Sub-Action 2. Funding of projects in leading-edge sectors - RRFQ: funding of basic research (horizontal support for all sciences)

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Improvements in the composition and atmospheric evolution of organic aerosols within the TM5-MP model

REINFORCE
IMPROVEMENTS IN THE SIMULATION OF AEROSOL-CLIMATE LINKAGES IN EARTH SYSTEM MODELS

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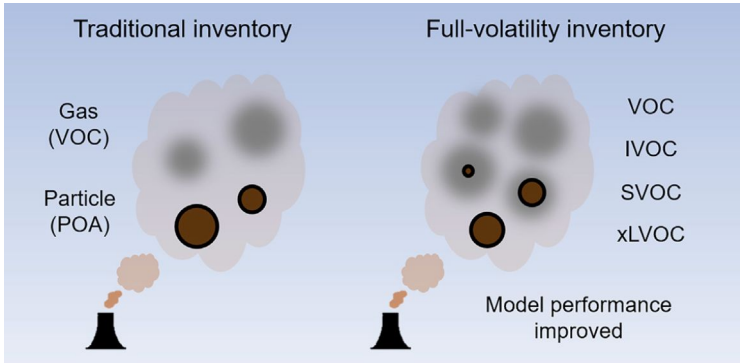
Formation and characterization of Organic Aerosols

- The concentration and composition of organic aerosols have long been **poorly reproduced by air-quality models**.
- **Traditional organic emission inventories** are oversimplified, resulting in significant biases in organic aerosol (OA) predictions.
- By introducing a new emission framework with **comprehensive volatility coverage**, improved model performance has been achieved in simulating organic aerosols, reshaping our understanding of their source contributions.
- The thousands of organic compounds can be **subdivided into groups** (surrogate species) with logarithmically spaced effective saturation concentrations (Donahue et al., 2006)
  - *…abandoning thus the traditional distinction between primary organic aerosol (POA) and secondary organic aerosol (SOA),*
  - *…allowing for efficient treatment of semivolatile primary emissions and SOA production, and*
  - *…enabling the simulation of the chemical evolution of these species within a unified framework.*



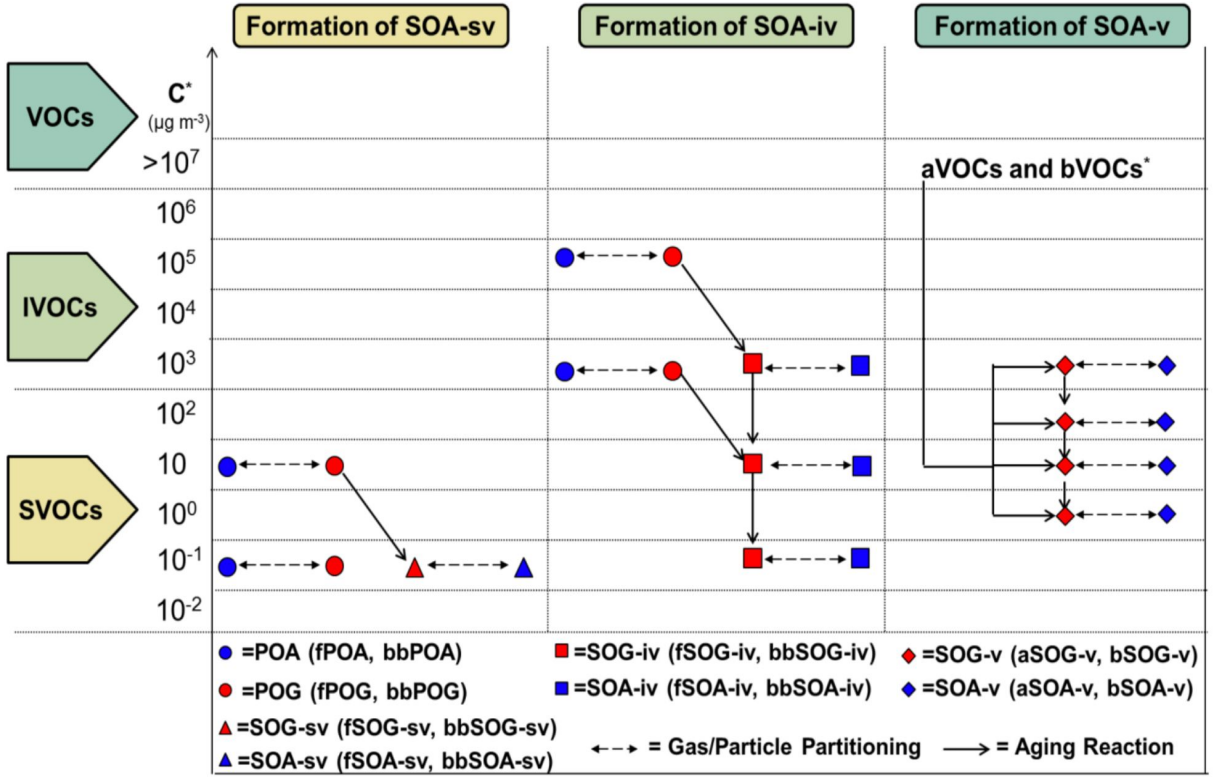
The VBS (Volatility Basis Set) framework describes the OA partitioning, where OA is assumed to be semivolatile, photochemically reactive, and distributed in logarithmically spaced volatility bins.

Aim of this work

To **improve OA simulation** - *within the framework of the* ***REINFORCE project*** - a lite version of the computationally efficient module **ORACLE** (Tsimpidi et al. 2014) has been coupled with TM5-MP that describes:

- the **partitioning** and **chemical aging** of organic aerosols (OA),
- the changes in OA **volatility** that accompany these **chemical transformations**,
- the formation of secondary organic aerosols (**SOA**) from semivolatile organic compounds (**SVOCs**) and intermediate-volatility organic compounds (**IVOCs**), in addition to the existing SOA formation scheme from biogenic volatile organic compounds (VOCs) (Bergman et al., 2021).

SOA formation procedures from SVOC, IVOC, and VOC emissions



Red indicates the compound is in the vapour phase.
Blue in the particulate phase.

- ***Circles*** *correspond to primary organic material emitted either in the gas phase or in the aerosol phase.*
- ***Triangles*** *indicate the formation of SOA from SVOCs by fuel combustion and biomass burning sources.*
- ***Squares*** *show SOA from IVOCs by fuel combustion and biomass burning sources.*
- ***Diamonds*** *indicate the formation of SOA from anthropogenic and biogenic VOC sources.*

Tsimpidi et al. 2014

The ORACLE module

- The ORACLE module adopts the **volatility basis set approach** (*VBS; Donahue et al., 2006*) by subdividing the organic compounds into surrogate species with logarithmically spaced effective saturation concentrations (**C***).
- ORACLE calculates the **bulk equilibrium** gas and aerosol concentrations (*Strader et al., 1999*), as:

$$c_{\mathrm{a},i} = c_{\mathrm{t},i} - x_i c_i^* \text{ for } i = 1, n$$

$$x_i = \frac{c_{\mathrm{a},i}/M_i}{\sum_{j=1}^{n} c_{\mathrm{a},j}/M_j},$$

where,

- $\mathbf{c_{t,i}}$ and $\mathbf{c_{a,i}}$ are the total and aerosol-phase concentrations of product ***i*** in μg m^{-3} , respectively;
- $\mathbf{c^*_i}$ is the effective saturation concentration of product ***i***;
- $\mathbf{x_i}$ is the mole fraction of product ***i*** in the absorbing organic phase; and
- $\mathbf{M_i}$ is the molecular weight of product ***i***.

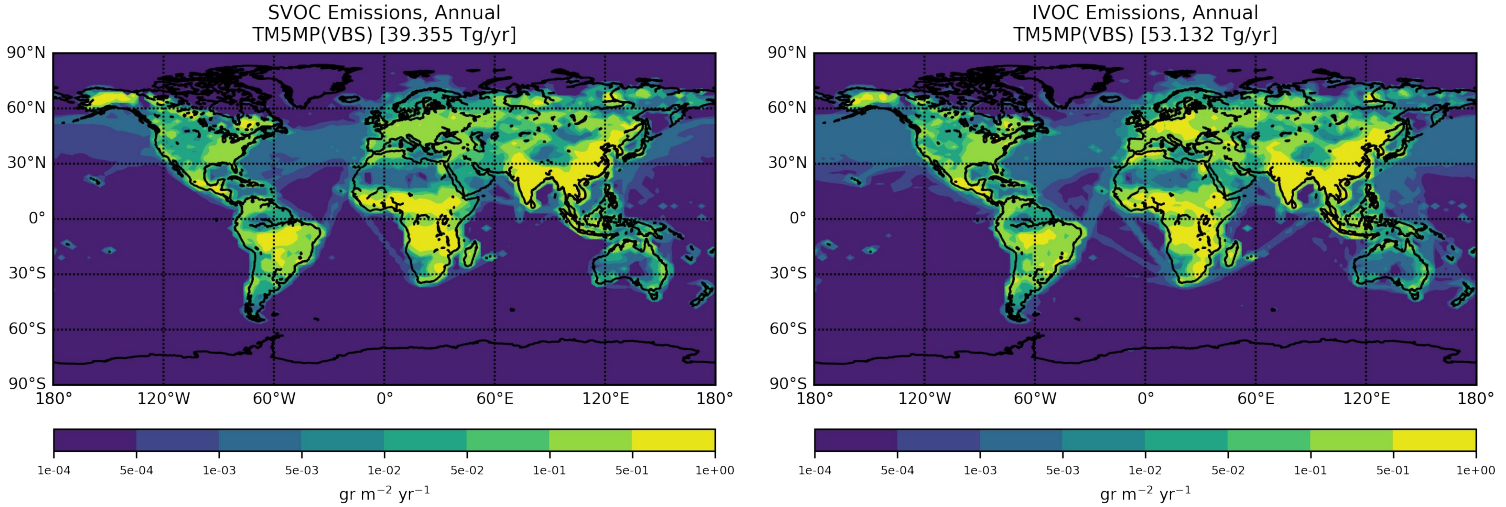
Note: The molecular weights of POA, SOA-sv, and SOA-iv components are assumed to be equal to 250 g mol^{-1}

The original ORACLE-lite code has been kindly provided to us by Alexandra Tsimpidi (Jülich) and Vlassis Karydis (Jülich).

The volatility distribution of POA emissions in the TM5-MP model

The volatility of traditional POA emissions is distributed into SVOCs and IVOCs emissions:

- SVOCs have saturation concentrations ***C**** between $\mathbf{10^{-2}}$ **and** $\mathbf{10^{2}}$ **μg m**$^{-3}$ and exist in both the gas and particulate phases under typical ambient conditions.
- IVOCs have saturation concentrations ***C**** between $\mathbf{10^{3}}$ **and** $\mathbf{10^{6}}$ **μg m**$^{-3}$ and exist only in the gas phase (Pandis et al., 2013).
  - *IVOC emissions are missing from traditional inventories, estimated to be between 0.25 and 2.8 times the traditional POA emissions (Schauer et al., 1999, 2001, 2002).*
    - *we assume here that the missing IVOC emissions are **1.2 times** the traditional emission inventory and are assigned to the fourth volatility bin with **C* = 10^{5} μg m^{-3}** (Tsimpidi et al. 2014).*



Chemical aging reactions

ORACLE treats all OA compounds as chemically reactive:

- Smog-chamber results indicate a net average decrease in volatility (and increase in SOA production)
- SVOCs and IVOCs can participate in up to three generations of oxidation, reaching a final OM / OC up to 1.8 (*assuming an initial OM / OC of 1.2*).
- Only homogeneous gas-phase ageing is considered since it is rapid compared to heterogeneous reactions with OH (*Donahue et al., 2013*).

$$SVOC_i + OH \rightarrow 1.15\ SOG\text{-}sv_{i-1}$$
$$SOG\text{-}sv_{i-1} \leftrightarrow SOA\text{-}sv_{i-1}$$

$$IVOC_i + OH \rightarrow 1.15\ SOG\text{-}iv_{i-1},$$
$$SOG\text{-}iv_{i-1} \leftrightarrow SOA\text{-}iv_{i-1}$$

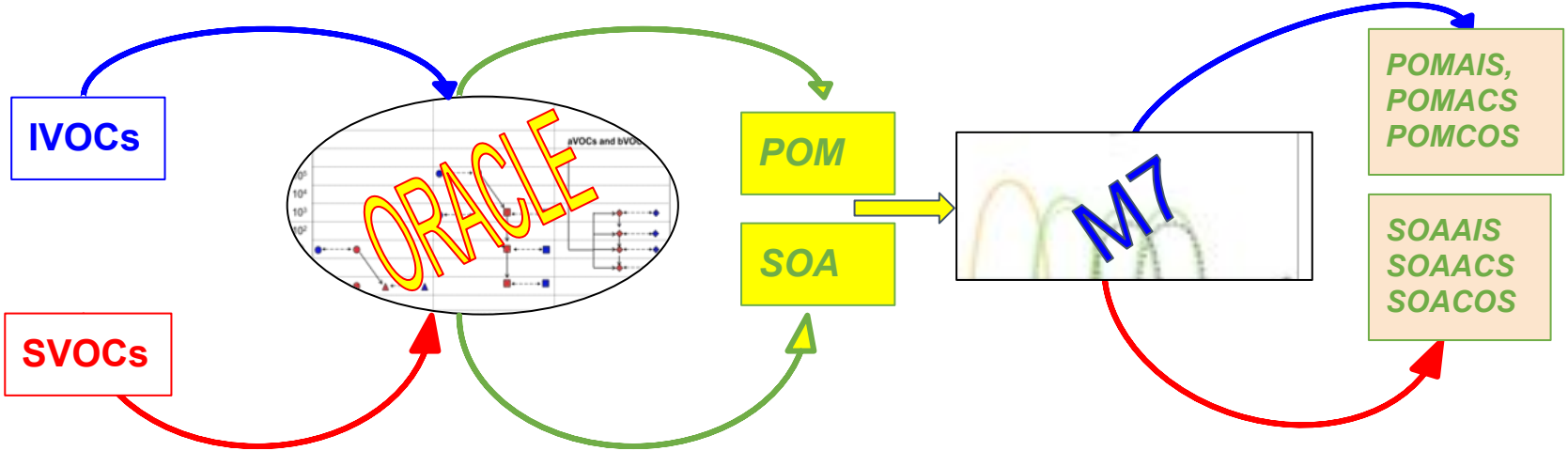
The volatilities of **SVOCs** and **IVOCs** are assumed to be reduced by a factor of 100 as a result of the OH reaction

- *a rate constant of 1.33×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and*
- *a 22.5 % increase in mass to account for two added oxygens, assuming a C15 precursor.*

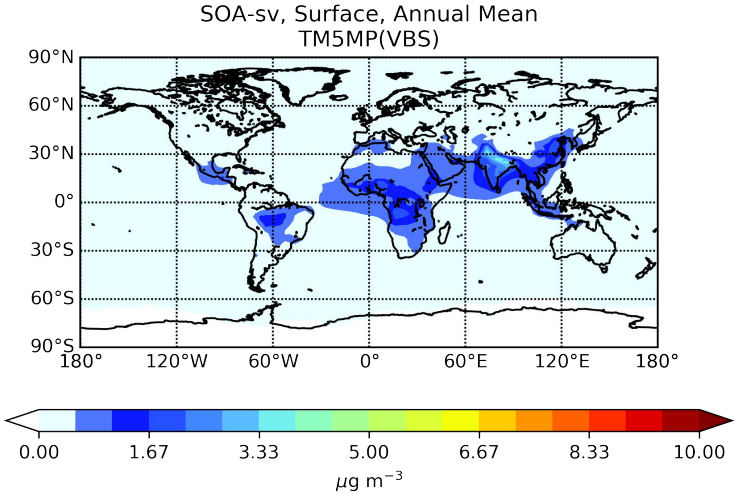
Aerosol size distribution

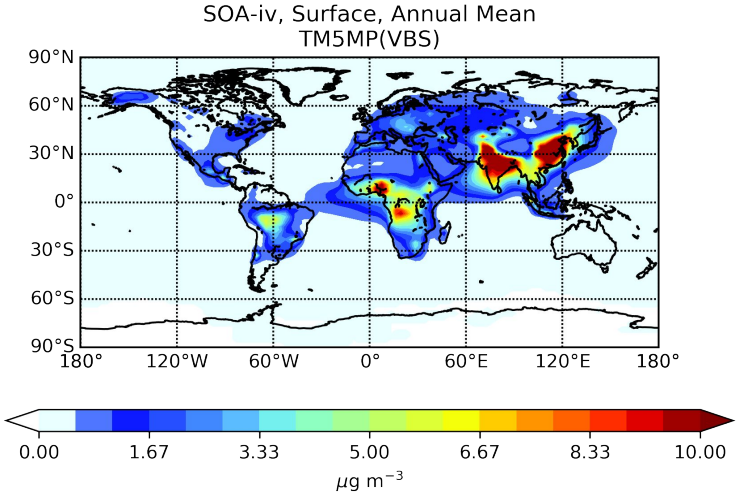
- For the VBS model configuration, primary organics are assumed to be emitted as either semi-volatile organic compounds (SVOCs; ~40%) or intermediate volatile organic compounds (IVOCs; ~60%).
- Upon applying the bulk equilibrium model (ORACLE), the aerosol size distributions for:
  - Primary organic matter (POM) from SVOC and IVOC, and
  - Semi volatile secondary organic aerosols (sv-SOA) and intermediate volatile secondary organic aerosols (iv-SOA)

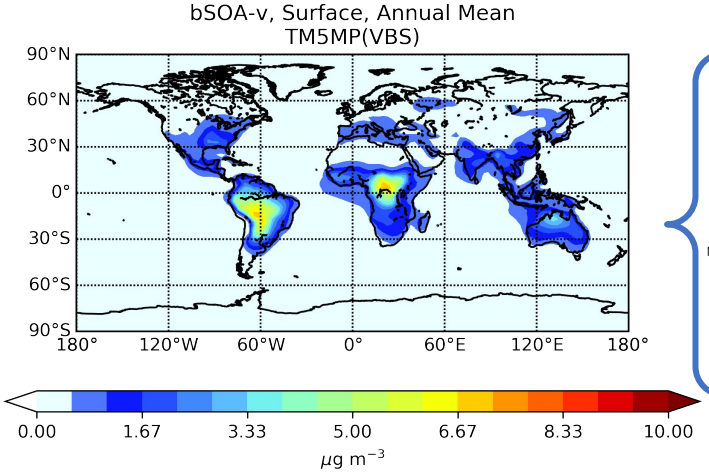
  are determined based on M7 calculations, which redistribute the change in OA mass per mode (i.e., AIS, ACS, and COS).
- The new SVOC and IVOC aerosol masses for POMs and SOAs correspond to the AIS, ACS, and COS aerosol modes in the model.

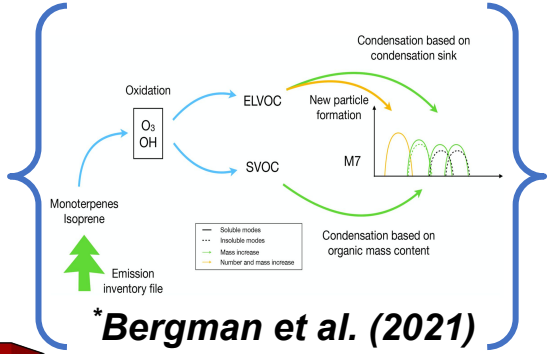


Modelled SOA concentration from SVOCs, IVOCs and bVOCs* emissions







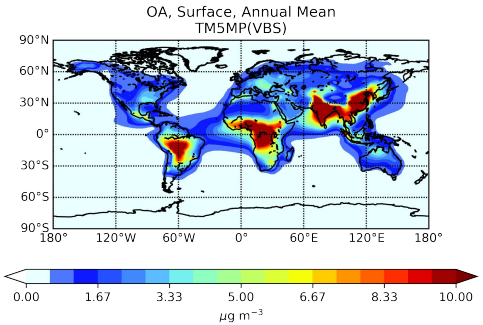


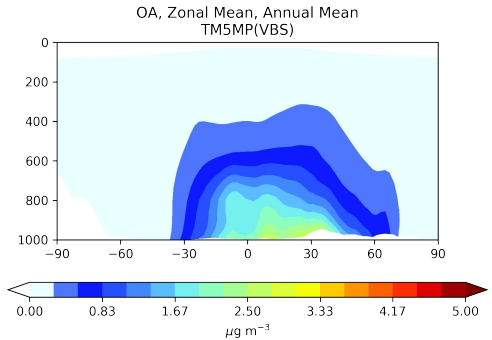
*Bergman et al. (2021)

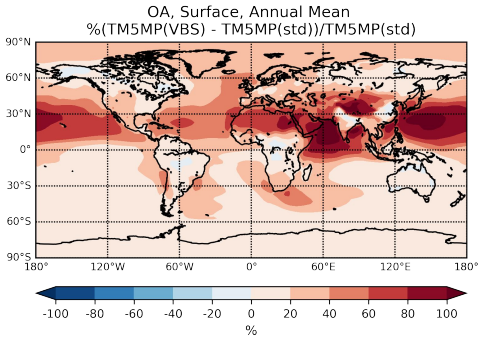
Modeled OA concentrations

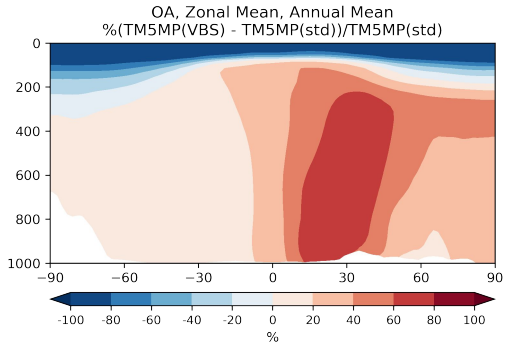
VBS results in higher surface OA concentrations across most regions compared to the standard (traditional) POM configuration of the model.

OA component	POM	SOA-sv	SOA-iv	bSOA-v
Burden (Tg)	*0.013*	*0.537*	*1.389*	*0.994*



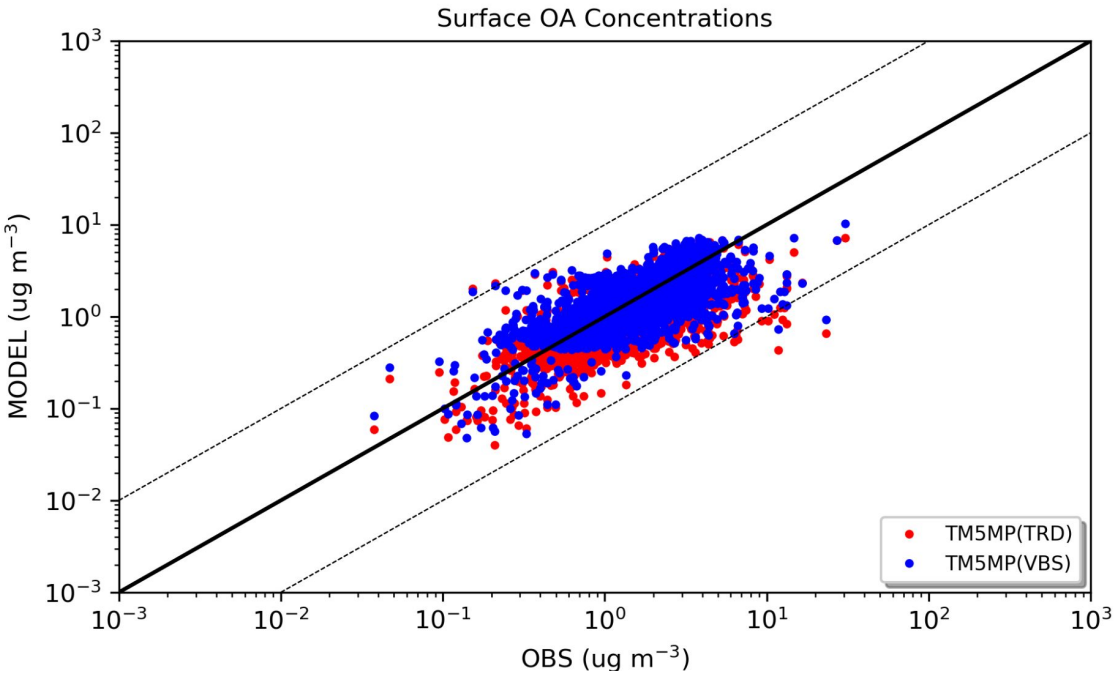






- The calculated global average surface OA concentration is ~1.15 μg m^{-3} (~29% higher than the standard OA).
- The main increases (>50%) in surface OA concentrations occur in the N. Hemisphere, mainly downwind of Southern Asia and at the outflow of the Pacific and Atlantic Oceans due to the photochemical ageing of anthropogenic IVOCs and SVOCs and their efficient transport away from the sources.
- In contrast, only slightly lower (<10%) surface concentrations occur over the tropical forests of South America (Amazon Basin) and the savannas of Africa (Congo Basin), where OA is primarily of biomass burning and biogenic SOA origin.

Model evaluation



Comparison of model calculated monthly mean OA surface concentrations (*μg m^{-3}*) for the standard TM5-MP configuration with a traditional description of POM emissions (**TRD**) and the new **VBS** scheme with observations from:

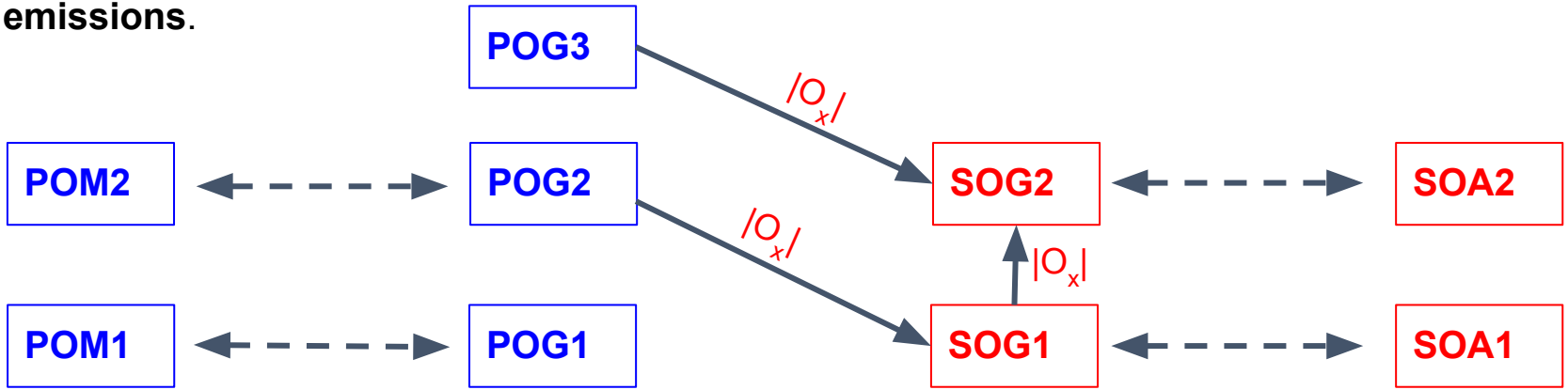
1. *the European Monitoring and Evaluation Programme (**EMEP**; http://nilu.no/projects/ccc/onlinedata/pm/)*
2. *the Interagency Monitoring of protected Visual Environments (**IMPROVE**; http://vista.cira.colostate.edu/improve/Data/ IMPROVE/improve_data.htm), as well as,*
3. *short-term measurement data collected over **East Asia** (Jo et al., 2013).*

- **TM5MP(TRD):** *N=2105, R=0.507, NMB=-13.364, RSME=1.610 μg m^{-3}, NME=44.837 μg m^{-3}*
- **TM5MP(VBS):** *N=2105, R=0.519, NMB=8.878, RSME=1.548 μg m^{-3}, NME=42.479 μg m^{-3}*

Collection of OA observations and data manipulation by Alexandra Tsimpidi (Jülich).

Summary

- A lite version of the computationally efficient VBS module **ORACLE** has been coupled to TM5-MP.
- A new emission framework based on the **volatility coverage** of POA emission inventories has been introduced in the model, replacing the previous traditional scheme.
- The **partitioning** and chemical **ageing** of OA have been included.
  - *The chemical oxidation in the volatility of organic vapours has been added to the chemical solver.*
- The **formation of SOA from SVOCs and VOCs** has been incorporated in the model, along with the existing SOA formation scheme from isoprene and monoterpenes.
- The **size distributions** of the new POA and SOA schemes are determined by the **M7** module based on changes in the total OA mass per mode (*AIS, ACS, and COS*).
- The new OA scheme shows i**ncreased surface OA concentrations** compared to the previous scheme's predictions, with most of the new particulate organic mass being associated with **IVOC emissions**.



Thank you for your attention

The authors acknowledge support from the REINFORCE (*improvements in the simulation of aerosol-climate linkages in earth system models: from global to Regional scalEs*) research project; the research project is implemented in the framework of H.F.R.I call “Basic research Financing (Horizontal support of all Sciences)” under the National Recovery and Resilience Plan “Greece 2.0” funded by the European Union — NextGenerationEU (H.F.R.I. Project Number: 15155).