

Secondary Inorganic Aerosols (SIA)

What do we know about SIA formation?

SAGE

esperanza.perdrix@imt-lille-douai.fr

- Secondary inorganic aerosols (SIA) are the predominant components of fine particulate matter (PM_{2.5}) in Europe, North America and Asia.
- They have significant impacts on:
 - air quality (high PM events),
 - visibility,
 - human health
 - ecosystems (nitrogen and sulfur cycles),
 - climate change (net negative radiative forcing mainly due to diffusion and cloud condensation nuclei)

SIA main (pure) species

SIA form from the neutralization of inorganic acids by ammonia gas. They are water soluble (cation + anion).

| cation\anion | sulfate | nitrate | chloride |
|-----------------|---|-------------------------------------|--------------------|
| ammonium | (NH₄)₂SO₄ NH ₄ HSO ₄ (NH ₄) ₄ H(SO ₄) ₂ | NH₄NO₃ | NH ₄ Cl |
| sodium | Na ₂ SO ₄ NaHSO ₄ | NaNO ₃ | |
| calcium | CaSO ₄ | Ca(NO ₃) ₂ | |

In bold, most common species in the atmosphere

- SIA are most probably in the form of mixed salts.
- Some of the salts in the table can be from primary origin (CaSO₄ from building materials, NH₄NO₃ from fertilizers...)
- All inorganic salts are not SIA because of primary emissions of NaCl, KCl, MgCl₂...

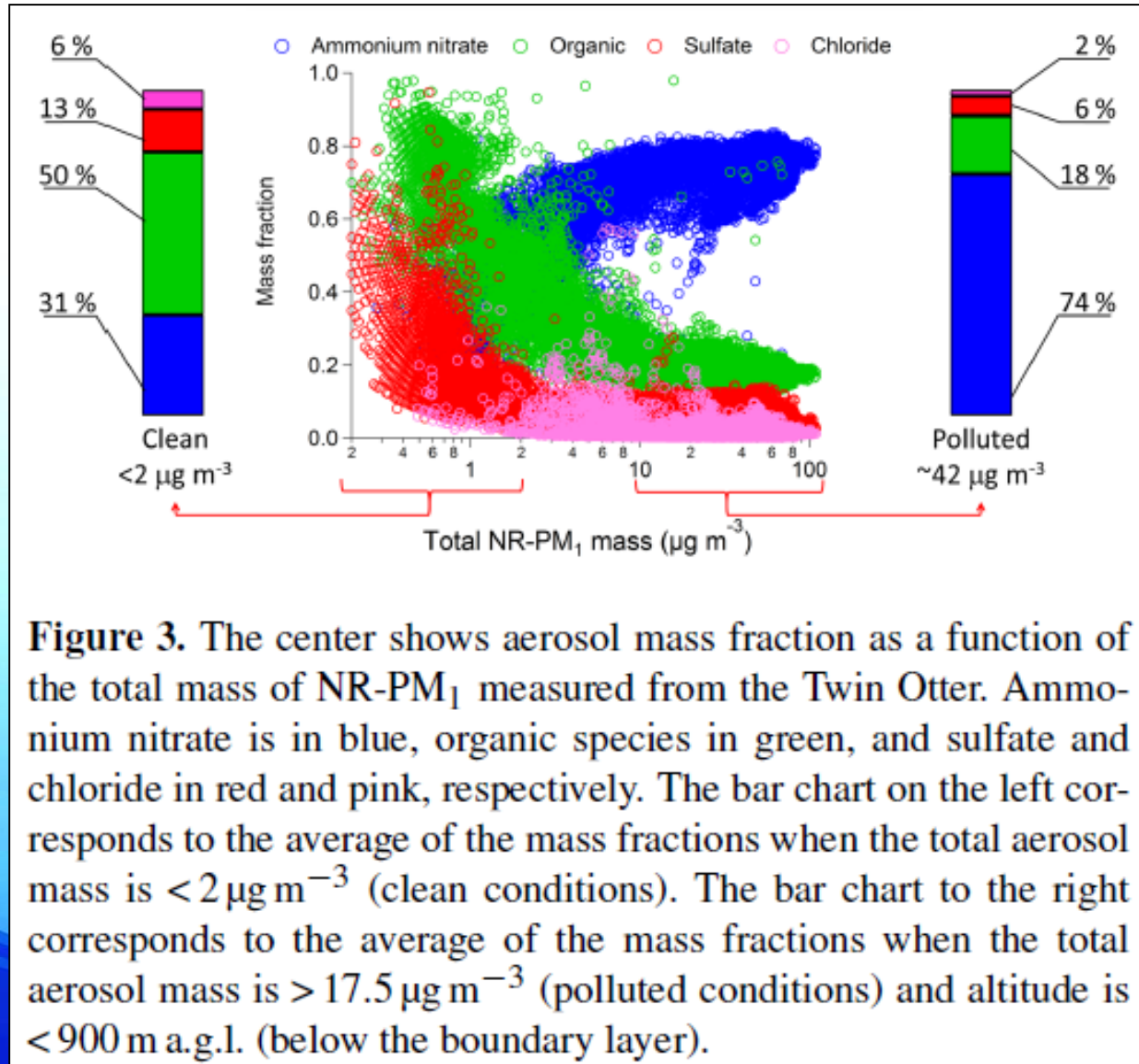
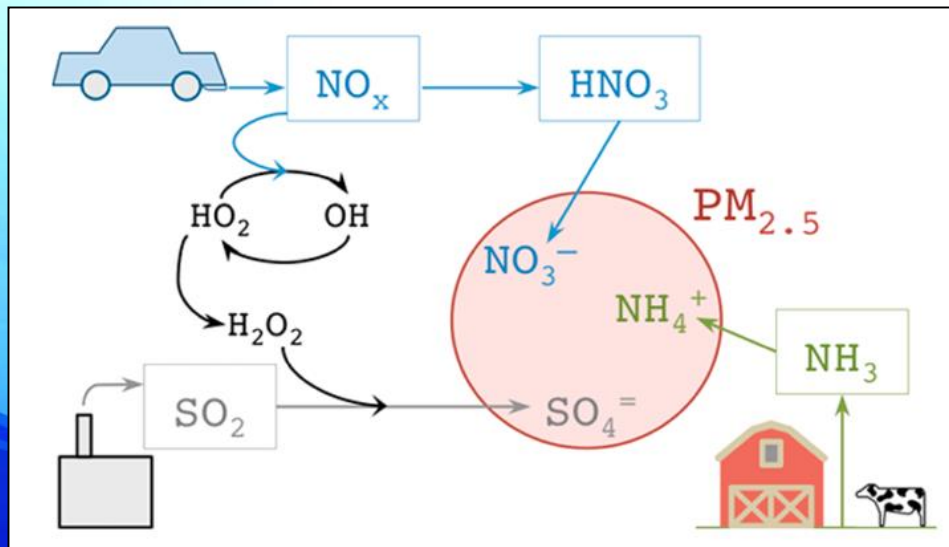


Figure 3. The center shows aerosol mass fraction as a function of the total mass of NR-PM₁ measured from the Twin Otter. Ammonium nitrate is in blue, organic species in green, and sulfate and chloride in red and pink, respectively. The bar chart on the left corresponds to the average of the mass fractions when the total aerosol mass is $< 2 \mu\text{g m}^{-3}$ (clean conditions). The bar chart to the right corresponds to the average of the mass fractions when the total aerosol mass is $> 17.5 \mu\text{g m}^{-3}$ (polluted conditions) and altitude is $< 900 \text{ m a.g.l.}$ (below the boundary layer).

A. Franchin et al.: Airborne and ground-based observations of ammonium-nitrate-dominated aerosols, *Atmos. Chem. Phys.*, 18, 17259–17276, 2018

SIA precursor gases

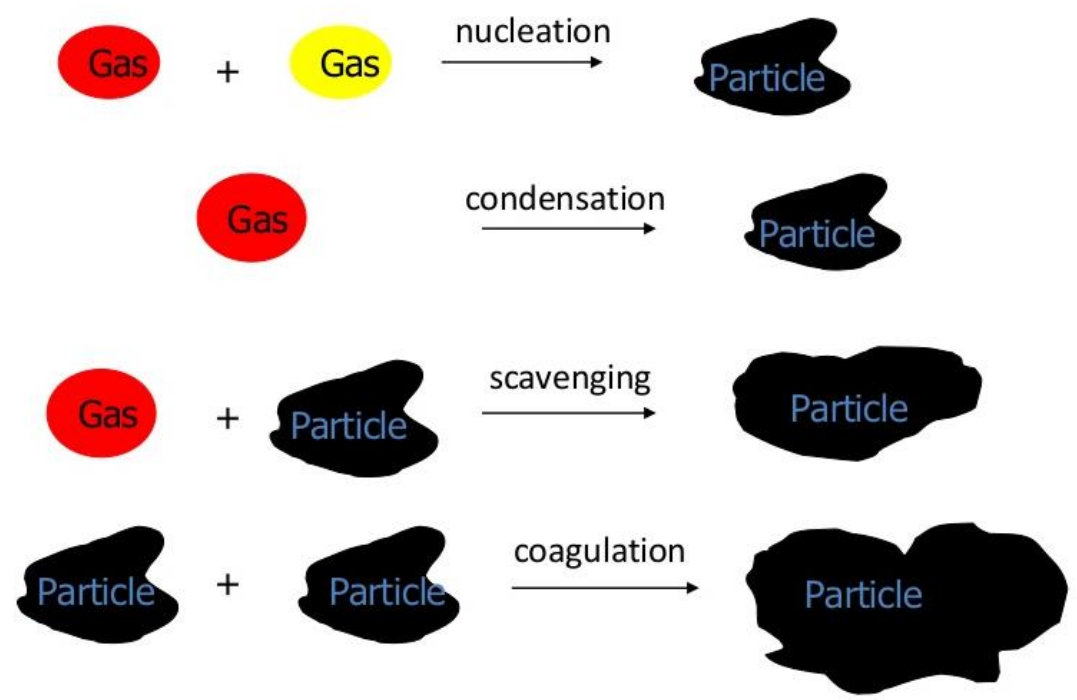
- **SO₂** (marine biogenic DMS, volcanoes, industrial processes)
- **NO_x** (combustion for transport, heating, cooking, industry; wildfires; lightning)
- **NH₃** and amines (fertilizers, agriculture, livestock farming)



http://www.selingroup.org/news2015/post_id-1

Secondary Sources

- Formation and growth of particles in the atmosphere



- Ammonium, sulfate, nitrate, secondary organic aerosol

Source: John Wenger, University College Cork

- **SO₂ oxidation** into sulfuric acid **H₂SO₄**
 - mainly in aqueous phase (clouds, haze, fog, wet surfaces)
 - oxidation by H₂O₂, O₃, NO₃ radical
 - catalyzed by metals such as Fe (in mineral particles...)
- **Nucleation** of low volatile **H₂SO₄** molecules
- Formation of clusters, coagulation, surface condensation
- **Hydration** depending on **RH**
- Uptake (absorption or adsorption) of ammonia gas **NH₃**
- **Salt** formation with speciation depending on **pH**:
(NH₄)₂SO₄ (full neutralization), NH₄HSO₄ (acidic aerosol)...
- Other pathways such as **heterogeneous** formation on pre-existing particules are reported.

Formation of secondary sulfate

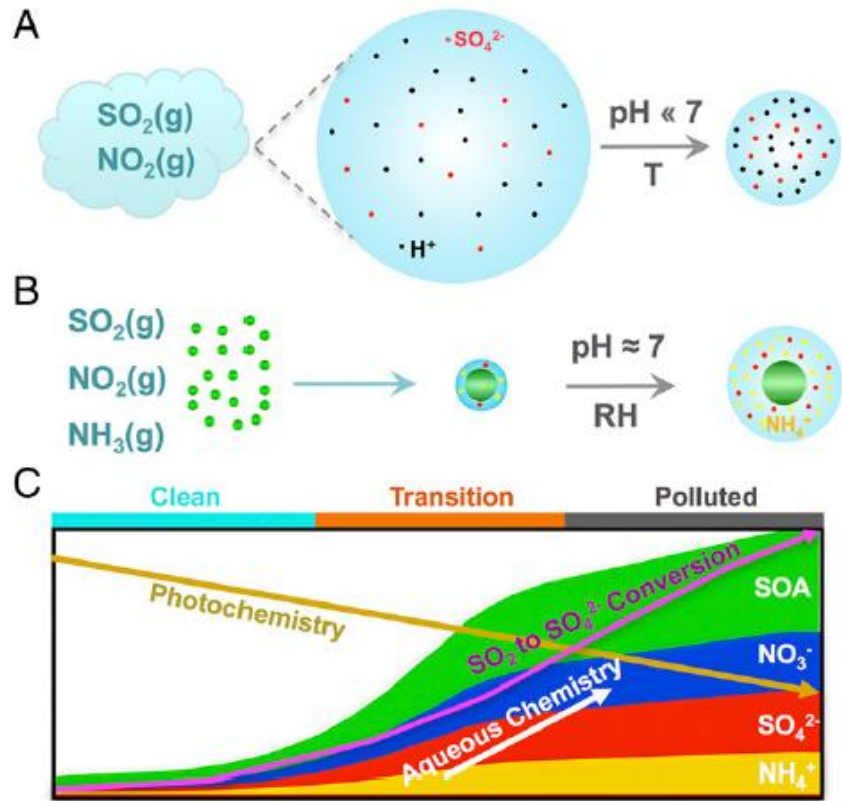


Fig. 4. Schematic of the sulfate formation mechanisms. Variations in temperature, RH, and particle size and acidity for the aqueous reactions between SO_2 and NO_2 leading to SO_4^{2-} formation under in-cloud conditions (A) and on fine PM (B). The red, black, yellow, and green colors in A and B represent SO_4^{2-} , H^+ , NH_4^+ , and SOA, respectively. (C) Anticorrelation between the photochemical activity and aqueous chemistry during the severe haze evolution (i.e., from the clean, transition, to polluted periods) in China, displaying the central role of the SO_2 to SO_4^{2-} conversion in facilitating aqueous production of the major secondary constituents.

Wang et al., 2016
www.pnas.org/cgi/doi/10.1073/pnas.1616540113

1. Formation of nitric acid from nitrogen dioxide

- **Daytime**

- mainly gas phase
- by O₃, HOx and ROx radicals



- **Nighttime**

- NO₂ **oxidation** by O₃ -> formation of **NO₃** radical and N₂O₅
- mainly on wet (aerosol) surfaces
- Hydrolysis of **N₂O₅** produces nitric acid:



(Karagulian et al., Atmos. Chem. Phys., 6, 1373–1388, 2006)

2. Neutralization of nitric acid by ammonia

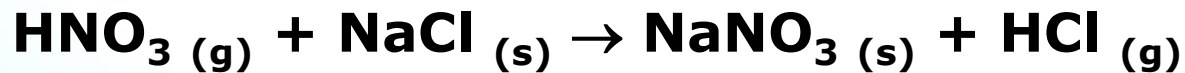


Formation of secondary nitrate or sulfate on coarse particles



- **Seasalt**

- Uptake of HNO₃ (gas) by NaCl aerosol forms NaNO₃



- Highly relevant in PM₁₀, less in PM_{2.5}
- Tracer of polluted marine air

- **Mineral dust: e.g. CaCO₃**

- Uptake of gas HNO₃ (or H₂SO₄) by alkaline CaCO₃ to form Ca(NO₃)₂ aerosol
- Highly relevant in PM₁₀, less in PM_{2.5}
- Same occurS with H₂SO₄ to form CaSO₄

Formation of secondary nitrate or sulfate on coarse particles

Lab observation of heterogeneous formation of sulfate from SO₂ and NO₂

| Particle | Gases | RH (%) | Whether sulfate was detected |
|---|---|--------|------------------------------|
| CaCO ₃ | SO ₂ (75 ppm) + NO ₂ (75 ppm) | 72 | Yes |
| Ca(NO ₃) ₂ droplet | SO ₂ (75 ppm) + NO ₂ (75 ppm) | 72 | Yes |
| CaCO ₃ | SO ₂ (150 ppm) | 72 | No |
| Ca(NO ₃) ₂ droplet | SO ₂ (150 ppm) | 72 | No |
| NaNO ₃ droplet | SO ₂ (75 ppm) + NO ₂ (75 ppm) | 72 | No |
| NH ₄ NO ₃ droplet | SO ₂ (75 ppm) + NO ₂ (75 ppm) | 72 | No |

Surprisingly, both SO₂ and NO₂ are needed to produce sulfate on calcite surface

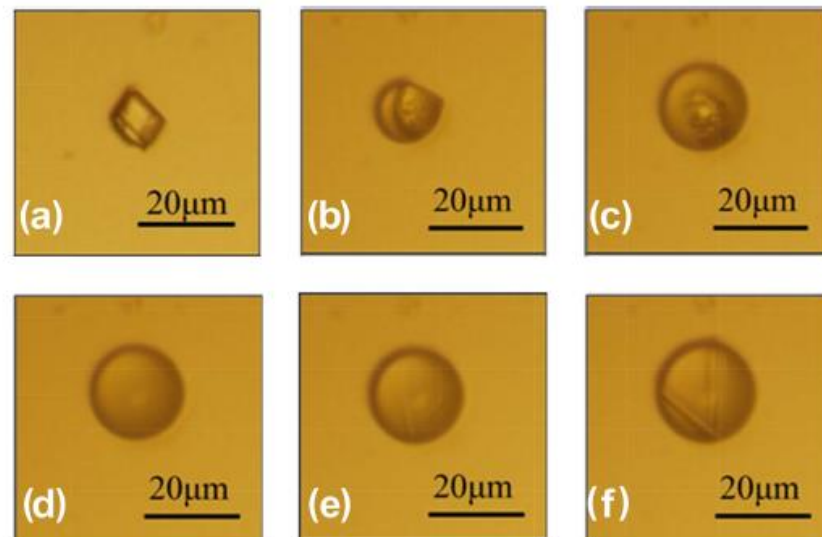


Figure 3. Microscopic images of an individual CaCO₃ particle (same as in Fig. 2) reacting with NO₂ (75 ppm) and SO₂ (75 ppm) at 72 % RH. Panels (a–f) correspond to the reaction time of 0, 6, 29, 37, 94, and 1050 min, respectively.

D. Zhao et al.: Multiphase oxidation of SO₂ by NO₂ on CaCO₃ particles, Atmos. Chem. Phys., 18, 2481–2493, 2018

- Ammonium **sulfate** salts are **stable**. Longer lifetime.
- Ammonium **nitrate dissociates** when T increases and RH decreases through equilibrium with the precursor gases:



- The equilibrium constant depends on T and RH.
- When RH is below the deliquescence state ($\text{RH} < \text{DRH}$), then NH_4NO_3 is solid with adsorbed water on its surface.
- When $\text{RH} > \text{DRH}$ then NH_4NO_3 is a liquid saline droplet.
- In case of competition for ammonia, **sulfate is neutralized first**.
- SIA are **hygroscopic, cloud condensation nuclei**
- Reactivity depends on deliquescence state (**water content**) and **acidity** (water pH).

Modelling

SIA variability is rather well modelled but improvements are still feasible, particularly for high temporal resolution.

➤ Annual mean

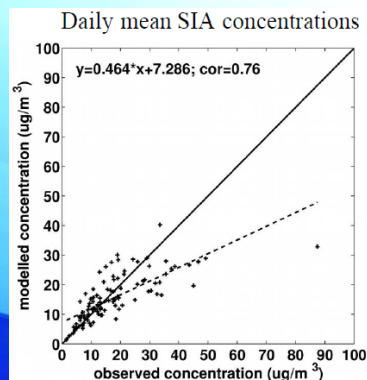
Regional modelling of SIA with MOCAGE

(Guth et al., Geosci. Model Dev., 9, 137–160, 2016)

- SO₂ overestimated, sulfate underestimated
=> knowledge on SO₂ emissions and reactivity
- Ammonium nitrate overestimation
=> uncertainties in ammonia emissions

➤ Daily variability

S. Banzhaf et al.: Impact of emission changes on SIA episodes across Germany, Atmos. Chem. Phys., 13, 11675–11693, 2013



Monthly

Surface EU (2000–2010)

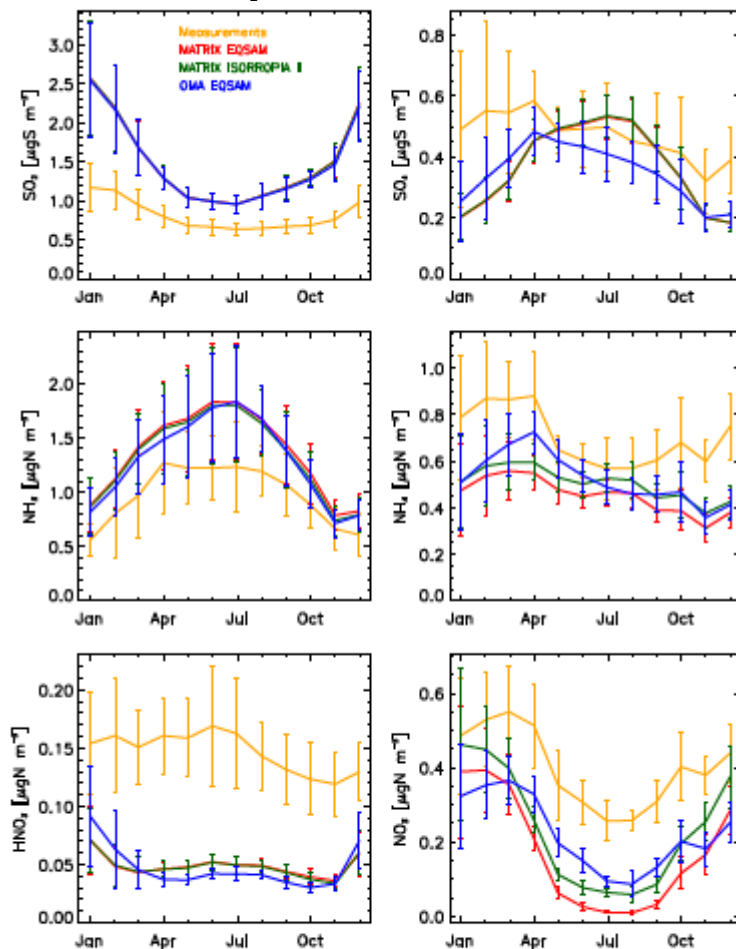


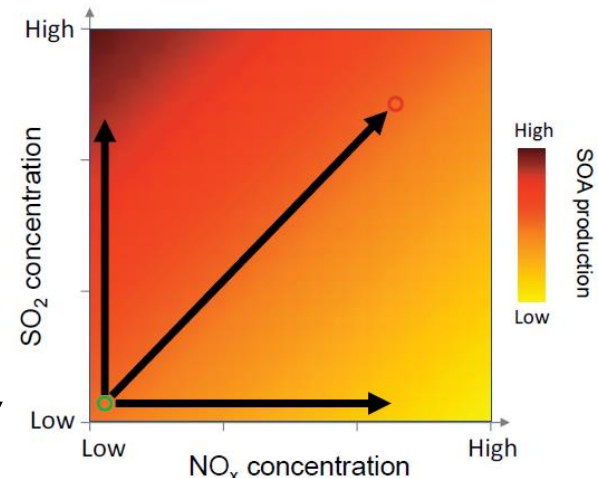
Figure 5. The 2000–2010 mean annual cycle over Europe, error bars represent ± 1 standard deviation. Measurements are in orange, MATRIX-EQSAM is in red, MATRIX-ISORROPIA II is in green, and OMA-EQSAM is in blue.

K. Mezuman et al.: Evaluating secondary inorganic aerosols in three dimensions, Atmos. Chem. Phys., 16, 10651–10669, 2016

Perspectives

Better knowledge of SIA/SOA chemistry (field & lab.)

- Investigate the **interactions** between:
 - ✓ inorganic & organic precursor gases (competition for oxidants)
 - ✓ Inorganic precursor gases & SOA formation
(sulfuric acid promotes SOA contrary to NO_x)
 - ✓ Organic precursor gases & SIA formation (effect of BVOCs on SIA?)
 - ✓ SIA & SOA (ammonium sulfate promotes SOA formation, synergy?)
- **Mixing state of primary/secondary aerosols**
(influences reactivity, optical properties)



Zhao et al., Atmos. Chem. Phys., 18, 1611–1628, 2018.

Need for more detailed field observations of SIA formation

- Aerosol water content and pH
- Aerosol surface and size distribution Role of heterogeneous chemistry ?
- Nighttime nitrate radical chemistry and SIA (and SOA) formation

Importance of nitrate radical chemistry ?

- Mixing state of aerosols

SIA shell on SOA core?
SOA shell on SIA core?
Mixed aerosols?

Identification of sources of SIA and inorganic precursor gases

- Sources of precursor gases?
- Areas of SIA formation?
- Local sources or transport?
- Contribution of satellite observations to accurately identify gas sources (e.g. NH_3)
- Influence of synoptic and local weather conditions on transport and/or formation of SIA

Surface NO_3 (2000–2010)

Surface SO_4 (2000–2010)

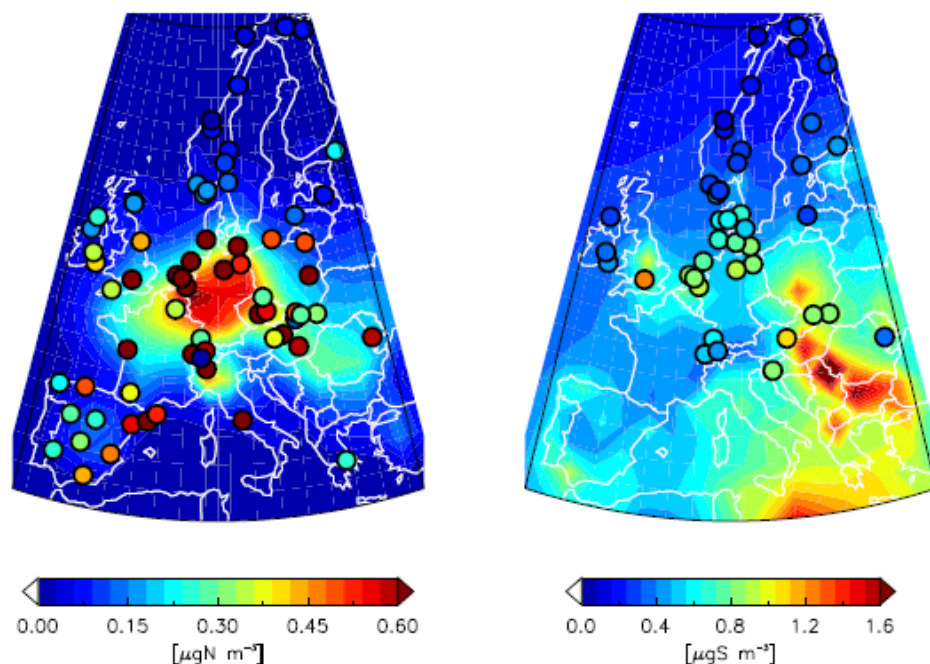


Figure 2. Mean nitrate (left panel) and sulfate (right panel) surface concentration (2000–2010) simulated by MATRIX-EQSAM overlaid by measurements from the EMEP network. The model data units match the units of the measured data ($\mu\text{g}X \text{ m}^{-3}$ with X being N for nitrate and S for sulfate).

Thank you for your attention

K. Mezuman et al.: Evaluating secondary inorganic aerosols in three dimensions, *Atmos. Chem. Phys.*, 16, 10651–10669, 2016

6 Mars 2019 – 5^{ème} journée scientifique CaPPA