Modeling atmospheric degradation of amine compounds H22-095

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HARMO

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Motivation :

Carbon capture utilization and storage (CCUS) technologies have become an essential component of the strategy to combat global warming by carbon dioxide emissions mitigation from industrial sources and power generation.

- CCUS will have a wide deployment for industries
- Technologies with amine-based absorption processes standing out as effective means to reduce CO_2 emissions

Problem : nitramines and nitrosamines are compounds classified as carcinogens by the World Health Organization, and their guideline level* (by NIPH) is set at **0.3 ng/m³** in air for the sum of the two.

** Derived Minimal Effect Level, associated with a cancer risk level of 1 to 10^{-6} after lifetime exposure, from Norwegian Institute of Public Health (NIPH).*

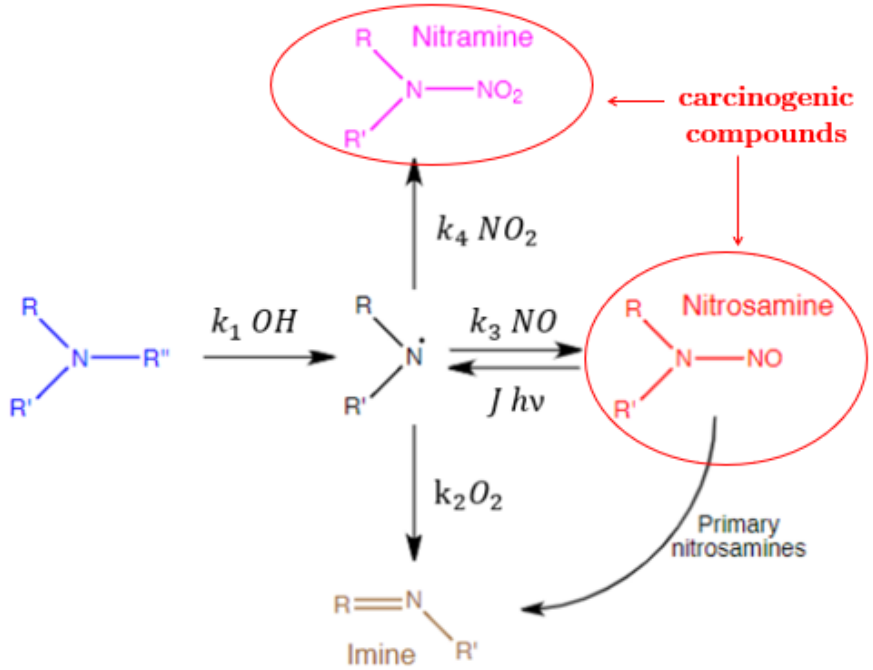


Figure 1. General degradation pathways for amine compounds.

Objectives

General objective : be able to assess new local health and environmental effects which involves emissions in atmosphere from CCUS technologies and provide modeling adapted tools.

Use of the **chemistry-transport model** (CTM) with improvements to the chemistry modules to take into account OH-initiated degradation pathways and particle formation.
Problem: *No access to air ambient measured data at ground level and in plumes to do comparisons yet.*

First solution before 3D modelling: Comparison with results of atmospheric chamber experiments.

➢ Experimental chamber setup and measured data from:
Tan, W., Zhu, L., Mikoviny, T., Nielsen, C. J., Tang, Y., Wisthaler, A., ... & Stenstrøm, Y. (2021). Atmospheric chemistry of 2-amino-2-methyl-1-propanol: a theoretical and experimental study of the OH-initiated degradation under simulated atmospheric conditions. The Journal of Physical Chemistry A, 125(34), 7502-7519.

Setting up

❖ Use of a **Plume-in-Grid** from the Polyphemus air quality plateform with **SSH-aerosol.**

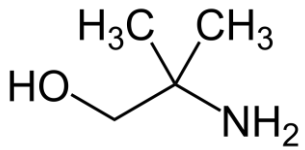
POLYPHEMUS Air Quality Modeling System

SSH aerosol

❖ Use of SSH-aerosol as a box model and results of **Euphore atmospheric chamber** photo-oxidation experiments.

CEAM FUNDACIÓN CENTRO DE ESTUDIOS AMBIENTALES DEL MEDITERRÁNEO

➢ Study of 2-amino-2-methyl-1-propanol [**AMP**] (CH3C(NH2)(CH3)CH2OH)



Methodology: comparison of measure/modelisation

0-dimensional modeling with SSH aerosol as box model:

- Recreate as possible conditions in atmospheric chamber during experiment : HO_2 and NO emission to reproduce Isopropyl nitrite (IPN) photolysis.
- OH profile calculated from AMP measured profile and ajusted with a coefficient.

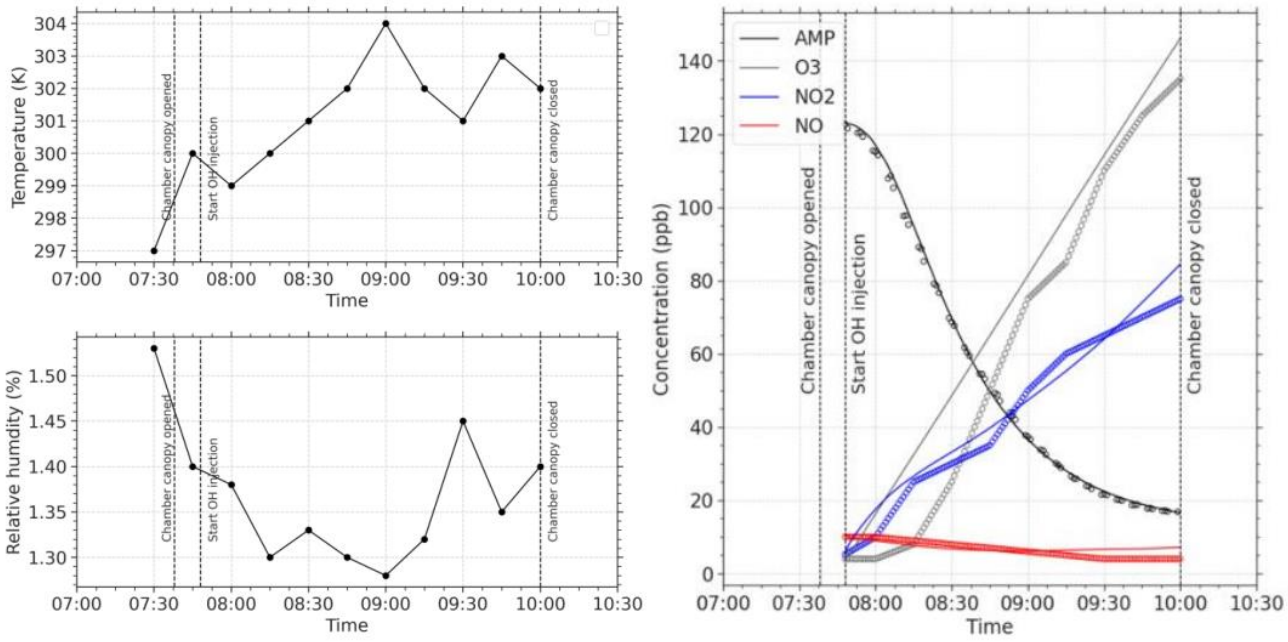


Figure 2. Temporal evolution of temperature and relative humidity / Measured (dotted curves) and modeled temporal profiles by SSH-aerosol for AMP and background species, Experimental d*ata from J. Phys. Chem. A 2021, 125, 34, 7502-7519*

Modeling amine chemistry:

- Consider only gaseous degradations.
- Work with a CB05 modified version.
- Focus on degradation compounds profiles.

Use of chemistry degradation pathways presented in Table 1 : *branching ratio of kinetic rate coefficient are unchanged.*

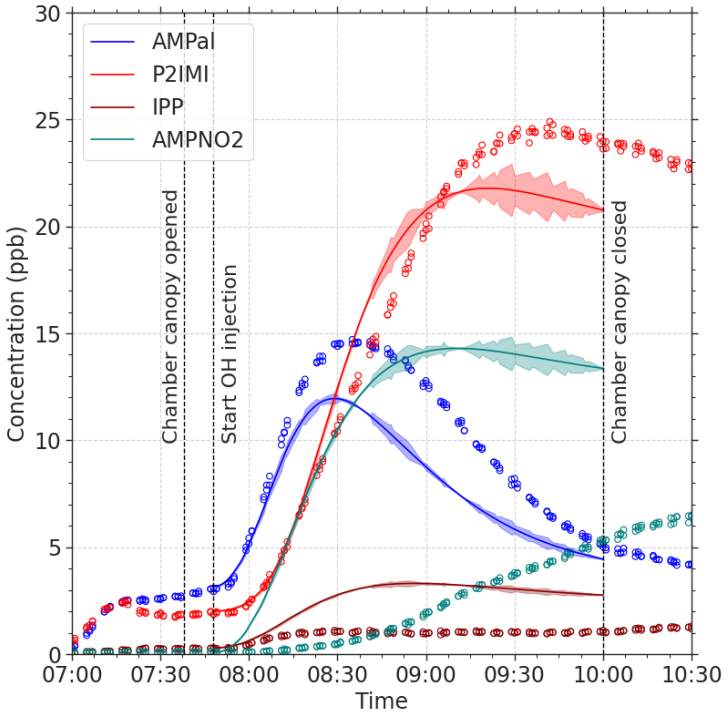
reaction	rate coefficient	ref.
$(CH_3)_2(CH_2OH)CNH_2 + OH \longrightarrow 0.06\,(CH_3)(CH_2OH)C{=}NH + 0.28\,CH_3C(O)NH_2 + 0.42\,(CH_3)_2(CHO)CNH_2 + 0.24\,(CH_3)_2(CH_2OH)CNH$	2.8×10^{-11}	a
$(CH_3)_2(CHO)CNH_2 + OH \longrightarrow 0.95\,(CH_3)_2C{=}NH + 0.05\,CH_3C(O)NH_2$	7.0×10^{-11}	b
$(CH_3)_2C{=}NH + OH \longrightarrow CH_3CN + CH_2O$	2.0×10^{-11}	b
$(CH_3)(CH_2OH)C{=}NH + OH \longrightarrow (CH_3)(CHO)C{=}NH$	2.0×10^{-11}	b
$(CH_3)_2(CH_2OH)CNH \longrightarrow (CH_3)_2C{=}NH + CH_2O$	4.6×10^{-3}	b
$(CH_3)_2(CH_2OH)CNH + NO \longrightarrow (CH_3)_2(CH_2OH)CNHNO$	$(8.5\pm1.4)\times10^{-14}$	c
$(CH_3)_2(CH_2OH)CNH + NO_2 \longrightarrow (CH_3)_2(CH_2OH)CNHNO_2$	$(3.2\pm0.5)\times10^{-13}$	c
$(CH_3)_2(CH_2OH)CNHNO + OH \longrightarrow (CH_3)C(O)CH_3 + CH_2O + N_2O$	1.0×10^{-10}	b
$(CH_3)_2(CH_2OH)CNHNO + h\nu \longrightarrow (CH_3)_2(CH_2OH)CNH + NO$	$0.34\times J_{NO2}$	d
$(CH_3)_2(CH_2OH)CNHNO_2 + OH \longrightarrow (CH_3)_2(CHO)CNHNO_2$	$(7.5\pm3.5)\times10^{-13}$	e,f

Table 1. AMP gaseous degradations pathways in atmospheric conditions (from Tan and al. 2021) employed in modeling, bimolecular rate coefficients in units of $cm^3.molecules^{-1}.s^{-1}$ and unimolecular rate coefficients in units of s^{-1}. a (Haris and al. 1983), b (Tan and al. 2021) ,c (Lazarou and al. 1994°, d (Nielsen and al. 2012) ,e (Borduas and al. 2015) , f (Barnes and al. 2010)

Results : Comparison measure/modelisation in 0d

Differences : Forcing OH concentrations, not complete initial conditions, not considering particles formation or other reactions, homogeneity hypothesis.
→ Good results with gaseous degradation only.

SSH-aerosol for $B_{CH3}/B_{CH2}/B_{NH2}$ = 6:42:24



SSH-aerosol for $B_{CH3}/B_{CH2}/B_{NH2}$ = 6:50:24

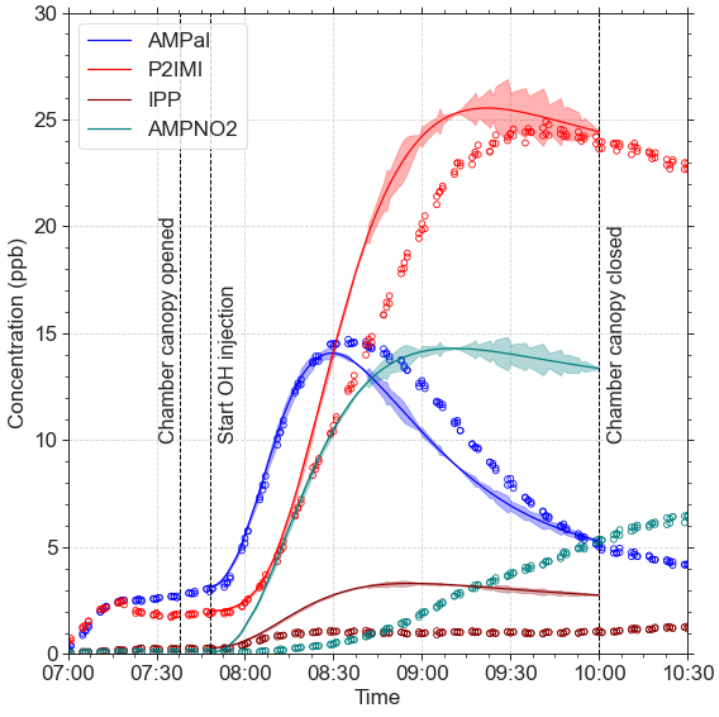


Figure 3. Measured (dotted curves) and modeled temporal profiles **(a)** for $B_{CH3}/B_{CH2}/B_{NH2}$ = 6:42:24 **(b)** for $B_{CH3}/B_{CH2}/B_{NH2}$ = 6:50:24, $(CH_3)_2(CHO)CNH_2$ (AMPal), $(CH_3)_2C{=}NH$ (P2IMI), $CH_3(CH_2OH)C{=}NH$ (IPP), and $(CH_3)_2(CH_2OH)NHNO_2$ (AMPNO2).

MESMER 3.0 for $B_{CH3}/B_{CH2}/B_{NH2}$ = 6:70:24

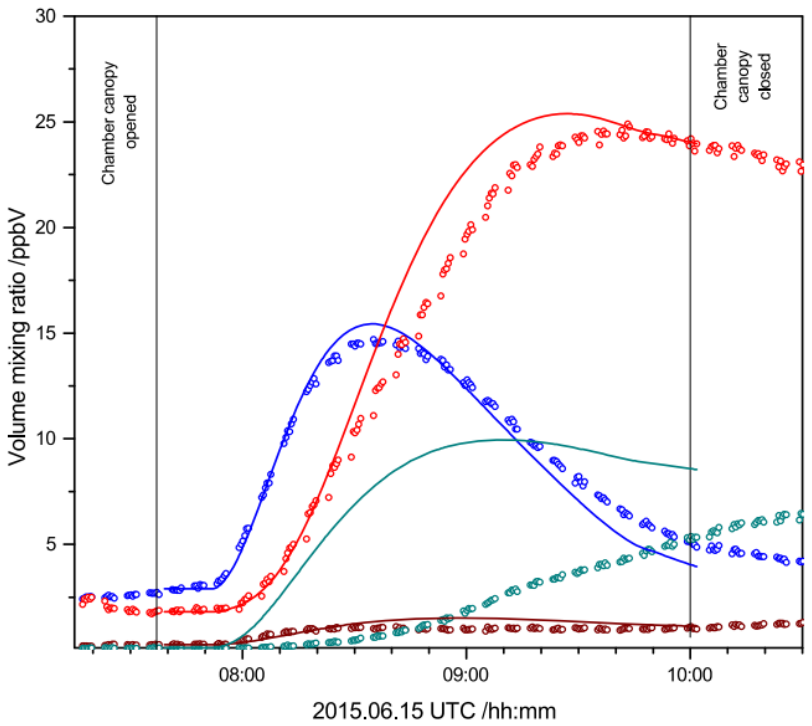


Figure 4. *Observed and modeled temporal profiles of products in the OH-initiated AMP photo-oxidation experiment on 2015.06.15. (CH3)2(CHO)CNH2 (blue color), (CH3)2C=NH (red color), CH3(CH2OH)C=NH (wine color), and (CH3)2(CH2OH)NHNO2 (dark cyan color). From J. Phys. Chem. A 2021, 125, 34, 7502-7519*

Comparison of ADMS and Plume-in-grid model to assess CCS

ADMS : World leading software for modelling industrial air pollution.

- Currently used for future impacts of CCS.
- Gaussian plume model : Constant meteorological and concentration fields in the whole domain.

Plume-in-Grid : combination of an eulerian model and a gaussian puff model.

- Eulerian model : chemistry and transport of atmospheric background pollutants.
- Gaussian puff model : chemistry and transport of industrial point emissions in interaction with the background.

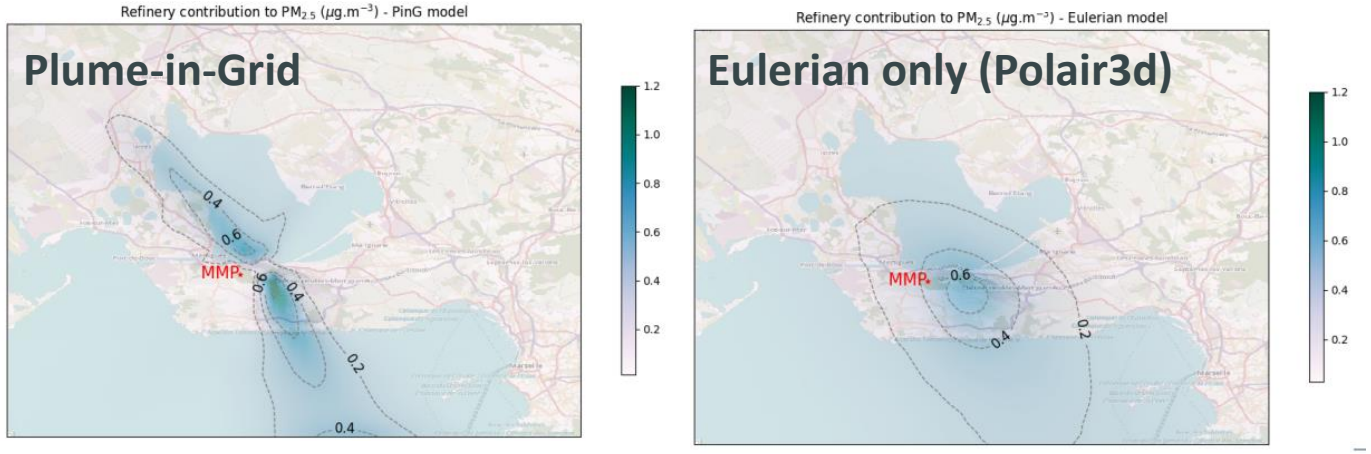


Figure 5. Comparison of impact location according to dispersion approach, (a) Plume-in-Grid model and (b) eulerian model from Polyphemus.

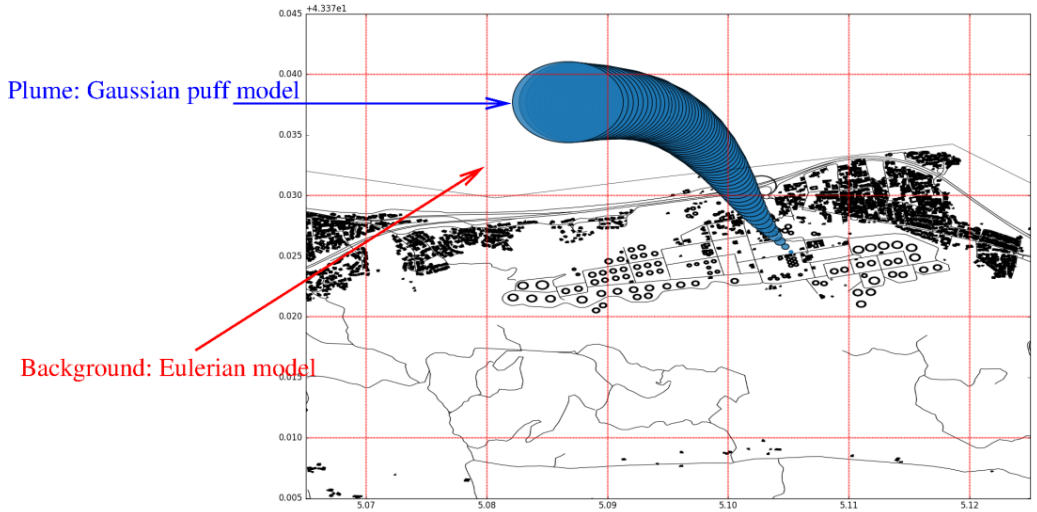


Figure 6. Plume-in-grid model.

Methodology : Theoretical case

Objective : perform two similar simulations between Plume-in-Grid and ADMS.

Amine atmospheric degradation pahways : gas only

- PinG : use of SSH-aerosol model with AMP specific degradation pathways. (previously presented)
- ADMS : use of amine chemistry module with general degradation pathways.

Case study on city area :

- PinG : 3-dimensional meteorological fields from WRF simulation.
- ADMS : extract meteorological data at source location from WRF simulation.

Source : AMP emission of 5.9 g/s

- Emissions corresponds to the leakage rate for the treatment of 1 Mtonne of CO_2/year

ADMS Amine chemistry

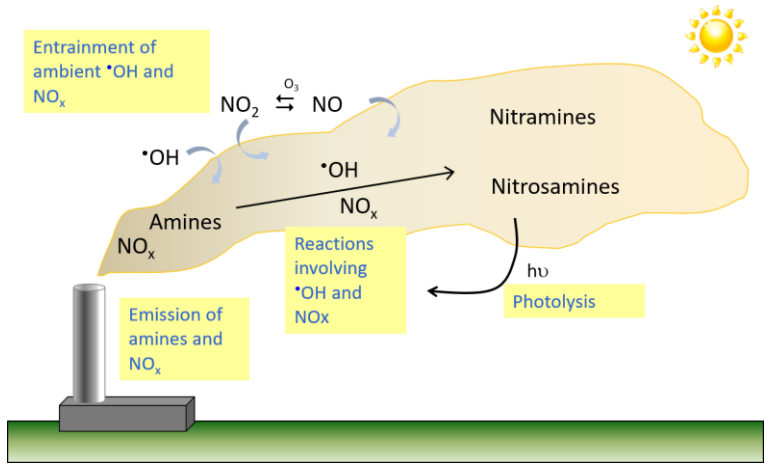


Figure 7. Model options included in ADMS amine chemistry module, *From CERC 2024*

AMINE + •OH	→	amino RADICAL + H_2O	(1a)
	→	RN(H)C•H_2 + H_2O	(1b)
amino RADICAL + O_2	→	imine + HO_2	(2)
amino RADICAL + NO	→	NITROSAMINE	(3)
amino RADICAL + NO_2	→	NITRAMINE	(4a)
	→	imine + HONO	(4b)
NITROSAMINE	hv →	amino RADICAL	(5)

Results : spatial impacts with different chemistry modelling

Importance of the 3D approach

- ❖ Inhomogeneous concentration/meteorological fields.
- ❖ highlighting the spatial and temporal variability of secondary compound formation → not possible with ADMS.

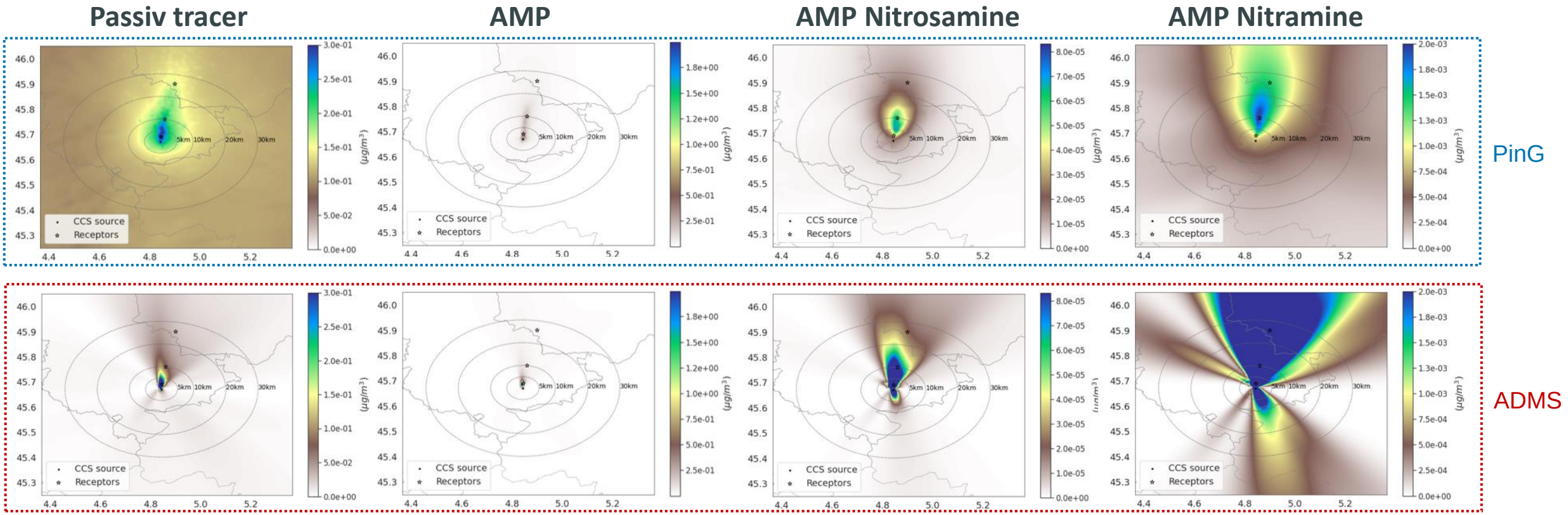


Figure 8. Comparisons between PinG (top maps) and ADMS (bottom maps) for a passiv tracer, AMP, $(CH_3)_2(CH_2OH)CNHNO$ (AMPNO) and $(CH_3)_2(CH_2OH)CNHNO2$ (AMPNO2) for averages concentration from 2018-04-02 to 2018-04-11 included (colorbar representation set up at the maximum concentration in PinG for each compounds).

Results : maximum concentration as a function of distance from source

Approach differences

- CTM approach gives more consistent results based on areas of high NOx emissions.
- PinG gives lower impacts close to the source contrary to ADMS.
- ADMS would tend to give concentration values that can be overestimated.

→ **Need air measurement data to compare concentration levels.**

→ **Highlight why CTM model must be used for CCS environmental assessment.**

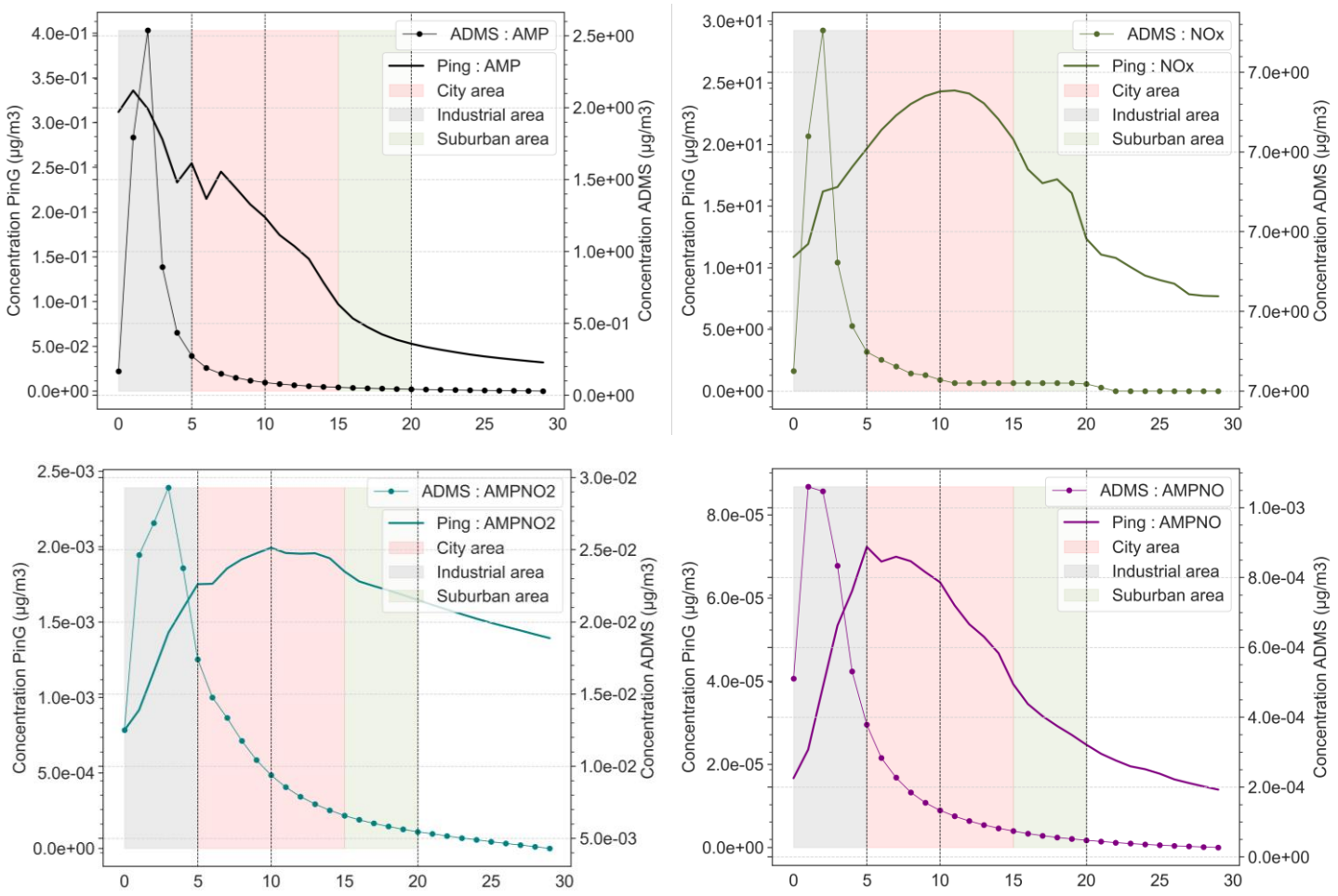


Figure 9. Comparisons between PinG (line curves) and ADMS (line dotted curves) for $(CH_3)_2(CH_2OH)CNH_2$ (AMP), Nox (sum of NO and NO_2), $(CH_3)_2(CH_2OH)CNHNO2$ (AMPNO2) and $(CH_3)_2(CH_2OH)CNHNO$ (AMPNO), from averages concentration 2018-04-02 to 2018-04-025.

Future work – emissions, impacts and modeling

MODEL VALIDATION : comparison with measurments in atmospheric chamber

- ❖ EUPHORE atmospheric chamber experiment for AMP.

- ➢ Comparisons between measured data and simulated data in 0D **including particles formation**.

MODEL APPLICATION :

SCOPE

- ➢ Setting up a 3D case and simulate one or more periods of CCUS use to estimate medium to long-range health and environmental impacts.
- ➢ possibility of adding new amine species and other products to best represent the solvents used.
- ➢ Emission assumptions based on SCOPE (Sustainable OPEration of post-combustion Capture plants) campaign data: extrapolation for full-scale sites

Water transfer, dry and wet depositions

NIVA

- ❖ FuNitr : Future Drinking Water Levels of Nitrosamines and Nitramines near a CO2 Capture Plant.

- ➢ Implementation of washing (wet deposition) for amines using FuNitr transfer coefficients.
- ➢ Quantification of dry and wet deposits in CTM and estimated transfers to drinking water (via watersheds).

Norway recommended drinking water limit for nitrosamine + nitramine level :

4 ng/L

Measure by mass spectrometer

LQA Laboratoire Qualité de l'Air

- ❖ PTR-MS-TOF : Proton Transfer Reaction Mass Spectrometer Time Of Flight

- ➢ Ultra-sensitive gas analyser for real-time measurment of volatil organic compounds (VOCS)
- ➢ measurement of amines / deg. Compounds :
  - ➢ in stack emissions for better emission.
  - ➢ In ambient air, comparison with modelling.

Aknowlegment:

Armin Wisthaler : providing experimental informations and amine measured data.

Thank you for your attention !