# High-resolution mapping of inorganic aerosol species over a SE Mediterranean urban area

**Stelios Myriokefalitakis, Eleni Athanasopoulou, Dimitris Karagiannis, Anastasia Kakouri, Eleni Liakakou, Georgios Grivas, Aikaterini Bougiatioti and Evangelos Gerasopoulos**

**Institute for Environmental Research and Sustainable Development, National Observatory of Athens (NOA), Athens, Greece**

*e-mail to* : steliosm@noa.gr

## INTRODUCTION

- ✓ City-scale modeling is a promising tool for resolving atmospheric processes at an ultra-high spatial resolution.
- ✓ Air quality simulations at a sub-grid level of an urban area can provide extra information not currently available from regional-scale modeling.

## AIM

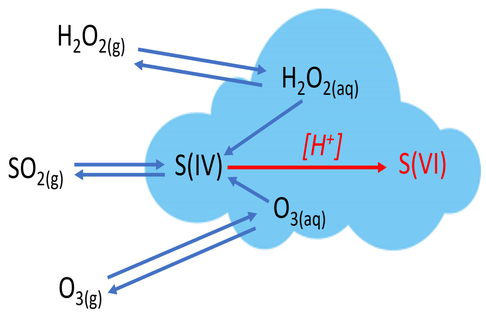
- ➢ To develop a framework for i) cloud sulfate production and ii) aerosol thermodynamic calculations, in the context of atmospheric city-scale spatial resolution.
- ➢ To estimate the contribution of secondary inorganic aerosols ($SO_4^{2-}$, $NO_3^-$, and $NH_4^+$) to the fine particulate mass in an urban area.

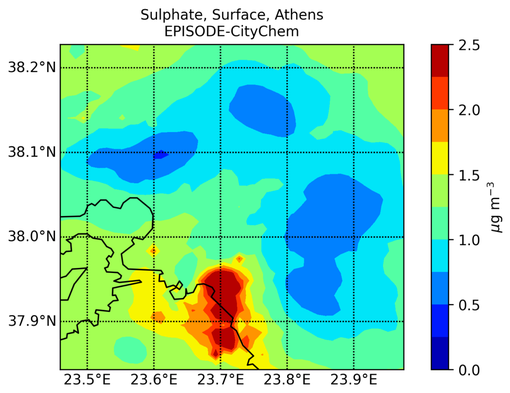
## EPISODE-CityChem

- ➢ Air quality simulations are performed here using the well-documented city-scale chemistry-transport model EPISODE-CityChem (Karl et al. 2019).
- ➢ The study area (45×45 cells of 1×1 km$^2$, with an embedded grid of 100×100 m$^2$) is the city of Athens (GR).
- ➢ The detailed EMEP gas-phase chemistry scheme applied here, includes about 70 species and more than 100 reactions.
- ➢ A local photochemistry scheme (EP10-Plume) is also applied in the receptor grid (100 × 100 m$^2$).
- ➢ The model is here modified to also account for the speciation of the main inorganic aerosol components ($SO_4^{2-}$, $NO_3^-$, $NH_4^+$).
- ➢ All simulations were here realized for the year 2019.

## Sulfate production in cloud droplets

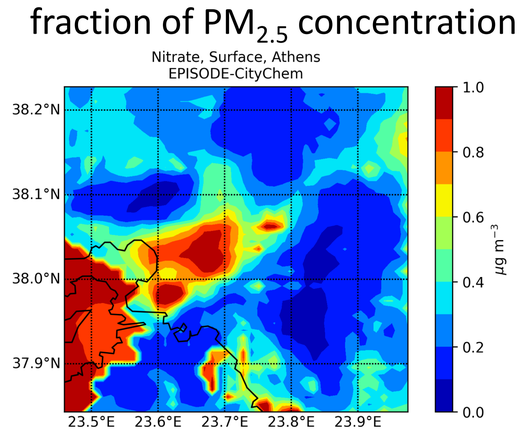
- ➢ Clouds play a key role in the production of sulfates, since the aqueous phase $SO_2$ oxidation via $H_2O_2$ and $O_3$ is much faster than the $SO_2$ oxidation via OH radicals in the gas phase.
- ➢ The cloud acidity governs the partitioning of soluble gas-phase species, and in EPISODE-CityChem is determined by the electro-neutrality of strong acids and bases (i.e., $H_2SO_4$, $SO_4^{2-}$, $HNO_3$, $NO_3^-$, and $NH_4^+$), followed by the dissociations of $CO_2$, $SO_2$, and $NH_3$.

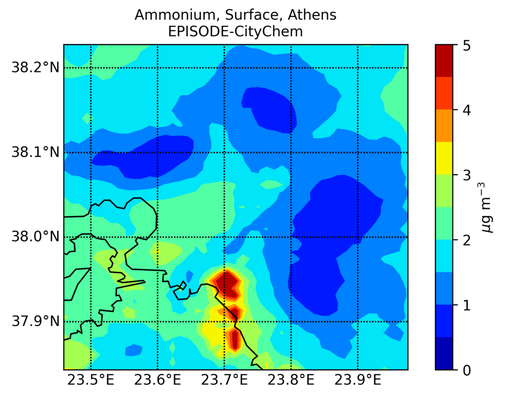


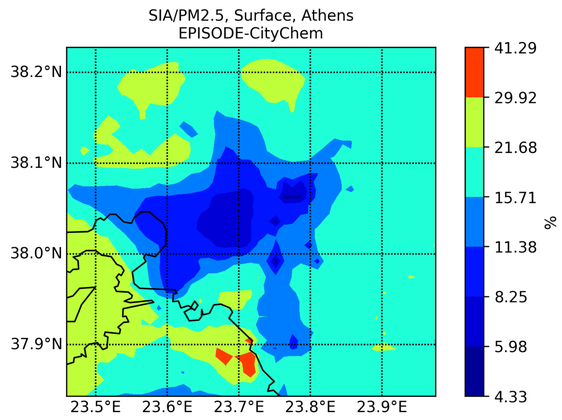

## THERMODYNAMIC CALCULATIONS

- ➢ The thermodynamic equilibrium model ISORROPIA II (Fountoukis and Nenes, 2007; available at https://www.epfl.ch/labs/lapi/software/isorropia/) has online coupled to the EPISODE-CityChem, to determine the gas/particle partitioning of $NH_3/NH_4^+$ and $HNO_3/NO_3^-$.
- ➢ ISORROPIA-II calculates the gas–liquid–solid equilibrium partitioning of the $K^+/Ca^{2+}/Mg^{2+}/NH_4^+/Na^+/SO_4^{2-}/NO_3^-/Cl^-/H_2O$ aerosol system, and it is used here in the forward mode, assuming that all aerosols are in a metastable (liquid) state.
- ➢ The presence of fine dust and sea salt aerosols are also taken into account in the thermodynamic calculations, considered here as a fraction of $PM_{2.5}$ concentration.



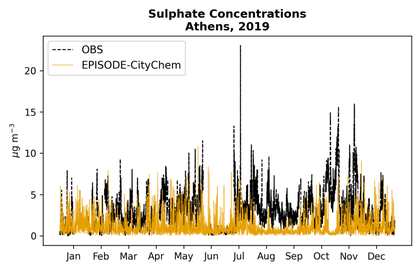



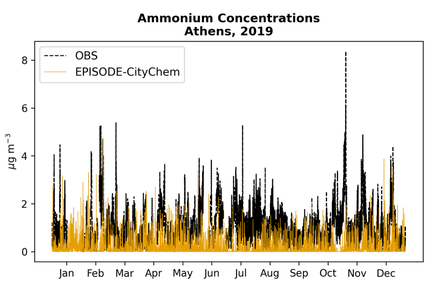

- ▪ The ambient precursor gases ($SO_2$, $NO_x$, and $NH_3$) are largely responsible for the SIA formation.
- ▪ SIAs represent a significant fraction of the $PM_{2.5}$ mass in the model domain, indicating here a ~24 ± 12 % contribution to the simulated total fine aerosol load in Athens.

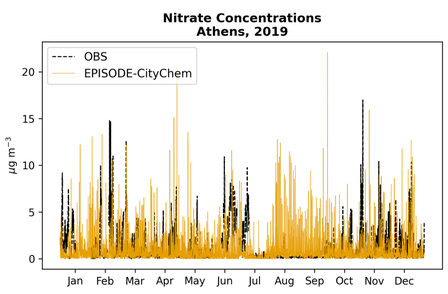



## MODEL EVALUATION

In situ data of secondary inorganic aerosols (SIA: $SO_4^{2-}$, $NH_4^+$, and $NO_3^-$), as retrieved from the NOA's supersite at Thission in the center of Athens, along with observations at Piraeus, are here used to evaluate the model.




EPISODE-CityChem tends to generally underestimate the SIA measurements in Athens, capturing however satisfactorily their observed daily variation at Piraeus (January-February) and at Thission (March-December) for the year 2019:

- ➢ The underestimation of the observed $SO_4^{2-}$ concentrations probably indicates too weak primary $SO_2$ sources or a slow $SO_2$-to-$SO_4^{2-}$ cloud conversion in the model domain.
- ➢ The lower $NH_4^+$ concentrations compared to the observed values, generally follow the simulated $SO_4^{2-}$ variation, pointing out possibly, missing $NH_3$ sources in the model domain.
- ➢ The $NO_3^-$ concentrations - although still lower compared to observations - are better simulated in the model compared to both $SO_4^{2-}$ and $NH_4^+$, suggesting a good representation of the $HNO_3/NO_3^-$ partitioning by the model.

## CONCLUSIONS

- ✓ In this work, we demonstrate the capacity of the city-scale model EPISODE-CityChem to represent atmospheric levels of the main secondary inorganic aerosol species in Athens, revealing their geospatial characteristics and sources in an urban agglomeration for the year 2019.
- ✓ The gas/particle partitioning of $NH_3/NH_4^+$ and $HNO_3/NO_3^-$ were simulated here with the ISORROPIA II thermodynamic model, providing insights into complex interactions in a SE Mediterranean urban area.
- ✓ The high spatiotemporal resolution of the model (i.e., down to 100x100 m$^2$, 1h), along with the improved representation of the inorganic aerosols, delivers a beyond state-of-the-art characterization of the fine ($PM_{2.5}$) particulate load over Athens.
- ✓ Although the model generally underestimates the observations, the inclusion of crustal species affects the ion balance and thus the partitioning of $HNO_3/NO_3^-$ and $NH_3/NH_4^+$ species in the model, especially downwind of regions with abundant mineral dust and/or sea spray aerosols.
- ✓ Overall, such model outputs can support new regulations and needed interventions, for better addressing air pollution inequalities and health impacts and allow for further development of mitigation measures and monitoring strategies.

**Acknowledgements.** This work was supported by the ERA-PLANET (www.era-planet.eu) trans-national project SMURBS (www.smurbs.eu; Grant Agreement n. 689443), funded under the EU Horizon 2020 Framework Programme. The authors thank A. Nenes for providing the ISORROPIA Version 2.1 code.