

Changes to manuscript ms-nr acpd-2013-1008

Uncertainties in assessing the environmental impact of amine emissions from a CO₂ capture plant

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Dear Dr. Thomas Karl,

We highly appreciate the reviews of our manuscript ms-nr acpd-2013-1008 that we received from Merched Azzi and one anonymous referee. We have replied to their comments in the Open Discussion. We have addressed all specific comments in the revised manuscript as will be described below. We carefully considered the concerns of Merched Azzi and the comments of the anonymous referee and largely followed their recommendation in the revised manuscript.

General

The first concern of Merched Azzi was the neglect of horizontal diffusion in the EMEP model which affects horizontal dispersion on the fine resolution grid especially under convective conditions. We quantified the error of maximum ground-level concentration of amines due to the missing horizontal diffusion operator and found that the error this introduces is less than 15% within 20 km distance from the source. We have added a note on this in section 2.2 (Description of the WRF-EMEP model system) of the revised manuscript and included a new section S3 (Evaluation of horizontal dispersion in the EMEP model) in the Supplement.

The second concern expressed by Merched Azzi is that the sensitivity of ground-level concentrations to plume rise treatment might be artificial, due to the coarse vertical resolution of the EMEP model. We performed several tests with a Gaussian plume model. Based on these we confirm the high sensitivity of the maximum ground level concentration to the respective parameterization of plume rise, especially under neutral and moderately stable conditions. We have added a note on this in section 3.4 (Results of the simulations) of the revised manuscript where the spatial distribution of modelled amine concentrations is discussed. We included the results from the tests with the Gaussian plume model in section S2 (Plume rise treatment in the EMEP model) of the Supplement.

We corrected Equation (1) which is used in the "NILU Plume" parameterization for calculation of the wind speed at plume height. The impact of not restricting z/L to the interval $[-2, 0]$ on the resulting final plume height computed with the WRF-EMEP model (based on meteorological data at the Mongstad site in July 2007) was found to be negligible. However, for the future use of the wind profile function in our model code we agree to limit z/L , as recommended by the reviewer.

To address the concern that peak concentrations calculated by the EMEP model might be subject to overshoot/undershoot of the numerical advection scheme, we have extended section 3.7 (Comparison with TAPM simulation results) with a comparison to ground-level concentrations of an inert tracer compound (emitted from the same source) for July 2007 computed by the TAPM model. The TAPM model (The Air Pollution Model), which has a built-in sub-grid Lagrangian particle dispersion model to resolve dispersion of a point source plume, has been used to evaluate the near-source concentrations computed by the WRF-EMEP model framework.

The anonymous referee (Referee #2) suggested to change the title of our manuscript since it seems to be too general. However, we decided to keep the title because the evaluated methodology can be transferred to other places in the world and to other amines, given that all necessary input data (kinetic parameters and branching ratios of amine oxidation, meteorology, CCP parameters, physicochemical properties, and catchment area) are available.

One concern expressed by Referee #2 is that the importance of the reaction of amines with the NO_3 radical was overestimated in the study. Another concern of Referee #2 is that the degradation rates of nitrosamines and nitramines used in the study are questionable.

With respect to the concern about the importance of NO_3 , we find that the annual average NO_3 concentrations computed by the EMEP model are realistic and consistent with commonly used average NO_3 nighttime concentrations (e.g. Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos. Environ.* 27, Supplement No.2, S197-S219, 2003). Based on this the atmospheric amine removal rate by NO_3 radicals will be approximately equal to the removal rate by OH radicals.

The degradation rates of nitrosamines and nitramines for air/soil/water/sediment used in our study are taken from the EPISuite™ software and are estimated using standard US EPA methodology. Although the degradation rate values are estimates based on the structure of these chemical compounds, they are not entirely unreasonable. Given the scarcity of experimental data on degradation rates of nitrosamines and nitramines, the chosen approach appears to be viable.

Both the relevance of the amine + NO_3 reaction and the relevance of degradation rates of nitrosamines and nitramines was adequately reflected in our Conclusions, therefore no changes were made to section 5 (Conclusions).

Further text changes:

In response to Referee #2 we added a statement in the Abstract about the specific meteorological conditions at Mongstad, west coast of Norway, to take into account the (limited) representativeness of the chosen region in the context of environmental impact assessment of CO₂ post-combustion capture by amine technology.

In section 2.3 (Fugacity level III multimedia model) a statement was added on the estimation of degradation rates of nitrosamines and nitramines in air, soil, water and sediment. We added an explanation on the different sets of degradation rates of nitrosamines and nitramines that are used in the baseline and in the sensitivity study (section 2.7: Sensitivity analysis).

In section 2.4 (Point source emissions) more details on the application of Equation (1) to calculate wind speed on plume height were provided.

In section 3.3 (Evaluation of atmospheric production yields) we added an explanation why photochemical reactivity of amines was relatively small in the vicinity of the source.

In section 3.5 (Mass balance of MEA) it is stated that the majority of the chemical turnover in the MEA + OH reaction leads to the production of carbonylic products which are not subject of the present study. Our follow-up work will address this knowledge gap. We added on page 8659, line 27: "A study of the complete product spectrum from the atmospheric oxidation of MEA for the environmental conditions at Mongstad is subject of our follow-up work (Karl et al., 2014)."

In the Discussion (section 4) the relevance of the amine + NO₃ reaction (scenario KNO3M) compared to the amine + OH reaction is now substantiated with an estimate of the annual average amine removal rates based on modelled concentrations of OH and NO₃.

Tables:

Table 4.

In the table header an explanation on the different sets of degradation rates of nitrosamines and nitramines that are used in the baseline and in the sensitivity study was included. Definitions of MNA and NDMA were added. A typo in the second last column for model aspect "Degradation rates of nitramines" was corrected.

Table 6.

Grid mean values (of the 40x40 km² study area) of the yearly average concentrations of amine and of the sum nitrosamines and nitramines were added in brackets below the grid maximum values.

Table 7.

Scenario names were corrected: "DegRateMNA" and "DegRateNDMA".

Table S1.

The table caption was extended to explain the method to estimate degradation rates of nitrosamines and nitramines in air, soil, water and sediment. The reference to the report by Yiannoukas (2011) was corrected.

Figures:

Figure 10.

A new figure, Figure 10, was added to the manuscript to show a comparison of modelled ground-level air concentration of a chemically inert tracer from the WRF-EMEP model framework and from the TAPM model.

Figure S2.

A new figure, Figure S2, was added to the Supplement showing the results from the sensitivity test on plume rise parameterisations with a Gaussian plume model.

Figure S3.

A new figure, Figure S3, was added to the Supplement showing the results from the test on horizontal dispersion for unstable conditions. The figure numbers in the Supplement were updated correspondingly

Figure S9 of the former Supplement was moved to the main manuscript, as part of the new Figure 10.