

## Reply to Referee #2

We thank Referee #2 for valuable comments, which helped to improve the manuscript. We will consider his/her comments in the revision of the manuscript, as it is stated below.

- 1. The title is perhaps too general - the authors actually only model the environmental impact of two amines MEA ( $\text{CH}_2\text{OHCH}_2\text{NH}_2$ ) and DEYA ( $\text{Et}_2\text{NH}$ ) emitted from a CCP at the West coast of Norway (Mongstad region). This region is characterized by meteorological conditions and air quality which both differ substantially from the "average industrialized world". This is in part compensated for in the abstract.**

### Response:

Although the title is quite general, we decided to keep the title as is, mainly because the methodology evaluated in this manuscript can be transferred to other places 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.

The specific conditions (meteorology and air quality) of the Mongstad region are discussed in quite some detail in the manuscript (sections 2.1, 3.1, and 3.2).

The following sentences were added to the Abstract (p. 8634, line 6):

"The study region is characterized by high precipitation amounts (typically exceeding 2000 mm per year), relatively few sunshine hours (about 1200 hours per year), predominantly westerly winds from the North Atlantic, and complex topography. Mongstad can be considered as moderately polluted due to refinery activities."

- 2. Page 8642, line 10:  $\text{SO}_4$  should be  $\text{SO}_3$ .**

### Response:

The referee is right that  $\text{SO}_x$  formally is the sum of  $\text{SO}_2$  and  $\text{SO}_3$ . However, in the WRF-EMEP model the treatment of anthropogenic emissions of oxidized sulphur compounds is simplified. In the model, 5% of the total anthropogenic emissions of sulphur oxides are in the form of particulate  $\text{SO}_4$ .

The statement on p. 8642, line 10, was corrected:

"Anthropogenic emissions of sulphur oxides (95% as  $\text{SO}_2$  and 5% as particulate  $\text{SO}_4$ )"

- 3. Page 8653, line 5: Closer to Mongstad high NO<sub>2</sub> concentrations led to a reduced production of OH radicals and hence less photochemical reactivity of the amine. This is not obvious to the Referee. Please explain.**

**Response:**

In the EMEP model, both the power plant equipped with CCP and the refinery of Mongstad are located in the same grid cell. In the plume from this source, NO can react with O<sub>3</sub> to form NO<sub>2</sub> and O<sub>2</sub>, thereby lowering ozone concentrations. In our model this occurs at the source (in the model grid cell that contains the industrial sources), due to the instantaneous volume mixing of the emissions. Since O<sub>3</sub> is the predominant OH precursor in our simulation, a reduction of O<sub>3</sub> will reduce the OH production directly at the source. In addition, the reaction of OH with NO<sub>2</sub> will be an important sink for OH radicals. Therefore it is to be expected that in our model simulations, OH levels are reduced directly at the source due to rapid consumption of O<sub>3</sub> (by NO) and OH (by NO<sub>2</sub>).

We added the following explanation to the manuscript, page 8653, line 5:

“Due to the instantaneous volume mixing of the emissions from Mongstad (from the power plant equipped with CCP and the refinery) in the EMEP model, emitted NO reacts with O<sub>3</sub> to form NO<sub>2</sub> and O<sub>2</sub>, thereby lowering ozone concentrations at Mongstad. In addition, the reaction of OH with NO<sub>2</sub> will be a relevant sink for OH radicals directly at the industrial source. Therefore, close to Mongstad, elevated NO<sub>2</sub> concentrations led to a reduced net production of OH radicals and hence less photochemical reactivity of the amine.”

- 4. The results from NO<sub>3</sub> chemistry sensitivity studies imply that NO<sub>3</sub> chemistry is important in the Mongstad region. With typical NO, NO<sub>2</sub> and O<sub>3</sub> mixing ratios of 0.2, 2 and 30 ppb, respectively, the NO<sub>3</sub> radical mixing ratio (nighttime) should be around 10<sup>7</sup> cm<sup>-3</sup>. With  $k(\text{amine}+\text{NO}_3) = 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the amine removal rate will be around 10<sup>-6</sup> s<sup>-1</sup>, which should be compared to the amine removal rate by OH radicals of around 10<sup>-5</sup> s<sup>-1</sup> ( $k(\text{OH}) = 10^{-11}$ ,  $\text{OH} = 10^6$ ). At best, around 10% of the amine removal can therefore be caused by NO<sub>3</sub> radicals in the Mongstad region. The Referee concludes that there must be something wrong in the code with respect to NO<sub>3</sub> radical chemistry. Please justify and elaborate on the results from the KNO3M scenario.**

**Response:**

For the yearly average, the duration of sunlight has to be taken into account. The typical sunshine hours in the region of Mongstad/Bergen is only 1200 hours per year, corresponding to a yearly fraction of 0.14. That means about 7600 hours are without sunshine (either night or clouds), corresponding to a yearly fraction of 0.86. The time with NO<sub>3</sub> as oxidant is potentially 6.3 times longer than the time with OH as oxidant on the yearly timescale. Taking this into account, and using the average concentration suggested by the referee, the amine removal rate by NO<sub>3</sub> would be  $0.86 \times 10^{-6} \text{ s}^{-1}$  and by OH is  $1.4 \times 10^{-6} \text{ s}^{-1}$  which means that 40% of the amine removal can be through NO<sub>3</sub> on the yearly average.

However, the annual average concentrations OH and NO<sub>3</sub> computed for the year 2007 at the location of Hamna (3km distant from Mongstad) by the WRF-EMEP model system are 8.9x10<sup>5</sup> molecules cm<sup>-3</sup> and 1.2x10<sup>8</sup> molecules cm<sup>-3</sup>, respectively.

With these explicitly calculated NO<sub>3</sub> concentrations of about 10<sup>8</sup> molecules cm<sup>-3</sup>, the amine removal rate by NO<sub>3</sub> becomes 10<sup>5</sup> s<sup>-1</sup>, thus equal to the amine removal by OH.

The following note was added to text in section 4 (“Discussion”) on page 8667, line 7:

“The annual average concentrations OH and NO<sub>3</sub> computed for the year 2007 at the location of Hamna (3 km distant from Mongstad) by the WRF-EMEP model system are 8.9x10<sup>5</sup> molecules cm<sup>-3</sup> and 1.2x10<sup>8</sup> molecules cm<sup>-3</sup>, respectively. With k(amine+NO<sub>3</sub>) in the order of 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and k(amine+OH) in the order of 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the atmospheric amine removal rate by NO<sub>3</sub> radicals will be approximately equal to the removal rate by OH radicals.”

- 5. On page 8667, line 4 is stated: “consideration of amine oxidation by NO<sub>3</sub> radicals increased maximum surface concentration of the sum of nitrosamines and nitramines by 150% in our simulations.” This cannot be correct. The results in Table 6 give max. surface air concentration sum 3.7 (BASE) and 5.6 (KNO<sub>3</sub>M). At best, this is a 50% increase. The danger of this table is that the numbers given are maximum numbers that do not necessarily relate to the same time of year. In other words, the authors are offering the reader to compare apples and bananas – pick whatever you like so to speak. It is suggested to present averages either for selected months or for the year modelled.**

**Response:**

We thank the referee for noting the wrong percentage number; it is actually a 50% increase.

All values in Table 6 are based on yearly averages and represent the grid maximum values inside the 40x40 km<sup>2</sup> study area from a one-year model calculation. Unfortunately, we did not mention this in the header of Table 6. The reason for choosing this metric is that the grid maximum of the yearly average air concentration of sum nitrosamines and nitramines can be compared to the safety limit value of 300 pg m<sup>-3</sup>, (as set by the Norwegian Environmental Directorate) indicated in the table.

In order to facilitate comparison of the air concentrations from the different cases with each other, we added now also the grid mean value (spatial average in the 40x40 km<sup>2</sup> study area) of the yearly average concentrations of the amines and the sum nitrosamines + nitramines.

Corrected on page 8667, line 4-5:

“Consideration of amine oxidation by NO<sub>3</sub> radicals increased the grid maximum of the yearly average surface concentration of the sum of nitrosamines and nitramines by 50% in our simulations

In Table 6, we added grid mean values (of the 40x40 km<sup>2</sup> study area) of the yearly average concentrations of amine and of the sum nitrosamines and nitramines.

- 6. Concerning the input parameters to the fugacity model, the reference to the data cannot be found at the link given (Yiannoukas, S., Morale, G., Williams, R., and Johnson, A.: Deposition and soil transport modelling of components from postcombustion amine-based CO<sub>2</sub> capture, Report for Gassnova SF. Det Norske Veritas Ltd, UK, Report No. PP011015, London, U.K, 2011. Available at: [http://www.gassnova.no/gassnova2/frontend/files/CONTENT/Rapporter/Depositionandsoiltransportmodelling\\_DNV.pdf](http://www.gassnova.no/gassnova2/frontend/files/CONTENT/Rapporter/Depositionandsoiltransportmodelling_DNV.pdf)).**

**Response:**

The correct link to the report (Yiannoukas et al., 2011) is:

[http://www.gassnova.no/no/Documents/Depositionandsoiltransportmodelling\\_DNV.pdf](http://www.gassnova.no/no/Documents/Depositionandsoiltransportmodelling_DNV.pdf).

The report is also found immediately using the title in a search on Google scholar.

The reference to the report, cited in the header of Table S1 in the Supplement, was corrected.

- 7. This may be, but the numbers given for the degradation time of nitrosamines and nitramines are highly questionable. The authors state on Page 8668, line 26 “More research on degradation rates of nitramines in soil and water is needed”, but the study does not include a sensitivity test of the nitrosamine and nitramine degradation rate in the dense compartments. This is surprising because the “worst case” scenario does not include a realistic degradation rate of nitramines in the aqueous phase (DT50 is actually around 1 year). In fact, the present study should actually conclude that the MAJOR uncertainty in the EIA is linked to the degradation of nitrosamines and nitramines in soil and water. It is not commendable to use fictional numbers from some unpublished report in a public domain publication without making proper reservations.**

**Response:**

While we appreciate the referee's comment on the importance of degradation rates in the fugacity model, we do not agree that the rates used in the modelling are "fictional numbers from some unpublished report". In fact, the degradation rates used in the report cited are taken from EPISuite™ and estimated using standard US EPA methodology (US EPA, 2012), and while being estimates, they are not entirely unreasonable. EPISuite™ presents the estimated degradation in terms of 'hours', 'days' or 'weeks', and standard US EPA values for transforming these half-lives correspond to 2.33, 8.67 and 15 days respectively. The estimated values are used in the aquatic compartment and scaling factors of 2 and 9 (i.e. degradation half-life in sediment = 9 \* degradation half-life in water), also standard US EPA approach. For example, for the nitramine degradation sensitivity simulation, DegRateMNA, (using degradation rates from methyl nitramine, short MNA) the degradation rate for primary degradation is reported as days, which have been implemented as a half-life of 2.3 for water, and 4.6 for soil and 21 (rounded up from 20.7) for sediments.

The referee also states that we did not include a sensitivity test of the degradation rates, but this is not correct. We used two sets of degradation rates for both compounds in all compartments as detailed in Table 4, model aspect “Degradation rates nitramines and nitrosamines”. Our baseline parameter values were chosen to reflect ultimate degradation (i.e. full degradation of the compound), while the shorter half-lives were thought of as degradation rates for the compound to transform to a metabolite. We used the longer of these half-lives in our worst case scenario. We do, however, completely agree with the reviewer that these degradation rates are extremely important for the predicted concentration in the water body and we feel that this is already reflected in our conclusions.

The following was added to section 2.3 (page 8643, line 10):

“The physiochemical parameters for the nitramine of MEA were approximated with data for methyl nitramine (MNA). The physiochemical parameters for nitramine and the nitrosamine of DEYA were approximated with data for dimethyl nitramine and NDMA, respectively. Degradation rates of nitramines and nitrosamines in air, soil, water and sediment were calculated using EPISuite™ based on standard US EPA methodology (US EPA, 2012).”

The following was added to section 2.7 (page 8649, line 22):

“We used two sets of degradation rates for nitrosamines and nitramines in all compartments as detailed in Table 4, model aspects “Degradation rates nitramines” and “Degradation rates nitrosamines”. Our baseline parameter values were chosen to reflect ultimate degradation (i.e. full degradation of the compound), while the shorter half-lives were thought of as degradation rates for the compound to transform to a metabolite.”

The caption of Table S1 (in the Supplement) was revised:

“Table S1: Physiochemical characteristics of the nitrosamine and the two nitramines for which the Fugacity III model was applied. The procedure to obtain the data is adopted from the report by Yiannoukas (2011). Degradation rates DT50 (degradation time for 50% of the substance, here values refer to ultimate degradation) in water, soil, sediment and air were derived from EPISuite™, in accordance with US EPA standard methodology (US EPA, 2012). MW: molecular weight; Kow: octanol-water partition coefficient; Koc: organic carbon partition coefficient between liquid and solid phases.”

**8. There is a misprint/inconsistency in Table 7. “DegrateMNA and DegrateNDMA” should be “DegRateMNA and DegRateNDMA” – by the way MNA and NDMA are not defined in the text or the Table header.**

**Response:**

Table 7 was corrected so the headers read (with capital letters as this):

DegRateMNA and DegRateNDMA

A typo in Table 4 was also corrected:

second last column (Degradation rates nitramines), last row should not be .../4.6 days, but instead: .../21 days.

Definitions of MNA and NDMA were given in the table caption of Table 4.

The caption of Table 4 reads now:

“Table 4: Summary of model aspects included in the sensitivity analysis of the fugacity model. Each parameter was changed independently. The degradation rates (expressed as degradation half-life in days) refer to the values for the compartments air / soil / water / sediment. Baseline degradation rates refer to ultimate degradation of the compound. For the alternate of the model aspect “Degradation rates nitramines”, the degradation rate of nitramines (MEA-nitramine and DEYA-nitramine) is based on the calculated primary degradation half-lives of methyl nitramine (MNA). For the alternate of the model aspect “Degradation rates nitrosamines”, the degradation rate of DEYA-nitrosamine is based on the calculated primary degradation half-lives of N-nitroso dimethyl amine (NDMA).”

## References:

US EPA: Estimation Programs Interface Suite for Microsoft Windows, v 4.00, United States Environmental Protection Agency, Washington, DC, USA, available at: <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm> (last access: 12 June 2014), 2012.

Yiannoukas, S., Morale, G., Williams, R., and Johnson, A.: Deposition and soil transport modelling of components from postcombustion amine-based CO<sub>2</sub> capture, Report for Gassnova SF. Det Norske Veritas Ltd, UK, Report No. PP011015, London, U.K.. available at: [http://www.gassnova.no/no/Documents/Depositionandsoiltransportmodellering\\_DNV.pdf](http://www.gassnova.no/no/Documents/Depositionandsoiltransportmodellering_DNV.pdf) (last access: 12 June 2014), 2011.