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## NEW DEVELOPMENTS ON RAMS-Hg MODEL

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## Mercury

- is a toxic metal
- the most toxic compound is methyl-mercury
- is increasingly recognized as a threat to the health of numerous wildlife species and tens of thousands of people around the world
- is bio-accumulated
- its physical and chemical processes are very complicated and need special treatment
- after deposited can evaporate and be re-emitted
- its annual amounts released into the atmosphere by human activities are 50-75 % of the total emissions
  
- Mercury is emitted as
  - elemental vapour ( $\text{Hg}^0$ )
  - gaseous divalent ( $\text{Hg}^{2+}$ )
  - particulate phase ( $\text{Hg}^p$ )
  
- Regulation of mercury emissions leading to positive impacts through reasonable cost is a key policy issue in Europe, USA and other countries

# BACKGROUND

(2/2)

- **Mercury fluxes include:**
  - anthropogenic emissions (e.g. power plants, waste incinerators, cement kilns)
  - natural emissions (e.g. water surfaces, soil / plants, volcanoes)
- **Mercury is a multi-scale transport pollutant from local to global**
- **Elemental mercury vapour is :**
  - relatively inert to chemical reactions with other atmospheric constituents
  - has an atmospheric residence time of approximately one year
  - once released to the atmosphere, can be dispersed and transported for long distances over hemispheric and global scales before being deposited to terrestrial and aquatic receptors
- **Gaseous divalent mercury :**
  - reacts with other atmospheric constituents
  - once released to the atmosphere, is expected to be removed in the vicinity of a few tens to a few hundreds km from sources
- **Particulate phase mercury :**
  - can be dispersed and transported for intermediate distances before being deposited to terrestrial and aquatic receptors

# GAPS IN THE CURRENT KNOWLEDGE

**The current knowledge on the mercury issue has uncertainties on :**

- mercury speciation for emissions of various anthropogenic sources
- rate reaction constants/ reaction paths (e.g. reduction of  $\text{Hg}^{2+}$  by  $\text{HO}_2$  at environmental conditions ?)
- the relationship between deposition of mercury compounds and surface hydrology

$\text{Hg}^0$  exchange at the air-water interface is known to occur both from oceans and inland waters - there is almost no complete data set to validate these processes in mercury models

The relative importance of Hg emitted from water surfaces compared to evasion from soils is still largely unknown

An integrated modeling tool is being developed at the framework of MERCYMS project, focusing on the above uncertainties

This modeling tool is aiming to become a policy tool of EU

# THE NEW MODEL CONCEPTS

**RAMS3b-Hg has been developed during MAMCS project to describe the Atmospheric Mercury Cycle**

**This version:**

- Oversimplified treatment of emissions from natural surfaces
- Used a rather simplified dry deposition scheme
- Used a simplistic approach of the scavenging processes that was leading to overestimation of wet deposition

**The new developments at the framework of MERCYMS project are based on RAMS4.3**

**A number of new processes with emphasis in physics have been included.**

**More specifically the modules implemented in the latest RAMS-Hg version consist of:**

- New treatment of anthropogenic emissions (area sources included)
- New air-surface exchange process parameterization
- New gas and aqueous phase chemistry
- A photochemical reaction scheme with on-line photolysis rate calculation
- New in-cloud processes and wet deposition scheme
- New dry deposition scheme

# ANTHROPOGENIC EMISSIONS

The various sources provided are automatically allocated within the model domain according to :

- the geographic co-ordinates
- the type of sources (e.g. power plants)
- speciation and stack characteristics

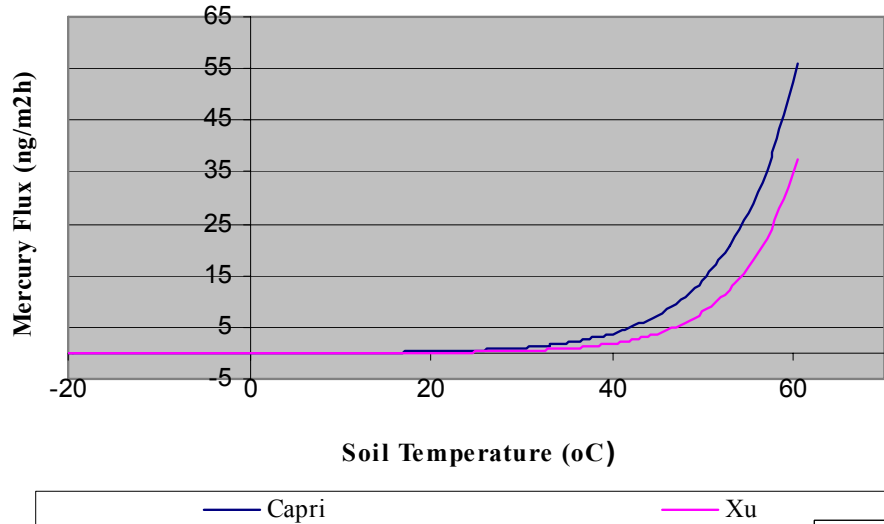
# AIR-SOIL EXCHANGE PARAMETERIZATION (1/2)

The air soil exchange parameterization is based on the following facts and assumptions

- Deposited mercury on the surface can be reduced chemically or bio-chemically to highly volatile species (primarily  $\text{Hg}^0$ )
- $\text{Hg}^0$  emission from soil depends on soil temperature and soil radiation

# AIR-SOIL EXCHANGE PARAMETERIZATION

(2/2)

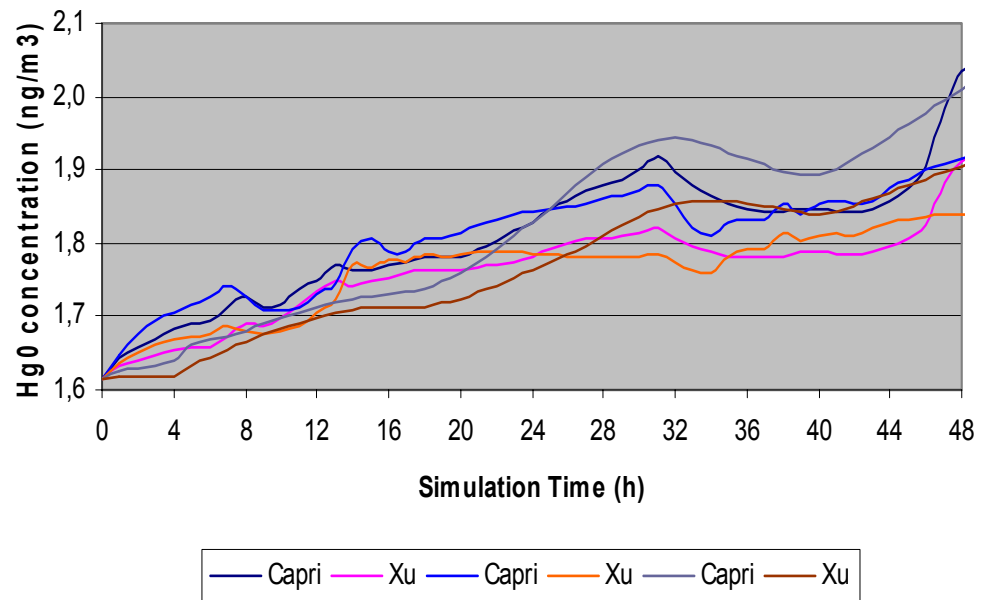


The air-soil exchange of elemental mercury has been developed by using the soil temperature dependent empirical functions proposed by:  
Capri and Lindberg (1998) – **case 1**  
Xu et al. (1999) – **case 2**  
The mercury flux is negligible for soil temperature below 20°C

Group of blue lines:  
soil grid points where case 1 is used  
Group of red lines:  
soil grid points where case 2 is used

For higher soil temperatures mercury fluxes (ng/m²h) in **case 1** can be twice the fluxes estimated in **case 2**.

The approach finally adopted was **case 2**





# AIR-WATER EXCHANGE PARAMETERIZATION (1/2)

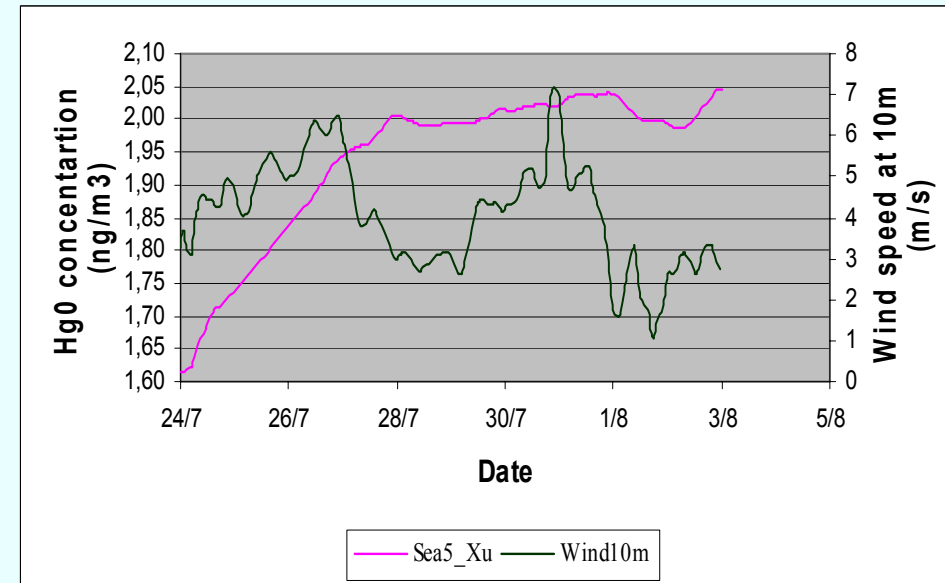
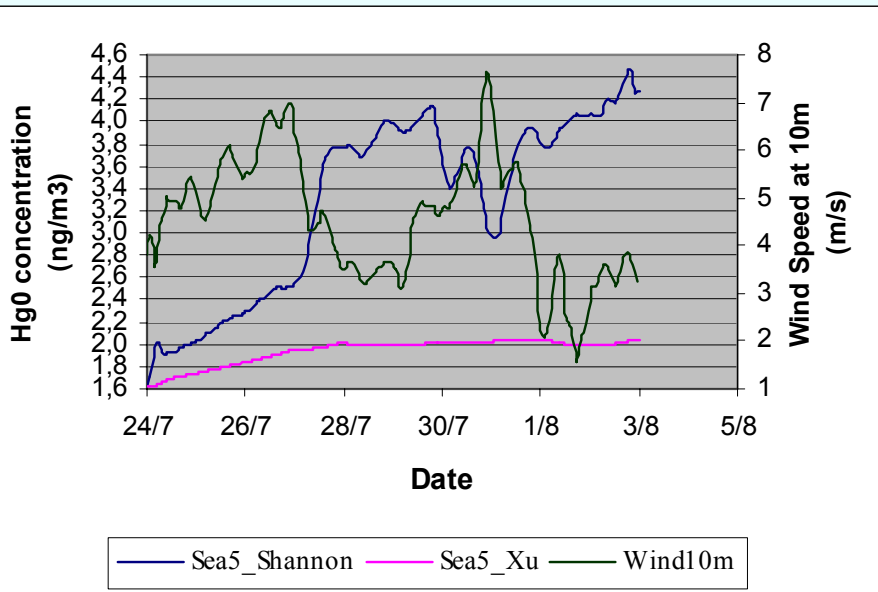
The assumptions used on the air water exchange parameterization are :

- $\text{Hg}^0$  is subject to volatilization from surface waters at ambient temperatures
- $\text{Hg}^0$  evasion occurs both from oceans and inland waters
- Air-water exchange is driven by the equilibrium between the vapor and dissolved phase mercury
- Air-water parameterization includes SST and sea state (wave conditions) effects

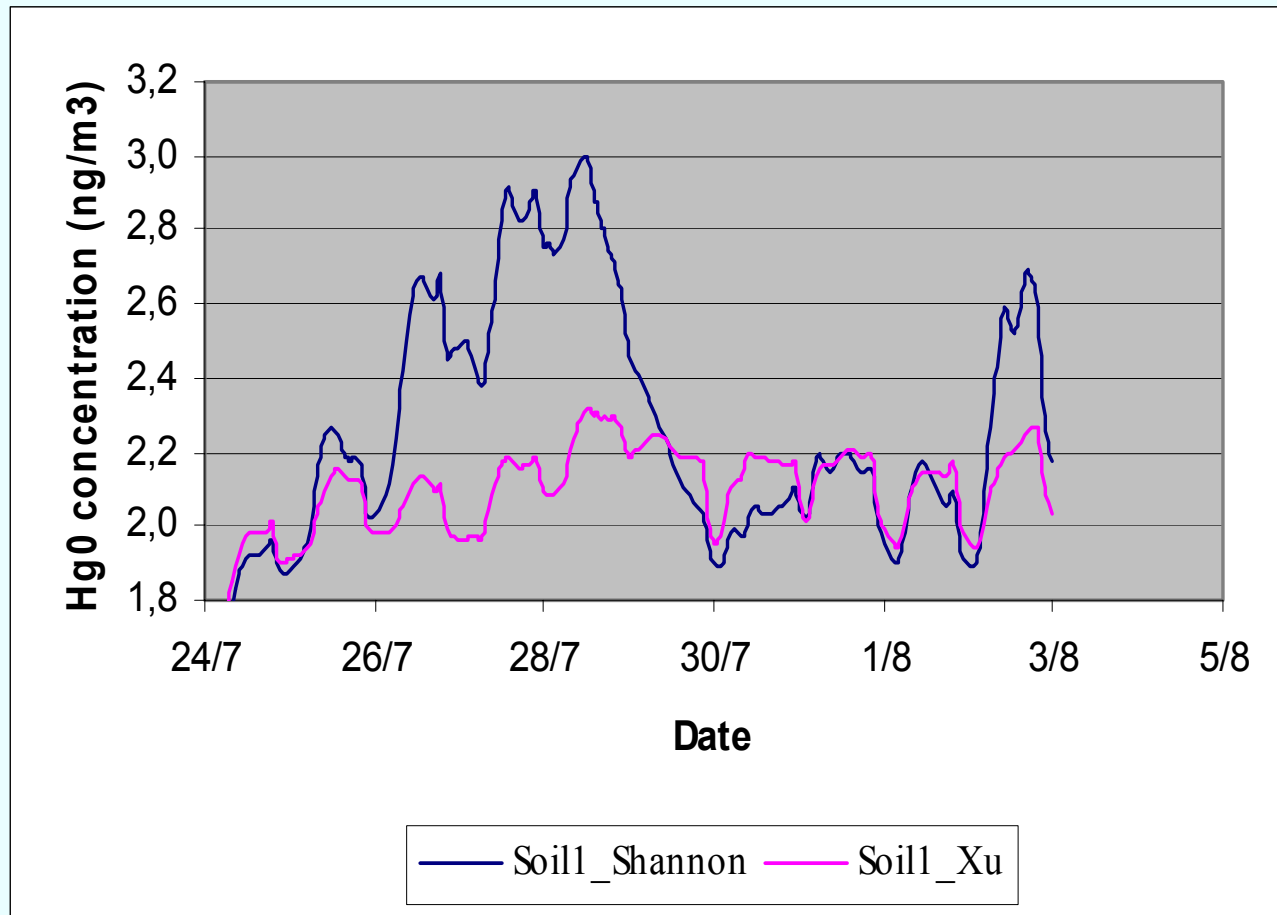
# AIR-WATER EXCHANGE PARAMETERIZATION (2/2)

- The air-water exchange of Hg<sup>0</sup> has been calculated by implementing either:
  - the formula proposed by Shannon et al. (1995) – **1st approach** , or
  - a combination of the Mackay and Yeun (1983) and Xu et al. (1999) expression – **2nd approach**
- For the 1st approach, the air-water exchange rate is a function of sea surface temperature only
- For the 2<sup>nd</sup>, the air-water exchange rate depends also on the friction velocity, wind speed at 10m above the surface and sea state

Sensitivity tests showed that the calculated values of Hg<sup>0</sup> are much higher, almost twice over sea, using the 1st approach



# NATURAL EMISSIONS-REEMISSIONS- ATMOSPHERE-SURFACE EXCHANGE

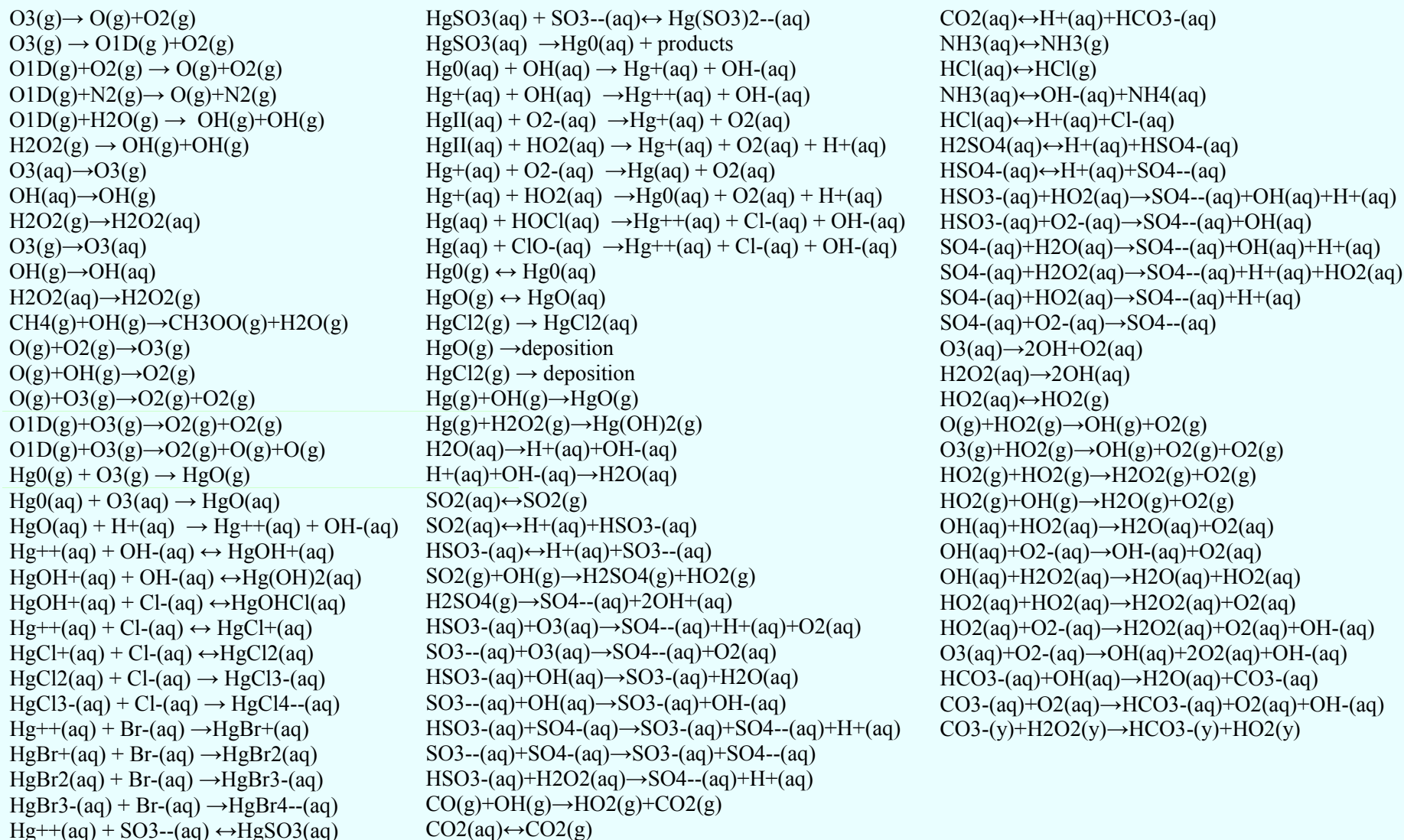


Air-water exchange parameterization also affects  $Hg^0$  concentration on coastal areas

# CHEMISTRY

- The modified chemistry module includes 107 reactions and deals with
  - the gas and aqueous phase chemistry reactions of mercury species with other reactants
  - Photochemical reactions of ozone ( $O_3$ ) and hydrogen peroxide ( $H_2O_2$ ) both in aqueous and gaseous phase
  - bimolecular and termolecular reactions that form these mercury reactants (e.g. bimolecular reactions of  $SO_x$ , CO and  $CO_2$  with  $O_2$ ,  $H_2O$ , OH and  $H_2O_2$ )
- The photochemical reactions of  $O_3$  and  $H_2O_2$  both in aqueous and gaseous phase are treated within the chemistry module using the Fast-J scheme proposed by Wild et al. (2000)
- The gas and liquid phase reactions of mercury considered in the chemistry module are those with  $O_3$ ,  $H_2O_2$ , Cl and sulphates (Munthe et al., 1991, Munthe 1992).
- The Benefits of this chemistry module are
  - flexibility
  - the ability to calculate on line the rate constants of the reactions for various temperatures, pressures and water content
  - the simplicity to add new reactions to the database

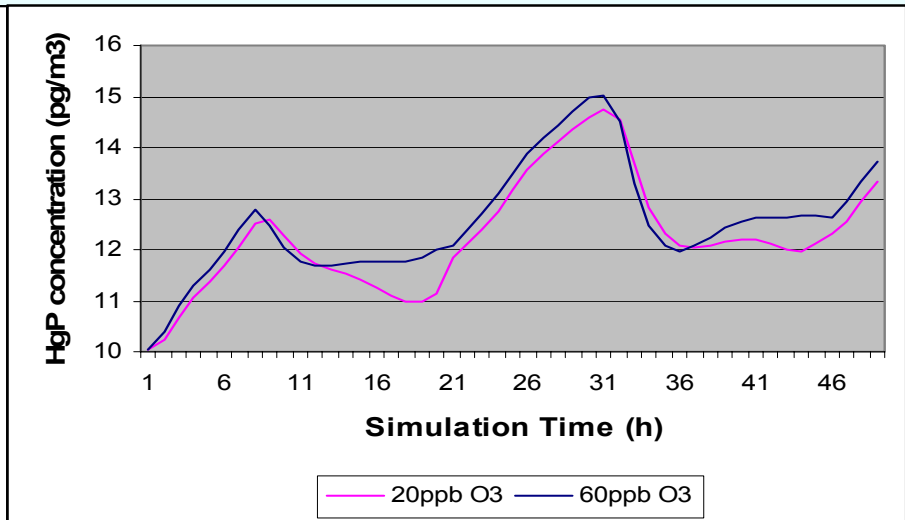
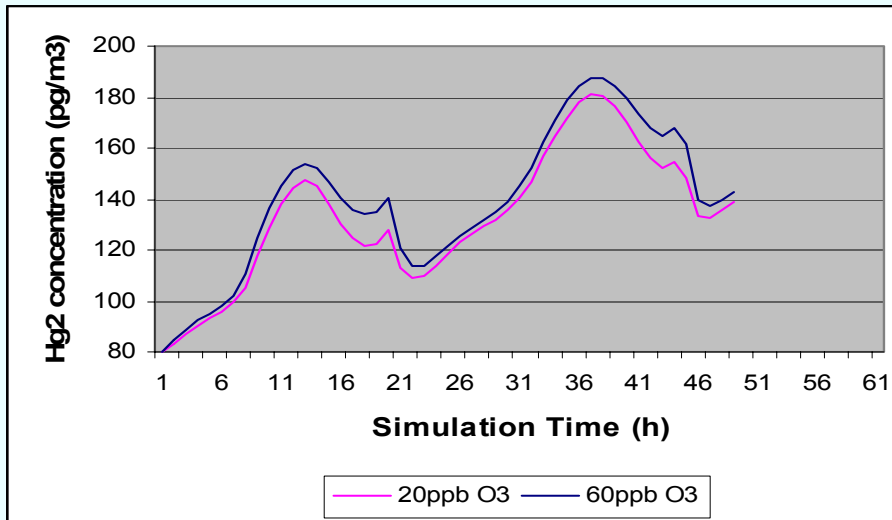
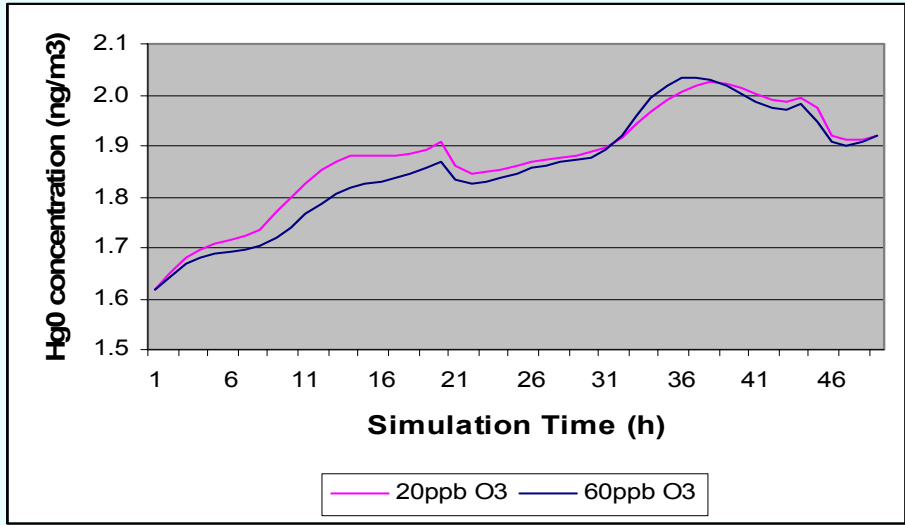
# LIST OF CHEMICAL REACTIONS



# SENSITIVITY TESTS ON O<sub>3</sub> BACKGROUND CONCENTRATIONS

- The predicted concentrations of Hg<sup>0</sup> and Hg<sup>P</sup> are relatively sensitive to O<sub>3</sub> levels.
- Reduction of O<sub>3</sub> (occurs during winter and/or night hours), results in increasing Hg<sup>0</sup> and decreasing Hg<sup>P</sup>. The opposite occurs when O<sub>3</sub> increases (e.g. during summer). The control experiment has been performed with 20 ppb O<sub>3</sub> background concentration while the background value of 60 ppb has also been examined. These results are consistent with the known photochemistry of mercury as Hg<sup>0</sup> is known to react with O<sub>3</sub> both in gas (Hall, 1995) and aqueous phase (Munthe, 1992). The products in each reaction are Hg<sup>P</sup> and Hg<sup>2</sup> respectively

- For regular simulations the background value of 40 ppb of O<sub>3</sub> is used.
- These preliminary results indicate a consistent behaviour of the implemented chemistry module



# WET DEPOSITION

**Wet deposition is the main removal path.**

The wet removal processes for Hg species have been developed by following the following facts and assumptions:

- Wet scavenging of  $\text{Hg}^2$  is assumed to occur in and below the clouds
- $\text{Hg}^2$  is assumed to be an irreversibly soluble gas and its scavenging coefficient is calculated accordingly
- In cloud,  $\text{Hg}^2$  can be removed by interstitial cloud air by dissolution into cloud drops
- The calculated local rate of removal of the irreversibly soluble gas with a concentration depends on the scavenging coefficient of the gas in the cloud and on the concentration of Hg
- The particulate matter scavenged only from below the precipitating level of clouds
- Scavenging coefficients in and below the clouds are different and in general are calculated according to Seinfeld and Pandis (1998) and Pielke (2002)

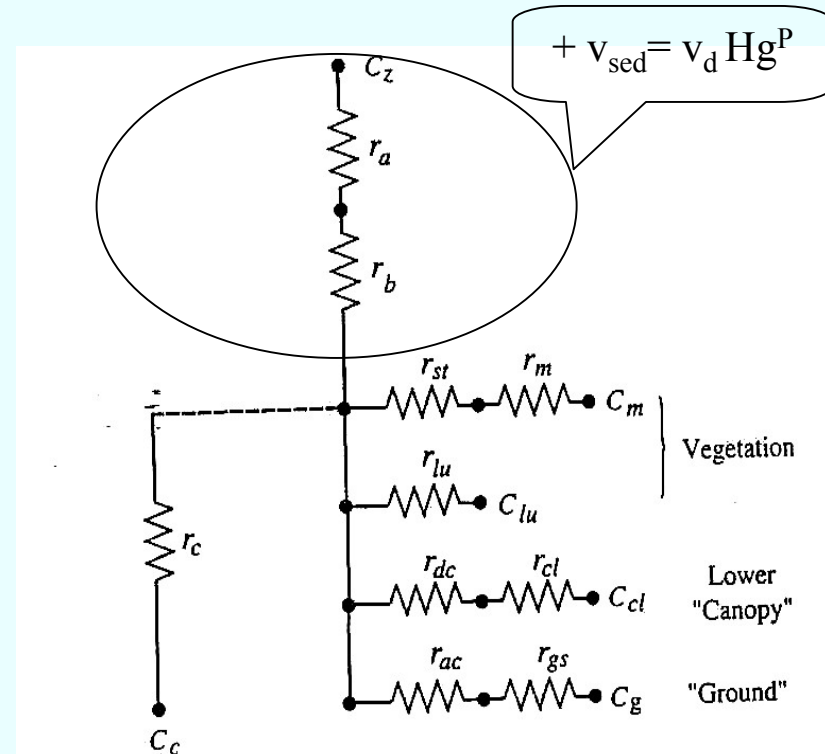
# DRY DEPOSITION

- The dry deposition of both  $Hg^2$  and  $Hg^P$  is calculated by using the classical formulation

$$F = -v_d C$$

where the flux of a pollutant (F) to the surface is the product of a characteristic deposition velocity ( $v_d$ ) and its concentration (C) in the “surface layer” plant canopy and deposit on the ground surface

- The deposition velocity is calculated using the resistance method
- The deposition velocity is calculated as the sum of various resistances for the gaseous species (Hicks, 1985) and the settling velocity for particles
- The values of the resistances depend upon meteorological conditions as well as on the properties of the surface





# DRY DEPOSITION OF Hg<sup>2</sup>

- A resistance module that incorporates the major elements described above. Deposition velocity  $v_d$  is calculated from three primary resistances  $r$  (s/m) in series (see Figure):

$$v_d = \frac{1}{r_a + r_b + r_c}$$

- The aerodynamic resistance  $r_a$  is calculated from:

$$r_a = \frac{1}{ku_*} \left[ \ln \left( \frac{z}{z_0} \right) - \phi_h \right]$$

where  $u^*$  is friction velocity (m/s),  $k$  is von Karmans' constant,  $z$  and  $z_0$  are the lowest model layer midpoint height (m) and landuse-dependent surface roughness length (m), respectively, and  $\Phi_h$  is a stability correction term

- The quasi-laminar sublayer (or boundary) resistance  $r_b$  is given by:

$$r_b = \frac{2 Sc^{2/3}}{ku_*}$$

where  $Sc$  is the Schmidt number, or the ratio of air viscosity to species molecular diffusivity.

- Over land, surface resistance  $r_c$  is further expressed as several serial and parallel resistances:

$$r_c = \left( \frac{1}{r_{st} + r_m} + \frac{1}{r_{lu}} + \frac{1}{r_{dc} + r_{cl}} + \frac{1}{r_{ac} + r_{gs}} \right)^{-1}$$

where the first serial resistance set represents the pathway into the stomatal and mesophyllic portions of active plants, the second is the pathway into the upper canopy, the third is the pathway into the lower canopy, and the fourth is the pathway to the ground surface. Many of these resistances are season- and landuse-dependent, and are built into Wesely's model; some in turn are adjusted within this module for solar insolation, moisture stress, and surface wetness

# DRY DEPOSITION OF Hg<sup>P</sup>

- Surface deposition of particles occurs via diffusion, impaction, and/or gravitational settling. Particle size is the dominant variable controlling these processes. The resistance approach of Slinn and Slinn (1980) - similar to the one implemented in UAM-AERO (Kumar et al., 1996) - has been adopted. Particle deposition velocity for a given aerosol size is calculated using the following resistance equation:

$$v_d = v_{sed} + \frac{1}{r_a + r_b + r_a r_b v_{sed}}$$

where  $v_{sed}$  is the gravitational settling (or sedimentation) velocity.

- This velocity is dependent on aerosol size and density:

$$v_{sed} = \frac{D_p^2 g C \rho_p}{18\nu}$$

where  $D$  is the log-mean particle diameter (m) of a given size section,  $D_p$  is particle density (g/m<sup>3</sup>),  $g$  is gravitational acceleration, and  $\nu$  is the viscosity of air.

- The factor  $C$  is the Cunningham correction for small particles
- Aerodynamic resistance  $r_a$  is identical to the value used for gaseous dry deposition.
- Boundary resistance  $r_b$  is and is given by

$$r_b = \frac{1}{u_* (Sc^{-2/3} + 10^{-3/St})}$$

- The stokes number  $St$  is calculated from:

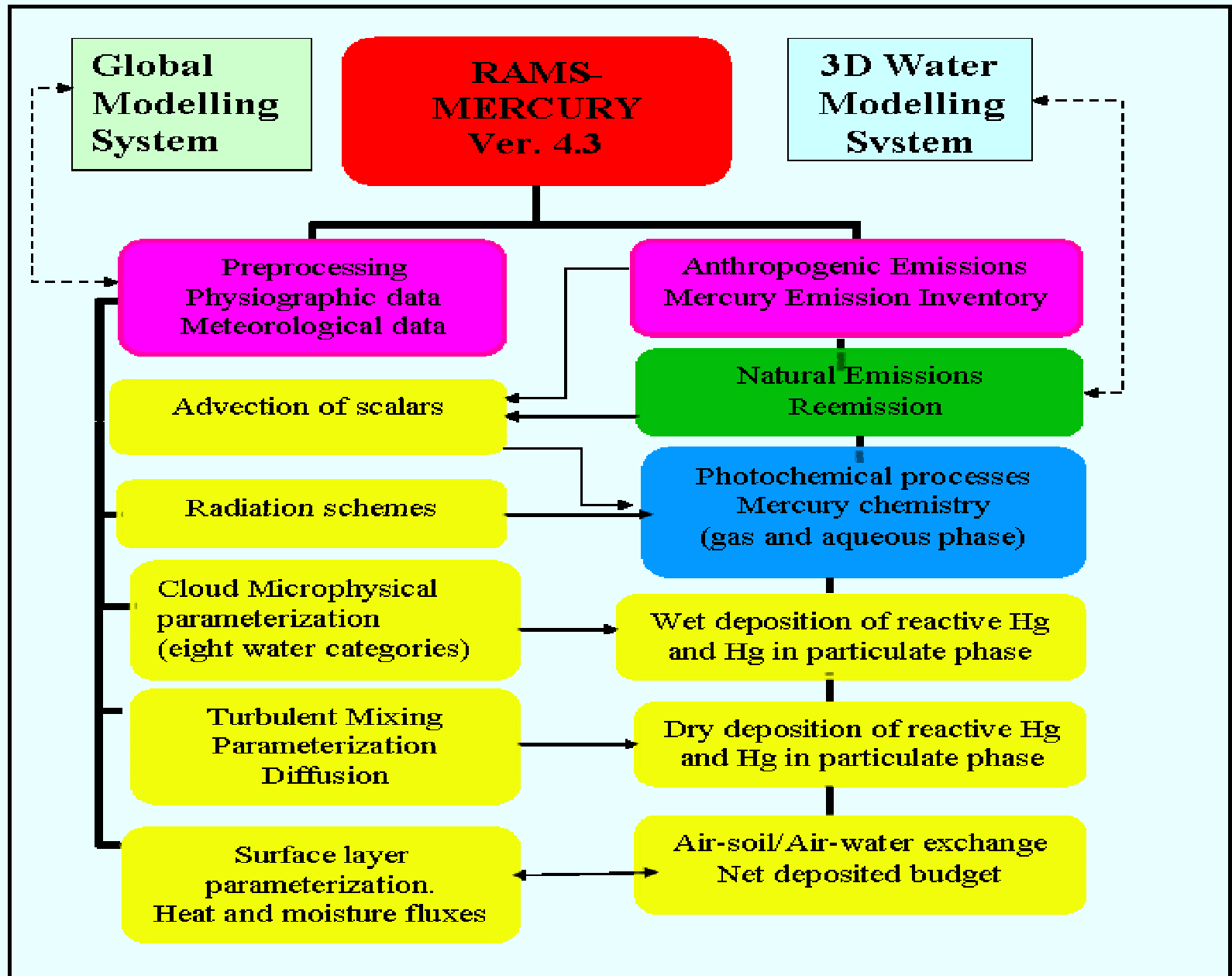
$$St = \frac{v_{sed} u_*^2}{\nu g}$$

# THE AM SYSTEM & THE MERCURY PROCESSES (SUMMARY)

The developed modules for the physico-chemical processes of mercury that have been incorporated in RAMS include:

- processing of emissions data
  - Point sources - information of the location, stack height, emission rates etc.
  - A module for handling area sources has been implemented
- handling of initial and boundary conditions for  $\text{Hg}^0$ ,  $\text{Hg}^2$  and  $\text{Hg}^p$ .
- implementation of dry deposition schemes for  $\text{Hg}^2$  and  $\text{Hg}^p$
- implementation of a gas-phase chemistry
- aqueous phase chemistry in the presence of liquid
- wet deposition using scavenging coefficients for in and below clouds
- fluxes from water bodies and soil

# RAMS 4.3-Hg



# PRELIMINARY MODEL SIMULATIONS

- Simulation period : 14 to 26 August 1997
- Models used : two versions of RAMS
  - RAMS ver. 4.3
  - RAMS ver. 3b
- The simulation domain covers the area of US East of the Rocky Mountains
- The New York State Department of Environmental Conservation provided the emission data used
- Walcek et al. (2003) performed the spatial distribution of total gaseous and particulate emission rates in eastern North America
- Mercury emissions extracted from the Global Mercury Emission Inventory have been also used for the rest computational domain

# MODEL – OBSERVATIONS INTERCOMPARISON (1/2)

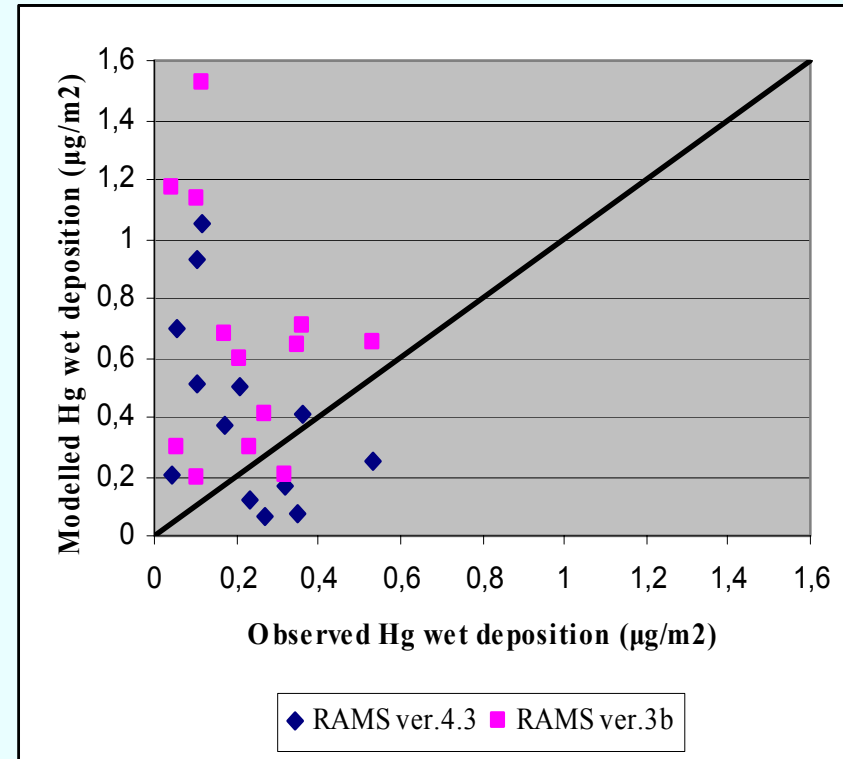
- Mercury Deposition Network (MDN) provided wet deposition observations
- Observations
  - represent weekly measured wet deposition of all mercury species,
  - were collected during the periods 12 to 19 August 1997 and 19 to 26 August 1997
- Model outputs
  - represent calculated wet deposition of all mercury species
  - wet deposition was accumulated for the 14 to 19 August simulation period and for 19 to 26 August simulation period

# MODEL – OBSERVATIONS INTERCOMPARISON (2/2)

As it was found in MAMCS and NYSERDA projects RAMS3b Hg development overestimates deposition

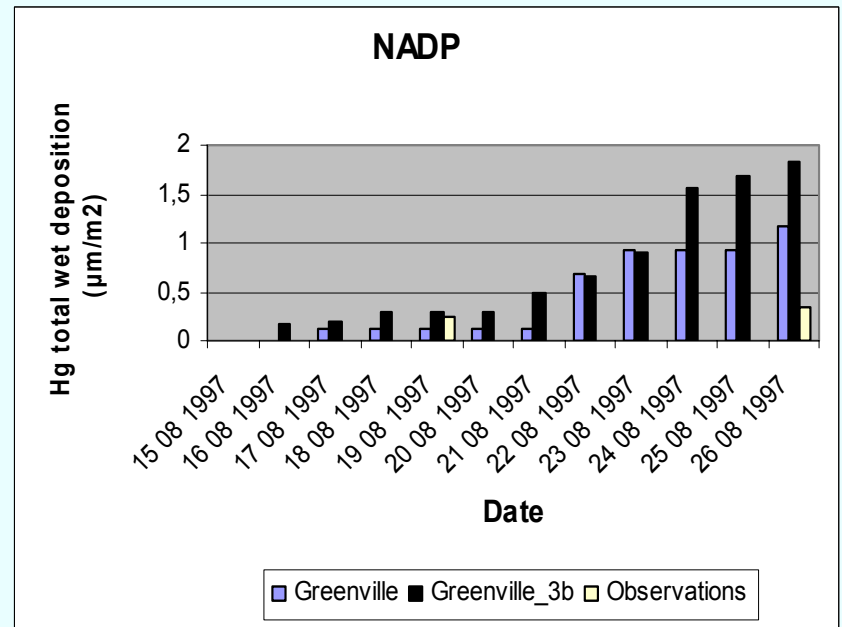
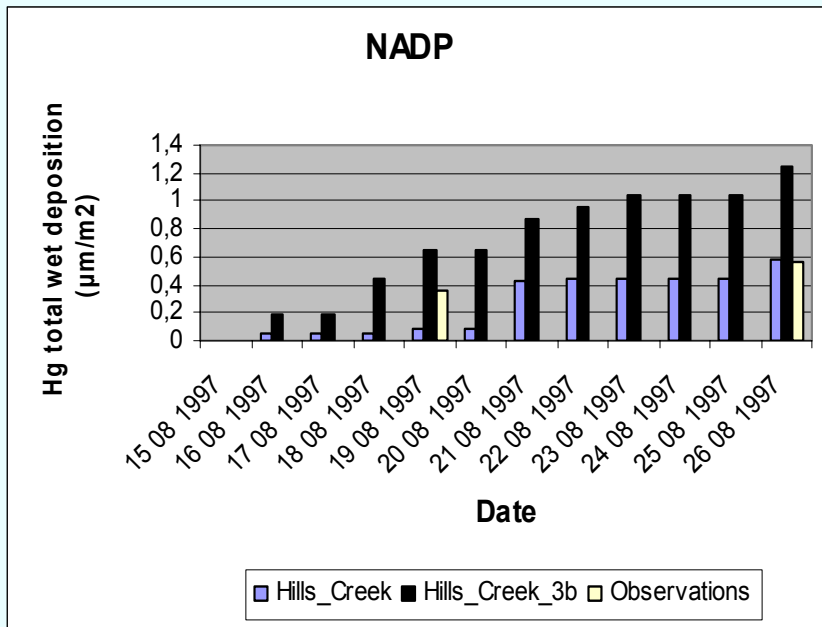
According to the model validation against the deposition data of NYSERDA, RAMS4.3 seems to perform better on this issue

Model (*)	BIAS ( $\mu\text{g}/\text{m}^2$ )	SD ( $\mu\text{g}/\text{m}^2$ )	RMSE ( $\mu\text{g}/\text{m}^2$ )
RAMS4.3	0.1915	0.3183	0.1936
RAMS3b	0.4349	0.4073	0.3898



\*A. Voudouri, I. Pytharoulis, G. Kallos (2004): Mercury Budget Estimates for the State of New York. *Env. Fluid Mech.* (in press)

# MODEL VALIDATION (NYSERDA Data)



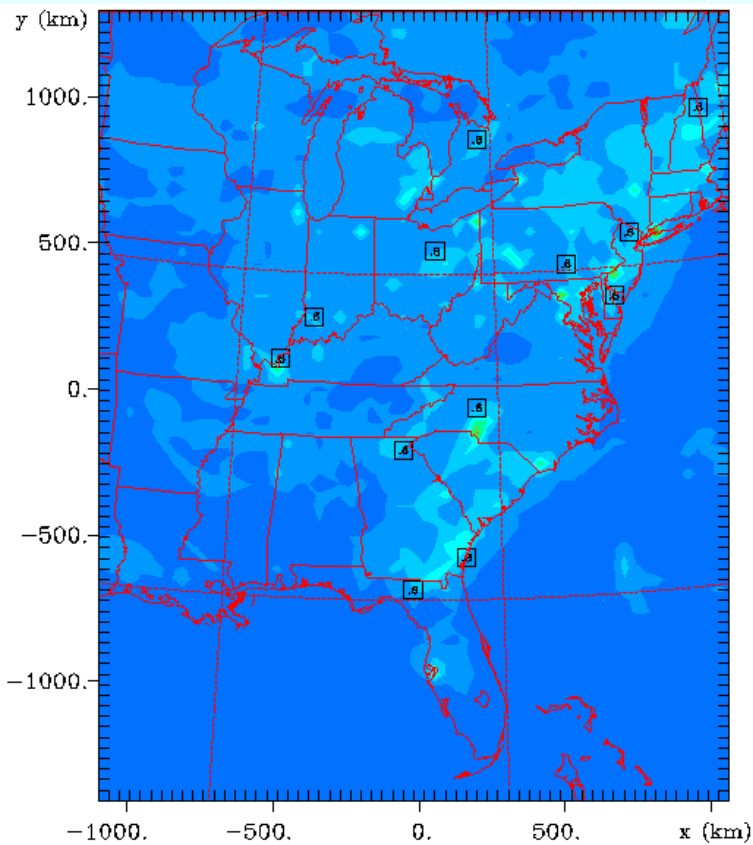


# DISCUSSION AND RESULTS

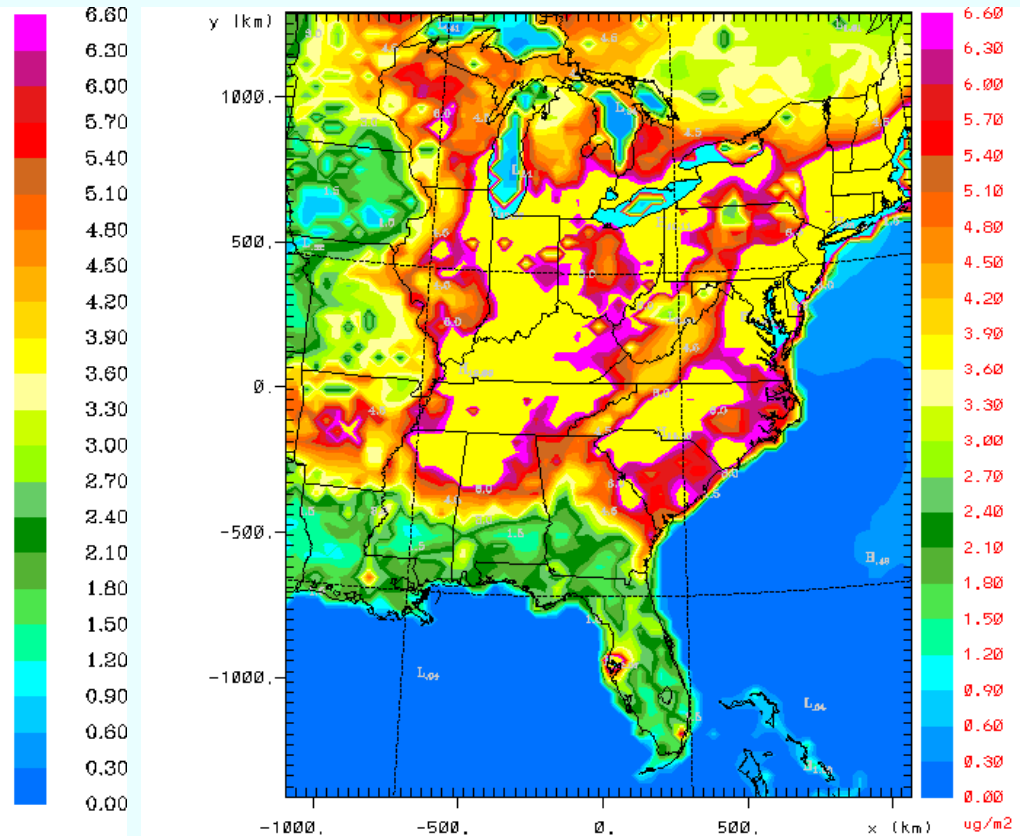
- Differences on the deposition pattern of  $\text{Hg}^2$  estimated using RAMS ver.3b and RAMS 4.3 are mainly allocated near the location of the sources
- The calculated deposited quantities of  $\text{Hg}^{\text{P}}$  using the new RAMS – Hg are one order of magnitude than the ones calculated using the previous version
- This can be attributed to :
  - differences in the microphysics of both versions of the original atmospheric model
  - the updated wet modules implemented on the new RAMS-Hg model and
  - the new dry deposition module used to calculate the dry deposited quantities of  $\text{Hg}^{\text{P}}$  and  $\text{Hg}^2$

# Total (wet and dry) deposited $\text{Hg}^{\text{P}}$ (in $\mu\text{g}/\text{m}^2$ ) at 0000 UTC on 26 August 1997 after 12 days of simulation

## RAMS3b



## RAMS 4.3



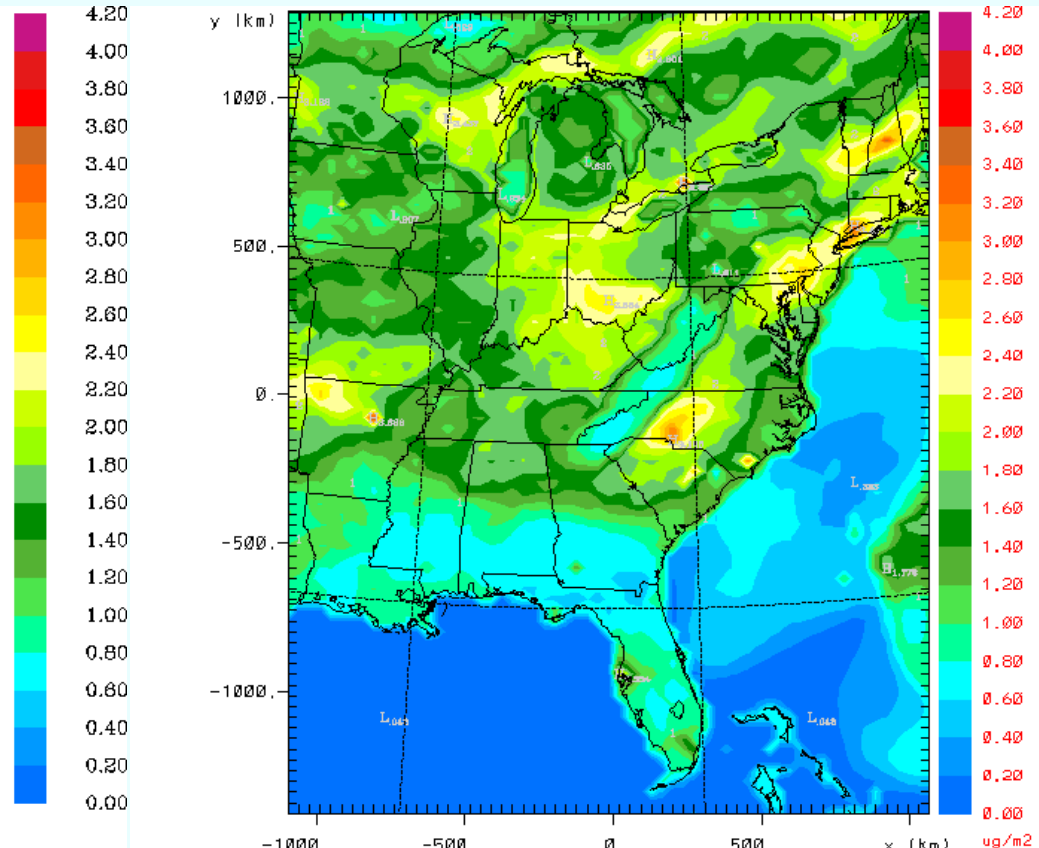
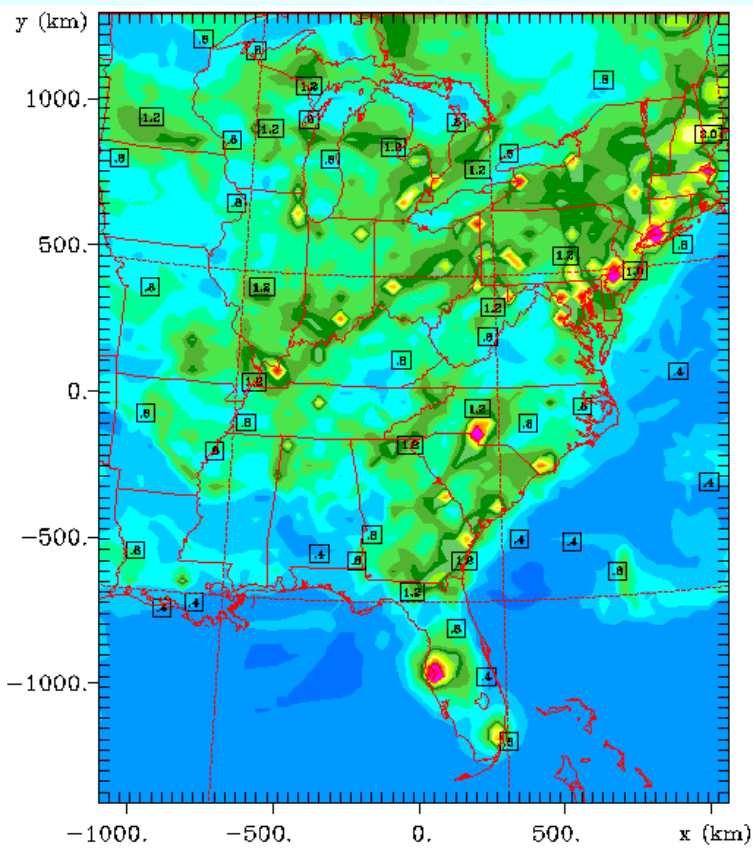
TEST		grid 1			
	1997-08-26-0000.00 UTC	min	max	inc	lab*
contours	Total depos. $\text{Hg}^{\text{P}}$ ( $\mu\text{g}/\text{m}^2$ )	0.4370E-01	25.84	0.3000	1e 0

Differences on the total deposited  $\text{Hg}^{\text{P}}$  are mainly attributed on higher dry deposited amounts of the pollutant calculated using the new dry deposition module for  $\text{Hg}^{\text{P}}$

# Total (wet and dry) deposited $\text{Hg}^{2+}$ (in $\mu\text{g}/\text{m}^2$ ) at 0000 UTC on 26 August 1997 after 12 days of simulation

## RAMS3b

## RAMS 4.3

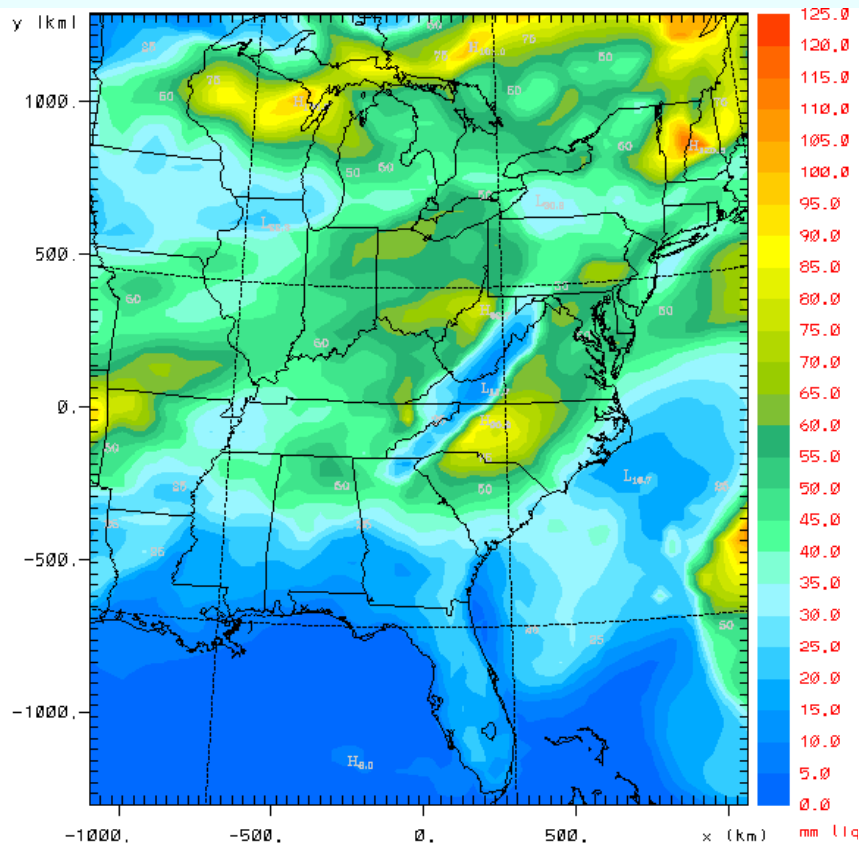


TEST	grid 1				
	1997-08-26-0000.00 UTC	min	max	inc	lab*
contours	Total depos. Hg2 (ug/m2)	0.4824E-01	3.887	0.2000	1e 0

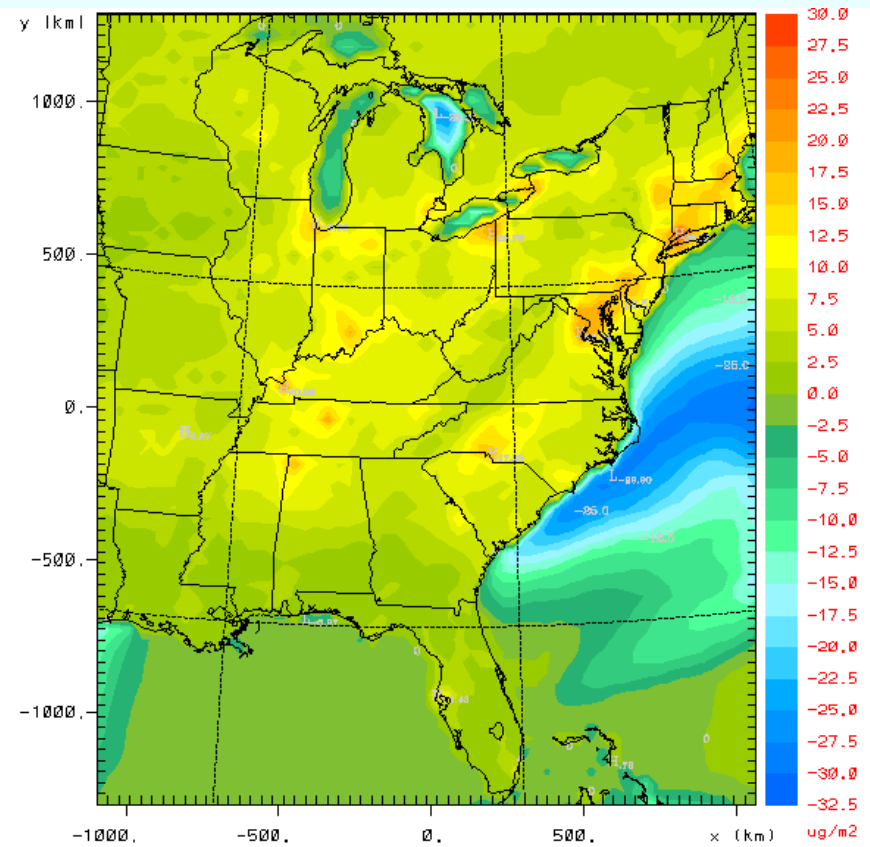
Differences on the deposition pattern of  $\text{Hg}^{2+}$  are mainly allocated near the location of the sources

# RAMS4.3 – Hg model outputs during 14 to 26 August 1997

## Total accumulated precipitation (mm)



## Net (deposited – emitted) Hg flux ( $\mu\text{g}/\text{m}^2$ )

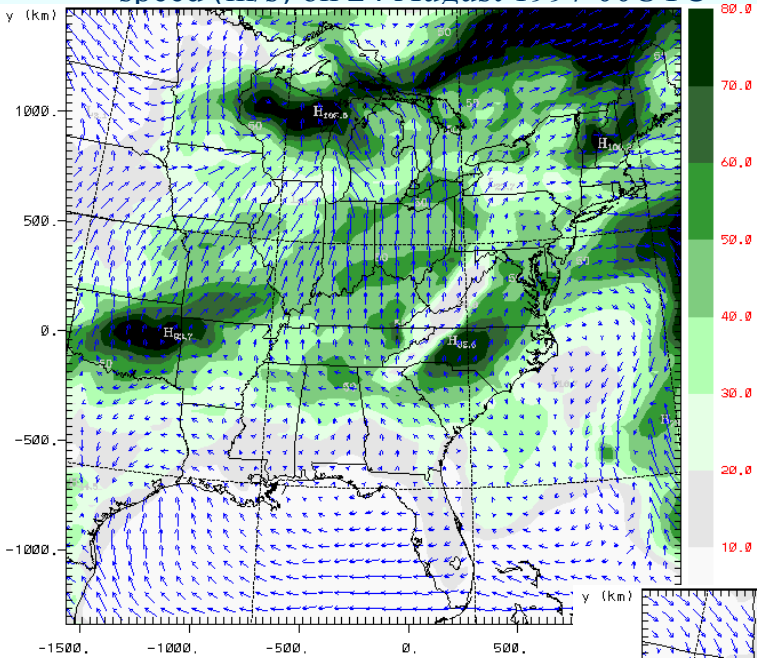


TEST	grid 1			TEST	grid 1				
	1997-08-26-0000.00 UTC	min	max	inc	1997-08-26-0000.00 UTC	min	max	inc	lab*
contours	total accum precip (mm liq)	0.8908E-02	120.5	5.000	Hg flux (depos.-emit.) (ug/m2)	-30.28	28.99	2.500	1e 0

- The net Hg flux is
  - **positive** over land - especially over areas where the precipitated quantity is high
  - **negative** over the sea - no sources, reemission from the water surface is the controlling factor.
- The budget seems to be in equilibrium over the soil surfaces at the western USA
 

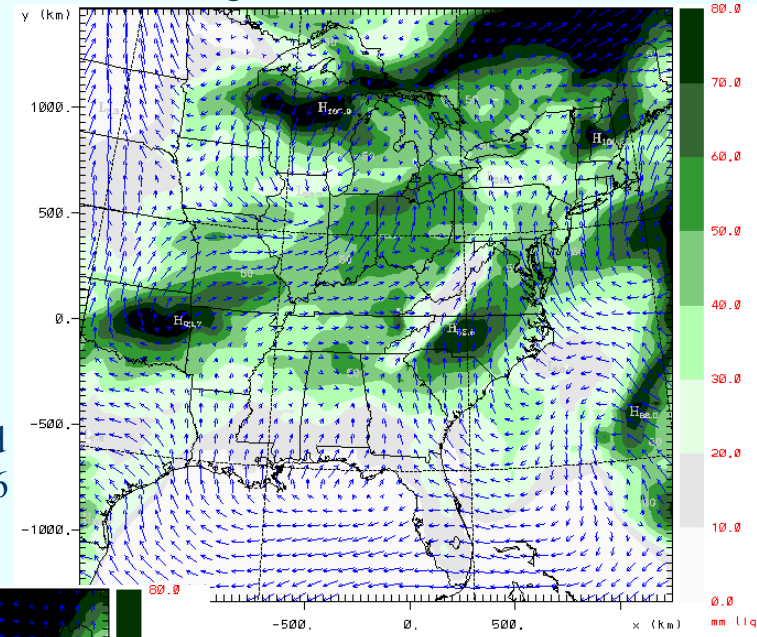
deposited quantity = emitted

### Total accumulated precipitation (mm) and wind speed (m/s) on 24 August 1997 00UTC



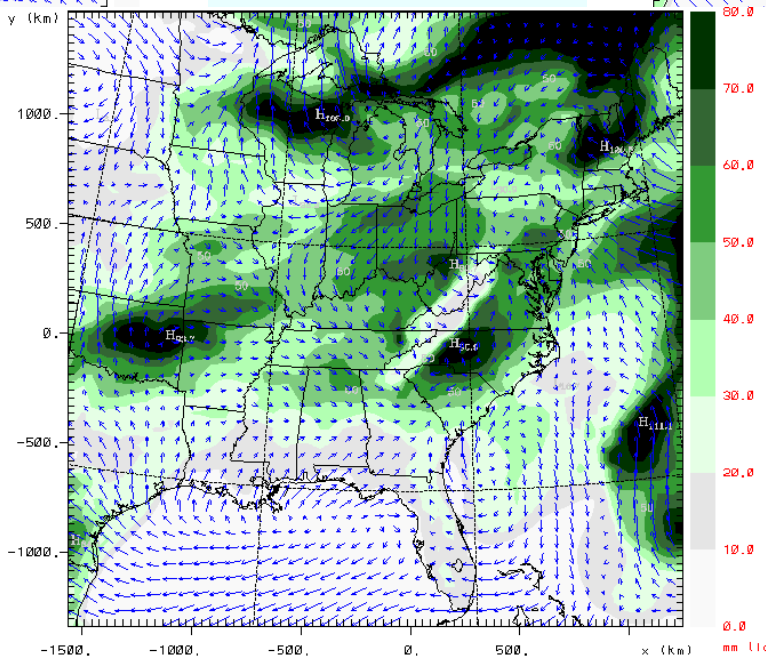
TEST		grid 1	
z =	69.2 m	1997-08-24-1200.00 UTC	
contours	total accum precip (mm liq)	0.000	168.
vectors	→	3 m/s horiz	0.2986E-01 10.

### Total accumulated precipitation (mm) and wind speed (m/s) on 25 August 1997 00UTC



	grid 1			
-08-25-0000.00 UTC	min	max	inc	leab*
accum precip (mm liq)	0.6345E-03	168.4	10.00	1e 0
m/s horiz	0.8000E-01	11.17		

### Total accumulated precipitation (mm) and wind speed (m/s) on 26 August 1997 00UTC



TEST		grid 1			
z =	69.2 m	1997-08-26-0000.00 UTC			
contours	total accum precip (mm liq)	0.1272E-02	168.0	10.00	1e 0
vectors	→	3 m/s horiz	0.6585E-01	12.87	

# CONCLUSIONS

In the new model development emphasis is given on accurate description of physical processes with direct coupling of mercury chemistry.

- This study presents an updated version of the RAMS - Hg atmospheric modeling system
- The latest system is based on the basic concepts adapted at the previous version
- New modules for describing the physical and chemical processes of mercury have been implemented
- The lack of systematic and detailed mercury measurements remains a problem for a detailed model validation
- Based on the limited deposition measurements from a previous study an attempt was made to evaluate the model performance
- The wet deposited amount of Hg calculated using the new modelling system was found to be in a closer agreement with observations compared to the previous one
- Further and more detailed validation is required
- This detailed validation will continue at the framework of the ongoing EU project MERCYMS

# ACKNOWLEDGEMENTS

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