Investigating Anthropogenic Emission Mitigation Effects on Biogenic SOA Formation using Simplified and GENOA-Generated Mechanisms in 3-D Modeling

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Background

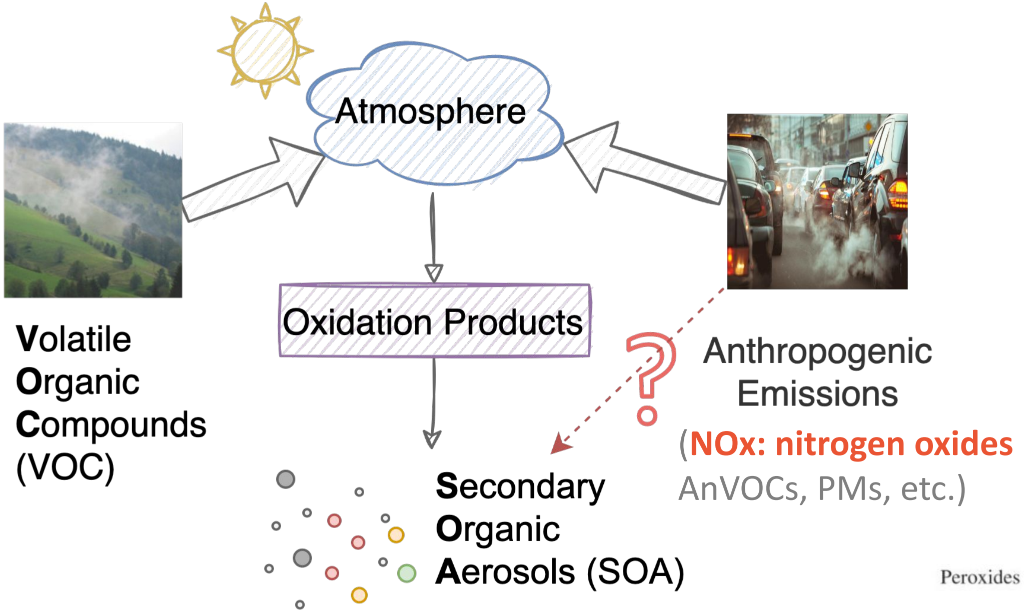
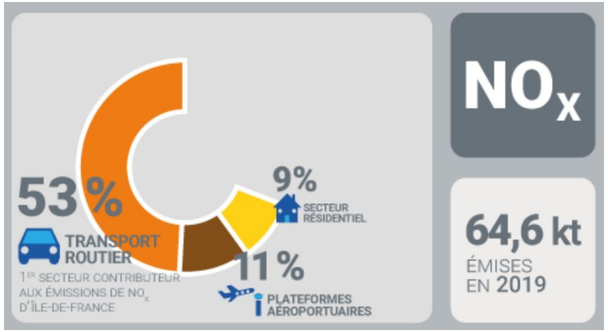


Fig.1 SOA Formation from Oxidized VOCs.

Fig.2 NOx emission at Ile-de-France in 2019. (Source: Airparif)



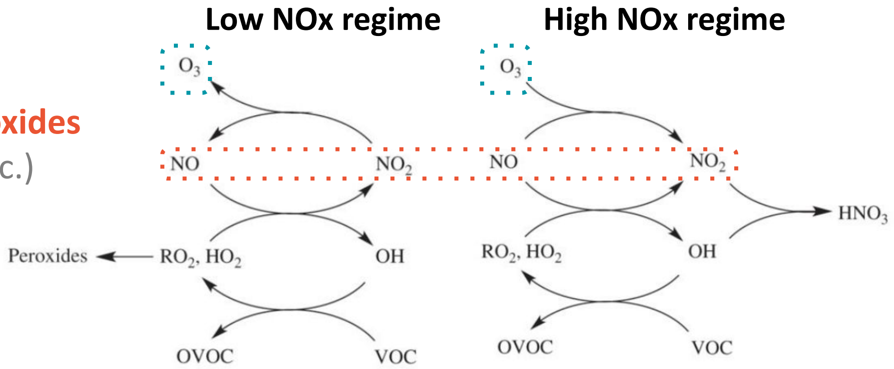


Fig.3 How NOx affects Ozone chemistry. (Source: Air pollution, 2019)

VOC Chemistry

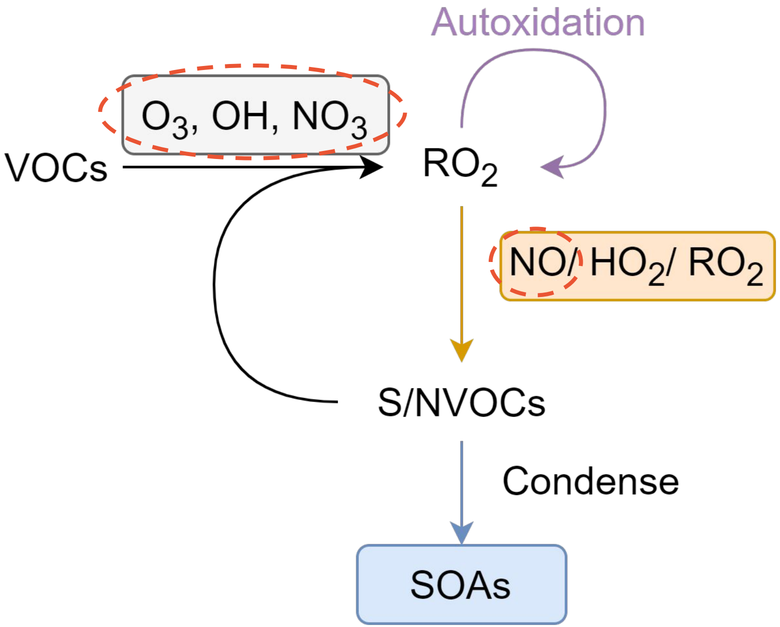


Fig.4 VOC degradation related to SOA formation.
S/NVOCs: semi-/non- volatile organic compounds

Anthropogenic Emission → **SOA Formation**

Non-linear

How can we simulate **accurate SOA responses** to anthropogenic emission mitigation?

SOA Formation Modeling

Bottom-up Approach

Add and evaluate **model species** and **lumped mechanism** for representative SOA precursors.

$$VOCs + Oxidants \longrightarrow \alpha_1 P_1 + \dots + \alpha_n P_n$$

Where α is SOA yield, P is model species: volatility bin or surrogate product.

Highly simplified VOC chemistry

Top-down Approach

Develop **protocols** to generate **detailed** VOC degradation schemes from targeted SOA precursors.

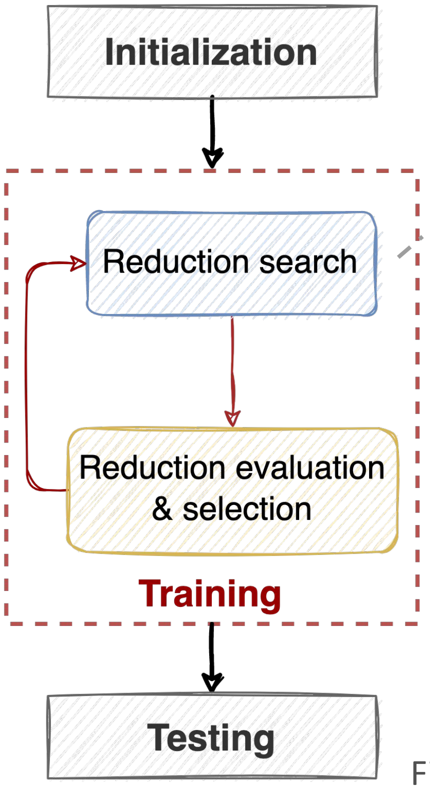
Multi-generation reactions & organic species

Overwhelming computational cost

⇩

Mechanism Reduction is Required

GENOA GENerator of reduced Organic Aerosol mechanisms



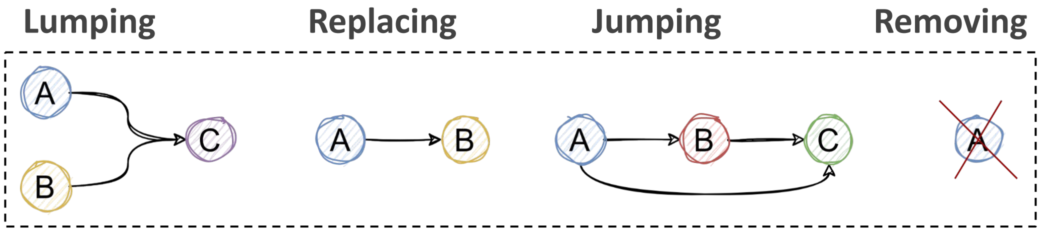


Fig.6 **Reduction Strategies** - Protocols to reduce species/ reactions

Semi-Explicit SOA Mechanisms

> Preserve complexity of VOC chemistry on SOA formation
- Condensable species (with structures)
- Reaction pathways forming SOAs

> Manageable Computational Costs
- Application to regional-scale air quality modeling

Fig.5 Schematic diagram of GENOA. (Wang et al., 2022)

GENOA GENerator of reduced Organic Aerosol mechanisms

GBM: GENOA v2.0-reduced Biogenic Mechanism

GENOA v2.0 (Wang et al. 2023):

Parallel Reduction on Mechanisms from Multiple SOA Precursors

Monoterpene (MT) SOA Formation

- ➔ Reference & starting point
  - ◆ α-pinene, β-pinene, and limonene degradation in
    - ● **M**aster **C**hemical **M**echanism (MCM v3.3.1) (Jenkin et al., 1997)
    - ● **P**eroxy **R**adical **A**utoxidation **M**echanism (PRAM) (Roldin et al., 2019)
      - ○ Highly **O**xygenated organic **M**olecules (**HOMs**)
- ➔ Result: Size < 8% of MCM+PRAM & error < 3%

Sesquiterpene (SQT) SOA Formation

- ➔ Reference & starting point
  - ◆ β-caryophyllene (BCARY) degradation in MCM v3.3.1 (Jenkin et al., 2012)
- ➔ Result: Size < 2% of MCM & error < 3%

3-D Simulations: Top-down v.s. Bottom-up

Chimere v2020
Chemistry-Transport Model
(Menut et al., 2021)
+
SSH-aerosol v1.3
Aerosol Box Model
(Sartelet et al., 2020)

SOA Mechanisms

Top-down: GBM - **G**ENOA v2.0-reduced **B**iogenic **M**echanism
Bottom-up: H^2O - **H**ydrophilic/**H**ydrophobic **O**rganic mechanism
(Couvidat et al., 2012)

Performance in 3-D Modeling

- Comparison with **Measurements** (**EBAS** database)
- Comparison Between Simulations

Response to Emission Reduction

- **50% NOx (NO, NO_2, HONO)** Reduction

GBM v.s. H^2O: monoterpene (MT)

Reduced by GENOA

Number	H^2O	GBM	MCM+PRAM
Reaction	22	197	3001
Species	15	110	1227
S/NVOC	6	23	975

Tab.1 Size of MT SOA schemes in different mechanisms.

MT SOAs = non-HOMs (MCM) + HOMs (PRAM):

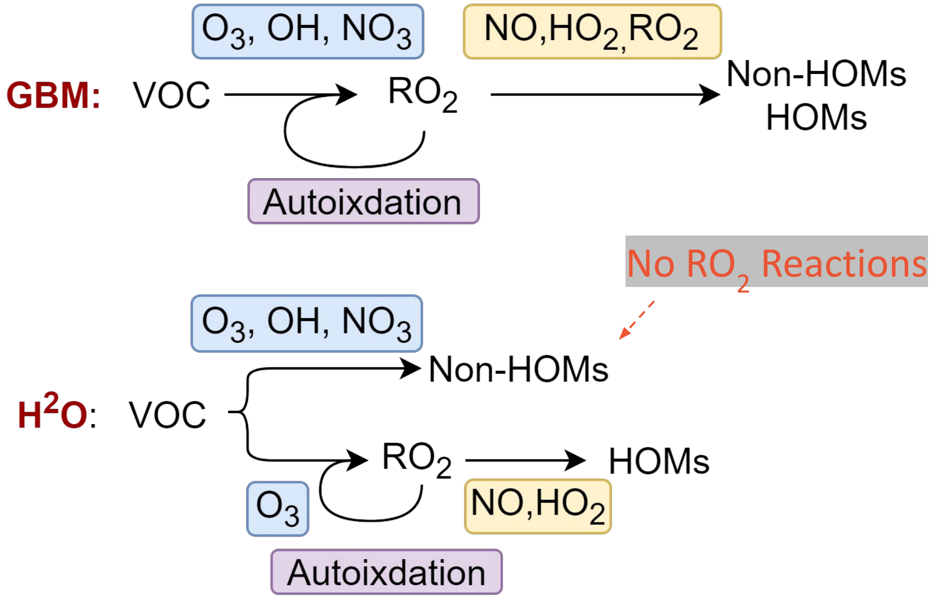


Fig.7 Comparison between GBM and H^2O MT schemes.

GBM v.s. H^2O: sesquiterpene (SQT)

H^2O: SQT + OH/O_3/NO_3 -> BiBmP + BiBlP

GBM:

Reduced by GENOA

Number	H^2O	GBM	MCM
Reaction	3	23	1625
Species	3	17	579
S/NVOC	2	6	365

Tab.2 Size of SQT SOA schemes in different mechanisms.

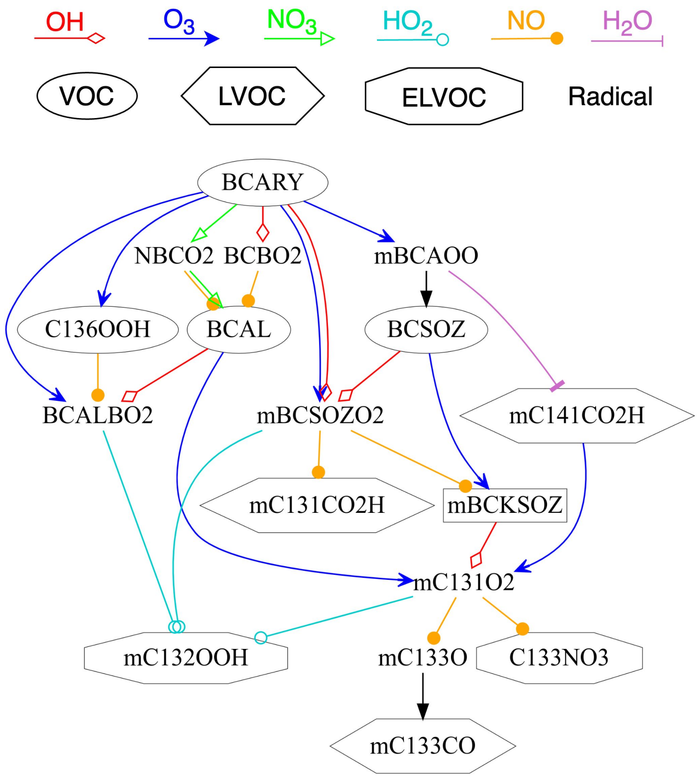


Fig.8 SQT SOA schemes in GBM.

v.s. Measurement

	PM_{10}	$PM_{2.5}$	$OC_{PM_{2.5}}$	OC_{PM_1}	OM_{PM_1}
No. station	80	61	25	2	2
No. measurement [b]	92	89	16	17	25
Measurement mean	13.5	7.9	2.5	2.3	4.2

Tab.3 Measurements extracted from EBAS database.

Simulation Setups

- 2018/6/1 to 2018/8/31 (15 days spin-up)
- Europe (32°N to 70°N & 17°W to 39.8°E)
- Resolution: 0.25° x 0.4°

Biogenic Emissions

- MEGAN v2.1
- MT × 3 & SQT × 3 & Isoprene / 3
  (Sindelarova et al., 2022; Ciccioli et al., 2023; etc.)

GBM better matches **measurements** than H^2O

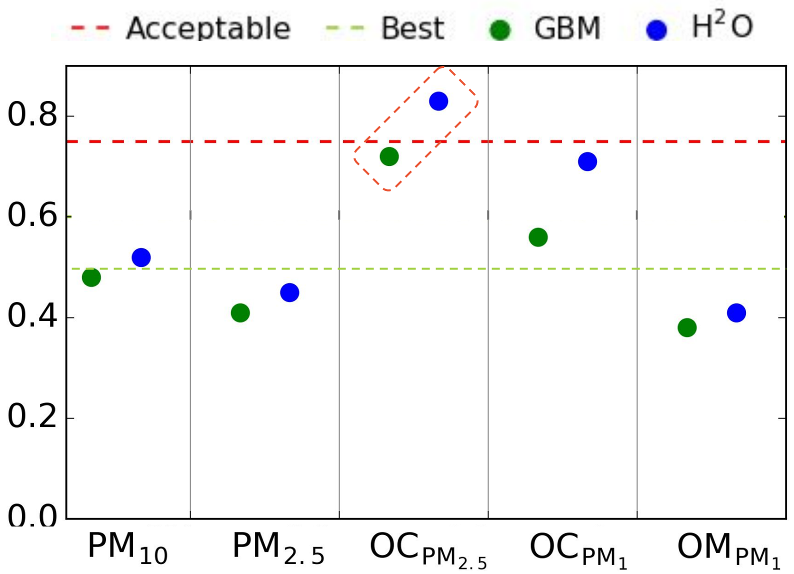
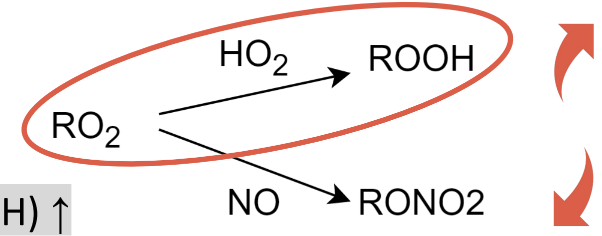


Fig.9 Mean fractional error (MFE) of OAs between simulation results and measurements. Criteria "Acceptable" ≤ 75%, "Best" ≤ 50% reported by Boylan et al., 2006.

Response to NOx Reduction:

Inorganics

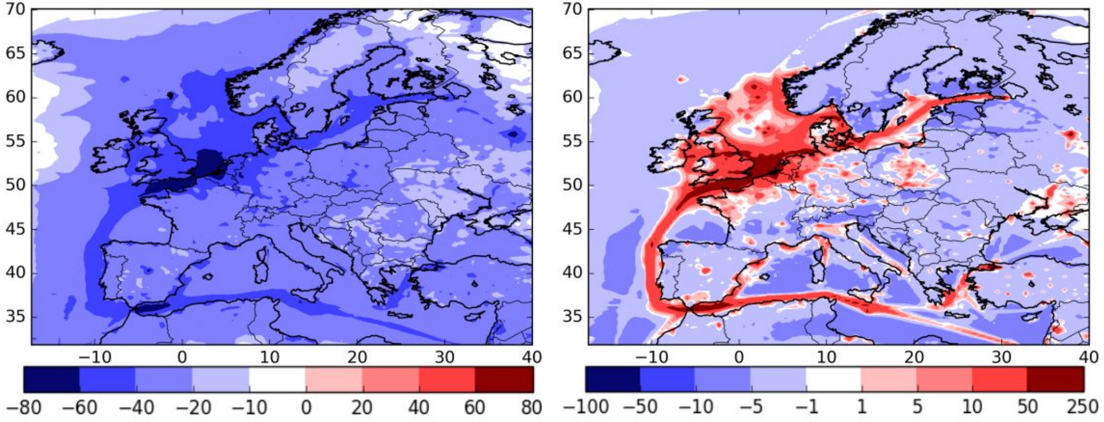


H2O & GBM: NOx ↓ => NO/HO_2 ↓ => RO_2 + HO_2 ↑ => Peroxides (ROOH) ↑

Tab.4 **Inorganic variations** due to NOx reduction

Regimes	Low NOx	High NOx
NO	↓↓	↓↓
Ozone	↓	↑
OH, NO_3	↓	↑
HO_2	↓	↑↑
NO/HO_2	↓	↓↓

NO **HO_2**



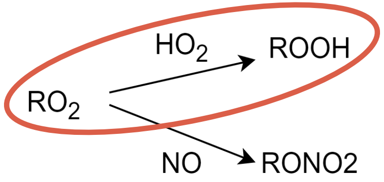
(a) NO NOx50 - REF Conc. (%) (b) HO2 NOx50 - REF Conc. (%)

Fig.10 NO and HO_2 variations due to NOx reduction simulated with GBM

Response to NOx Reduction:

SOAs

Anthropogenic Emission ⇨ **Biogenic SOA Conc.**



Conc. (μg/m³)	GBM	H^2O
SOAs	+0.08	+0.04
MT SOA	+0.09	+0.03
HOMs	+0.05	+0.04
Non-HOMs	+0.04	-0.01
SQT SOA	-0.01	≤0.001

Tab.5 Conc. variations due to NOx reduction

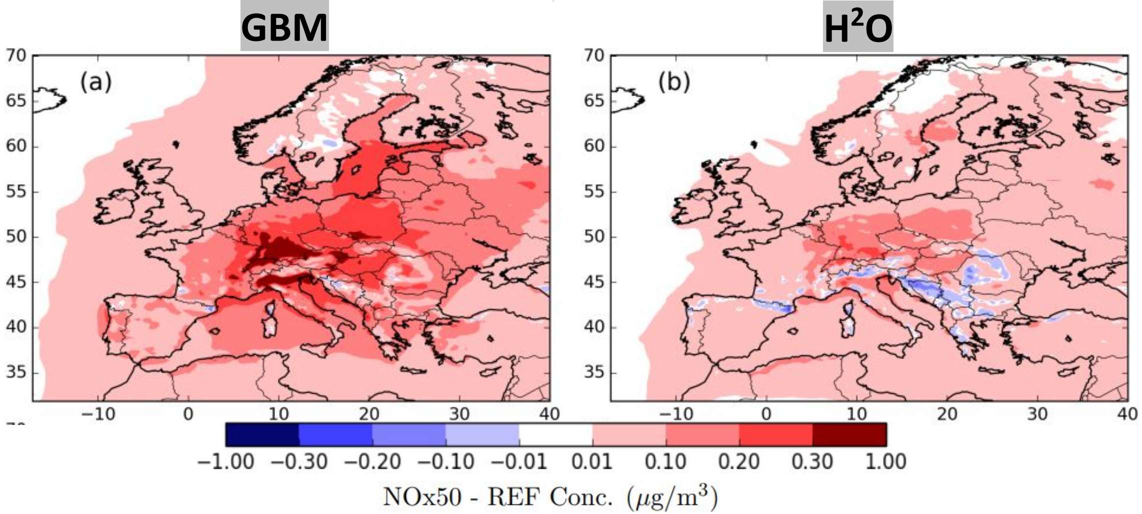


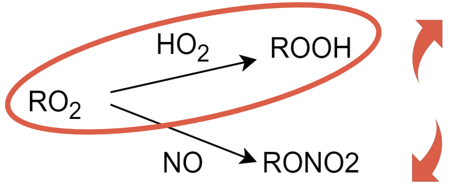
Fig.11 SOA variations due to NOx reduction simulated with GBM/H^2O

H^2O & GBM: **MT ROOHs** are less volatile than RO_2+NO Products

Response to NOx Reduction:

Monoterpene (MT) SOAs

Anthropogenic Emission ⇨ **Biogenic SOA Conc.**



Conc. (μg/m³)	GBM	H²O
SOAs	+0.08	+0.04
MT SOA	+0.09	+0.03
HOMs	+0.05	+0.04
Non-HOMs	+0.04	-0.01
SQT SOA	-0.01	≤0.001

Tab.5 Conc. variations due to NOx reduction

Usual response in current 3-D modeling

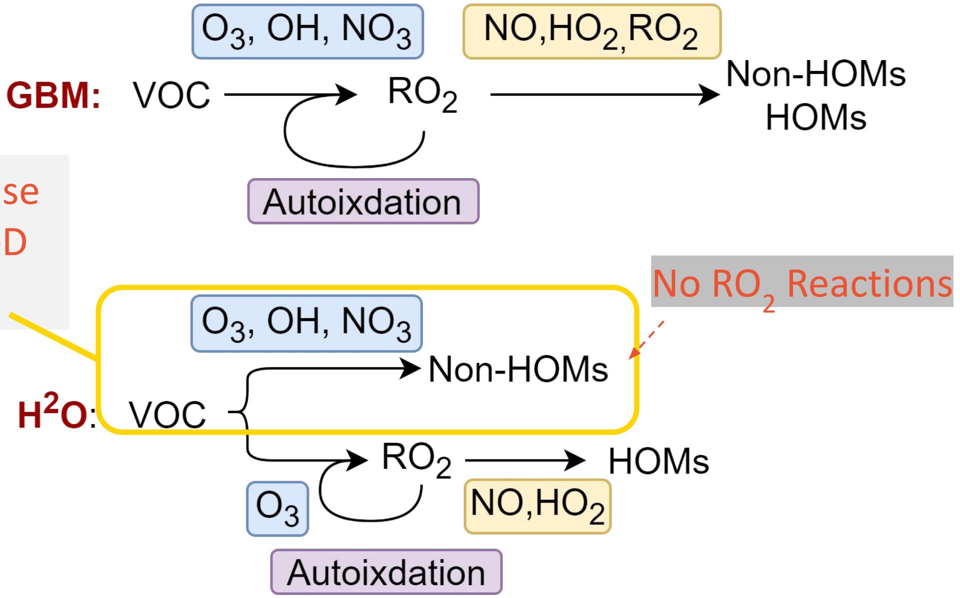
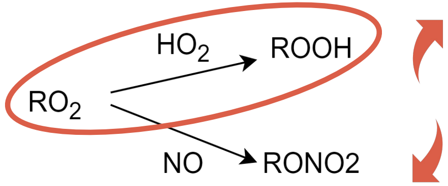


Fig.12 Comparison between GBM and H²O MT schemes.

Response to NOx Reduction:

Sesquiterpene (SQT) SOAs

Anthropogenic Emission ⇨ **Biogenic SOA Conc.**



Conc. (μg/m^3)	GBM	H^{2}O
SOAs	+0.08	+0.04
MT SOA	+0.09	+0.03
HOMs	+0.05	+0.04
Non-HOMs	+0.04	-0.01
SQT SOA	-0.01	≤0.001

Tab.5 Conc. variations due to NOx reduction

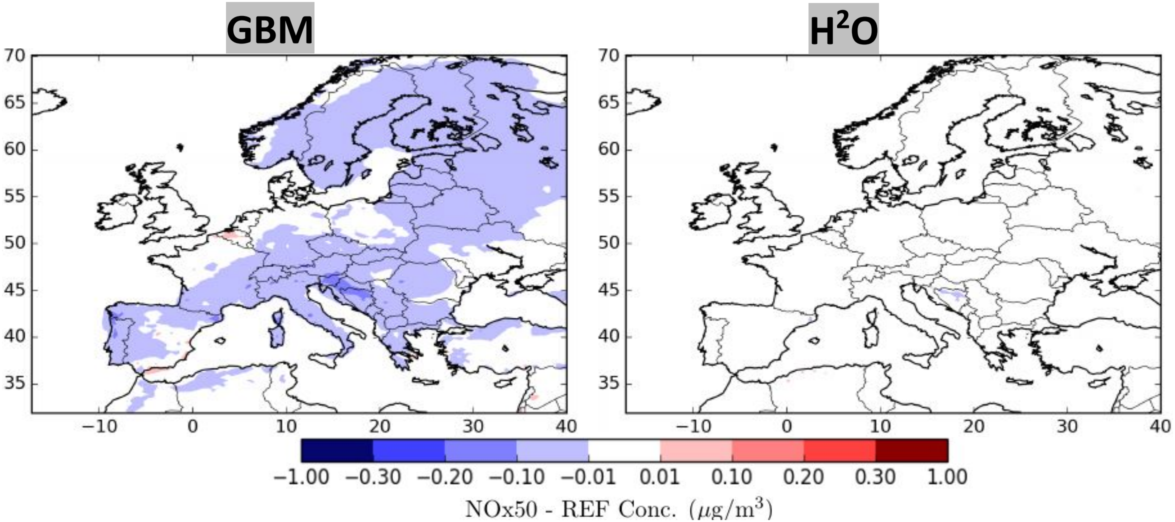


Fig.13 SQT SOA variations due to NOx reduction

H^{2}O & GBM: **SQT SOAs** are not sensitive to NOx

Conclusions

Mechanism Reduction

- **GBM** trained from MCM + PRAM using **GENOA v2**
  - Monoterpene and sesquiterpene SOA Formation

3-D Simulations with **Top-down** (**GBM**) and **Bottom-up** (**H^2O**) SOA mechanisms

- GBM better matches **measurements** than H^2O
- **NOx** ↓ -> **SOAs** ↑ w/ H^2O & **SOAs** ↑↑ w/ GBM
  - **Monoterpene:** NOx ↓ -> NO/HO_2 ↓ -> RO_2 + HO_2 = ROOH ↑ -> SOAs ↑
    - Significant SOAs from **HOM** formation via RO_2 Autoxidation
  - **Sesquiterpene**: SOA not sensitive to NOx

Detailed SOA Mechanisms => Appropriate Response of SOAs to Emission Mitigation in 3-D Air Quality Modeling

What is going on now …

Model development

- Preserve formation of other pollutants from VOC degradation
  - Ozone, NOx, …
- Apply to **Fully Explicit VOC Mechanisms** (EPA STAR Agreement # 84000701)
  - GECKO-A (Aumont et al., 2005), MechGen (Carter et al., 2023), …

Model application

- Generate condensed SOA mechanisms from other SOA precursors
  - Aromatics, isoprene, …
  - **Final goal:** Build **One For All** Key SOA Precursors
- Investigate SOA formation variations on other scenarios
  - Shipping routine, Agriculture zone, …

Thank you!

Check Out Our Poster 👉 **"3-D Simulations of Toluene SOA Formation at Regional and Street Scales"** in Poster Session!