Atmospheric Chemistry of Amines

Modelling nitrosamine and nitramine formation in the atmospheric gas phase photo-oxidation of Cansolv DC103 amine.

Claus Nielsen

Department of Chemistry

University of Oslo

September 2014

This page is intentionally left blank

Atmospheric Chemistry of Amines

Modelling nitrosamine and nitramine formation in the atmospheric gas phase photo-oxidation of Cansolv DC103 amine.

Claus Nielsen

Department of Chemistry, University of Oslo

September 2014.

This page is intentionally left blank

Table of Contents

This page is intentionally left blank

Executive Summary

The present report is an anonymized extract of the report “Atmospheric Chemistry of Amines - A theoretical study of the OH initiated atmospheric gas phase photo-oxidation of DC103” intended for dispersion modeling purpose only.

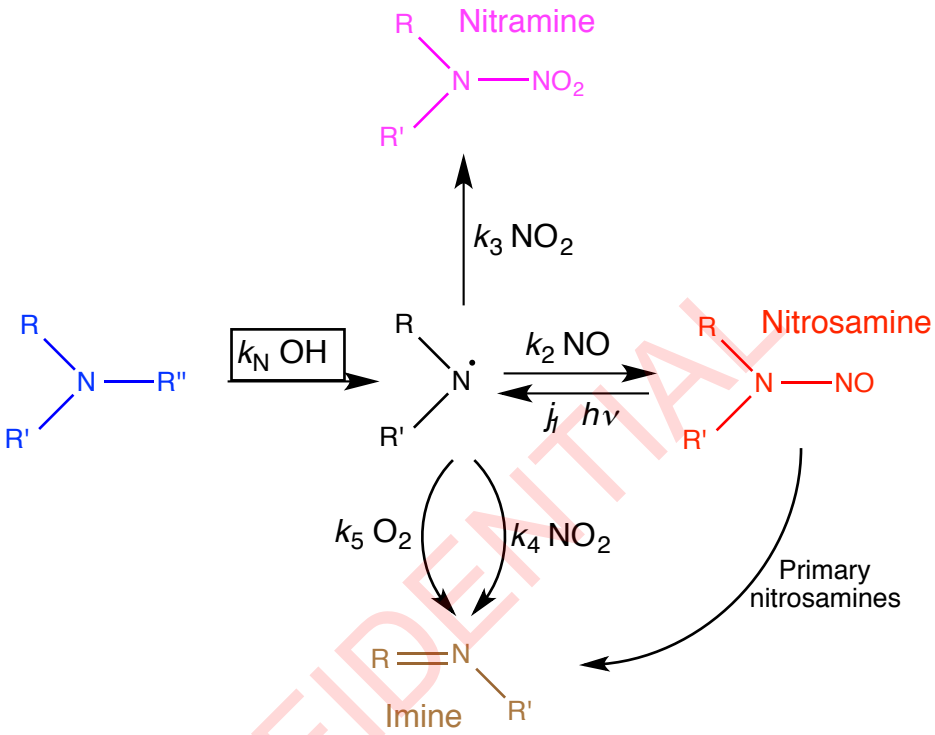
The atmospheric gas phase photo-oxidation of the DC103 amine is dominated by reaction with OH radicals. The rate coefficient for the OH radical reaction with DC103 is not reported in the literature; a best estimate based on available available data for structurally similar compounds suggests room temperature rate coefficient k_{OH} = 2.5 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} at 298 K. The average atmospheric lifetime of DC103 with respect to reaction with OH is consequently estimated to be around 70 min in the Boundary Dam area.

The study shows that the DC103 potential to form first generation nitrosamines and nitramines is smaller than that of dimethylamine, $(CH_3)_2NH$, but larger than that of MEA, $NH_2CH_2CH_2OH$. The amount of nitramines formed in the atmospheric photo-oxidation of DC103 is conservatively estimated to be respectively 2.8 % after 2 h, and 3.4 % after complete photo-oxidation in the Boundary Dam area. For comparison, the numbers for dimethylamine are 1.4 % after 2h and 3.9 % after complete photo-oxidation under the same conditions.

This page is intentionally left blank

Nitrosamine and nitramine formation in atmospheric amine photo-oxidation

Estimates of nitrosamine and nitramine formation in the OH initiated photo-oxidation of DC103 is based on the general mechanism shown in Scheme 1, in which nitrosamine formation from primary amines has been included. Primary nitrosamines do, however, isomerize and react with O_2 followed by N-N bond scission within seconds to give the corresponding imines.[1]



Scheme 1. Atmospheric photo-oxidation scheme for DC103 showing the routes to nitramines and nitrosamines.

The photolysis rate coefficient, j_1, is proportional to to NO_2 photolysis rate coefficient, j_{NO2}: $j_{Rel} = j_1/j_{NO2}$ = 0.37.[2]

The initial amine reaction with OH radicals constitutes the rate-limiting step in the formation of nitrosamines, nitramines and imines. The amount of nitrosamine and nitramine formed at a given time in the atmospheric oxidation of DC103 depends on the rate coefficient of the initial hydrogen abstraction reaction, the branching ratio in the reaction (here: k_N/k_1), and the branching in the subsequent amino radical reactions:

$$B_{Nitramine} = k_3\cdot[NO_2]/(k_2\cdot[NO]+k_3\cdot[NO_2]+ k_4\cdot[NO_2]+ k_5\cdot[O_2])$$

$$B_{Nitrosamine} = k_2\cdot[NO]/(k_2\cdot[NO]+k_3\cdot[NO_2]+ k_4\cdot[NO_2]+ k_5\cdot[O_2])$$

$$B_{Imine} = (k_3\cdot[NO_2]+k_5\cdot[O_2])/(k_2\cdot[NO]+k_3\cdot[NO_2]+ k_4\cdot[NO_2]+ k_5\cdot[O_2])$$

The total yield of amino radicals formed in the DC103 + OH reaction is estimated to be ~37 % (k_N/k_1 = 0.37), which is comparable to that of the $(CH_3)_2NH$ + OH reaction (k_N/k_1 = 0.42).[2]

The Boundary Dam area (48˚59'N) is characterized by NOx-levels in the region 2-4 ppb. Table 1 summarises the estimated average NO_2-photolysis rate coefficient, and the NO and NO_2 mixing ratios in the Boundary Dam area.

Table 1. Assumed annual average values of the NO_2 photolysis rate, OH radical concentration, and NO and NO_2 volume mixing ratios in the Boundary Dam area.

j_{NO2}	/s^{-1}	1.6×10^{-3}
OH	/molecules cm^{-3}	1.0×10^{6}
NO	/ppb	2.2
NO_2	/ppb	3.7

Estimates of the branching in the DC103 amino radical reactions with O_2, NO and NO_2 (k_2/k_3, k_4/k_3, k_5/k_3) are given in Table 2 together with other parameters needed in estimating the annual average nitramine yield and the steady state nitrosamine mixing ratio.

The average wind speed in the Boundary Dam area is around 4 m s^{-1}. During 2 hours an air parcel will therefore, on average, travel 30 km. It is of interest to know not only the theoretical maximum nitramine yield, but also the nitramine yield during the first hours after emission. Table 2 includes the calculated nitramine yield 2 hours after emission as well as the maximal yield (100 % photo-oxidized amine). The results reported in Table 2, are based on annual averages listed in Table 1.1.

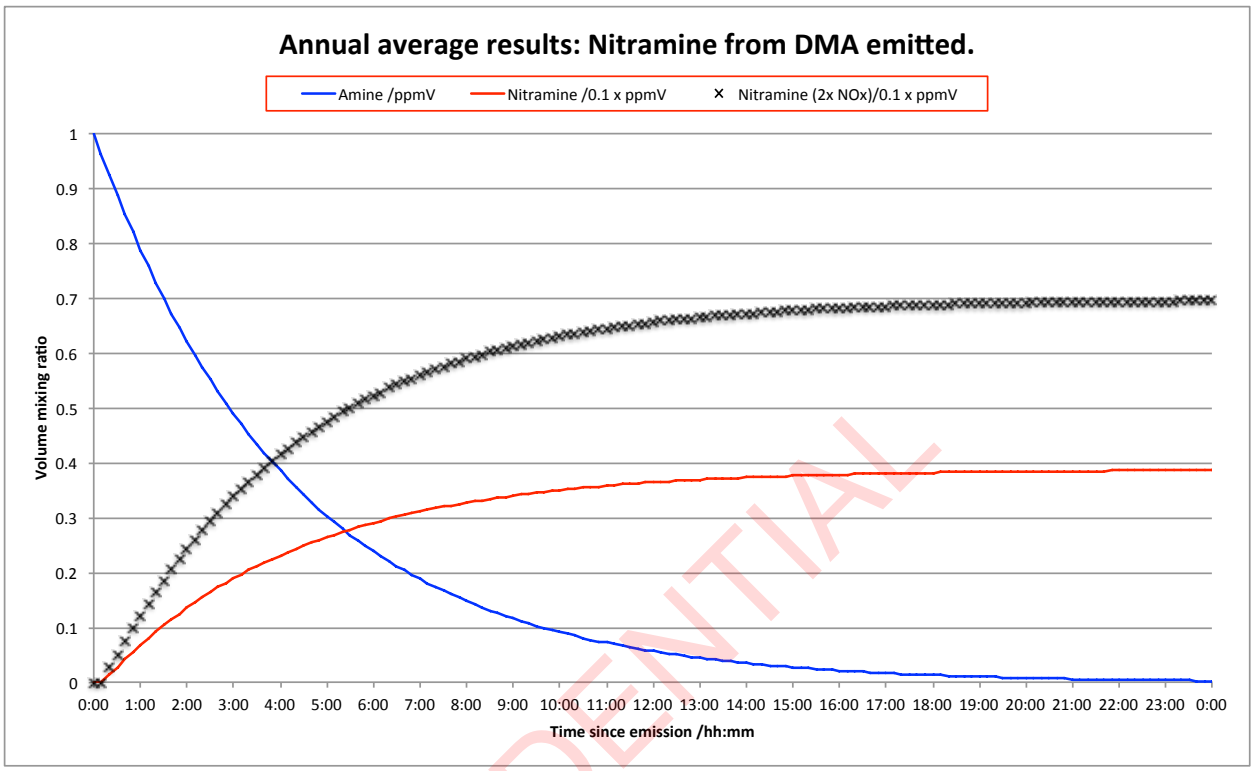
Table 2. Reaction rate coefficients and branching ratios for formation of the corresponding amino radical and its reactions with NO, O_2 and NO_2. See Scheme 1 for definition of rate coefficients.

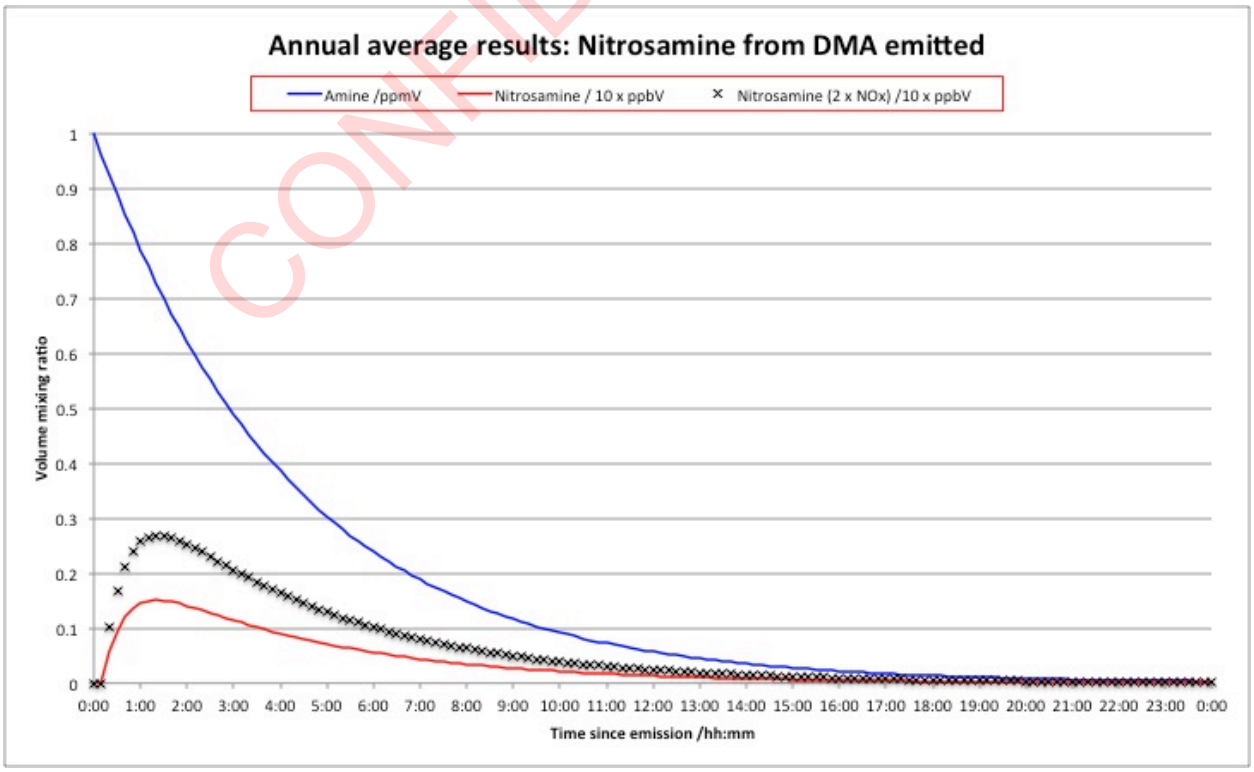
Amine	$k_{Amine+OH}$ [a]	J_{rel} [b]	k_N/k_1	k_2/k_3 [b]	k_4/k_3 [b]	k_5/k_3 [b]	Nitramine yield	
							2h	∞
DC103	2.5×10^{-10}	0.34	0.37	0.67	0.20	1.7×10^{-7}	2.8 %	3.4 %
MEA [c]	7.6×10^{-11}	0.34	0.09	0.67	0.20	1.7×10^{-7}	0.3 %	0.8 %
$(CH_3)_2NH$	6.5×10^{-11}	0.34 [d]	0.42 [d]	0.67 [d]	0.20 [d]	1.7×10^{-7} [d]	1.4 %	3.9 %

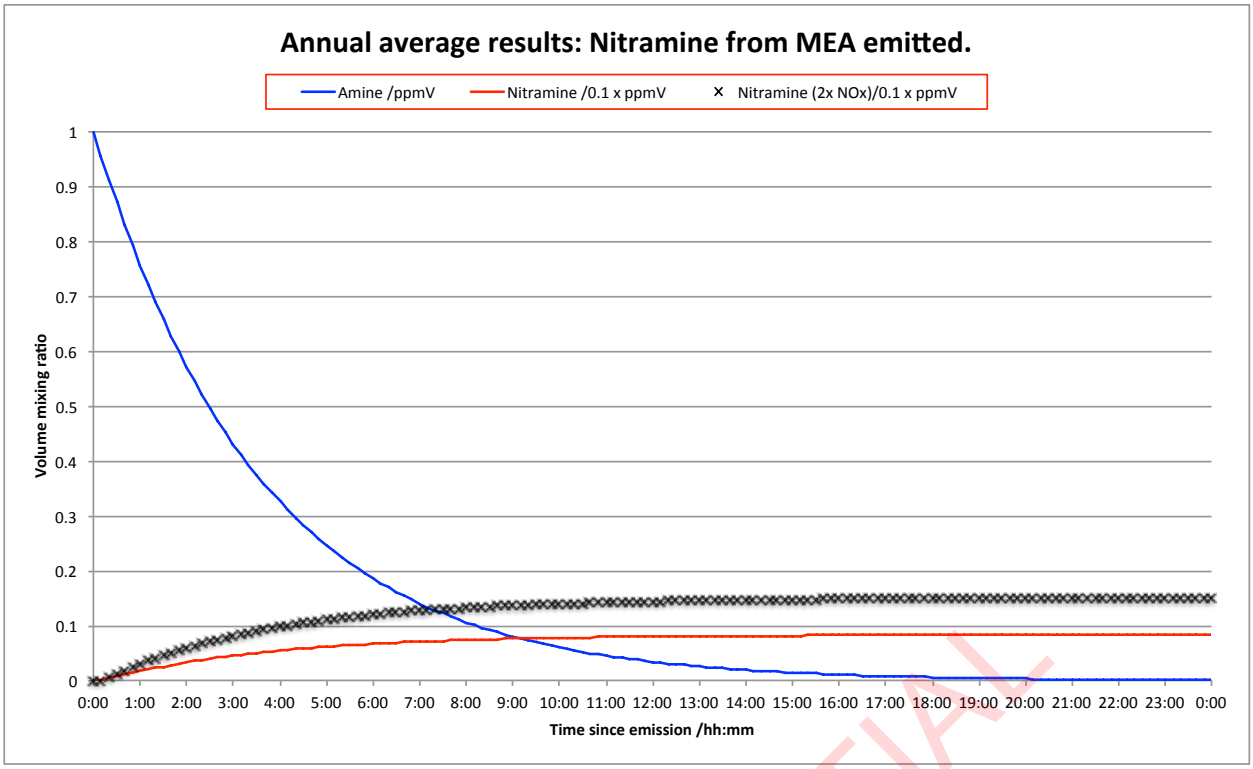
[a] Unit: cm^3 $molecule^{-1}$ s^{-1}. [b] Assumed to be the same in DC103, MEA and $(CH_3)_2NH$. [c] From ref .3 [d] From Ref. 2.

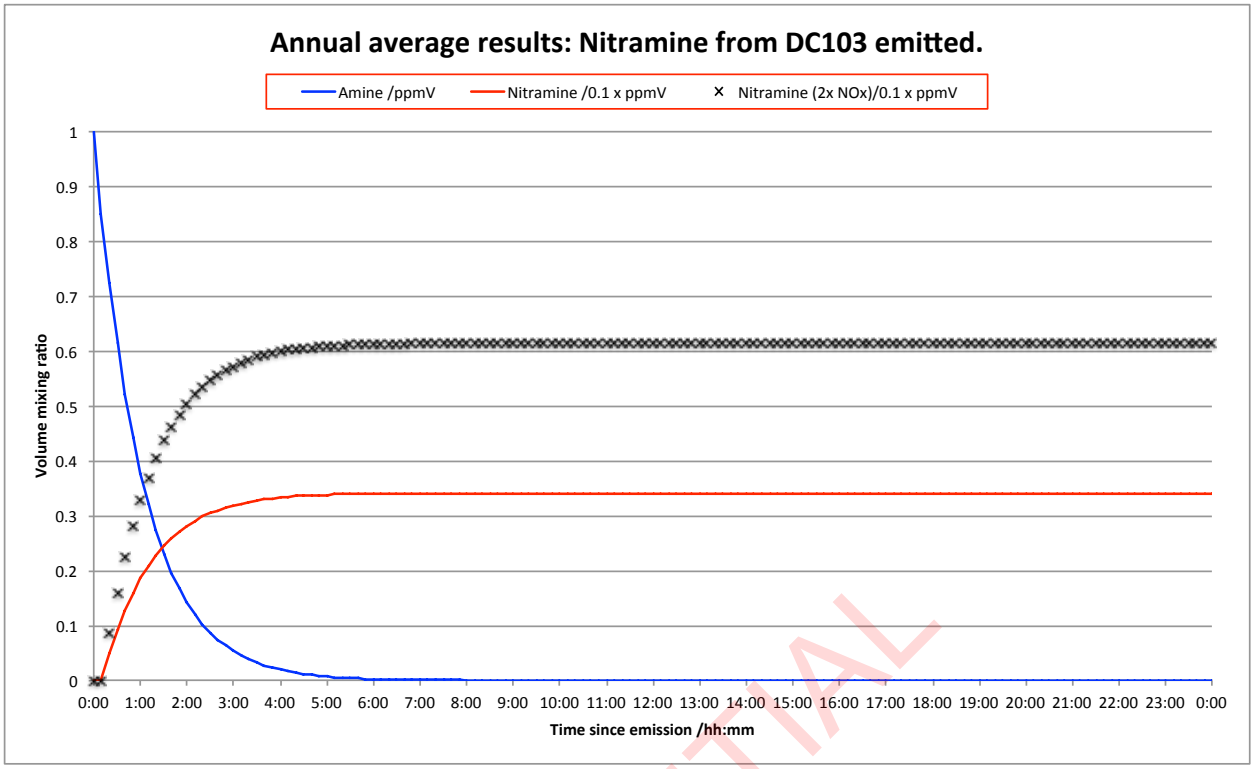
Box model results

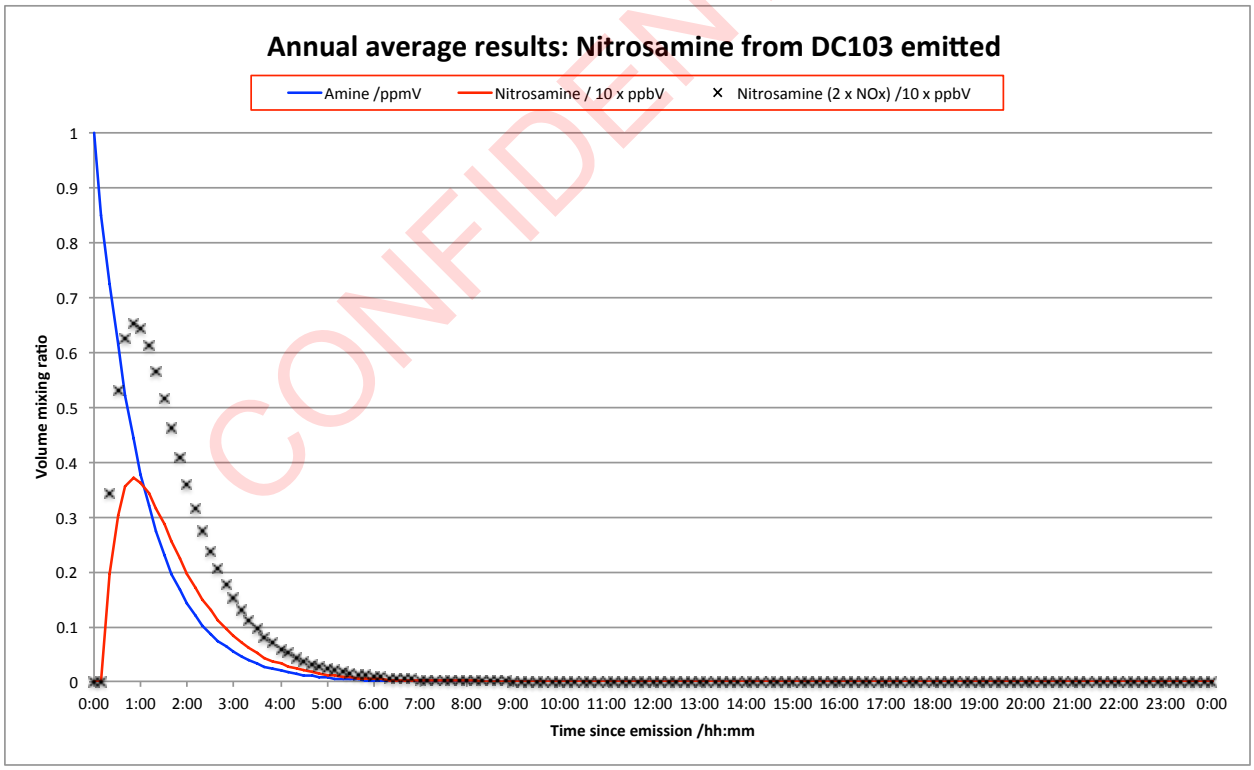
The results from simple box model calculations of nitramine and nitrosamine mixing ratios in an closed air parcel following emission are shown below. The box model is based on the parameters given in Table 1.











Literature

1. Nielsen, C. J.; D'Anna, B.; Karl, M.; Aursnes, M.; Boreave, A.; Bossi, R.; Bunkan, A. J. C.; Glasius, M.; Hansen, A.-M. K.; Hallquist, M.; Kristensen, K.; Mikoviny, T.; Maguta, M. M.; Müller, M.; Nguyen, Q.; Westerlund, J.; Salo, K.; Skov, H.; Stenstrøm, Y.; Wisthaler, A. *Summary Report: Photo-oxidation of Methylamine, Dimethylamine and Trimetahylamine. Climit project no. 201604*; NILU OR 2/2011, ISBN 978-82-425-2357-0; NILU: 2011.

2. Nielsen, C. J.; Herrmann, H.; Weller, C., Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS). *Chem. Soc. Rev.* **2012,** *41* (19), 6684-6704.

3. Nielsen, C. J.; D'Anna, B.; Dye, C.; George, C.; Graus, M.; Hansel, A.; Karl, M.; King, S.; Musabila, M.; Müller, M.; Schmiedbauer, N.; Stenstrøm, Y.; Wisthaler, A. *Atmospheric Degradation of Amines (ADA). Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA)*; NILU OR 8/2010, ISBN 978-82-425-2172-9; NILU: 2010.