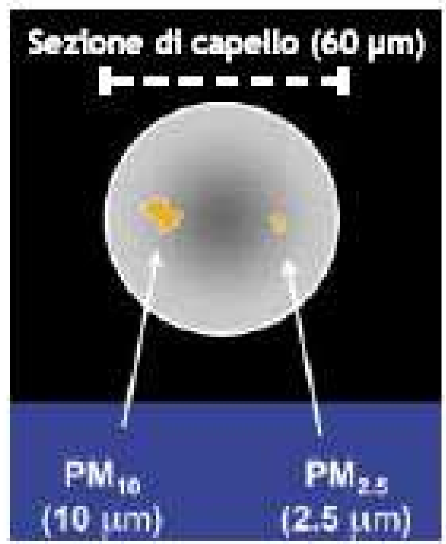
Corso di formazione
Attività di monitoraggio della qualità dell’aria: i modelli di dispersione degli inquinanti in atmosfera e le misure in atmosfera

L’aerosol atmosferico e la sua modellizzazione

Camillo Silibello

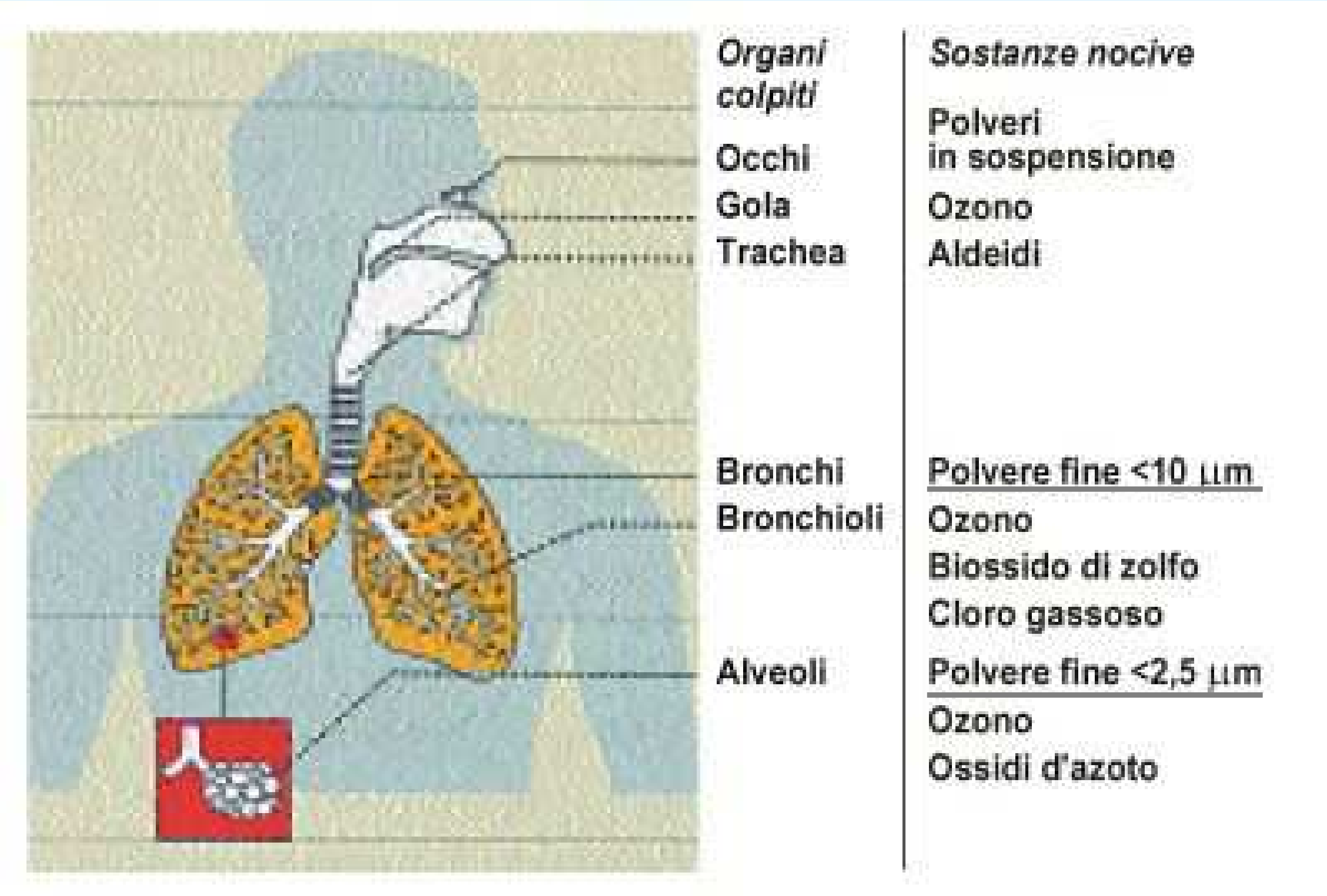
Definizione

- Aerosol è una sospensione di particelle liquide e/o solide in un gas.
- L'aerosol atmosferico consiste di piccole particelle solide o liquide sospese in aria.
- <u>Le dimensioni dell'aerosol sono espresse in </u>(mm)
  - 1 mm = 10^{-6} m
  - 1 mm = 10^{4} angstrom (Å)



Effetti sulla salute

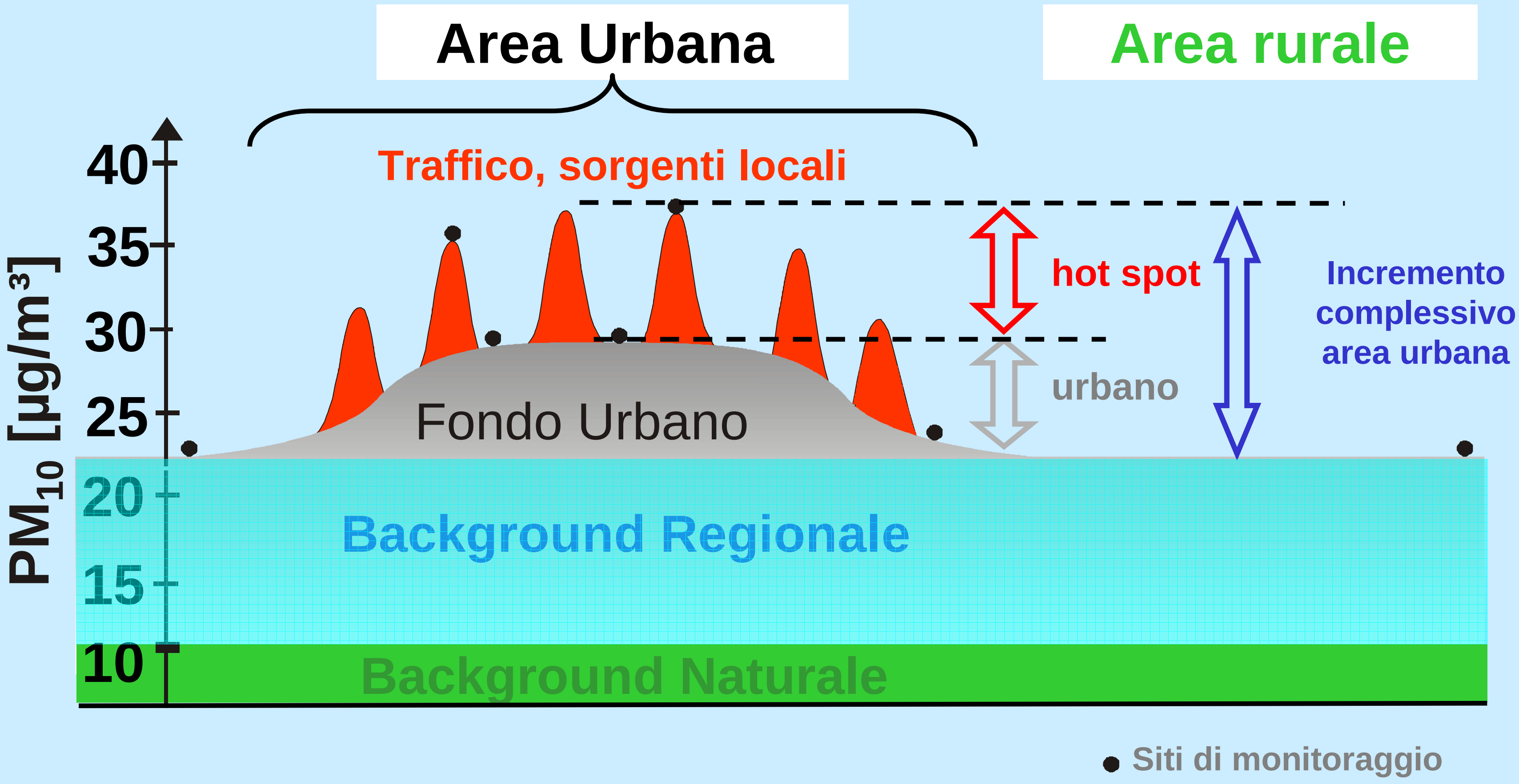
Si tratta di sostanze particolarmente pericolose, perché talmente sottili da penetrare profondamente nei bronchi e nei polmoni. Aggravano le malattie respiratorie e possono inoltre veicolare altre sostanze inquinanti.



Effetti sulla visibilità

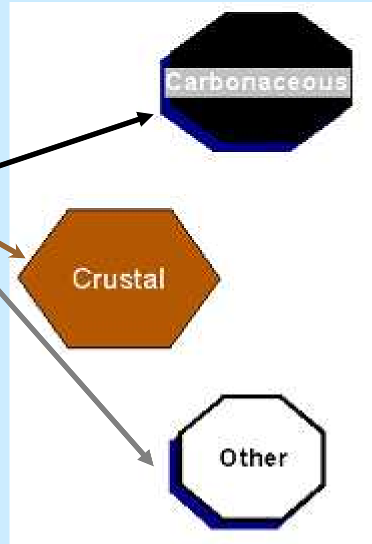
Pittsburg, from Spyros Pandis

“urban increment”

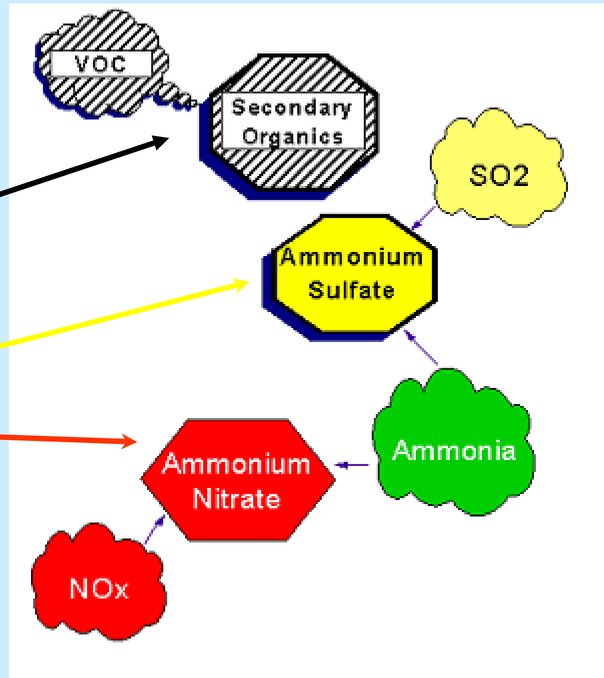


Primary and Secondary Aerosol

- ***Primary aerosol***: Directly emitted from sources as particles: crustal species, sea salts, carbonaceous.



- ***Secondary aerosol***: Formed in the atmosphere from directly emitted gases (condensation processes):
  - ***Secondary organic aerosol***: Many oxygenated and nitrated compounds;
  - ***Secondary inorganic aerosol***: Sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate.



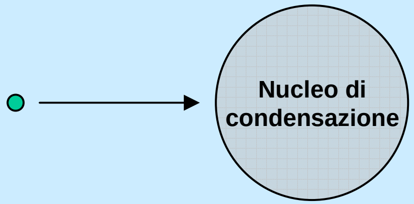
Processi chimico-fisici

gas condensabili

Nucleazione

formazione di particelle per agglomerazione di molecole di vapore supersature

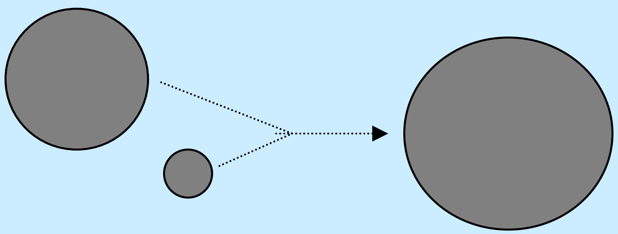
gas condensabili



Condensazione

- Diffusione di specie gassose verso la superficie delle particelle e successiva cattura;
- Dissoluzione;
- Equilibrio termodinamico tra le specie chimiche inorganiche ed organiche in fase gassosa, liquida e solida.

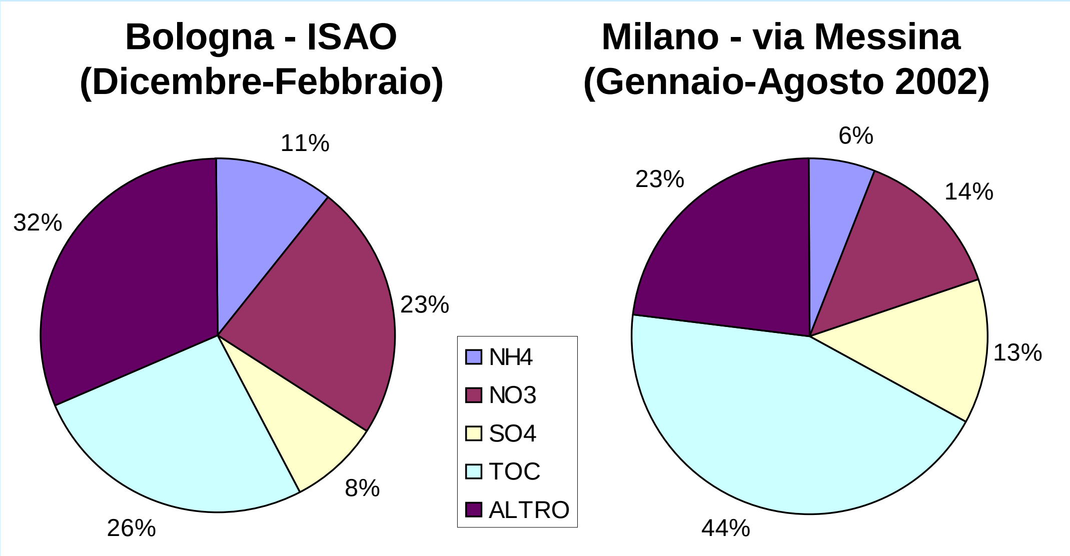
Particelle esistenti

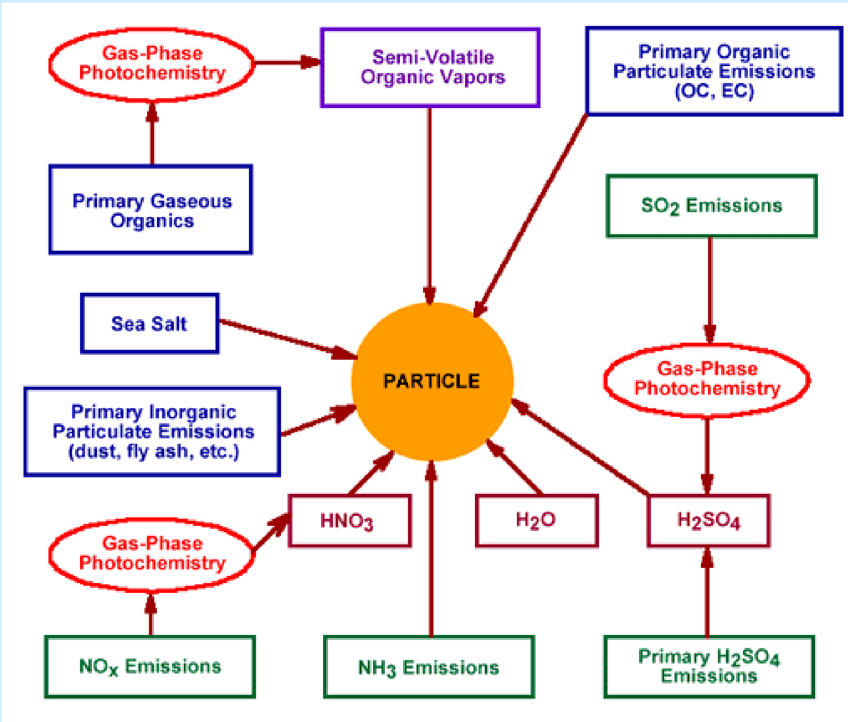


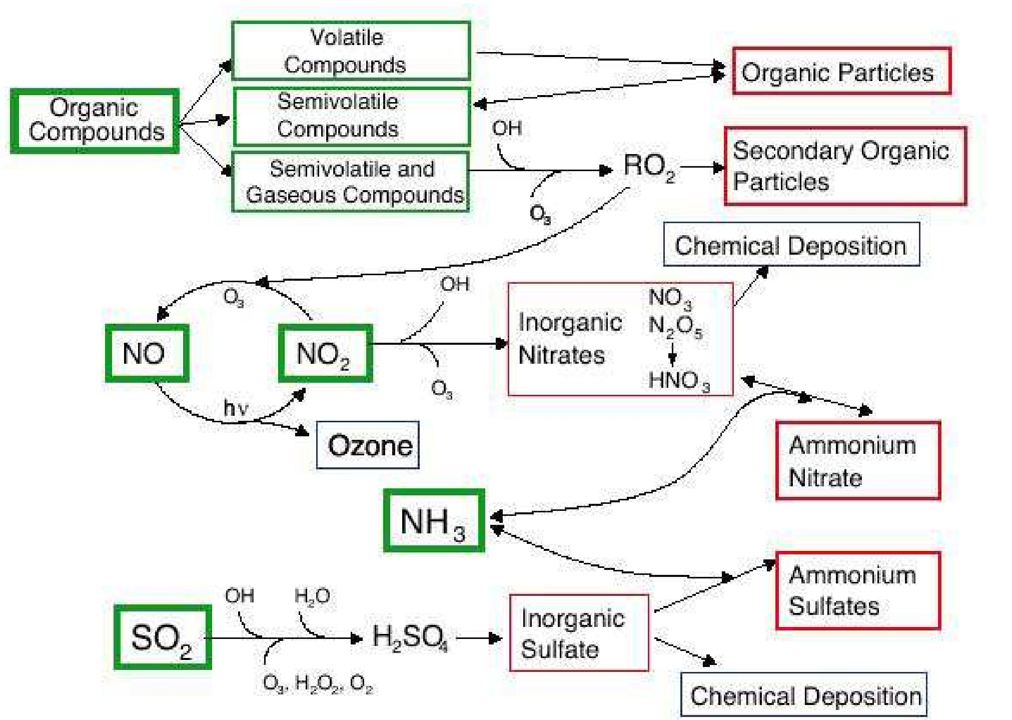
Coagulazione

collisione ed adesione di particelle: accrescimento

Atmospheric aerosol processes







FORMATION OF SECONDARY INORGANIC AEROSOLS

Ammonia reacts with sulfuric acid and nitric acid to form ammonium sulphate and ammonium nitrate. Ammonium sulphate formation is preferential under most conditions, though ammonium nitrate is favoured by low temperature and high humidity.

<table>
<tr><th>Sulphate</th><th>Nitrate</th></tr>
<tr><td>$SO_2 + OH \rightarrow HOSO_2$
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow$ sulphate aerosol

aqueous phase:
$SO_2 + H_2O_2 \rightarrow$ S(VI) sulphate aerosol
$SO_2 + O_3 \rightarrow$ S(VI) sulphate aerosol

solid
NH_3 (g) + H_2SO_4(g) $\leftrightarrow$ $(NH_4)_2SO_4$, NH_4HSO_4,…
aqueous solution
NH_4^+, HSO_4^-, $SO_4^=$</td><td>$NO_2 + OH = HNO_3 \rightarrow$ nitrate aerosol
$NO_2 + O_3 = NO_3 + O_2$
$NO_2 + NO_3 = N_2O_5 \rightarrow$ nitrate aerosol

low RH (RH<DRH):
NH_3 (g) + HNO_3 (g) $\leftrightarrow$ NH_4NO_3(s) ammonium nitrate aerosol (solid state)
high RH (RH<DRH):
NH_3 (g) + HNO_3 (g) $\leftrightarrow$ NH_4^+ + NO_3^- ammonium nitrate aerosol (aqueous state)</td></tr>
</table>

PM_{10} ioni inorganici

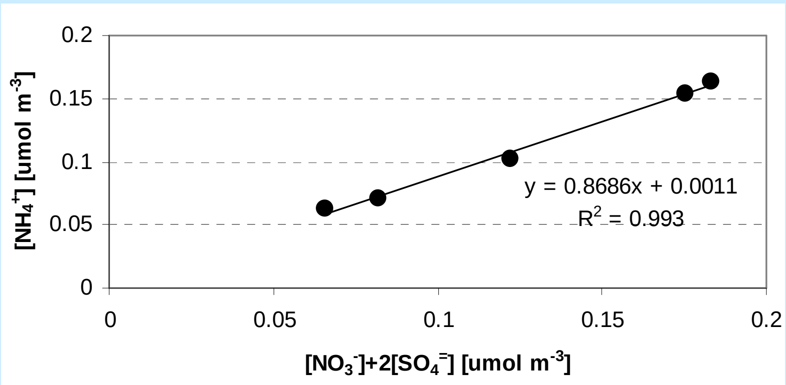
NO_3^- e $SO_4^=$ sono composti che risultano dalla decomposizione degli acidi corrispondenti (HNO_3 e H_2SO_4). NH_4^+ risulta invece dell'accezione di uno ione H^+ da un composto basico (NH_3).

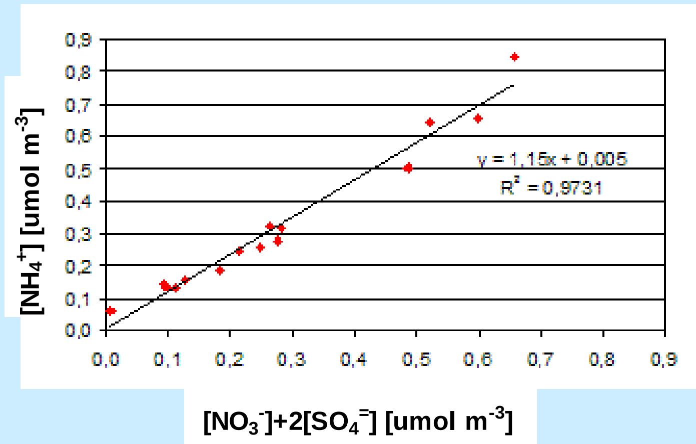
Per ogni equivalente di NO_3^- e $SO_4^=$ si hanno rispettivamente 1 e 2 equivalenti di H^+ nella fase liquida dell'aerosol.

Nelle figure è stata correlata la concentrazione di NO_3^- + $2SO_4^=$ in umol m^{-3} (ascissa), con la concentrazione di NH_4^+ in **μmol**/m3 (ordinata). Un coefficiente angolare della retta di regressione uguale all'unità indica completa neutralizzazione.

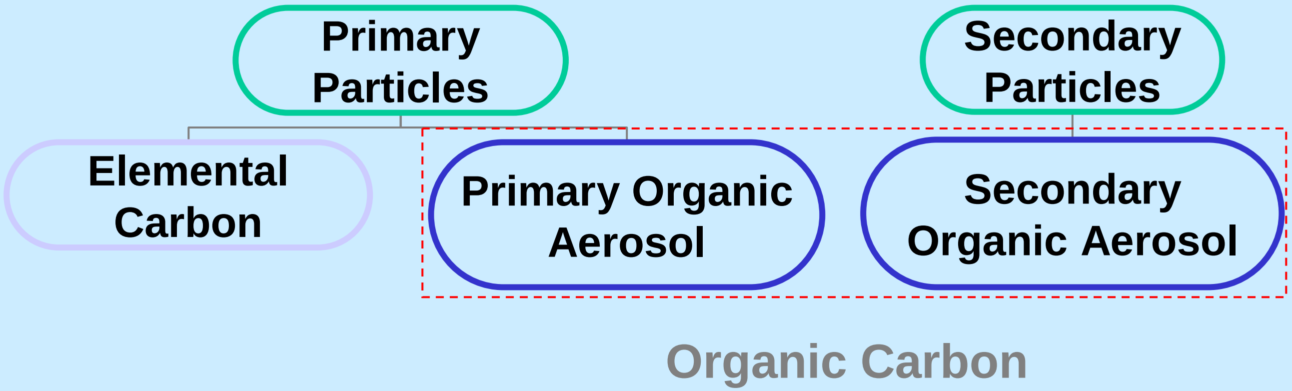
La riduzione di emissioni di NH_3 può determinare l'aumento dell'acidità dell'aerosol e delle deposizioni e della formazione di composti organici secondari

Montelibretti (giugno 2005)	**Milano** (marzo - giugno 2002)
Il coefficiente angolare (0.87) indica l'incompleta neutralizzazione di NO_3^- e $SO_4^=$ (condizioni acide).	Il coefficiente angolare (1.15) indica che le concentrazioni di NH_4^+ sono tali da neutralizzare completamente quelle di NO_3^- e $SO_4^=$. in tali condizioni l'ammonio osservato è presente come nitrati e solfati d'ammonio.





Organic Carbon (OC)
Definitions

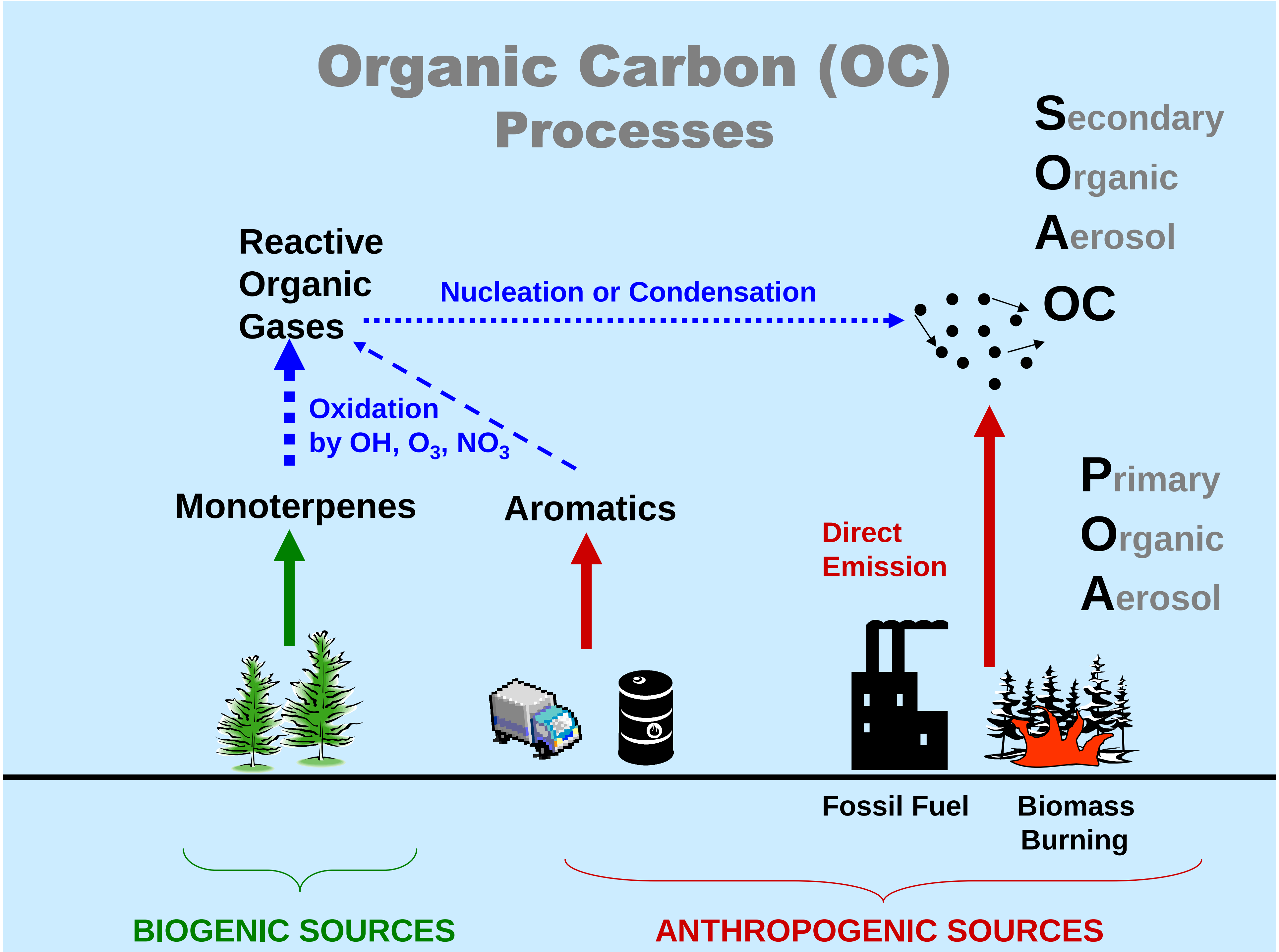


- Primary Particles
  - Elemental (Black) Carbon (EC-BC)
  - Primary Organic Aerosol (POA)
  - Primary Carbon = EC (BC) + POA
- Secondary Particles
  - Secondary Organic Aerosol (SOA) , formed in-situ by condensation of low-volatility products of the photo-oxidation of hydrocarbons
- Organic Carbon = POA + SOA

Organic Carbon (OC)

Organic aerosols are solid or liquid particles suspended in the atmosphere containing organic carbon (OC) .

- **Organic carbon is a substantial fraction (20% to 70%) of average $PM_{2.5}$ at urban and non-urban locations;**
- **OC derives from many sources, both natural and manmade, of ancient (fossil fuels >1M years old) and recent (<100 year) origin;**
- **OC derives from directly emitted particles (primary organic aerosol, POA), high molecular weight VOC that condense readily when emitted to ambient air (considered direct organic carbon particle) and semi-volatile organic compounds (SVOC). SVOC are distributed between gas and particle phases (partitioning/reversibly condensable gaseous) and their sources are:**
  - **Direct emissions (alkanes, PAHs, PCBs, PCDDs, nitro-aromatics, terpenes, acids, carbonyls, lipids, others);**
  - **Atmospheric reaction products (from VOC, SVOC), secondary organic aerosol (SOA);**


Organic Carbon (OC)
Processes
Secondary
Organic
Aerosol
OC
Reactive
Organic
Gases
Nucleation or Condensation
Oxidation
by OH, O_3, NO_3
Monoterpenes
Aromatics
Direct
Emission
Primary
Organic
Aerosol
Fossil Fuel
Biomass
Burning
BIOGENIC SOURCES
ANTHROPOGENIC SOURCES

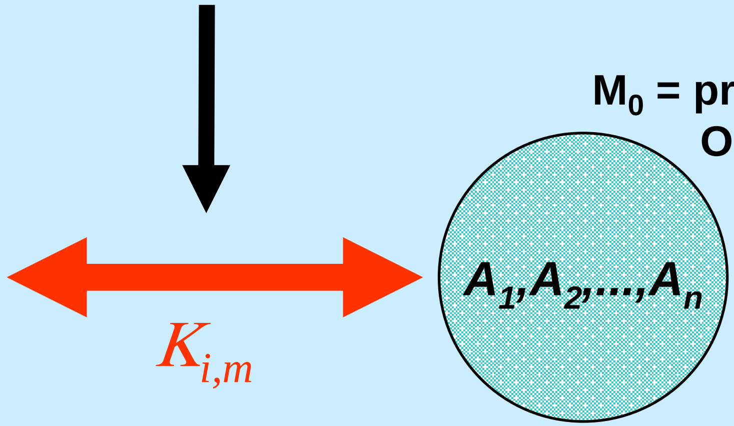
GAS/PARTICLE PARTITIONING

VOC + oxidant → P_1, P_2, …P_n

Oxidation by OH, O_3, NO_3

M_0 = pre-existing OC aerosol

G_1, G_2, …G_n



Gas-Phase

$$\frac{d[\mathrm{G}]_i}{dt} = -\sum_m k_{i,m}\left([\mathrm{G}]_i - [\mathrm{G}]^*_{i,m}\right)$$

Aerosol-Phase

$$\frac{d[\mathrm{A}]_{i,m}}{dt} = k_{i,m}\left([\mathrm{G}]_i - [\mathrm{G}]^*_{i,m}\right)$$

P_1, P_2, …P_n: SVOC (condensible organic compounds)
A_1, A_2, …A_n: particulate-phase associated adsorbed/absorbed SVOC
G_1, G_2, …G_n: gas-phase associated SVOC

GAS/PARTICLE PARTITIONING

ADSORPTION
dominate when
TSP is mainly of
mineral origin

ABSORPTION
dominate when
TSP contains
organic material

The gas-particle partitioning coefficient K_P $[m^3\ \mu g^{-1}]$ is defined as follows:

$$\boldsymbol{K_P = C_P / (C_G \cdot \mathrm{TSP})}$$

where *TSP* is the concentration of suspended particulate material [$\mu g\ m^{-3}$], C_P and C_G respectively the particulate-associated and gaseous concentration of a given adsorbed/absorbed SVOC [$ng\ m^{-3}$].

Strategie di controllo del $PM_{2.5}$

- La riduzione di emissioni di **NH_3** può determinare l'aumento dell'acidità dell'aerosol e delle deposizioni e della formazione di composti organici secondari;
- La riduzione delle emissioni di **NOx**:
  - può determinare una riduzione dei processi di ossidazione maggiore disponibilità di radicali (in particolare OH) e conseguentemente della formazione di solfati e SOA;
  - è più efficace ai fini della riduzione dei livelli di $PM_{2.5}$ durante il periodo invernale (nitrato d'ammonio)
- La riduzione di emissioni di **SO_2** determina la riduzione dei livelli di $PM_{2.5}$ (e può causare un aumento dei livelli di nitrato). Potrebbe essere più efficace, ai fini della riduzione dei livelli di $PM_{2.5}$, durante il periodo estivo (formazione di H_2SO_4);
- La riduzione di emissioni **VOC** può determinare una significativa riduzione dei livelli di $PM_{2.5}$. Si stima che i composti aromatici - toluene, xylene e trimethyl-benzene possano esser responsabili per circa il 50-70% dei SOA. Potrebbe essere più efficace, ai fini della riduzione dei livelli di $PM_{2.5}$, durante il periodo estivo (formazione fotochimica di SOA e elevate emissioni biogeniche).

Il modello FARM

The FARM model

(Flexible Air quality Regional Model)

Eulerian grid model for dispersion, transformation and deposition of **reactive pollutants** (photochemistry and aerosols)

Derived from **STEM**

prof. G.R. Carmichael *et al.*,
CGRER (Center for Global and Regional Environmental Research),
University of Iowa

a long history…

STEM

80's

Comprehensive regional model

Regional applications
(Asia, N & Latin America, Europe…)

Chemical mechanisms

90's

Numerical aspects

Aersols
Biomass burnings

Regional vs. global chemistry

00's

Chemical forecast

Data assimilation

. . . . .

FARM

Regional & urban

Episodic & long-term
(AQ assessment, scenarios, …)

System integration

Multi-domain

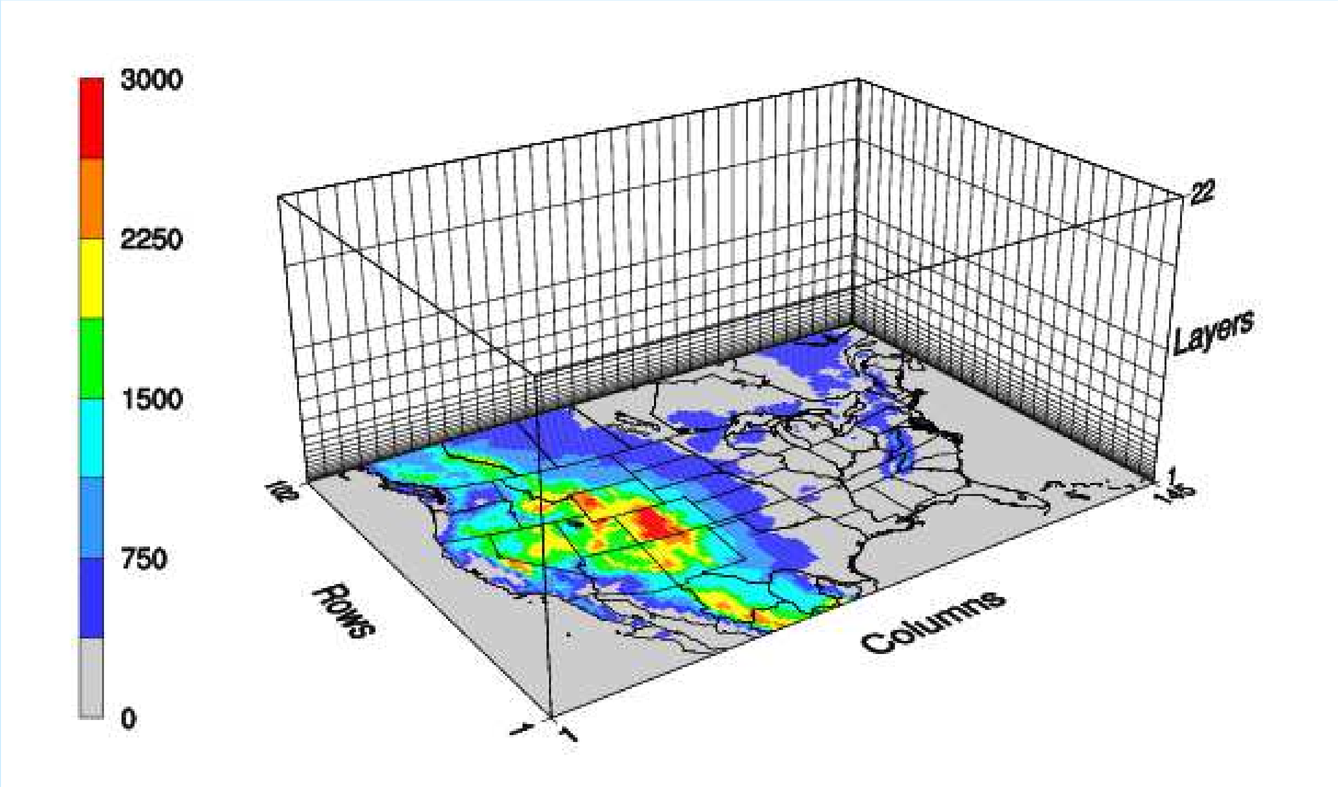
Forecast systems

Data assimilation

. . . . .

FARM (Flexible Air quality Regional Model)

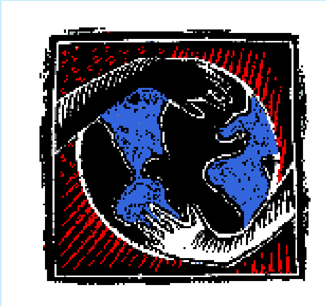
Eulerian grid model for dispersion, transformation and deposition of reactive pollutants



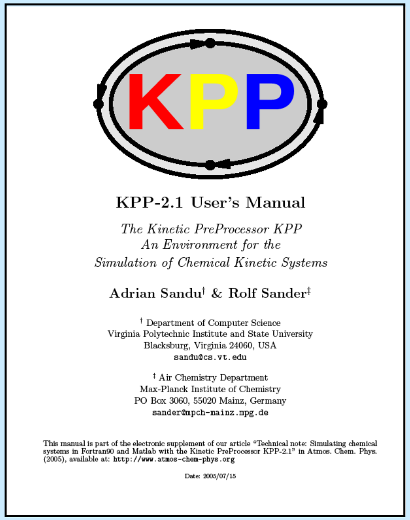
FARM model, information are provided at following sites:
Cost Model Inventory: http://www.mi.uni-hamburg.de/index.php?id=539
MDS - Model Documentation System: http://pandora.meng.auth.gr/mds/mds.php.

FARM (Flexible Air quality Regional Model)

Eulerian grid model for dispersion, transformation and deposition of reactive pollutants



- Derived from **STEM-II**, Prof. G.R. Carmichael et al., CGRER (Center for Global and Regional Environmental Research), University of Iowa



KPP

KPP-2.1 User's Manual

The Kinetic PreProcessor KPP
An Environment for the
Simulation of Chemical Kinetic Systems

Adrian Sandu† & Rolf Sander‡

† Department of Computer Science
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24060, USA
sandu@cs.vt.edu

‡ Air Chemistry Department
Max-Planck Institute of Chemistry
PO Box 3060, 55020 Mainz, Germany
sander@mpch-mainz.mpg.de

This manual is part of the electronic supplement of our article "Technical note: Simulating chemical systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1" in Atmos. Chem. Phys. (2005), available at: http://www.atmos-chem-phys.org

Date: 2005/07/15

- **SAPRC99** gas phase chemical mechanism implemented using KPP (Kinetic PreProcessor, Sandu and Sanders, 2005). **Rosenbrock** (ROS3) and **LSODE** solvers used for the integration of stiff equations. A mechanism for the treatment of **POPs** Has been implemented

- **aero3** (CMAQ) aerosol module:
  - Lognormal size distributions: ***Aitken mode*** (0.01 -0.1 µm); ***Accumulation mode*** (0.1-2.5 µm) and **Coarse mode** (2.5-10 µm);
  - Aerosol processes: Nucleation; Coagulation; ISORROPIA equilibrium model (SIA); SOA treatment.

<u>F</u>lexible <u>A</u>ir quality <u>R</u>egional <u>M</u>odel (FARM)

http://air-climate.eionet.europa.eu/databases/MDS/

Main features and developments:

- ✓ **Emission** of pollutants from area and point sources, with plume rise calculation and mass assignment to vertical grid cells
- ✓ **3D dispersion** by advection and turbulent diffusion
- ✓ Transformation of chemical species by **gas-phase chemistry**, with flexible mechanism configuration (SAPRC-99, **POPs-Hg**) through KPP pre-processor (KPP, Kinetic Pre-Processor: Damian et al, 2002; Sandu et al., 2003; Daescu et al. 200).
- ✓ Treatment of $\mathbf{PM_{10}}$ and $PM_{2.5}$ (*aero0* inorganic equilibrium module, *aero3* modal aerosol module)
- ✓ **Dry removal** of pollutants dependent on local meteorology and land-use
- ✓ Removal through **precipitation scavenging** processes
- ✓ One- and two-way **nesting** on arbitrary number of grids
- ✓ Treatment of additional inert **tracers**
- ✓ **Parallel processing** using **OpenMP** paradigm
- ✓ Inclusion of **data assimilation** techniques
- ✓ Online calculation of photolysis rates using **TUV** model (Tropospheric Ultraviolet and Visible radiation model; Madronich *et al*, 1989)
- ✓ Inclusion of **map factors** and **different coordinate systems**
- ✓ **SW management and code optimization**
- **MPI parallelization** (under work)

Modelling atmospheric composition

Mass balance equation for chemical species (up to 150 in state-of-the-art Chemical Transport Models)

$$\frac{\partial c_i}{\partial t} + \mathbf{V}_h . \nabla_h c_i + \frac{\partial}{\partial z} w_c c_i - \frac{\partial}{\partial z} K_Z \frac{\partial c_i}{\partial z} = E + R - D$$

Transport

Source and Sinks

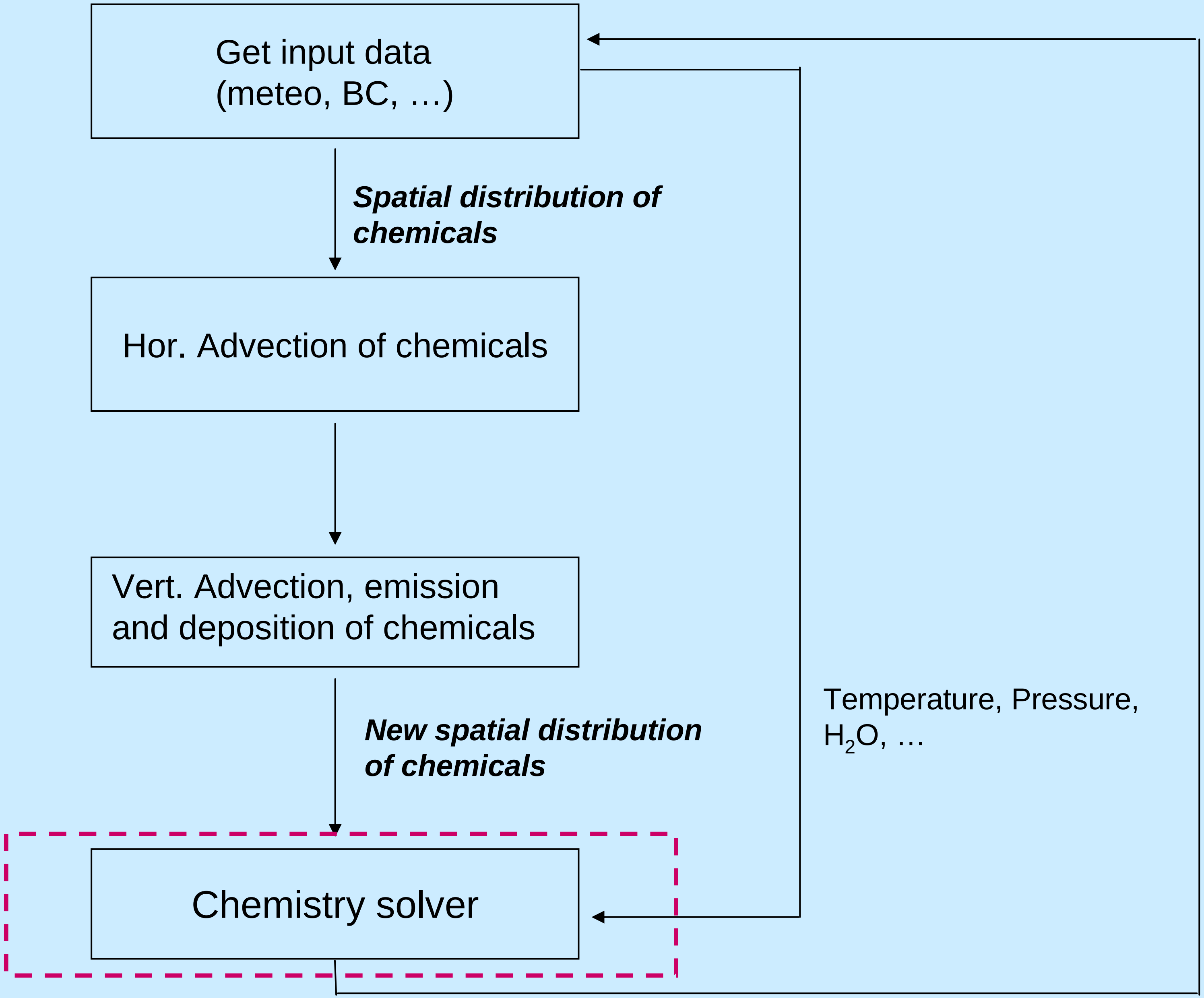
c_i concentration of species i

$E_i \neq f(c_i)$ ... Emission

$R_i = f(c_i, c_j, c_k, c_{m,} ...)$ ... Chemical conversion

$D_i = l_{Dep} c_i$ ... Deposition

Photochemistry models



Chemical rates required in FARM

Chemical rates k = k (Temperature, Pressure)

…are stored as constants

as Arhenius function parameters

or as specific functions

Photolysis rates $J = \int q_\lambda \, \sigma_\lambda \, I_\lambda \, d\lambda$ **where** q_λ **= quantum yield**

σ_λ **= cross section**

I_λ **= actinic flux**

…are stored as 'look-up tables' of J (λ, I) or calculated using radiative models (e.g. TUV, …)

PM Treatment in FARM

- **Primary Components**
  - **AORPA (Primary organic aerosol)**
  - **AEC (Primary elemental carbon)**
  - **A25 (Unspeciated fine PM/dust)**
- **Secondary Components**
  - **ASO4 (Sulfate aerosol)**
  - **ANH4 (Ammonium aerosol)**
  - **ANO3 (Nitrate aerosol)**
  - **AORA,B (Secondary organic aerosol)**
- **Particle size distribution represented as the superposition of three lognormal subdistributions, called modes**
  - **Aitken mode (up to ~ 0.1 microns) (typically for fresh particles)**
  - **Accumulation mode (0.1 – 2.5 microns) (typically for aged particles)**
  - **Coarse mode (2.5 – 10 microns)**
  - **PM_{10} is the sum of all three modes**
  - **Predict particle number, total surface area, total mass for each mode**

Ref: Binkowski *et al*, JGR 2003

Continuous Distribution (Modal Approach)

Aitken Mode

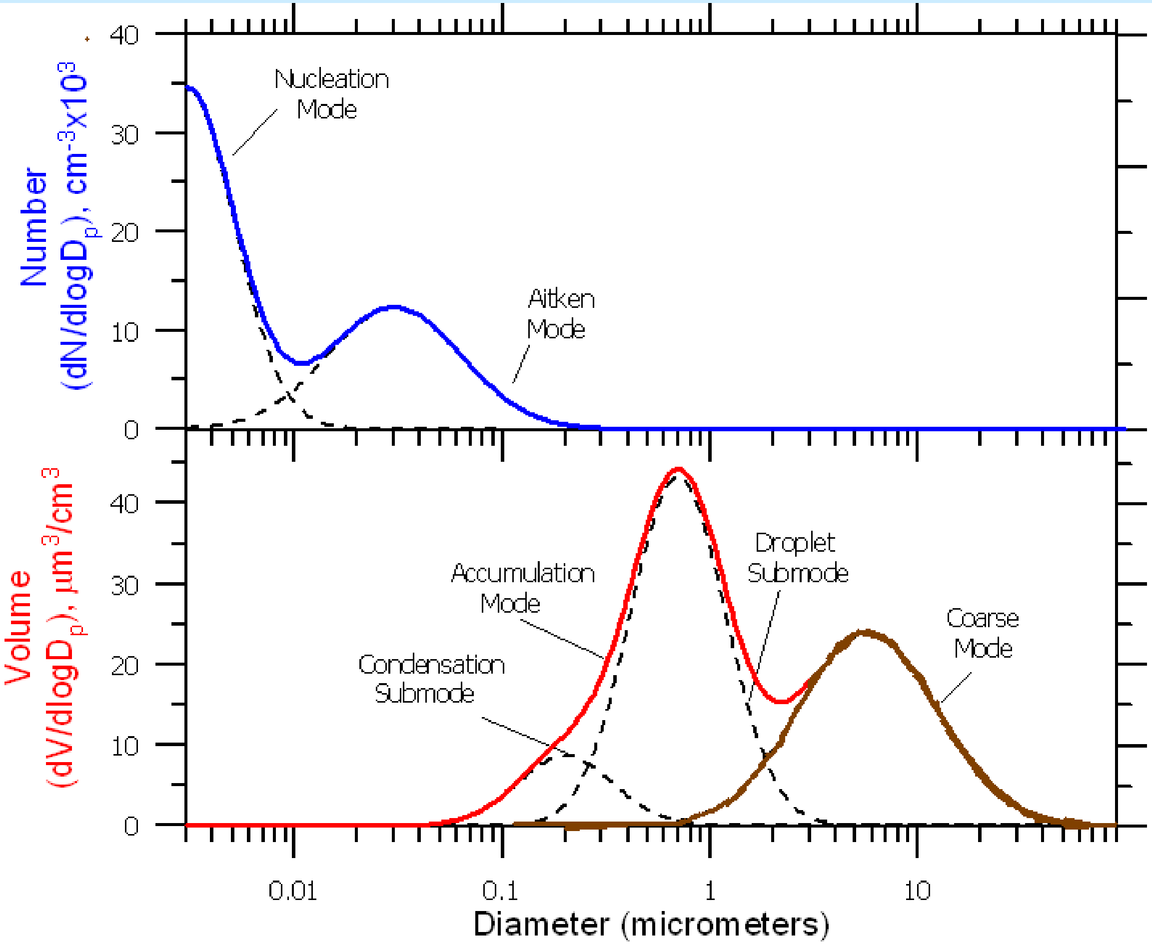
(0 - 0.1 µm)

Accumulation mode

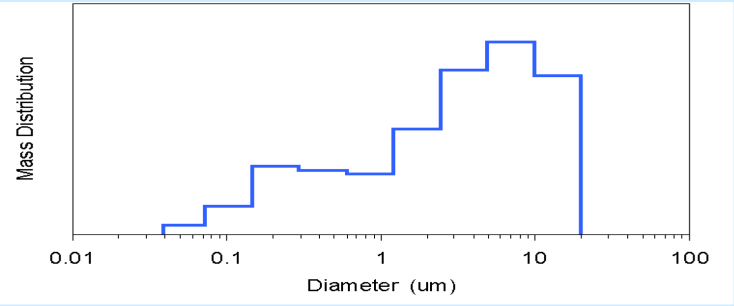
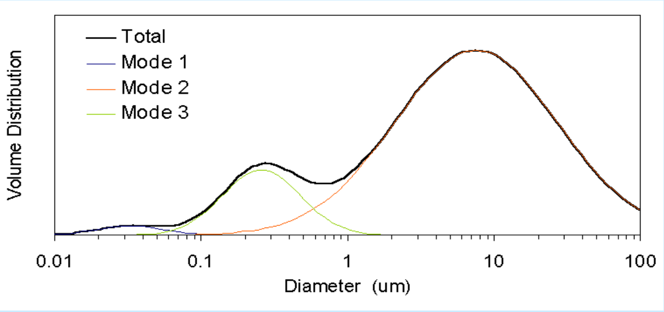
(0.1-2.5 µm)

Coarse mode

(2.5 – 10 µm)



Mathematical Representations of the Aerosol Size Distribution

Discrete Distribution (Sectional Approach)	Continuous Distribution (Modal Approach)
• uses discrete size bins • very expensive for good size resolution  	• uses moments of log normal distributions • CMAQ uses 3 modes: Aitken, Accumulation, Coarse modes. Three integral properties are included: particle number concentration, surface area concentration, mass concentration of the individual chemical components 

Aerosol chemistry in FARM

SIA - ISORROPIA

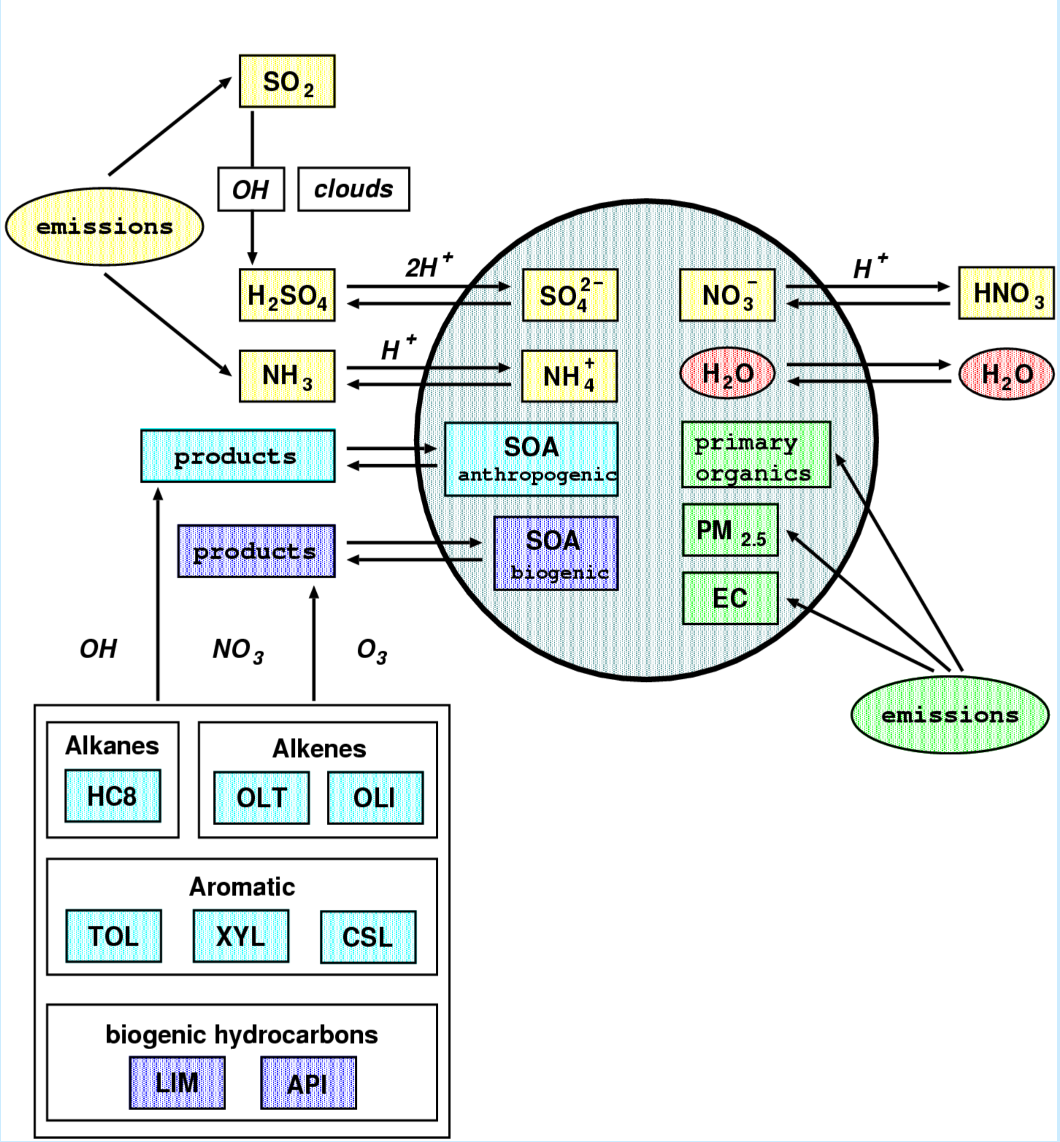
Ammonia-sulfate-nitrate-water-system

SOA - SORGAM

Secondary Organic Aerosol Module

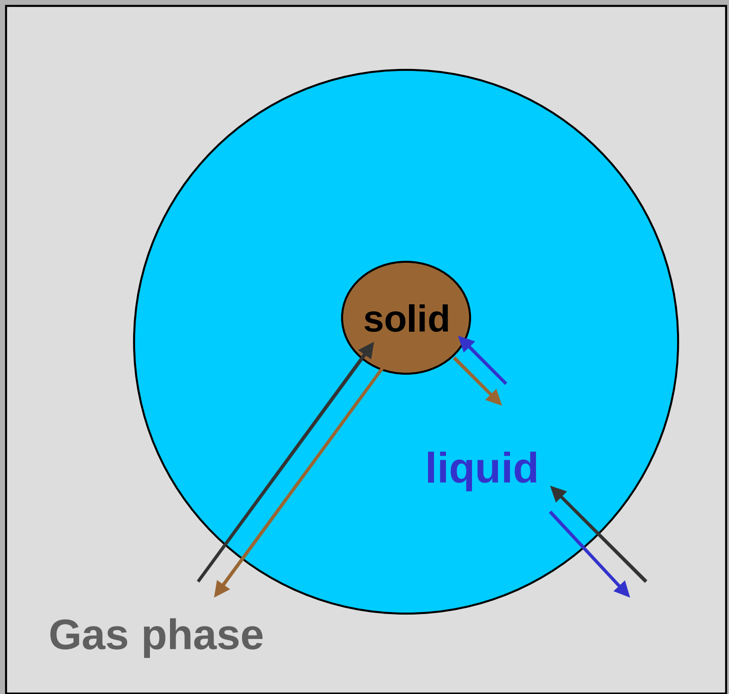
Photochemistry: ROG + (OH,NO3,O3)
Semivolatile condensable products
Gas/particle partitioning
Secondary organic aerosol

Binkowski, EPA, Models-3 CMAQ
Ackermann et al., 1998, Atmos. Envi.
Schell et al., 2001, J. Geophys. Res.
Nenes et al., 1998



The “ISORROPIA” model (Nenes *et al.*, 1998)

http://nenes.eas.gatech.edu/ISORROPIA



Solid phase:

$NaHSO_4$, NH_4HSO_4 , Na_2SO_4 , NaCl, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaNO_3$,

Liquid phase:

Na^+, NH_4^+, H^+, OH^-, HSO_4^-, SO_4^{2-}, NO_3^-, Cl^-, H_2O, $HNO_{3(aq)}$,$HCl_{(aq)}$, $NH_{3(aq)}$,

Gas phase: HNO_3, HCl, NH_3, H_2O

The "ISORROPIA" model (Nenes *et al.*, 1998)

Some reactions…

$$HSO^-_{4(aq)} \xleftrightarrow{K_1} H^+_{(aq)} + SO^{2-}_{4(aq)}$$

$$NH_{3(g)} \xleftrightarrow{K_{21}} NH_{3(aq)}$$

$$NH_{3(aq)} + H_2O_{(aq)} \xleftrightarrow{K_{22}} NH^+_{4(aq)} + OH^-_{(aq)}$$

$$HCl_{(g)} \xleftrightarrow{K_3} H^+_{(aq)} + Cl^-_{(aq)}$$

$$HNO_{3(g)} \xleftrightarrow{K_4} H^+_{(aq)} + NO^-_{3(aq)}$$

$$Na_2SO_{4(s)} \xleftrightarrow{K_5} 2Na^+_{(aq)} + SO^{2-}_{4(aq)}$$

$$NH_4Cl_{(s)} \xleftrightarrow{K_6} NH_{3(g)} + HCl_{(g)}$$

$$(NH_4)_2SO_{4(s)} \xleftrightarrow{K_7} 2NH^+_{4(aq)} + SO^{2-}_{4(aq)}$$

$$NaHSO_{4(s)} \xleftrightarrow{K_{11}} Na^+_{(aq)} + HSO^-_{4(aq)}$$

$$NH_4HSO_{4(s)} \xleftrightarrow{K_{12}} NH^+_{4(aq)} + HSO^-_{4(aq)}$$

$$(NH_4)_3H(SO_4)_{2(s)} \xleftrightarrow{K_{13}} 3NH^+_{4(aq)} + HSO^-_{4(aq)} + SO^{2-}_{4(aq)}$$

$$H_2O_{(aq)} \xleftrightarrow{K_w} H^+_{(aq)} + OH^-_{(aq)}$$

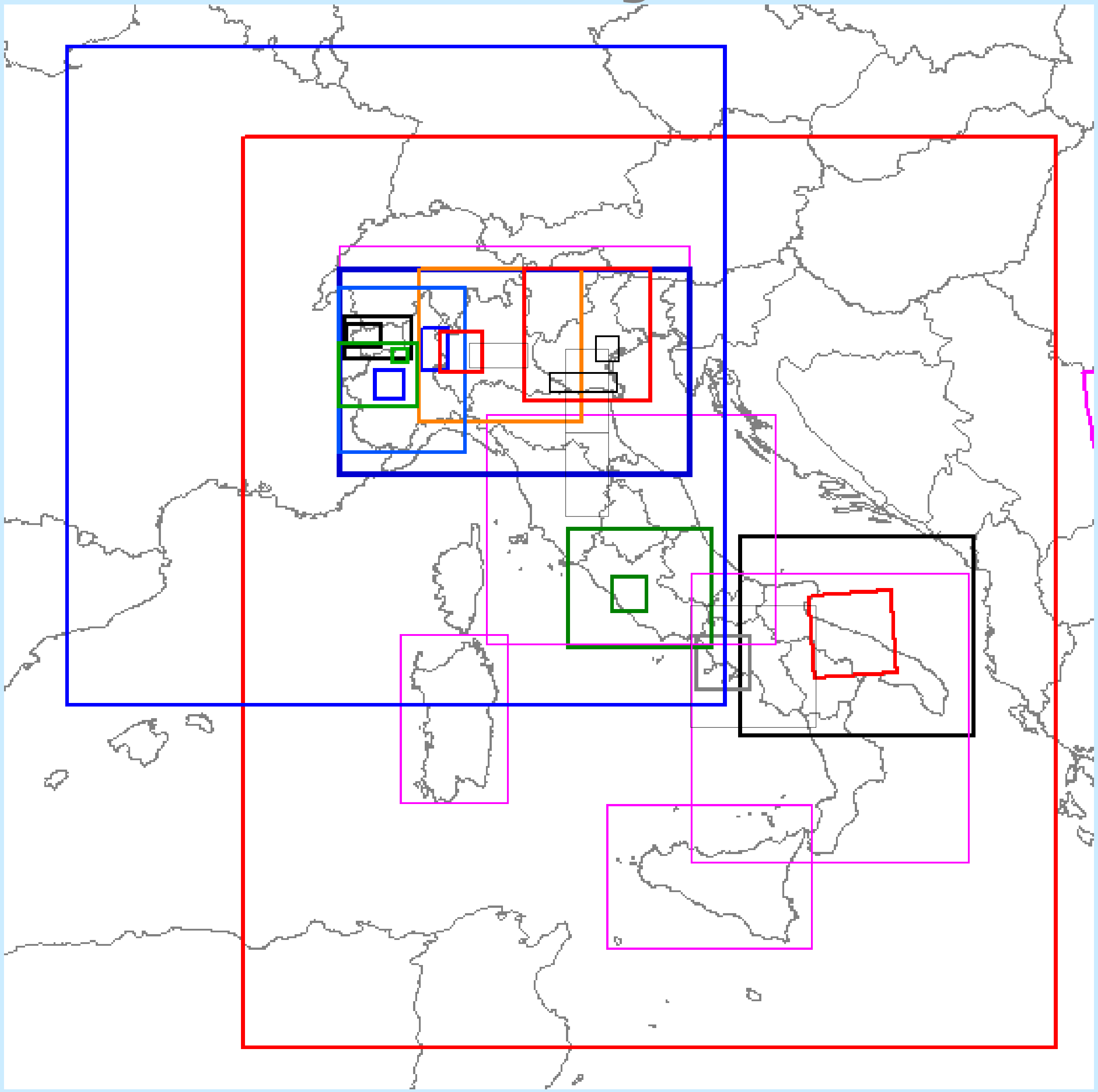
$$NaCl_{(s)} \xleftrightarrow{K_8} Na^+_{(aq)} + Cl^-_{(aq)}$$

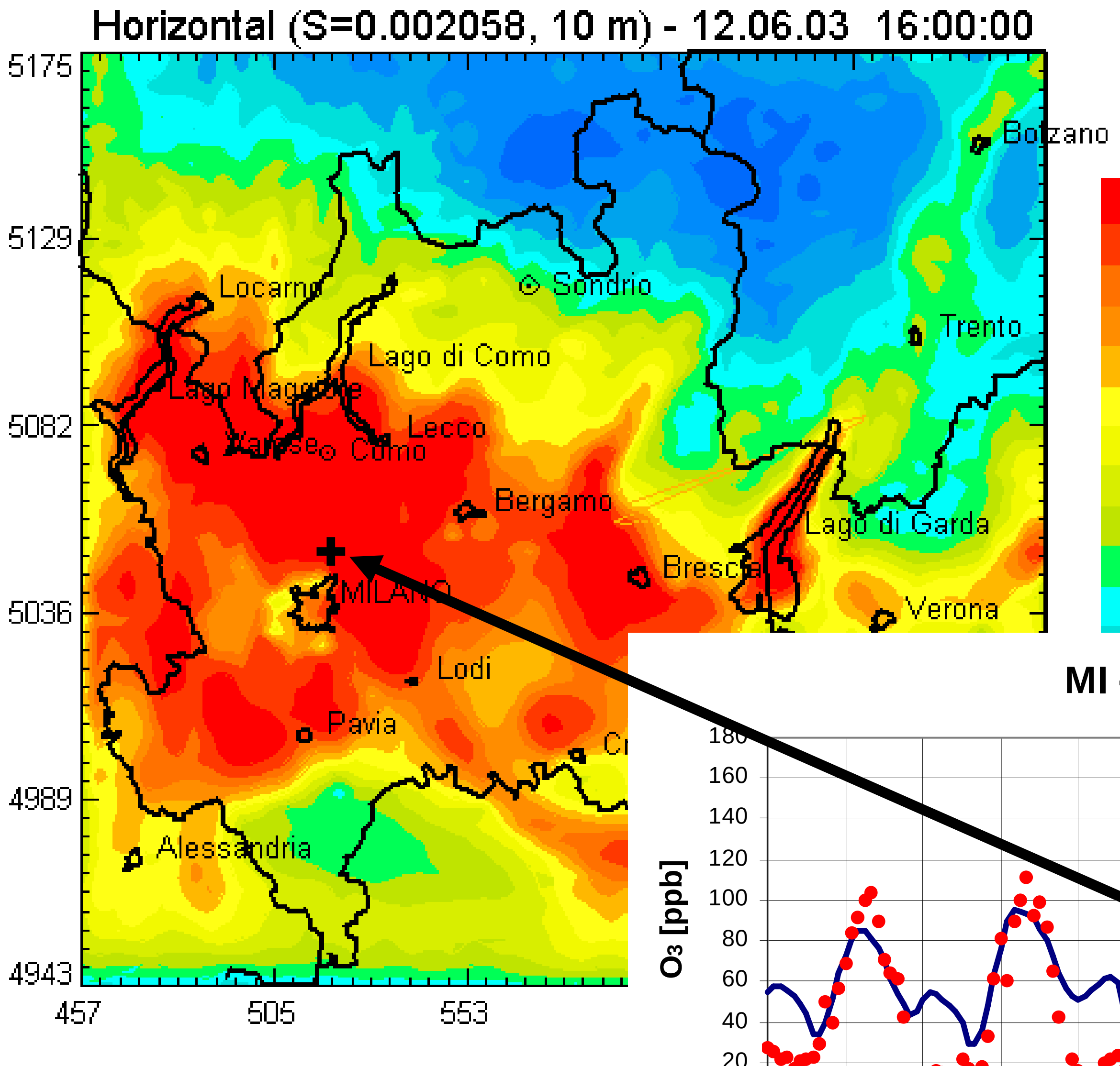
$$NaNO_{3(s)} \xleftrightarrow{K_9} Na^+_{(aq)} + NO^-_{3(aq)}$$

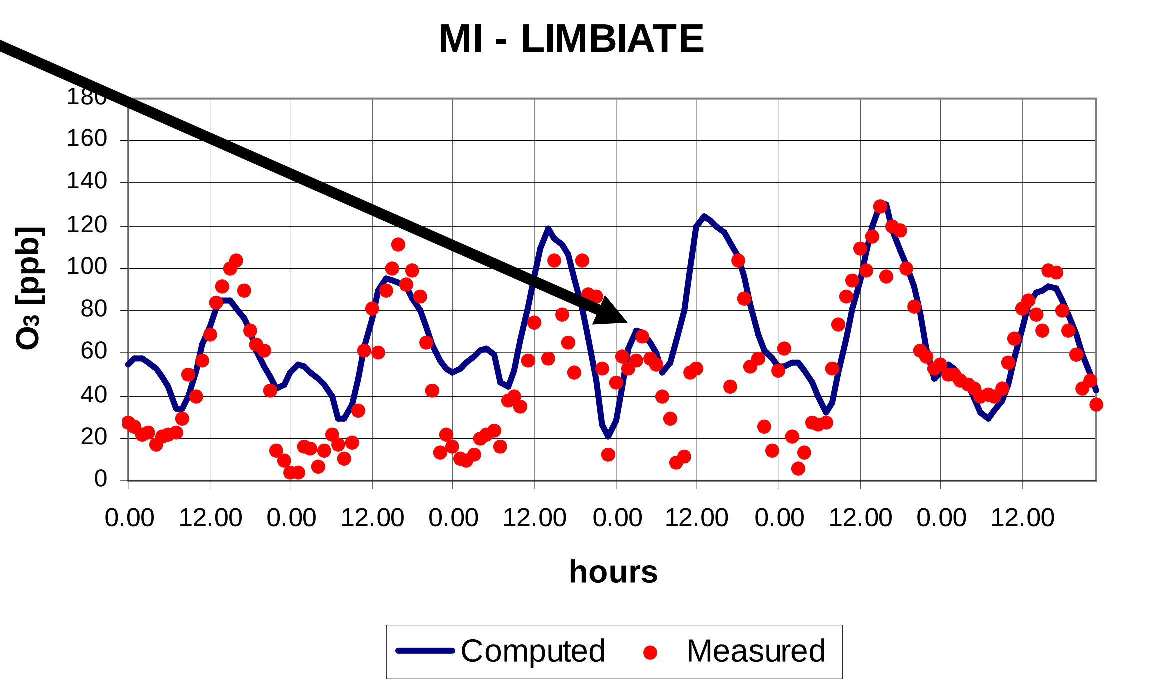
$$NH_4NO_{3(s)} \xleftrightarrow{K_{10}} NH_{3(g)} + HNO_{3(g)}$$

Esempi di utilizzo di FARM

Where FARM has it been applied in Italy ?







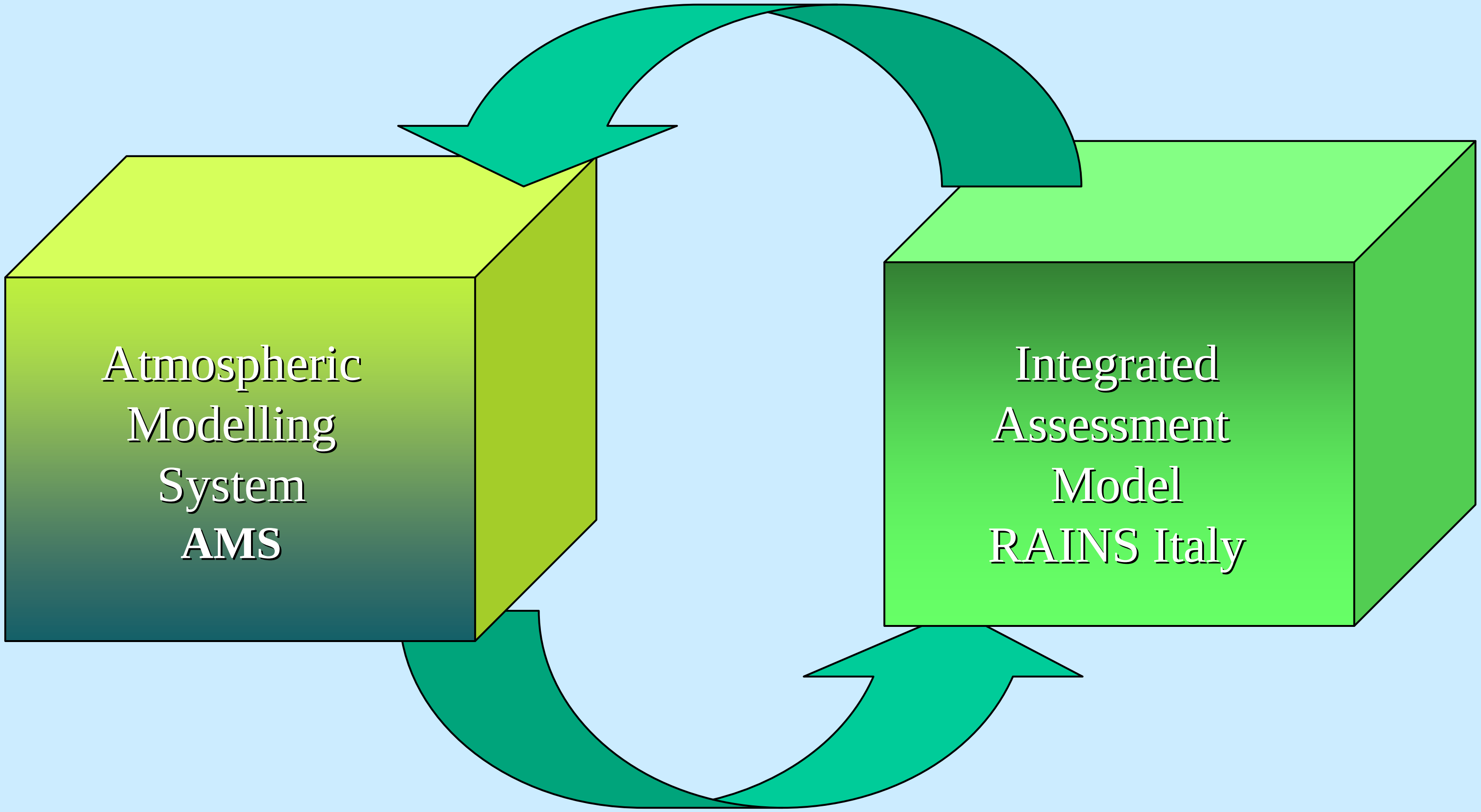
O_3 "nocturnal peak"

The MINNI Project
Summary Info

- A 3 year project for the development of a National Integrated Modelling System (closing in mid 2006);
- Financed by ENEA and the Italian Ministry for the Environment (total investment 1,268 million euros);
- Carried out under the leadership of ENEA in cooperation with ARIANET and IIASA.

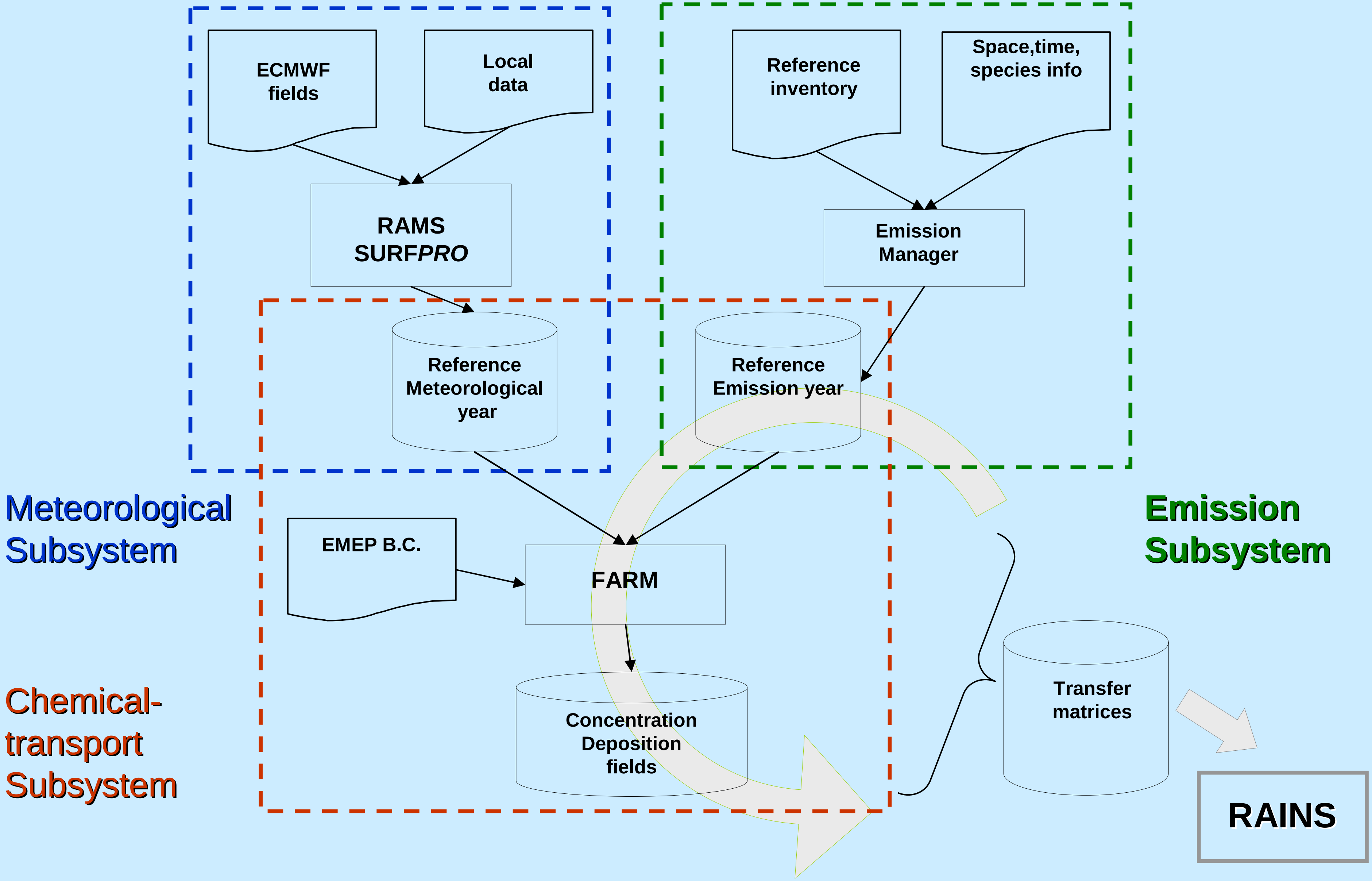
The MINNI Project

Main components



The MINNI Project

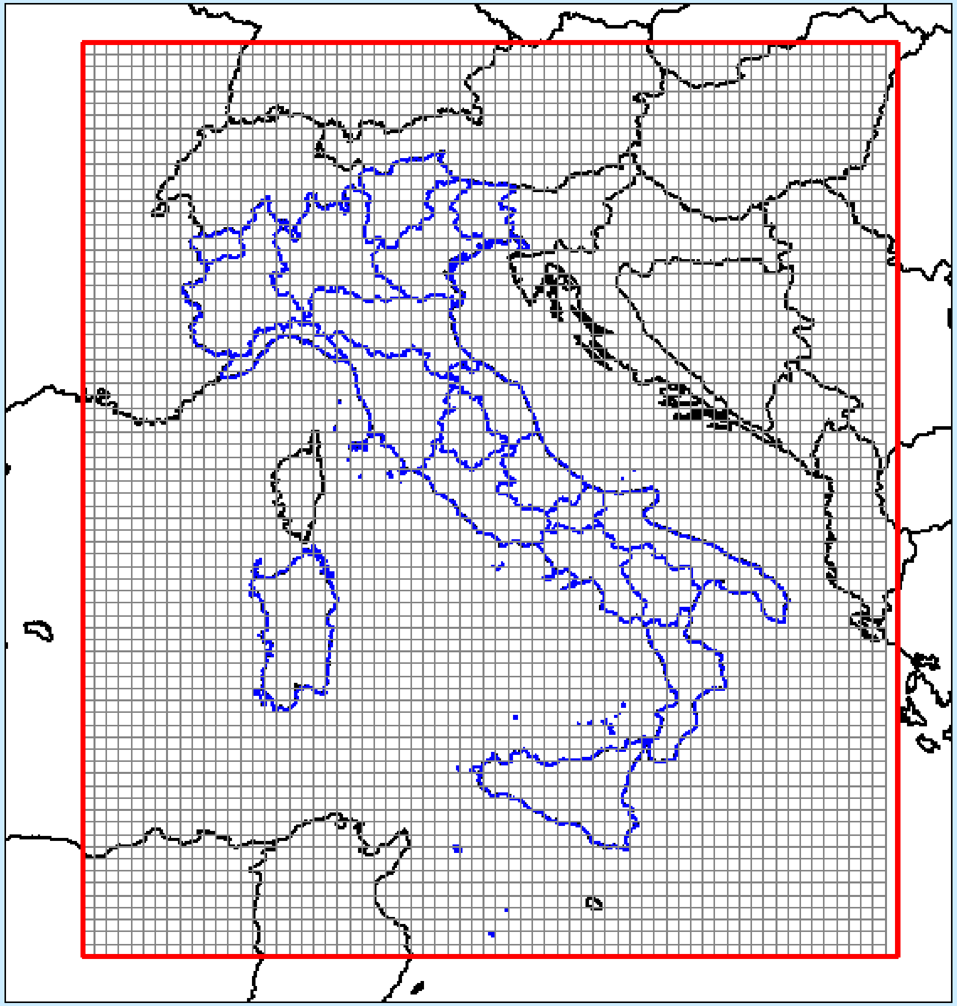
Atmospheric modelling system



MINNI domains

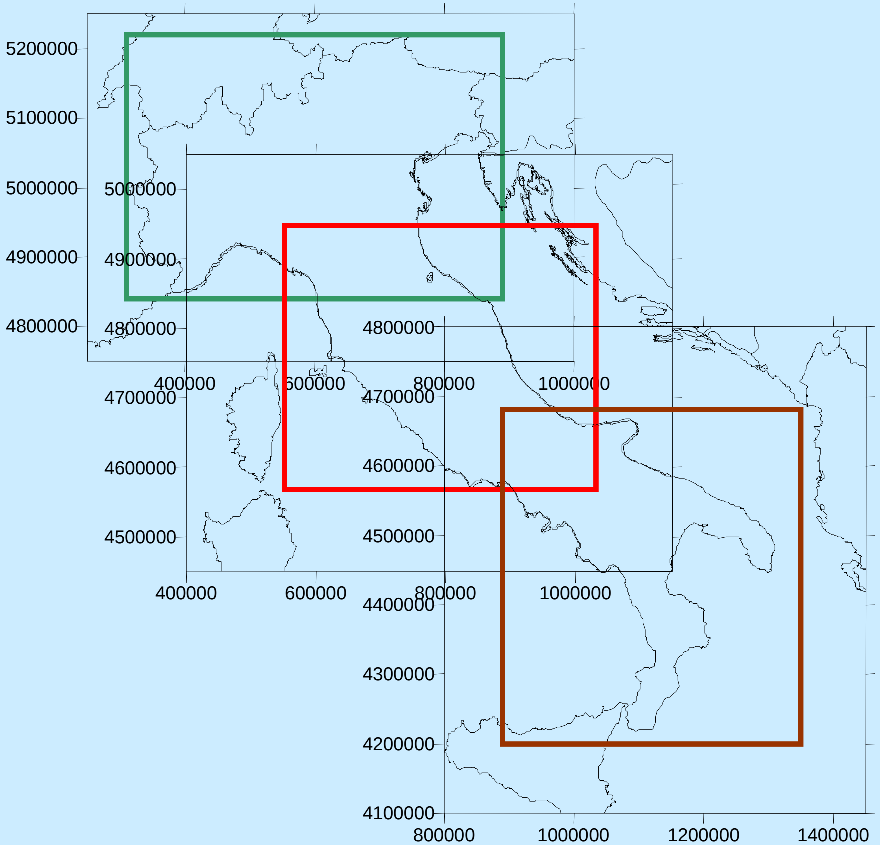
- 1 domains - Italy - (20 km horizontal resolution)
- 5 subdomains - Macro-regions - (4 km horizontal resolution);

National domain



Grid square cells
20 x 20 km^2

Macro-region domains

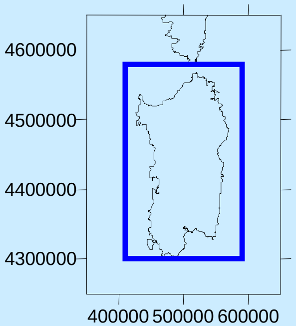


Northern Italy (NI0)

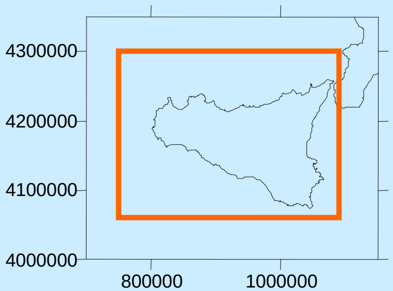
Central Italy (CI0)

Southern Italy (SI0)

Sardinia (SA0)



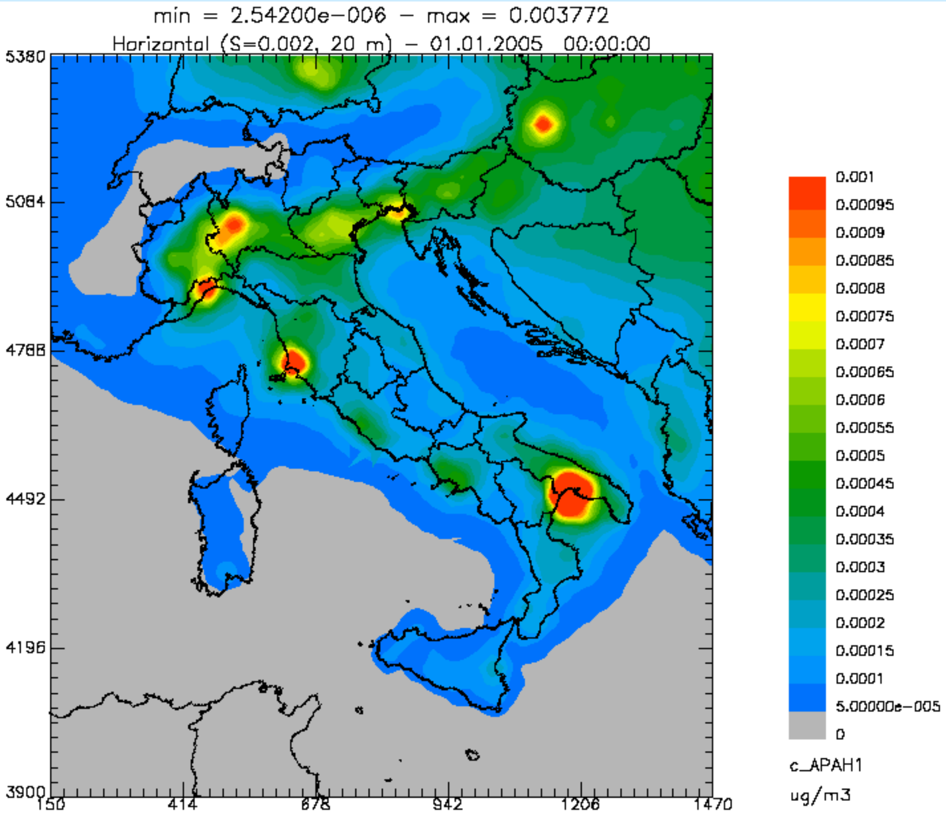
Sicily (SC0)



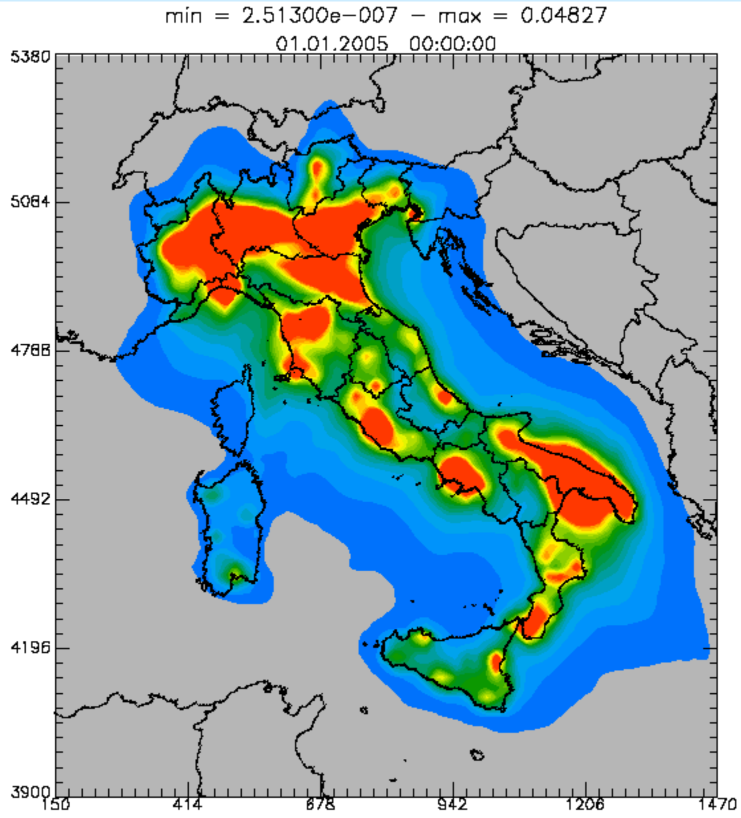
B[a]P

Spatial distribution of annual mean concentrations

EMEP



MINNI



Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation

THEME FP7-ENV-2007.1.1.2.1: *Megacities and regional hot-spots air quality and climate*
Collaborative Project (medium-scale focused research project)
Grant agreement no.: 212520

The research leading to these results has received funding from the European Union's Seventh Framework Programme FP/2007-2011 within the project MEGAPOLI, grant agreement n°212520

COMPARISON OF COMPUTED AND MEASURED AEROSOL OPTICAL DEPTH (AOD) OVER EUROPE FOR A YEAR LONG CHEMICAL TRANSPORT MODEL SIMULATION

C. Silibello, A D'Allura, S. Finardi, P. Radice

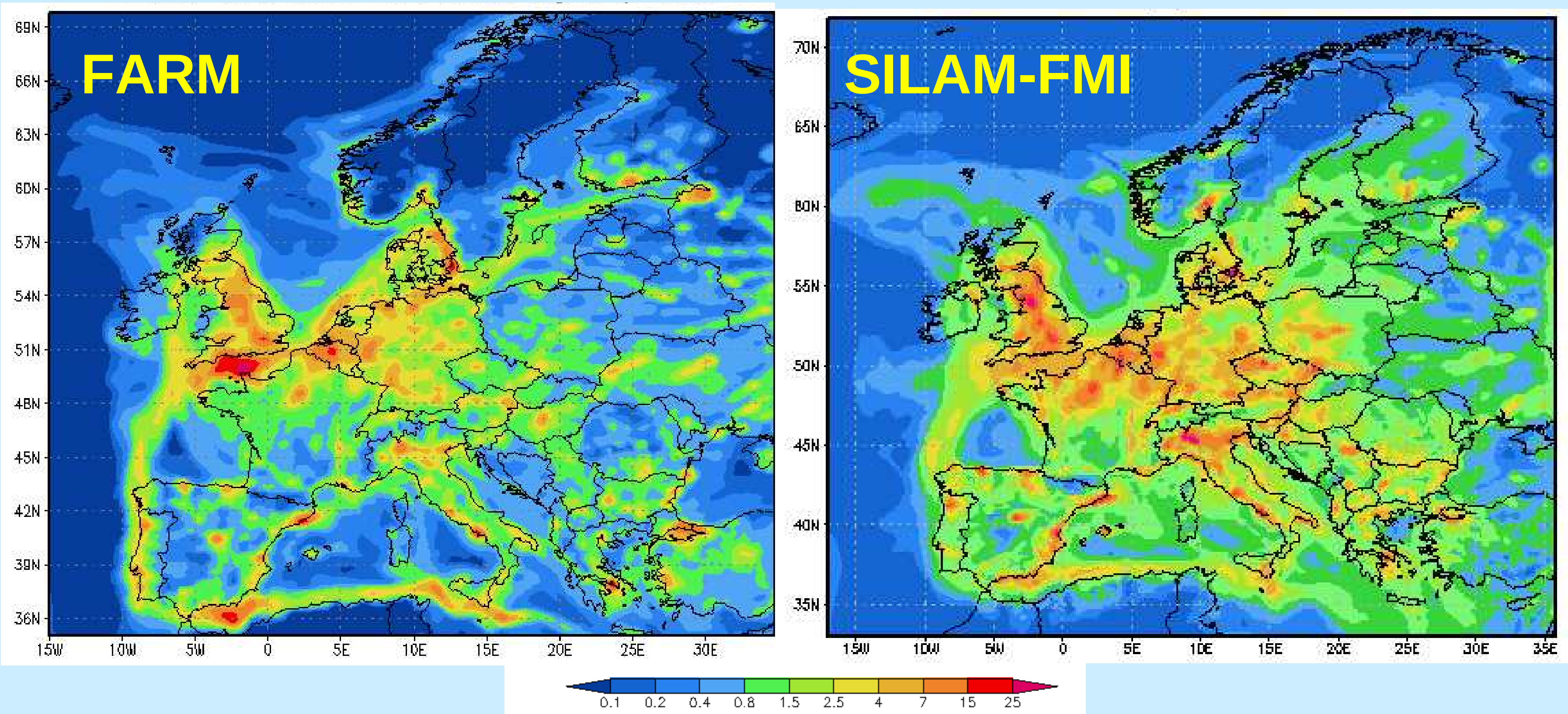
ARIANET

14th International Conference on Harmonisation within Atmospheric Dispersion Modelling for Regulatory Purposes
Kos Island, Greece, 2-6 October 2011

MEGAPOLI

Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation

FARM (Flexible Air quality Model) participated to MEGAPOLI regional multi-model ensemble (CHIMERE, CMAQ, FARM, SILAM-FMI, LOTOS-EUROS) and intercomparison of model results. Benchmark test case: full year 2005.



1.7.2009, NO_2 near-surface concentrations from FARM and SILAM-FMI

FARM runs CONFIGURATION

Spatial resolution:

- 25 km (horizontal); 16 levels, up to 10 km (vertical)

Emissions:

- **Anthropogenic:** TNO data set (~ 7 km resolution);
- **Biogenic/natural:**
  - Isoprene and Terpenes from vegetation (Guenther *et al.*, 1993);
  - PM (fine and coarse) from Aeolian resuspension (Vautard *et al.*, 2005);
  - sea salts, wind influence (Zhang *et al.*, 2005).

Meteorology:

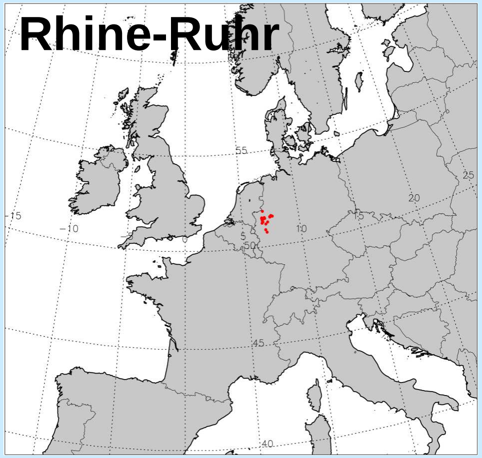
- **ECMWF** analysis;

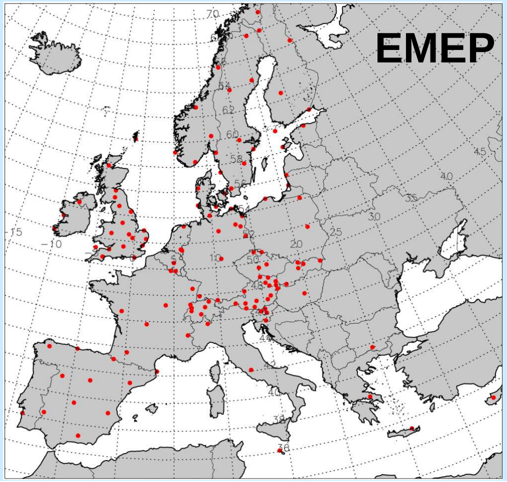
IC/BC:

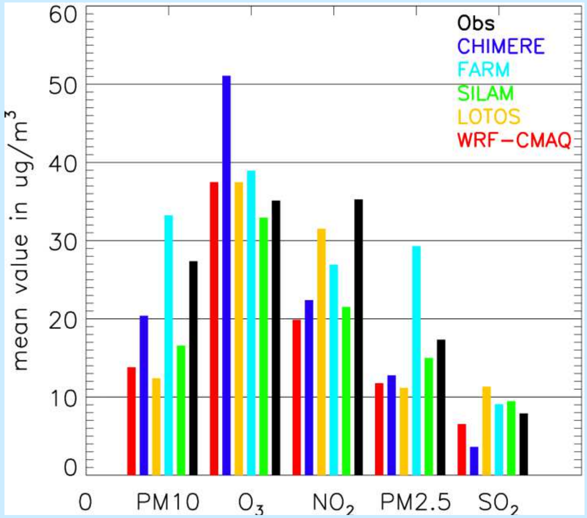
- **MPI MATCH – Global scale:** gaseous species
- **GOCART – Global scale:** aerosols, Climatological fields

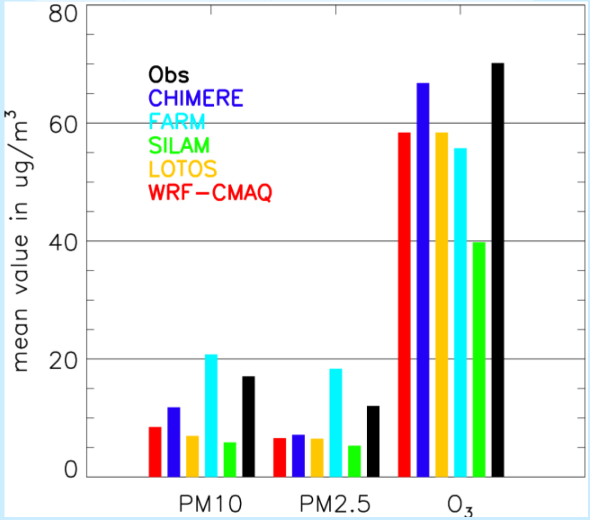
MEGAPOLI regional ensemble for year 2005

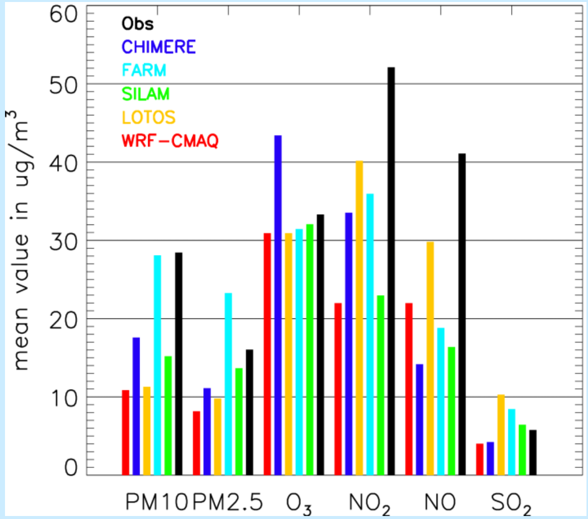
Operational evaluation: Annual means











Evaluation of concentration simulations for remote and two urban areas

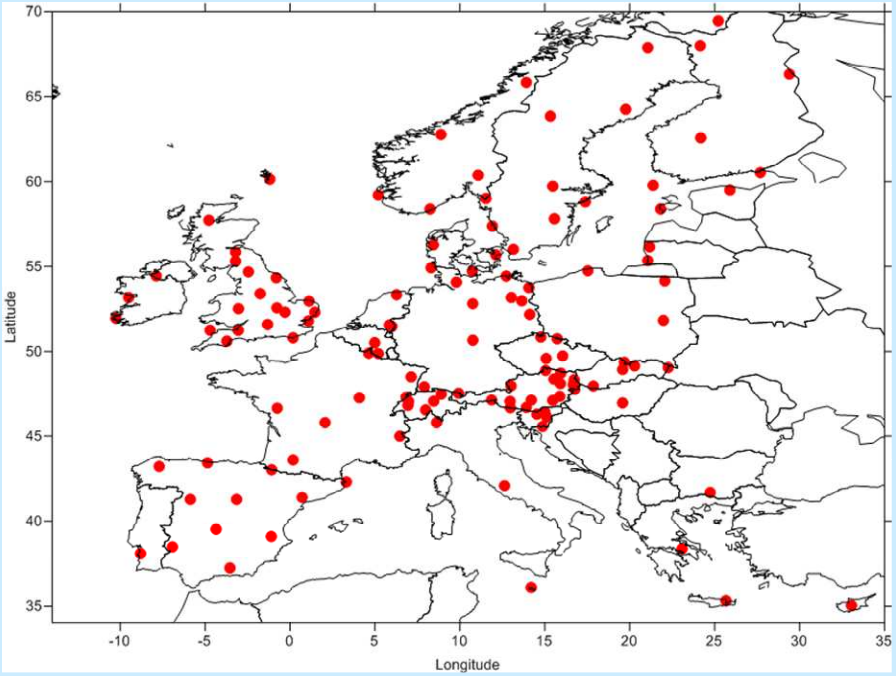
Michael Haller, *K. Heinke Schlünzen, G. Bedbur, K. Conrady, S. Finardi, S. Gimmerthal, D. Grawe, P. Hoffmann, M. Prank, V. Reinhardt, A. Segers, C. Silibello, G. Siour, M. Sofiev, R. Sokhi, M. Uphoff, J. Theloke, X. Vazhappilly-Francis*

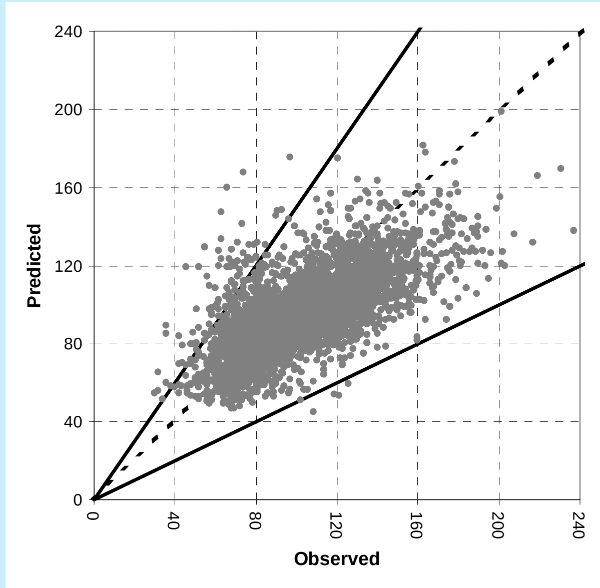
11 EMS, 12 – 16 September 2011, Berlin

FARM modelled concentrations agree with other models simulation results (higher PM concentrations) !

Ozone model performances
FARM vs EMEP stations

(http://tarantula.nilu.no/projects/ccc/emepdata.html)





Performance Metrics	Range	O_3		
		P.C.	G.	June
Correlation coefficient (R)	*-1 to 1*	0.65	0.78	0.70
Mean Fractional Bias (MFB)	*-200 to +200 %*	| 30 |	| 15 |	-1.64
Mean Fractional Error (MFE)	*0 to +200 %*	45	30	4.27
Fraction of prediction within a factor of 2 of observations (FAC2)	*0 to +100 %*	50	60	99.54

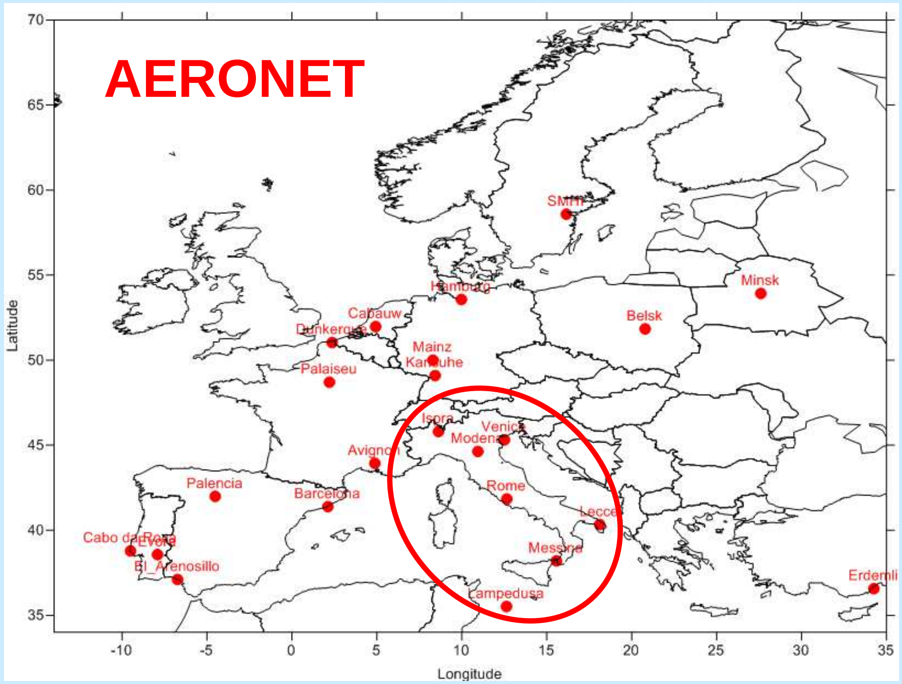
AOD analysis

The aerosol module ***aero3*** model does not include coarse mode particles in its visual range calculations. AOD (Aerosol Optical Depth), a dimensionless quantification of visibility impairment, is defined by the following equation:

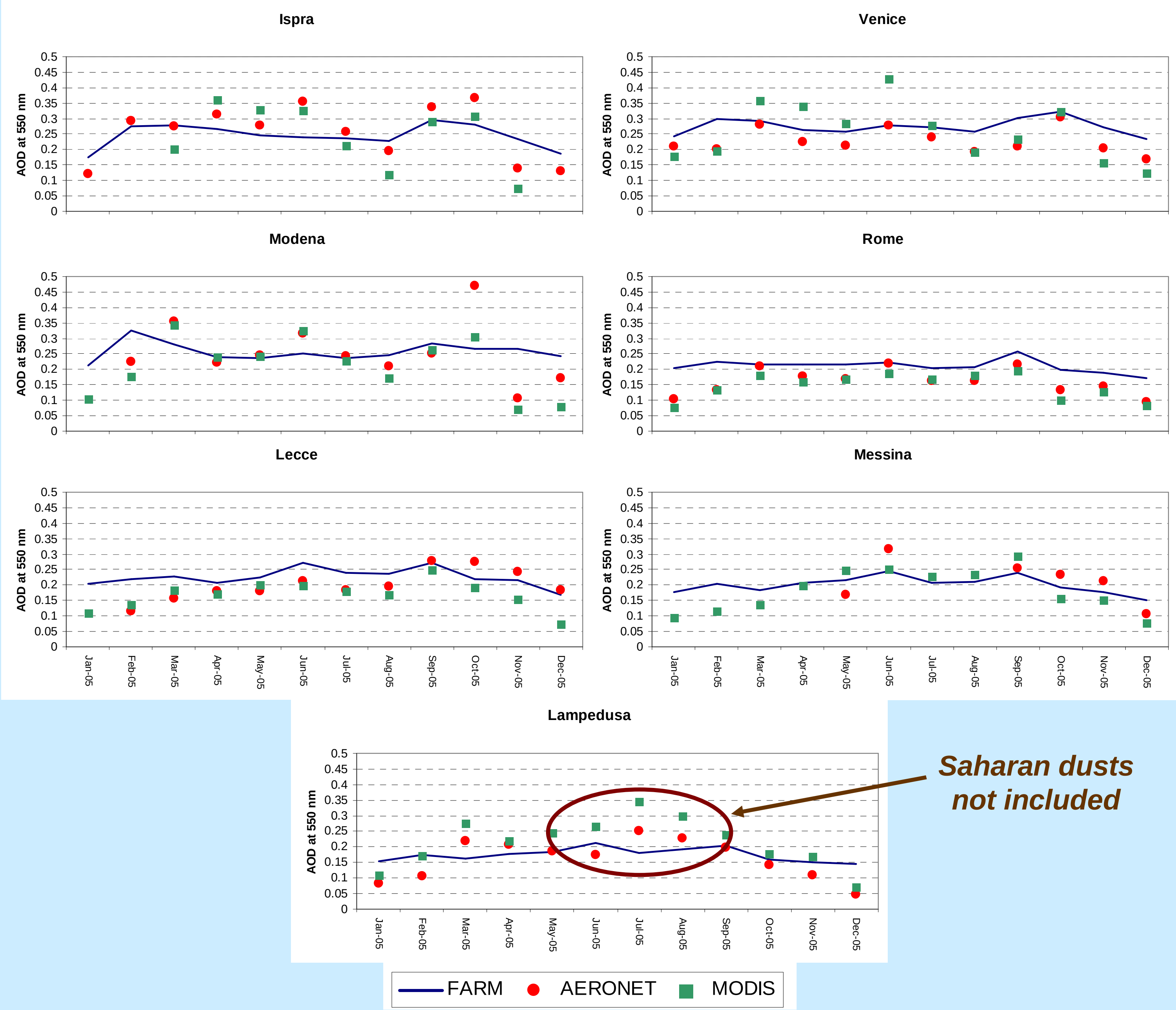
$$AOD = \int_{z=0}^{z_{top}} B_{sp}\,dz$$

where B_{sp} is the aerosol extinction coefficient in km^{-1} and z is altitude in km. B_{sp} is calculated through the extinction efficiency, a measure of light scattering efficiency, which in turn is estimated using approximations to the Mie theory (Binkowski, 1999).

To evaluate the model predicted columnar AOD against observations we have used data from MODIS satellite sensor and sun photometer measurements of the direct (collimated) solar radiation (AERONET network).



AOD analysis FARM vs MODIS & AERONET data, monthly averages



Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation

THEME FP7-ENV-2007.1.1.2.1: *Megacities and regional hot-spots air quality and climate*
Collaborative Project (medium-scale focused research project)
Grant agreement no.: 212520

The research leading to these results has received funding from the European Union's Seventh Framework Programme FP/2007-2011 within the project MEGAPOLI, grant agreement n°212520

Analysis of Po Valley emission influence on the surrounding region air quality in winter and summer circulation regimes

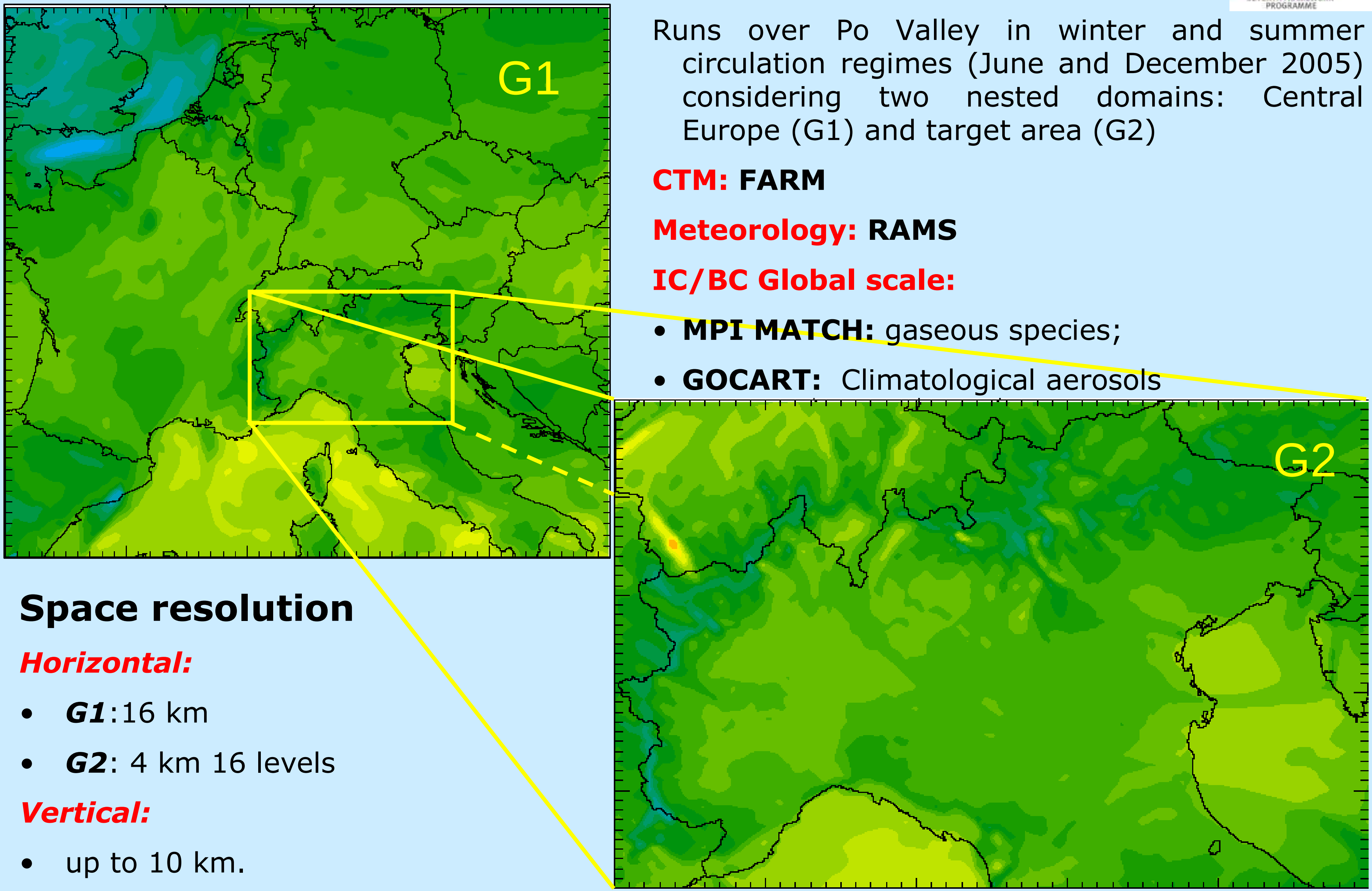
A. D'Allura, S. Finardi, P. Radice, C. Silibello

ARIANET

EGU General Assembly 2011 03-08 April 2011 Vienna, Austria

Po Valley simulations

Nested domains



Runs over Po Valley in winter and summer circulation regimes (June and December 2005) considering two nested domains: Central Europe (G1) and target area (G2)

CTM: FARM

Meteorology: RAMS

IC/BC Global scale:

- **MPI MATCH:** gaseous species;
- **GOCART:** Climatological aerosols

Space resolution

Horizontal:

- ***G1***:16 km
- ***G2***: 4 km 16 levels

Vertical:

- up to 10 km.

Process Analysis

Hourly balance terms computed runtime over inner model grid (G2)

Hourly production and destruction terms for the species of interest due to the following processes:

- horizontal inflow/outflow through the ***lateral boundaries***;
- net variation of mass due to flow through the ***top boundary*** (inflow minus outflow);
- increase of mass due to the ***emissions***;
- net variation due to gas-phase ***chemistry*** (production minus destruction);
- net variation of mass due to ***aerosol*** processes (production minus destruction);
- decrease of mass due to ***dry deposition***;
- decrease of mass due to ***wet deposition***.

$$\frac{\partial c_i}{\partial t} = -u\frac{\partial c_i}{\partial x} - v\frac{\partial c_i}{\partial y} - w\frac{\partial c_i}{\partial z} + K_{xx}\frac{\partial^2 c_i}{\partial x^2} + K_{yy}\frac{\partial^2 c_i}{\partial y^2} + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial c_i}{\partial z}\right) +$$

$$\left(\frac{\partial c_i}{\partial t}\right)_{emis} + \left(\frac{\partial c_i}{\partial t}\right)_{chem} + \left(\frac{\partial c_i}{\partial t}\right)_{aerosol} + \left(\frac{\partial c_i}{\partial t}\right)_{drydep} + \left(\frac{\partial c_i}{\partial t}\right)_{wetdep}$$

u, v, w: components of wind velocity vector, K_{xx}, K_{yy}, K_{zz}: diagonal components of the diffusivity tensor

PM - dimensional analysis

Net flows vs deposition processes (June 2005)

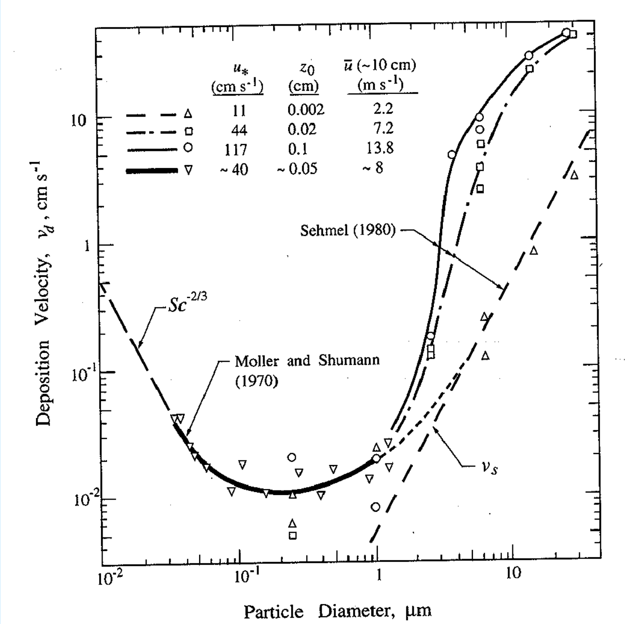
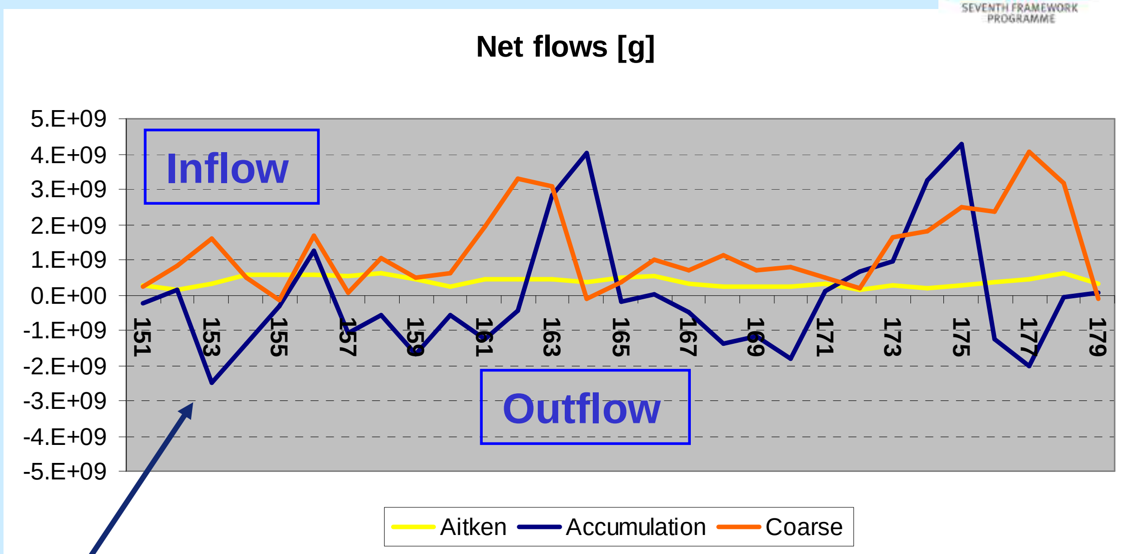
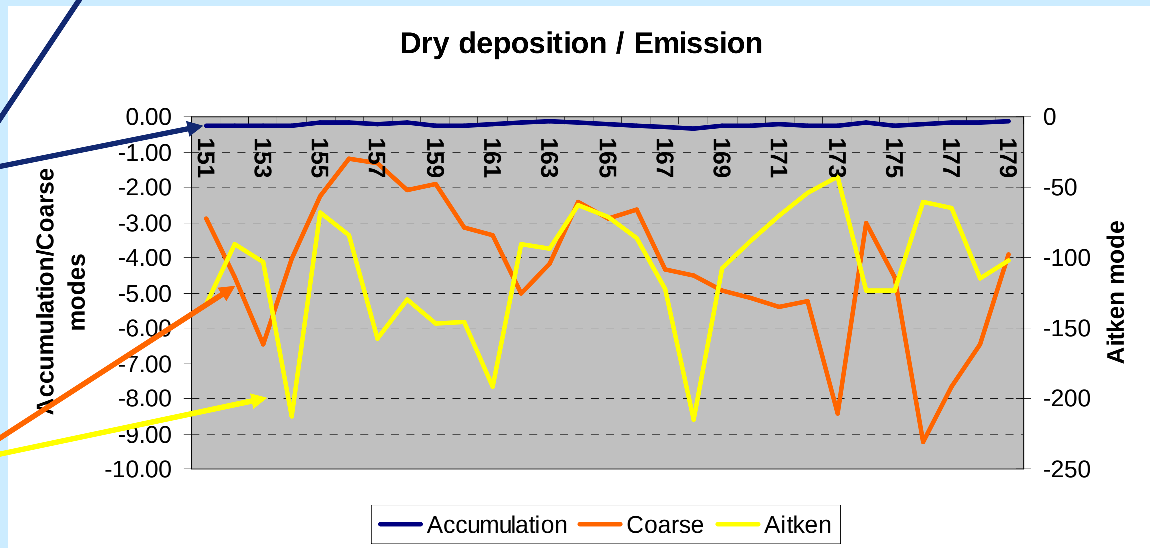


FIGURE 19.2 Particle dry deposition velocity data for deposition on a water surface in a wind tunnel (Slinn et al. 1978).



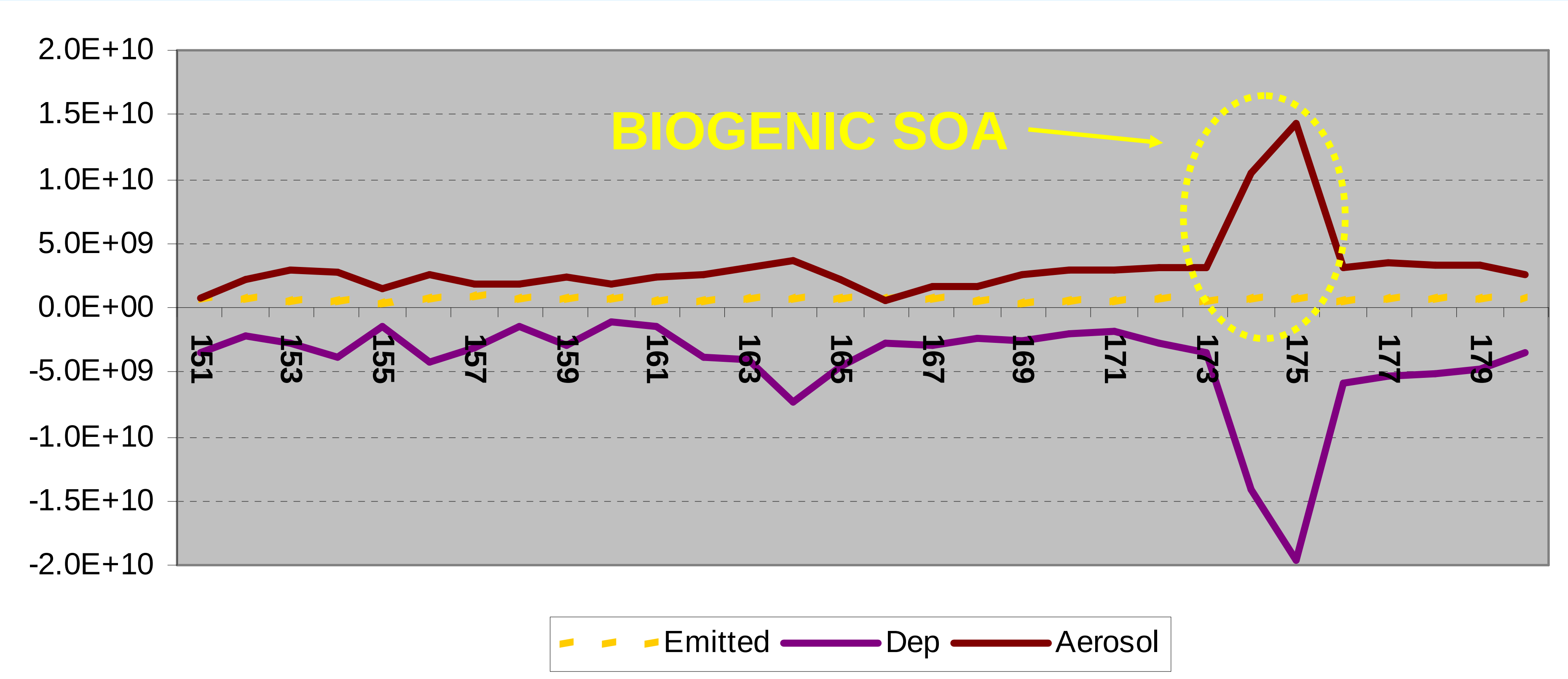


***Accumulation** mode particles may be transported outside Po Valley region (because of lower dry deposition).*

*Negligible outflow from Po Valley region, for **Aiken** and **Coarse** mode particles, due to dry deposition process.*

Process contribution to $PM_{2.5}$ [g]

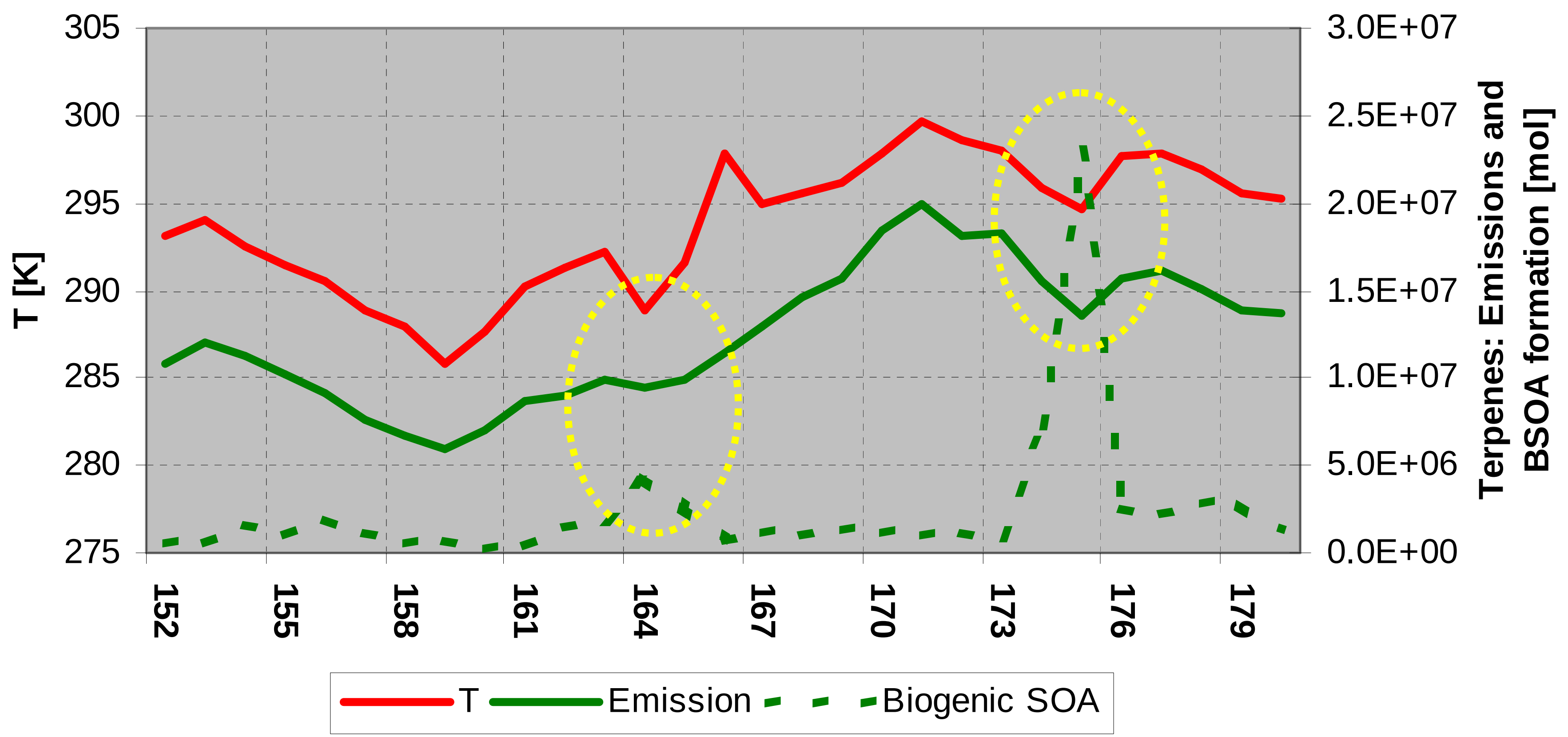
Other processes (June 2005)



Process contribution to $PM_{2.5}$ [g]

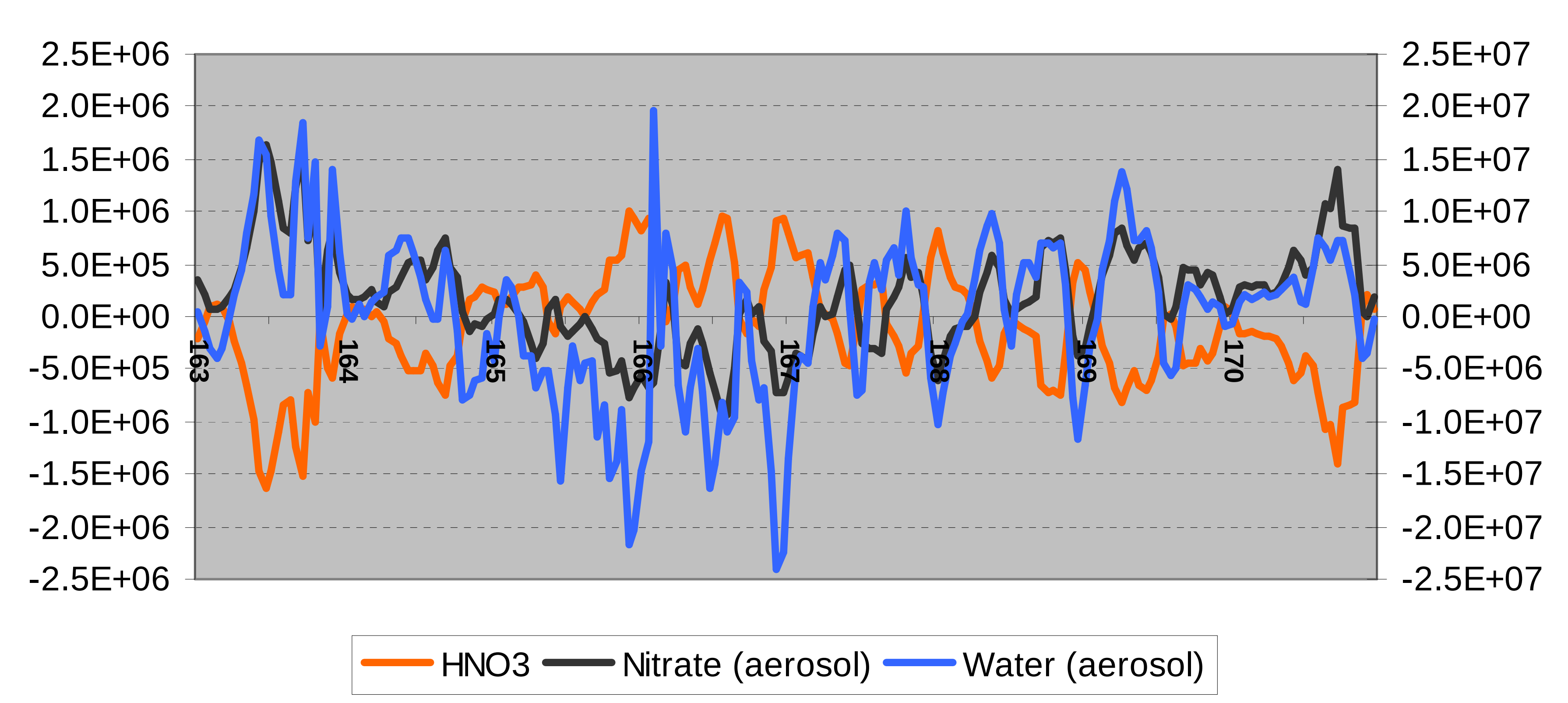
Aerosol processes interpretation

T: ground level average temperature at noon;
Terpenes emissions (full year, Temperature dependence) and **BSOA formation: daily integral over all domain**



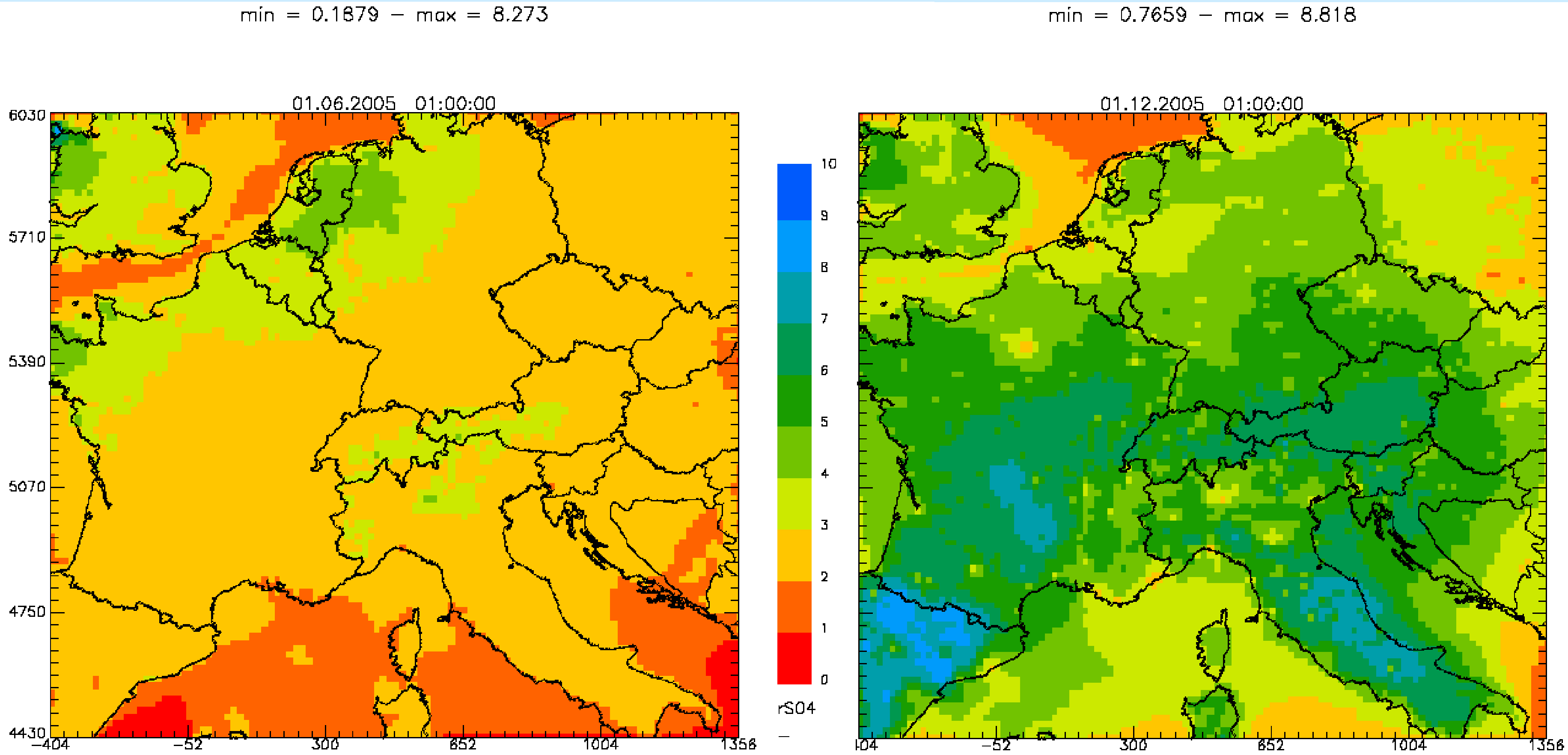
Because of their volatility, these compounds are also capable of evaporating from the particle-phase back to the gas-phase as temperatures increases.

Po Valley simulations
Process contribution to HNO_3 [mol]
Aerosol processes



The decrease in the PM liquid water content leads to less dissolution of HNO_3 in the particles

$$R_{SO_4} = \frac{[NH_4^+]}{[SO_4^=]}$$



June 2005

Dec. 2005

In summer, due to photochemistry, aerosol is sulfate richer than winter. During cold season excess ammonia can react with the other species (HNO_3, HCl) to form volatile salts.