CNR – Institute of Atmospheric Pollution Research, Italy

Influences of shipping emissions on Mediterranean air quality and radiative forcing

Enhancement of Mercury emissions at the sea water – atmosphere interface driven by regional climate change

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Rende, 12 June 2014

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Research activities are conducted within the framework of International, European and National projects. These activities often combine multiple disciplines, integrating the experimental, modeling, and regulatory components of atmospheric pollution research

- **Pollution in Urban and Industrial Areas**
- **Emerging Air Contaminants in Environmental Emissions**
- **Pollutant Cycles Across different Spatial Scales**
- **Global and Regional Atmospheric Modeling**
- **Sharing of Geospatial Information and Environmental Knowledge**

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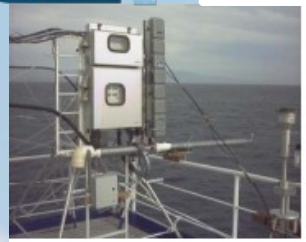

Taken from:http://www.gmos.eu/freedocuments/pirrone_presentation.pdf

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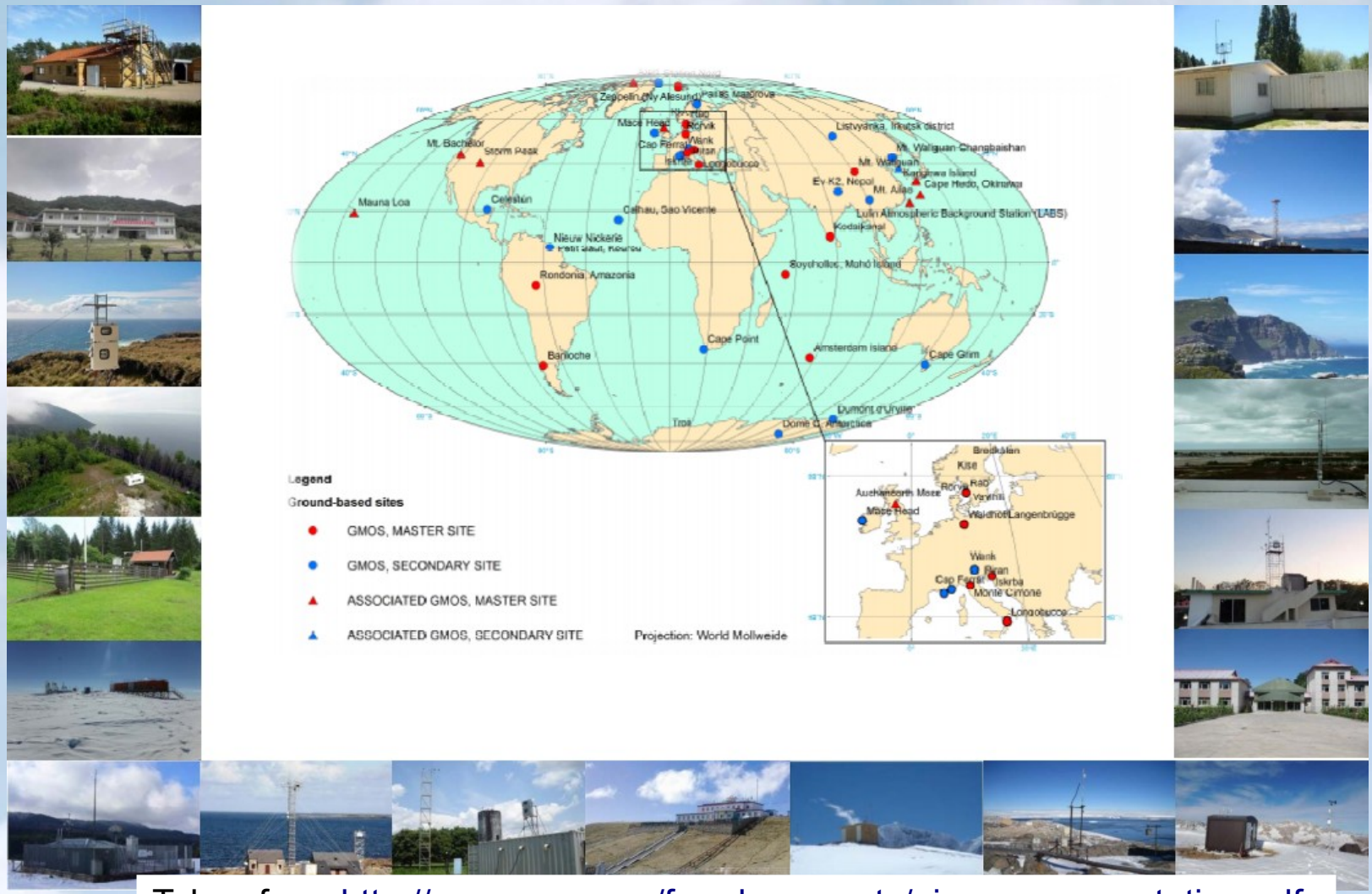

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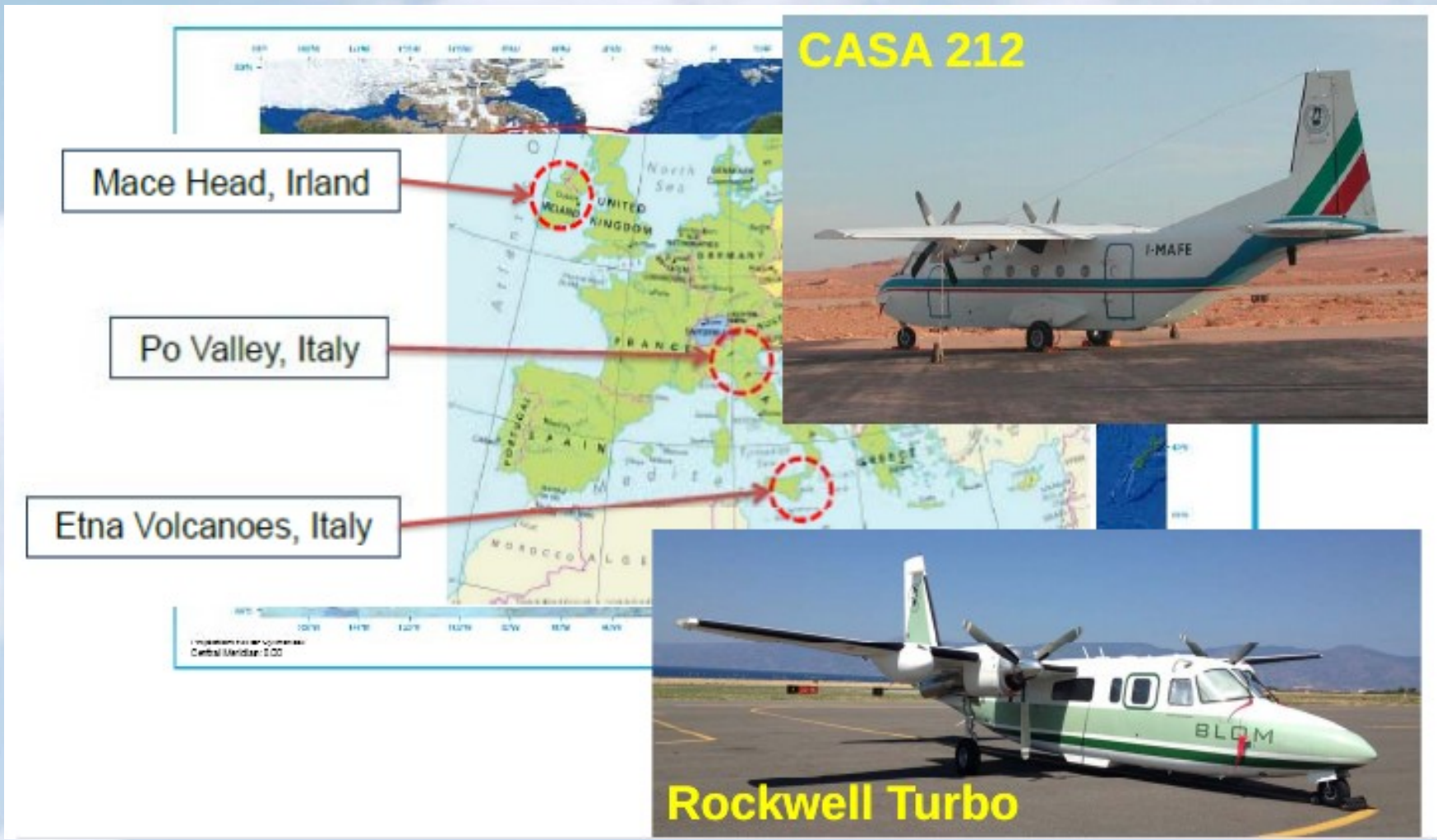

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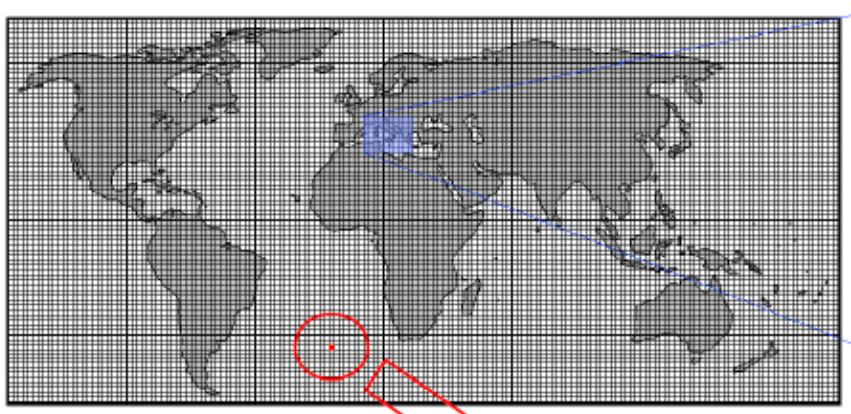
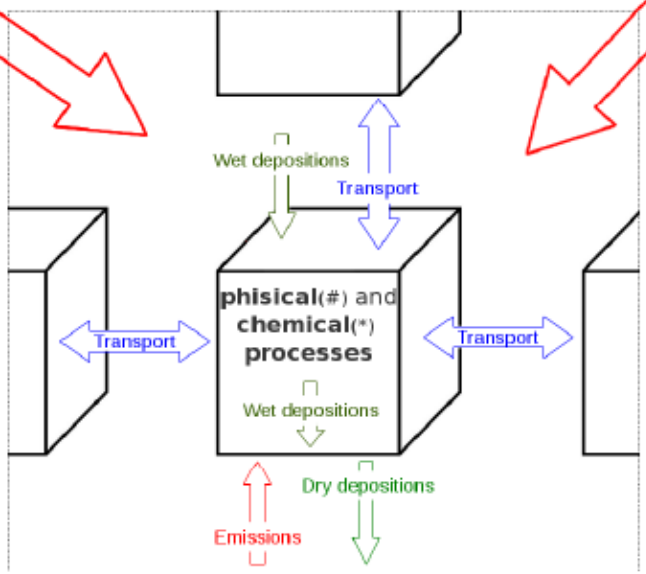


WRF/Chem Model

GLOBAL MODEL
Horizontal grid resolution
~ 200 Km
Temporal resolution
~ 30 min

ECHMERIT Model



REGIONAL MODEL
Horizontal grid resolution
~ 3 Km
Temporal resolution
< 1 min

(#) Interaction atmosphere - solar radiations
(#) Interaction atmosphere - soil/sea surface
(#) Cloud and atmospheric microphysics

(*) Emissions
(*) Photolisys
(*) Dry deposition
(*) Gaseous and acqueous phase reactions
(*) Wet deposition

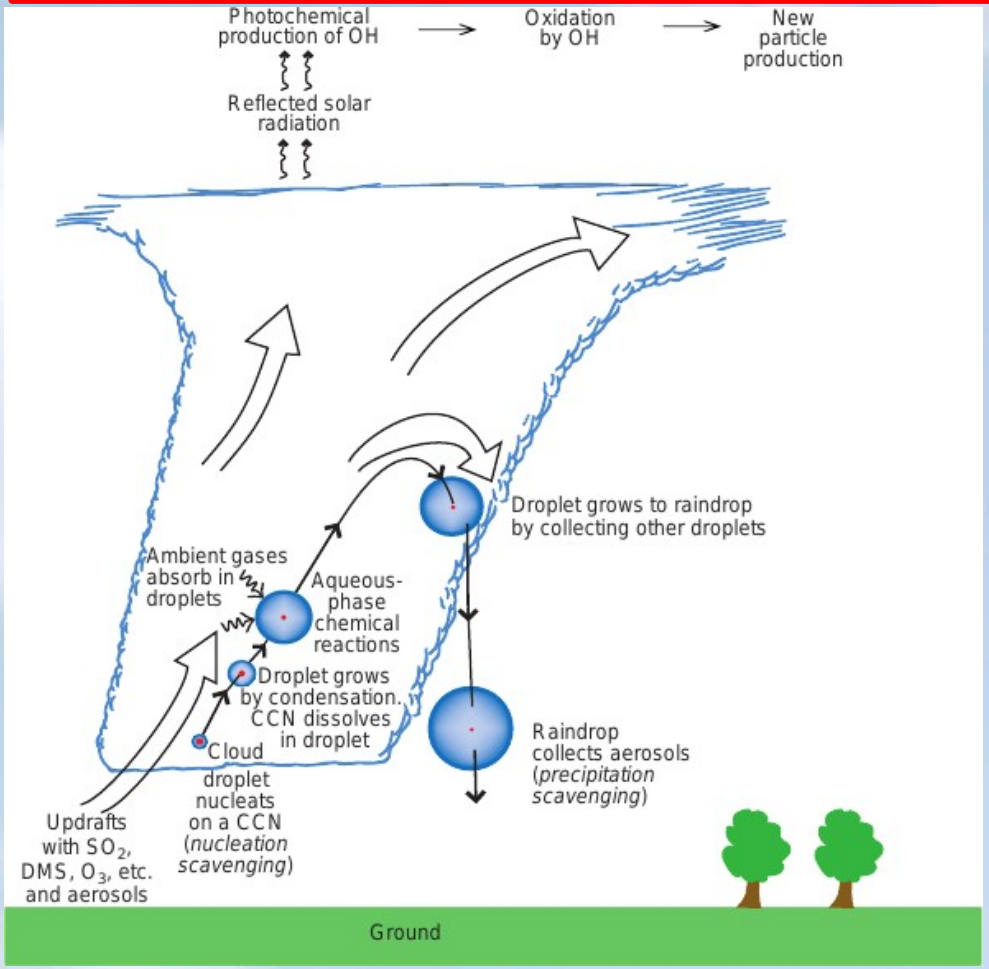
Taken from:http://www.gmos.eu/freedocuments/pirrone_presentation.pdf

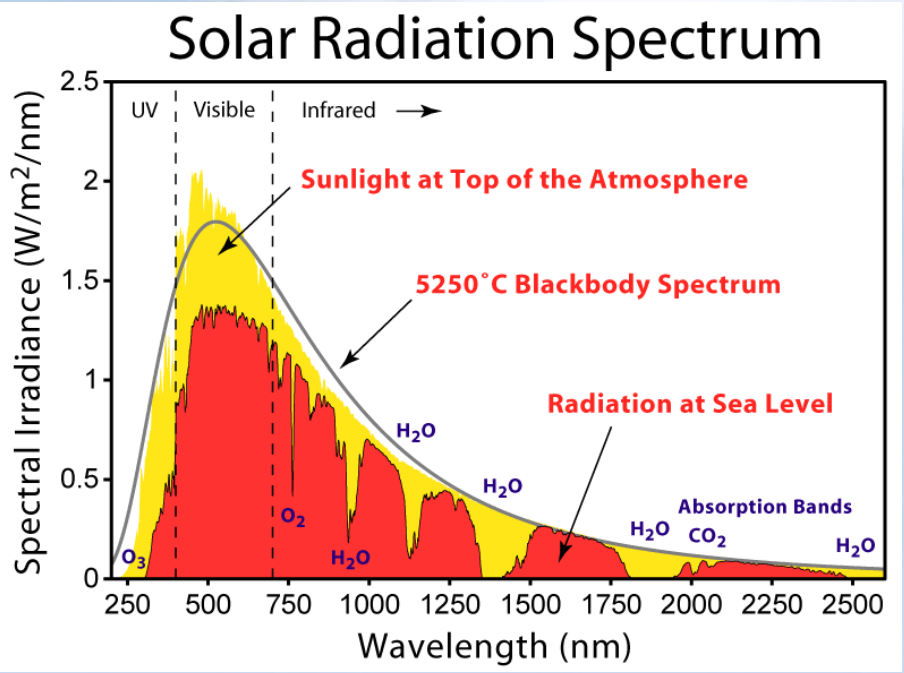
Hydrology ↔ Air quality

Air quality → Hydrology

Precipitations: Cloud Condensation Nuclei

Solar radiation: photolysis, scattering, absorption, ...

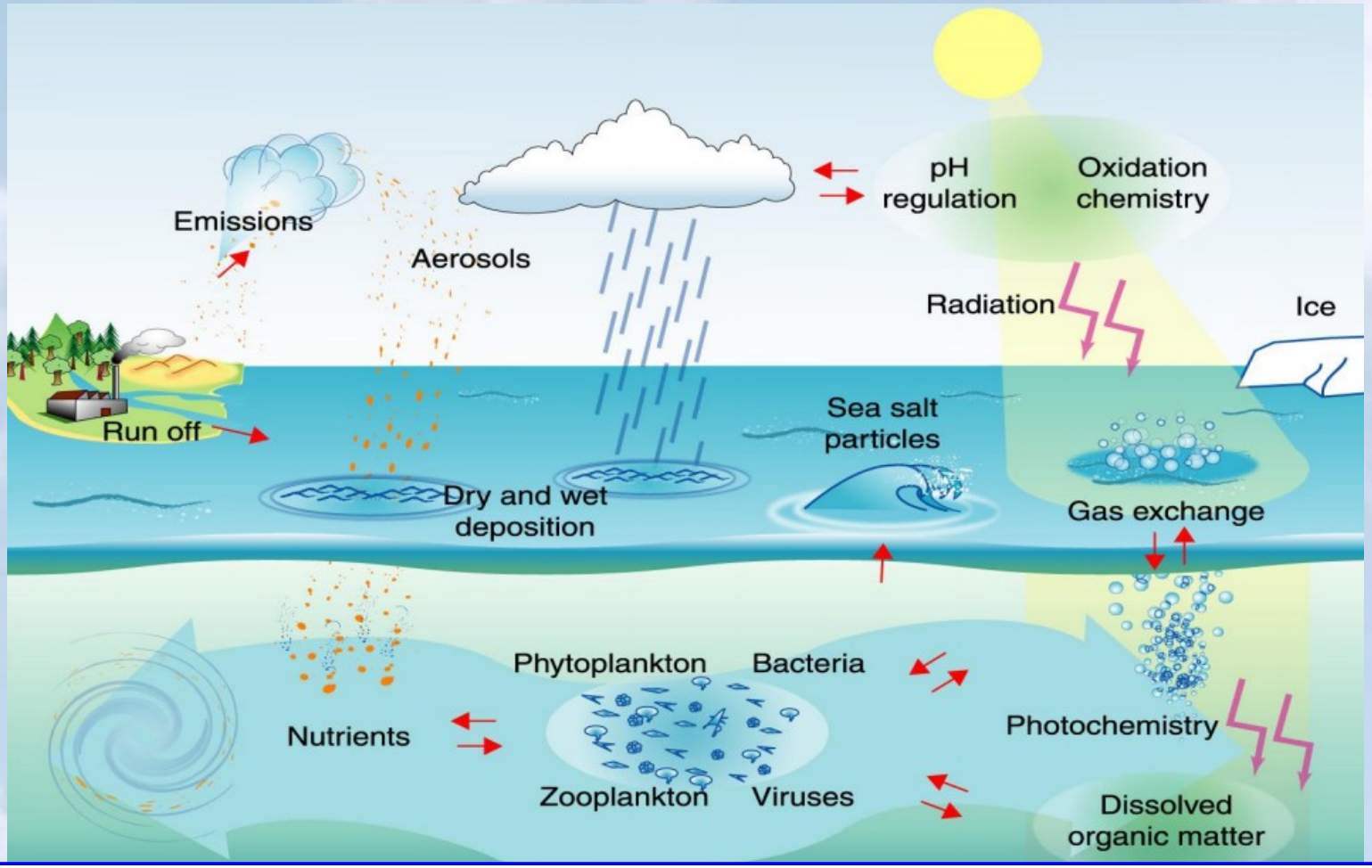




Hydrology ↔ Air quality

Hydrology → Air quality

Removal processes, interface exchange, aqueous phase oxidation, ...



Hydrology ↔ Air quality

A measure of the amount of potentially harmful or damaging substances there are in the air: **POLLUTION**, defined as the presence of a substance that may have harmful effects on human health and/or on the environment

Air Quality Modelling

- gives the opportunity to understand and simulate the dynamics of complex systems
- provides an estimation which is more extensive in time and space of the concentration fields and deposition of pollutants
- investigates the role of individual processes or reactions on air quality

WRF/Chem Model

- **weather conditions**, which determine dispersion, transport and deposition

TOGETHER WITH

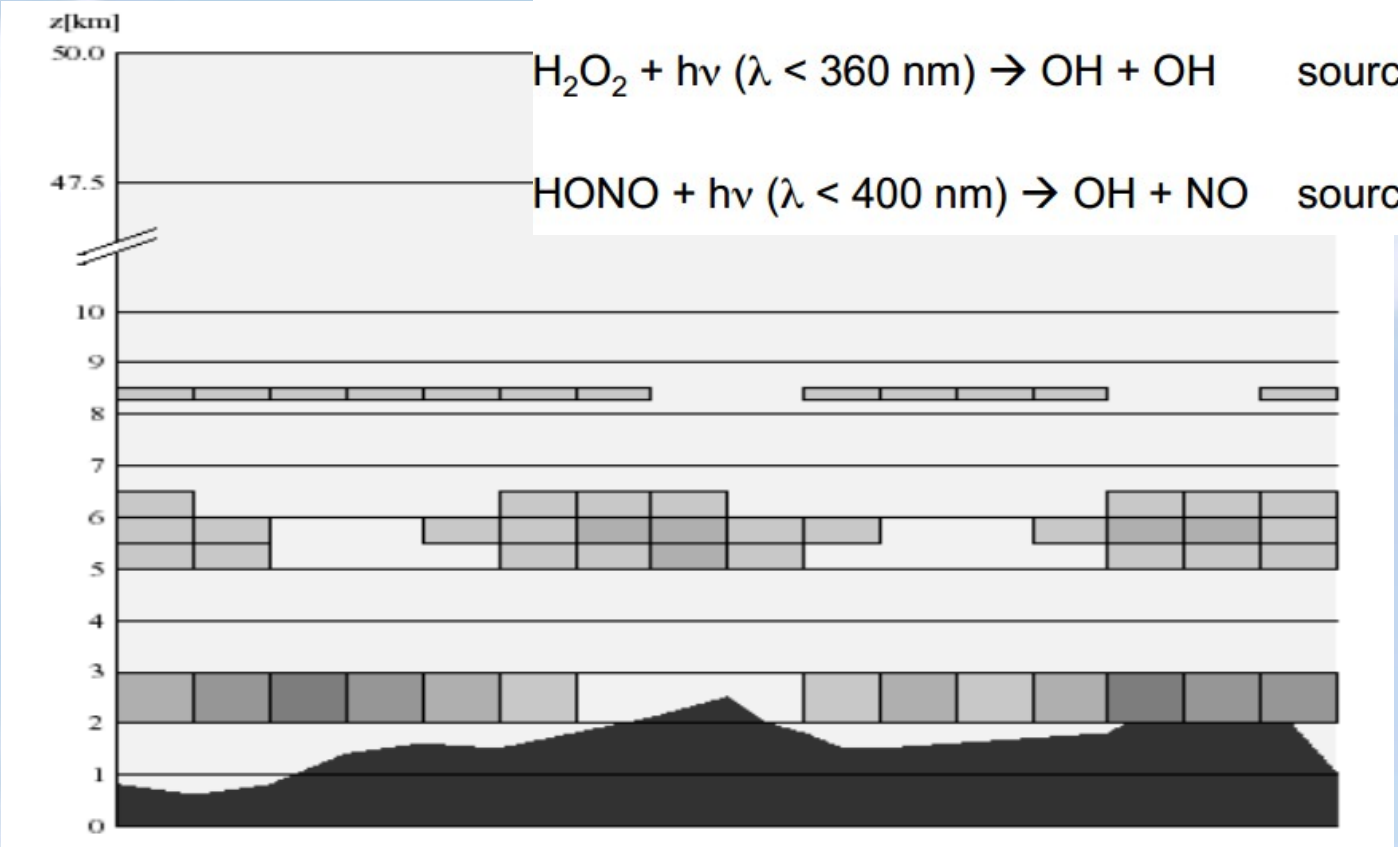
- **chemical interactions** between atmospheric constituents

the atmospheric physics and chemistry are solved in the same time-step

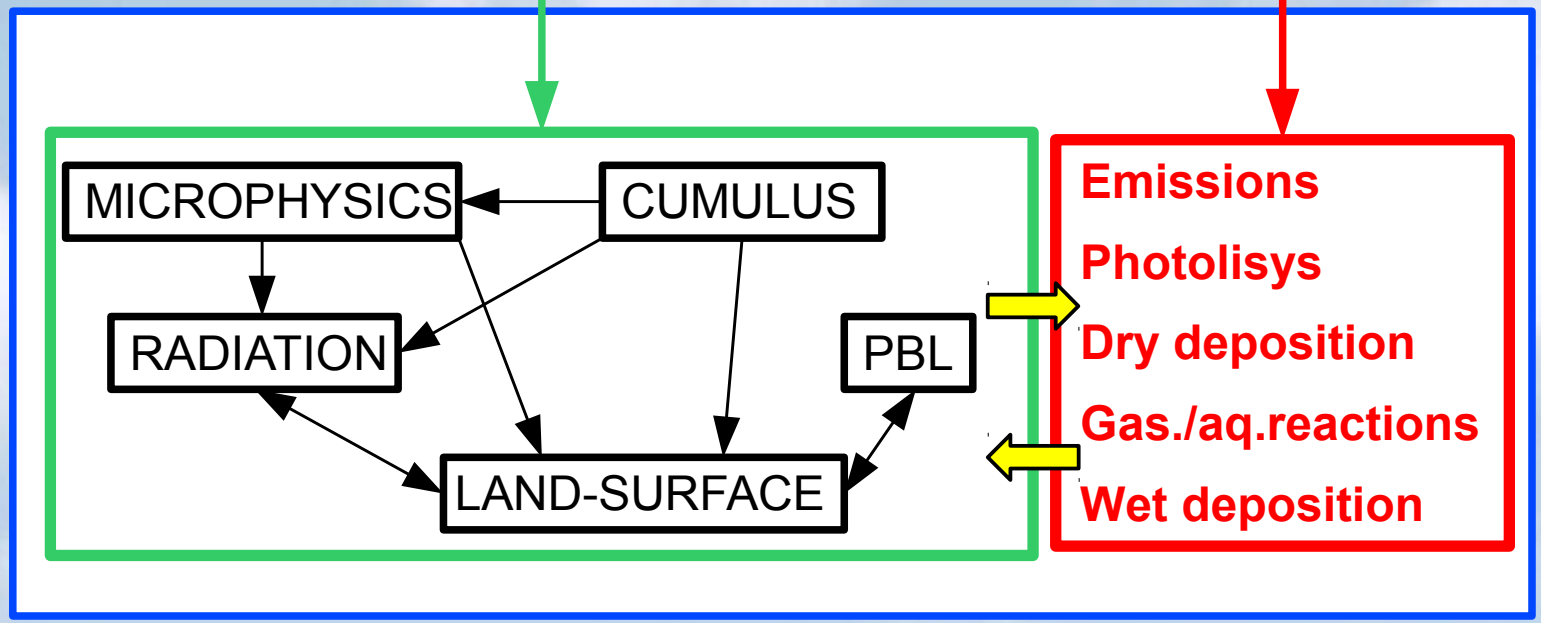
$O^3P + O_2 \rightarrow O_3$
$O^3P + O_3 \rightarrow 2\,O_2$
$O^1D + N_2 \rightarrow O^3P + N_2$
$O^1D + O_2 \rightarrow O^3P + O_2$
$O^1D + H_2O \rightarrow HO + HO$
$O_3 + HO \rightarrow HO_2 + O_2$
$O_3 + HO_2 \rightarrow HO + 2\,O_2$
$HO + HO_2 \rightarrow H_2O + O_2$
$H_2O_2 + HO \rightarrow HO_2 + H_2O$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + H_2O$
$O^3P + NO \rightarrow NO_2$
$O^3P + NO_2 \rightarrow NO + O_2$
$O^3P + NO_2 \rightarrow NO_3$
$HO + NO \rightarrow HONO$
$HO + NO_2 \rightarrow HNO_3$
$HO + NO_3 \rightarrow NO_2 + HO_2$
$HO_2 + NO \rightarrow NO_2 + HO$
$HO_2 + NO_2 \rightarrow HNO_4$
$HNO_4 \rightarrow HO_2 + NO_2$
$HO_2 + NO_3 \rightarrow 0.3\,HNO_3 + 0.7\,NO_2 + 0.7\,HO + O_2$
$HO + HONO \rightarrow NO_2 + H_2O$
$HO + HNO_3 \rightarrow NO_3 + H_2O$
$HO + HNO_4 \rightarrow NO_2 + O_2 + H_2O$
$O_3 + NO \rightarrow NO_2 + O_2$
$O_3 + NO_2 \rightarrow NO_3 + O_2$
$NO + NO + O_2 \rightarrow NO_2 + NO_2$
$NO_3 + NO \rightarrow NO_2 + NO_2$
$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$
$NO_3 + NO_2 \rightarrow N_2O_5$
$N_2O_5 \rightarrow NO_2 + NO_3$
$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$
$HO + H_2 \rightarrow H_2O + HO_2$
$HO + SO_2 \rightarrow SULF + HO_2$
$CO + HO \rightarrow HO_2 + CO_2$

WRF/Chem Model

$O_2 + h\nu\ (\lambda < 240\ nm) \rightarrow O + O$	source of O_3 in stratosphere
$O_3 + h\nu\ (\lambda < 340\ nm) \rightarrow O_2 + O(^1D)$	source of OH in troposphere
$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O(^3P)$	source of O_3 in troposphere
$CH_2O + h\nu\ (\lambda < 330\ nm) \rightarrow H + HCO$	source of HOx, everywhere
$H_2O_2 + h\nu\ (\lambda < 360\ nm) \rightarrow OH + OH$	source of OH in remote atm.
$HONO + h\nu\ (\lambda < 400\ nm) \rightarrow OH + NO$	source of radicals in urban atm.



WRF/Chem Model

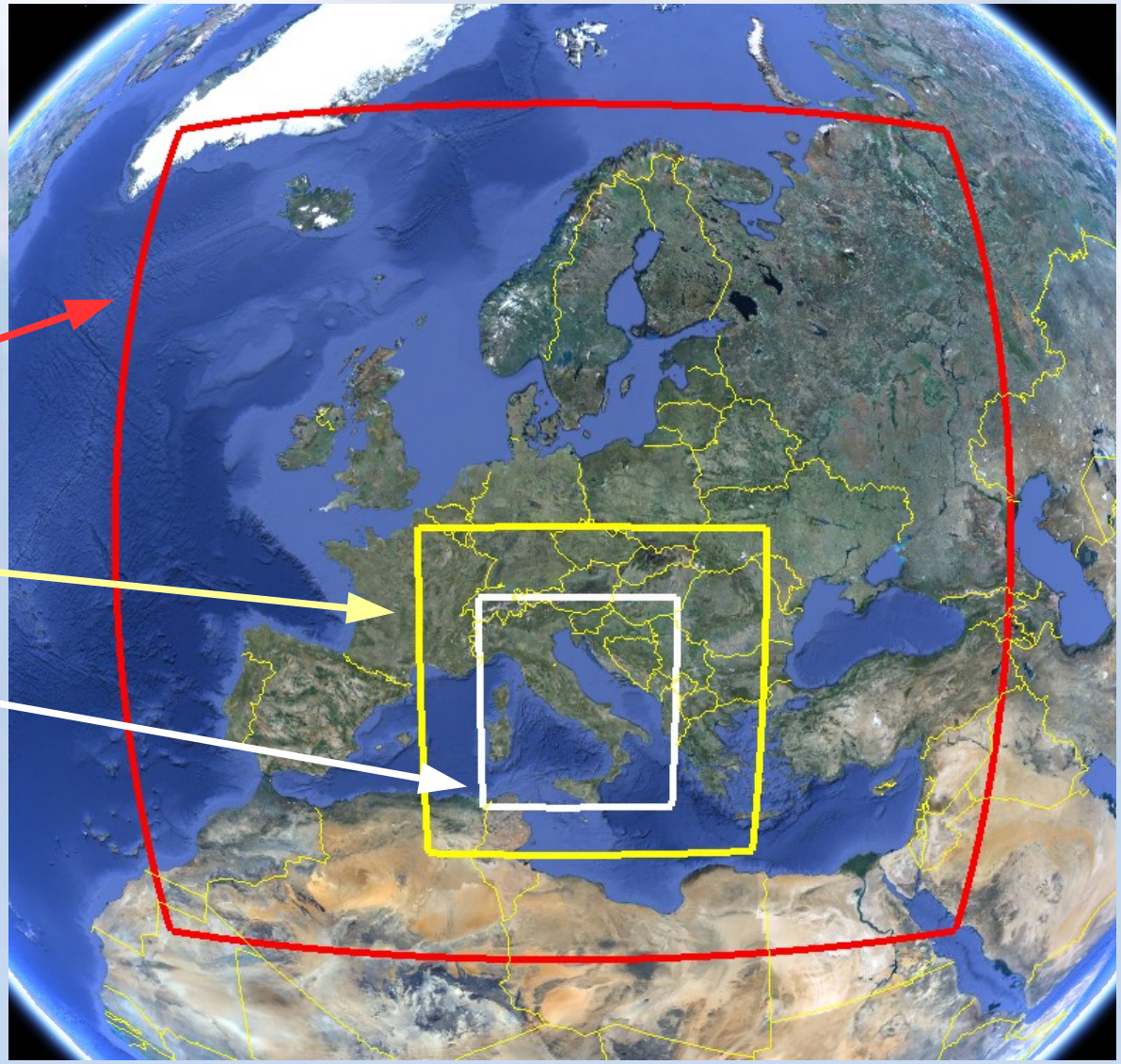


WRF/Chem Model

81 km²

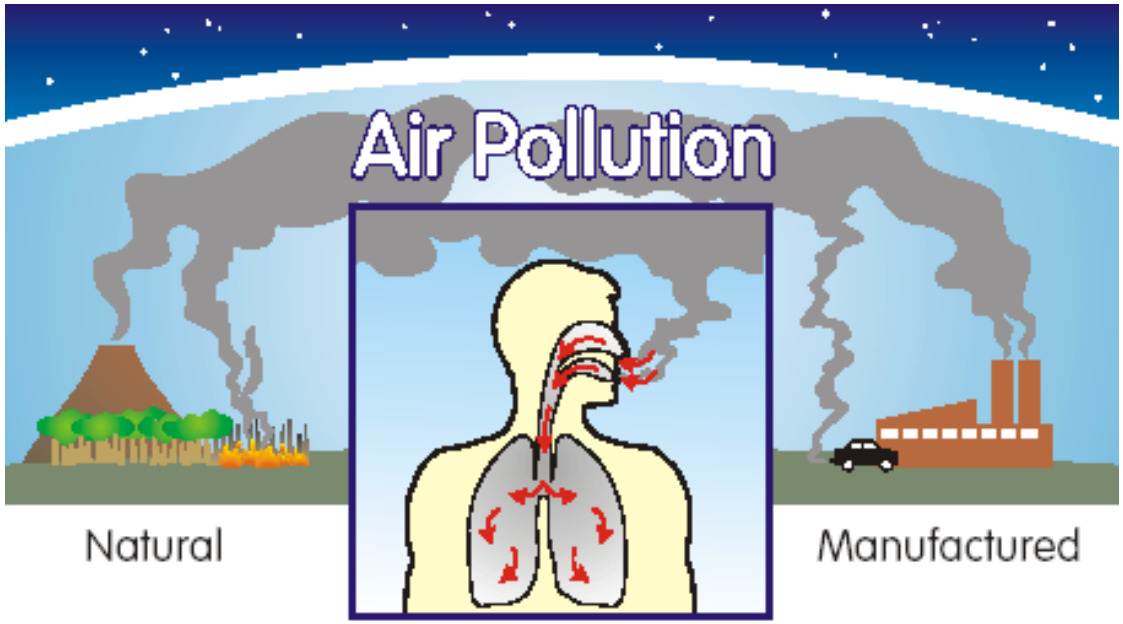
27 km²

9 km²



WRF/Chem Model

Influences of shipping emissions on Mediterranean air quality and radiative forcing



TROPOSPHERIC OZONE

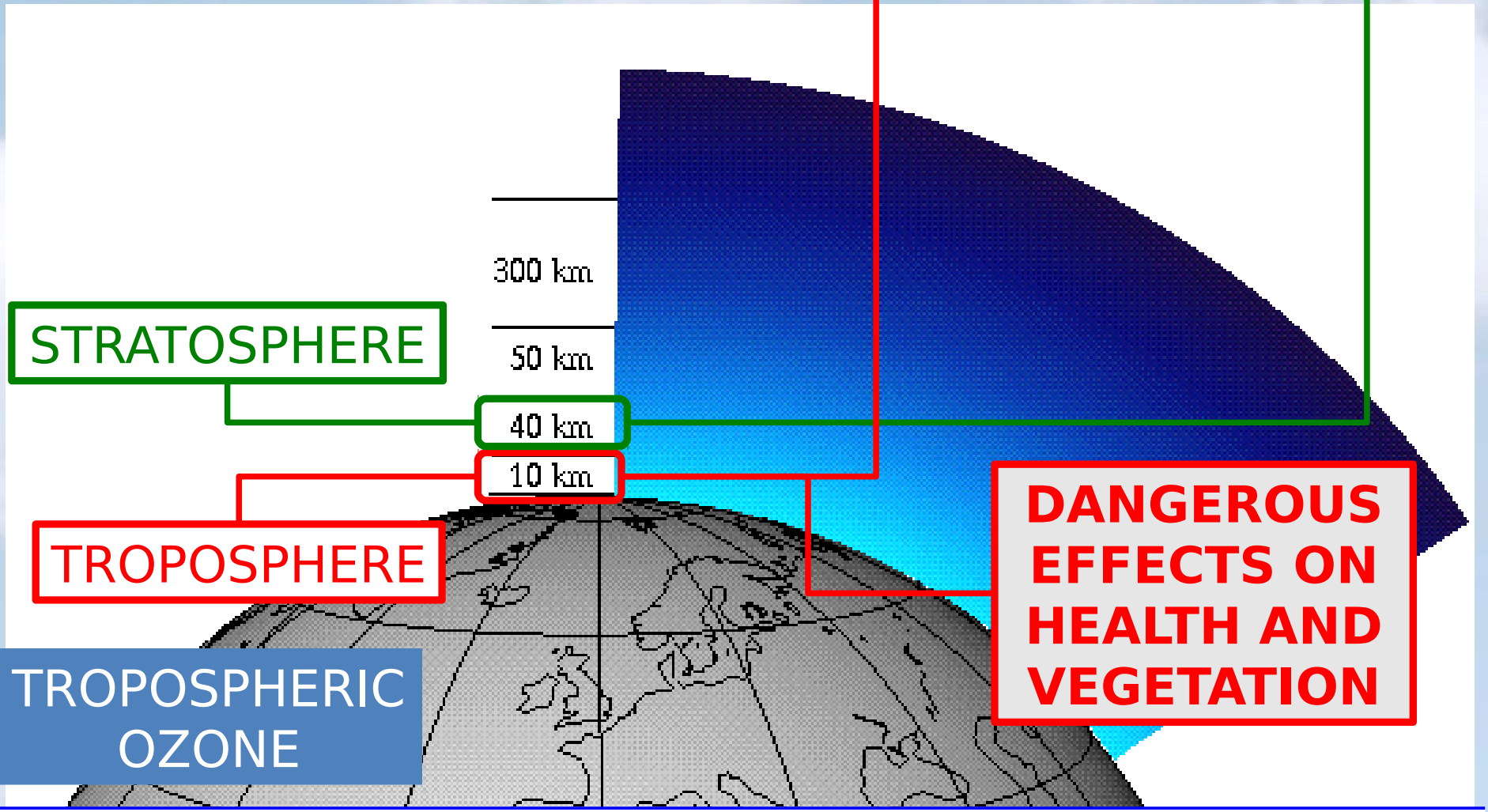
Enhancement of Mercury emissions at the sea water – atmosphere interface driven by regional climate change

MERCURY

WRF/Chem Model

dangerous pollutant

UV filters



WRF/Chem Model

Ozone is a secondary pollutant...

$$NO_2 + h\nu(\lambda < 424\,nm) \longrightarrow NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

PRODUCED BY NO_2

$$NO + O_3 \longrightarrow NO_2 + O_2$$

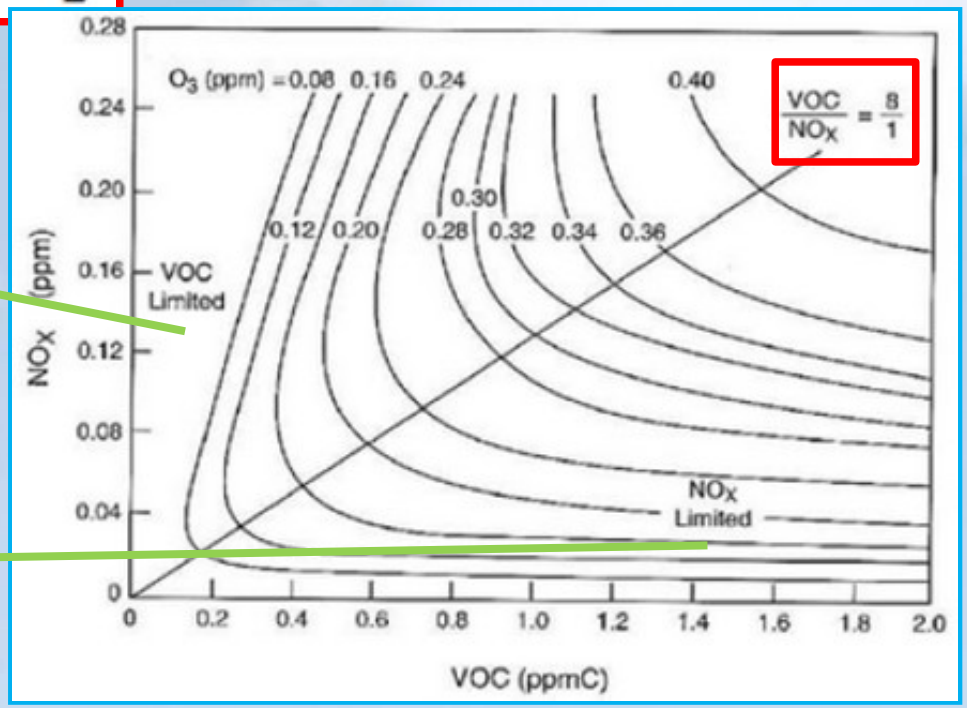
DESTROYED BY NO

Cycle and atmospheric interactions complex: further reactions

Urban areas

Rural areas

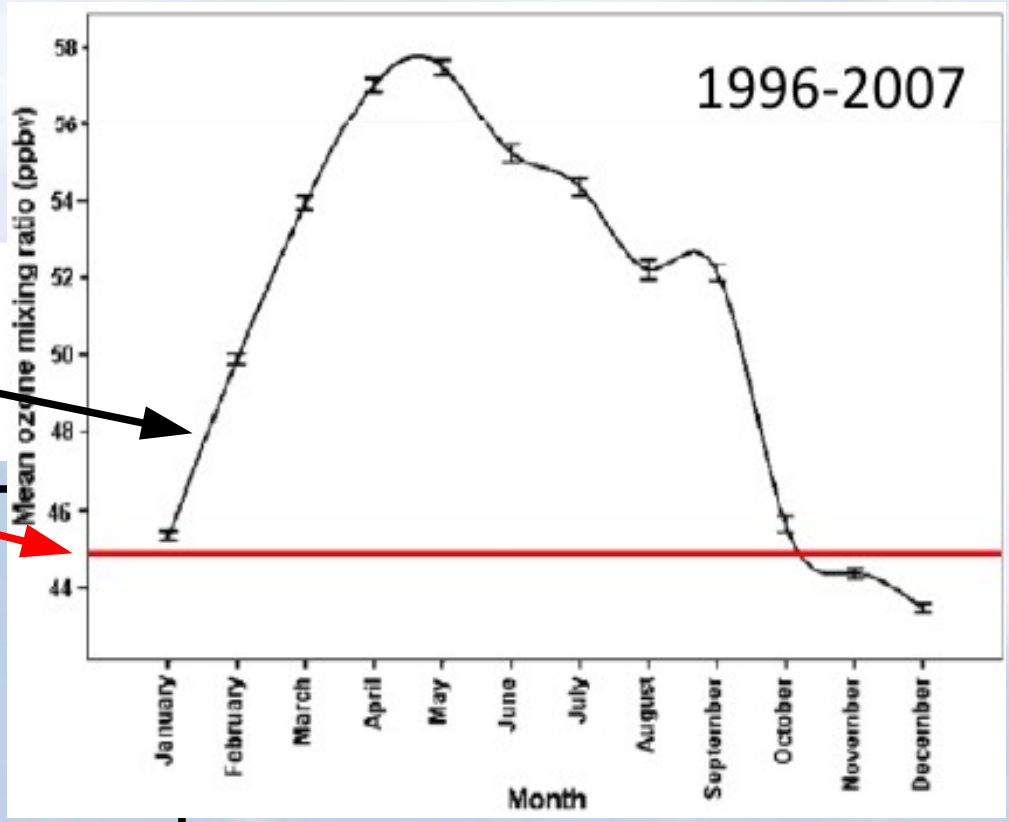
TROPOSPHERIC OZONE



High concentrations of tropospheric ozone in Mediterranean Region

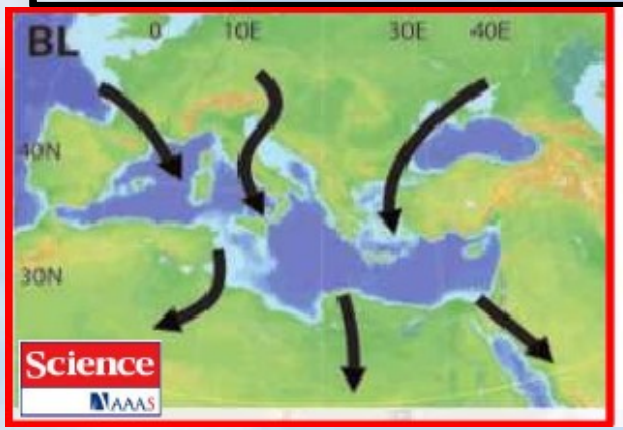
Mediterranean Mean

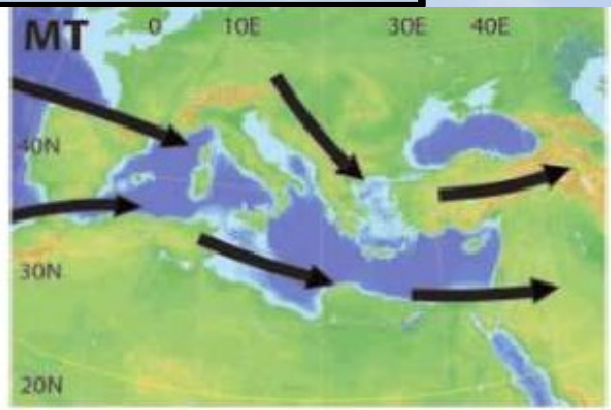
Global Mean

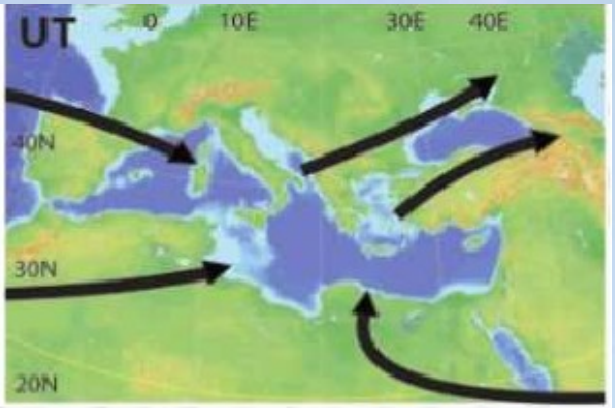


Validate the model result with oceanographic measurements

Estimate the influence of ship emissions

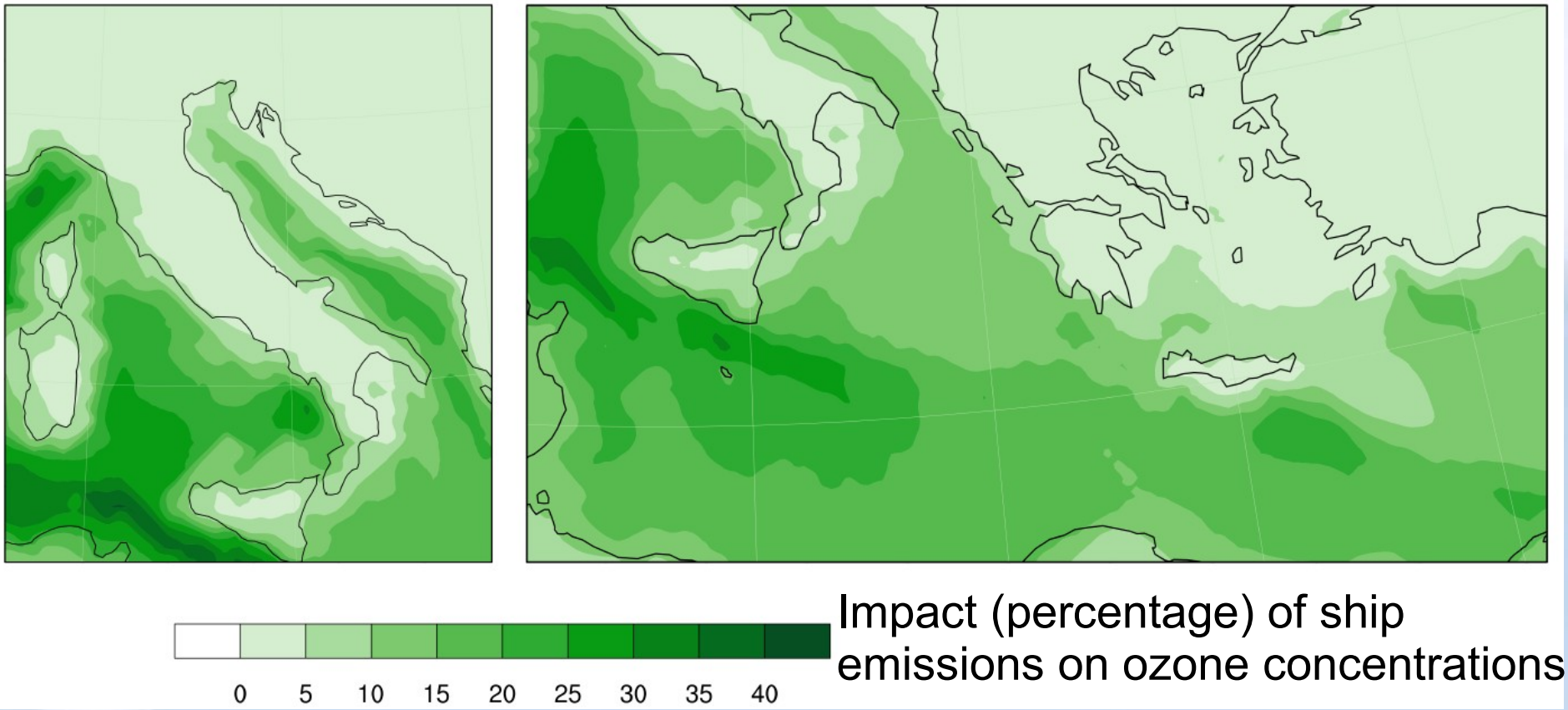






WRF/Chem Model

~ 5% inland
~ 10% costal
~ 30 % intense traffic



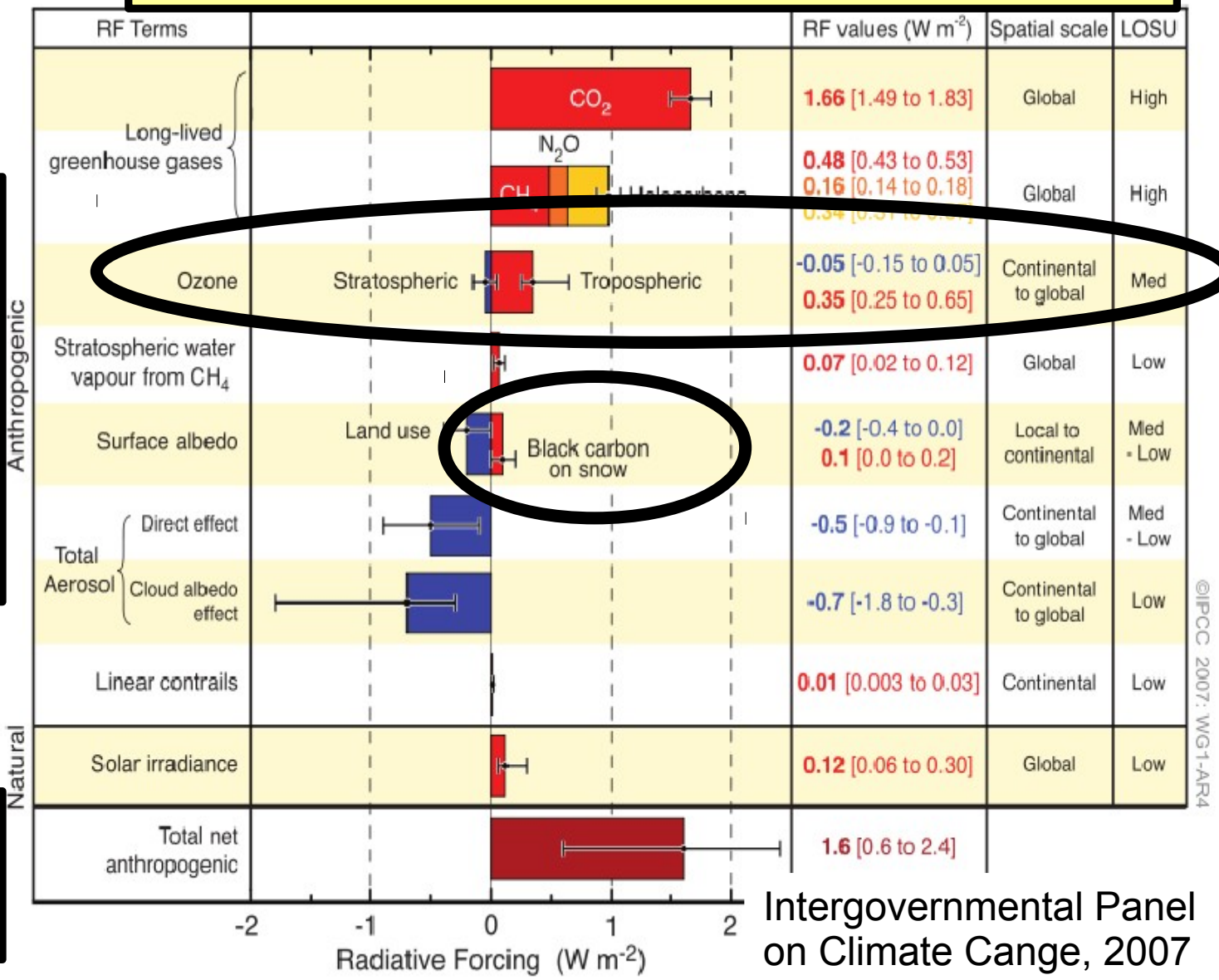
Impact (percentage) of ship emissions on ozone concentrations

WRF/Chem Model

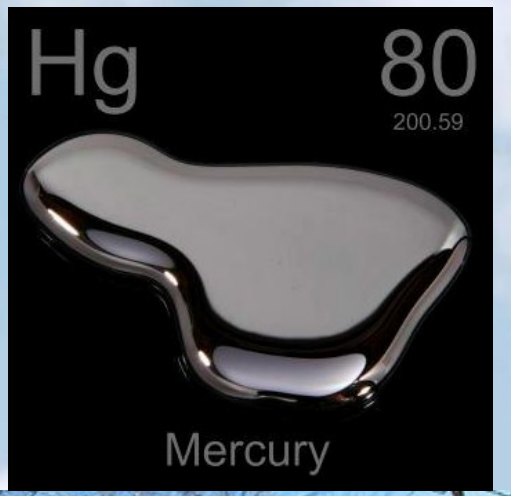
Short-lived climate forcers

It is possible to estimate the change in the radiation budget

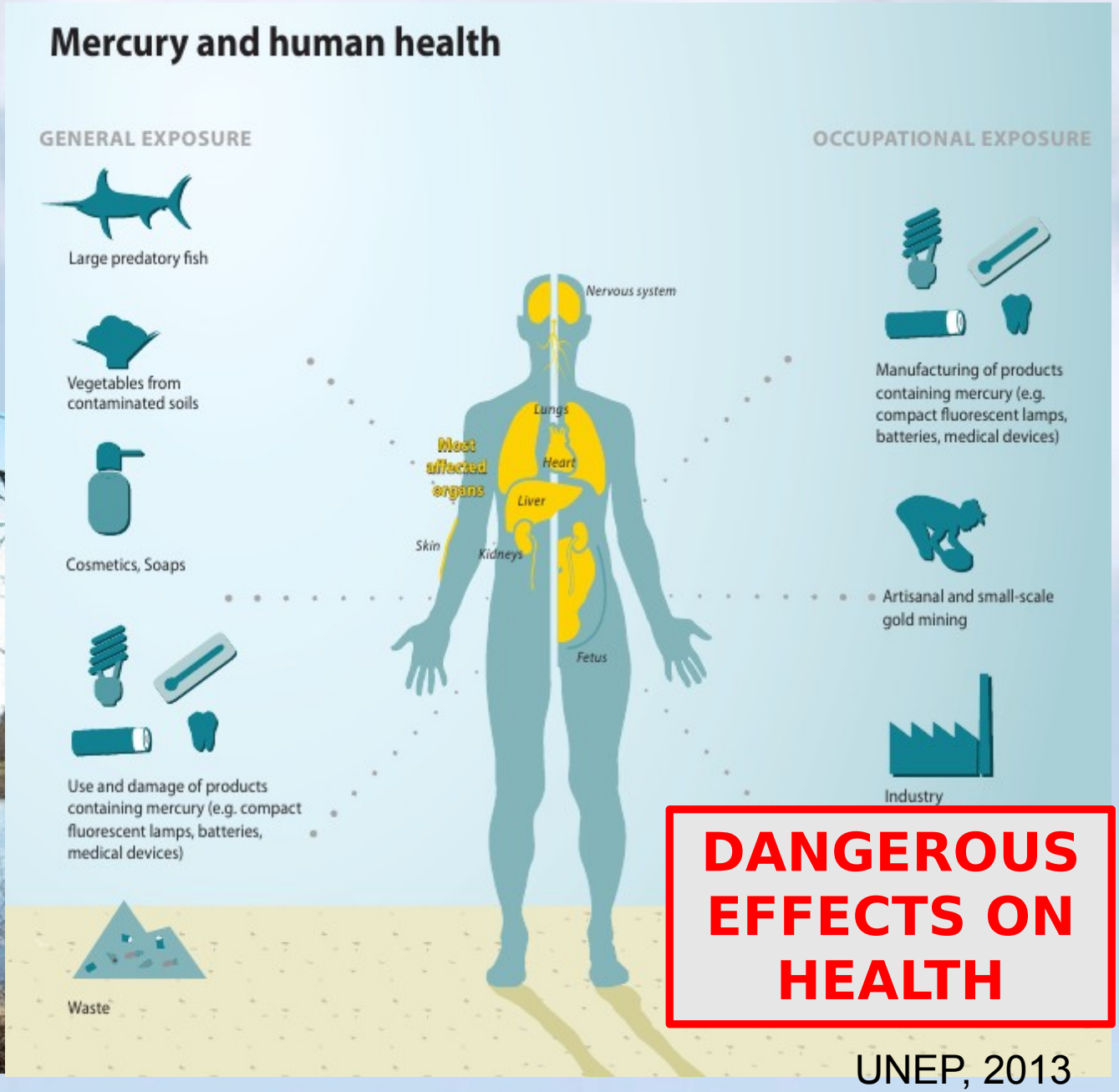
Work in progress...



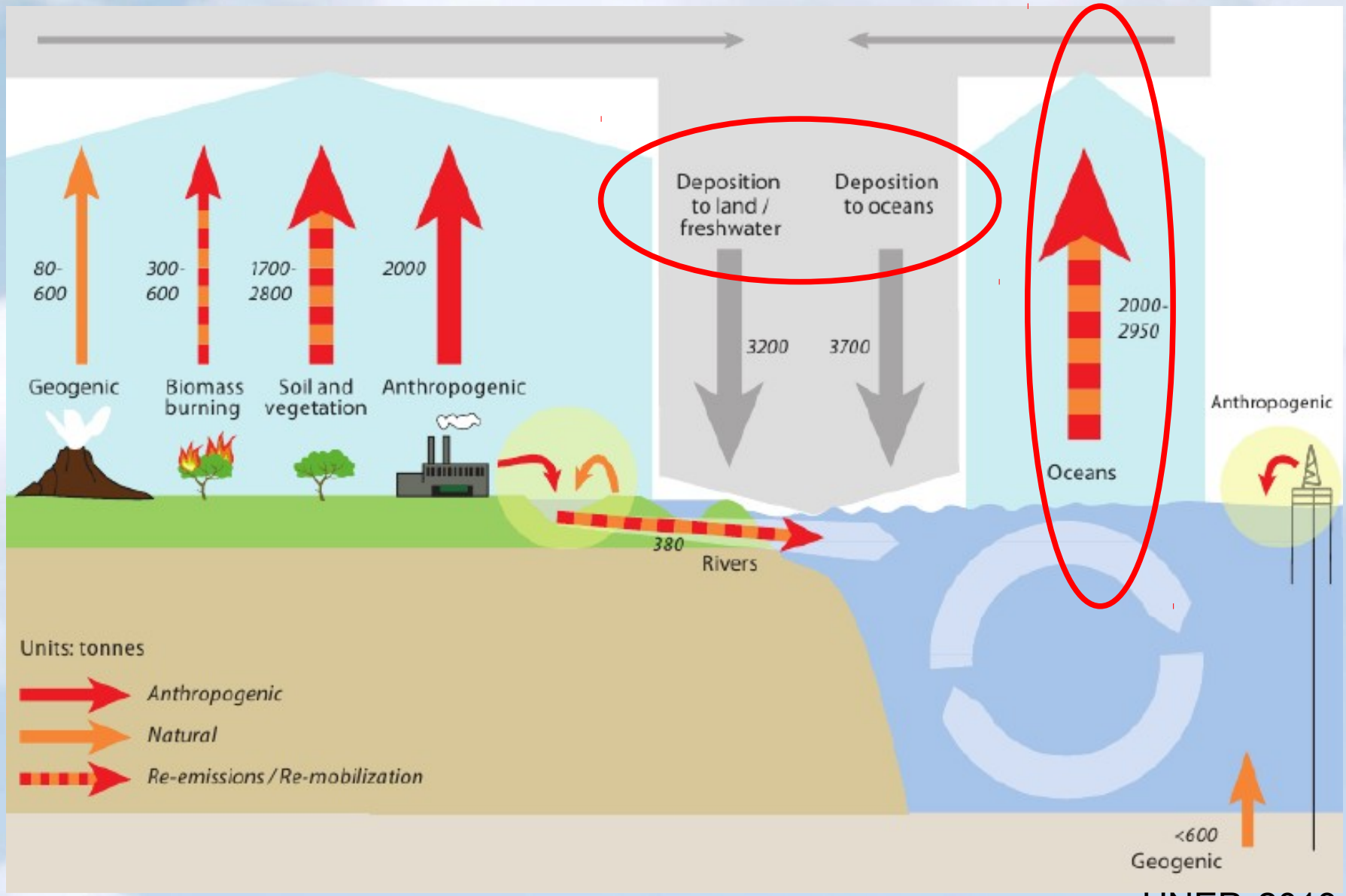
Intergovernmental Panel on Climate Cange, 2007


Hg
80
200.59
Mercury


WARNING
Sudbury River Fish
Fish Contaminated With Mercury
DO NOT EAT
Pescado Contaminado Con Mercurio
No Se Puede Comer

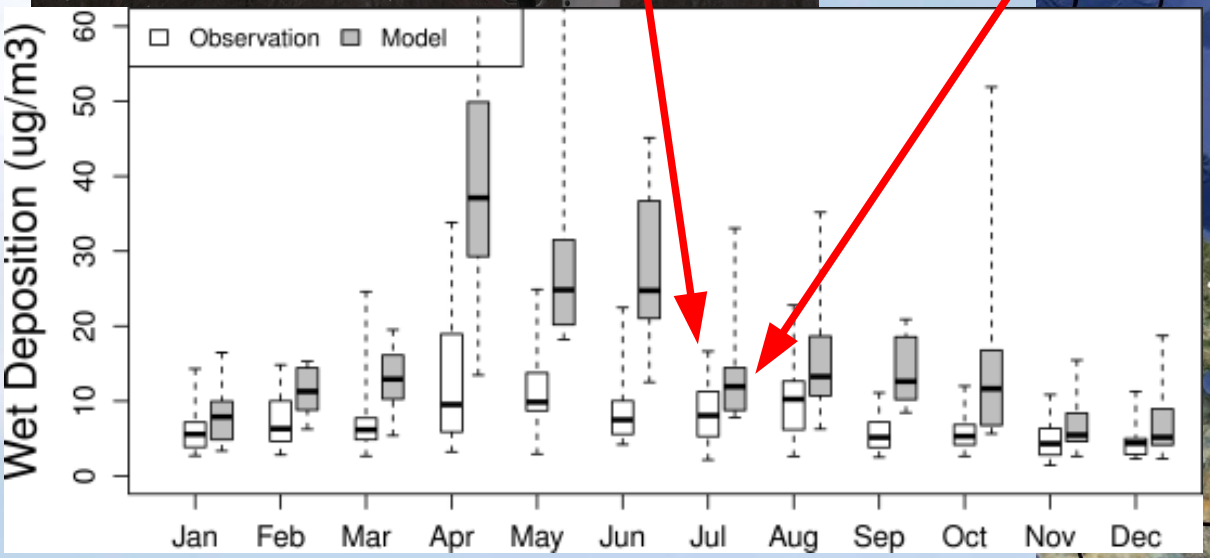

Mercury and human health
GENERAL EXPOSURE
OCCUPATIONAL EXPOSURE
Large predatory fish
Vegetables from contaminated soils
Cosmetics, Soaps
Use and damage of products containing mercury (e.g. compact fluorescent lamps, batteries, medical devices)
Waste
Nervous system
Lungs
Most affected organs
Heart
Liver
Skin
Kidneys
Fetus
Manufacturing of products containing mercury (e.g. compact fluorescent lamps, batteries, medical devices)
Artisanal and small-scale gold mining
Industry
DANGEROUS EFFECTS ON HEALTH

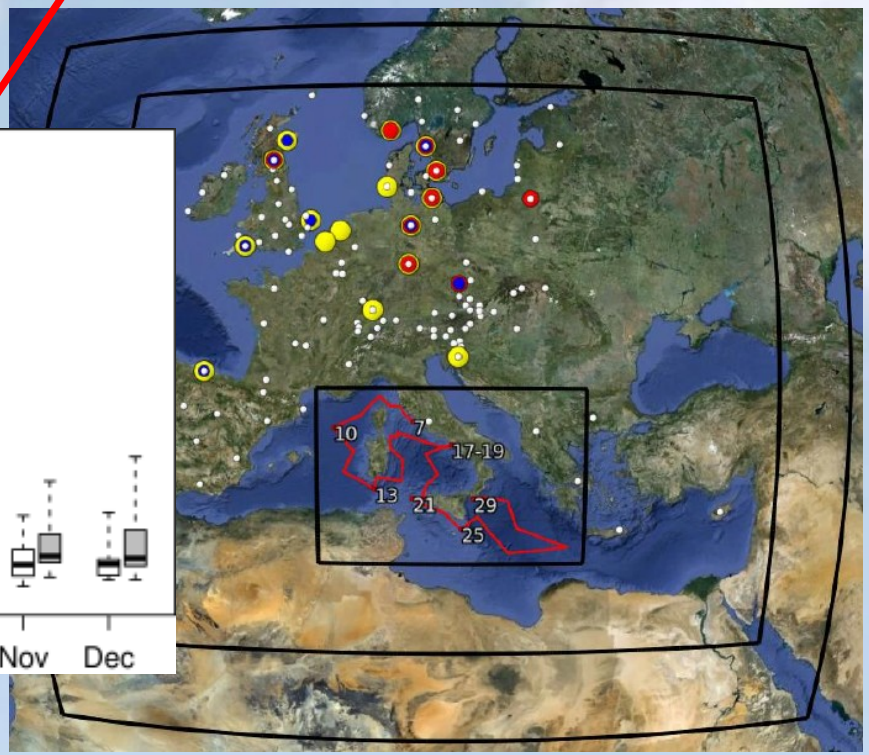
UNEP, 2013


80-600
300-600
1700-2800
2000
Geogenic
Biomass burning
Soil and vegetation
Anthropogenic
Deposition to land / freshwater
Deposition to oceans
3200
3700
2000-2950
Oceans
Anthropogenic
380
Rivers
Units: tonnes
Anthropogenic
Natural
Re-emissions / Re-mobilization
<600
Geogenic

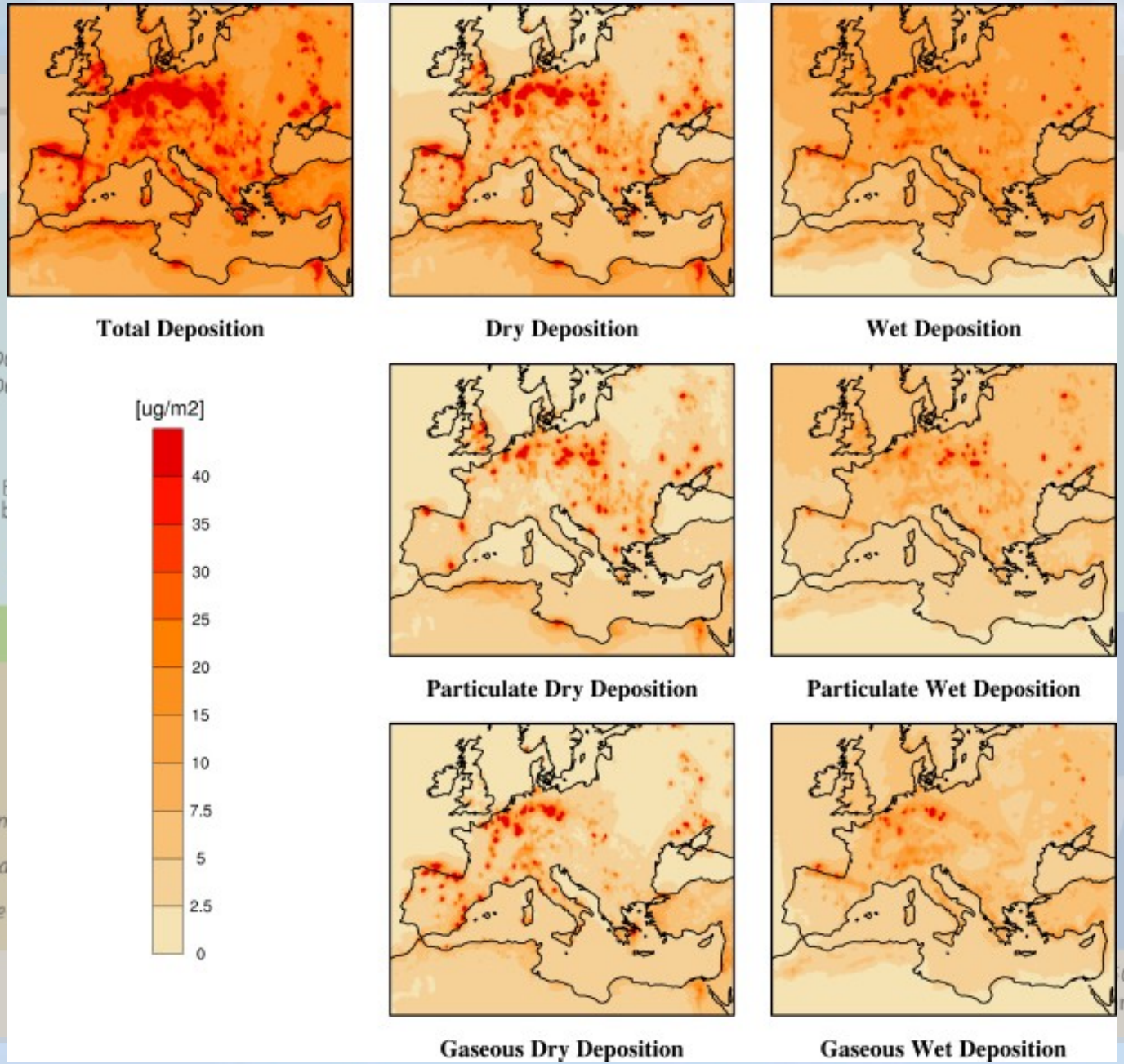
UNEP, 2013

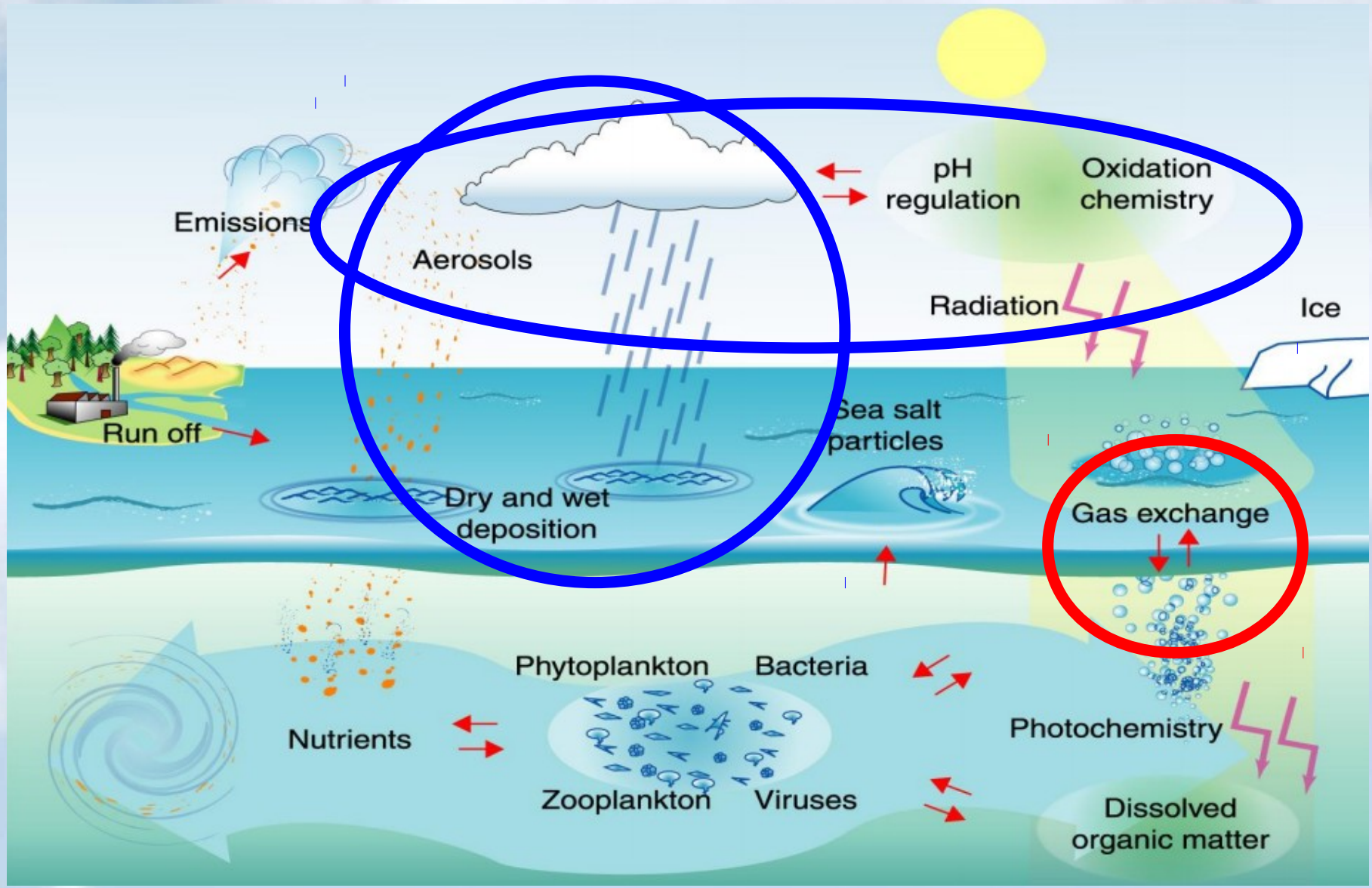
WRF/Chem with Hg





Gencarelli et al. (2013) ESPR
DOI: 10.1007/s11356-013-2162-3


Total Deposition
Dry Deposition
Wet Deposition
[ug/m2]
40
35
30
25
20
15
10
7.5
5
2.5
0
Particulate Dry Deposition
Particulate Wet Deposition
Gaseous Dry Deposition
Gaseous Wet Deposition


pH
regulation
Oxidation
chemistry
Emissions
Aerosols
Radiation
Ice
Run off
Sea salt
particles
Dry and wet
deposition
Gas exchange
Phytoplankton
Bacteria
Nutrients
Photochemistry
Zooplankton
Viruses
Dissolved
organic matter

Specifically, in the model the Hg^0 fluxes are computed using the two-layer gas exchange model introduced by Liss and Slater (1974):

$$F = K_w(C_w - C_a/H(T))$$

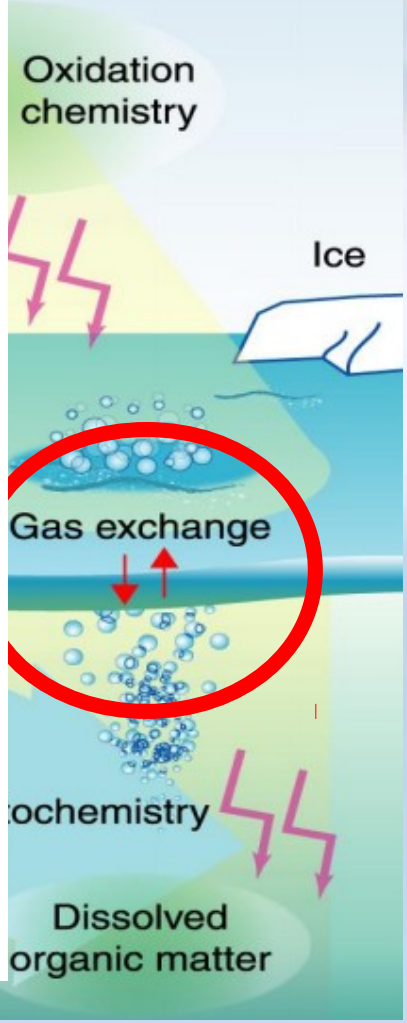
where F is the Hg^0 flux, in ng m^{-2} h^{-1}, K_w is the water-side mass transfer coefficient, in m h^{-1}, $H(T)$ is the Henry's Law constant corrected for the temperature T, and C_w and C_a, both expressed in ng m^{-3}, are the Hg^0 concentrations in seawater and in air, respectively. The water-side mass transfer coefficient K_w was calculated by using the parameterization of Wanninkhof (1992):

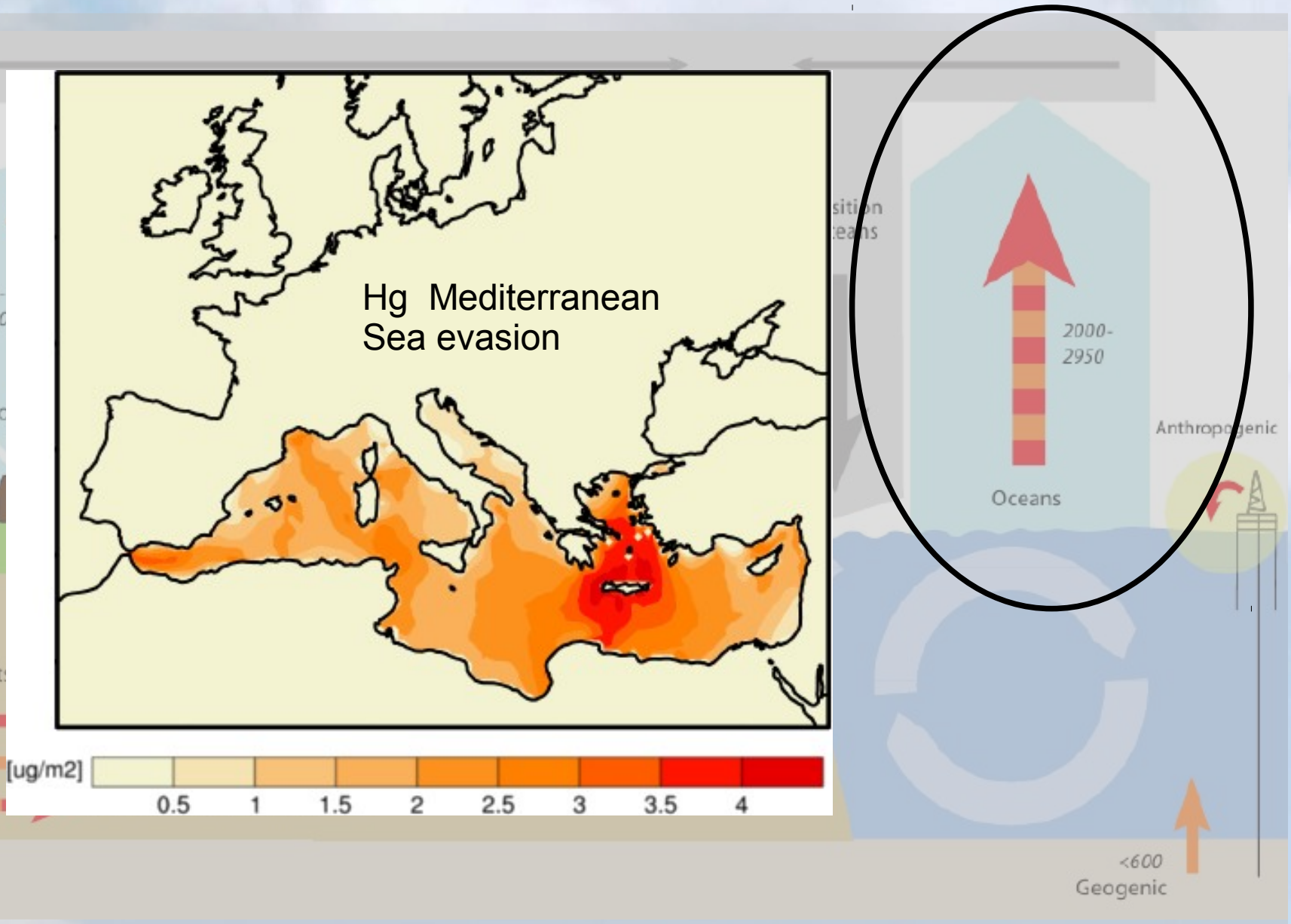
$$K_w = 0.31 \times u_{10}^2 (Sc_{Hg}/Sc_{CO})^{-0.5}$$

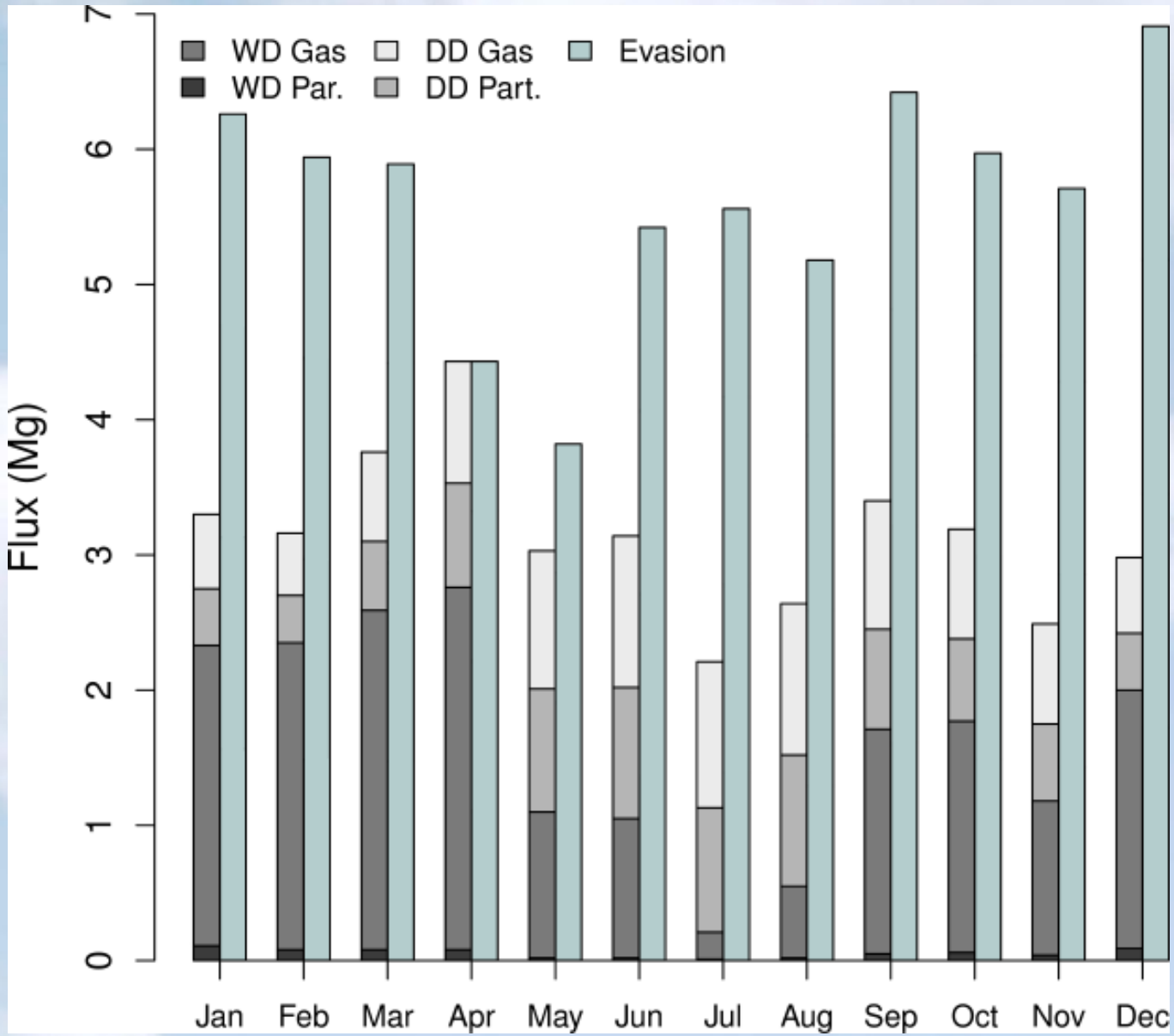
where u_{10} is the wind speed 10 meter above sea surface and Sc_{Hg} and Sc_{CO} are the Schmidt number of mercury and Carbon Oxide, respectively. The parameterization of Andersson *et al.* (2008) was used to calculate the temperature dependent Henry's law constant:

$$H(T) = e^{(\frac{-2404.3}{T} + 6.92)}$$

A positive value of F indicates a net Hg flux from the ocean to atmosphere whereas a negative flux would indicate deposition to the ocean.



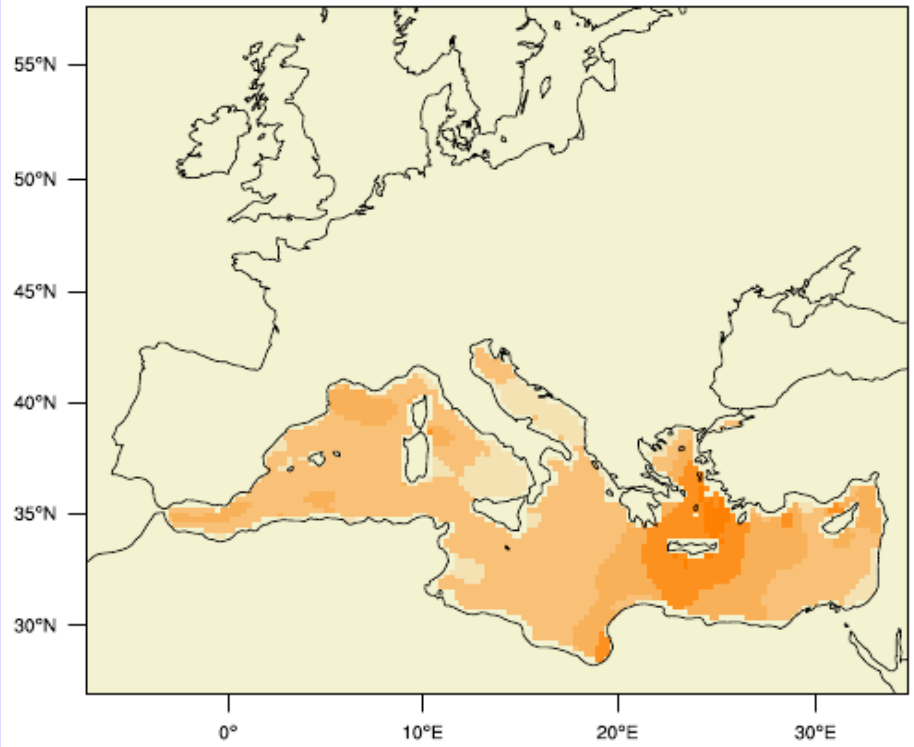

Hg Mediterranean
Sea evasion
[ug/m2]
0.5
1
1.5
2
2.5
3
3.5
4
2000-
2950
Oceans
Anthropogenic
<600
Geogenic



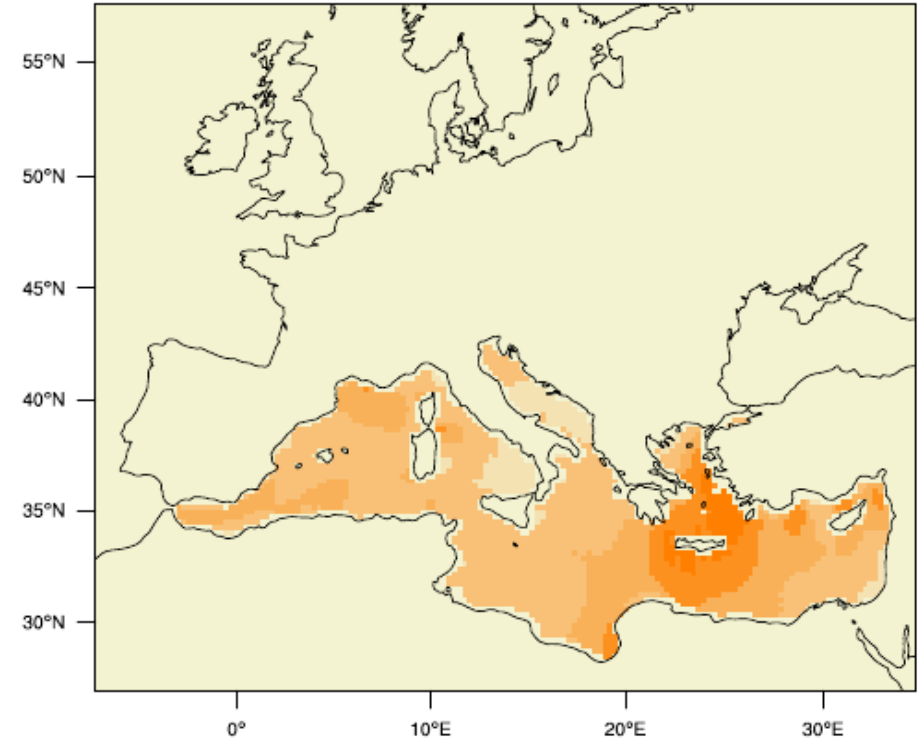
The Mediterranean Sea is a quite significant mercury source for the region with around 70 Mg emitted in 2009

70 Mg emitted and 40 Mg deposited

June – July 2009



Real conditions:
10.9 Mg



Hypothesis, T + 1°C:
11.5 Mg

0.6 Mg

Resume and conclusions

- Model results suggest that ship emissions increase average O_3 (that is a Short-lived climate forcers) concentrations by roughly 10 % over the Mediterranean Sea and between 5 and 10 % over coastal and inland areas, while close to areas where maritime traffic is intense the modelled O_3 concentration increase exceeds 30 %. Shipping emissions clearly play an important role in local and regional air quality in Mediterranean coastal areas, however they also influence the local energy budget because O_3 absorbs radiative energy and has a local heating effect (as does the black carbon emitted by maritime traffic)

- The Hg emission flux from the Mediterranean Sea has been estimated for present day conditions and for a modified scenario: an increase of 1 ° C of the atmospheric temperature causes a greater evasion of Hg from Mediterranean (0.6 Mg in June-July)