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Evaluation of worst case assumptions – atmospheric chemistry.

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Content

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Preface

The NILU report "CO2 Technology Centre Mongstad – updated air dispersion calculations, Update of OR 12/2008" by Tore Flatlandsmo Berglen, Dag Tønnesen, Christian Dye, Matthias Karl, Svein Knudsen, and Leonor Tarrasón describes the calculation and assessment of the dispersion of emissions to air of carbon dioxide (CO_2), nitrogen oxides (NO_x), ammonia (NH_3), amines and amine degradation products from activities at CO2 Technology Centre Mongstad (TCM). The report is an update of the report "Test Centre Mongstad, Dispersion calculations for emissions to air from Test Centre Mongstad (TCM)" (Berglen et al., 2008). The calculated maximum hourly mean concentrations and yearly averages are well below norms and guidelines for NH_3, CO_2, MEA, formaldehyde, acetaldehyde, and piperazine. "Worst case calculations" for nitrosamines in air show that there may be a problem, but further research must be done to reduce the uncertainties. Based on the "worst case calculations" for water it is not possible to conclude that there will be a problem, but the uncertainties have to be reduced, especially concerning nitrosamine degradation.

The main objective of the present work is to make an assessment of all the assumptions made in the referred to NILU report with respect to atmospheric chemistry and the formation and fate of nitrosamines post emission. A second objective is to evaluate the potential for nitrosamine degradation by photolysis in air and water.

1   The NILU report.

1.1   Dispersion and deposition models.

NILU has applied 2 models in their calculation of dispersion of emissions. To calculate maximum hourly mean concentrations in the vicinity of TCM (up to a few kilometres from Mongstad) the CONCX model was used (reference, Bøhler 1987, missing in the report). CONCX is Gaussian distribution model that calculates concentrations downwind of an emission source at various wind speeds and under various atmospheric stability conditions. There is no chemical degradation included, nor loss by deposition. This means that the compounds are assumed to chemically inert. The calculated maximum hourly mean concentrations are lower than the administrative norms for NH_3, CO_2, NO_2, MEA, piperazine, CH_2O, CH_3CHO, CH_3NH_2, $CH_3CH_2NH_2$, $(CH_3)_2NH$ and $(CH_3CH_2)_2NH$, and lower than the guidelines from FHI for MEA, MDEA, AMP, piperazine, CH_2O, CH_3CHO.

To calculate annual mean and 8-hours mean concentrations, annual deposition and concentration in drinking water of compounds resulting from emission at TCM, NILU has applied "The Air Pollution Model" (TAPM) developed by CSIRO, Australia. Annual mean air concentrations calculated by the model are used to represent long-term air concentrations, while the computed maximum 8-h (8-h running average) air concentrations are used to represent short-term air concentrations. The emitted compounds and their photo-oxidation products were assumed to be chemically inert in the atmosphere but to undergo both wet and dry deposition processes. It is explicitly stated that deposition was treated in the same way as for sulphur dioxide.

Large-scale weather information for Norway from the synoptic analyses of the year 2007 was supplied as input to the model. Site-specific wind data with a 6-h resolution and rainfall data on a daily basis for year 2007 were retrieved from the Norwegian Meteorological Institute (met.no) eKlima service (http://sharki.oslo.dnmi.no) and used for the evaluation of simulated local wind and precipitation. Monthly average and 8-h maximum air concentration fields together with dry and wet deposition fields were obtained from the model output.

It is assumed in the NILU study that photochemical degradation products are formed instantaneously when they leave the stack of the CO_2 capture plant, with a fixed formation yield. The emission rate of the degradation product corresponds to a certain fraction of the total amine emission.

The dispersion model generates monthly fields of dry and wet deposition fluxes for a unity emission of 1 g s^{-1}. For the comparison of the compound's deposition flux to the critical deposition, only wet deposition was used. For water-soluble compounds wet deposition is the major deposition route.

Long-term and short-term air concentrations and yearly wet deposition flux of all formed products were assumed to have the same regional distribution as the parent amine(s). The air concentrations and wet deposition fluxes of amine degradation products were obtained by scaling the TAPM results for the parent amine(s) with the respective fractional formation yield.

The only stated reservation with respect to the performance of the TAPM model is (quote):
TAPM calculates the atmospheric meteorological parameters (advection/wind, temperature, humidity, rainfall) based on the laws of physics that governs the atmosphere. There are uncertainties in these calculations. The uncertainty or error for TAPM is less than 30 % for

predictions of observed mean concentrations of passive agents released from stacks.

It is also important to emphasize that the meteorological data ("weather") represents the year 2007. In the real atmosphere there are inter-annual variations in weather. Hence the dispersion from TCM will change accordingly. This means that deposition, location and magnitude of maxima etc. may vary from year to year. However the results presented here are considered representative for the situation that will occur in the vicinity of Mongstad when TCM will be in operation.

The model performance vis-à-vis the meteorological data used in the model is not well documented in the report; the model calculations are better described in a recent paper by Karl *et al.*[1] (quote): *The seasonality of wind direction and wind speed at the met.no stations Takle, 30 km northeast of Mongstad, and Fedje, an island 18 km to the west of Mongstad, were well reproduced by the dispersion model. Monthly averaged wind speed is underestimated by ca. 10–50% at both stations. TAPM systematically overestimated the monthly rainfall amounts during the year 2007 by up to a factor 2–3. The yearly rainfall pattern, however, was well captured by the model. The frequency of days with rain (rainfall amount >0.1 mm) in TAPM was about 20% higher than observed. Due to the nature of the wet deposition in the dispersion model, where the amines are assumed to be completely dissolved in the rain water, it is the frequency and timing of rainfall, rather than the quantity that determines the total wet deposition. In this regard it is expected that TAPM overestimates wet deposition by 20–30%.*

1.2 Model and Chemistry assumptions

The model assumes that a certain percentage of an emitted amine will converted to other compounds such as nitrosamines, and that this percentage is independent upon distance from emission point. This is obviously not the case and the error originating in this assumption is easy to demonstrate.

Taking an average wind speed of $<v>$ (the wind speed is always > 0.4 m s^{-1}) the distance, d, travelled by an (expanding) air parcel in the time, t, will be $d = <v> \times t$. Neglecting that chemical transformation will not start at emission point, the relative amount of amine reacted in an expanding air parcel can be calculated from second order kinetics without considering the dispersion:

$$\frac{d[\text{Amine}]}{dt} = -k_{OH} \times [\text{Amine}] \times [\text{OH}]$$

The Figure 1 shows the percentage of amine reacted as a function of distance in km from emission point taking average wind speeds $<v> = 0.5$, 1 and 2 m s^{-1}, $k_{OH} = 6.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (the room temperature value for OH reaction with dimethylamine) and an annual average OH concentration of 5×10^5 cm^{-3} corresponding to lifetime with respect to reaction with OH of $\tau_{OH} \approx 9$ h. This simplified treatment overestimates the percentage conversion of amine as a function of distance from emission point. It can be seen that for $<v> = 0.5$ m s^{-1} less than 50% of the amine will have reacted within the first 10 km, and less than 80% within the first 25 km from emission point. For higher average wind speeds the amount of amine reacted as a function of distance from emission point will be lower.
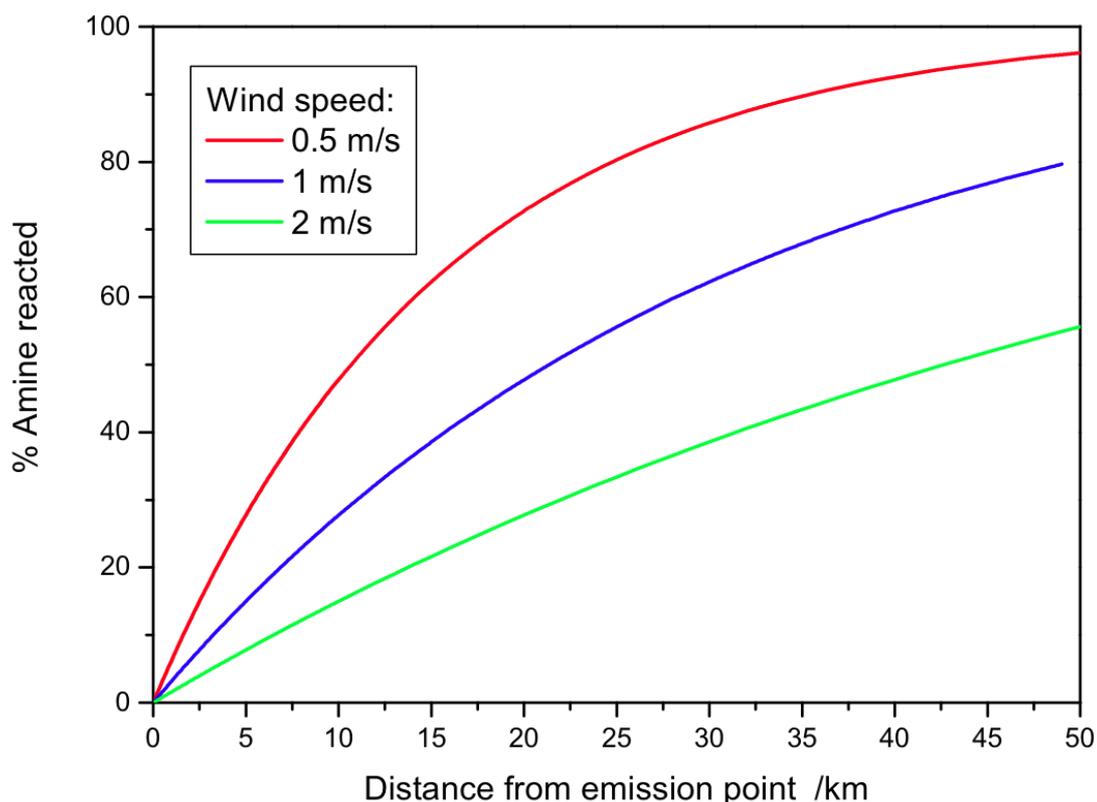
Figure 1. Per cent amine reacted as a function of distance from emission point assuming constant wind speeds of 0.5, 1 and 2 m s^{-1}, an average OH concentration of 5×10^{-5} cm^{-3} and $k_{OH} = 6.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Taking a 2% nitrosamine yield as representative, the maximum concentration of the nitrosamine at 10 km from emission point will then be less than 1% of the amine emitted. The amount of nitrosamine relative to amine present in the expanding emission parcel can be estimated using a simple reaction scheme:

$$
\begin{array}{ccccc}
& X\ \%\ \text{yield} & & \text{Photolysis} & \\
& \tau_{OH} \approx 9\ \text{h} & & \tau_{sunlight} = Y\ \text{hours} & \\
\text{Amine} & \rightarrow & \text{Nitrosamine} & \rightarrow & \text{Other products}
\end{array}
$$
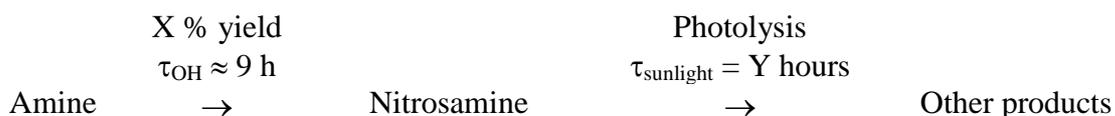
Figure 2 shows the effect of nitrosamine photolysis lifetime for an average wind speed of 0.5 m s^{-1} and a 2 % nitrosamine yield of amine reacted. In the case of no photolysis the amount of nitrosamine will eventually reach 2% of the amine emitted. However, even for a photolysis lifetime of 10 h the maximum amount of nitrosamine in an expanding air parcel is reduced to less than 0.8 % of the original amine in the air parcel. For a photolysis lifetime of ½ h the maximum amount of nitrosamine will be less than 0.1 % of the amine originally in the expanding air parcel.
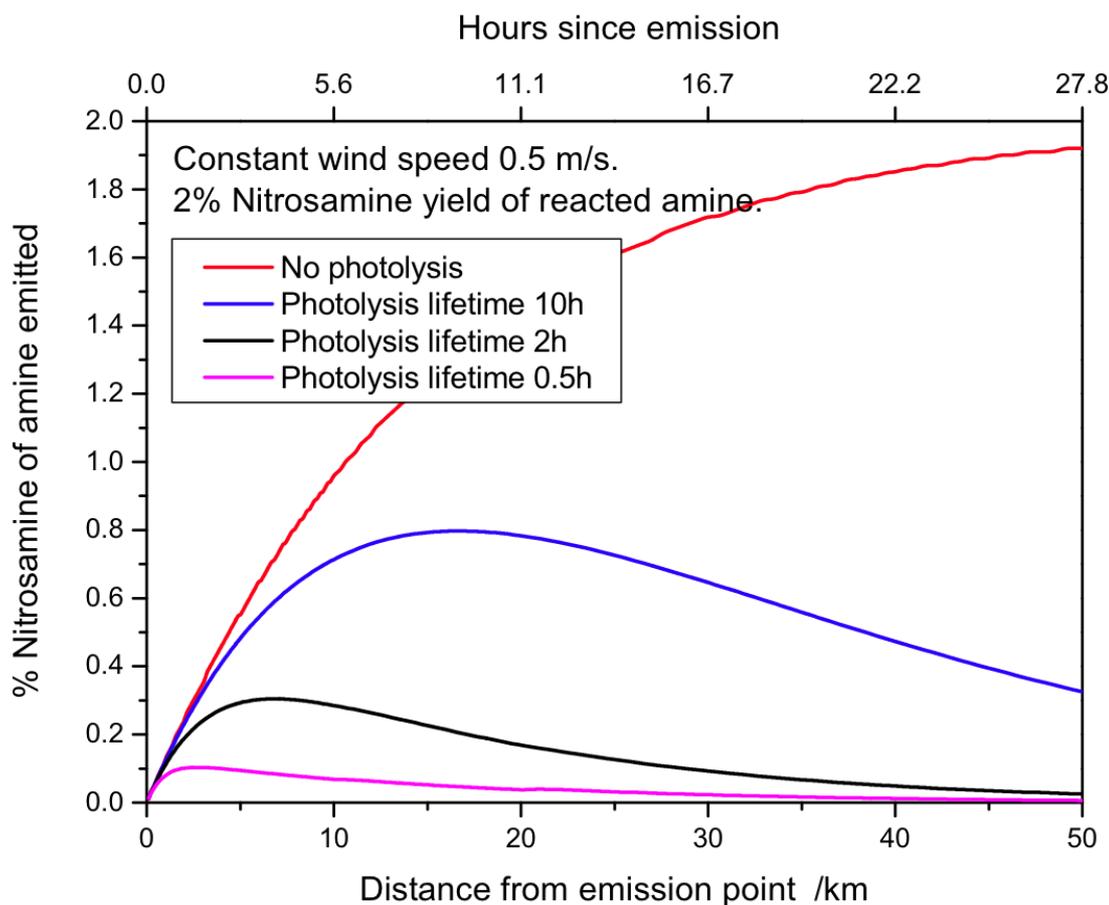
Figure 2. Amount of nitrosamine in an expanding air parcel as a function of distance from emission point for different nitrosamine photolysis lifetimes. The calculations assume a 2% yield of nitrosamine from photo-oxidized amine, an average OH concentration of 5×10^{-5} cm^{-3}, $k_{OH} = 6.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and a constant wind speed of 0.5 m s^{-1}.

Similar calculations have been carried out for average wind speeds of 1 and 2 m s^{-1}; the results are shown in Figures 3 and 4, respectively. A doubling of the wind speed halves the time to reach 50 km from emission point. This means that less amine will have reacted and consequently less nitrosamine will have formed. It also means that less nitrosamine will have had time to photolyze, and, consequently, the maximum amount of nitrosamine in an air parcel will be more or less the same independent of the wind speed.
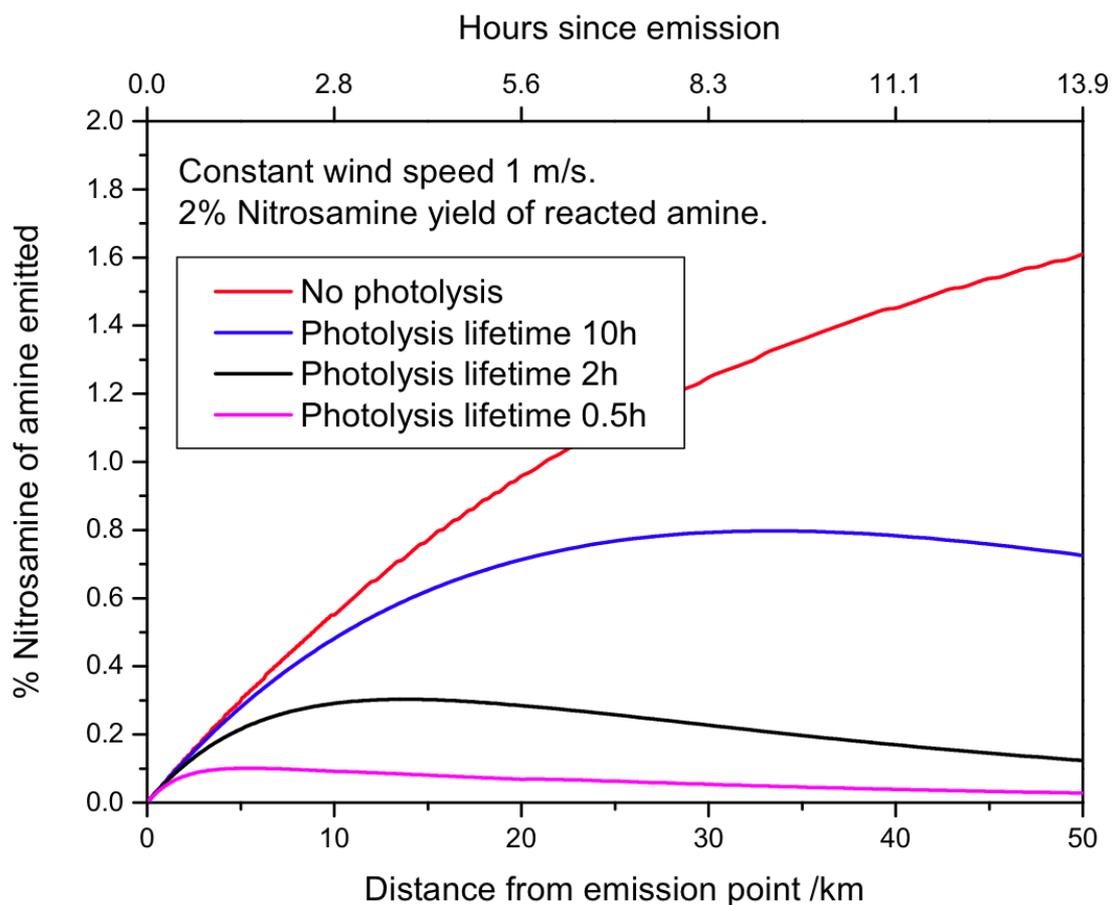
Figure 3. Amount of nitrosamine in an expanding air parcel as a function of distance from emission point for different nitrosamine photolysis lifetimes. The calculations assume a 2% yield of nitrosamine from photo-oxidized amine, an average OH concentration of 5×10^{-5} cm^{-3}, $k_{OH} = 6.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and a constant wind speed of 1 m s^{-1}.
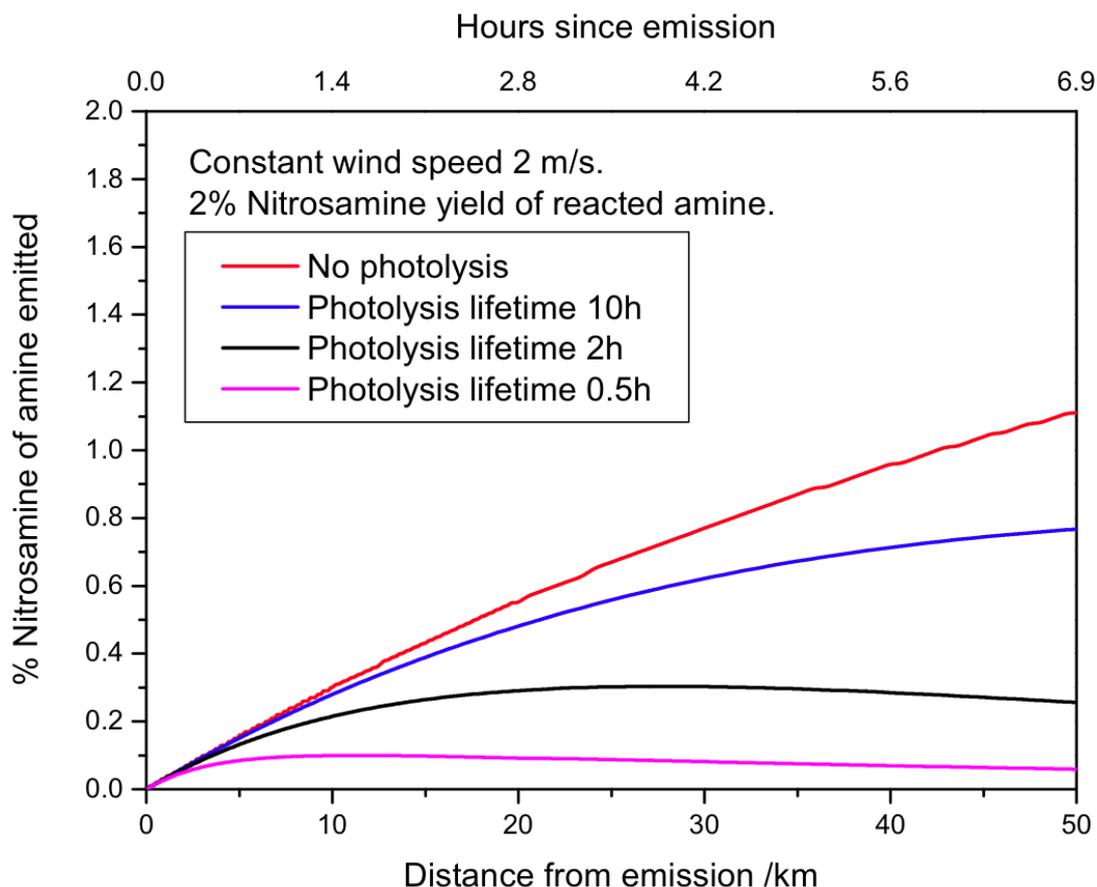
Figure 4. Amount of nitrosamine in an expanding air parcel as a function of distance from emission point for different nitrosamine photolysis lifetimes. The calculations assume a 2% yield of nitrosamine from photo-oxidized amine, an average OH concentration of 5×10^{-5} cm^{-3}, $k_{OH} = 6.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and a constant wind speed of 2 m s^{-1}.

The open issue is then the actual atmospheric photolysis lifetime of nitrosamines in the Mongstad region. Since the photolysis rate constant for nitrosamines (dimethylnitrosamine) has been determined relative to that of NO$_2$, information about the latter photolysis rate is needed. The estimated NO$_2$ photolysis rate at Mongstad (60°N 5°E) is shown in Figure 5 for mid winter, spring equinox, mid summer and fall equinox. The calculations are based on an idealized situation with clear sky conditions, a stratospheric ozone layer of 300 DU and a local albedo of 0.1.[2] Inclusion of the local cloudiness may reduce the photolysis rates by 30-40 %. The estimated annual average effective photolysis rate constant for NO$_2$ in the Mongstad area is $\langle j_{NO2} \rangle_{y,eff} \approx 1.25 \times 10^{-3}$ s^{-1} taking the cloudiness into consideration. This corresponds to an annual average NO$_2$ photolysis lifetime of around 13 min.
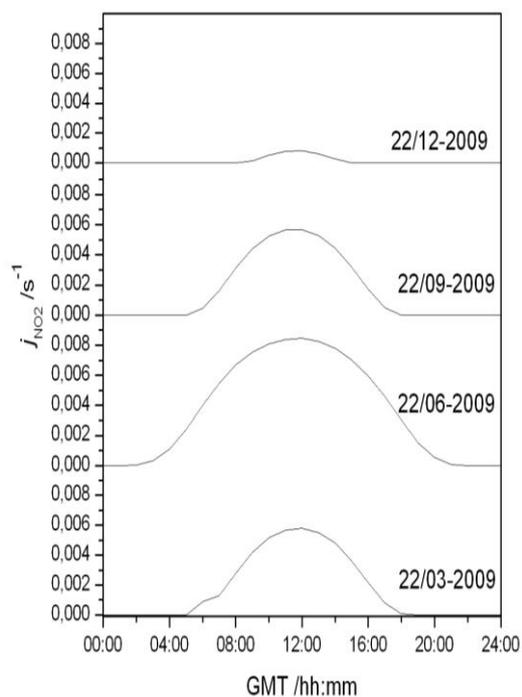
Figure 5. Calculated NO$_2$ photolysis rate at Mongstad (60°N 5°E)**.**

Tuazon et al.[3] determined the photolysis rate constant of nitroso dimethylsamine (NDMA) relative to that of NO_2 to be $j_{NDMA} = 0.53 \times j_{NO2}$. This is the only published value for the effective atmospheric photolysis rate constant of nitrosamines. The ADA-2010 project has carried out a series of NDMA photolysis experiments from which a value of $j_{NDMA} = 0.25 \times j_{NO2}$ was derived.[4] Assuming that all nitrosamines have the same atmospheric photolysis rate constant then suggests an annual average nitrosamine photolysis lifetime of 25 minutes in the Mongstad area for $j_{NDMA} = 0.53 \times j_{NO2}$, or 52 minutes for $j_{NDMA} = 0.25 \times j_{NO2}$.

Summary: A very simple model of the real world complex atmospheric chemistry allows one to conclude that the amount of nitrosamine from amine photo-oxidation in an (expanding) air parcel will be far less than indicated by the yield of nitrosamine in the amine photo-oxidation. For a nitrosamine photolysis lifetime of 2 hours a 2% nitrosamine yield in the amine photo-oxidation only results in around 0.3% nitrosamine in the air parcel – all due to photolysis of the nitrosamine.

The ACC emission data includes nitrosamines emitted directly from the absorber (worst-case 3 pbbV, 0.138 mg s^{-1}). Figure 6 shows the amount of nitrosamine remaining in an expanding air parcel after photolysis as a function of distance from emission point for different average air speeds assuming a photolysis lifetime of 2h. It is self-evident that the higher wind speed will result in worst-case dispersion of the nitrosamine emitted directly. However, even an average photolysis lifetime of 2 h will result in a 50% loss of nitrosamine within the first 10 km from the emission point. Shorter photolysis lifetimes obviously result in increased removal.
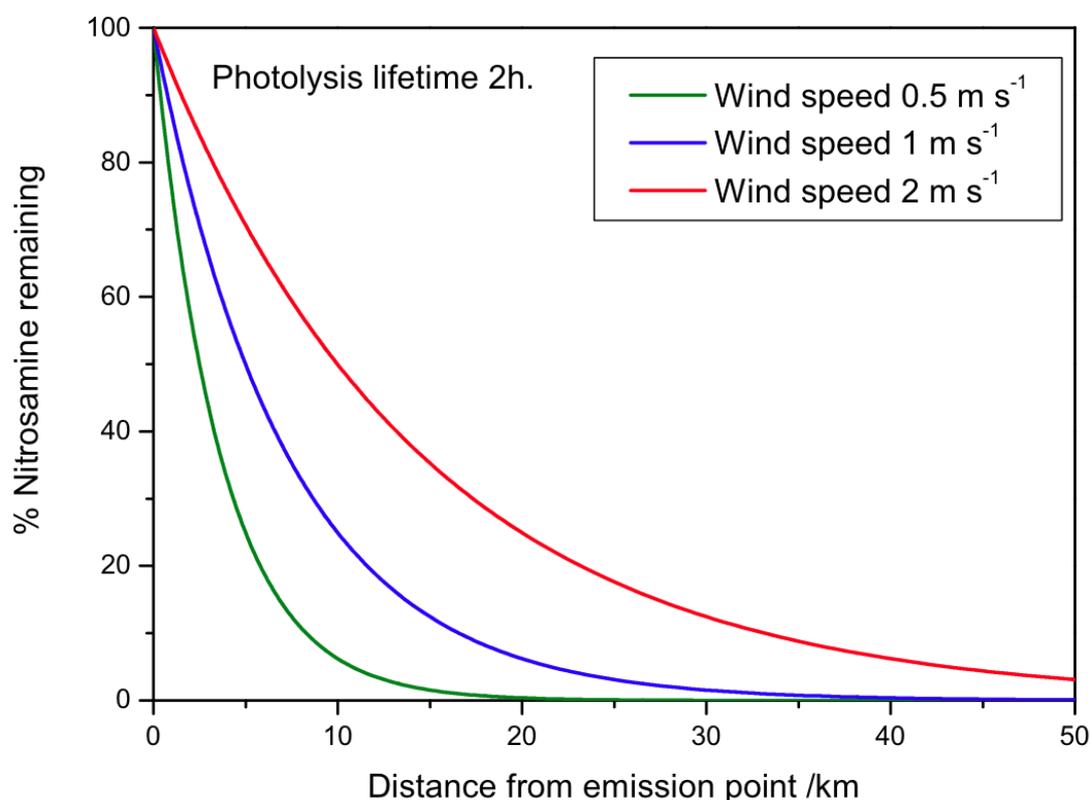
Figure 6. Per cent nitrosamine remaining from a direct emission as a function of distance from the emission point for different wind speeds assuming a photolysis lifetime of 2h.

Figure 7 shows the loss of nitrosamine as a function of distance for different photolysis lifetimes given a constant wind speed of 2 m s^{-1}. The photolysis lifetime of nitrosamines will vary through the year and through the day. Results from ADA-2010 [4] suggest that the average photolysis lifetime of NDMA will be less than 1 h in the Mongstad area. This is twice as long as the earlier results of Tuazon *et al*.[3] would suggest. With a photolysis lifetime of 1 h the amount of directly emitted nitrosamine will be reduced by 50% within the first 5 km form emission point.
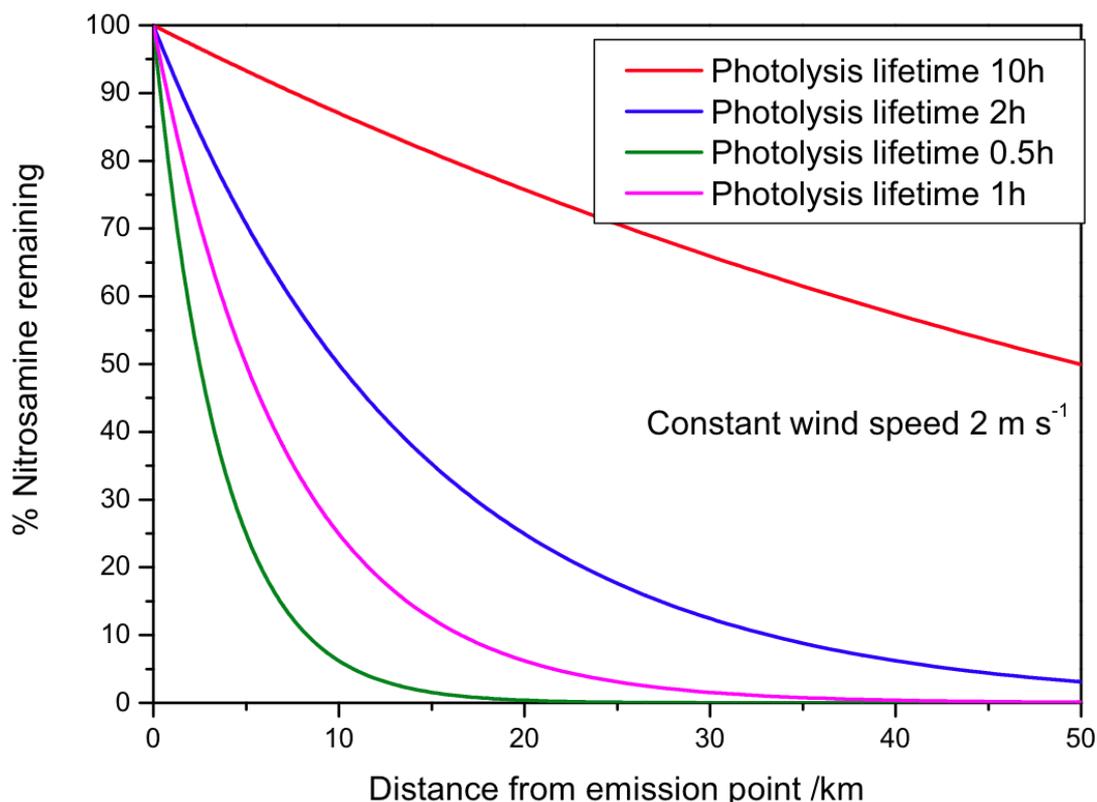
Figure 7. Per cent nitrosamine remaining from a direct emission as a function of distance from the emission point for different photolysis lifetimes assuming a constant wind speed of 2 m s^{-1}.

Summary: Even the simplest implementation of atmospheric chemistry in a dispersion model will result in a >50% reduction in the amine photo-oxidation product formation within the first 25 km from emission point (average wind speed 1 m s^{-1}). If one includes photolysis of nitrosamines the assumed 2% nitrosamine yield of amine emitted is additionally reduced further by almost an order of magnitude for a (conservative estimated average) photolysis lifetime of 2 h. It is not possible to give an exact answer to the question "to what extent the worst case can be reduced" because this requires dispersion model information that is not available. The prevailing wind directions in the Mongstad region can be deduced from the various plots in the NILU report, but there is no information about the average wind speed. Since there is a non-linear relationship between the atmospheric lifetime of a chemical component and its regional atmospheric concentration and deposition, one would have to carry out a separate dispersion model sensitivity study to answer the question. Assuming a linear relationship between atmospheric lifetime of a chemical component and its regional atmospheric concentration and deposition the worst-case scenario for nitrosamine deposition should be reduced by at least one order of magnitude.

The TAPM model assumes that "*The amines are assumed to be highly soluble and totally removed by wet deposition. Amines are deposited directly to the ground. Further degradation in soil/vegetation surfaces is not considered.*" This is then implicitly assumed to be the case for nitrosamines as well. This assumption is correct for alkanolamines and the corresponding nitrosamines. However the assumption is not correct for the alkanamines and alkan nitrosamines, for which the Henrys Law constant is only around 550 M atm^{-1}, see sections 2.3 and 2.5. The alkanamines and their corresponding nitrosamines will therefore not be totally removed by wet deposition.

1.3 Emissions assumptions

It is stated in the NILU report that the emission from Alstom does not contain any toxic substances, only NH_3, CO_2 and water vapour + "normal air" (N_2, O_2 and Ar).

1.4 Degradation of nitrosamines in water

Two cases of nitrosamine degradation in water are considered in the NILU report, (1) no degradation, and (2) degradation in soil water. Photolysis is lake surface water is not considered. Experimental data on the photolysis of nitrosamines in water exist, see section 2.3 "Photolysis of nitrosamines in water". The study of Plumlee and Reinhard[5] is of particular importance, since they have calculated the average NDMA photodecay rate constant for surface water. Figure 8 shows their predicted NDMA photodecay rate constants for three different sites at 2º S, 33º N and 51º N.
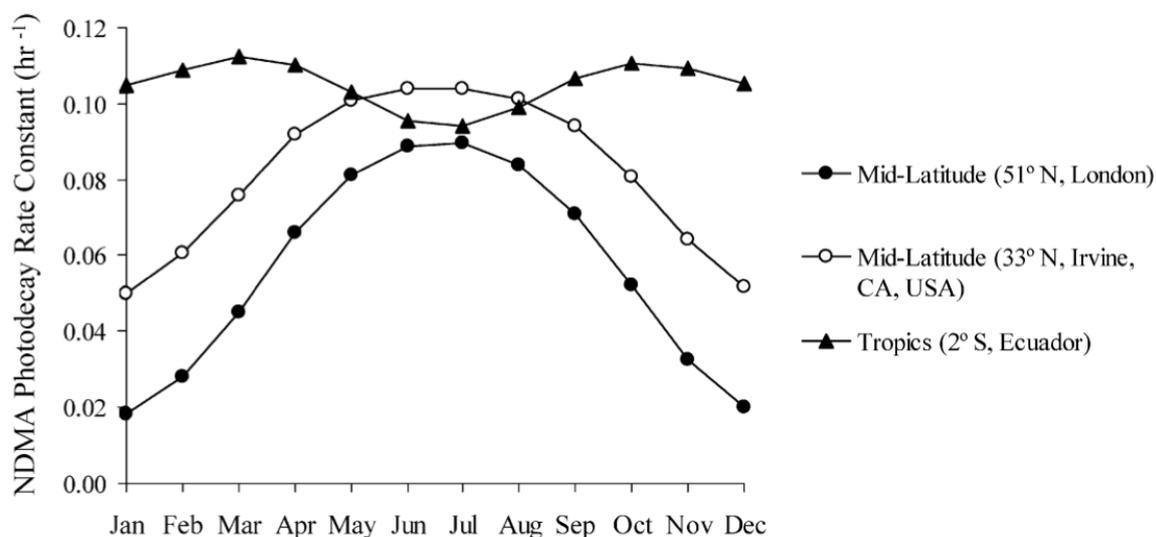
Figure 8. Average NDMA photodecay rate constants predicted for midday solar irradiance in mid-latitude and tropical zones in surface water with intermediate light screening and a depth of 1 m. From Plumlee and Reinhard.5

For comparison NO_2 photolysis rate constant (clear sky conditions) at mid summer in London (51º N, Zenith angle 27º) is around 10% higher that at Mongstad (60º N, Zenith angle 36º).[2] Due to the larger solar Zenith angle at Mongstad, the light screening is around 10% larger here than at London. The predicted photodecay rates calculated for London correspond to half-lives over the year of 8-38 hours. A conservative estimate for the half-lives of nitrosamines in surface water over the year in the Mongstad region will be < 1 week. This should be included in the calculation of the equilibrium nitrosamine concentration the drinking water. It is emphasised that more modelling work is needed to carry out a better

quantification of the photolysis lifetimes of nitrosamines in the water catchments around Mongstad. The organic content in the lakes in lakes in question is also needed to estimate the light screening.

1.5 Loss pathways of nitrosamines in soils

As mentioned above, the NILU report considers nitrosamine degradation in soil water. Recent field and laboratory studies show that NDMA did not leach through turfgrass soils following intensive irrigation with NDMA-containing wastewater effluent.[6,7] Application of ^{14}C-NDMA showed less than 3% of the applied ^{14}C was incorporated into the plants, suggesting only a minor role for plant uptake in removing NDMA from the vegetated soils. The observed rapid dissipation and limited downward movement of NDMA through the soil suggests volatilization as a significant loss pathway.

The soil type at Mongstad may differ considerably from the ones studied by Gan et al.[6] and Arienzo et al.[7]. It is suggested that this should be followed up.

1.6 Erroneous statements in the NILU report

In section 5.4 "Worst case scenario – nitrosamines in air" is stated that:

In general, primary amines have little potential to form nitrosamines, tertiary amines have higher potential and secondary amines have the highest potential to form nitrosamines. Also cyclic amines like piperazine have large potential to form nitrosamines. The potential to form nitrosamines of the different amines is not easy to quantify. However, based on common knowledge in the literature it is most likely between 2 and 10% (see e.g. Pitts et al., 1978, Karl et. al 2008, Bråten et. al 2008). It may be lower (e.g. 1%), or it may be higher than 10% (Grosjean, 1991 refer to a 30% potential), but 2-10% is considered as a plausible range. The various amines have different chemical properties, and their atmospheric lifetimes vary. In the same manner nitrosamines are a group of compounds and their chemical properties and toxicity differ. In this "worst case" analysis we have chosen to give a range of nitrosamine formation potential. We emphasize the 10% value according to the maximizing principle as it is appropriate to carry out in a "worst case scenario" analysis.

The original literature (Pitts *et al*., 1978)[8] does not mention or even suggest a likely range for the potential to form nitrosamines of 2-10%. In fact, the authors state in the abstract of their work that the nitrosamine yields under dark conditions were ≈3% for diethylamine and ≈1% for triethylamine. However, the authors quote an extreme conditions experiment in which their reactor air contained NOx and around 200 ppbV HONO, and that an injection of 500 ppbV diethylamine resulted in a 14% yield of diethylnitrosamine. Concerning nitrosamine formation from "dark chemistry" involving dimethylamine, the authors mention "about 1% yield". The work of Grosjean[9] (Grosjean, 1991) does not anywhere refer to a 30% potential for nitrosamine formation. Grosjean[9] cites the dimethylamine dark experiments by Hanst *et al*.[10] which involved a mixture of 1 ppm dimethylamine, 2 ppm each of NO and NO_2 and 0.5 ppm HONO in humid air showed a 10-30% dimethylnitrosamine yield. It should be noted that Glasson later proved the nitrosamine formation in the Hanst *et al*. experiments to be the result of a surface reaction.[11]

Summary: There is no scientific basis for statements in the NILU report concerning the potential for nitrosamine formation. The concept of "potential for nitrosamine formation" is

misunderstood. For secondary amines the concept refers to the N-H:C-H branching in the initial photo-oxidation reaction. Taking dimethylamine as example:

$(CH_3)_2NH + OH \rightarrow (CH_3)_2N + H_2O$ *This amino radical has the potential to form nitrosamines*

$\rightarrow CH_3NHCH_2 + H_2O$ *The alkyl radical will not result in nitrosamines*

The experimental N-H:C-H branching ratio for the OH-initiated photo-oxidation of dimethylamine has been reported to be 0.63:0.37 [12] and 0.58:0.42,[4] and one could therefore claim that dimethylamine has a potential for nitrosamine formation of around 40%!

For tertiary amines it refers to branching of the alkoxy radical reactions following the initial photo-oxidation step. Taking trimentylamine as example:

$(CH_3)_3N + OH \rightarrow (CH_3)_2NCH_2 + H_2O$

$(CH_3)_2NCH_2 + O_2 \rightarrow (CH_3)_2NCH_2\ OO$

$(CH_3)_2NCH_2OO + NO \rightarrow (CH_3)_2NCH_2O + NO_2$

$(CH_3)_2NCH_2O + O_2 \rightarrow (CH_3)_2NCHO + HO_2$

$(CH_3)_2NCH_2O \rightarrow (CH_3)_2N + CH_2O$ *This amino radical has the potential to form nitrosamines*

The most important paper in relation to nitrosamine formation, the fundamental study of Lindley *et al.*,[12] is not included in the NILU report reference list. This publication presents all the rate constants necessary to calculate the amount of nitrosamine that will be formed from dimethylamine in the atmosphere. Quoting Lindley *et al.*: "*The most favorable condition for nitrosamine generation occurs at low* [NO_2]/[NO] *ratios; a ratio less than 1 is not common except during the early morning hours. Taking* [NO_2]/[NO] ≈ 1 *and* [NO] $= 0.1$ *ppm gives* [$(CH_3)_2NNO$]$_{ss}$ $= (4.0 \times 10^{-3})$ [Me_2NH]." Note the high NOx-level (100 pptV NO and 100 pptV NO_2) employed in the estimation.

The ADA-2010 project studied the photo-oxidation of dimethylamine in more detail and derived all branching ratios in the atmospheric degradation, Scheme 1.

Scheme 1. Atmospheric photo-oxidation of dimethylamine. From Nielsen *et al.*, ref. 4.

Because NDMA is constantly formed and destroyed through photolysis it makes little sense to quantify the yield *per se*. It is the amount of NDMA present in the atmosphere that is of interest, and this can be estimated from steady-state considerations leading to the following expression:

$$\frac{\left[(CH_3)_2NNO\right]_{SS}}{\left[(CH_3)_2NH\right]} = \frac{k_{1a}\left[OH\right]}{j_5} \cdot \frac{\left(k_3/k_{4a}\right) X_{NO}}{\left(k_2/k_{4a}\right) X_{O2} + (1+k_{4b}/k_{4a}) \cdot X_{NO2}}$$

in which X_{NO}, X_{NO2} and X_{O2} are the mixing ratios of NO, NO_2 and O_2, respectively.
Table 1 compares the experimental rate constants relevant to dimethylnitrosamine formation. For a situation with $[OH]=10^6$, $[NO_2]/[NO] = 1$, $[NO] = 0.1$ ppmV and $j_{NO2} = 10^{-3}$ s^{-1}, the difference between predictions based on the older data and the new ADA-2010 results is that the new results indicate a factor of 10 times more nitrosamine at steady state.

Table 1. Comparison of relative rate constants relating to the branching of the dimethylamino radical reactions in the atmosphere.

	k_2/k_{4a}	k_{4b}/k_{4a}	k_3/k_{4a}	j_5/j_{NO2}
Lindley et al.[33]	$(3.90 \pm 0.28) \times 10^{-7}$	0.22 ± 0.06	0.26	
Tuazon et al.[37]				0.53
Nielsen et al.[4]	3.0×10^{-7}	0.10	0.75	0.25

Summary: Emissions from TCM at Mongstad will be diluted to background levels very fast compared to the timescale of the atmospheric amine photo-oxidation. The nitrosamine yield in the photo-oxidation process will therefore depend on the local NOx conditions. For the Mongstad area (measurements carried out 2006-2007 at Leirvåg-Hamna) the annual average amount of NO_2 is 4.6-7.4 μg m^{-3} corresponding to a mixing ratio of 2.5-4 ppbV. Taking the recent results from ADA-2010 concerning nitrosamine formation, and assuming a NO:NO_2 ratio of 1:2 and an average day-night-summer-winter oxidative capacity corresponding to 5 × 10^5 cm^{-3} OH radicals (upper limit) and an annual average actinic flux corresponding to j_{NO2} = 5 × 10^{-4} s^{-1} (lower limit) places the steady state dimethylnitrosamine concentration at less than 0.1% of the dimethylamine present in the air mass.

1.7 Recommended values for gas phase chemistry modelling

The maximum nitrosamine concentration (NOT YIELD) can for dimethylnitrosamine be set to 1% of the amount of dimethylamine in the same air mass in the Mongstad area. This is 10 times the estimated annual average steady state concentration. The most likely concentration of dimethylnitrosamine should be set to a conservative value of 2 times the estimated steady state concentration, that is 0.2% of the amount of dimethylamine in the same air mass in the Mongstad area. There are no experimental data for the nitrosamine formation for other amines. A best estimate for these will be to use the same values for other secondary amines.

The amount of nitramines formed in the atmospheric photo-oxidation of amines in the Mongstad area depend on the NO_2 concentration. The ADA-2010 project has derived upper limit yields of nitramine formation of 0.4% for methylamine and 2.5% for dimethylamine assuming 10 ppbV NO_2. As the annual average NO_2 concentration is below this in the Mongstad area, it is suggested to keep these upper limit values as representative for nitramine formation for primary and secondary amines in the Mongstad area. The most likely values for the nitramine yields will be a factor of 2 lower.

The atmospheric lifetime of nitrosamines with respect to gas phase photolysis is given by the photolysis rate constant, j. There is only experimental gas phase data for one single nitrosamine, dimethylnitrosamine (NDMA). Tuazon *et al.*[3] derived the photolysis rate constant of NDMA relative to that of NO_2 to be $j_{NDMA} = 0.53 \times j_{NO2}$. The ADA-2010 project presented a 50% smaller value, $j_{NDMA} = 0.25 \times j_{NO2}$.[4] It is suggested to use the smallest photolysis rate constant for atmospheric chemistry modelling.

2 Nitrosamines in the aqueous phase

2.1 Hydrolysis of nitrosamines in water

Tate and Alexander[13] found that N-nitroso dipropylamine (NDPA) did not degrade in lake water incubated at 30 ℃ for 108 days. They also concluded NDPA was not susceptible to microbiological degradation.

Plumlee and Reinhard[5] studied the chemical hydrolysis of NDPA and also demonstrated the stability of this compound. Even at the elevated temperature of 51 ℃, no degradation of NDPA was detected during a 32-day study at any pH. They concluded that it is probable that NDPA will not degrade in water in the absence of light.

Summary: Hydrolysis of nitrosamines in water is slow at any pH and will not constitute an important sink for this class of molecules.

2.2 OH radical reactions with nitrosamines and nitramines in water.

Mezyk *et al.*[14] determined absolute rate constants for the reactions of the OH radical with *N*-nitroso dimethylamine (NDMA) in water at room temperature using electron pulse radiolysis and transient absorption spectroscopy, and reported a rate constant of $(4.30 \pm 0.12) \times 10^8$ M^{-1} s^{-1}. DMPO spin-trapping experiments demonstrated that the hydroxyl radical reaction with NDMA occurs by hydrogen atom abstraction from a methyl group, and the rate constant for the subsequent reaction of this radical transient with dissolved oxygen was measured as $(5.3 \pm 0.6) \times 10^6$ M^{-1} s^{-1}. This relatively slow rate constant implies that regeneration of the parent nitrosoamine from the oxidized transient could occur in natural waters containing dissolved organic compounds.

Mezyk *et al.*[15] later determined absolute rate constants for OH radical reactions with low-molecular-weight nitrosamines and nitramines in water at room temperature using the techniques of electron pulse radiolysis and transient absorption spectroscopy. The bimolecular rate constants obtained, k (M^{-1} s^{-1}), were as follows: methylethylnitrosamine, $(4.95 \pm 0.21) \times 10^8$; diethylnitrosamine, $(6.99 \pm 0.28) \times 10^8$; dimethylnitramine, $(5.44 \pm 0.20) \times 10^8$; methylethylnitramine, $(7.60 \pm 0.43) \times 10^8$; and diethylnitramine, $(8.67 \pm 0.48) \times 10^8$, respectively. MNP/DMPO spin-trapping experiments demonstrated that hydroxyl radical reaction with these compounds occurs by hydrogen atom abstraction from an alkyl group.

Landsman *et al.*[16] determined absolute rate constants and degradation efficiencies for hydroxyl radical reactions with seven low-molecular-weight nitrosamines in water using a combination of electron-pulse radiolysis/absorption spectroscopy and steady-state radiolysis/GCMS measurements. The hydroxyl radical oxidation rate constants were found to depend upon nitrosamine size and to have a very good linear correlation with the number of methylene groups in these compounds. This correlation, given by $\ln(k_{OH}) = (19.72 \pm 0.14) + (0.424 \pm 0.033)(\#CH_2)$, suggests that hydroxyl radical oxidation predominantly occurs by hydrogen atom abstraction from constituent methylene groups in each of these nitrosamines. From steady-state radiolysis measurements under aerated conditions, specific hydroxyl radical degradation efficiencies for each nitrosamine were evaluated. For larger nitrosamines, the efficiency was constant at 100%; however, for the smaller alkyl substituted species, the efficiency was significantly lower, with a minimum value of only 80% determined for *N*-nitrosodimethylamine. The reduced efficiency is attributed to radical repair reactions competing with the slow peroxyl radical formation.

Minakata *et al.*[17] has developed a group contribution method (GCM) to predict the aqueous phase HO• rate constants for the following reaction mechanisms: (1) H-atom abstraction, (2)

HO• addition to alkenes, (3) HO• addition to aromatic compounds, and (4) HO• interaction with sulfur (S)-, nitrogen (N)-, or phosphorus (P)-atom-containing compounds. The GCM hypothesizes that an observed experimental rate constant for a given organic compound is the combined rate of all elementary reactions involving HO•, which can be estimated using the Arrhenius activation energy, E_a, and temperature. Each E_a for those elementary reactions can be comprised of two parts: (1) a base part that includes a reactive bond in each reaction mechanism and (2) contributions from its neighbouring functional groups. The GCM includes 66 group rate constants and 80 group contribution factors, which characterize each HO• reaction mechanism with steric effects of the chemical structure groups and impacts of the neighbouring functional groups, respectively. Literature-reported experimental HO• rate constants for 310 and 124 compounds were used for calibration and prediction, respectively. The genetic algorithms were used to determine the group rate constants and group contribution factors. The group contribution factors for H-atom abstraction and HO• addition to the aromatic compounds were found to linearly correlate with the Taft constants, σ*, and electrophilic substituent parameters, σ+, respectively. The best calibrations for 83% (257 rate constants) and predictions for 62% (77 rate constants) of the rate constants were within 0.5-2 times the experimental values. This accuracy may be acceptable for model predictions of the advanced oxidation processes (AOPs) performance, depending on how sensitive the model is to the rate constants.

Using the method presented in Minakata *et al*.[17] the following OH radical rate constants for the reactions with nitramines, amines, amides and nitrosamines in aqueous solution have been calculated and compared to experimental data.

Table 2. Observed and calculated rate coefficients for OH radical reaction with amines, nitrosamines, nitramines and amides in water.

Compound	SMILES	k_{2nd}, calc $M^{-1}s^{-1}$	k_{2nd}, obs $M^{-1}s^{-1}$	Reference
Diethylnitramine	CN(CC)[N+](=O)[O-]	1.23×10^9	5.44×10^8	Mezyk *et al*.[15]
Methylethylnitramine	CN(CC)[N+](=O)[O-]	6.78×10^8	7.60×10^8	Mezyk *et al*.[15]
Dimethylnitramine	CN(C)[N+](=O)[O-]	1.24×10^8	8.67×10^8	Mezyk *et al*.[15]
N-nitrosomethylethylamine	CN(CC)N=O	4.30×10^8	4.95×10^8	Mezyk *et al*.[15]
N-nitrosodiethylamine	CCN(CC)N=O	8.52×10^8	6.99×10^8	Mezyk *et al*.[15]
N-nitrosodimethylamine	CN(C)N=O	7.41×10^6	4.3×10^8	Landsman *et al*.[16]
N-nitrosodipropylamine	CCCN(CCC)N=O	3.54×10^9	2.3×10^9	Landsman *et al*.[16]
N-nitrosoethylbutylamine	CCN(CCCC)N=O	3.61×10^9	3.1×10^9	Landsman *et al*.[16]
N-nitrosodibutylamine	CCCCN(CCCC)N=O	6.36×10^9	4.71×10^9	Landsman *et al*.[16]
N-nitrosomorpholine	O=NN1CCOCC1	1.35×10^9	1.75×10^9	Landsman *et al*.[16]
N-nitrosopyrrolidine	C1CCN(C1)N=O	2.44×10^9	1.75×10^9	Landsman *et al*.[16]
N-nitrosopiperidine	O=NN1CCCCC1	4.23×10^9	2.98×10^9	Landsman *et al*.[16]
Methylamine	CN	4.57×10^9	1.2×10^8	Lee *et al*.[18]
Dimethylamine	CNC	1.25×10^7	6.0×10^7	Getoff and Schwörer [19]
Monoethanolamine	OCCN	6.75×10^9	3.0×10^8	Kishore *et al*.[20]
Diethanolamine	OCCNCCO	5.60×10^9	4.8×10^8	Kishore *et al*.[20]
Triethanolamine	OCCN(CCO)CCO	1.18×10^{10}	2.0×10^9	Kishore *et al*.[20]
Methyldiethanolamine	N(C)(CCO)CCO	9.61×10^9	4.7×10^8	Lee *et al*.[18]
N-methylformamide	CNC=O	1.84×10^9	1.2×10^9	Hayon *et al*.[21]
Formamide	C(=O)N	5.17×10^9	3.7×10^8	Munoz *et al*.[22]

Summary: Kinetic information on reactions of nitrosamines and nitramines in aqueous solution is restricted to OH radical reactions. No study on the reactivity towards NO_3 and other radicals has been found so far. Lee et al.[18] found the reactivity of NDMA towards ozone in aqueous solution to be very slow and probably insignificant for the degradation in the atmosphere. Also the reaction of N-nitroso diethylamine with O_3 is very slow as shown by Xu et al.[23]

The reactivity of nitrosamines and nitramines towards OH is lower compared to other compounds classes such as alcohols or carbonyl compounds. The lifetimes of nitrosamines during the night hours remains highly uncertain since the reaction with night-time oxidants are not investigated so far. It can be only speculated that they have probably much longer lifetimes during the night or under low radiation conditions. The oxidation of NDMA by OH radicals leads to the formation of methylamine, formaldehyde, nitrate and nitrite (Heur et al.,[24] Lee et al.[18] and Xu et al.[25]).

The group contribution method developed by Minakata et al.[17] seem to be very useful to estimate kinetic data of nitrosamines and nitramines in aqueous solution. However, the method seems to clearly overestimate the reactivities of amines and amides.

2.3 Photolysis of nitrosamines in water.

The photolysis of various dialkylnitrosamines has been studied by several groups. Chow[26] observed that dialkylnitrosamines were rapidly photo-degraded in the presence of acid but were stable in neutral solution. Burns and Alliston[27] studied the photolysis of *N*-nitroso dibutylamine in aqueous solution and observed degradation at all pH's (range of 0.7 to 9.2) studied but also observed degradation was more rapid at low pH. Polo and Chow[28] observed that dimethylnitrosamine photodegraded in solution up to pH 10 but also found that the rate at pH 10 was about one-tenth that observed at pH 1. The latter two studies indicated the photolysis occurred via first-order kinetics with tendencies toward zero-order kinetics at higher concentrations. Aubert *et al.*[29] studied the degradation of *N*-nitroso dimethylamine over a 15-day period and found that the degradation was accelerated by light and was slower in seawater than in fresh water.

Saunders and Mosier[30] studied the photolysis of *N*-nitroso dipropylamin (NDPA) in lake water and several other aqueous systems. In lake water sunlight photolysis experiments, dissipation of NDPA was significant but variable. Other laboratory studies demonstrated NDPA photodegraded readily in neutral solution and the photo-degradation rate was not pH dependent in the 3 to 9 range. The major photoproduct was found to be *n*-propylamine, but the formation of di-*n*-propylamine was also observed.

Plumlee and Reinhard[5] studied the aqueous photolysis of seven alkyl nitrosamines (*N*-nitroso dimethylamine, *N*-nitroso methyl-ethylamine, *N*-nitroso diethylamine, *N*-nitroso dipropyl-amine, *N*-nitroso dibutylamine, *N*-nitroso piperidine, and *N*-nitroso pyrrolidine) by irradiation in a solar simulator. Direct photolysis at irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. Absorption cross-sections were reported (see Figure 9) and the quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43\text{-}0.61$ for the other nitrosamines. Quantified products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98 and 79%, respectively. Indirect photolysis of nitrosamines in surface water was not observed; increasing dissolved organic carbon slowed the NDMA photolysis rate because of light

screening. Removal of NDMA measured in tertiary treated effluent flowing in a shallow, sunlit engineered channel agreed with photolysis rates predicted based on the measured quantum yield and system parameters.
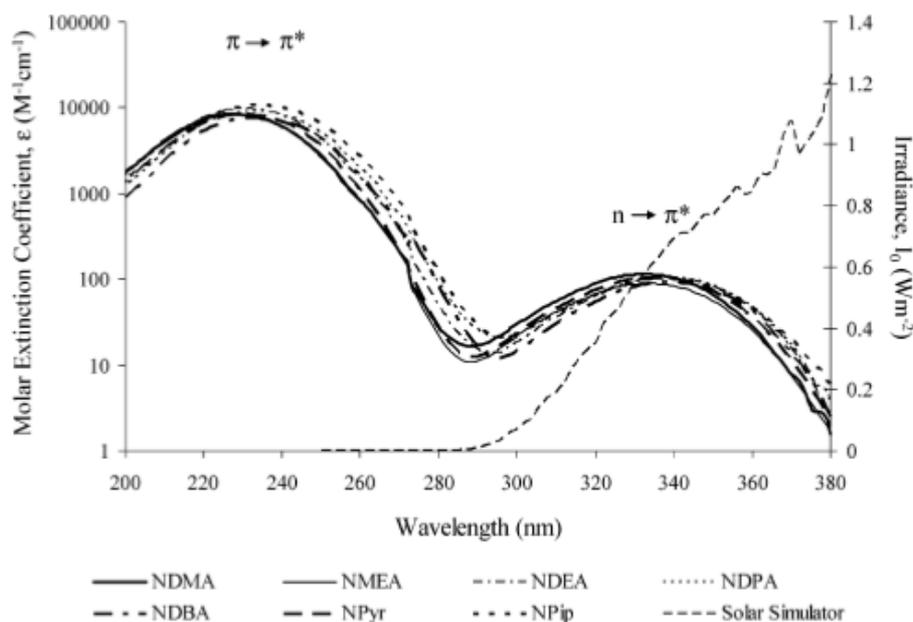
Figure 9. UV molar extinction of nitrosamines reported by Plumlee and Reinhard.[5]

Plumlee and Reinhard further calculated the average NDMA photodecay rate constant for midday solar irradiance in midlatitudes and tropical zones in surface water with light screening and a depth of 1m. For 51 °N the predicted rates corresponds to half-lifes over the year of 8-38 h. For the Mongstad region (60 °N) the corresponding half-lives will somewhere between 50 and 100% longer.

Xu *et al.*[31] studied the direct photolysis of *N*-nitroso diethylamine (NDEA) in water with ultraviolet (UV) irradiation. Results showed that NDEA could be completely degraded under the direct UV irradiation. The effects of the experimental conditions, including the initial concentration of NDEA, humic acid and solution pH, were studied. The degradation products of NDEA were identified and quantified with gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC). It was confirmed that methylamine (MA), dimethylamine (DMA), ethylamine (EA), diethylamine (DEA), NO_2^- and NO_3^- were the main degradation products.

Lee *et al.*[32] studied the direct ultraviolet (UV) photolysis of *N*-nitroso dimethylamine (NDMA) in aqueous solution with its degradation products analyzed quantitatively. NDMA is photolyzed either to dimethylamine (DMA) or to methylamine (MA) by two distinct pathways. The two pathways of NDMA photolysis were found to be strongly dependent on the initial NDMA concentration and solution pH. Increasing the initial NDMA concentration clearly favoured the DMA formation path. DMA production was optimized in the region of pH 4-5. The nitrite ion (NO_2^-) produced from the NDMA photolysis was identified as a key reagent in directing the NDMA photolysis toward DMA production. The quantum yield of NDMA photolysis measured from the kinetic measurements of NDMA photolysis with varying initial NDMA concentration was observed to be constant as 0.28 ± 0.0022, regardless of the initial NDMA concentration.

Jahan *et al.*[33] studied the photolysis of NDMA employing 253.7 nm radiation from Hg lamps. They report quantum efficiencies of 0.3% at pH 6.8 and 4.7 at pH 3.0. The results are not

relevant to the troposphere.

Chen *et al.*[34] studied the photolysis of 8 nitrosamines (*N*-nitrosodimethylamine, *N*-nitrosodiethylamine, *N*-nitrosodipropylamine, *N*-nitrosodibutylamine, *N*-nitrosopiperidine, *N*-nitrosomethylethylamine, *N*-nitrosopyrrolidine and *N*-nitrosopiperidine) under both natural (outdoor experiments in Tempe, Arizona, USA) and artificial sunlight conditions. They report both rate constants (pseudo-first order) and quantum yields. The half-lives were around 8-10 minutes with a solar intensity of 1150-1300 W cm^{-2}.

Stefan and Bolton [35] studied the direct ultraviolet (UV) photolysis of *N*-nitroso dimethylamine (NDMA) in aqueous solution by kinetic and product studies. Identified photolysis products are dimethylamine (DMA), nitrite and nitrate. They found that the photolysis occurs much faster at pH = 3 than pH = 7 with quantum yields of 0.25 and 0.13 respectively. The authors stated that the formation of dimethylamine and nitrite can lead to a re-formation of NDMA in the absence of light. Furthermore, it was mentioned that the photolysis products nitrite and nitrate will compete with NDMA for the light and reduce the efficiency of the NDMA destruction.

Summary: The Lee et al.[32] study reveals a new mechanistic pathway of NDMA photolysis to DMA by identifying the factors influencing the photolysis pathway. The observed photolytic behaviours of NDMA photolysis could be successfully explained in terms of the new mechanism involving NO_2^-. However, the mechanism through which NDMA is photolyzed to DMA is not clearly understood. At the moment it can be only assumed that this mechanism is general for N-nitroso alkylamines. This means that the aqueous photolysis process re-generates the precursors for the nitrosamine formation.

Because nitrosamine hydrolysis reactions, biodegradation and OH reactions with nitrosamines are relatively slow, aquatic photolysis of nitrosamines is expected to be the major loss process even at relatively low levels of solar irradiation.

In order to check if the partitioning of nitrosamines into the atmospheric aqueous phase (clouds and aqueous particles) delays the degradation of nitrosamines by gas phase photolysis a simplified box model run was performed. The modelled concentration time profile of *N*-nitroso dimethylamine in the presence of aqueous particles (Tilgner and Herrmann[36]) and clouds with a liquid water content of 5 x 10^{-5} L cm^{-3} for summer and winter conditions are shown in Figures 10 and 11.
The simplified box model was initialized as follows:
- Starting NDMA concentration of 0.1 ppt (no other compounds in either phases)
- Gas phase photolysis: *$j_{NDMA} = 0.25 \times j_{NO2}$* ; no aqueous phase photolysis process
- OH reactions in the gas ($3.0 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}; Tuazon *et al.*[3]) and aqueous phase ($4.3 \cdot 10^8$ M^{-1}s^{-1}; Landsman *et al.*[16])
- Phase transfer description based on a Henrys law constant of H = $1.82 \cdot 10^{-6}$ atm m^3 mol^{-1} (experimental, Mirvish *et al.*[37]) and an assumed mass accommodation coefficient of $\alpha = 1$
- An photolytic OH source
- A model run in the absence of clouds and with a cloud period (marked in blue in Figures 10 and 11)
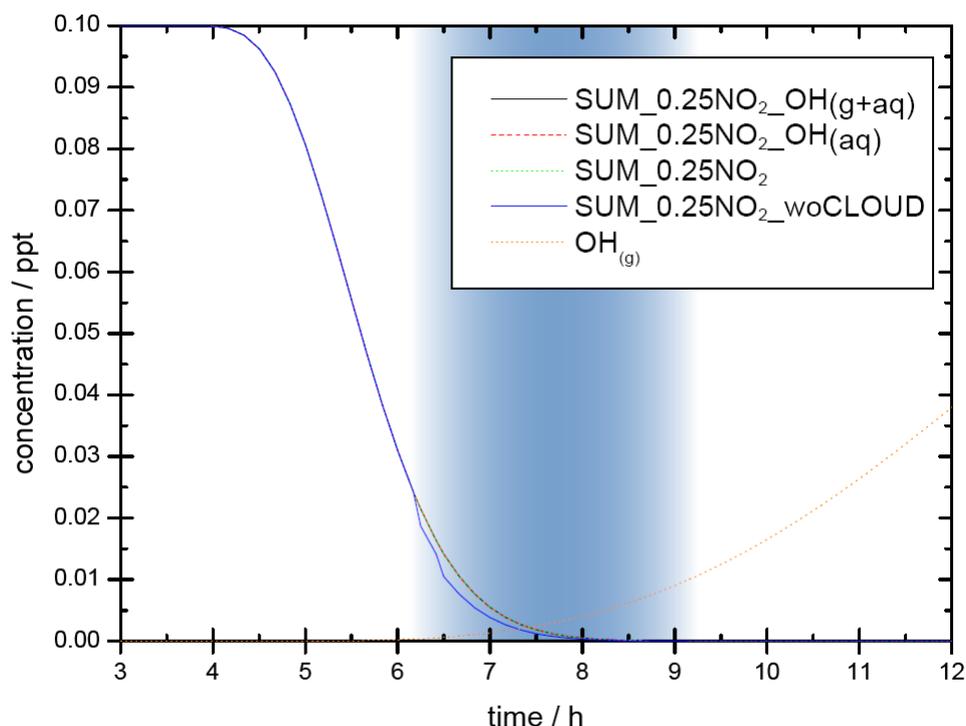
Figure 10. Summary of the box model runs performed under summer conditions. Abbreviations: **SUM_0.25NO₂_woCloud**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in summer without cloud (only wet particles); **SUM_0.25NO₂**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in summer with cloud (blue) and wet particles; **SUM_0.25NO₂_OH(aq)**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in summer with cloud (blue) and wet particles + OH reaction in water; **SUM_0.25NO₂_OH(g+aq)** NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in summer with cloud (blue) and wet particles + OH reaction in water and gas phase.
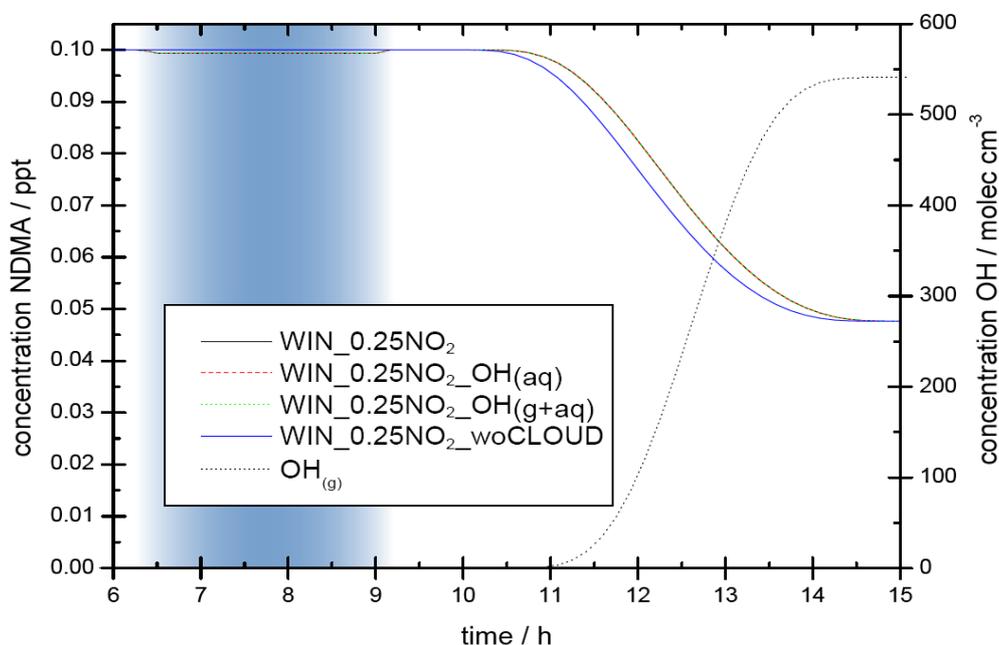
Figure 11. Summary of the box model runs performed under winter conditions. Abbreviations: **WIN_0.25NO₂_woCloud**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in winter without cloud (only wet particles); **WIN_0.25NO₂**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in winter with cloud (blue) and wet particles; **WIN_0.25NO₂_OH(aq)**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in winter with cloud (blue) and wet particles + OH reaction in water; **WIN_0.25NO₂_OH(g+aq)**, NDMA photolysis ($j_{NDMA} = 0.25 \times j_{NO2}$) in winter with cloud (blue) and wet particles + OH reaction in water and gas phase.

The results show that the aqueous phase can act as a reservoir for NDMA in summer and winter. However, the effect is in the order of a few minutes only due to the fast photolysis in the gas phase and the re-adjustment of the partitioning equilibrium. Furthermore, the results shown in Figures 10 and 11 indicate that OH radical reactions in either phase do not affect the modelled concentration profiles significantly.

2.4   Field measurements

A recent study from Herckes et al.[38] detected small nitrosamines (such as NDMA) in the hydrophobic neutral fraction of fog water samples in California. A preliminary testing revealed concentration up to 240 ng/L. However, Herckes and co-workers[38] did not present a list with nitrosamines (other than NDMA) found in the fog water samples. This magnitude is also confirmed by the collected field data presented in Hutchings et al.[39] Furthermore, amines (precursors for nitrosamines) have been detected in fog water samples by Herckes et al.[38] and in other studies e.g. Zhang and Anastasio.[40]

Hutchings et al.[39] investigated sources and sinks as well as the partitioning of NDMA in the troposphere by laboratory, field and modelling studies. They measured product yields for the NDMA formation in presence of dimethylamine and nitrite at different pH values. The experimental results obtained demonstrate very low product yields (< 1%) under all tested conditions. Furthermore, no increasing NDMA formation over the time was measured. Hutchings et al.[39] concluded that the formation of NDMA in aqueous solution is not efficient enough to explain the results from field measurements and that the partitioning from the gas phase is an important source for NDMA in the tropospheric aqueous phase.

Keefer and Roller report that the nitrosation of secondary amines take place even in neutral and basic media and that the reaction is catalyzed by formaldehyde.[41] They report significant yields of nitrosamines in presence of HCHO after 17 hours reaction time. Therefore, it is recommended to check the nitrosamines yields at atmospherically relevant time scales in presence of HCHO. Nonetheless, worst case scenarios should also consider a more efficient nitrosation of amines than reported by Hutchings and co-workers.

The modelling studies performed support also the conclusions from other studies that the lifetimes of NDMA during the daytime is determined by photolysis processes. However, they outline that it might persist in the atmosphere for hours in the dark and that photolysis processes in aqueous solution could be less efficient than in the gas phase.

Summary: The available field measurements and modelling studies demonstrate that one should expect nitrosamines in the tropospheric aqueous phase. However, the efficiency and consequently the importance of aqueous phase nitrosation reactions in comparison to phase transfer processes are still not clear. Therefore, experimental studies considering also the potential catalytic effect of HCHO are recommended. For worst case studies also model runs with higher nitrosamines product yields than the ones reported by Hutchings et al.[39] should be performed.

2.5   Air – aqueous aerosol partitioning of nitrosamines

There are only few, and in part inconsistent, studies of Henry´s Law constants (HLC) for nitrosamines. Mirvish et al.[37] reported air-water distribution ratios for 17 nitrosamines at 37 ºC. Klein[42] reported vapour pressures of 30 nitrosamines between 0 and 40 ºC, and the partial

pressures of N-nitroso dimethylamine, N-nitroso diethylamine and N-nitroso pyrrolidine over aqueous solutions. More recently, Hiatt[43] measured relative volatility values for 114 organic compounds including 5 nitrosamines. Abraham and Al-Hussaini[44] have been employed the available for deriving a general solvation description of N-nitroso dialkylamines. The available HLC data are summarized in Table 2.

The Henry´s Law constant for nitrosodimethylamine (Table 3) is 2×10^{-06} atm m^3 mol^{-1}. For a cloud having liquid water content of 5% (5×10^{-5} L cm^{-3}) around 6% of nitrosodimethylamine will be in the liquid phase. It is complicated to calculate the "below-cloud" scavenging of trace gases, but nitrosamines having HLC´s comparable to nitrosodimethylamine will not be totally removed by wet deposition.

Henry´s Law constants can be estimated using the EPI (Estimation Programs Interface) Suite 4.0 software (http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm). This software delivers two calculated HLC constants using the bond contribution description and the group contribution description. In the first step experimental and calculated data were compared for a number of nitrosamines in order to check the reliability and applicability of the two estimation methods, Table 3.

Table 3. Observed and calculated Henry´s Law constants for nitrosamines.

Compound	SMILES	Bond-Method H (calc) atm m^3/mol	Group-Method H (calc) atm m^3/mol	Experiment H (exp) atm m^3/mol
Nitrosodimethylamine	CN(C)N=O	2.06×10^{-06}	1.20×10^{-06}	1.82×10^{-06}
Nitrosodiethylamine	CCN(CC)N=O	3.63×10^{-06}	1.73×10^{-06}	6.60×10^{-06}
Nitrosodipropylamine	CCCN(CCC)N=O	6.39×10^{-06}	3.46×10^{-06}	5.38×10^{-06}
Nitrosodibutylamine	CCCCN(CCCC)N=O	1.13×10^{-05}	6.89×10^{-06}	1.32×10^{-05}
Nitrosodiisopropylamine	CC(C)N(C(C)C)N=O	6.39×10^{-06}		7.83×10^{-06}
Nitrosobutylmethylamine	CCCCN(C)N=O	4.81×10^{-06}	2.87×10^{-06}	5.75×10^{-06}
Methylamylnitrosamine	CCCCCN(C)N=O	6.39×10^{-06}	4.06×10^{-06}	4.65×10^{-06}
Nitrosoethylbutylamine	CCN(CCCC)N=O	6.39×10^{-06}	3.46×10^{-06}	9.54×10^{-06}
Nitrosomethylbenzylamine	CN(CC1=CC=CC=C1)N=O	1.66×10^{-07}		1.20×10^{-05}
Nitrosoazetidine	C1CN(C1)N=O	1.20×10^{-06}	1.41×10^{-07}	4.89×10^{-08}
Nitrosopyrrolidine	C1CCN(C1)N=O	1.60×10^{-06}	1.99×10^{-07}	4.89×10^{-08}
Nitrosopiperidine	O=NN1CCCCC1	2.12×10^{-06}	2.81×10^{-07}	8.44×10^{-07}
Nitrosohexamethyleneimine	C1CCCN(CC1)N=O	2.82×10^{-06}	3.97×10^{-07}	2.20×10^{-07}
Nitrosomorpholine	C1COCCN1N=O	1.41×10^{-08}	2.13×10^{-10}	2.45×10^{-08}
2,6-Dimethylnitrosomorpholine	CC1CN(CC(O1)C)N=O	2.48×10^{-08}	1.17×10^{-09}	2.69×10^{-07}
Dinitrosopiperazine	N1(N=O)CCN(CC1)N=O	3.36×10^{-11}	4.06×10^{-13}	4.89×10^{-08}
2,6-Dimethyldinitrosopiperazine	CC1CN(CC(N1N=O)C)N=O	5.93×10^{-11}		4.89×10^{-08}
Methylnitrosoacetamide	CC(=O)N(C)N=O	3.04×10^{-09}		1.10×10^{-04}
Methylnitrosourea	CN(C(=O)N)N=O	9.91×10^{-11}		4.89×10^{-08}
Methylnitrosourethan	O(CC)C(=O)N(C)N=O	1.43×10^{-08}		2.45×10^{-05}
Ethylnitrosocyanamide	N#CN(CC)N=O	1.20×10^{-05}		3.67×10^{-05}

As can be seen in Table 3 that the group contribution method fails to calculate the HLC data for a couple of compounds. The bond method was able to calculate all data. However, deviations between calculated and experimental data are sometimes large in particular for more complex molecules.

HLC of nitrosamines with simple alkyl chains are reasonable well described by both methods (see Figure 12). However, the performance of the bond method is slightly better.
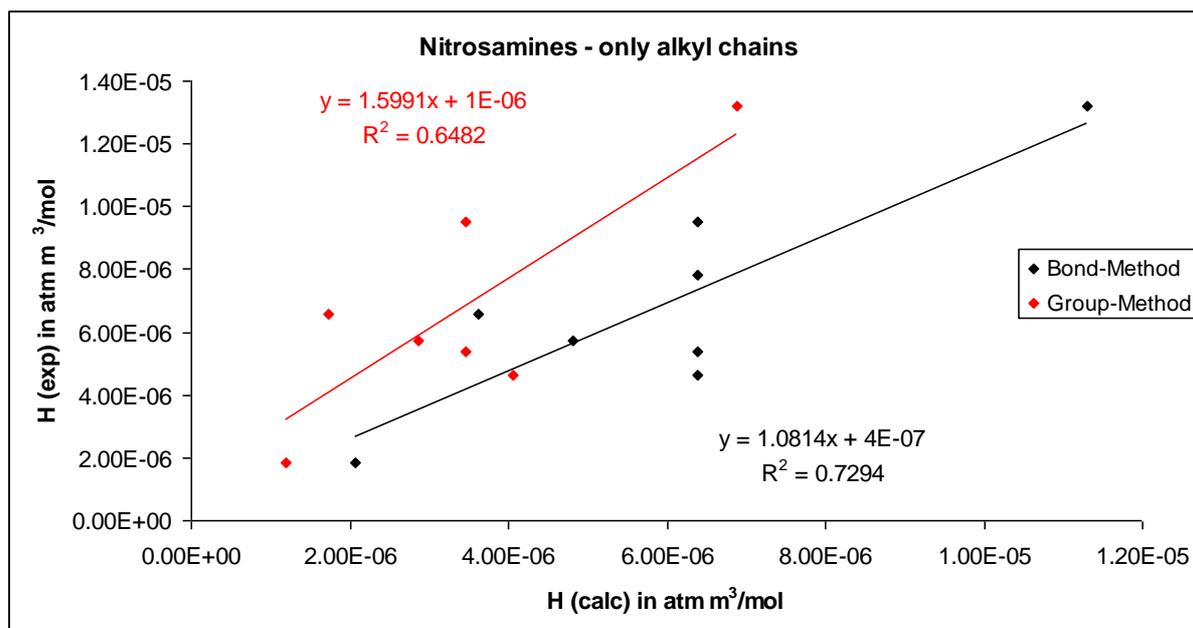
Figure 12. Correlation plot of observed and estimated Henry´s Law constants for *N*-nitroso alkylamines.

Looking at all nitrosamine data (see Table 4) shows at the first glance a better performance of the group contribution method. However, not all data were accessible with the group method and in particular these data show the highest deviations with the bond contribution method (see Table 4) which lowers the correlation coefficient.
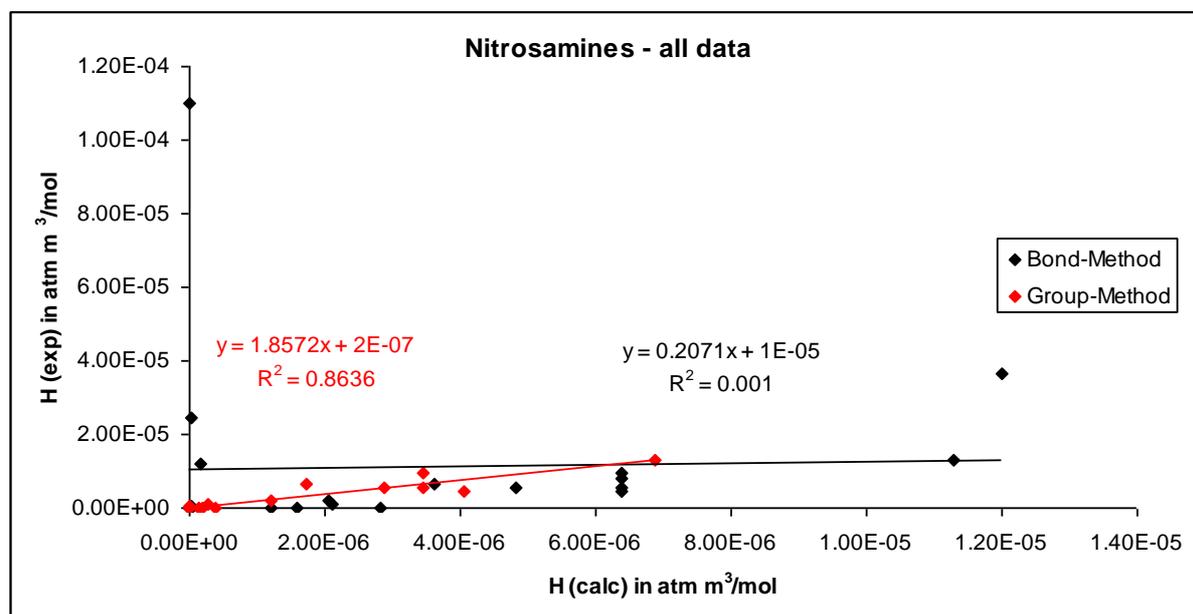
Figure 13. Correlation plot of observed and estimated Henry´s Law constants for all *N*-nitrosamines.

Overall, the EPA software offers a possibility to estimate HLC for nitrosalkylamines. HLC data for other nitrosamines with cyclic structures or functional groups are highly uncertain and great care has to be taken if these data are used.

Apparently, the offered bond method has also problems as the method produces identical results for compounds with the same number of carbon atoms independently of the

molecule's structure, *e.g* for Nitrosodipropylamine, Nitrosodiisopropylamine, Methyl-amylnitrosamine and Nitrosoethylbutylamine.

Experimental studies are highly recommended if HLC data for nitrosamine compounds are missing rather then estimation results.

In addition to the first test Henrys law constants of other nitrosalkanolamines have been calculated in order to see the influence of the chain length and the substituents. The results are shown in Table 4. The above statements need to be considered for the accuracy of these results.

Table 4. Predicted Henry´s Law constants *N*-nitroso alkanolamines.

Compound	SMILES	H (calc) Bond-Method atm m^3/mol	H (calc) Group-Method atm m^3/mol
Dinitrosomethanolamine	OCN(CO)N=O	$1.10 \cdot 10^{-9}$	-
Dinitrosoethanolamine	OCCN(CCO)N=O	$4.85 \cdot 10^{-12}$	$2.28 \cdot 10^{-16}$
Dinitrosopropanolamine	OCCCN(CCCO)N=O	$8.54 \cdot 10^{-12}$	$4.55 \cdot 10^{-16}$
Methyl hydroxymethyl nitrosoamine	OCN(C)N=O	$1.50 \cdot 10^{-9}$	-
Ethyl hydroxymethyl nitrosoamine	OCN(CC)N=O	$1.99 \cdot 10^{-9}$	-
Propyl hydroxymethyl nitrosoamine	OCN(CCC)N=O	$2.65 \cdot 10^{-9}$	-
Methyl hydroxyethyl nitrosoamine	OCCN(C)N=O	$9.99 \cdot 10^{-11}$	$1.65 \cdot 10^{-11}$
Ethyl hydroxyethyl nitrosoamine	OCCN(CC)N=O	$1.33 \cdot 10^{-10}$	$1.99 \cdot 10^{-11}$
Propyl hydroxyethyl nitrosoamine	OCCN(CCC)N=O	$1.76 \cdot 10^{-10}$	$2.81 \cdot 10^{-11}$

As can be seen, there can be dramatic differences depending on which method is used.

Summary: New experimental data on partitioning coefficients for nitrosamines have not been found in the literature. Therefore, any description of the nitrosamine partitioning will rely on the existing experimental as well as estimated data.

Based on this data estimation exercise the following conclusions should be drawn.

Preference is to be given to experimental data rather than estimated ones

Since NDMA was measured in fog water samples (see Hutchings *et al.*[39]) also other such as the nitrosoalkylamines and nitrosoalkanolamines have to be expected in the atmospheric aqueous phase.

There is only a small effect of the carbon atom number on the Henrys law data for nitrosoalkylamines.

It seems that the applied software has large problems to estimate Henrys law constants for cyclic and functionalized nitrosamines.

Even with the uncertainties in the estimations the following holds: Calculated Henrys law constants for nitrosoalkanolamines are higher than for the nitrosoalkylamines. The magnitude of calculated Henrys law constants for nitrosoalkanolamines is similar to poly-alcohols.

In summary, for a worst case scenario a complete partitioning of nitrosoalkanolamines in the atmospheric aqueous phase should be considered.

2.6   Recommended values for atmospheric aqueous phase modeling

Nitrosamine yields. Experiments from Hutchings *et al.*[39] revealed yields for *N*-nitroso dimethylamine formed in the reaction between nitrite and dimethylamine below 1% in the pH range between 3 and 6. However, Keefer and Roller[41] report that the nitrosation reaction is catalyzed by HCHO. Their results indicate that the nitrosamine yields can be even higher than 1% under acidic conditions in the presence of HCHO. Since Keefer and Roller did not characterize the product yields below pH = 7 it is not possible to provide reliable maximum or "most likely" nitrosamine yields under atmospheric conditions. For box model studies it is desirable to have worst and best case scenarios recommended. However this is very difficult when additional experimental data are not available. It is safe to state that best case studies should use the values presented by Hutchings and co-workers. However, worst case studies should use significantly higher yields. As a starting point one could use yields around 10 % but without more experimental work this cannot be regarded a safe "worst case", i.e. a reliable upper limit of yields.

Life time of nitrosamine due to photolysis (air, water, aerosol)

Daytime: The performed model simulations (Figure 10 and 11) indicate that the life times for *N*-nitrosodimethylamine due to photolysis in aerosol/water droplets are determined by the photolysis in the gas phase and the partitioning of NDMA in between the gas and the aqueous phase. Model simulations indicate that radical reactions can not compete with photolysis processes as a sink for nitrosamines during the daytime.

 Assumption: Lifetime due to photolysis in aerosol/water droplets ≈ lifetime due to photolysis in the gas phase.

Night time: Life times in aerosols/water droplets strongly rely on the reactivity towards the NO_3 radical since the reactivity towards ozone seems to be too low. However, since no experimental data on NO_3 radical reactions in either phase are available no serious recommendation can be given at the moment.

Nitrosamine recycling processes during the night. The effectiveness of recycling processes in aerosols/water droplets during the night depends strongly on the nitrosamine formation yields and reaction kinetics. Hutchings *et al.*[39] report very low yields for the formation of NDMA in presence of DMA and NO_2^-, which could result in a less effective recycling in particular in presence of other sinks for DMA such as NO_3 radicals during the night. However, a catalyzed nitrosation of secondary amines could increase the effectiveness of the recycling process in particular during the winter time. There is a clear need for further experimental (NO_3 kinetics and nitrosamine formation yields) and modelling studies at this point.

3 Annual variation in atmospheric lifetime of nitrosamines

The estimated annual variation in the clear sky NO_2 photolysis rate at Mongstad was shown previously in Figure 5 for mid-winter, spring equinox, mid-summer and fall equinox. The variation in the atmospheric gas phase photolysis lifetimes of nitrosamines can be derived directly from this figure. Figures 14-17 show the estimated gas phase photolysis lifetimes assuming a 33% reduction in the actinic flux by clouds and $j_{Nitrosamine} = 0.25 \times j_{NO2}$.

The surface albedo will change during the year. As an example, snow cover will increase the albedo and thereby the intensity of the reflected sunlight. This will lead to shorter atmospheric lifetime of the nitrosamines than indicated in the figures.
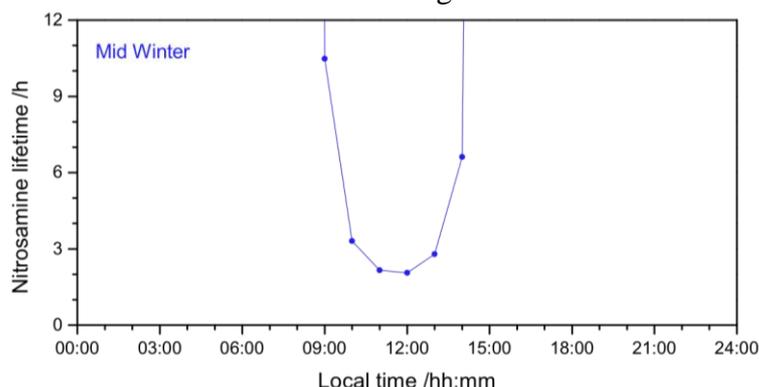
Figure 14. Estimated atmospheric gas phase photolysis lifetime of nitrosamines in the Mongstad area at mid-winter conditions.
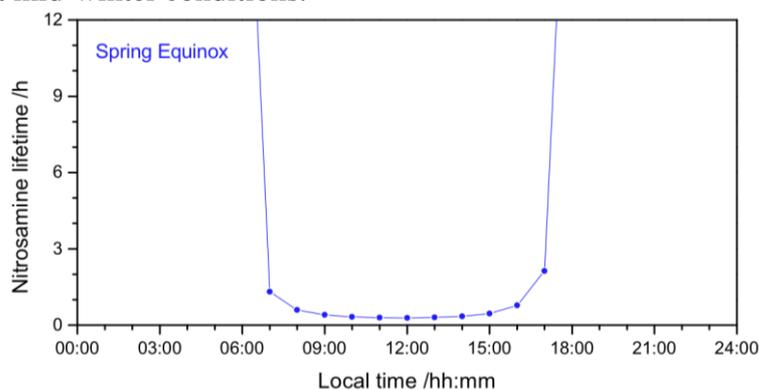
Figure 15. Estimated atmospheric gas phase photolysis lifetime of nitrosamines in the Mongstad area at spring Equinox conditions.
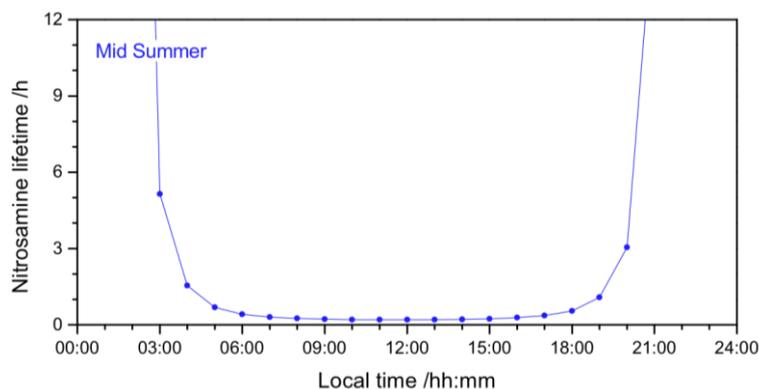
Figure 16. Estimated atmospheric gas phase photolysis lifetime of nitrosamines in the Mongstad area at mid-summer conditions.
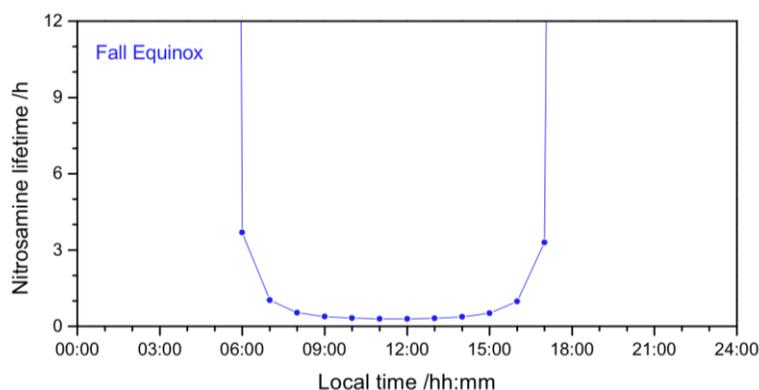
Figure 17. Estimated atmospheric gas phase photolysis lifetime of nitrosamines in the Mongstad area at fall Equinox conditions.

The average diurnal nitrosamine lifetime at mid-winter conditions is estimated to be around 13 hour, which at first sight is of concern. The lifetime should, however, be compared to the actual amount of nitrosamines formed under the same conditions. The oxidative capacity of the atmosphere is, to a first approximation, related to the photolysis rate of O_3 leading to $O(^1D)$ and subsequently to OH radicals. This photolysis rate shows and even stronger annual variation than j_{NO2} does, and it is almost negligible at mid-winter conditions in the Mongstad area. There will therefore be almost no photo-oxidation of amines emitted in the mid-winter period and, consequently, very little nitrosamines formed.

The average diurnal gas phase nitrosamine photolysis lifetime at Equinox is estimated to be around 56 minutes while the mid-summer value is 26 minutes.

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