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MODELING AMINES AND DEGRADATION PRODUCTS IN THE PLUME OF ASSET WITH CARBON CAPTURE TECHNOLOGY

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Abstract: This work aims to develop tools enabling to assess the atmospheric concentrations of toxic amine degradation products linked to carbon capture technologies. Due to the unavailability of ambient air measurements, measurement/modeling comparisons were made on the basis of atmospheric chamber measurements (in EUPHORE) and a box model (SSH-aerosol) for 2-amino-2-methyl-1-propanol (AMP). This first evaluation step allows us to use in the following with greater confidence the amine chemistry modules developed in SSH-aerosol. This latter has also been included in a new version of a chemistry-transport model relying on a Plume-in-Grid approach (PinG) to treat emissions from point sources. Fictitious impact studies were carried out with PinG and compared with a model widely used by industrialists and engineering firms: ADMS. The chemistry-transport model approach offers the possibility of taking into account variable meteorological fields and background concentrations in 3 dimensions with all the qualities needed to assess the potential impact on health and the environment of a Carbon Capture and Storage unit (CCS).

Key words: *Amine , atmospheric dispersion, chemistry-transport model, carbon capture*

INTRODUCTION

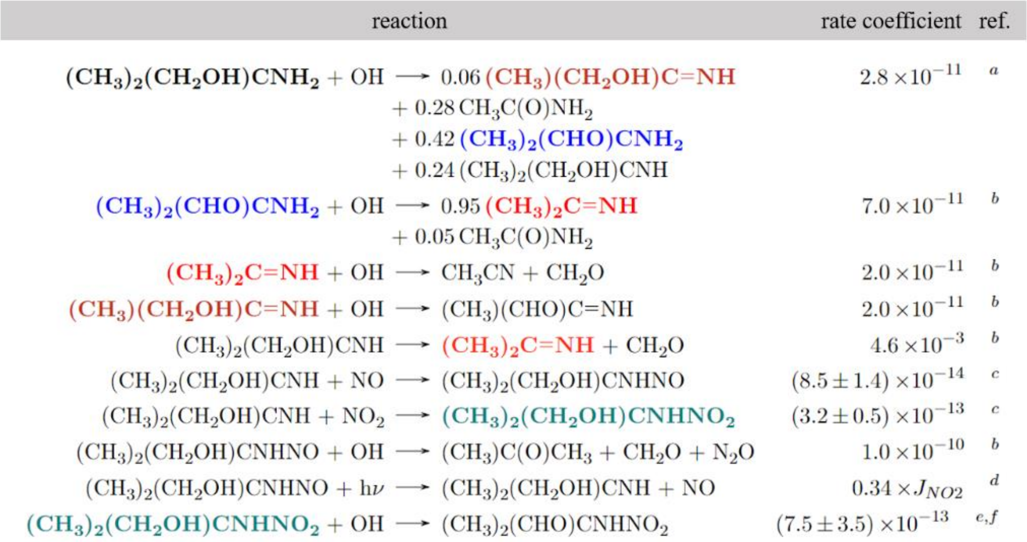
Carbon capture technologies have become an essential component of the strategy to combat climate change and specifically to mitigate the increasing levels of atmospheric carbon dioxide from industrial sources and power generation. Technologies with amine-based absorption processes standing out as effective means to reduce CO_2 emissions.(Martin and al. 2021) However, it leads to minor releases of solvent into the atmosphere and consequently to amines emissions fluxes. The atmospheric degradation processes to which the amines are subjected lead to the formation of secondary compounds that are carcinogenic and harmful to the environment: nitrosamines and nitramines.(Manzoor and al. 2014, Nielsen and al. 2010) It is therefore relevant to investigate the atmospheric fate of amines, particularly their chemical degradation pathways by including them in chemical-transport model to assess risk for health and environment.

Even if the current lack of data for direct atmospheric measurements of amine and degradation products currently prevents comprehensive comparisons with 3D simulations, the comparisons between atmospheric chamber measurements of OH initiated degradation of 2-amino-2-methyl-1-propanol (AMP) (Tan and al. 2021) and SSH-aerosol (Sartelet and al. 2020) as a box model represent a first evaluation step. The second objective is to compare two modeling frameworks to highlight the impact of a simplifying assumption on the spatial description of concentrations. So, beyond this evaluation against observations, we proceed to a comparison between a commercial gaussian plume model (ADMS 5.2) and a Plume-in-Grid (Ping) (Korsakissor and Mallet 2010) model in order to highlight the importance of variable atmospheric conditions, especially for nitrogen oxides concentration variation. We aim to present the developments made in SSH-aerosol to include amine degradation pathways. This multiphase chemistry model has been plugged within the plume-in-grid approach proposed within the Polyphemus air quality platform (http://cerea.enpc.fr/polyphemus/) to assess the potential impact of a CCS unit.

METHODOLOGY

Amine chemistry

The OH-initiated degradation of AMP $(CH_3)_2(CH_2OH)CNH_2$ was studied by Tan and al. 2021 during photo-oxidation experiments in the EUPHORE atmospheric chamber. The major reaction routes implemented in SSH-Aerosol, with their associated rate coefficients and branching ratios are compiled in Figure 1. The formation of secondary aerosols is not be considered for the time being.



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

Figure 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)

Model presentation

The models used are . The two models used, ADMS5.2 and Polyphemus Plume-in-Grid (PinG), are not based on the same dispersion approach: ADMS is a Gaussian plume model, while the PinG model is a combination of an Eulerian model, for background concentrations management, and a Gaussian puff model to represent the plume of point source emissions. The PinG model is adapted and validated to reproduce emissions of industrial sources.(Kim and al. 2014) Different chemistry modeling approaches are used in both models. In ADMS, only the chemical patterns of NO_x (reaction of NO with O_3, photolysis of NO_2) and the general chemical reactions of amines released during carbon capture and storage (CCS) for OH-initiated oxidation are included. The PinG model is coupled to the SSH-aerosol model, a suitable multiphase chemical modeling framework that represents the physico-chemical transformation undergone by particles and gases in the troposphere, using a modified version of the Carbon Bond v5 (CB05) model. (Sartelet and al. 2020)

Model setup

The 0-dimensional modeling case with SSH-aerosol, used as a box model, recreate as possible conditions in the EUPHORE atmospheric chamber during the experiment. OH radicals concentration was estimated and adaptated from gaseous AMP measured concentration and is forced during simulation. The experiment environment was reproduced by emissions of HO_2 and NO to reproduce isopropyl nitrite photolysis (used in experiment to produce OH). Concentrations of background species like NO_x and O_3 have been adjusted as much as possible to measured data with these continuous emissons. Meteorological data have been reconstructed and photolysis rates have been adjusted to measures rates. The 3-dimensional modeling case is based on a test case on Lyon area with southerly winds. All data are issued from Polyphemus preprocessing and directly used in case of PinG and extracted at source location for ADMS. The emission rate of AMP is 5.9 $g.s^{-1}$ and corresponds to the leakage rate for the treatment of 1 Mtonne of CO_2/year. (-). This case study is theoretical and does not take into account NO_x or nitrosamine emissions at source.

RESULTS

Modeling-measurments 0-dimensional comparison

Here we choose to present results for the chemistry degradation pathways presented in Figure 1, branching ratio of kinetic rate coefficient being unchanged. Figure 2 (a) present time evolution of background species and Figure 2 (b) show evolution of degradation products. The right reproduction of AMP profile allows to compare the evolution of concentration of degradation products. In their article, Tan and al. (2021) show modeling results from MESMER 3.0, that are closer to the experimental data, but employing different branching ratio for the in the OH-initiated AMP reaction (first reaction in Figure 1) (B_{CH3} /B_{CH2} /B_{NH2} = 6:70:24). (Tan and al. 2021) Figure 2 (b) highlights choice of adjust branching ratio, by Tan and al. 2021, B_{CH2} : a higher proportion of AMPal would also increase P2IMI concentration. IPP, which is predicted by theorical study as the minor product is slightly overestimated. One explanation could be that particles are not taken into account, and OH concentration forcing may not be totally appropriate in this case, as AMP concentrations variations are dependent on OH oxidation and particle formation. About AMPNO2 profiles, a large discrepancy is observed, as in the modelling of Tan and al. 2021. Other simulations have been made with other branching ratio to improve results: (B_{CH3} /B_{CH2} /B_{NH2} = 6:50:24).

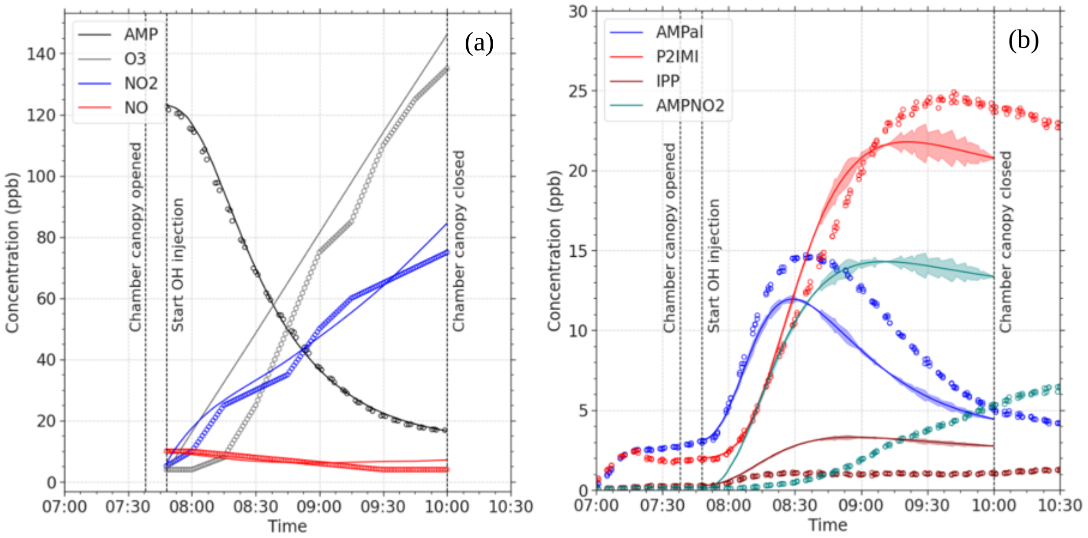


Figure 2. Measured (dotted curves) and modeled temporal profiles **(a)** of background species and AMP, **(b)** of degradation products in the OH-initiated AMP reaction, $(CH_3)_2(CHO)CNH_2$ (AMPal), $(CH_3)_2C{=}NH$ (P2IMI), $CH_3(CH_2OH)C{=}NH$ (IPP), and $(CH_3)_2(CH_2OH)NHNO_2$ (AMPNO2).

Comparison of PinG-SSH and ADMS simulations

In this second part, comparisons between the both model are made. Differences are expected because background concentrations and meteorological fields are three-dimensional and time-dependent in the PinG modeling. OH concentrations fields are take into account in PinG simulation, in ADMS there is a coefficient which depend of O_3, OH average concentrations and NO_2 photolysis rate are used to setup simulation, this two approches impact considerably degradation of AMP. In addition, ADMS's amine degradation pathways are more simple and general than thoses included in SSH-aerosols, presented in Figure 1. Nitrosamines and nitramines are not degraded by reactions with OH and imine concentrations are not available. Figure 3 shows comparisons at various points for AMP and Namines (sum of nitrosamines and nitramines) for the two models, . AMP concentrations are generally of the same order of magnitude or even higher in the case of PinG, except near the source. In fact, simulations carried out with ADMS show a tendency to impact at ground level closer to the source than PinG. This effect, combined with the differences in the chemical scheme, results in significantly higher concentrations of Namines in the ADMS simulation. The plumes formed in the case of ADMS have uniform concentrations in the direction of propagation, the distribution of compound formation being carried out directly at source.

In the case of the PinG model, the Gaussian puff model enables chemistry to be maintained under conditions of high amine concentrations, prior to background puff dilution and pollutant deposition at ground level. Figure 4 shows dispersion maps for AMP, nitrosamine and nitramine, with an adapted scale on the lower maximum between the two models.

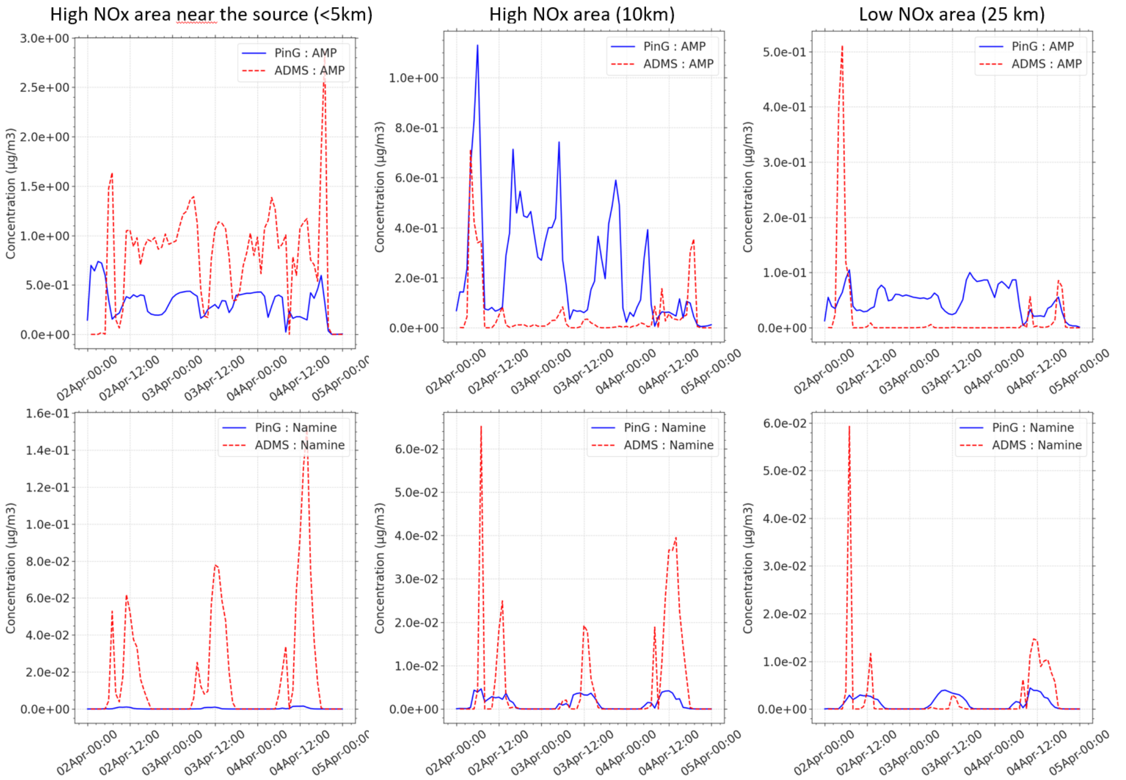


Figure 3. Comparisons between PinG (blue line curves) and ADMS (red dotted curves) for AMP and Namine, sum of $(CH_3)_2(CH_2OH)CNHNO$ (AMPNO) and $(CH_3)_2(CH_2OH)CNHNO2$ (AMPNO2) for different NOx levels, from 2018-04-02 to 2018-04-025.

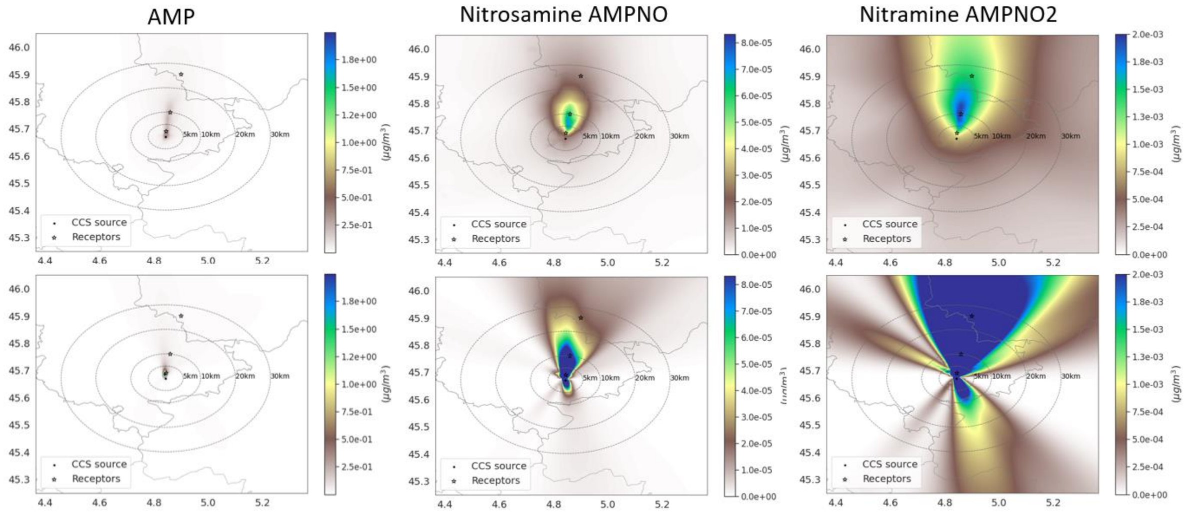


Figure 4. Comparisons between PinG (top maps) and ADMS (bottom maps) for $(CH_3)_2(CH_2OH)CNH_2$ (AMP) ,$(CH_3)_2(CH_2OH)CNHNO$ (AMPNO) and $(CH_3)_2(CH_2OH)CNHNO2$ (AMPNO2) for averages concentration from 2018-04-02 to 2018-04-11 included.

Nitrosamine and nitramine concentrations depend on NO_x concentrations, and the PinG approach gives more consistent results based on areas of high NO_x emissions, unlike ADMS modeling, which only takes fixed NO_x concentrations into account, keeping these species in the plume. Differences in the dispersion approach used between the two models directly affect plume dilution, and simulations with a passive tracer were carried out for each model, showing that PinG dilutes concentrations by an order of magnitude more than ADMS.

CONCLUSION AND OUTLOOK

Work carried out on 0-dimensionnal modeling show good results as a first approach and hightlighted importance of specific OH-initiated degradation pathways consideration. Inclusion of particles formation by condensation/evaporation would allow to remove contraints on OH concentration by consideration of all sinks and sources of AMP in the EUPHORE experimental chamber. The optimisation of branching ratios will be discussed after comparison to a complete chemistry simulation with experimental results. This first test phase is important in view of the concentration differences observed between the PinG and ADMS models for 3-dimensionnal simulations. Good results in 0-dimensional comparisons, taking into account aerosol formation, will enable PinG to be used with greater confidence for impact studies on future sites that will host carbon capture installations.

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