_x, NMVOC and PM₁₀ pollutants has been considered.

All things considered, the impacts of the emissions of these countries have different meanings. From the point of view of total annual emissions, Bulgaria has the smallest total emission in these countries. At this point, its contributions seem significant. Similar things could be said about Romania. Although its annual total emissions are approximately twice as big as those of Bulgaria, they are still small when we compare emissions from Poland or Russia. In the following figure, a comparison can be made in terms of total emissions for these countries.

On the other hand, their locations also deserve to be given consideration. Although Bulgaria and Romania have less annual emission totals, the short distances help to transport a big portion of aerosols easily to north-western Turkey and Istanbul. When the situation is evaluated from this point of view, the impact of Ukraine and Poland aerosol transport also become important in spite of the far distances.

It is worth to note that, besides country locations and potential emissions, dominant atmospheric dynamics play a significant role in forming ambient air quality of Istanbul. While Greece is very close to the related area and Russia has the biggest potential emissions and there is not much distance to the North of Turkey, no significant effect was observed for Greece during the simulation period. Russian emissions influenced Istanbul PM₁₀ in a short period.

Besides country based emission changes, brute force emission sensitivity analyses were performed on a regional base. Previous efforts related to country base approach had given clear evidences as to which part of the Europe emissions affect Northern and Western Turkey. Actually, similar information had been obtained before, by the

backward trajectory study. Brute force sensitivity runs added quantitative information over the visualized results.

In the light of the first approach of brute force sensitivity analyses and backward trajectory studies; regional base sensitivity analyses were carried out for the same period which covered the entire Eastern European regions. Besides Romania, Bulgaria, Poland, Ukraine and Russia; Hungary, Slovakia, Moldova, Belarus, Lithuania, Latvia and Estonia were added for regional analyses (Figure 7.23-a).

First, a continuous response of Istanbul PM10 attracted our attention during all the simulations. Naturally, the quantity of these responses changed from time to time, but 12% average increase and 9% average decrease were observed over Istanbul as a result of 50% increase and decrease in brute force sensitivity analyses. The results of the analyses could reach up to 24% increase and 26% decrease of PM10 during the simulations for Istanbul grid.

Figure 7.23: Time evolution of PM10 concentration in Istanbul, Turkey during simulation period. (a) to (b) are experiments with an increase of 50% anthropogenic emissions for Regional and Regional + Turkey respectively. The light gray area indicates the PM10 result from the base case and dark gray indicates the discrepancy of each experiment from base case.

Another regional base brute force analysis was performed, but this time in addition to regional perturbation emissions, emissions from Turkey had been taken into consideration (Figure 7.23-b). Turkey is also a big source for its ambient air pollution. It has 420Gg PM10 annual total (EMEP). In addition to European sourced air pollution transport to Northern and Western Turkey, this area is already a serious source by itself with a big population and industrial activities. As a result of this, all these factors might create an inevitable poor air quality ambiance from time to time. The approach naturally covers both local and long-range pollutant transport.

Therefore, the model run should give an approximate impact to any related area as much as perturbations. Adding emissions from Turkey into brute force sensitivity analysis for the regional base approach, the model gave almost the same results as expected. As can be seen from Figure 7.23 (b), 45% average increased results and 46% decreased results were observed during the simulation period. Backward trajectory and individual country base brute force studies had indicated this conclusion before.

8. CONCLUSIONS AND FUTURE STUDIES

In this study, the trans-boundary particulate matter transfer from Eastern European countries to Turkey has been presented. Actually, a study of this magnitude for Turkey had never been carried out before. In addition to difficulties of setting and running atmospheric models, emission modeling alone has been the most challenging task. A new emission processing module has been developed for this study and large quantities of data had to be handled.

A significant impact of Eastern European emissions to PM₁₀ concentrations in Istanbul has been demonstrated. The brute-force sensitivity simulations indicated that, during the simulation period, aerosol transport from Europe to northern and western Turkey can be seen all the time in the regional framework. Although this transport generally accounted for a small percentage of Istanbul PM₁₀ levels, sometimes trans-boundary pollution could constitute a quarter of the Istanbul air pollution during the simulation. As a result, while air pollution of the northern or western Turkey is evaluated, the contribution of long-range transport from Europe must strictly be kept in mind. It was found that episodes with relatively high concentrations of PM₁₀ in Turkey are accompanied by northwesterly winds indicating the effects of especially Eastern European countries.

Together with the back-trajectory study and brute-force sensitivity analysis; origins, routes and quantity of the PM₁₀ concentrations were attempted to be identified. The PM₁₀ emitted from Eastern Europe sources could be transported to the northwest of Turkey between 12 and 48 hours depending on the distance of each country. Furthermore, assuming a linear response, the contribution of each county/region can be estimated as twice the response to 50% emission changes modeled in this study. As a result, one can say that the contribution of these countries can be responsible for as much as half of the total Istanbul PM₁₀ levels under certain conditions. The PM₁₀ concentration distributions during the long-range transport were dominated by atmospheric dynamics.

As mentioned before, the MM5 on-line tracer model (MM5T) and backward trajectory were studied qualitatively for two high-pollution events that occurred in Istanbul, Turkey on 7-8 and 10-11 January 2002. The simulated tracer evolution provided qualitative proof that transport of PM₁₀ emitted from Eastern Europe could have contributed to the high-pollutant events in Istanbul. The model suggests that PM₁₀ transport to Istanbul took from hours to a few days for different locations in the related area during these events. Furthermore, trajectory studies showed that the major pollution transport routes occurred in Eastern Europe. Results obtained from this tracer and backward trajectory studies were quite reasonable and qualitatively support the hypothesis that the long-range transport from the north and northwest played an important role in both high PM₁₀ events in Istanbul. They are a very preliminary, qualitative study for understanding the causes of these high pollution events

Observations of PM₁₀ air pollutants were conducted in line with the air quality model in a case study to clarify the extent of transboundary air pollution from eastern European countries. Discrepancies between the model and the observations are likely to be due to horizontal and vertical coarse grid resolution and uncertainties in emission data. However, it should be noted that the model correctly reproduces the temporal pattern of PM₁₀ values observed in Istanbul. A finer model resolution, information of aerosol chemical composition and more reliable emission data may provide appropriate conclusions for the comparison. In the future, it is planned that more accurate and high resolution databases and calculation procedures will be integrated into the EME. The model has enough flexibility to react and to adapt to the changing requirements of national and international emission reporting.

Understanding of cause-effect relationships among atmospheric pollutants, exposures and deposition, and impacts on human health, visibility, and ecological systems is very popular among atmospheric scientists. Recently, studies show that airborne particles cause more visibility decrease and more likely health problems than do gases. The World Health Organization estimates that 2.7 million people die each year from air pollution (WHO, 2000). Furthermore, epidemiological studies have led to growing concern about the effects of particles on human health (e.g. UK Expert Panel on Air Quality Standards, 1995). A summary of several studies by Pope (2000) concluded that short-term (acute) increases of $10 \mu\text{g m}^{-3}$ PM₁₀ were associated with

a 0.5 to 1.5 percent increase in daily mortality, higher hospitalization and health-care visits for respiratory and cardiovascular diseases and enhanced outbreaks of asthma and coughing. Increased death rates usually occurred within 1 to 5 days following an air pollution episode. Long-term exposures of PM_{2.5} particles above background levels ($\sim 5\mu\text{gm}^{-3}$) resulted in a variety of cardiopulmonary problems, including increased mortality, increased disease and decreased lung function in adults and children (Pope and Dockery, 1999). There is a considerable and growing body of evidence showing an association between increases in adverse health effects, especially of the cardiac and respiratory systems, and elevated levels of PM in air. According to the EMEP database, Turkey has the biggest PM emissions after Russia, France and Ukraine in Europe. However, PM researches are hardly available in Turkey. Actually, we can not comment on the relationship between gases and health problems, either. In addition, these particles are small enough and gases have suitable compositions to remain in suspension for some hours or days and travel considerable distances from the source. It is a fact that air pollution is a major concern for determining health effects and producing government regulations in many countries. At this point, having correct and detailed information of potential of local emissions is becoming an essential requirement. The CORINAIR/EMEP emission inventory has a coarse resolution and doubtful data covering a lot of countries, including Turkey.

Besides studying qualitative and quantitative aspects of long range PM₁₀ transport from Europe to Turkey, this study has given a chance to see the deficiency of air quality modeling and management in Turkey. Difficulties and absences which were encountered during the study provided an overview of air quality in Turkey. According to these experiments, some conclusions and recommendations might be summarized as follows:

- A dense observation network system for atmospheric pollutants must be installed covering the entirety of Turkey, including urban and rural areas. In addition to PM₁₀ observations, PM_{2.5} and also PM₁ observational variety should be added to the system with regard to increasing concern about ultra fine particulate matters, especially in terms of health effects.
- In the framework of a national emission inventory development, anthropogenic emission database of air pollutions for Turkey must be prepared as soon as possible.

Fortunately, each source category and its sub-categories have already been classified and documented by the CORINAIR emission inventory. This newly formed national emission inventory will gain a high spatial and temporal resolution with detailed studies. As a result, it can be used for air dispersion modeling, national or regional strategy development, regulation setting; air toxics risk assessment and tracking emissions trends over time. Furthermore, this effort will help scientists or researchers to stay away from misleading results arising from expert estimated data filled with experts' estimates when they are incomplete or inconsistent.

- Since natural emissions are an important component of the earth system responsible for determining the composition of the atmosphere, the magnitudes, distributions, controlling processes and uncertainties associated with natural emissions of Turkey must be studied again in the framework of a national emission inventory development. Guenther et al. (1995) demonstrated that, especially biogenic emission of VOC accounted for more than 90% global VOC emissions and forests are the main source of biogenic emissions. As a result of this, to reduce uncertainties in air quality modeling in Turkey, an accurate and fine land-use dataset (plant species composition and dominance) has to be obtained. In addition, appropriate emission factors, environmental conditions (which influence species physiology and production) and environmental correction algorithms must be developed for the characteristic forests and other vegetation in Turkey.

- An emission processing strategy should be developed considering national characteristics. For the purpose of developing an emission modeling, existing models (e.g. SMOKE, EMS95) can be modified or a new process can be prepared immediately.

- As mentioned above, more accurate and high resolution databases and calculation procedures must be developed for Turkey. This emission inventory and emission modeling processes should match and be made suitable for the current studies and technologies in Europe.

- In the course of the whole study, prevailing wind direction was westerly or northwesterly, a significant fraction of the pollutants emitted from Europe are transported to and deposited in Turkey. But, to say something about the magnitude, frequency and conditions of the transport, an evaluation should be researched for a long period of time.

- There is a growing concern about long-range transboundary transport of particulate matter from the distance sources in the atmosphere. Several international agencies, including the International Joint Commission (IJC), the Organization for Economic Co-operation and Development (OECD) and the United Nations Economic Commission for Europe (UN-ECE) have formed task groups tackling this problem. Due to the political and economical consequences of this ongoing debate, it is important to clearly outline how far "long range" really is and how large the pollutant transports actually are. In this thesis, the first study has been carried out in a comprehensive approach for the long-range PM₁₀ transport, but plenty of sensitivity analyses should be performed for other pollutants in an ensemble way of thinking.

Unfortunately, this study exposed that air quality studies have not been performed in a systematic approach in Turkey. An observation network, an emission inventory, an emission modeling, a meteorological model and an air quality model are the part of the entire system. If one of them does not exist, it is not possible to explain sources and impacts of air pollution. A study which is performed out of this concept will never bring a realistic contribution to the evaluation of air quality problem in Turkey. It is a fact that this study has filled in an important gap about transboundary pollution studies between Europe and Turkey. What is more, this study will force to change our approach to the air pollution problem and gain a comprehensive and systematic way of approach for further studies.

Northern and western parts of Turkey frequently experience air pollution episodes. However, transport of air pollutants from Europe to these regions has not been studied sufficiently. At the beginning of the study, it was claimed that trans-boundary pollution was an important problem for Istanbul. At the end of this study, a significant impact of Eastern European emissions to PM₁₀ concentrations in Istanbul has been demonstrated clearly. This study shows that trans-boundary sources can be responsible for half of the poor air quality of Istanbul. In the light of the results of brute force sensitivity analyses, backward trajectory and tracer studies; while air pollution of the North or West of Turkey is evaluated, the contribution of trans-boundary pollution from Europe should also be added to obtain a comprehensive and realistic assessment.

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APPENDICES

Appendix 1 Lists of Landuse/Vegetation and Soil Categories

Table 1.1	Description of 25-category (USGS) vegetation categories and physical parameters for North Hemisphere summer (15 April - 15 October) and winter (15 October - 15 April)
Table1.2	Description of 17-category Soil categories and physical parameters.

Appendix 2 Chemical Mechanisms Included in the CMAQ System

Table2.1	CB4 Mechanism Species List
Table2.2	RADM2 Photolysis Reactions (Adapted from Stockwell et al., 1990)
Table2.3	CB4 Mechanism (CB4_AE_AQ Mechanism)

Appendix 3 CMAQ Predefined Vertical Profiles for Initial and Boundary Concentrations

Table3.1	CMAQ Predefined Vertical Profiles for Initial Concentrations
Table3.2	CMAQ Predefined Vertical Profiles for Boundary Conditions

Appendix 4 Aerosol

Table4.1	Aerosol Species Concentrations
Table4.2	Equilibrium Relations and Constants (Kim et al., 1993a)
Table4.3	Organic Aerosol Yields in Terms of Amount of Precursor Reacted (From Pandis et al. (1992) and Bowman et al. (1995))

Appendix 5 Landuse Data Relationship

Table5.1	Relations Among MM5, CMAQ/RADM, and USGS Landuse Categories
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Appendix 1 Lists of Landuse/Vegetation and Soil Categories

Table 1.1 Description of 25-category (USGS) vegetation categories and physical parameters for North Hemisphere summer (15 April - 15 October) and winter (15 October - 15 April)

Vegetation Integer Identification	Vegetation Description	Albedo(%)		Moisture Avail. (%)		Emissivity (% at 9 μ m)		Roughness Length (cm)		Thermal Inertia (cal cm ⁻² k ⁻¹ s ^{-1/2})	
		Sum	Win	Sum	Win	Sum	Win	Sum	Win	Sum	Win
1	Urban	18	18	10	10	88	88	50	50	0.03	0.03
2	DryInd Crop. Past.	17	23	30	60	92	92	15	5	0.04	0.04
3	Irrg. Crop. Past.	18	23	50	50	92	92	15	5	0.04	0.04
4	Mix. Dry/Irrg.C.P.	18	23	25	50	92	92	15	5	0.04	0.04
5	Crop./Grs. Mosaic	18	23	25	40	92	92	14	5	0.04	0.04
6	Crop./Wood Mosaic	16	20	35	60	93	93	20	20	0.04	0.04
7	Grassland	19	23	15	30	92	92	12	10	0.03	0.04
8	Shrubland	22	25	10	20	88	88	10	10	0.03	0.04
9	Mix Shrb./Grs.	20	24	15	25	90	90	11	10	0.03	0.04
10	Savanna	20	20	15	15	92	92	15	15	0.03	0.03
11	Decids. Broadlf.	16	17	30	60	93	93	50	50	0.04	0.05
12	Decids. Needlf.	14	15	30	60	94	93	50	50	0.04	0.05
13	Evergm. Broadlf.	12	12	50	50	95	95	50	50	0.05	0.05
14	Evergrn. Needlf.	12	12	30	60	95	95	50	50	0.04	0.05
15	Mixed Forest	13	14	30	60	94	94	50	50	0.04	0.06
16	Water Bodies	8	8	100	100	98	98	.01	.01	0.06	0.06
17	Herb. Wetland	14	14	60	75	95	95	20	20	0.06	0.06
18	Wooded wetland	14	14	35	70	95	95	40	40	0.05	0.06
19	Bar. Sparse Veg.	25	25	2	5	85	85	10	10	0.02	0.02
20	Herb. Tundra	15	60	50	90	92	92	10	10	0.05	0.05
21	Wooden Tundra	15	50	50	90	93	93	30	30	0.05	0.05
22	Mixed Tundra	15	55	50	90	92	92	15	15	0.05	0.05
23	Bare Gmd. Tundra	25	70	2	95	85	95	.10	5	0.02	0.05
24	Snow or Ice	80	82	95	95	95	95	0.01	0.01	0.05	0.05
25	No data										

Table1.2 Description of 17-category Soil categories and physical parameters.

Soil Integer Identification	Soil Description	Max moisture content	Reference soil moisture	Wilting point soil moisture	Air dry moist content limits	Saturation soil potential	Saturation Soil conductivity (10^{-6})	B parameter	Saturation soil diffusivity (10^{-6})	Soil diffu./condu. coef.
1	Sand	0.339	0.236	0.010	0.010	0.069	1.07	2.79	0.608	- 0.472
2	Loamy Sand	0.421	0.283	0.028	0.028	0.036	14.10	4.26	5.14	- 1.044
3	Sandy Loam	0.434	0.312	0.047	0.047	0.141	5.23	4.74	8.05	- 0.569
4	Silt Loam	0.476	0.360	0.084	0.084	0.759	2.81	5.33	23.9	0.162
5	Silt	0.476	0.360	0.084	0.084	0.759	2.81	5.33	23.9	0.162
6	Loam	0.439	0.329	0.066	0.066	0.355	3.38	5.25	14.3	- 0.327
7	Sandy Clay Loam	0.404	0.314	0.067	0.067	0.135	4.45	6.66	9.90	- 1.491
8	Silty Clay Loam	0.464	0.387	0.120	0.120	0.617	2.04	8.72	23.7	- 1.118
9	Clay Loam	0.465	0.382	0.103	0.103	0.263	2.45	8.17	11.3	- 1.297
10	Sandy Clay	0.406	0.338	0.100	0.100	0.098	7.22	10.73	18.7	- 3.209
11	Silty Clay	0.468	0.404	0.126	0.126	0.324	1.34	10.39	9.64	- 1.916
12	Clay	0.468	0.412	0.138	0.138	0.468	0.974	11.55	11.2	- 2.138
13	Organic Materials	0.439	0.329	0.066	0.066	0.355	3.38	5.25	14.3	- 0.327
14	Water	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
15	Bedrock	0.200	0.108	0.006	0.006	0.069	141.0	2.79	136.0	- 1.111
16	Other	0.421	0.283	0.028	0.028	0.036	14.10	4.26	5.14	- 1.044
17	No data									

Appendix 2 Chemical Mechanisms Included in the CMAQ System

Table2.1 CB4 Mechanism Species List

Nitrogen Species NO Nitric oxide NO2 Nitrogen dioxide HONO Nitrous acid NO3 Nitrogen trioxide N2O5 Nitrogen pentoxide HNO3 Nitric acid PNA Peroxynitric acid	Oxidants O3 Ozone H2O2 Hydrogen peroxide	Sulfur Species SO2 Sulfur dioxide SULF Sulfuric acid	Atomic Species O Oxygen atom (triplet) O1D Oxygen atom (singlet)
Carbon oxides CO Carbon monoxide	Hydrocarbons PAR Paraffin carbon bond (C-C) ETH Ethene (CH ₂ =CH ₂) OLE Olefinic carbon bond (C=C) TOL Toluene (C ₆ H ₄ -CH ₃) XYL Xylene (C ₆ H ₅ -(CH ₃) ₂) ISOP Isoprene	Carbonyls and phenols FORM Formaldehyde ALD2 Acetaldehyde and higher aldehydes MGLY Methyl glyoxal (CH ₃ C(O)C(O)H) CRES Cresol and higher molecular weight phenols	Organic nitrogen PAN Peroxyacyl nitrate (CH ₃ C(O)OONO ₂) NTR Organic nitrate
Organic Radicals C2O3 Peroxyacyl radical (CH ₃ C(O)OO·) ROR Secondary organic oxy radical CRO Methylphenoxy radical	Operators XO2 NO-to-NO ₂ Operation XO2N NO-to-nitrate operation	Products of organics TO2 Toluene-hydroxyl radical adduct OPEN High molecular weight aromatic oxidation ring fragment ISPD Products of isoprene reactions	Species added for aerosols SULAER Counter species for H ₂ SO ₄ production TOLAER Counter species for toluene reaction XYLAER Counter species for xylene reaction CSLAER Counter species for cresol reaction TERPAER Counter species for terpene reaction TERP Monoterpenes
Species added for aqueous chemistry FACD Formic acid AACD Acetic and higher acids PACD Peroxy acetic acid UMHP Upper limit of methylhydroperoxide			

Table2.2 RADM2 Photolysis Reactions (Adapted from Stockwell et al., 1990)

Reaction	Description
$O_3 + h\nu \rightarrow O_2 + O^1D$	Ozone Photolysis to O^1D
$O_3 + h\nu \rightarrow O_2 + O^3P$	Ozone Photolysis to O^3P
$NO_2 + h\nu \rightarrow NO + O^3P$	Nitrogen Dioxide Photolysis
$NO_3 + h\nu \rightarrow NO + O_2$	Nitrate Photolysis to NO
$NO_3 + h\nu \rightarrow NO_2 + O^3P$	Nitrate Photolysis to NO_2
$HONO + h\nu \rightarrow OH + NO$	Nitrous Acid Photolysis
$HNO_3 + h\nu \rightarrow OH + NO_2$	Nitric Acid Photolysis
$HNO_4 + h\nu \rightarrow HO_2 + NO_2$	Pernitric Acid Photolysis
$H_2O_2 + h\nu \rightarrow OH + OH$	Hydrogen Peroxide Photolysis
$HCHO + h\nu \rightarrow H + HCO$	Formaldehyde Photolysis to Radicals
$HCHO + h\nu \rightarrow H_2 + CO$	Formaldehyde Photolysis to Molecular Hydrogen
$CH_3CHO + h\nu (+2O_2) \rightarrow CH_3OO + HO_2 + CO$	Acetaldehyde Photolysis
$CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$	Acetone Photolysis
$CH_3COC_2H_5 + h\nu \rightarrow ACO_3 + ETH$	Methyl Ethyl Ketone Photolysis
$HCOCHO + h\nu \rightarrow HCHO + CO$	Glyoxal Photolysis to Formaldehyde
$HCOCHO + h\nu \rightarrow 2CO + H_2$	Glyoxal Photolysis to Molecular Hydrogen
$CH_3COCHO + h\nu \rightarrow ACO_3 + HO_2 + CO$	Methyl Glyoxal Photolysis
$HCOCH=CHCHO + h\nu \rightarrow 0.98HO_2 + TCO_3 + 0.02ACO_3$	Unsaturated Dicarbonyl Photolysis
$CH_3OOH + h\nu \rightarrow CH_2O + OH + HO_2$	Methyl Hydrogen Peroxide Photolysis
$CH_3ONO_2 + h\nu \rightarrow 0.2ALD + 0.8KET + HO_2 + NO_2$	Organic Nitrate Photolysis
$C_3H_4O + h\nu \rightarrow \text{products}$	Acrolein Photolysis

Table2.3 CB4 Mechanism (CB4_AE_AQ Mechanism)

Reaction List

{1}	NO2	+	hv	-->	NO	+	O
{2}	O	+	[O2]	-->	O3		
{3}	O3	+	NO	-->	NO2		
{4}	O	+	NO2	-->	NO		
{5}	O	+	NO2	-->	NO3		
{6}	O	+	NO	-->	NO2		
{7}	O3	+	NO2	-->	NO3		
{8}	O3	+	hv	-->	O		
{9}	O3	+	hv	-->	O1D		
{10}	O1D	+	[N2]	-->	O		
{11}	O1D	+	[O2]	-->	O		
{12}	O1D	+	[H2O]	-->	2.000*OH		
{13}	O3	+	OH	-->	HO2		
{14}	O3	+	HO2	-->	OH		
{15}	NO3	+	hv	-->	0.890*NO2 + 0.890*O + 0.110*NO		
{16}	NO3	+	NO	-->	2.000*NO2		
{17}	NO3	+	NO2	-->	NO + NO2		
{18}	NO3	+	NO2	-->	N2O5		
{19}	N2O5	+	[H2O]	-->	2.000*HNO3		
{20}	N2O5			-->	NO3 + NO2		
{21}	NO	+ NO	+ [O2]	-->	2.000*NO2		
{22}	NO	+ NO2	+ [H2O]	-->	2.000*HONO		
{23}	OH	+	NO	-->	HONO		
{24}	HONO	+	hv	-->	OH + NO		
{25}	HONO	+	OH	-->	NO2		
{26}	HONO	+	HONO	-->	NO + NO2		
{27}	OH	+	NO2	-->	HNO3		
{28}	OH	+	HNO3	-->	NO3		
{29}	HO2	+	NO	-->	OH + NO2		
{30}	HO2	+	NO2	-->	PNA		
{31}	PNA			-->	HO2 + NO2		
{32}	PNA	+	OH	-->	NO2		
{33}	HO2	+	HO2	-->	H2O2		
{34}	HO2 + HO2	+ [H2O]		-->	H2O2		
{35}	H2O2	+	hv	-->	2.000*OH		
{36}	H2O2	+	OH	-->	HO2		
{37}	CO	+	OH	-->	HO2		

{38}	FORM	+	OH	-->	HO2 + CO
{39}	FORM	+	hv	-->	2.000*HO2 + CO
{40}	FORM	+	hv	-->	CO
{41}	FORM	+	O	-->	OH + HO2 + CO
{42}	FORM	+	NO3	-->	HNO3 + HO2 + CO
{43}	ALD2	+	O	-->	C2O3 + OH
{44}	ALD2	+	OH	-->	C2O3
{45}	ALD2	+	NO3	-->	C2O3 + HNO3
{46}	ALD2	+	hv	-->	XO2 + 2.000*HO2 + CO + FORM
{47}	C2O3	+	NO -	->	NO2 + XO2 + FORM + HO2
{48}	C2O3	+	NO2	-->	PAN
{49}	PAN			-->	C2O3 + NO2
{50}	C2O3 + C2O3			-->	2.000*XO2 + 2.000*FORM + 2.000*HO2
{51}	C2O3 + HO2			-->	0.790*FORM+0.790*XO2+0.790*HO2+ 0.790*OH
{52}	OH			-->	XO2 + FORM + HO2
{53}	PAR	+	OH	-->	0.870*XO2+0.130*XO2N+0.110*HO2+ 0.110*ALD2 + 0.760*ROR - 0.110*PAR
{54}	ROR			-->	1.100*ALD2 + 0.960*XO2 + 0.940*HO2 - 2.100*PAR + 0.040*XO2N + 0.020*ROR
{55}	ROR			-->	HO2
{56}	ROR	+	NO2	-->	NTR
{57}	OLE	+	O	-->	0.630*ALD2 + 0.380*HO2 + 0.280*XO2 + 0.300*CO + 0.200*FORM + 0.020*XO2N+ 0.220*PAR + 0.200*OH
{58}	OLE	+	OH	-->	FORM + ALD2 + XO2 + HO2 - PAR
{59}	OLE	+	O3	-->	0.500*ALD2 + 0.740*FORM + 0.330*CO + 0.440*HO2 + 0.220*XO2 + 0.100*OH - PAR
{60}	OLE	+	NO3	-->	0.910*XO2 + 0.090*XO2N + FORM + ALD2 - PAR + NO2
{61}	ETH	+	O	-->	FORM+0.700*XO2+ CO+ 1.700*HO2 + 0.300*OH
{62}	ETH	+	OH	-->	XO2 + 1.560*FORM + HO2+ 0.220*ALD2
{63}	ETH	+	O3	-->	FORM + 0.420*CO + 0.120*HO2
{64}	TOL	+	OH	-->	0.080*XO2+0.360*CRES+0.440*HO2+ 0.560*TO2
{65}	TO2	+	NO	-->	0.900*NO2+0.900*HO2+0.900*OPEN+ 0.100*NTR
{66}	TO2			-->	CRES + HO2
{67}	CRES	+	OH	-->	0.400*CRO+0.600*XO2+0.600*HO2+ .300*OPEN
{68}	CRES	+	NO3	-->	CRO + HNO3+CSLAER
{69}	CRO	+	NO2	-->	NTR
{70}	XYL	+	OH	-->	0.700*HO2 + 0.500*XO2 + 0.200*CRES +0.800*MGLY+1.100*PAR+0.300*TO2+XYLAER
{71}	OPEN	+	OH	-->	XO2 + 2.000*CO + 2.000*HO2+ C2O3 + FORM

{72}	OPEN	+	h _v	-->	C2O3 + HO2 + CO
{73}	OPEN	+	O3	-->	0.030*ALD2 + 0.620*C2O3 + 0.700*FORM + 0.030*XO2 + 0.690*CO + 0.080*OH + 0.760*HO2 + 0.200*MGLY
{74}	MGLY	+	OH	-->	XO2 + C2O3
{75}	MGLY	+	h _v	-->	C2O3 + HO2 + CO
{76}	ISOP	+	O	-->	0.750*ISPD + 0.500*FORM + 0.250*XO2 + 0.250*HO2 + 0.250*C2O3 + 0.250*PAR
{77}	ISOP	+	OH	-->	0.912*ISPD + 0.629*FORM + 0.991*XO2 + 0.912*HO2 + 0.088*XO2N
{78}	ISOP	+	O3	-->	0.650*ISPD + 0.600*FORM + 0.200*XO2 + 0.066*HO2 + 0.266*OH + 0.200*C2O3 + 0.150*ALD2 + 0.350*PAR + 0.066*CO
{79}	ISOP	+	NO3	-->	0.200*ISPD + 0.800*NTR + XO2 + 0.800*HO2 + 0.200*NO2 + 0.800*ALD2 + 2.400*PAR
{80}	XO2	+	NO	-->	NO2
{81}	XO2	+	XO2	-->	
{82}	XO2N	+	NO	-->	NTR
{83}	SO2	+	OH	-->	SULF + HO2+SULAER
{84}	SO2			-->	SULF+SULAER
{85}	XO2	+	HO2	-->	UMHP
{86}	XO2N	+	HO2	-->	
{87}	XO2N	+	XO2N	-->	
{88}	XO2N	+	XO2	-->	
{89}	ISPD	+	OH	-->	1.565*PAR + 0.167*FORM + 0.713*XO2 + 0.503*HO2 + 0.334*CO + 0.168*MGLY + 0.273*ALD2 + 0.498*C2O3
{90}	ISPD	+	O3	-->	0.114*C2O3 + 0.150*FORM + 0.850*MGLY + 0.154*HO2 + 0.268*OH + 0.064*XO2 + 0.020*ALD2 + 0.360*PAR + 0.225*CO
{91}	ISPD	+	NO3	-->	0.357*ALD2 + 0.282*FORM + 1.282*PAR + 0.925*HO2 + 0.643*CO + 0.850*NTR + 0.075*C2O3 + 0.075*XO2 + 0.075*HNO3
{92}	ISPD	+	h _v	-->	0.333*CO + 0.067*ALD2 + 0.900*FORM + 0.832*PAR + 1.033*HO2 + 0.700*XO2 + 0.967*C2O3
{93}	ISOP	+	NO2	-->	0.200*ISPD + 0.800*NTR + XO2 + 0.800*HO2 + 0.200*NO + 0.800*ALD2 + 2.400*PAR
{94}	TERP	+	OH	-->	TERPAER + OH
{95}	TERP	+	NO3	-->	TERPAER + NO3
{96}	TERP	+	O3	-->	TERPAER + O3

Rate Expression	Rate Constant
k(1) uses photo table NO2_CBIV88 , scaled by 1.00000E+00	{0.00000E+00}
k(2) is a falloff expression using: $k_0 = 6.0000\text{E-}34 * (T/300)^{*(-2.30)}$ $k_{inf} = 2.8000\text{E-}12 * (T/300)^{(0.00)}$ $F = 0.60, \quad n = 1.00$	{1.37387E-14}
k(3) = $1.8000\text{E-}12 * \exp(-1370.0/T)$	{1.81419E-14}
k(4) = $9.3000\text{E-}12$	{9.30000E-12}
k(5) is a falloff expression using: $k_0 = 9.0000\text{E-}32 * (T/300)^{*(-2.00)}$ $k_{inf} = 2.2000\text{E-}11 * (T/300)^{(0.00)}$ $F = 0.60, \quad n = 1.00$	{1.57527E-12}
k(6) is a falloff expression using: $k_0 = 9.0000\text{E-}32 * (T/300)^{*(-1.50)}$ $k_{inf} = 3.0000\text{E-}11 * (T/300)^{(0.00)}$ $F = 0.60, \quad n = 1.00$	{1.66375E-12}
k(7) = $1.2000\text{E-}13 * \exp(-2450.0/T)$	{3.22581E-17}
k(8) uses photo table NO2_CBIV88 , scaled by 5.30000E-02	{0.00000E+00}
k(9) uses photo table O3O1D_CBIV88 , scaled by 1.00000E+00	{0.00000E+00}
k(10) = $1.8000\text{E-}11 * \exp(107.0/T)$	{2.57757E-11}
k(11) = $3.2000\text{E-}11 * \exp(67.0/T)$	{4.00676E-11}
k(12) = $2.2000\text{E-}10$	{2.20000E-10}
k(13) = $1.6000\text{E-}12 * \exp(-940.0/T)$	{6.82650E-14}
k(14) = $1.4000\text{E-}14 * \exp(-580.0/T)$	{1.99920E-15}
k(15) uses photo table NO2_CBIV88 , scaled by 3.39000E+01	{0.00000E+00}
k(16) = $1.3000\text{E-}11 * \exp(250.0/T)$	{3.00805E-11}
k(17) = $2.5000\text{E-}14 * \exp(-1230.0/T)$	{4.03072E-16}
k(18) is a falloff expression using: $k_0 = 2.2000\text{E-}30 * (T/300)^{*(-4.30)}$ $k_{inf} = 1.5000\text{E-}12 * (T/300)^{*(-0.50)}$ $F = 0.60, \quad n = 1.00$	{1.26440E-12}
k(19) = $1.3000\text{E-}21$	{1.30000E-21}
k(20) = k(18) / Keq, where $\text{Keq} = 2.700\text{E-}27 * \exp(11000.0/T)$	{4.36029E-02}
k(21) = $3.3000\text{E-}39 * \exp(530.0/T)$	{1.95397E-38}
k(22) = $4.4000\text{E-}40$	{4.39999E-40}
k(23) is a falloff expression using: $k_0 = 6.7000\text{E-}31 * (T/300)^{*(-3.30)}$ $k_{inf} = 3.0000\text{E-}11 * (T/300)^{*(-1.00)}$ $F = 0.60, \quad n = 1.00$	{6.69701E-12}

$k(24)$ uses photo table NO2_CBIV88 , scaled by 1.97500E-01 {0.00000E+00}
 $k(25) = 6.6000\text{E-}12$ {6.60000E-12}
 $k(26) = 1.0000\text{E-}20$ {1.00000E-20}
 $k(27)$ is a falloff expression using: {1.14885E-11}
 $k_0 = 2.6000\text{E-}30 * (T/300)^{*(-3.20)}$
 $k_{inf} = 2.4000\text{E-}11 * (T/300)^{*(-1.30)}$
 $F = 0.60, \quad n = 1.00$
 $k(28)$ is a special rate expression of the form: {1.47236E-13}
 $k = k_0 + \{k_3[M] / (1 + k_3[M]/k_2)\}$, where
 $k_0 = 7.2000\text{E-}15 * \exp(785.0/T)$
 $k_2 = 4.1000\text{E-}16 * \exp(1440.0/T)$
 $k_3 = 1.9000\text{E-}33 * \exp(725.0/T)$
 $k(29) = 3.7000\text{E-}12 * \exp(240.0/T)$ {8.27883E-12}
 $k(30)$ is a falloff expression using: {1.48014E-12}
 $k_0 = 2.3000\text{E-}31 * (T/300)^{*(-4.60)}$
 $k_{inf} = 4.2000\text{E-}12 * (T/300)^{(0.20)}$
 $F = 0.60, \quad n = 1.00$
 $k(31) = k(30) / K_{eq}$, where $K_{eq} = 2.100\text{E-}27 * \exp(10900.0/T)$ {9.17943E-02}
 $k(32) = 1.3000\text{E-}12 * \exp(380.0/T)$ {4.65309E-12}
 $k(33) = 5.9000\text{E-}14 * \exp(1150.0/T)$ {2.79783E-12}
 $k(34) = 2.2000\text{E-}38 * \exp(5800.0/T)$ {6.23927E-30}
 $k(35)$ uses photo table HCHOmole_CBIV88 , scaled by 2.55000E-01 {0.00000E+00}
 $k(36) = 3.1000\text{E-}12 * \exp(-187.0/T)$ {1.65514E-12}
 $k(37) = 1.5000\text{E-}13 * (1.0 + 0.6 * \text{Pressure})$ {2.40000E-13}
 $k(38) = 1.0000\text{E-}11$ {1.00000E-11}
 $k(39)$ uses photo table HCHOrad_CBIV88 , scaled by 1.00000E+00 {0.00000E+00}
 $k(40)$ uses photo table HCHOmole_CBIV88 , scaled by 1.00000E+00 {0.00000E+00}
 $k(41) = 3.0000\text{E-}11 * \exp(-1550.0/T)$ {1.65275E-13}
 $k(42) = 6.3000\text{E-}16$ {6.30000E-16}
 $k(43) = 1.2000\text{E-}11 * \exp(-986.0/T)$ {4.38753E-13}
 $k(44) = 7.0000\text{E-}12 * \exp(250.0/T)$ {1.61972E-11}
 $k(45) = 2.5000\text{E-}15$ {2.50000E-15}
 $k(46)$ uses photo table ALD_CBIV88 , scaled by 1.00000E+00 {0.00000E+00}
 $k(47) = 3.4900\text{E-}11 * \exp(-180.0/T)$ {1.90766E-11}
 $k(48) = 2.6300\text{E-}12 * \exp(380.0/T)$ {9.41356E-12}
 $k(49) = 2.0000\text{E+}16 * \exp(-13500.0/T)$ {4.23268E-04}
 $k(50) = 2.5000\text{E-}12$ {2.50000E-12}
 $k(51) = 6.5000\text{E-}12$ {6.50000E-12}
 $k(52) = 1.1000\text{E+}02 * \exp(-1710.0/T)$ {3.54242E-01}
 $k(53) = 8.1000\text{E-}13$ {8.10000E-13}

k(54) = 1.0000E+15 * exp(-8000.0/T)	{2.19325E+03}
k(55) = 1.6000E+03	{1.60000E+03}
k(56) = 1.5000E-11	{1.50000E+11}
k(57) = 1.2000E-11 * exp(-324.0/T)	{4.04572E-12}
k(58) = 5.2000E-12 * exp(504.0/T)	{2.82173E-11}
k(59) = 1.4000E-14 * exp(-2105.0/T)	{1.19778E-17}
k(60) = 7.7000E-15	{7.70000E-15}
k(61) = 1.0000E-11 * exp(-792.0/T)	{7.01080E-13}
k(62) = 2.0000E-12 * exp(411.0/T)	{7.94340E-12}
k(63) = 1.3000E-14 * exp(-2633.0/T)	{1.89105E-18}
k(64) = 2.1000E-12 * exp(322.0/T)	{6.18715E-12}
k(65) = 8.1000E-12	{8.10000E-12}
k(66) = 4.2000E+00	{4.20000E+00}
k(67) = 4.1000E-11	{4.10000E-11}
k(68) = 2.2000E-11	{2.20000E-11}
k(69) = 1.4000E-11	{1.40000E-11}
k(70) = 1.7000E-11 * exp(116.0/T)	{2.50901E-11}
k(71) = 3.0000E-11	{3.00000E-11}
k(72) uses photo table HCHOrad_CBIV88 , scaled by 9.04000E+00	{0.00000E+00}
k(73) = 5.4000E-17 * exp(-500.0/T)	{1.00858E-17}
k(74) = 1.7000E-11	{1.70000E-11}
k(75) uses photo table HCHOrad_CBIV88 , scaled by 9.64000E+00	{0.00000E+00}
k(76) = 3.6000E-11	{3.60000E-11}
k(77) = 2.5400E-11 * exp(407.6/T)	{9.97368E-11}
k(78) = 7.8600E-15 * exp(-1912.0/T)	{1.28512E-17}
k(79) = 3.0300E-12 * exp(-448.0/T)	{6.73819E-13}
k(80) = 8.1000E-12	{8.10000E-12}
k(81) = 1.7000E-14 * exp(1300.0/T)	{1.33359E-12}
k(82) = 8.1000E-12	{8.10000E-12}
k(83) = 4.3900E-13 * exp(160.0/T)	{7.51005E-13}
k(84) = 1.3600E-06	{1.36000E-06}
k(85) = 7.6700E-14 * exp(1300.0/T)	{6.01684E-12}
k(86) = 7.6700E-14 * exp(1300.0/T)	{6.01684E-12}
k(87) = 1.7300E-14 * exp(1300.0/T)	{1.35712E-12}
k(88) = 3.4500E-14 * exp(1300.0/T)	{2.70640E-12}
k(89) = 3.3600E-11	{3.36000E-11}
k(90) = 7.1100E-18	{7.11000E-18}
k(91) = 1.0000E-15	{1.00000E-15}
k(92) uses photo table ACROLEIN , scaled by 3.60000E-03	{0.00000E+00}
k(93) = 1.4900E-19	{1.49000E-19}

$k(94) = 1.0700\text{E-}11 * \exp(549.0/T)$	$\{6.75269\text{E-}11\}$
$k(95) = 3.2300\text{E-}11 * \exp(-975.0/T)$	$\{1.22539\text{E-}12\}$
$k(96) = 7.2900\text{E-}15 * \exp(-1136.0/T)$	$\{1.61125\text{E-}16\}$

Appendix 3 CMAQ Predefined Vertical Profiles for Initial and Boundary Concentrations

Table3.1 CMAQ Predefined Vertical Profiles for Initial Concentrations

1	Optional boundary condition: The vertical coordinate of the model to								
2	generate these b.c. is the terrain-following sigma coordinate. The number of								
3	sigma layers and defined sigma levels are listed below.								
4	6	47	1.00	0.98	0.93	0.84	0.60	0.30	0.00
5									
6	SO2	0.300E-03	0.200E-03	0.100E-03	0.100E-03	0.200E-04	0.100E-04		
7	SULF	0.150E-03	0.150E-03	0.100E-03	0.100E-03	0.200E-04	0.100E-04		
8	NO2	0.200E-04	0.200E-04	0.100E-04	0.000E+00	0.000E+00	0.000E+00		
9	NO	0.200E-04	0.200E-04	0.100E-04	0.000E+00	0.000E+00	0.000E+00		
10	O3	0.350E-01	0.350E-01	0.400E-01	0.500E-01	0.600E-01	0.700E-01		
11	HNO3	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.700E-04	0.100E-03		
12	H2O2	0.100E-02	0.100E-02	0.150E-02	0.100E-02	0.800E-03	0.200E-03		
13	ALD	0.300E-04	0.350E-04	0.300E-04	0.200E-04	0.200E-04	0.100E-04		
14	HCHO	0.250E-03	0.250E-03	0.250E-03	0.200E-03	0.100E-03	0.500E-04		
15	OP1	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07		
16	OP2	0.300E-07	0.350E-07	0.300E-07	0.200E-07	0.200E-07	0.100E-07		
17	PAA	0.300E-04	0.300E-04	0.300E-04	0.250E-04	0.200E-04	0.150E-04		
18	ORA1	0.100E-05	0.100E-05	0.500E-06	0.500E-06	0.500E-06	0.000E+00		
19	ORA2	0.100E-05	0.100E-05	0.500E-06	0.500E-06	0.500E-06	0.000E+00		
20	NH3	0.100E-03	0.100E-03	0.300E-04	0.200E-04	0.200E-04	0.100E-04		
21	N2O5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00		
22	NO3	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00		
23	PAN	0.200E-04	0.200E-04	0.100E-04	0.100E-04	0.100E-04	0.000E+00		
24	HC3	0.400E-04	0.400E-04	0.320E-04	0.120E-04	0.400E-05	0.000E+00		
25	HC5	0.400E-04	0.400E-04	0.320E-04	0.120E-04	0.400E-05	0.000E+00		
26	HC8	0.200E-04	0.200E-04	0.160E-04	0.600E-05	0.200E-05	0.000E+00		
27	ETH	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00		
28	CO	0.800E-01	0.800E-01	0.800E-01	0.700E-01	0.650E-01	0.500E-01		
29	OL2	0.500E-05	0.300E-05	0.200E-05	0.100E-05	0.100E-05	0.000E+00		
30	OLT	0.200E-06	0.200E-06	0.100E-06	0.000E+00	0.000E+00	0.000E+00		
31	OLI	0.100E-06	0.100E-06	0.000E+00	0.000E+00	0.000E+00	0.000E+00		
32	TOL	0.100E-05	0.100E-05	0.100E-05	0.100E-05	0.000E+00	0.000E+00		
33	XYL	0.200E-06	0.200E-06	0.100E-06	0.000E+00	0.000E+00	0.000E+00		
34	ACO3	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08		
35	TPAN	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07		
36	HONO	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08		

37	HNO4	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08
38	KET	0.300E-04	0.350E-04	0.300E-04	0.200E-04	0.200E-04	0.100E-04
39	GLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
40	MGLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
41	DCB	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
42	ONIT	0.200E-04	0.200E-04	0.160E-04	0.600E-05	0.200E-05	0.000E+00
43	CSL	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
44	ISO	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05
45	HO	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
46	HO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
47	ASO4I	4.810E-02	3.207E-02	1.603E-02	1.603E-02	3.207E-03	1.603E-03
48	ASO4J	1.154E+00	7.696E-01	3.848E-01	3.848E-01	7.696E-02	3.848E-02
49	NUMATKN	1.437E+10	9.583E+09	4.791E+09	4.791E+09	9.583E+08	4.791E+08
50	NUMACC	4.110E+08	2.740E+08	1.370E+08	1.370E+08	2.740E+07	1.370E+07
51	ASOIL	1.000E+00	8.000E-01	4.000E-01	4.000E-01	8.000E-02	4.000E-02
52	NUMCOR	1.740E+04	1.392E+04	6.960E+03	6.960E+03	1.392E+03	6.960E+02

Table3.2 CMAQ Predefined Vertical Profiles for Boundary Conditions

1	Optional boundary condition: The vertical coordinate of the model to
2	generate these b.c. is the terrain-following sigma coordinate. The number of
3	sigma layers and defined sigma levels are listed below.
4	6 47 1.00 0.98 0.93 0.84 0.60 0.30 0.00 4
5	
6	North
7	
8	SO2 0.300E-03 0.200E-03 0.100E-03 0.100E-03 0.200E-04 0.100E-04
9	SULF 0.150E-03 0.150E-03 0.100E-03 0.100E-03 0.200E-04 0.100E-04
10	NO2 0.200E-04 0.200E-04 0.100E-04 0.000E+00 0.000E+00 0.000E+00
11	NO 0.200E-04 0.200E-04 0.100E-04 0.000E+00 0.000E+00 0.000E+00
12	O3 0.350E-01 0.350E-01 0.400E-01 0.500E-01 0.600E-01 0.700E-01
13	HNO3 0.500E-04 0.500E-04 0.500E-04 0.500E-04 0.700E-04 0.100E-03
14	H2O2 0.100E-02 0.100E-02 0.150E-02 0.100E-02 0.800E-03 0.200E-03
15	ALD 0.300E-04 0.350E-04 0.300E-04 0.200E-04 0.200E-04 0.100E-04
16	HCHO 0.250E-03 0.250E-03 0.250E-03 0.200E-03 0.100E-03 0.500E-04
17	OP1 0.250E-06 0.250E-06 0.250E-06 0.200E-06 0.100E-06 0.500E-07
18	OP2 0.300E-07 0.350E-07 0.300E-07 0.200E-07 0.200E-07 0.100E-07
19	PAA 0.300E-04 0.300E-04 0.300E-04 0.250E-04 0.200E-04 0.150E-04
20	ORA1 0.100E-05 0.100E-05 0.500E-06 0.500E-06 0.500E-06 0.000E+00
21	ORA2 0.100E-05 0.100E-05 0.500E-06 0.500E-06 0.500E-06 0.000E+00
22	NH3 0.100E-03 0.100E-03 0.300E-04 0.200E-04 0.200E-04 0.100E-04
23	N2O5 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
24	NO3 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
25	PAN 0.200E-04 0.200E-04 0.100E-04 0.100E-04 0.100E-04 0.000E+00
26	HC3 0.400E-04 0.400E-04 0.320E-04 0.120E-04 0.400E-05 0.000E+00
27	HC5 0.400E-04 0.400E-04 0.320E-04 0.120E-04 0.400E-05 0.000E+00
28	HC8 0.200E-04 0.200E-04 0.160E-04 0.600E-05 0.200E-05 0.000E+00
29	ETH 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
30	CO 0.800E-01 0.800E-01 0.800E-01 0.700E-01 0.650E-01 0.500E-01
31	OL2 0.500E-05 0.300E-05 0.200E-05 0.100E-05 0.100E-05 0.000E+00
32	OLT 0.200E-06 0.200E-06 0.100E-06 0.000E+00 0.000E+00 0.000E+00
33	OLI 0.100E-06 0.100E-06 0.000E+00 0.000E+00 0.000E+00 0.000E+00
34	TOL 0.100E-05 0.100E-05 0.100E-05 0.100E-05 0.000E+00 0.000E+00
35	XYL 0.200E-06 0.200E-06 0.100E-06 0.000E+00 0.000E+00 0.000E+00
36	ACO3 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08
37	TPAN 0.100E-07 0.100E-07 0.100E-07 0.100E-07 0.100E-07 0.100E-07
38	HONO 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08

39	HNO4	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08
40	KET	0.300E-04	0.350E-04	0.300E-04	0.200E-04	0.200E-04	0.100E-04
41	GLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
42	MGLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
43	DCB	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.100E-06	0.500E-07
44	ONIT	0.200E-04	0.200E-04	0.160E-04	0.600E-05	0.200E-05	0.000E+00
45	CSL	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
46	ISO	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05
47	HO	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
48	HO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
49	ASO4I	2.405E-02	2.405E-02	1.603E-02	1.603E-02	3.207E-03	1.603E-03
50	ASO4J	5.772E-01	5.772E-01	3.848E-01	3.848E-01	7.696E-02	3.848E-02
51	NUMATKN	7.187E+09	7.187E+09	4.791E+09	4.791E+09	9.583E+08	4.791E+08
52	NUMACC	2.055E+08	2.055E+08	1.370E+08	1.370E+08	2.740E+07	1.370E+07
53	ASOIL	5.000E-01	5.000E-01	4.000E-01	4.000E-01	8.000E-01	3.000E-01
54	NUMCOR	8.750E+03	8.750E+03	7.000E+03	7.000E+03	1.400E+03	5.250E+02
55	East						
56							
57	SO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
58	SULF	0.200E-03	0.200E-03	0.200E-03	0.200E-03	0.200E-04	0.100E-04
59	NO2	0.100E-04	0.100E-04	0.000E+00	0.000E+00	0.000E+00	0.000E+00
60	NO	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
61	O3	0.300E-01	0.350E-01	0.400E-01	0.500E-01	0.600E-01	0.700E-01
62	HNO3	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.150E-03
63	H2O2	0.200E-02	0.200E-02	0.200E-02	0.200E-02	0.150E-02	0.150E-02
64	ALD	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04
65	HCHO	0.250E-03	0.250E-03	0.250E-03	0.200E-03	0.150E-03	0.100E-03
66	OP1	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
67	OP2	0.400E-07	0.400E-07	0.400E-07	0.400E-07	0.400E-07	0.400E-07
68	PAA	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.500E-04
69	ORA1	0.150E-05	0.500E-06	0.500E-06	0.500E-06	0.500E-06	0.500E-06
70	ORA2	0.150E-05	0.500E-06	0.500E-06	0.500E-06	0.500E-06	0.500E-06
71	NH3	0.500E-04	0.500E-04	0.500E-04	0.200E-04	0.200E-04	0.200E-04
72	N2O5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
73	NO3	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
74	PAN	0.100E-04	0.100E-04	0.100E-04	0.100E-04	0.100E-04	0.100E-04
75	HC3	0.120E-04	0.120E-04	0.120E-04	0.800E-05	0.400E-05	0.400E-05
76	HC5	0.120E-04	0.120E-04	0.120E-04	0.800E-05	0.400E-05	0.400E-05
77	HC8	0.600E-05	0.600E-05	0.600E-05	0.400E-05	0.200E-05	0.200E-05
78	ETH	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00

79	CO	0.800E-01	0.800E-01	0.800E-01	0.750E-01	0.700E-01	0.650E-01
80	OL2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
81	OLT	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
82	OLI	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
83	TOL	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
84	XYL	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
85	ACO3	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
86	TPAN	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07
87	HONO	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
88	HNO4	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08
89	KET	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04
90	GLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
91	MGLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
92	DCB	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
93	ONIT	0.600E-05	0.600E-05	0.600E-05	0.400E-05	0.200E-05	0.200E-05
94	CSL	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
95	ISO	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05
96	HO	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
97	HO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
98	ASOI	3.207E-02	3.207E-02	3.207E-02	3.207E-02	3.207E-03	1.603E-03
99	ASOJ	7.696E-01	7.696E-01	7.696E-01	7.696E-01	7.696E-02	3.848E-02
100	NUMATKN	9.583E+09	9.583E+09	9.583E+09	9.583E+09	9.583E+08	4.791E+08
101	NUMACC	2.740E+08	2.740E+08	2.740E+08	2.740E+08	2.740E+07	1.370E+07
102	ASOIL	8.000E-01	8.000E-01	8.000E-01	8.000E-01	8.000E-02	4.000E-02
103	NUMCOR	1.392E+04	1.392E+04	1.392E+04	1.392E+04	1.392E+03	6.960E+02
104	South						
105							
106	SO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
107	SULF	0.200E-03	0.200E-03	0.200E-03	0.100E-03	0.500E-04	0.200E-04
108	NO2	0.100E-04	0.100E-04	0.000E+00	0.000E+00	0.000E+00	0.000E+00
109	NO	0.100E-04	0.100E-04	0.000E+00	0.000E+00	0.000E+00	0.000E+00
110	O3	0.300E-01	0.350E-01	0.400E-01	0.500E-01	0.600E-01	0.700E-01
111	HNO3	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.500E-04	0.150E-03
112	H2O2	0.200E-02	0.200E-02	0.200E-02	0.200E-02	0.150E-02	0.100E-02
113	ALD	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.500E-05
114	HCHO	0.250E-03	0.250E-03	0.250E-03	0.200E-03	0.150E-03	0.100E-03
115	OP1	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
116	OP2	0.400E-07	0.400E-07	0.400E-07	0.400E-07	0.400E-07	0.500E-08
117	PAA	0.100E-03	0.100E-03	0.100E-03	0.100E-03	0.500E-04	0.500E-04
118	ORA1	0.150E-05	0.500E-06	0.500E-06	0.500E-06	0.500E-06	0.500E-06

119	ORA2	0.150E-05	0.500E-06	0.500E-06	0.500E-06	0.500E-06	0.500E-06
120	NH3	0.500E-04	0.500E-04	0.500E-04	0.300E-04	0.200E-04	0.200E-04
121	N2O5	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
122	NO3	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
123	PAN	0.100E-04	0.100E-04	0.100E-04	0.100E-04	0.100E-04	0.100E-04
124	HC3	0.120E-04	0.120E-04	0.120E-04	0.400E-05	0.400E-05	0.400E-05
125	HC5	0.120E-04	0.120E-04	0.120E-04	0.400E-05	0.400E-05	0.400E-05
126	HC8	0.600E-05	0.600E-05	0.600E-05	0.200E-05	0.200E-05	0.200E-05
127	ETH	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
128	CO	0.700E-01	0.700E-01	0.700E-01	0.700E-01	0.650E-01	0.550E-01
129	OL2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
130	OLT	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
131	OLI	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
132	TOL	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
133	XYL	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
134	ACO3	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
135	TPAN	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07	0.100E-07
136	HONO	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
137	HNO4	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08	0.200E-08
138	KET	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.400E-04	0.500E-05
139	GLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
140	MGLY	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
141	DCB	0.250E-06	0.250E-06	0.250E-06	0.200E-06	0.150E-06	0.100E-06
142	ONIT	0.600E-05	0.600E-05	0.600E-05	0.200E-05	0.200E-05	0.200E-05
143	CSL	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08	0.100E-08
144	ISO	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05	0.250E-05
145	HO	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
146	HO2	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
147	ASO4I	3.207E-02	3.207E-02	3.207E-02	1.603E-02	3.207E-03	1.603E-03
148	ASO4J	7.696E-01	7.696E-01	7.696E-01	3.848E-01	7.696E-02	3.848E-02
149	NUMATKN	9.583E+09	9.583E+09	9.583E+09	4.791E+09	9.583E+08	4.791E+08
150	NUMACC	2.740E+08	2.740E+08	2.740E+08	1.370E+08	2.740E+07	1.370E+07
151	ASOIL	8.000E-01	8.000E-01	8.000E-01	4.000E-01	8.000E-02	4.000E-02
152	NUMCOR	1.400E+04	1.400E+04	1.400E+04	7.000E+03	1.400E+03	7.000E+02
153	West						
154							
155	SO2	0.300E-03	0.200E-03	0.200E-03	0.100E-03	0.000E+00	0.000E+00
156	SULF	0.300E-03	0.200E-03	0.200E-03	0.100E-03	0.000E+00	0.000E+00
157	NO2	0.100E-03	0.100E-03	0.100E-03	0.500E-04	0.000E+00	0.000E+00
158	NO	0.500E-04	0.500E-04	0.500E-04	0.200E-04	0.000E+00	0.000E+00

159 O3 0.350E-01 0.400E-01 0.450E-01 0.500E-01 0.600E-01 0.700E-01
 160 HNO3 0.500E-03 0.500E-03 0.500E-03 0.500E-03 0.200E-03 0.100E-03
 161 H2O2 0.200E-02 0.200E-02 0.200E-02 0.200E-02 0.800E-03 0.200E-03
 162 ALD 0.400E-04 0.400E-04 0.400E-04 0.400E-04 0.400E-04 0.500E-05
 163 HCHO 0.400E-03 0.400E-03 0.400E-03 0.400E-03 0.100E-03 0.500E-04
 164 OP1 0.400E-06 0.400E-06 0.400E-06 0.400E-06 0.100E-06 0.500E-07
 165 OP2 0.400E-07 0.400E-07 0.400E-07 0.400E-07 0.400E-07 0.500E-08
 166 PAA 0.250E-04 0.250E-04 0.250E-04 0.250E-04 0.200E-04 0.100E-04
 167 ORA1 0.250E-05 0.250E-05 0.250E-05 0.250E-05 0.500E-06 0.500E-06
 168 ORA2 0.250E-05 0.250E-05 0.250E-05 0.250E-05 0.500E-06 0.500E-06
 169 NH3 0.300E-03 0.300E-03 0.300E-03 0.200E-03 0.100E-03 0.500E-04
 170 N2O5 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
 171 NO3 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
 172 PAN 0.100E-03 0.100E-03 0.100E-03 0.500E-04 0.100E-04 0.100E-04
 173 HC3 0.800E-04 0.800E-04 0.800E-04 0.600E-04 0.800E-05 0.400E-05
 174 HC5 0.800E-04 0.800E-04 0.800E-04 0.600E-04 0.800E-05 0.400E-05
 175 HC8 0.400E-04 0.400E-04 0.400E-04 0.300E-04 0.400E-05 0.200E-05
 176 ETH 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
 177 CO 0.800E-01 0.800E-01 0.800E-01 0.800E-01 0.650E-01 0.500E-01
 178 OL2 0.100E-04 0.100E-04 0.500E-05 0.500E-05 0.100E-05 0.000E+00
 179 OLT 0.200E-05 0.100E-05 0.500E-06 0.300E-06 0.000E+00 0.000E+00
 180 OLI 0.100E-05 0.200E-06 0.100E-06 0.000E+00 0.000E+00 0.000E+00
 181 TOL 0.100E-04 0.500E-05 0.500E-05 0.300E-05 0.000E+00 0.000E+00
 182 XYL 0.300E-05 0.200E-05 0.400E-06 0.400E-06 0.000E+00 0.000E+00
 183 ACO3 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08
 184 TPAN 0.100E-07 0.100E-07 0.100E-07 0.100E-07 0.100E-07 0.100E-07
 185 HONO 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08
 186 HNO4 0.200E-08 0.200E-08 0.200E-08 0.200E-08 0.200E-08 0.200E-08
 187 KET 0.400E-04 0.400E-04 0.400E-04 0.400E-04 0.400E-04 0.500E-05
 188 GLY 0.400E-06 0.400E-06 0.400E-06 0.400E-06 0.100E-06 0.500E-07
 189 MGLY 0.400E-06 0.400E-06 0.400E-06 0.400E-06 0.100E-06 0.500E-07
 190 DCB 0.400E-06 0.400E-06 0.400E-06 0.400E-06 0.100E-06 0.500E-07
 191 ONIT 0.400E-04 0.400E-04 0.400E-04 0.300E-04 0.400E-05 0.200E-05
 192 CSL 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08 0.100E-08
 193 ISO 0.250E-05 0.250E-05 0.250E-05 0.250E-05 0.250E-05 0.250E-05
 194 HO 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
 195 HO2 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.000E+00
 196 ASO4I 4.810E-02 3.207E-02 3.207E-02 1.603E-02 3.207E-03 1.603E-03
 197 ASO4J 1.154E+00 7.696E-01 7.696E-01 3.848E-01 7.696E-02 3.848E-02
 198 NUMATKN 1.437E+10 9.583E+09 9.583E+09 4.791E+09 9.583E+08 4.791E+08

199	NUMACC	4.110E+08	2.740E+08	2.740E+08	1.370E+08	2.740E+07	1.370E+07
200	ASOIL	1.000E+00	8.000E-01	8.000E-01	4.000E-01	8.000E-02	4.000E-02
201	NUMCOR	1.750E+04	1.400E+04	1.400E+04	7.000E+03	1.400E+03	7.000E+02

Appendix 4 Aerosol

Table 4.1 Aerosol Species Concentrations

Units: mass [$\mu\text{g m}^{-3}$], number [$\# \text{m}^{-3}$]

{ a1 }	ASO4 J	Accumulation mode sulfate mass
{ a2 }	ASO4I	Aitken mode sulfate mass
{ a3 }	ANH4J	Accumulation mode ammonium mass
{ a4 }	ANH4I	Aitken mode ammonium mass
{ a5 }	ANO3J	Accumulation mode nitrate mass
{ a6 }	ANO3I	Aitken mode aerosol nitrate mass
{ a7 }	AORGAJ	Accumulation mode anthropogenic secondary organic mass
{ a8 }	AORGAI	Aitken mode anthropogenic secondary organic mass
{ a9 }	AORGAJ	Accumulation mode primary organic mass
{ a10 }	AORGAJ	Aitken mode mode primary organic mass
{ a11 }	AORGBJ	Accumulation mode secondary biogenic organic mass
{ a12 }	AORGBI	Aitken mode biogenic secondary biogenic organic mass
{ a13 }	AECJ	Accumulation mode elemental carbon mass
{ a14 }	AECI	Aitken mode elemental carbon mass
{ a15 }	A25J	Accumulation mode unspecified anthropogenic mass
{ a16 }	A25I	Aitken mode unspecified anthropogenic mass
{ a17 }	ACORS	Coarse mode unspecified anthropogenic mass
{ a18 }	ASEAS	Coarse mode marine mass
{ a19 }	ASOIL	Coarse mode soil-derived mass
{ a20 }	NUMATKN	Aitken mode number
{ a21 }	NUMACC	Accumulation mode number
{ a22 }	NUMCOR	Coarse mode number
{ a23 }	SRFATKN	Aitken mode surface area
{ a24 }	SRFACC	Accumulation mode surface area
{ a25 }	AH2OJ	Accumulation mode water mass
{ a26 }	AH2OI	Aitken mode water mass

PM2.5

ASO4J + ASO4I + ANO3J + ANO3I + ANH4J + ANH4I + AORGAJ + AORGAI + AORGAJ +
AORGAJ + AORGBJ + AORGBI + AECJ + AECI + A25J + A25I

PM10

ASO4J + ASO4I + ANO3J + ANO3I + ANH4J + ANH4I + AORGAJ + AORGAI + AORGAJ +
AORGAJ + AORGBJ + AORGBI + AECJ + AECI + A25J + A25I + ACORS + ASEAS + ASOIL

CURRICULUM VITAE

Tayfun Kındap was born in Ankara in 1970. He obtained his bachelor degree from Istanbul Technical University, Faculty of Aeronautics and Astronautics, Meteorological Engineering (1988-1992). After getting his M.Sc. degree in the same department (1992-1996), he registered a Ph.D. program in Istanbul Technical University, Eurasia Institute of Earth Sciences in 2001.