SINTEF REPORT

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TITLE

PROTOCOL FOR EVALUATION OF SOLVENTS - PROCESS AND ATMOSPHERIC CHEMISTRY
(Report for H&ETQP Amine 4 project)

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ABSTRACT

Abstract WP1

In the present report we have evaluated the importance of different process parameters in affecting the emissions from a CO2 capture plant. This assessment is mainly qualitative in nature; we do not feel that there is sufficient experimental data available to quantify the contribution from different parameters.

The efficiency of the water-wash section is one of the key parameters in determining the emission level. Another key parameter is the extent of entrainment and demister efficiency. The level of NOx entering the CO2 capture plant is also identified as a key parameter.

A set of experiments are recommended to estimate worst-case scenario emissions from a CO2 capture plant.

We have looked at the relative risk of emission presented by the different solvents. Among the solvents considered we believe that piperazine presents the greatest risk, followed by MDEA, while MEA and AMP have the lowest risk.

A extensive review and a theoretical evaluation has been carried out of the degradation products likely to form for the different solvents.

It is with our present knowledge very difficult to predict worst-case emissions from a CO2 capture plant. A set of activities are however suggested to estimate worst-case emissions.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Environment/Health	Miljø/Helse
GROUP 2	Absorption	Absorpsjon
SELECTED BY AUTHOR	CO_2 capture	CO_2 fangst
	Amines	Aminer
	Degradation Products	Degraderingsprodukter

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Overview of terminology used in report

The following terminology has been used throughout the document:

Parent amine or PA – any of the amines used within the process for capturing CO2 (e.g. MEA, AMP, MDEA and piperazine).

Atmospheric degradation products or ADPs – these are the degradation products which are formed in the atmosphere through degradation of the parent amine.

Process degradation products or PDPs – these are the degradation products which are formed during the process through degradation of the parent amine and subsequently released into the atmosphere.

Secondary atmospheric degradation products or 2ADPs – these are the degradation products which are formed in the atmosphere through further degradation of the PDPs.

Atmospheric environment – any process which occurs in the atmosphere.

Terrestrial environment – any process which occurs on land (e.g. in soils).

Aqueous environment – any process which occurs in fresh waters (lakes, rivers and ground water) or marine systems (seawater and sediments).

1 WP1. Theoretical evaluation of the potential to form and emit harmful compounds

In Table 1 provideds a summary of the extent to which we believe different process parameters may affect the emissions from a CO_2 capture plant. The table summarizes both the importance of different parameters under normal operation and in a worst case scenario.

Table 1. *Summary of the extent to which process parameters effect emissions from the plant*

Process parameter	Importance to emissions from plant under normal operation [a]	Importance to emissions from plant in worst case scenario [b]
Water wash operation	3	3
Demister/entrainment	3	3
Variations in NOx level	3	3
Foam formation	2	3
Reclaimer operation frequency	2	2
Solvent composition	2	0
Reboiler operation	1	2
Absorber and desorber operation	1	2
Variations in exhaust gas composition (other than NOx)	1	2
Materials in plant	1	2
CO_2 loading	1	1
Flue gas DCC treatment (quenching)	1	1
Reclaimer technology	1	1
Inter-cooling	1	1

a: How important is a given process parameter in determining the emissions from a CO_2 capture plant under normal operation, 3 very important, 2 important, 1 somewhat important. b: How significant effect can a failure in this process parameter be to worst-case emissions.

1.1 The Effect of Process Conditions and Process Units

The formation and emission of the harmful compounds may be affected by the process conditions and the various process units. The process elements or parameters that may affect the emissions include:

- Solvent composition
- Variations in flue gas composition, oxygen and NOx level in particular
- CO_2 loading
- Flue gas DCC treatment (quenching)
- Absorber and desorber operation
- Reclaimer technology
- Reclaimer operation frequency
- Reboiler
- Water wash
- Demister
- Materials in plant
- Inter-cooling
- Foam formation
- Solvent additives

1.1.1 Solvent composition

The composition of solvent will affect the solvent degradation rates. In general we expect that higher solvent concentration will result in higher degradation rates. An example of this is shown in Figure 1. The degradation rate, in terms of MEA loss, of 40wt% MEA is slightly higher than those of 30 wt% MEA at an initial CO_2 loading of 0.4 and 135°C (Davis and Rochelle, 2009). This effect is likely to be dependent on the solvent, and there may be exceptions to this trend. It should be noted that Figure 1 shows degradation rates at a high temperature, and these rates are not representative of what will be encountered in a CO_2 capture plant.

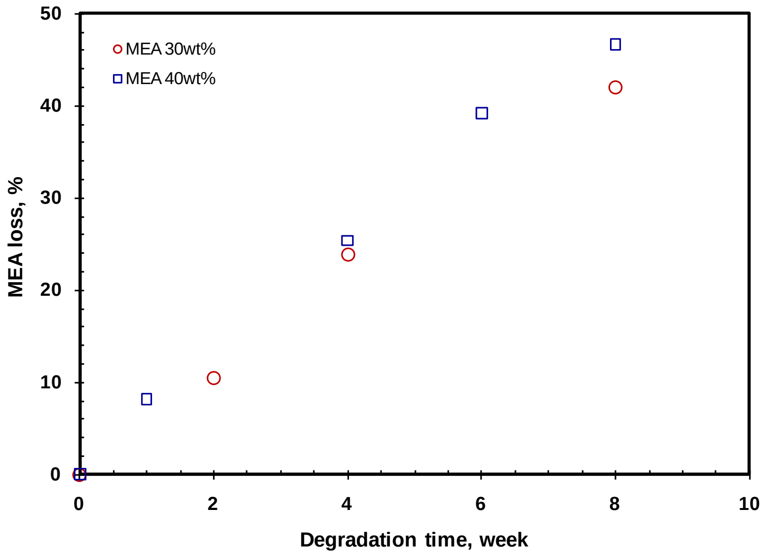


***Figure 1**. Effect of MEA concentration on the degradation rates at CO_2 loading of 0.4 and 135 ℃.*

In addition, the composition of solvent and its degradation products also effect on their partial pressures according to equation:

$$p_i = \gamma_i \, x_i \, P_i^o \tag{1}$$

where γ, x, and P^o are the activity coefficient, mole fraction, and vapor pressure of component i, respectively. The higher the mole fraction of component i, the higher the partial pressure of it. All other things being equal this would result in a higher emission level.

The vapor pressure is a function of the free amine in the liquid. Reactions that bind up the amine as carbamate or protonated amine will result in lower concentrations of free amine and lower vapor pressure.

The activity coefficient of a component in a solution depends on both its composition and temperature. Figures 2 and 3 show the activity coefficients of MEA, MDEA and water varying with MEA/MDEA concentrations and temperatures. For a dilute MEA solution, the activity coefficient of MEA is about 0.2 at 40 °C and increases to about 0.4 at 100 °C. At a constant temperature, the higher the concentrations of MEA, the higher the activity coefficients and will end up to 1.0 at x_{MEA} = 1.0 (pure MEA).

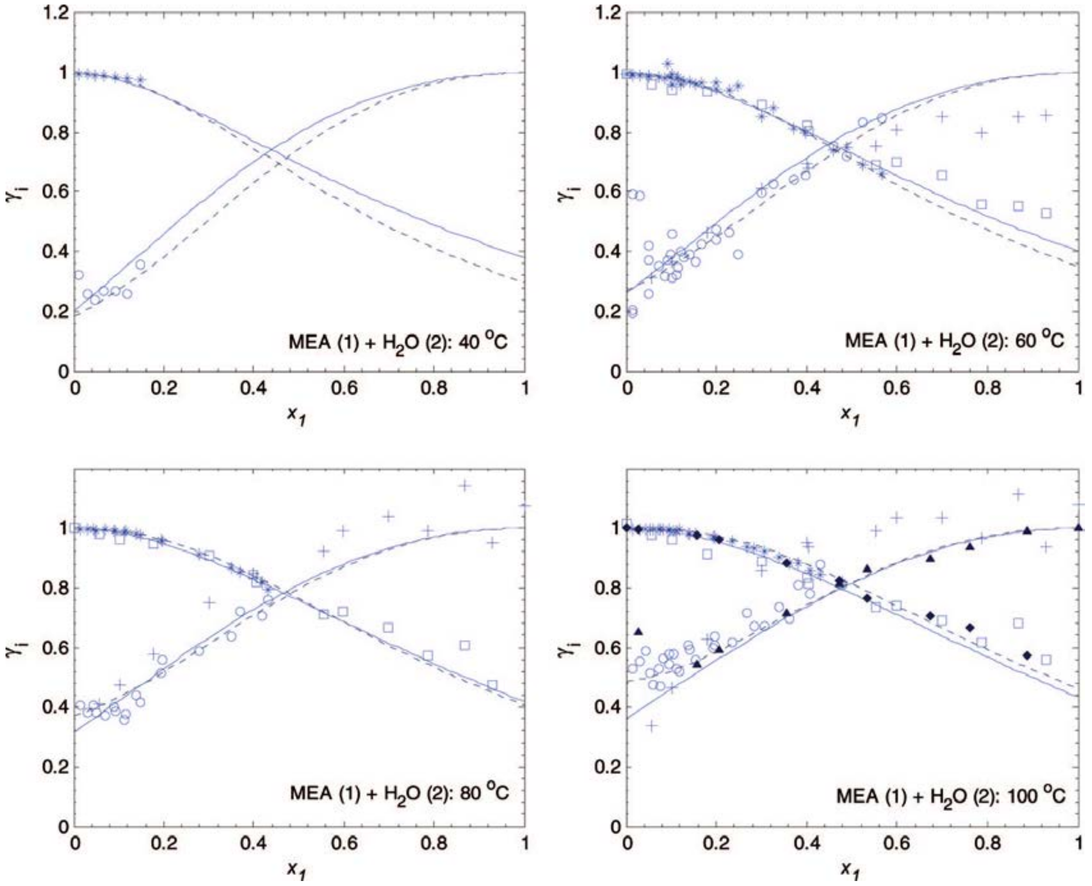


Figure 2. *Activity coefficients of MEA (γ_1) and water (γ_2), depending on composition at different temperatures: ○, MEA; *, H_2O; solid lines, calculated using Wilson model; dashed lines, calculated using NRTL model (reproduced from Kim et al., 2008)*

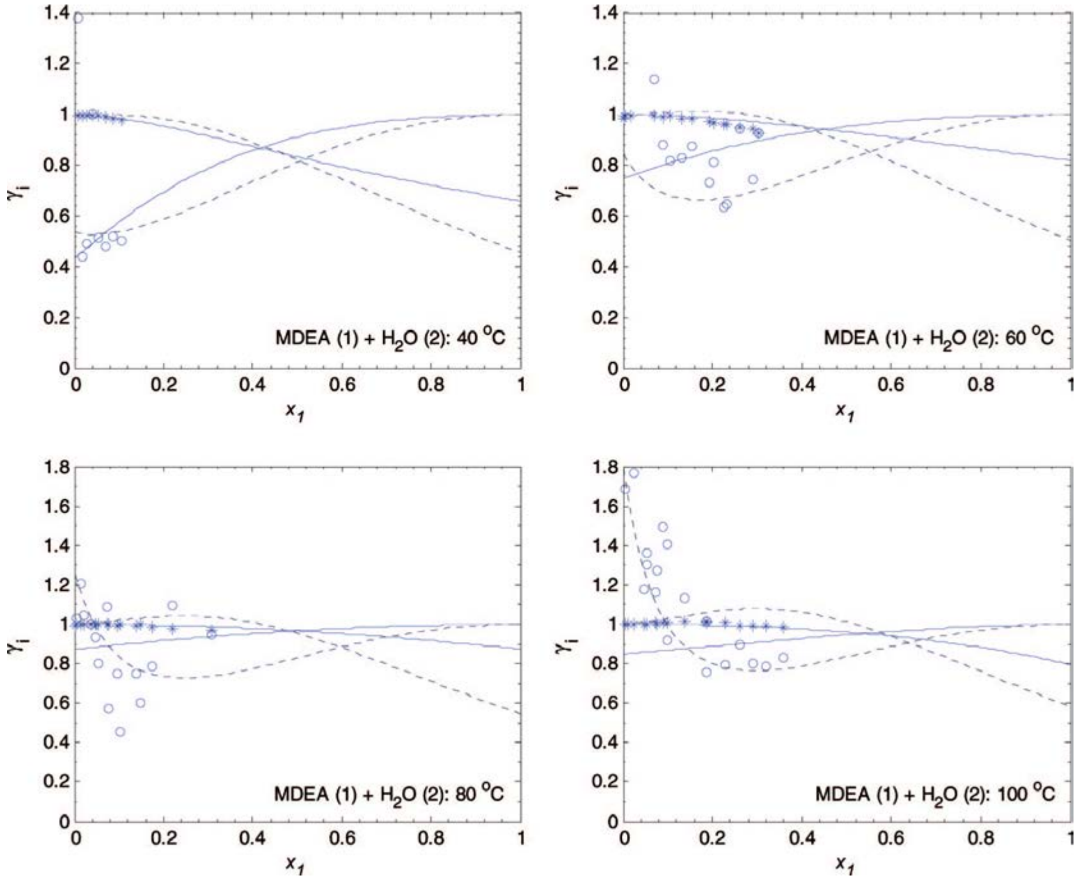


Figure 3. *Activity coefficients of MDEA (γ_1) and water (γ_2), depending on composition at different temperatures: ○, MDEA; *, H_2O; solid lines, calculated using Wilson model; dashed lines, calculated using NRTL model (reproduced from Kim et al. 2008)*

According to Eq. (1), the volatility of the component *i* also depends on its vapor pressure which can be predicted by use of an empirical equation as follows:

$$\ln P_i^o = b_1 + b_2 / T + b_3 \ln(T) + b_4 T^{b_5} \qquad (2)$$

where P_i^o in Pa and T in K. Table 1 and Figure 4 show parameters *b* for selected amines and the relationship between ln P^o vs 1/*T*, respectively.

Table 1. *Vapor Pressure Parameters of some Amines obtained from DIPPR Database*

Component	b_1	b_2	b_3	b_4	b_5	**Error, %**	$P^o_{40\,°C}$, **Pa**
MEA	92.624	-10367	-9.4699	1.9×10^{-18}	6	< 10	164.0
Piperazine	70.503	-7914.5	-6.6461	5.2106×10^{-18}	6	< 5	1143
MDEA	253.07	-18378	-33.972	2.3348×10^{-5}	2	< 10	4.245
AMP$^{a)}$	$P^o = 1\times10^3 \exp\left(15.155 - \frac{3472.6}{(T-107.32)}\right)$						179.7

$^{a)}$Pappa et al. (2006)

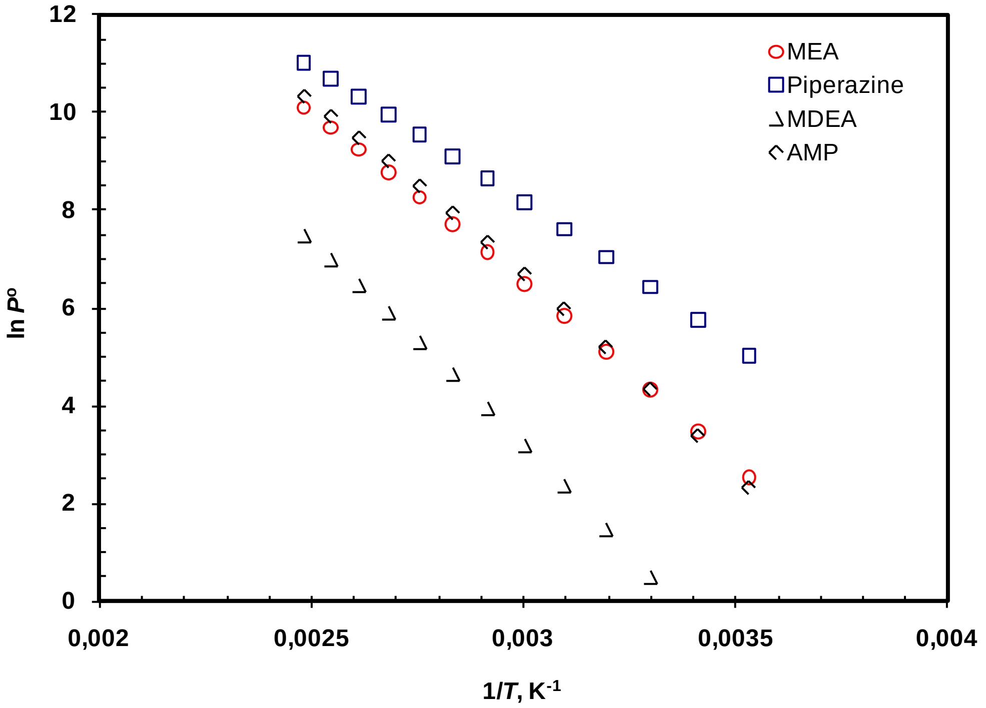


Figure 4. Relationship between ln P^o vs 1/T for some pure amines

1.1.2 Variations in flue gas composition

A flue gas from a power plant will contain NOx compounds in addition to other compounds such as CO, CO_2, SO_2, volatile organic compounds (VOCs), and particulate matter (PM). In Table 2 are given the expected exhaust gas conditions for the full scale CO_2 capture plant at Mongstad.

Table 2. *Flue gas conditions (Source: CCM)*

Property	**Place of measurement**	**Value**
Temperature (°C)	Inlet DCC	120
	Inlet absorber	20-45
Pressure (bara)	Inlet DCC	1.01
Gas flow (t/h)		1550
Gas composition	**Component**	
(mol %)	CO_2	3.4
	N_2	76
	O_2	13.8
	H_2O	6.8
(ppmv)	NOx	3
	NH_3	2

The impurity that has the greatest impact on harmful emissions from the plant may be NOx. NOx may react with the amines to form nitrosamines and nitramines. These are the degradation products that would raise the greatest concern in terms of emissions. To our knowledge there has been no experimental studies to studies to study correlation between NOx levels in a CO_2 capture plant and formation rates of nitrosamines, it would however seem likely that nitrosamine formation rates are proportional to the NOx levels entering the plant.

Oxidative degradation is expected to be the dominant form of solvent degradation in a post-combustion CO_2 capture plant. The level of oxygen entering the plant is expected to affect the level of oxidative degradation.

1.1.3 CO_2 loading

Primary and secondary amines are known to react directly with CO_2 to form carbamate species. According to Austgen *et al.* (1989), peak formation of MEA carbamate occurs at a loading of about 0.5 mol CO_2/mol amine and decreases at higher loadings. Formation of carbamate and amine protonation will result in lower amine vapor pressure.

The carbamate form of the amine is susceptible to thermal degradation. Consequently, there may be formation of thermal degradation products if the system is running at high loadings. The thermal degradation occurs at desorption condition. Figure 5 shows an effect of CO_2 loadings on the degradation rates for 30wt% MEA at 135°C (Davis and Rochelle, 2009).

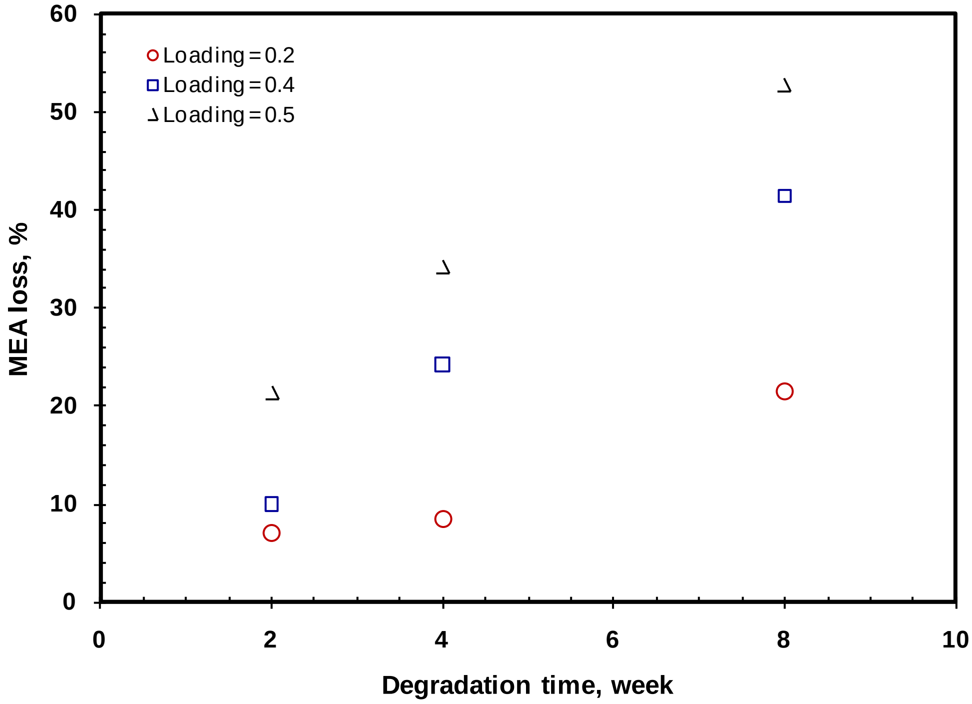


Figure 5. Effect of CO_2 loading on the degradation rates for 30wt% MEA at 135°C.

1.1.4 Flue gas DCC treatment

Flue gas from Flue Gas Desulfurization (FGD) unit is cooled in Direct Contact Cooler (DCC) by a circulating water stream. By lowering the gas temperature in this way, some amount of water contained in the flue gas will condense. The condensed water from the flue gas is removed from the DCC with the hot circulating water. A slip stream of excess water is taken from the circulating water stream to maintain the water balance around the DCC. This DCC excess water contains little dissolved CO_2 and is sent to a cooling tower, for waste water treatment or to be used as makeup water for water-wash section. In addition, CO_2 compression and drying units produce water as well as reclaimer waste and filter residue. A schematic of the water balance in a CO_2 capture plant is shown in Figure 6.

The net amount of wash water required becomes zero if the amount of water supplied by the flue gas equals the amount of water contained in the purified gas and the CO_2 stream. Ideally, in a complete water balance, no bleed or water make-up would be required. This operation can be ensured by controlling the flue gas temperatures on the inlet and outlet of the absorption column.

Flue gas temperature from DCC has a direct effect on the gas velocity in the absorber. Higher temperatures result in higher gas velocities. We do not know if the DCC will have a significant effect on the NOx composition entering the CO_2 capture plant

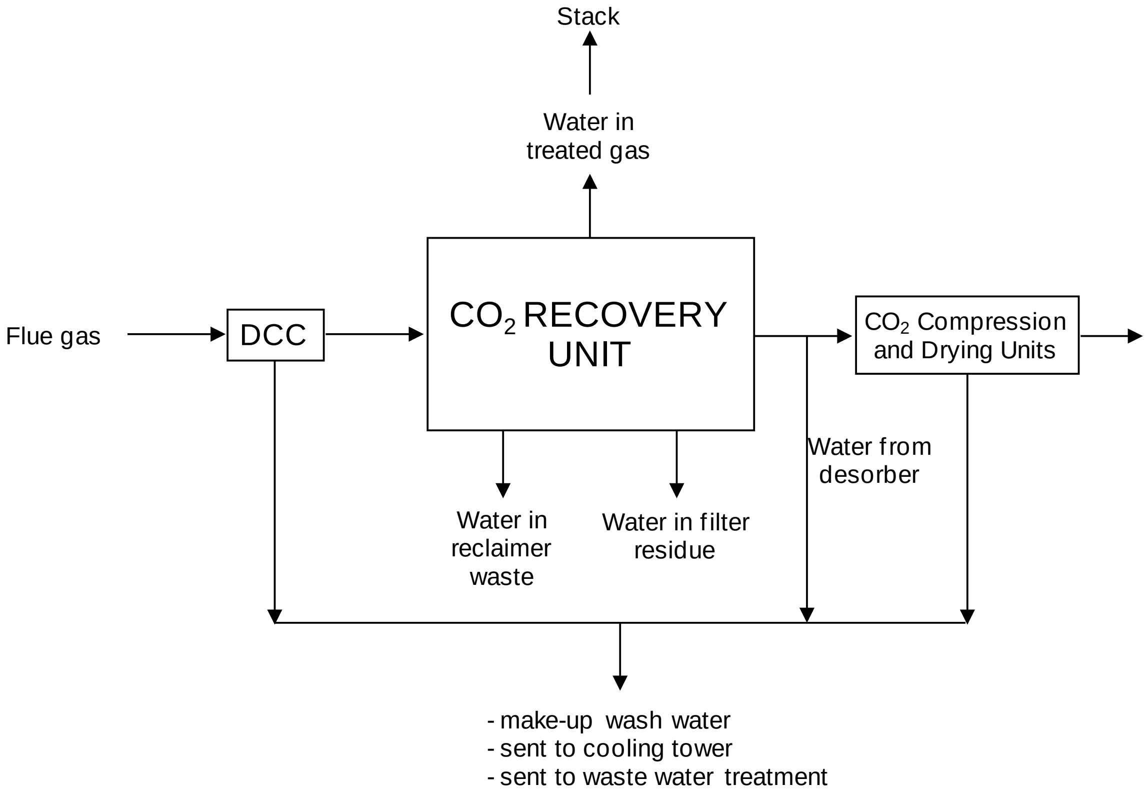


Figure 6. Water balance in a CO_2 capture plant

1.1.5 Absorber and Desorber

Entrainment in absorber and desorber columns may result in harmful compound emissions. As mentioned above that gas velocity will affect on entrainment formation. According to Molokanov et al. (1969), the effect of gas velocity on the entrainment in a column cross-section with certain methods may follow Eq. (4).

$$e = Av^4 \tag{4}$$

where *e*, *A*, and *v* are entrainment (%), an empirical coefficient, and gas velocity, respectively. Figure 7 shows the effect of gas velocity on entrainment measured by different methods. The gas velocity in the absorber is probably one of the key parameters in determining entrainment in a CO_2 capture plant.

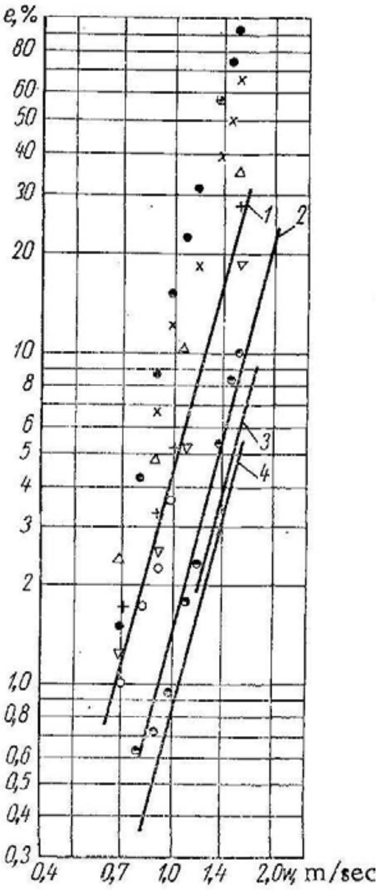


Figure 7. *Average relative entrainment e along the plate as a function of gas velocity v measured by different methods (reproduced from Molokanov et al., 1969).*

Degradation rate in a column could be affected by the design of absorber/desorber bottom. By taking the same surface area of different design of column bottom (e.g. conical and elliptical cross section profiles), the volume of these two bottom designs will be different in which the bottom design having larger volume will have much degradation products compared to that with smaller volume.

In addition to the effect of the bottom design on the degradation rate, uptake of oxygen in liquid phase in the column will also affect degradation rate (oxidative degradation).

The obvious initial assumption regarding oxidative solvent degradation is that it would take place in the absorber. There is however an argument that the main issue may be the combination of oxygen and higher temperatures encountered in the stripper. The risk of oxygen being transported to the stripper probably depends on plant design.

1.1.6 Reclaimer

A thermal reclaimer is usually used to regenerate amines by removing the high boiling point and non volatile impurities, such as heat stable salts (HSS), suspended solids, volatile acids, and iron products, from the plant solution. It plays an important part in reducing corrosion, foaming, and fouling. The reclaimer is used, in most cases, if the degradation level of the amine reaches a given level (Ballard, 1966 gave a value of 1 percent). It should be noted that the extent/frequency of reclaimer operation should probably be reconsidered to take into account emissions control. If the focus is on controlling emissions from the plant, this would suggest more extensive reclaimer operation than would otherwise have been the case.

The heat stable salts are formed from reaction between flue gas impurities, e.g. SO_2, NO_2 and HCl, and the amines. These impurities reduce the alkalinity of the solvent which leads to a reduction in its capacity to bind CO_2. In the reclaimer the amines bound in HSS and organic acids are neutralized by the addition of NaOH or $NaHCO_3$. The amine can then be recovered by distillation. A sludge containing non-regenerable degradation products will be the bottom products from the reclaimer. In addition, a variety of other components will be present depending on the solvent formulation used and the composition of the flue gas. If the amine to be regenerated has a high boiling point, the reclaimer should be operated under low pressure in order to avoid high temperatures which lead to further degradation. However, frequency of reclaiming determines build up of degradation products.

1.1.7 Reboiler

Reboiler is a heat exchanger typically used to provide heat to the bottom of a distillation column. The selection of the proper type of reboiler for a specific service is the most critical element of reboiler design. Shell and tube heat exchanger is one of the most used reboiler types with steam as the heat source.

Since rebolier operates at a high temperature, the highest degradation rate can happen in this section. To control degradation, a maximum surface temperature needs to be controlled as well as liquid residence time (Stewart and Lanning 1994). A high surface temperature together with a high residence time will lead to high degradation rate. In addition, type of reboiler, risk of high local temperatures, and formation of gas-pockets could also affect degradation.

1.1.8 Water wash

For environmental and economical reasons, the amount of evaporated solvent in the purified gas needs to be minimized by adding a water wash section in the column. The purpose of the water wash section at the top of the absorber is to minimize solvent loses not only due to evaporation but also mechanical entrainment. This is accomplished by scrubbing the flue gas with counter-current flow of water. Wash water pump takes water from the bottom of the water wash section and circulates it back to the top.

Water wash is a matter of design which depends on several factors such as volatility, make-up water, temperature, number of stages, and CO_2 loading. The more volatile such an amine used the more efficient water wash required. In addition, it is important to maintain a low solvent concentration in the circulating water to keep the driving force high by adding relatively clean water, while an equal amount of solvent loaded water is drawn out. The temperature on the absorber top should always be kept low to increase solvent vapor solubility in circulating water. The number of stages will also affect the efficiency of the water wash section.

Stable carbamate formation from the reaction between amine (primary and secondary) and CO_2 generally reach a peak at a higher loading (e.g. MEA case, Austgen *et al.* 1989). Carbamate formation can reduce solvent vapor pressure which leads to a reduction in the water wash section duty.

1.1.9 Demister and Entrainment

Demister is a device which is often used in a vapor liquid separator to enhance the removal of liquid droplets entrained in a vapor stream by aggregating the mist into droplets which are heavy enough to separate from the vapor stream. There are several types of demisters such as a mesh-type coalescer, vane pack, and other structure.
The demister efficiency depends on several factors such as gas physical properties, gas velocity, vapor pressure, liquid velocity, type of entrainment, and column/vessel structure (Kirkpatrick, 1938).

Stewart and Lanning (1994) discuss possible causes of entrainment in amine plants. They mention amine distributors as a potential source of mist. Entrainment is probably the type of emission that can change most dramatically. It can also result in emission of components that would otherwise not have been emitted due to low vapor pressure.

1.1.10 Material in plant

Alkanolamines tend to be corrosive solvents; thereby a proper material type in the plant should be used. Corrosion is still an issue as a potential operating problem in a CO_2 capture plant.

Since CO_2 absorption releases heat, water vapor condensation can occur on wall surfaces which are not wetted by the amine solution. CO_2 may react with water condensate to form carbonic acid which may result in aggressive attacks on carbon steel. Corrosion is likely to catalyze solvent degradation.

1.1.11 Intercooling

Absorber intercooling is used to reduce the temperature in the middle of the absorber column, see Figure 10. The intercooling affects on increasing the overall absorption rate of CO_2 and the rich loading, i.e. increasing the cyclic capacity (Reddy et al., 2003; Plaza et al., 2009).

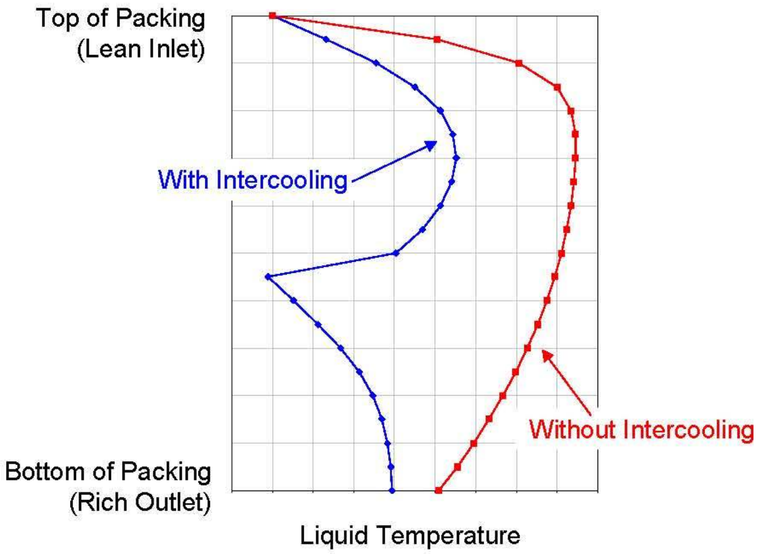


Figure 10. *Absorber temperature profile with intercooling (reproduced from Reddy et al., 2003).*

Intercooling reduces the absorber temperatures, something which should result in lower degradatation rates. How significant this contribution is likely to be is however hard to quantify.

1.1.12 Foam formation

Foam may result in formation of satellite droplets from liquid film rupture (sub micron). In other words this can lead to increased entrainment in the plant, resulting in higher emissions. Foaming can reduce the plant performance, increase amine loses, prevent adequate regeneration, and reduce process efficiency (Ballard, 1966). Several factors can cause foam formation, i.e. foam promoters. According to Ballard (1966), some foam promoters are:

- Finely divided suspended solids
- Organic acids in the gas stream
- Field corrosion inhibitors
- Dissolved hydrocarbons
- Degradation products such as thiosulfate and volatile acids
- Plug valve greases with a soap base
- Makeup water with a high inorganic chemical content.

Foaming can, in many cases, be controlled by adding a foam inhibitor, but the success of the foam inhibitor usually depends on when and how it is added (before/after the foam generated) in batchwise in the range of 5 to 300 ppm. The addition of too much foam inhibitor is usually worse than no foam inhibitor. Silicone compounds and high-boiling point alcohols (oleyl alcohol or octylphenoxythanol) are usually used as foam inhibitors. The commercial foam inhibitors for amine systems are Dow Corning DB-100 Antifoam Compound, Dow Corning DB-31 Antifoam Emulsion, Tretolite VEZ D-83, etc. (Kohl and Nielsen, 1997). Another potential risk related to foam formation is that foam will carry over into the water wash. This can probably result in quite dramatic loss in water wash efficiency. Onset of foam formation is difficult to predict, and this is perhaps one of the phenomena that can result in unexpected variations in plant emissions.

1.1.13 Solvent additives

There are a number of potential operating problems in a CO_2 capture plant such as corrosion, foaming, chemical losses, and degradation. To prevent or reduce these problems, additives can then be added to the system. However, in recent years there is a trend towards minimizing the use of additives. One reason for this is that additives may have undesired side effects, for example, corrosion inhibitors may not only catalyze solvent degradation but also cause foaming problem. It can also be hard to control the concentration of additives and determine when to replace them.

There are two main risks related to the use of solvent additives. One is the issue of emission of the additive itself; another is the risk of additives catalyzing solvent degradation.

For any additive that is a potential reaction catalyst, such as metal ions, its effect on solvent degradation should be tested. Catalysts may significantly change the emission profile from the plant.

1.2 Summary of Degradation Chemistry

This chapter provides a summary of some of the main features of solvent degradation. It must be noted that while some of the main trends are well understood, there are still knowledge gaps in solvent degradation.

This summary is based on MEA, the solvent for which degradation under post combustion CO_2 capture conditions are best understood. The other solvents are expected to undergo similar reactions.

1.2.1 Oxidative degradation

Oxidative degradation is expected to be the dominant form of degradation in a post-combustion CO_2 capture plant. While the mechanistic details of oxidative degradation are not known, the overall chemistry is reasonably well understood. Oxygen (O_2) in the liquid phase will react with the amine through radical reactions. The main degradation products are organic acids and ammonia, but some other components are also formed. The degradation reactions are probably mostly exothermic reactions.

It is known that oxidative degradation can be catalyzed by metal ions.

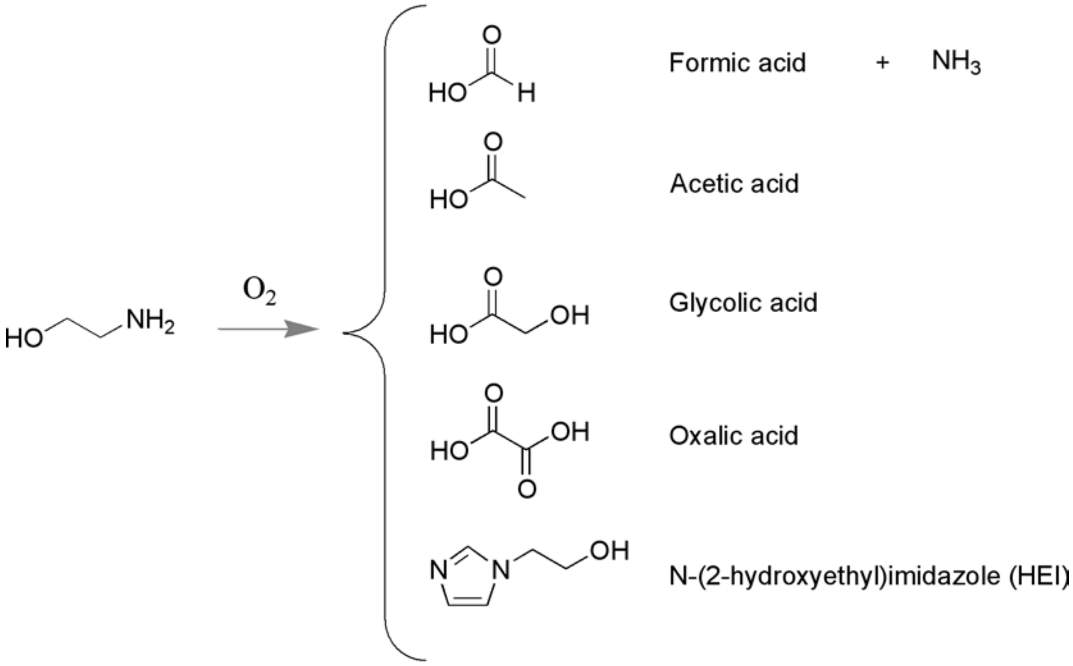


Figure 11. *Oxidative degradation of MEA and its products.*

1.2.2 Thermal degradation

Thermal degradation usually refers to degradation of the carbamate form of the amine. The mechanisms for this type of degradation is fairly well understood. It is believed that this form of degradation is dominant in CO_2 removal from natural gas (where oxygen is not an issue), but is perhaps of less importance in post-combustion CO_2 capture.

It should be noted that while the first steps in thermal degradation are the same in CO_2 removal from natural gas and post-combustion CO_2 capture the following reactions step may be different. In a post-combustion CO_2 capture plant the degradation products from thermal degradation products will be exposed to a different chemical environment with oxygen and oxidative degradation products. As a result they may react to form different degradation products.

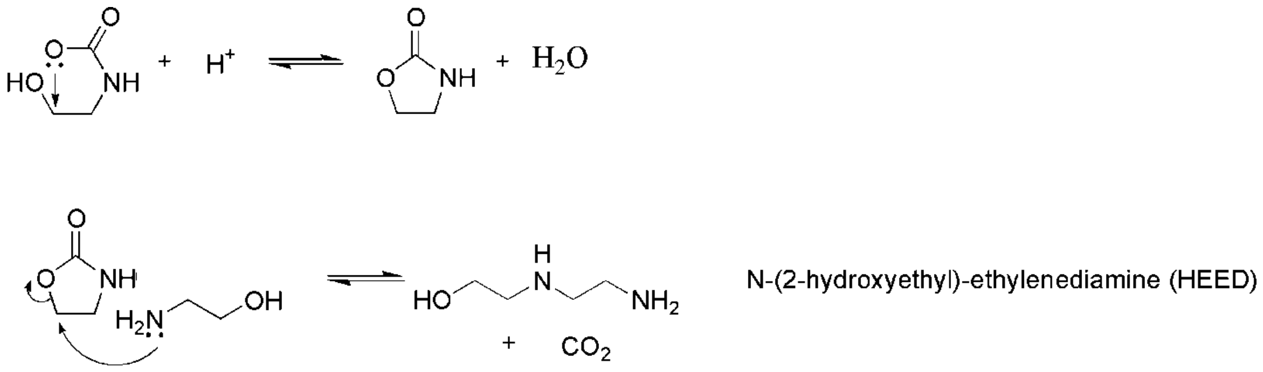


Figure 12. *Mechanism of thermal degradation.*

1.2.3 Secondary solvent degradation

We have recently looked at reactions between degradation products and the solvent. There is clear evidence that organic acids (formed during oxidative degradation) can go on to react with the solvent (Lepaumier et al. 2010).

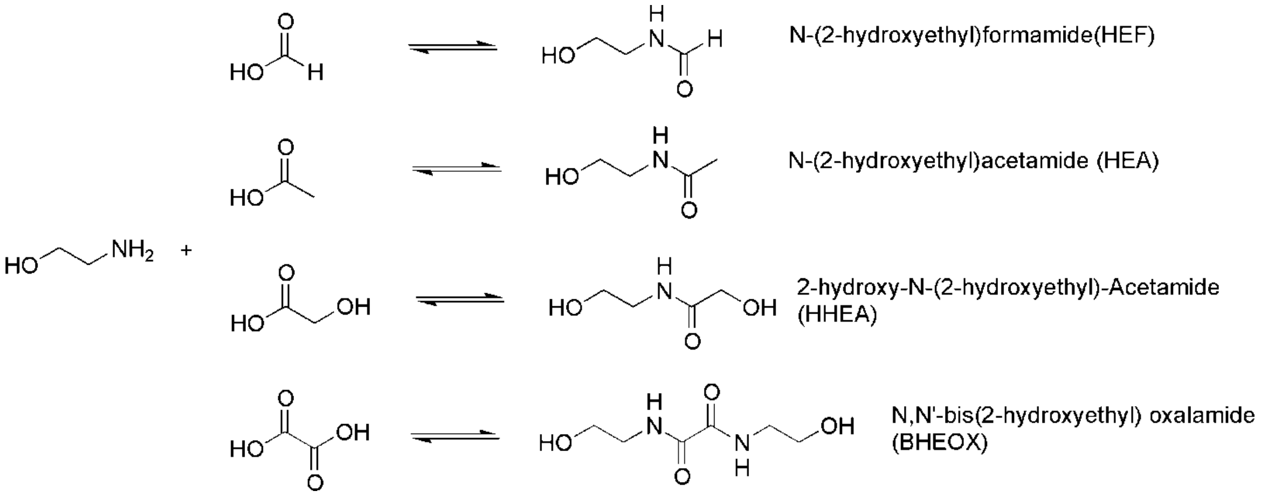


Figure 13. *Degradation of secondary solvent*

In addition to these secondary degradation products formed here, there are likely to be other such reactions. Some degradation products may be so thermodynamically stable or have so high reaction barriers that they do not react further; many degradation products are however likely to some extent to undergo further reactions.

1.2.4 Alkylamine formation

It has been suggested that methylamine can form during oxidative degradation of alkanolamines (Rooney, Dupart et al. 1998). Since the mechanistic details of oxidative degradation is unknown, this suggestion should be regarded as uncertain but entirely plausible.

Methylamines have been observed experimentally in degradation tests where MEA has been exposed to NOx (Pedersen, Sjøvoll et al. 2010).

The extent to which compounds such as alkylamines are formed during solvent degradation is uncertain. Since alkylamines are very volatile, they may be emitted to a significant degree even if they form only a small fraction of degradation products formed.

1.2.5 Reactions with NOx

The main potential issue with degradation as a result of reactions with NOx is the formation of nitrosamines and nitramines. This issue is addressed in detail in 3 appendices (I-III) to this report.

One of the overall conclusions from this assessment is that nitrosamine formation is likely to be bigger issue than nitramine formation.

Among the solvents considered in this project the risk would appear to be greatest for piperazine. In contrast, the risk would be the lowest for primary amines.

1.3 Degradation Products

A spread sheet detailing likely degradation products from the solvent MEA, MDEA, AMP and Piperazine are given in an excel sheet submitted together with this report (Appendix IV). The spread sheet contains references to observations of the components in the CO_2 capture literature (if they have been observed experimentally).

The data given in the spread sheets are also summarized in Table 3, Table 4 and Table 5. These tables do however contain less information than the spread sheet.

In the tables are given simple estimates of emissions of different degradation products. It should be emphasized that these represent informed guesswork. To our knowledge, there are no broad quantitative studies in open literature on the formation of degradation products in post-combustion CO_2 capture plants. The available data also comes from different CO_2 capture plants and different lab-scale experiments. Great caution should be used when comparing data on solvent degradation obtained under different degradation conditions.

The numbers given are also mostly conservative (high). The sum of the degradation products in the tables would imply a higher level of overall solvent degradation than is usually allowed in CO_2 capture plants.

The estimates of emissions are based on a few simple assumptions. For volatile degradation product emissions are assumed to be proportional to the rate of formation. The rate of formation is given as a fraction of the ammonia emission number. The underlying assumption is that ammonia formation is an indicator of the overall degradation rate in the plant and that volatile degradation products do not accumulate in the plant. This is probably a reasonable model assumption, but probably not equally valid for all degradation products. It is for example not valid for nitrosamines that may be formed in reaction with secondary amine solvents.

For Table 3 calculations we have assumed an ammonia emission of 1 ppmv for MEA, 0.5 ppmv for MDEA, and 0.05 ppmv for AMP and Piperazine. This is based on a simple estimate of the relative stability of the solvents.

For medium volatility degradation products vapor emissions are assumed to be proportional to volatility and concentration in the liquid. The concentrations in the liquid are based on informed guesswork.

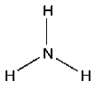
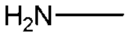
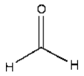
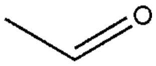
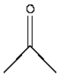
In Table 3 are listed volatile degradation products. These are defined as any component having a free energy of solvation higher than -5 kcal/mol. In Table 4 are listed medium volatility degradation products. Medium volatility degradation products are defined as a component having a free energy of solvation (dG solv) < -5 kcal/mol and that are not on ionic form. In Table 5 are listed non-volatile degradation products. These are defined as compounds that are expected to be on ionic form in post-combustion CO_2 capture plant.

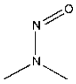
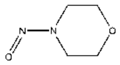
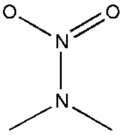
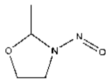
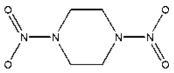
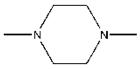
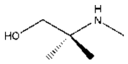
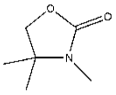
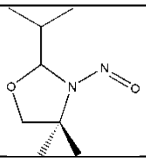
In a conventional post-combustion CO_2 capture power plant volatile degradation products probably presents the greatest challenge in terms of emissions, since it is difficult to keep such components from escaping the plant with a conventional water wash.

Nitrosamines and nitramines are marked with red in the tables. These compounds probably present the greatest health and environmental risk among the emitted compounds.

We have in this work considered the degradation of each solvent component separately. In a solvent system with two components, there will most likely be formed other degradation products in addition to those formed by the solvents in single component systems. We do however not believe that such additional degradation products would significantly change the emission profile of the solvent system. There are also very few studies in open literature looking at degradation in mixed solvent systems.

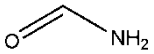
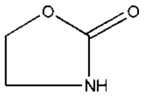
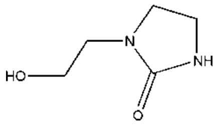
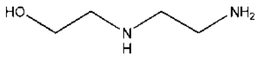
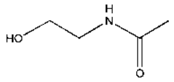
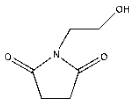
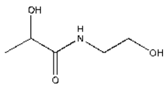
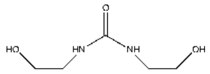
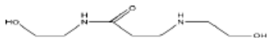
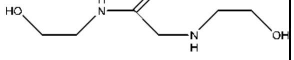
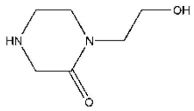
Table 3. *Volatile degradation products*

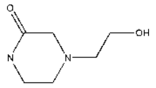
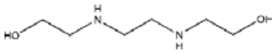
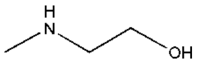
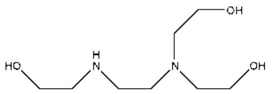
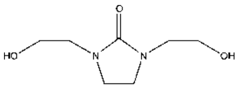
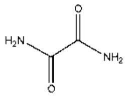
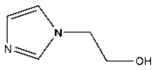
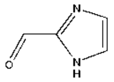
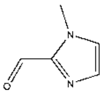
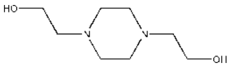
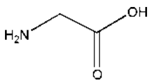
Degradation product	**CAS.**	**Structure**	**Emission[a] [ppmv]**	**Ref./Comment**
Ammonia	7664-41-7		1 (MEA) 0.05 (Pip) 0.5 (MD) 0.05 (AMP)	Oxidative degradation product, expected for all solvents.
Methylamine	74-89-5		0.006 (MEA) $3*10^{-4}$ (Pip) 0.03 (MD) $3*10^{-4}$ (AMP)	May form from oxidative degradation.
Formaldehyde	50-00-0		0.08 (MEA) 0.004 (Pip) 0.004 (MD) 0.004 (AMP)	
Acetaldehyde	75-07-0		0.02 (MEA) 0.001 (Pip) 0.009 (MD) 0.001 (AMP)	
Acetone	67-64-1		0.002 (MEA)	
dimethylamine	124-40-3		0.01 (MEA) $5*10^{-5}$ (Pip) $5*10^{-4}$ (MD) $5*10^{-5}$ (AMP)	
ethylamine	75-04-7		0.01 (MEA) $3.5*10^{-5}$ (Pip) $3.5*10^{-4}$ (MD) $3.5*10^{-5}$ (AMP)	
diethylamine	109-89-7		0.01 (MEA) $7*10^{-5}$ (Pip) $7*10^{-4}$ (MD) $7*10^{-5}$ (AMP)	

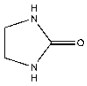
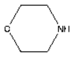
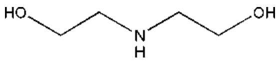
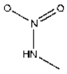
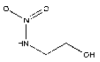
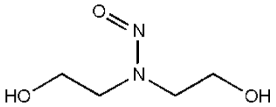
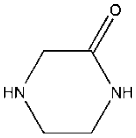
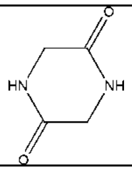
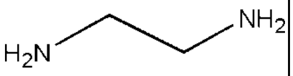
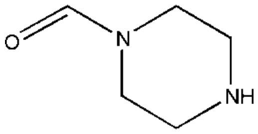
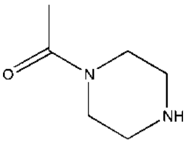
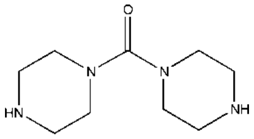
N-nitrosodimethylamine	62-75-9		0.02 (MEA) 0.001 (Pip) 0.01 (MD) 0.001 (AMP)	
4-nitroso-morpholine	59-89-2		0.01 (MEA) $4*10^{-4}$ (MD)	
Dimethylnitramine	4164-28-7		0.02 (MEA) $1*10^{-4}$ (Pip) 0.001 (MD) $1*10^{-4}$ (AMP)	
2-methyl-3-nitroso-oxazolidine	39884-53-2		0.003 (MEA)	Degradation product suggested by R. Loeppky
1,4 dinitropiperazine	140-79-4		$1*10^{-4}$ (Pip)	
1,4 dimethylpiperazine	106-58-1		0.004 (MD)	
2-methyl-2-(methylamino)- 1-Propanol	27646-80-6		$3*10^{-4}$ (AMP)	Degradation product observed in the work of H. Lepaumier.
3,4,4-trimethyl oxazolidin-2-one	15833-17-7		$5*10^{-4}$ (AMP)	Degradation product observed in the work of H. Lepaumier.
4,4 dimethyl-2-isopropyl-3-nitrosooxazolidine	39884-58-7		0.015 (AMP)	

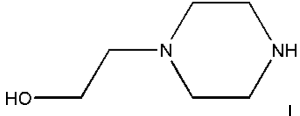
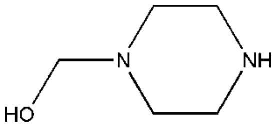
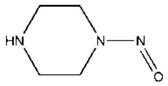
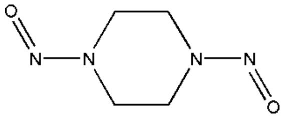
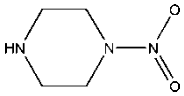
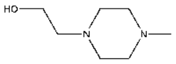
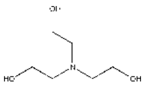
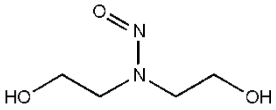
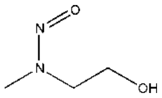
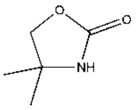
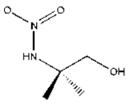
a: MD is short for MDEA, N-methyl diethanolamine

Table 4. *Medium volatility degradation products*

Degradation product	CAS.	Structure	Emission[a] [ppmv]	Ref./Comment
Formamide			0.007 (MEA) 0.003 (Pip) 0.006 (MD) 0.003 (AMP)	
Oxazolidin-2-one			0.004 (MEA)	
1-(2_hydroxyethyl)-2-imidazolidinone	3699-54-5		0.003 (MEA)	
N-(2-hydroxyethyl)-ethylenediamine	111-41-1		0.003 (MEA)	
N-(2-hydroxyethyl)-acetamide/N-acetylethanolamine	142-26-7		0.003 (MEA)	
1-(2-hydroxyethyl)-2,5-Pyrrolidinone	18190-44-8		0.003 (MEA)	
N-(2-Hydroxyethyl)lactamide	5422-34-4		0.003 (MEA)	
N,N-di(2-hydroxyethyl)urea	15438-70-7		0.003 (MEA)	
N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]-Propanamide	587876-41-3		0.003 (MEA)	
N-(2-hydroxyethyl)-2-[(hydroxyethyl)amino]-acetamide	144236-39-5		0.003 (MEA)	
1-(2-hydroxyethyl)-2-piperazinone	59702-23-7		0.003 (MEA)	

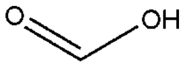
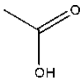
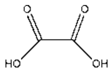
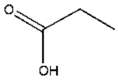
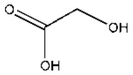
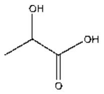
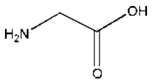
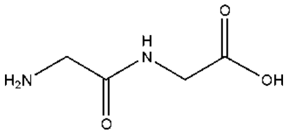
4-(2-hydroxyethyl)-2-piperazinone	23936-04-1		0.003 (MEA)	
2-((2-[(2-hydroxyethyl)amino]ethyl)amino)ethanol	4439-20-7		0.003 (MEA)	
2-methylaminoethanol	109-83-1		0.01 (MEA)	
2,2'-[[2-[(2-hydroxyethyl)amino]ethyl]imino]bis-Ethanol	60487-26-5		0.003 (MEA)	
1,3-bis(2-hydroxyethyl)-2-Imidazolidinone	71298-49-2		0.003 (MEA)	
Oxalamide	471-46-5		0.003 (MEA)	
1-(2-Hydroxyethyl)imidazole	1615-14-1		0.03 (MEA)	
1H-imidazole-2-carboxaldehyde	10111-08-7		0.003 (MEA)	
1-methyl-1H-imidazole-2-carboxaldehyde	13750-81-7		0.003 (MEA)	
N,N-bis(hydroxyethyl)piperazine	122-96-3		0.003 (MEA)	
Glycine	56-40-6		0.003 (MEA)	
Hydroxy-Acetaldehyde	141-46-8		0.003 (MEA)	

2-imidazolidinone	120-93-4		0.003 (MEA)	
morpholine	119-91-8		0.02 (MEA)	
diethanolamine	111-42-2		0.003 (MEA)	
methylnitramine	598-57-2		0.02 (MEA) 0.002 (Pip)	
2-(nitroamino) ethanol	74386-82-6		0.006 (MEA)	Not known to what extent nitramines may form in CO_2 capture plants
N-nitroso ditethanolamine	1116-54-7		0.0005 (MEA) 0.001 (MD)	Nitrosamines have been detected in CO_2 capture plants.
2-oxopiperazine	5625-67-2		0.002 (Pip)	Possible oxidative degradation product
2,5-piperazinedione	106-57-0		0.002 (Pip)	Possible oxidative degradation product
Ethylenediamine	107-15-3		0.002 (Pip)	
1-Piperazinecarboxaldehyde	7755-92-2		0.003 (Pip)	
1-Acetylpiperazine	13889-98-0		0.003 (Pip)	
1,1'-carbonylbis piperazine	17159-16-9		0.002 (Pip)	

1-Piperazineethanol	103-76-4		0.005 (Pip)	
N-(hydroxymethyl)piperazine	90324-69-9		0.002 (Pip)	
1-nitrosopiperazine	5632-47-3		0.002 (Pip)	Possible nitrosamine degradation product
1,4 dinitrosopiperazine	140-79-4		0.2 (Pip)	Possible nitrosamine degradation product
1-nitropiperazine	42499-41-2		0.003 (Pip)	Possible nitramine degradation product
4-methyl-1-Piperazineethanol	5464-12-0		0.2 (MD)	Observed experimentally
triethanolamine	102-71-6		0.006 (MD)	
N-nitroso ditethanolamine	1116-54-7		$8*10^{-4}$ (MD)	
2-(methylnitrosoamino) ethanol	26921-68-6		0.3 (MD)	
4,4-dimethyl-2-Oxazolidinone	26654-39-7		0.01 (AMP)	
nitro 2-amino-2-methylpropanol	no cas		$3*10^{-4}$ (AMP)	

a: MD is short for MDEA, N-methyl diethanolamine

Table 5. *Non volatile degradation products*

Degradation product	**CAS.**	**Structure**	**Emission[a] [ppmv]**	**Ref./Comment**
Formic acid/formate	64-18-6		0.003 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Acetic acid/acetate	64-19-7		0.03 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Oxalic acid	144-62-7		0.003 (MEA) 0.002 (Pip) 0.003 (MD) 0.002 (AMP)	Known oxidative degradation product
Propanoic acid/Propinoic acid	79-09-4		$3*10^{-3}$ (MEA)	
Hydroxy-acetic acid/glocolate/glycolic acid	79-14-1		$3*10^{-3}$ (MEA)	
Lactic acid/Lactate	598-82-3		$3*10^{-3}$ (MEA)	
Glycine	56-40-6		$3*10^{-3}$ (MEA)	Possible oxidative degradation product
N-Glycylglycine	556-50-3		$2*10^{-3}$ (Pip)	Likely oxidative degradation product

a: MD is short for MDEA, N-methyl diethanolamine

1.4 Worst-Case Scenarios

It is hard to identify or define a single-worst case scenario in a CO_2 capture plant. There however a number of things that can go wrong in a CO_2 capture plant, potentially resulting in higher emissions of harmful compounds. The things that can go wrong in the plant are mainly unrelated to each other, and we do not feel it makes sense do define them into a single-worst case scenario.

The factors that contribute to higher emissions can be separated into three classes:

- Entrainment
- Volatility losses
- Higher degradation rates

High entrainment is probably the factor that can have the most immediate and largest effect on the emission. High entrainment can lead to significant emissions of components that would usually not be expected to be emitted from the plant.

Higher volatility losses (resulting from a water-wash failure) can also result in significant emissions. But the emission profile of the plant is likely to change less dramatically than the case is for higher entrainment.

Higher degradation rates can lead to large solvent losses, and make plant operation more challenging. The effects of high degradation rates on emissions is however likely to be less dramatic. It would probably take some time for degradation products to build up to a level where they significantly change the overall emissions from the plant.

On the other hand higher degradation rate may be the more difficult to handle once it is observed. It may be difficult to identify the cause of the high degradation rates, and the remedies may be less obvious than for issues related to entrainment and volatility losses.

Higher than expected degradation rates may also result in the water-wash becoming saturated with some degradation products. In this case the emission of some degradation products could increase quite dramatically.

1.4.1 Extreme entrainment

The most likely cause of extreme entrainment may be changes to the properties of the liquid in the absorber. Accumulation of degradation products may lead to higher viscosity or foam formation, which could again result in entrainment.

The simplest and most conservative estimate that can be made regarding entrainment is that they have the same composition as the liquid in the absorber.

To quantify a worst case scenario for entrainment is difficult since we do not even have measures of entrainment from a CO_2 capture plant under normal operation.

1.4.2 Too high temperatures

Too high temperatures in the reboiler and in the stripper may have quite dramatic effect on the degradation rates of the solvent. Degradation products will accumulate to high levels and one may see the formation of compounds that are not otherwise formed.

1.4.3 High levels of NOx coming into plant

Higher levels of NOx in the plant will probably result in higher formation rates for nitrosamines and nitramines. It would seem reasonable to assume that the formation rates of nitrosamines and nitramines are proportional to the amount of NOx entering the plan.

We do not at present know what the worst-case level on NOx that can be expected in the CO_2 capture plant is.

1.4.4 Catalyzed degradation

There is the possibility that components that catalyze degradation are formed/introduced into the system. The most obvious possibility is metal ions, but there may also components that can have a catalytic effect on degradation.

Such degradation catalysts may have a dramatic effect on the extent to which certain degradation products are formed.

From what we know today catalysis of oxidative degradation would seem to be the most likely.

1.4.5 Water-wash failure

There are probably a number of ways in which a water-wash may fail to operate as intended. The result of a failure is any case likely to be that the water-wash becomes saturated in one or more components. Saturation in the solvent components and ammonia is the most likely to occur since these components will tend to dominate emissions.

A water-wash failure would have the most dramatic effect for relatively volatile solvents such as AMP and piperazine. For an extremely hydrophile solvent such as MDEA the emissions are likely to stay on a low level in the absence of a water-wash.

For AMP and piperazine a 10-fold increase in emissions in the absence of a water-wash would seem likely.

1.4.6 How to quantify worst-case scenarios

In the present report we have to a large extent avoided putting numbers on the worst-case scenarios. This is mainly due to a lack of experimental data and validated models for the different process units. Instead we suggest a set of experimental activities to quantify worst case scenarios.

These experimental activities can be run in a CO_2 capture pilot plant and in lab-scale experiments on degradation (with apparatus proposed as part of test protocol).

The recommended tests are summarized in Table 6. Recommended worst-case scenario tests.

For each test a solvent system is recommended. These are the solvents that would be expected to perform worst in each test; this would provide an overall worst-case scenario. One could of course also do a set of such worse-case tests for each solvent system.

Table 6. *Recommended worst-case scenario tests*

Parameter	Apparatus	Test
Extreme entrainment	Pilot	Operate with 150% of standard gas velocity in absorber. Measure change in emissions for non-volatile component.
High temperatures	Lab –scale	Increase temperatures in stripper to 145C for 1 week. MEA as solvent. Worst case is defined by % increase in degradation products.
Water-wash failure	Pilot	Operate water wash with no freshwater 1 week. Look at relative change in emissions. AMP and Piperazine as solvent.
Catalyzed degradation	Lab-scale	Spike solution with metal ions, (Cr, Ni and Fe). Look at relative change in degradation over 1 week. MEA as solvent.
High NOx levels	Lab-scale	Increase NOx to whatever is deemed realistic worst case for plant. Look at relative change in nitrosamine and nitramine concentration. Piperazine as solvent.
Foaming	Pilot	Operate pilot at 150% of standard gas velocity. Solvent MEA-AMP 2:1 mole ratio.

There is some arbitrariness in the recommended duration and the extremeness of the conditions in the worst-case scenarios. These could be revised to reflect what degree of failure is realistic in a full scale plant. If the solvents are exposed to extreme enough conditions such as persistent temperatures over a 140C, it is likely that most solvents will degrade completely. Extreme testing should therefore not be given too much weight in ranking of solvent systems.

It is also not clear if there is that much to gain by testing the solvents at conditions that will not realistically occur at the full scale CO_2 capture plant.

Testing for worst-case foaming is very difficult, since this is a phenomenon that is very sensitive to the liquid phase properties. We do not know what types of impurities at what concentrations will lead to the most extreme foaming. The recommended solvent system is a mixture reported to give significant foaming (Thitakamol and Veawab 2008).

1.5 Ranking of solvents

There are a number of factors to consider in ranking the solvents with respect to their potential to form and emit harmful compounds to the air. The weighting of these factors depends on their toxicity and fate in the environment. At present there is no predefined way to carry out such a ranking.

From what we know at present the compounds that present the greatest health and environmental risk are the nitrosamines. The risk is highest for secondary amines, lower for tertiary amines and the lowest for primary amines. Based on this we could make the following raking:

Piperazine>MDEA> AMP=MEA.

Another aspect is to what extent the solvent degrades, forming alkylamines, secondary amines (that may go on to form nitrosamines) and volatile degradation products. Different solvents have somewhat different degradation pathways and form somewhat different degradation products. We do however believe it is reasonable to assume that degradation products of different solvents will have similar composition. We then assume that formation rates of alkylamines, secondary amines and volatile degradation products are all proportional to the overall rate of degradation.

In terms of degradation rates the following ranking is likely:

MEA>MDEA>Piperazine=AMP

If we add these rankings together, giving the most weight to the risk of nitrosamine formation we obtain the following ranking:

Piperazine>MDEA>MEA>AMP

If we had looked at the risks from the worst-case scenarios the ranking would be somewhat different. AMP and piperazine are more volatile than MEA and MDEA and their emissions could potentially increase a lot in a worst-case emission scenario. Considering such worst-case risk we obtain the following ranking:

Piperazine>AMP>MEA>MDEA

We do believe that this can be generalized to the following statements:

- Secondary amines have highest risk of nitrosamine formation, followed by tertiary amine, while primary amines have the lowest risk of nitrosamine formation.
- All other things being equal solvents with low vapour pressure are safer than solvents with high vapour pressure.
- All other things being equal a more stable solvent is safer than a less stable solvent. This since it will have lower emissions of degradation products.

In the present ranking we have considered each solvent component separately. In ranking solvent systems consisting of two components, the ranking could be based on the component that has a highest risk. An AMP-Piperazine system would be ranked as Piperazine, while a MEA-MDEA system would be ranked as MDEA.

1.5.1 Other solvents

The present set of solvents (Piperazine, MEA, MDEA and AMP) does cover a broad range of amine chemistry. The list includes both primary, secondary, tertiarty, cyclical and sterically hindered amines.
The present set of solvents should therefore span most of the emission risk presented by amine solvents.

There are however some types of solvents that are not represented on this list, the most important are open chain secondary amines and amino acids.

Open chain secondary amines, such as DEA (diethanolamine) have a chemistry that is likely to differ from that of piperazine (secondary, but cyclical). The risk of formation of nitrosamines from open chain secondary amines would appear to be relatively high. Compared to piperazine the nitroso components formed would be less volatile. Open chain secondary amines are likely to have degradation rates comparable to solvents such MEA.

To our knowledge there have been no studies published in the open scientific literature on the degradation of amino acids in CO_2 capture process conditions. There is probably also very little experience with such solvents in post-combustion CO_2 capture plants. The risk from such solvent would on the whole appear to be less than for amine solvents. Amino acids are much less volatile than amines and many are ubiquitous chemicals in nature, many of the degradation products formed are also likely to be naturally occurring compounds. The risk of nitrosamine formation for amino acid solvents has to our knowledge not been studied.

References

Ballard, D. *How to operate an amine plant*. Hydrocarbon Process., 1966, **45** (4): p. 137–144.

Davis, J. and G.T. Rochelle. *Thermal degradation of monoethanolamine at stripper conditions*. Energy Procedia, 2009, **1**: p. 327 – 333.

Kim et al. *Ebulliometric determination of vapor-liquid equilibria for pure water, monoethanolamine, N-methyldiethanolamine, 3-(methylamino)-propylamine, and their binary and ternary solutions.* J. Chem. Eng Data, 2008, **53**: p. 2521-2531.

Kirkpatrick, G.M. *Liquid entrainment separators*. Ind. Eng. Chem, 1938, **30**: p. 1207 – 1210.

Kohl, A.L. and R.B. Nielsen, *Gas Purification*. 1997, Houston, USA: Gulf Professional Publishing.

Lepaumier, H. da Silva, E. F. Einbu, A. Grimstvedt, A. Knudsen, J. N., Zahlsen, K. Svendsen, H. F. 210 *Comparison of MEA degradation in pilot-scale with lab-scale experiments,* to be presented at GHGT10.

Miller, J.A. and C.T. Bowman. *Mechanism and modeling of nitrogen chemistry in combustion*. Prog. Energy Combust. Sci., 1989, **15**: p. 287 – 338.

Modi, K.A. and R.T. Waibel. *NOx emissions from process heaters and boilers: improving emissions estimates*. NPRA Refinery & Petrochemical Plant Environmental Conference 1995. San Francisco.

Molokanov et al. *Effect of nonuniform distribution of liquid entrainment by gas stream over plate area on entrainment measurement by different methods*. Chemical and Petroleum Engineering, 1969, **5**: p. 113 – 116.

Pappa et al. *Measurement and thermodynamic modeling of the phase equilibrium of aqueous 2-amino-2-methyl-1-propanol solutions.* Fluid Phase Equilibria, 2006, **243**: p. 193 – 197.

Pedersen, S., Sjøvoll, M. and Fostås, B. F. Flue gas degradation of amines, IEA GHG workshop, 2010.

Plaza et al. *Absorber intercooling in* CO_2 *absorption by piperazine-promoted potassium carbonate*. AIChE J., 2009, **56**: p. 905 – 914.

Reddy et al. *Fluor's econamine FG Plus*^{SM} *technology. An enhanced amine-based CO2 capture process*. Second National Conference on Carbon Sequestration 2003. Alexandria.

Rooney, P. C., M. S. Dupart, et al. (1998). "Oxygen's role in alkanolamine degradation." Hydrocarbon processing(International ed.) 77(7): 109-113.

Stewert, E. J. and R. A. Lanning (1994). "Reduce amine plant solvent losses." Hydrocarbon Processing (May 1994).

Thitakamol, B. and A. Veawab (2008). "Foaming Behavior in CO2 Absorption Process Using Aqueous Solutions of Single and Blended Alkanolamines." Industrial & Engineering Chemistry Research 47(1): 216-225.

2 WP 2 Theoretical evaluation of the fate of these compounds post emission

When conducting a full environmental risk assessment of a potentially harmful chemical it is typical to focus on both fate and toxicity (e.g. EU Technical Guidance Document; US EPA). Environmental fate assessment includes both abiotic processes (e.g. atmospheric deposition, soil adsorption, dissolution into aqueous systems) and biotic processes (e.g. biodegradation). Although the scope of this project defines abiotic process as the main focus of activities, it is therefore suggested that the inclusion of biotic processes (especially biodegradation) is an essential part of environmental fate studies. Therefore it is recommended that biodegradation of hazardous chemicals should also be considered within the scope of this project in order to fully evaluated their environmental fate. It is acknowledged that biotic processes have been included as part of the scope of service for the H&ETQP Amine 3 project. As a result, theoretical biodegradation data based on a QSAR approach (e.g. from EPI Suite and TOXNET) has been generated and evaluated as part of this project. This is relevant to the work completed within sub-tasks T1 and T11.

2.1 Theoretical reaction rate constants of parent amines

Quantitative structure activity relationship (QSAR) method was applied to predict rate constants of parent amines with the atmospheric hydroxyl radical, short *k*(OH). For this purpose the program suite EPI Suite™ of the U.S. Environmental Protection Agency (EPA) was used (http://www.epa.gov/oppt/exposure/pubs/episuite.htm). The EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physical/chemical property and environmental fate estimation programs developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation (SRC).

EPI Suite™ uses a single input to run the following estimation programs: KOWWIN™, AOPWIN™, HENRYWIN™, MPBPWIN™, BIOWIN™, BioHCwin, KOCWIN™, WSKOWWIN™, WATERNT™, BCFBAF™, HYDROWIN™, KOAWIN and AEROWIN™, and the fate models WVOLWIN™, STPWIN™ and LEV3EPI™. ECOSAR™, which estimates ecotoxicity, is also included in EPI Suite™. EPI Suite™ is a screening-level tool and should not be used if acceptable measured values are available. A clear understanding of the estimation methods and their appropriate application is very important. AOPWIN™: Estimates the gas-phase reaction rate for the reaction between the most prevalent atmospheric oxidant, hydroxyl radicals, and a chemical. Gas-phase ozone radical reaction rates are also estimated for olefins and acetylenes. In addition, AOPWIN™ informs the user if nitrate radical reaction will be important. Atmospheric half-lives for each chemical are automatically calculated using assumed average hydroxyl radical and ozone concentrations.

In this project, rate constants of the reaction for a range of different primary, secondary, and tertiary amines, including heterocyclic amines with OH were predicted using EPI Suite™ and compared to experimental data of *k*(OH). A list of the studied amines and their experimental and predicted *k*(OH) is in given *Table 1*. A more complete list is given in Appendix V.

Table 1: *Predicted and experimental rate constants for the reaction of parent amines (alkylamines and parent amines) and the atmospheric hydroxyl radical.*

Parent Amine	**Formula**	**CAS nr.**	***k*(OH) in molec cm^3 s^{-1} (at 298 K)**		
			EPI Suite predicted	**Exp.**	**Experiment Reference**
Monomethylamine	CH3 NH2	74-89-5	22.26E-12	22.0E-12	Atkinson et al. (1977)
Dimethylamine	(CH3)2 NH	124-40-3	65.53E-12	65.4E-12	Atkinson et al. (1978)
Trimethylamine	(CH3)3 N	75-50-3	69.79E-12	60.9E-12	Atkinson et al. (1978)
Monoethylamine	CH3 CH2 NH2	75-04-7	29.85E-12	27.7E-12	Atkinson et al. (1978)
Diethylamine	(CH3 CH2)2 NH	109-89-7	80.7E-12		—
Triethylamine	(CH3CH2)3N	121-44-8	92.6E-12		—
N-N-Diethylhydroxylamine	(CH3 CH2)2 NOH	3710-84-7	83.71	100E-12	Gorse and Saunders, 1977
N-N-dimethylethanolamine	(CH3)2NCH2CH2OH	108-01-0	83.4E-12	90E-12	Anderson and Stephens, 1988
AMP	(CH3)2C(NH2)CH2OH	124-68-5	25.5E-12	28E-12	Harris and Pitts, 1983
MEA	NH2CH2CH2OH	141-43-5	35.8E-12		—
Diethanolamine	NH(CH2CH2OH)2	111-42-2	92.7E-12		—
Triethanolamine	N(CH2CH2OH)3	102-71-6	111E-12		—
Piperazine	C4H10N2	110-85-0	169E-12		—
MDEA	CH3N((CH2)2OH)2	105-59-9	97E-12		—

Comparison of predicted and experimental *k*(OH) values shows usually good agreement. Still, the predicted rate constants for the more complex amines such as the heterocyclic amines might be highly uncertain. The predicted *k*(OH) value of piperazine (1.69E-10 molecules cm^3 s^{-1}) indicates a very fast reaction of this amine with OH radicals and an e-fold atmospheric lifetime of <1 hr (at constant [OH] = 2E06 molecules cm^{-3}). Experimental verification of this particular rate constant is urgently recommended.

Figure 1 displays measured (full symbols) and predicted (open symbols) *k*(OH) of primary (green), secondary (red), and tertiary (blue) amines versus the number of carbon atoms in the amine molecules. At least for the primary amines, for which a sufficient number of amines have been studied experimentally, a linear relationship between *k*(OH) and number of carbon atoms is found. Thus it seems that QSAR provides reliable results for primary amines. For secondary amines, *k*(OH) appears to increase as well with the number of carbon atoms in the amine molecule. For tertiary amines, too little experimental data exists to derive such a relationship. Predicted *k*(OH) of tertiary amines show a linear trend with a similar slope as for the secondary amines. There exists however no experimental basis for such a relationship and thus predicted rate constants for tertiary amines and heterocyclic amines should be critically examined.

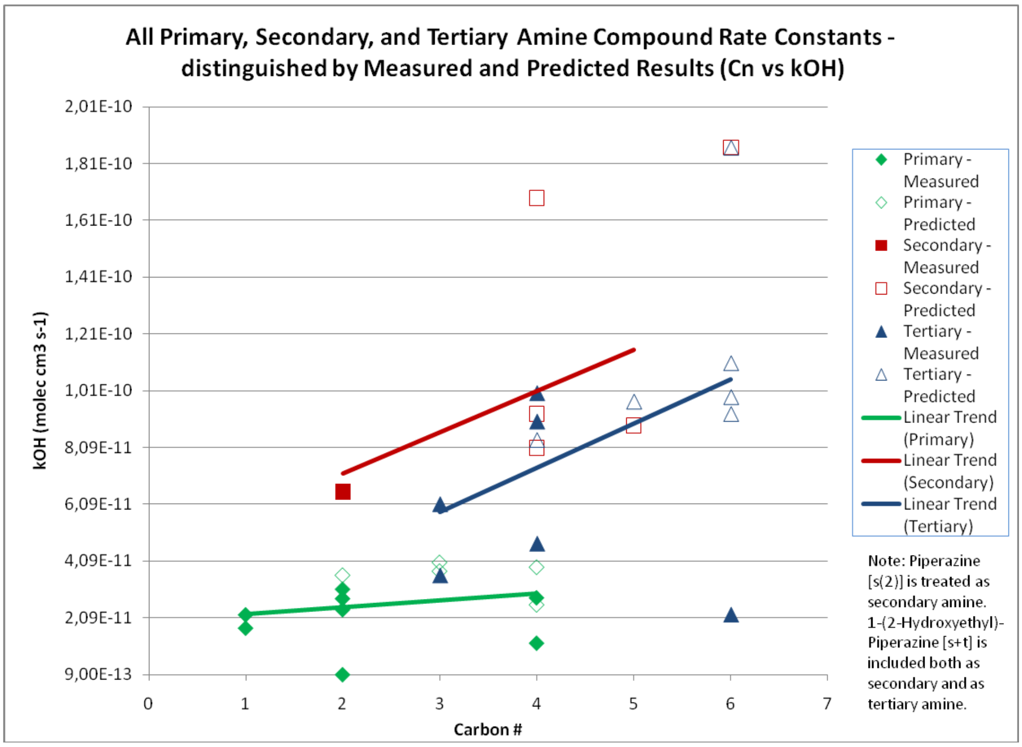


Figure 1: *Measured (full symbols) and predicted (open symbols) rate constants for the reaction of primary amines (green), secondary amines (red), and tertiary amines (blue) with the hydroxyl radical, k(OH), in units molecules cm^3 s^{-1}, versus the number of carbon atoms of the amine. Linear trend lines for primary (green line), secondary (red line), and tertiary (blue line) amines using both predicted and experimental data are also displayed. Note that piperazine (s2) is treated is a secondary amine (s) and that 1-(2-hydroxyethyl)-piperazine (s+t) is included both as secondary and as tertiary amine.*

Koch et al. (1997) studied 3 simple, commercially available amines (TBA, TFEA and DABCO) to test the predictions of the Atkinson SAR (which is the conceptual basis of the AOPWIN™ module) and to explore the ground for improvements. The data for these amines is also included in Appendix V. The discrepancy between observed and predicted rate constants was more than a factor of 20 for TFEA and a factor of 6 for DABCO. On this basis the authors concluded that the predictive power of the SAR for amines appears to be extremely poor. In particular the SAR does not give a sound indication to where the hydrogen abstraction actually takes place in the molecule. Therefore, Bråten et al. (2008) argued that the Atkinson SAR does not work well for amines. It is added here, that the Atkinson SAR seems to perform well for the primary amines, but that predicted rate constant for secondary and tertiary amines should be used with caution.

2.2 Particle formation potential

Gas phase aliphatic amines may play a significant role in secondary aerosol formation via photo-oxidation and gas-to-particle conversion in regions with high amine concentrations (Murphy et al., 2007; Angelino et al., 2001). Aerosol particles forming in the atmospheric oxidation of amines can be either organic salt particles or organic non-salt particles, the latter are commonly referred to as *secondary organic aerosol* (SOA) particles. Acid-base reactions between amines and acids commonly present in the atmosphere (i.e. nitric acid and sulphuric acid) and in the emissions (e.g. from the power plant) appear to play an important role in the formation of the salt particles.

In a comprehensive particle study on several aliphatic amines, Murphy et al. (2007) demonstrated that only the two tertiary amines studied (trimethylamine and triethylamine) formed significant non-salt organic aerosol (i.e. low-volatile condensable organics and secondary organic aerosol) when oxidized by OH or ozone. However, the non-salt organic aerosol fraction appeared to be more stable than the alkyl ammonium nitrate (*aminium nitrate*) salts and did not quickly repartition back to the gas phase. Experimentally determined mass-based aerosol yields of non-salt organic aerosol in the oxidation of amines available in literature are summarized in Appendix VI, Table 1. With the exception of trimethylamine, the formation yield of non-salt organic aerosol in the oxidation of amines is 10% or smaller.

Alkylamines react with strong inorganic acids like nitric acid and sulphuric acid in a reversible thermodynamic equilibrium reaction, according to:

$NR_3\ (g) + HNO_3\ (g) \rightleftarrows HNR_3NO_3\ (s)$ (R1)

$NR_3\ (g) + H_2SO_4\ (g) \rightleftarrows (HNR_3)_2SO_4\ (s)$ (R2)

The equilibrium of these two reactions depends on temperature, relative humidity, and particle acidity (Murphy et al., 2007; Pratt et al., 2009). In addition to gas-to-particle conversion by equilibrium reactions, reactive uptake into liquid aerosol may also occur. The thermodynamic equilibrium reactions R1 and R2 are governed by the dissociation constant *Kp* (*Kp*(R1) = $p(NH_3) \cdot p(HNO_3)$). The dissociation constant of an aminium salt can be estimated using the integrated form of the Van't Hoff equation and estimated or experimentally determined values of thermodynamic parameters (Murphy et al., 2007):

$$\ln Kp = \frac{\Delta S^0_{diss} - \Delta C_{P,diss}}{R} - \frac{\Delta H^0_{diss} - T_0 \Delta C_{P,diss}}{RT} + \frac{\Delta C_{P,diss}}{R} \ln\left(\frac{T}{T_0}\right) \quad (1)$$

Depending on which literature source is used for the heat of formation (ΔH_f^0), the predicted dissociation constant using Equation (1) can vary by several orders of magnitude, see Appendix VI, Table 2. Until now, only one peer-reviewed publication on the experimental determination of the dissociation constant for one amine exists (trimethylamine; Murphy et al, 2007).

Among the amines which are used as solvents in carbon capture only the nitrate salt of MEA has been studied. The predicted and experimentally derived *Kp* value for the nitrate salt of MEA is several times smaller than the relatively well known *Kp* value of ammonium nitrate (Nielsen et al., 2010). This implies that the MEA-nitrate salt is far more stable in the atmosphere than ammonium nitrate, a commonly present aerosol constituent. Due to the lack of thermodynamic data for AMP, MDEA, and Piperazine, the *Kp* values for their aminium nitrate salts could not be estimated. There appears to be no clear rule about the relationship between molecule structure of the parent amine and the stability of the formed salt.

Based on experimental Kp data and SOA yields, both trimethylamine and MEA have the potential to form aerosol salt particles of atmospheric relevance.

2.3 Identification of process degradation products

Piperazine

In addition to the observed degradation products, n-formylethylene amide, n-formyl piperazine have been shown to be produced from piperazine (Freeman, Dugas et al. 2010). Many possible ring-opening reactions of piperazine derivatives should be considered as a part of a complete degradation scheme for piperazine. Such reactions would lead to a number of smaller amines which would have potential to form nitrosamines and nitramines.

MDEA

MDEA is a tertiary amine which requires dealkylation to form nitrosamines and nitramines. Simple dealkylation gives two possible products N-nitroso ditethanolamine and 2-(methylnitrosoamino) ethanol which are observed. There are no other direct pathways, however some cyclic compounds are observed which can react in several different ways. Among its other degradation products is diethylamine which can form diethylnitrosamine and diethylnitramine.

MEA

For MEA a number of secondary amines are observed as process degradation products. These may react with radicals in the presence of NO_x and NO_2 to form nitramines and nitrosamines. 2-methylaminoethanol and diethanolamine for instance will lead to the formation of N-nitroso ditethanolamine and 2-(methylnitrosoamino) ethanol which are observed degradation products in MDEA. Diethylamine is an observed degradation product in all four solvents which can be expected to form diethylnitrosamine.

AMP

AMP is a smaller molecule and its potential to form nitramines and nitrosamines other than those observed is limited.

The observed process degradation products can degrade in the gas phase after emission and form further secondary degradation products.

In the test protocol, the highest priority should be to identify any primary or secondary (alkyl) amines produced in the process and to draw up atmospheric degradation pathways for these. Of the four parent amines, the compound with the highest potential to form additional toxic compounds in the process is piperazine as ring-opening reactions could potentially form a number of smaller amines.

2.4 Experimental and theoretical rate constants for atmospheric degradation products

Quantitative structure activity relationship (QSAR) method was applied to predict rate constants of relevant harmful atmospheric degradation products with the atmospheric hydroxyl radical, short *k*(OH). Predicted atmospheric degradation products from the reaction of amines (MEA, AMP, MDEA, and piperazine) with OH radicals were based on CO2&Amines phase I report on theoretical chemistry (Bråten et al., 2008). The program suite EPI Suite™ of the U.S. EPA was used (http://www.epa.gov/oppt/exposure/pubs/episuite.htm), which makes use of SAR and experimental data. The EPI Suite™ also contains a database of experimental k(OH). In addition the NIST (U.S. National Institute of Standards and Technology) Chemical Kinetics Database on the web (http://kinetics.nist.gov/kinetics/index.jsp) was searched for the atmospheric degradation products. In this project, the rate constants of the complete list of relevant atmospheric degradation products (Table 5.4 in Appendix A of Bråten et al., 2008) have been predicted using EPI Suite™. Experimental data is scarce and only available for atmospheric relevant compounds. A list of the compounds together with the predicted rate constant and the experimental rate constants available in EPI Suite™ and in NIST is compiled in Appendix VII . *Table 2* lists all compounds for which experimental *k*(OH) values were provided in the NIST database.

Table 2: *Predicted and experimental rate constants for the reaction of relevant atmospheric degradation products and the atmospheric hydroxyl radical.*

Compound	**Formula**	**CAS nr.**	***k*(OH) in molec cm^3 s^{-1} (at 298 K)**			
			EPI Suite predicted	**EPI Suite exp.**	**NIST exp.**	**NIST Reference**
Formaldehyde	C H2 O	50-00-0	8.13E-12	9.37E-12	9.37E-12	Atkinson et al. (2001)
Methanol	C H4 O	67-56-1	0.62E-12	0.99E-12	0.93E-12	Atkinson et al. (2001)
Ethanedial	C2 H2 O2	107-22-2	25.3E-12	11.4E-12	11.0E-12	Atkinson et al. (1997)
Acetaldehyde	C2 H4 O	75-07-0	17.0E-12	15.8E-12	14.9E-12	Atkinson et al. (2001)
Acetaldehyde, hydroxyl-	C2 H4 O2	146-46-8	23.4E-12	9.90E-12	10.0E-12	Atkinson et al. (2001)
Formamide, N-Methyl-	C2 H5 N O	123-39-7	6.76E-12		8.60E-12	Solignac et al. (2005)
Methanamine, N-Methyl-N-nitroso	C2 H6 N2 O	62-75-9	2.53E-12	2.53E-12	3.01E-12	Tuazon et al. (1984)
Methanamine, N-Methyl-N-nitro	C2 H6 N2 O2	4164-28-7	3.83E-12	3.84E-12	4.5E-12	Tuazon et al. (1984)
2-Propanone	C3 H6 O	67-64-1	0.20E-12	0.22E-12	0.22E-12	Atkinson et al. (1997)
Formamide, N,N-Dimethyl-	C3 H7 N O	68-12-2	17.5E-12		14.0E-12	Solignac et al. (2005)
Acetamide, N-Methyl-	C3 H7 N O	79-16-3	6.16E-12	5.20E-12	5.20E-12	Koch et al. (1997)
Acetamide, N,N-Dimethyl-	C4 H9 N O	127-19-5	16.2E-12	13.6E-12	19.0E-12	Solignac et al. (2005)

Comparison of predicted and experimental *k*(OH) of relevant atmospheric degradation products (*Table 2*) shows that the predicted rate constants are at least within factor of two of the experimental values. For many compounds, the predicted rate constants are in excellent agreement with the measured ones, probably due to the fact that experimental data is used in the QSAR procedure (Atkinson SAR). But good agreement is also found in the case of compounds for which experimental data was not included in EPI Suite™, such as N-methyl-formamide and N,N-dimethyl-formamide (*Table 2*).

Experimental evaluation of rate constants with the OH radical is in particular required for those atmospheric degradation products that are expected to have a high toxicological potential such as the respective nitroso compounds (nitrosamines and nitramines). No experimental data is currently available for the nitrosamines and nitramines predicted to form in the OH-initiated oxidation of MDEA, AMP, and piperazine.

2.5 Experimental and theoretical rate constants for process degradation products

The process degradation products identified for the four parent amines include aldehydes, organic acids, amides, nitrosamines, nitramines, alcohols and other aliphatic amines. Of particular concern for human health effect are nitrosamines and nitramines and well as certain amides and aldehydes. These compounds are known to be carcinogenic, and their emission levels and atmospheric residence times need to be determined for risk assessment. In the following we consider only gas phase chemical removal, and for many compounds, the primary atmospheric gas phase removal process is reaction with the hydroxyl radical (OH). OH radicals are formed photochemically during the daylight hours, and the average concentration in the Mongstad region is $\sim 5\times10^5$ molecules cm^{-3}.

The observed process degradation products can degrade in the gas phase after emission and form further secondary degradation products. The main concern for health and safety are nitramines and nitrosamines. These are formed in the photochemical degradation of an amine by H-abstraction from the amine group by a radical followed by reaction with NO and NO_2. The simplest reaction scheme for a primary or secondary amine is as follows:

$$R_2NH + X \longrightarrow R_2N\cdot + HX \quad (R3)$$
$$R_2N\cdot + NO \longrightarrow R_2NNO \quad (R4)$$
$$R_2N\cdot + NO_2 \longrightarrow R_2NNO_2 \quad (R5)$$

In this case the H-abstraction occurs from the amine nitrogen, but it can also occur from the alkyl groups which leads to complex degradation schemes, but no important pathways to form nitrosamines and nitramines. Formation of these compounds can only happen via hydrogen-shift reactions in some degradation products that aren't energetically feasible under atmospheric conditions (Nielsen et al., 2010). The branching ratio between H-abstraction from the nitrogen and the alkyl groups is needed to assess the potential to form nitramines and nitrosamines. For alcohols, abstraction from the OH-group is a very minor pathway, but there are no reliable studies of the extent of H-abstraction from the amine hydrogen. Primary amine alkanolamines however lead to the formation amides which in turn form nitramines. Cl and NO_3 radicals react by hydrogen abstraction similarly to OH, and in most cases the reaction pathways can be expected to be similar. However this should be verified by quantum chemical mechanistic studies and experimental product studies.

In general, very little data for the OH reaction rate is available for the process degradation products. All four parent amines, Piperazine, MEA, MDEA and AMP, lead to the emission of certain small molecules such as formaldehyde, acetaldehyde, methylamine and other small aliphatic amines and for these the OH rate constants are well established (R. Atkinson 2008). For the parent amines themselves only the rate for AMP has been measured (Harris and Pitts 1983). For the nitrosamines and nitramines, the OH rate has been indirectly measured in a smog chamber for N-nitrosodimethylamine and dimethylnitramine(Tuazon, Carter et al. 1984), for the remaining compounds there is no data available. For MEA a number of larger aliphatic amines are formed during the process and these are generally known to react with OH with rates of the order of $1\text{-}7\times10^{-11}$ $molecule^{-1}$ cm^3 s^{-1} (Bråten et al., 2008, Bunkan et al. 2009).
For those compounds for which no experimental rate data is availble, the rates have been estimated using the EPI Suite™ which employs a quantitative structure-activity relationship (QSAR) method as described in section T3.

Table 3*: OH reaction rates of 11 identified nitrosamines and nitramines estimated by the EPI Suite™***.** *For all other process degradation products the rates are given in the detailed spreadsheet.*

Process Degradation Product	**Parent amine**	***k*(OH) molecule^{-1} cm^{3} s^{-1}**	***k*(OH)** Tuazon et al. (1984)
1-nitrosopiperazine	Piperazine	1.06E-10	
1,4 dnitrosopiperazine	Piperazine	4.27E-11	
1-nitropiperazine	Piperazine	1.07E-10	
1,4 dinitropiperazine	Piperazine	4.53E-11	
N-nitrosodimethylamine	Piperazine, MEA, MDEA, AMP	2.53E-12	3.01E-12
methylnitramine	Piperazine, MEA, MDEA, AMP	1.30E-13	4.5E-12
dimethylnitramine	Piperazine, MEA, MDEA, AMP	3.83E-12	
N-nitroso ditethanolamine	MDEA	2.97E-11	
2-(methylnitrosoamino) ethanol	MDEA	1.61E-11	
4-nitroso-morpholine	MEA	7.48E-11	
2-(nitroamino) ethanol	MEA	1.48E-11	

It should be noted that the QSAR calculations produce very fast reaction rates for the piperazine degradation products that may not be very accurate. It is not obvious based on the molecular structure why 1,4 dinitrosopiperazine should react a factor of 10 faster with OH than N-nitrosodimethyl amine, and it should be given high priority that these reaction rates be checked experimentally.

In addition to OH reactions, photolysis and reactions with chlorine radicals (Cl), ozone (O_3) and nitrate radicals (NO_3) can be important chemical removal processes. Cl radicals are produced photochemically during daylight hours in coastal areas, and could potentially be a significant removal process at the Mongstad location. The NO_3 radical is the most important reactant at night at concentrations around 100 times the daytime OH concentration (2.5×10^{8} molecules cm^{-3}). Ozone initiates complex series of reactions with unsaturated compounds such as imines, and for these species the ozone reaction and its possible products should be considered. For the identified process degradation product NO_3 and Cl rate data is available for ammonia, formaldehyde, acetaldehyde and formic and acetic acid (R. Atkinson 2008). For all other process degradation products as well as the parent amines there's no available data.

2.6 Atmospheric half-life/lifetimes of nitrosamines and nitramines

The atmospheric lifetime of a molecule is the measure for how long an emitted or produced compound remains in the atmosphere until it is destroyed or removed. In terms of human exposure to harmful compounds the atmospheric lifetime is a determining factor for the risk assessment of a species. How long a molecule resides in the atmosphere is governed by many different complex processes such as transport, gas phase chemistry, aerosol and cloud chemistry, photolysis, emission and deposition. In order to better understand these processes one can use models to solve mathematical equations that represent these processes. In this way, many scenarios can be explored without performing costly laboratory experiments or field measurements. Results from the models can be used to identify the processes most important to validate. Atmospheric models range in scale from global models to small box models and cover times scales ranging from fractions of seconds to several years. Larger models include atmospheric physics and transport, whereas smaller models are useful for studying individual processes in more detail.

For the present purpose a zero-dimensional box-model has been constructed to study the chemistry of the process degradation products of the four parent amines. Such a model can later be incorporated in a larger scale model. The model includes at present 179 chemical reactions involving the identified process degradation products and, where known, their secondary degradation products. All of these compounds react with the OH radical and for those with known rate constants for NO_3 and Cl these have been included. The OH reaction rates were taken from the literature where available, otherwise they were obtained by QSAR calculations (S.P. Sander 2006; R. Atkinson 2008). The Cl rate constant has been crudely estimated for the model for N-nitrosodimethylamine by extrapolating from the OH data. The photolysis data in the model have been generated by the NCAR Tropospheric Ultraviolet and Visible (TUV) Radiation Model (NCAR) for the geographical location of the Mongstad plant. Initial concentrations of other atmospheric species (H_2O, NO_x, etc.) have been taken from literature(Seinfeld and Pandis 2006). Very limited data for the emitted concentrations of process degradation products is available, these were based on the assumption that the emissions are proportional to the vapour pressure of the compounds.

The atmospheric lifetime of a molecule with respect to OH degradation is usually expressed as $\tau_{OH}=1/(k(OH)*[OH])$, where k(OH) is the rate of reaction with OH and [OH] is the average tropospheric OH concentration. For the present initial tests of the model, the lifetimes of the process degradation products have been determined by the model and compared to the standard lifetime.

Table 4*: Atmospheric lifetimes in hours of nitramines and nitrosamines produced in the process, τ_{OH}, based on the average tropospheric OH concentration, 1.5×10^{6} molecules cm^{-3}, and those determined by the chemical reaction model using flux data for Mongstad at 60.8°N.*

Compound	τ_{OH} 1/(*k*(OH)×[OH])	τ_{OH} Model	*k(OH)*
1-nitrosopiperazine	1.8	4.5	1.06E-10
1,4 dnitrosopiperazine	4.3	9.9	4.27E-11
1-nitropiprazine	1.7	4.0	1.07E-10
1,4 dinitropiperazine	4.1	9.4	4.53E-11
Nnitrosodimethylamine	61.7	165.4	2.53E-12
Methylnitramine	1424.5	2217.1	1.3E-13
Dimethylnitramine	41.2	116.0	3.83E-12
N-nitroso ditethanolamine	6.2	13.4	2.97E-11
2-(methylnitrosoamino) ethnol	12.5	29.9	1.61E-11
4-nitroso-morpholine	2.5	5.9	7.48E-11
2-(nitroamino) ethanol	11.5	26.4	1.48E-11

It is worth noting that, 1) the model predicts longer lifetimes than the lifetime calculated based on the rate and, 2) the lifetimes vary widely from 4 hours to ~92 days. The model predicts longer lifetimes simply because the OH concentrations calculated by the model are lower than the tropospheric average. This is because the solar flux at 60.8°N is lower than average and hence the concentration of radicals is lower. This illustrates that using the standard lifetime can lead to compounds being classified as short-lived, when in fact they might not be at high latitudes. The model and the standard lifetime is based on the same *k*(OH) data. For these nitrosamines and nitramines, no experimental rate data is available and QSAR predicted rate constants have been used. As discussed in section T12 the reliability of the QSAR data for nitrosamines and nitramines is essentially unknown. The very slow reaction rate predicted for methylnitramine which corresponds to a lifetime of 92 days is questionable and it is recommended that high priority is given to test this rate as methylnitramine is toxic and is produced from all four parent amines. In contrast, the cyclic piperazine derivatives have very fast reaction rates according to the QSAR calculation and corresponding very short lifetimes of a few hours.

The chemical reaction model is a useful tool for studying chemical degradation schemes and lifetimes of species based on site-specific flux data and temperatures. It can form a part of a test protocol for risk assessment of emitted compounds, however the quality of the results depends on the quality of the reaction rate data. It is imperative to verify the OH reaction rates experimentally for at least some of these compounds for use in modelling. It can also be used for quantitative modelling of compounds after emission for comparison with toxicological limit values, but the quality of such results are dependent on accurate measurements of the concentrations of emitted compounds. It is recommended that measurements of emitted concentrations be made from a full-scale test plant at the earliest possible stage.

2.7 Determination of photolysis rates

In addition to reaction with OH and other radicals, certain compounds can be broken down in the atmosphere directly by UV light. Photolysis can be the dominant removal process so it is important to evaluate the photolysis rate for each important compound to establish the atmospheric lifetime. UV transitions in a molecule correspond to electronic excitations between the energy levels that correspond to the molecular orbitals of the system. In particular, transitions involving p orbitals and lone pairs are important for the range of light available in the troposphere. The unit of the molecule that is responsible for the absorption is called the chromophore, of which the most common are C=C (π to π *) and C=O,N,S (n to π*) systems. Aliphatic compounds can only undergo $\sigma \rightarrow \sigma^*$ transitions, and compounds with non-bonding electrons such as amines can undergo $n \rightarrow \sigma^*$ transitions. Both of these require higher energies and hence shorter wavelengths (< 250 nm) than are available in the troposphere so these compounds do not photolyze to a significant degree. Tropospheric photolysis of organic compounds is thus based on transitions of *n* or π electrons to the π^* excited state which generally happen at wavelengths >300 nm. These transitions occur in unsaturated compounds such and alkenes and also in e.g. nitrosamines.

The parent amines are thus not expected to photolyze in the troposphere, but some of the degradation products, such as aldehydes, nitramines and particularly nitrosamines can be expected to photolyze. The only available UV data for the relevant nitrosamines are for N-nitrosodimethylamine (Bamford 1939; Lindley, Calvert et al. 1979; Tuazon, Carter et al. 1984). Tuazon *et al*. established that the photolysis rate of N-nitrosodimethylamine was very fast, of the order of minutes under average conditions. The photolysis rate of a compound depends on the absorption cross section of the molecule and the amount of radiation available. For the Mongstad location, which is at high latitude, the amount of radiation varies widely throughout the year (Figure 1). It is therefore important to consider the photolysis lifetime at maximum radiation in the summer as well as at the minimum in winter. Photolysis might be an important removal process in summer but not in winter, at which time other removal channels have to be considered.

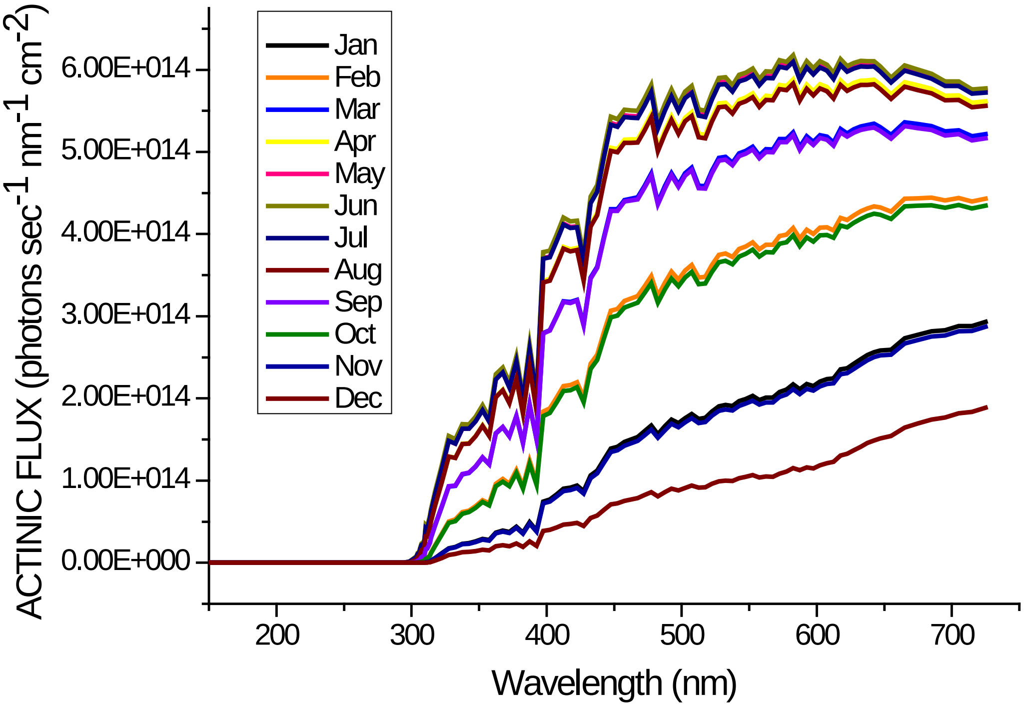


***Figure 2:** The solar flux at midday at the Mongstad site (60.8°N;5.03°E) for each month of the year 2008.*

The lifetimes with respect to photolysis for some of the process degradation products are estimated from UV spectra calculated by ab initio methods. The UV spectra are used to determine the photolysis rates of the compounds. The photolysis rate constant, J, is calculated using the following expression:

$$J = \int I(\nu)\Phi(\nu)\sigma(\nu)\, \mathrm{d}\nu \qquad \text{(Quantum yield, } \Phi(\nu) = 1)$$

Where I(v) is the solar flux at a given time of the year and sigma(v) is the absorption cross section from the spectrum. The quantum yield $\Phi(\nu)$ is assumed to be 1, an assumption which is supported by an experimentally determined value of 1.03 ± 0.10 for N-nitrosodimethylamine (Geiger and Huber 1981). The solar flux data is calculated using the NCAR TUV model for the Mongstad location (NCAR). Excitation energies and oscillator strengths are calculated in the Gaussian package by the B3LYP method and using a 6-311G++ basis set (Frisch, Cheeseman et al. 2003). This is a lower level of theory which can give a good indication of what the spectra will look like, although an error margin of ±25nm is typically to be expected. Similar calculations at a higher level have been used previously to calculate UV-spectra with good results (Christiansen and Jorgensen 1998; Christiansen, Gauss et al. 1999; Lane and Kjaergaard 2008; Yekutiel, Lane et al. 2010). The absorption cross sections are obtained by convoluting the obtained line spectrum with a broadening Gaussian band profile. These are relatively fast, low-level calculations that are sufficient for an initial evaluation of the photolysis rates of the compounds of interest. The cross sections can be more accurately determined by state of the art calculations at the CC3 level of theory but this is computationally more costly.

Table 5*: Photolysis lifetimes in summer and winter of 11 nitrosamines and nitramines that have been identified as process degradation products. The UV spectra have been calculated at the B3LYP(6-311G++) level, and photolysis rates calculated bases on solar flux data from the NCAR TUV model for the two seasons in the year 2008 (NCAR).*

Process Degradation Product	***Lifetime summer (hrs)***	***Lifetime winter (hrs)***
1-nitrosopiperazine	9.54E-04	1.60E-02
1,4 dnitrosopiperazine	1.45E-03	2.80E-02
1-nitropiperazine	1.51E-04	3.46E-03
1,4 dinitropiperazine	7.85E+01	1.40E+03
N-nitrosodimethylamine	4.08E-03	6.42E-02
methylnitramine	9.65E+01	1.52E+03
dimethylnitramine	8.68E+01	1.37E+03
N-nitroso ditethanolamine	4.29E-04	6.76E-03
2-(methylnitrosoamino) ethanol	3.48E-03	5.49E-02
4-nitroso-morpholine	2.62E-03	4.13E-02
2-(nitroamino) ethanol	1.06E+02	1.66E+03

For the present purposes the lifetimes have been determined for mid-June and mid-December for 11 nitrosamines and nitramines that have been observed as degradation products at the pilot plant (Table 5). The calculated spectra for all 11 species are shown in Appendix VIII, two examples are shown in Figure 3. The calculated lifetime of N-nitrosodimethylamine is 15 seconds in summer and just under four minutes in winter so this compound can be assumed to photolyze very rapidly which lowers the potential risk to humans and the environment. The other nitrosamines have similar short lifetimes which is consistent with the -N-N=O chromophore absorbing light in the 300-400 nm region. The nitramines on the contrary are very long-lived with respect to UV light and the spectra exhibit no absorption features at wavelengths longer than 300 nm where there is radiation available (*Figure 2*). The one exception is 1-nitropiperazine which does have a higher absorption cross section than the other nitramines in the 320 nm region. This result should ideally be verified by a higher-level calculation or a direct measurement. The photolysis lifetimes of the other nitramines are around 100 hours in summer and they therefore will be removed by other means.

The lifetime with respect to photolysis should be considered as part of the test protocol for the risk of these compounds. If the compound is photolyzed very rapidly it is not necessary to consider its further atmospheric fate. However, if photolysis is slow for all or part of the year, then other removal processes will dominate. Calculations of the UV spectra can be carried out initially at a low level as has been done in the present study to determine which compounds absorb in the relevant region of the spectrum (wavelengths longer than 300 nm) and which ones absorb near the edge of this region. For those compounds a complete quantum chemistry study should be carried out, including calculations at the benchmark (CC3) level, for the most accurate results possible.

Ideally, the UV spectra and cross sections should be measured in the laboratory for these compounds. Some compounds have relatively low vapour pressures that can make it difficult to keep a stable pressure in a small gas cell. For these compounds theoretical calculations of the UV spectra might be more practical.

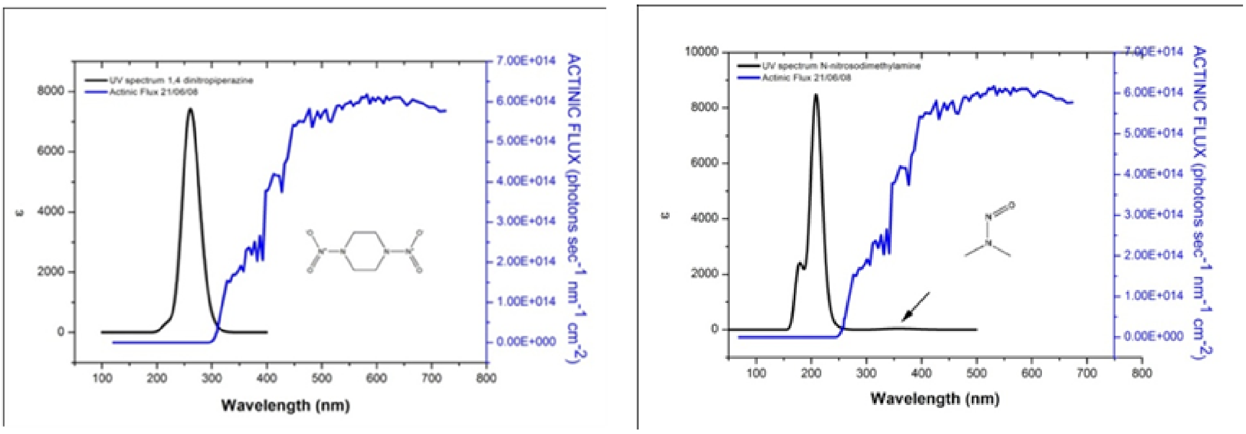


__Figure 3:__ The calculated spectra of N-nitrosodimethylamine and dinitropiperazine shown with the solar flux (for June 21st 2008). The spectrum for N-nitrosodimethylamine has an absorption feature around 350 nm which make the compounds will photolyze rapidly. Dinitropierazine has no absorption features in the region where there is available sunlight.

2.8 Environmental fate of atmospheric degradation products in soil and water

Atmospheric degradation products are defined in this project as the reaction products of the parent amines with atmospheric oxidants (OH, NO_3, O_3, halogen atoms) under atmospheric conditions (temperature, pressure, etc.). During daytime, reaction of amines with the hydroxyl radical (OH) is the most important atmospheric gas-phase degradation pathway for gas-phase amines (Bråten et al., 2008). Predicted atmospheric degradation products from the reaction of amines (MEA, AMP, MDEA, and Piperazine) with OH radicals were based on CO2&Amines phase I report on theoretical chemistry (Bråten et al., 2008). During night-time, the most important atmospheric gas-phase degradation pathway for amines is the reaction with nitrate (NO_3) radicals. NO_3 radicals are present in the atmosphere during night time. NO_3 radicals photolyze rapidly in sunlight and hence are not present in the atmosphere during the sunlit period of the day. The atmospheric degradation products from this reaction might be the same as in the reaction with OH, but additional products like organic nitrates may form. Possible products from the reaction with NO_3 have not been studied in the report by Bråten et al. (2008) and therefore could not be included here. In the marine boundary layer halogen chemistry can be important.

The environmental fate of predicted atmospheric degradation products in air, soil and water was evaluated based on available data records in TOXNET (http://toxnet.nlm.nih.gov/). Both abiotic and biotic degradation of predicted atmospheric degradation products was retrieved from the TOXNET database. Environmental fate data was not available for all of the atmospheric degradation compounds included in the CO2&Amines phase I report. On the other hand, all relevant information for the major products from MEA, like formamide and formaldehyde, was found. It is noted that the rate constant for the reaction of formamide with OH in the TOXNET database is predicted using a structure activity relationship (SAR) method and not determined experimentally.

The complete list obtained from the TOXNET search is included in the Appendix IX.

In the atmosphere the fate is determined by abiotic processes:

- the reaction with the hydroxyl radical (OH),
- the reaction with ozone (O_3),
- the reaction with the nitrate radical (NO_3) at night,
- *the reaction with halogen atoms like Cl, Br, and I*,
- the photolysis in sunlight,
- the gas phase/particle partitioning controlled by its vapour pressure,
- *the uptake into the liquid phase of aerosols and clouds.*

Items in italic are not included in the TOXNET database.

In general the atmospheric processing leads to the formation of increasingly water soluble products which are scavenged by dry and wet deposition. OH radicals are often referred to as being the detergents of the atmosphere which remove all harmful pollutant within relatively short time. The OH concentration characterizes the self-cleansing capability of the atmosphere.

In the aqueous environment the fate is determined by:

- the volatilization from the water surface,
- the retention on suspended solids and in the sediments,
- abiotic processes (hydrolysis, photolysis, etc.),
- biodegradation,
- bioconcentration in aquatic organisms.

In the terrestrial environment the fate is determined by:

- the volatilization from the soil surface,
- biodegradation,
- retention in soil minerals or humic soil constituents.

The abiotic fate in soil is not included in the TOXNET database. Degradation of organic compounds in soil predominantly occurs through microbial activity and abiotic processes are slower than the biotic processes. As an example, it has been found that formaldehyde readily biodegrades under both aqueous aerobic and anaerobic conditions. Soil properties like pH, anaerobic or aerobic conditions, soil texture, and soil organic matter content affect the fate of organics in the terrestrial environment.

2.9 Environmental fate of process degradation products in soil and water

The environmental fate of the predicted process degradation products in soil and water was evaluated based on theoretical data generated by the EPI Suite™ *programmes* (US EPA, 2009a). A list of the programmes used and the parameters evaluated are given below in *Table 6*.

Table 6: *EPI Suite™ programs used to assess the environmental hazard associated with the process degradation products and the parameters they estimate.*

EPI Suite™ Program	Parameters calculated
KOWWIN Program (v1.67)	Octanol/water partition coefficient (Log K_{ow})
WSKOWWIN Program (v1.41)	Water Solubility at 25 °C (mg/L)
ECOSAR Program (v0.99h)	Fish 14-day LC50 (mg/L or ppm) Fish 96-hr LC50 (mg/L or ppm) Daphnid 48-hr LC50 (mg/L or ppm) Green Algae 96-hr EC50 (mg/L or ppm) Green Algae 96-hr ChV (mg/L or ppm) Fish ChV 30-day (mg/L or ppm) Daphnid 16-day EC50 (mg/L or ppm) Fish (SW) 96-hr ChV (mg/L or ppm) Mysid Shrimp 96-hr LC50 (mg/L or ppm) Earthworm 14-day LC50 (mg/kg or ppm dry wt soil)
BIOWIN Program (v4.10)	Biowin1 (Linear Model Prediction) Biowin2 (Non-Linear Model Prediction) Biowin3 (Ultimate Biodegradation Timeframe) Biowin4 (Primary Biodegradation Timeframe) Biowin5 (MITI Linear Model Prediction) Biowin6 (MITI Non-Linear Model Prediction) Biowin7 (Anaerobic Model Prediction) Ready Biodegradability Prediction
PCKOCWIN Program (v1.66)	K_{oc} (Soil adsorption coefficient)*
HYDROWIN Program (v1.67)	Aqueous hydrolysis rate constant Aqueous hydrolysis half-life (days)
BCFWIN Program (v2.17)	Bioconcentration factor (BCF) Log BCF

*the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium.

2.9.1 Octanol/water partition coefficient (K_{ow})

The water solubility and K_{ow} are closely linked parameters which are dependent upon the physico-chemical characteristics of a given chemical. Knowledge of the physical and chemical properties of a chemical can give significant insight into:

- Partitioning in the environment
- Potential for environmental exposure
- Potential routes of human exposure
- Toxicity and biological effects

K_{ow} is a physical property used extensively to describe a chemical's lipophilic or hydrophobic properties. It is the ratio of a chemical's concentration in the octanol-phase to its concentration in the aqueous phase of a two-phase system at equilibrium. Determination of K_{ow} provides information on how a chemical will partition between a highly non-polar organic media (e.g. octanol) and a highly polar media (e.g. water). This information effectively provides the concentration of the chemical in octanol and in water (e.g. water solubility). Since measured values range from $<10^{-4}$ to $>10^{8}$ (at least 12 orders of magnitude), the logarithm (Log K_{ow}) is commonly used to characterize its value (US EPA, 2005; 2006a).

K_{ow} can be used to estimate how a chemical partitions in biological systems and potential for absorption through membranes. In this case octanol is used to mimic the fat present in organisms. The higher the K_{ow}, the more likely a chemical will partition to octanol and, therefore, be present in fat. The lower the K_{ow}, the more likely a chemical will partition to water and, therefore, be present in the body tissues. As a result K_{ow} can be used directly to calculate/estimate a number of other properties essential for environmental risk assessment (US EPA 2006a):

- Water solubility
- Bioconcentration
- Soil adsorption
- Aquatic toxicity

The US EPA (2006a) provides a summary and interpretation of the log K_{ow} values (*Table 7*). Low log K_{ow} values (<1) indicate a chemical is highly soluble in water (hydrophilic), and will therefore partition into aqueous media where available. This will mean a chemical is very mobile in the environment, but also likely to be dispersed to low concentrations in large bodies of water. Furthermore, the high water solubility means such chemicals are likely to be very bioavailable, although unlikely to bioaccumulated in organisms. Medium log K_{ow} values (2-6) indicate a chemical will not be very soluble in water (hydrophobic), and will therefore partition to organic media. In general, the chemical is less likely to exhibit significant mobility through the environment and may remain concentrated in small areas. Although increased hydrophobicity leads to low aqueous concentrations and therefore low bioavailability, any of the chemicals dissolved in water will rapidly partition into the tissue of exposed organisms and is a potential for bioaccumulation and bioconcentration. However, log K_{ow} values can result in quite different behaviour within this range. Liquids with a log K_{ow} of 2-4 tend to absorb well through the skin. Chemicals with a log K_{ow} > 4 tend to not absorb well. Chemicals with a log K_{ow} of 5-6 tend to bioconcentrate. In contrast, high log K_{ow} values (>8) are not bioavailable as they are essentially insoluble in water.

Table 7: *K_{ow} classifications as recommended by the US EPA (2006a).*

Log K_{ow}	Indicates to the Assessor:
<1	Highly soluble in water (hydrophilic)
>4	Not very soluble in water (hydrophobic)
>8	Not readily bioavailable
>10	Difficult to measure experimentally. Essentially insoluble in water. Not bioavailable.

In the case of the present study, a range of log K_{ow} values were returned by EPI Suite™ for the parent amines and process degradation products studied. However, all of the log K_{ow} values were below 1 indicating that the chemicals involved with CO_2 capture would be highly hydrophilic. For some of the studied chemicals EPI Suite™ also reported experimentally determined log K_{ow} values. In general there was good agreement between the predicted and experimental values. This indicates that the use of predicted values for chemicals where no experimental data is available can be considered reliable. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document.

The low log K_{ow} values for the studied chemicals indicate they are highly soluble in water (hydrophilic), and will therefore partition into aqueous media where available. As a result these chemicals are expected to be very mobile in the environment, quickly being dispersed to low concentrations in large or moving bodies of water. The high log K_{ow} values also indicate that the chemicals are likely to be very bioavailable, with the potential to be present in the body tissues. However, this also means that they are unlikely to bioaccumulate/bioconcentrate in fat stores within organisms. Although the low log K_{ow} values do imply parent amines and their process degradation products will be bioavailable, rapid transport and dispersion through aqueous compartments, together with the low potential for bioconcentration indicate that these compounds are in general not hazardous. However, release to, and accumulation in groundwaters and drinking waters should be considered further. A key issue in assessing the risk of individual parent amines and process degradation products will be to understand their individual toxic or non-toxic nature.

2.9.2 Water solubility

Water solubility plays a major role in defining the movement, distribution and ultimate fate of chemicals in the environment. For example, high solubility leads to rapid distribution in water, i.e., chemicals will be transported along with the general flow of water. High solubility is generally associated with a very low affinity for adsorption to solids in water (e.g. soil particles or sediment). Determining water solubility provides the degree to which a chemical will dissolve in 1 L of water. Water solubility can be effectively calculated for a compound if the K_{ow} is known, although more accurate data can be achieved if melting point values are also available. Water solubility can also significantly affect the degradation potential of a chemical. Water insoluble chemicals may not degrade in the environment as micro-organisms may be unable to absorb them. Higher water solubility values are generally associated with more rapid (ready) biodegradation (US EPA 2005; 2006a).

The water solubility of a chemical also indicates to the assessor the potential for environmental exposure through release to aquatic compartments and the risk of human exposure through ingestion of drinking water. Environmental exposure occurs when a water soluble chemical is present in surface waters (e.g. lakes and rivers). Human exposure occurs through ingestion of drinking water contaminated by the water soluble chemical (often sourced from reservoirs or groundwater). A water solubility value of <0.01 mg/L is suggested by the US EPA as the lower limit of concern for adverse affects, aquatic exposure and general population exposure (US EPA 2005; 2006a).

The US EPA (2006a) provides a summary and interpretation of water solubility values (*Table 8*). Chemicals with high water solubility values (e.g. >1,000 mg/L) have a greater possibility of human and aquatic exposure, and are more likely to be absorbed through gastro-intestinal tract or lungs. However, high water solubility is associated with limited bioconcentration in organisms. Chemicals with a low water solubility (e.g. <1 mg/L) are less likely to be absorbed into tissues, but do have a higher potential to bioconcentrate within organisms. The distribution of a chemical between different environmental compartments can also be accurately predicted from water solubility. Higher water solubilities indicate partitioning to water phases which can result in removal from soil into ground water by rain runoff and removal from the atmosphere into ground water by rain washout.

Table 8: *Water solubility classifications as recommended by the US EPA (2006a).*

Water solubility (mg/L)	Classification
>10,000	Very soluble
>1,000 – 10,000	Soluble
>100 – 1,000	Moderately soluble
>0.1 – 100	Slightly soluble
<0.1	Insoluble

In the case of the present study, the water solubility values were returned by EPI Suite™ for the parent amines and process degradation products studied ranged between 10^{+4} mg/L to $>10^{+6}$ mg/L. As all log K_{ow} values are above 10^{+3} mg/L, the chemicals involved with CO_2 capture are considered as water soluble. For some of the studied chemicals EPI Suite™ also reported experimentally determined water solubility values. In general there was good agreement between the predicted and experimental values (within an order of magnitude). This indicates that the use of predicted values for chemicals where no experimental data is available can be considered reliable. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document.

The high water solubility values for the studied chemicals indicate they will be rapidly distributed/dispersed in water and transported along with the general flow of water. They will exhibit a very low affinity for adsorption to solids in water (e.g. soil particles or sediment), implying rapid removal from soil into groundwater by rain runoff and removal from the atmosphere into ground water by rain washout. The high water solubility values suggest rapid biodegradation is possible, although this will still depend highly on the chemical structure of the chemical in question. Chemicals with water solubility values (e.g. >1,000 mg/L) have a greater possibility of human and aquatic exposure. For the chemicals studied, environmental exposure is expected to occur as highly water soluble chemicals are often present in surface waters (e.g. lakes and rivers). Similarly, there is a potential for human exposure through ingestion of drinking water containing these chemicals. However, bioconcentration of these chemicals in organisms in not predicted. Chemicals with a water solubility value of <0.01 mg/L is suggested by the US EPA as the lower limit of concern for adverse affects, aquatic exposure and general population exposure. All of the chemicals studies exhibited water solubilities orders of magnitudes higher than 0.01 mg/L and so are therefore considered a concern. Release to, and accumulation in groundwaters and drinking waters should be considered further, together with understanding their individual toxic or non-toxic potential.

2.9.3 Biodegradation

In order to complete a thorough QSAR assessment of the environmental fate of a compound, biodegradation processes must be considered. Biodegradation is widely recognised as one of the most important degradation and removal routes for chemicals released into the environment. The other major degradation routes are abiotic processes, comprising hydrolysis, photolysis and chemical decomposition. As a result, biodegradation features as a major parameter in all environmental risk assessment documents (e.g. EU TGD, 2003 and US EPA, 2005; 2006b).

Determining the biodegradation of a chemical provides the assessor with an indication of the persistence in soil, water, and sediment. Where relevant, it can also provide an estimation of the amount of a chemical that may be removed in sewage treatment plants. Biodegradation can be ‘aerobic’, which occurs in oxygenated environments such as surface water and soil, or anaerobic, which occurs in oxygen-free systems such as sediment and groundwater. Anaerobic biodegradation is generally much slower than aerobic degradation. The degree of degradation to which a compound undergoes can be classified in a number of ways. The most commonly used terms are ‘primary biodegradation’ and ‘ultimate biodegradation’. Primary biodegradation is the initial step in the degradation process and results in the formation of a new compound. Ultimate biodegradation meanwhile, is the complete mineralisation of the study compound to CO_2 and water (US EPA, 2006b). The EU TGD (2003) suggests that biodegradation >20% may be regarded as evidence of inherent, primary biodegradability, whereas biodegradation above 70% may be regarded as evidence of inherent, ultimate biodegradability.

The EPI Suite™ (2009a) Biodegradation Probability Program (BIOWIN) provides estimates of biodegradability useful in chemical screening, including the likelihood of passing a ready biodegradability test plus the approximate time required for a compound to biodegrade in a stream. Biodegradation is the destruction of a compound by biota, typically microorganisms, in the environment (US EPA, 2005). The current BIOWIN (v4.02) program contains six separate models, designated as follows (see also Boethling et al, 2003):

Biowin1 = linear probability model
Biowin2 = nonlinear probability model
Biowin3 = expert survey ultimate biodegradation model
Biowin4 = expert survey primary biodegradation model
Biowin5 = Japanese MITI linear model
Biowin6 = Japanese MITI nonlinear model

The linear and non-linear models, called Biowin1 and Biowin2, are based upon fragment constants that were developed using regression analyses (Howard et al., 1992; US EPA, 2005). Biowin3 and Biowin4 estimate the approximate time required for ultimate and primary biodegradation, respectively, of an organic compound in streams (Boethling et al., 1994; US EPA, 2005). Biowin5 and Biowin6 estimate the probability of passing the OECD 301C ready biodegradability test (MITI-1 test). They are based on linear (Biowin5) and nonlinear (Biowin6) regressions of data from the Japanese MITI database (Tunkel et al., 2000; US EPA, 2005).

BIOWIN (v4.02) also had provides a "Ready Biodegradability Prediction" (YES or NO), based on combining the results from Biowin3 and either Biowin5 or 6. This method is based on ready biodegradation data from all six OECD301 test methods plus OECD310 (Boethling et al., 2004), and is considered a stringent test as false positives for ready biodegradability are significantly reduced in number as compared to any individual model (US EPA, 2005; US EPA, 2006b). In addition, BIOWIN (v4.02) also provides an estimate of the potential for a chemical to biodegrade under anaerobic conditions (Biowin7), however this is not discussed within the current study.

The US EPA (2005; 2006b) provide a summary and interpretation of the biodegradation estimates/values generated by BIOWIN.

- Biodegradation Probability > 0.5 from Biowin1 or 2 indicates "Rapid Biodegradation"; for Biowin5 or 6 it indicates "Readily Degradable".
- Biodegradation Probability < 0.5 from Biowin1 or 2 indicates "Not Rapid Biodegradation"; for BIiowin5 or 6 it indicates "NOT Readily Degradable".
- Biodegradation of "weeks" or faster from BIOWIN3 in combination with biodegradation probability > 0.5 from BIOWIN5 (or BIOWIN6) is even more reliable in indicating if a compound is "Readily Degradable".

The ultimate (Biowin3) and primary (Biowin4) biodegradation models provide a semi-quantitative estimate of rate of aerobic biodegradation. The results are converted to a relative time frame, which in turn can be used to estimate half-lives of the chemicals (*Table 9*).

Table 9: *Biodegradation results to half-life as recommended by the US EPA (2006b).*

BIOWIN Output	**Half-Life (days)**
Hours	0.17
Hours to Days	1.25
Days	2.33
Days to Weeks	8.67
Weeks	15
Weeks to Months	37.5
Months	60
Recalcitrant	180

In the case of the present study, the results of the Ready Biodegradation prediction test in BIOWIN have been used to assess the biodegradability of the CO2 capture parent amines and process degradation products. This test has been selected owing to the strict requirements for a chemical achieving a result of ‘readily biodegradable. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document. The chemicals tested showed a distribution between readily biodegradable (YES) and not readily biodegradable (NO). For example, the parent amine piperazine was estimated YES, but all of the predicted process degradation products (nitrosamines and nitramines) were estimated as not readily biodegradable. AMP and one of its process degradation products were estimated to be readily biodegradable, whilst the remaining two process degradation products were not readily biodegradable. MDEA and three of its process degradation products (2 alkylamines and nitrosodiethanolamine) were classed as readily biodegradable. In contrast, the three remaining process degradation products (2 piperazine-based compounds and another nitrosamine) were classed as not readily biodegradable. As there is such a large number of process degradation products predicted for the parent amine MEA, the results are presented in *Table 10*. Of the 25 process degradation products studied, 19 and the parent amine MEA were classed as being readily biodegradable, including the alkylamines. Only 6 of the process degradation products were classed as not readily biodegradable, of which 4 were nitrosamines and nitramines.

All of the parent amines were classed as being readily biodegradable, indicating that these compounds represent less of a hazard in the environment. Based on these results it was possible to calculate the percentage of the process degradation products for each of the parent amines which were classed as readily biodegradable.

MEA = 76%
MDEA = 50%
AMP = 33%
Piperazine = 0%

These data indicate that MEA represents the least hazardous of the parent amines as it produces the fewest number of environmentally persistent process degradation products. In contrast, piperazine appears to be the most hazardous as all of its process degradation products are not readily biodegradable. In most cases, the process degradation products from the different parent amines which were not readily biodegradable comprised of nitrosamine and nitramine compounds. It is therefore suggested that these compounds present the greatest risk from an environmental perspective and thorough experimental assessment is recommended. However, chemicals with very long biodegradation times may be highly persistent in the environment if they are not subject to destruction by other processes such as photolysis, hydrolysis, etc (US EPA, 2005).

Table 10: *Prediction of ready biodegradation for MEA and its associated process degradation products using the BIOWIN program in EPI Suite™.*

Chemical	Ready Biodegradation
MEA	YES
Ammonia	YES
Methylamine	YES
Formaldehyde	YES
Acetaldehyde	YES
Oxalic acid	YES
Oxazolidin-2-one	NO
1-(2_hydroxyethyl)-2-imidazolidinone, HEIA/HEI	YES
N-(2-hydroxyethyl)-ethylenediamine, HEED/HEEDA/AEEA	YES
N-(2-hydroxyethyl)-acetamide/N-acetylethanolamine/HEA	YES
N-(2-hydroxyethyl)-Formamide/N-formylethanolamine/HEF	YES
N,N-di(2-hydroxyethyl)urea/MEA-urea	YES
1-(2-hydroxyethyl)-2-piperazinone	YES
4-(2-hydroxyethyl)-2-piperazinone	NO
Acetone	YES
Nitric acid/Nitrate	YES
Nitrous acid/Nitrite	YES
1-(2-Hydroxyethyl)imidazole/HEI	YES
Dimethylamine	YES
Ethylamine	YES
Diethylamine	YES
N-nitrosodimethylamine	NO
4-nitroso-morpholine	NO
Methylnitramine	NO
Dimethylnitramine	NO
2-(nitroamino) ethanol	YES

2.9.4 Soil adsorption coefficient (K_{oc})

Soil adsorption coefficients (K_{oc}) provide a measure of a chemicals ability to sorb to the organic portion of soil and sediment. Determining the K_{oc} indicates to the assessor the potential for the chemical to leach through soil and be introduced into ground water, the potential for partitioning of the chemical between water and suspended solids and sediment. K_{oc} is an important parameter as strong adsorption of a chemical will impact other environmental fate properties (US EPA 2005; 2006b).

The Soil Adsorption Coefficient Program (PCKOCWIN) estimates the soil adsorption coefficient (K_{oc}) of organic compounds. K_{oc} can be defined as "the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium" (Lyman, 1990); it is represented by the following equation (Lyman, 1990):

$$K_{oc} = \text{(ug adsorbed/g organic carbon) / (ug/mL solution)}$$

The US EPA (2006b) provides a summary of and interpretation of the K_{oc} values (*Table 11*). Low K_{oc} values indicate a chemical will not bind tightly to soil, and will therefore leach into the soil. This will cause a reduction in surface level concentration of the chemical, but could lead to contamination of groundwaters. However, such mobile chemicals will also result in contamination of surface waters with storm runoff. In contrast, high K_{oc} values indicate a chemical will bind tightly to soil, and will therefore be removed from the water column via sorption to sediment and particulate matter. Furthermore, there will be a reduced rate of degradation because the chemical is not available to microorganisms.

Table 11: *K_{oc} classifications as recommended by the US EPA.*

K_{oc} Classifications	**Predicted log K_{oc} Values**
Very Strong	≥ 4.5
Strong	3.5 – 4.4
Moderate	2.5 – 3.4
Low	1.5 – 2.4
Negligible	< 1.5

In the case of the present study, the results of the PCKOCWIN have been used to assess the adsorption of the CO_2 capture parent amines and process degradation products to soil. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document.

For piperazine and its associated process degradation products, log K_{oc} values in the range 1.7 – 2.7. This indicates that all of the compounds exhibit low to moderate adsorption to soils. For AMP and its associated process degradation products, log K_{oc} values in the range 0.3 – 1.5. This indicates that all of the compounds exhibit negligible to low adsorption to soils. For MDEA and its associated process degradation products, log K_{oc} values in the range 0.0 – 1.9. This indicates that all of the compounds exhibit negligible to low adsorption to soils. For MEA and its associated process degradation products, log K_{oc} values in the range 0.0 – 1.7. This indicates that all of the compounds exhibit negligible to low adsorption to soils.

Virtually all of the parent amines and their associated process degradation products have predicted log K_{oc} values which indicate negligible or low adsorption to soils. It is difficult to conclude whether a high or low K_{oc} value is the most hazardous result for the process degradation products. A high K_{oc} indicates that a chemical will be bound to soils and sediments making it less bioavailable (important if it is toxic), less mobile through the environment and unlikely to accumulate in groundwaters. However, it is likely to increase its persistence in the environment for these reasons. A low K_{oc} indicates that a chemical will not bind to soils and sediments, making it more bioavailable (important if it is toxic), more mobile through the environment and likely to accumulate in groundwaters. A key issue in assessing the risk of individual process degradation products will be to understand their individual toxic or non-toxic nature.

A number of other factors which will have an impact on the final K_{oc} values include pH (soil adsorption decrease as ionization increases), clay content (some chemicals may absorb very strongly to high-clay content soils) and bond formation with humic matter (some chemicals may form chemicals bonds with organic matter, decreasing the potential for leaching). It is suggested that these parameters are determined independently in the area local to the Mongstad facility.

It is concluded that this QSAR program is highly suitable for estimating the K_{oc} of the process degradation products relevant to the current project. Further study into the effect of K_{oc} on the process degradation products is recommended.

2.9.5 Aqueous hydrolysis

Aqueous hydrolysis is a chemical reaction in which water reacts with a compound to produce other compounds. The mechanism involves the splitting of a bond and the addition of the hydrogen cation and the hydroxide anion from the water molecule. Determining the aqueous hydrolysis of a compound indicates to the assessor the degree to which the test compound is persistent and when hydrolysis products need to be considered in an environmental risk assessment. When a compound is susceptible to rapid aqueous hydrolysis there is a risk of forming of degradation products which are more hazardous than the parent compound (US EPA 2005; 2006b).

The Aqueous Hydrolysis Rate Program (HYDROWIN) estimates aqueous hydrolysis rate constants for the following chemical classes: esters, carbamates, epoxides, halomethanes and selected alkyl halides. HYDROWIN estimates acid- and base-catalyzed rate constants; it does NOT estimate neutral hydrolysis rate constants. The estimated acid- and base-catalyzed rate constants are used to calculate hydrolysis half-lives and selected pHs (US EPA, 2009a). The US EPA (2006b) suggests that compounds with a hydrolysis half-life of >14 days can be considered as having a low potential to undergo aqueous hydrolysis and should remain as the parent compound.

In the case of the present study, only a very small number of the predicted process degradation products were members of the chemical classes suited for calculation. As a result, no aqueous hydrolysis values were returned for most of the study compounds. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document. However, of the few compounds which did return a value, the estimated half-lives were significantly above these thresholds >1 year.

It is concluded that this QSAR program is not suitable for the process degradation products relevant to the current project. However, the few compounds for which aqueous hydrolysis half-lives could be estimated can be considered as having a low hazard. Further study into the effect of aqueous hydrolysis on the process degradation products is recommended. The focus of these studies should be on those process degradation products which have atmospheric life times of >3 days. Such compounds will not be degraded in the atmosphere and are likely to undergo deposition to terrestrial and aqueous environments. As a result these compounds are of most relevance to environmental fate processes such as aqueous hydrolysis.

2.9.6 Bioaccumulation and bioconcentration

Bioaccumulation, bioconcentration and biomagnification are frequently confused terminologies and often used in correctly. Bioconcentration is the increase in the concentration of a chemical over that in an organism’s surroundings (e.g.,water). Biomagnification is the increase in the concentration of a chemical over that in an organism’s diet. Bioaccumulation is the increase in the concentration of a chemical through all routes of exposure (US EPA, 2006b). Therefore:

Bioaccumulation = Biomagnification & Bioconcentration

The BCF is related to biomagnification effects. Many chemical compounds, especially those with a hydrophobic component partition easily into the lipids and lipid membranes of organisms and bioaccumulate. If the compounds are not metabolised as fast as they are consumed, there can be significant magnification of potential toxicological effects up the food chain. Only minimal experimental and monitoring information has been gathered on the bioaccumulation properties of many currently used chemical compounds.

The EPI Suite™ (2009a) BCFWIN calculates the bioconcentration factor and its logarithm from the log K_{ow}. A bioconcentration factor (BCF) is the ratio (in L/kg) of a chemical’s concentration in the tissue of an aquatic organism (e.g. fish) to its concentration in the ambient water, when exposure of the organism is to waterborne chemicals only (i.e., not to a chemical in the organism’s diet or sorbed to ingested particles). Bioconcentration occurs through gill membranes or other external body surfaces (US EPA, 2005). However no simple “BCF/log K_{ow}” relationship applies at higher values of log K_{ow}, therefore, estimated BCF from BCFWIN is best used only below log K_{ow} 6 (US EPA, 2005). In addition, BCFWIN does not account for metabolism under field conditions; therefore, compounds that metabolise would have a lower BCF than predicted.

The US EPA (2006b) provides a summary of and interpretation of BCF and log BCF values generated by BCFWIN (*Table 12*). It is suggested that compounds with a BCF of <1000 and a log BCF of <3 can be considered as having a low bioaccumulation concern. All of the process degradation products and parent amines studies had calculated BCF and Log BCF values significantly below these thresholds. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document. It is therefore concluded that none of the studied process degradation products are likely to bioaccumulate in aquatic organisms. From this perspective all of the compounds can be considered as being a low bioaccumulation concern and therefore a low hazard.

Table 12: *BCF and log BCF classifications as recommended by the US EPA (2006b).*

Bioaccumulation	Low Bioaccumulation Concern	Bioaccumulation Concern	
Fish BCF	<1000	≥1000	≥5000
Fish log BCF	<3	≥3	≥3.7

2.10 Identification of hazardous process degradation products

The aim of this study was to identify the most hazardous components of the process degradation products by use of a QSAR-based approach. Process degradation products are defined in this project as the reaction products of the parent amines formed within the CO_2 capture process. The predicted process degradation products from the reaction of amines (MEA, AMP, MDEA, and Piperazine) are theorised and reported in Work Package 1. Once released into the atmosphere, these chemicals are subject to both further atmospheric degradation processes (discussed in T1-T8 above) and/or deposition to terrestrial and aqueous (freshwater and marine) environments. Section T9 (above) describes an environmental fate assessment of the parent amines and their associated process degradation products. Using the information generated in the environmental fate study, together with the QSAR data generated for toxicity in this section the most hazardous of the chemicals associated with CO_2 capture will be identified.

2.10.1 Ecotoxicity (aqueous)

The ecotoxicity of the parent amines and predicted process degradation products in soil and water was evaluated based on theoretical data generated by the ECOASR program in EPI Suite™ (US EPA, 2009a). An understanding of the chemical's aquatic toxicity helps the risk assessor estimate if the release of the chemical will adversely affect aquatic biota and the aquatic ecosystem (US EPA, 2005). A full description of the principles behind ecotoxicity tests is beyond the scope of the current study and is a major focus for the CCM 3/TQP Amine 3 project. However, a brief rationale behind toxicity risk assessment is provided herein.

The US EPA (2006c) suggests that ecotoxicological risk assessment should follow three steps:
Toxicity - Identify potential adverse effects and concentrations (effect level) at which effects may occur.
Exposure - How much of the chemical will the environment or human population be exposed to?
Risk Characterization - Compare hazardous effect levels to potential exposure concentrations to evaluate potential risk.

Typically, only aquatic toxicity is studied as most industrial releases go to freshwater. As a result, terrestrial and marine organisms are only assessed on a case-by-case basis depending on release. In order to ensure adequate risk assessment, three trophic levels are usually studied. In freshwater these are fish, aquatic invertebrates (daphnids) and green algae. Toxicity to these surrogate species is then used to predict toxicity to species in the aquatic environment (US EPA, 2006c).

Aquatic toxicity is typically assessed using acute toxicity (short-term exposure) tests which determine effect concentrations (LC50/EC50) for the compound being studied. When possible, chronic toxicity (long-term exposure) tests which are assessed using a chronic toxicity value (ChV) or No Effect Concentration (NOEC) should be completed. As always, use of existing or generation of new experimental ecotoxicity data is preferred. If this is not available, an appropriate analog chemical may be used which is from the same chemical class and exhibits a similar log kow value (US EPA, 2006c). However, not all endpoints are available for the chemical of interest or an appropriate analog, assessing study quality (validity) is not always possible and ChV is not usually reported. In this situation, use of structure activity relationships (SARs) may be the most suitable approach. The acute and chronic toxicity of a chemical to fish (both fresh and saltwater), water fleas (daphnids), and green algae has been the focus of the development of SARs, although for some chemical classes SARs are available for other organisms (e.g., earthworms) (US EPA, 2009b). Although predicted where possible and present in Appendix X, the toxicity data for earthworms is not discussed within the scope of this study.

The EPI Suite™ (2009a) ECOSAR Class Program is a computerized version of the ecotoxicity analysis procedures as currently practiced by the US EPA Office of Pollution Prevention and Toxics (OPPT) when data are lacking for regulatory endpoints (US EPA, 2009b). ECOSAR can predict the potential toxicity of the chemical to plant and animal live in the water body. The model uses measured data to predict toxicity of chemicals lacking data. Acute (48-hr or 96-hr) and Chronic (14-day, 16-day, or 30-day) values in mg/L (ppm) for fish, invertebrate (Daphnids), and green algae are provided (US EPA, 2005). If a chemical is not soluble enough to reach effects concentrations (referred to as “No Effects at Saturation or NES”) this is also indicated. Toxicity is predicted at pH 7, TOC < 2 mg/L, moderate water hardness (150 mg/L CaCO3), with 100% active ingredient assumed (US EPA, 2006c).

The US EPA (2005; 2006c) provides a summary of and interpretation of the acute and chronic toxicity values generated by ECOSAR (*Table 13*). It is suggested that compounds with an acute toxicity of <1 mg/L or ppm are of high concern, those with an acute toxicity of 1 - 100 mg/L or ppm are of moderate concern, and those with an acute toxicity of >100 mg/L or ppm are of low concern. For compounds with a chronic toxicity of <0.1 mg/L or ppm are of high concern, those with a chronic toxicity of 0.1 - 10 mg/L or ppm are of moderate concern, and those with a chronic toxicity of >10 mg/L or ppm are of low concern.

Table 13: *Assignment of toxicity concern levels as recommended by the US EPA (2005; 2006c).*

Concern Level	Acute Toxicity Definition	Chronic Toxicity Definition
High	< 1 mg/L or ppm	<0.1 mg/L or ppm
Moderate	1 - 100 mg/L or ppm	0.1 - 10 mg/L or ppm
Low	>100 mg/L or ppm*	>10 mg/L or ppm*

* no effects predicted at saturation (below the solubility limit); or log Kow is greater than the cut-off of 8

In the case of the present study, the amount of data returned by the ECOSAR program varied considerably between the different parent amines and process degradation products studied. For some chemicals, data was returned for all of the listed acute and chronic tests for each organism used in the program. For other chemicals only a partial data set was returned. These data are presented in the individual chemical information sheets provided in Appendix X at the end of this document.

For the parent amine piperazine and its associated nitrosamine and nitramine process degradation products, the results indicate that in most of the acute and chronic tests all of the studied compounds are considered low concern. Piperazine and 1-nitrosopiperazine were considered a moderate level of concern in some of the tests, including both acute and chronic tests. For the parent amine AMP and its associated process degradation products, the results indicate that all of the compounds studied are classed as being of moderate concern for some of the acute and chronic tests. For the parent amine MDEA and its associated process degradation products, the results indicate that in most of the acute and chronic tests all but two of the studied compounds are considered low concern. The process degradation products methylamine (an alkylamine) and 1,4 dimethylpiperazine were considered a moderate level of concern in some of the tests, including both acute and chronic tests.

As there is such a large number of process degradation products predicted for the parent amine MEA, the results are presented in *Table 14*. Each chemical is listed as being of low, moderate or high concern based upon its ‘worst case’ result from the list of acute and chronic data. For the parent amine MEA and its associated process degradation products, the results indicate an even distribution between low and moderate concern. Of the 25 process degradation products studied, 10 and the parent amine MEA were classed as being of moderate concern in at least one of the acute or chronic tests. Therefore, 15 of the process degradation products were classed as being of low concern. The chemicals classed as being of moderate concern comprised predominantly the alkylamines, nitrosamines and aldehydes.

Based on these results it was possible to calculate the percentage of the process degradation products for each of the parent amines which were classed as being of moderate concern.

Piperazine = 25%
MDEA = 33%
MEA = 40%
AMP = 100%

These data indicate that piperazine represents the least hazardous of the parent amines as it produces the fewest number of process degradation products classed as being of moderate concern. In contrast, AMP appears to be the most hazardous, as all of its process degradation products are considered of moderate concern. In most cases, the process degradation products from the different parent amines which were classed of being of concern were the alkylamines, aldehydes and nitrosamines. It is therefore suggested that these compounds present the greatest hazard from an environmental perspective and thorough experimental assessment is recommended. However, it should be stated that the available data sets for piperazine, AMP and MDEA contained only a very small number of process degradation products compared to the data set for MEA. As a result, the percentage values presented above should not be considered definitive.

Table 14: *Prediction of ready biodegradation for MEA and its associated process degradation products using the BIOWIN program in EPI Suite™.*

Chemical	Ecotoxicity Concern Level
MEA	Moderate
Ammonia	Low
Methylamine	Moderate
Formaldehyde	Moderate
Acetaldehyde	Moderate
Oxalic acid	Low
Oxazolidin-2-one	Moderate
1-(2_hydroxyethyl)-2-imidazolidinone, HEIA/HEI	Low
N-(2-hydroxyethyl)-ethylenediamine, HEED/HEEDA/AEEA	Low
N-(2-hydroxyethyl)-acetamide/N-acetylethanolamine/HEA	Low
N-(2-hydroxyethyl)-Formamide/N-formylethanolamine/HEF	Low
N,N-di(2-hydroxyethyl)urea/MEA-urea	Low
1-(2-hydroxyethyl)-2-piperazinone	Low
4-(2-hydroxyethyl)-2-piperazinone	Low
Acetone	Low
Nitric acid/Nitrate	Low
Nitrous acid/Nitrite	Low
1-(2-Hydroxyethyl)imidazole/HEI	Moderate
Dimethylamine	Moderate
Ethylamine	Moderate
Diethylamine	Moderate
N-nitrosodimethylamine	Moderate
4-nitroso-morpholine	Moderate
Methylnitramine	Low
Dimethylnitramine	Low
2-(nitroamino) ethanol	Low

2.11 Literature review of nitrosamines and nitramines

Of the identified process degradation products, nitrosamines and nitramines are considered some of the most environmentally hazardous and therefore important compounds. The aim of this review is to provide a summary of the available literature specific to nitrosamines and nitramines regarding their environmental occurrence, fate and concentration limits. A study of the toxicity and ecotoxicity of nitrosamines and nitramines is not part of this literature review.

Following an extensive literature search, little information was found regarding the environmental occurrence and fate of nitramine compounds. A significant amount of data was available for nitro-aromatics and cyclic nitramines used as explosives (e.g. RDX, HMX, HIVIX and CL-20). However, many of these compounds are too unrelated (especially in chemical structure) to be of relevance to the current project. No literature directly containing environmental fate information could be found for nitramines.

In contrast, a reasonable quantity of data was available concerning the environmental fate of nitrosamines. However, most of the studies focused on N-nitrosodimethylamine (NDMA), with little information available for other related nitrosamine compounds. NDMA is a carcinogenic by-product of chlorination that is frequently found in municipal wastewater effluent and has therefore been the focus of many studies. Very little data was available for the environmental occurrence and fate of other nitrosamines.

2.11.1 Environmental Occurrence

Mitch and Sedlak (2002; 2004) report that chlorine disinfection of secondary wastewater effluent and drinking water can result in the production of the potent carcinogen N-nitrosodimethylamine (NDMA) at concentrations of approximately 100 and 10 parts per trillion (ng/L), respectively. Laboratory experiments indicated that NDMA formation was occurring during the chlorination of dimethylamine and other secondary amines. Gunnison et al., (2000) report that N-nitrosodimethylamine (NDMA) was detected in groundwater collected from the dewatering and recharge zones of an intercept-and-treat groundwater remediation system. Zhao et al., (2006) where able to determine the presence of NDMA, N-nitrosopyrrolidine (NPyr), N-nitrosopiperidine (NPip) and N-nitrosodiphenylamine (NDPhA) in drinking water samples collected from four locations within the same distribution system. Charrois et al., (2004) studied authentic drinking water samples, and were able to detect N-nitrosodimethylamine (2-180 ng/L) as well as N-nitrosopyrrolidine (2-4 ng/L) and N-nitrosomorpholine (I ng/L.

Rywotycki (2003) suggest that some crop plants (e.g. red beets, carrots, spinach, green peas, turnips, grasses, cereals and cucumbers) can take up and accumulate nitrosamines and similar compounds. The amount of nitrosamines accumulated in plants depends on many physico-chemical factors in soils, such as soil reaction. Nitrosamines have been shown to remain in soils for between 90 and 128 days and in aquatic environment (country wells, lakes, fish ponds and rivers) for 80–110 days (Hill, 1988; Preussman, 1983; Smyk et al, 1990; Wyllie and Morehouse, 1990-1991).

2.11.2 Environmental fate (biodegradation and soil adsorption)

Biodegradation:

Biodegradation of nitrosamines in soils and aqueous systems have been reported (Yang et al, 2005; Kaplan and Kaplan, 1985). However it has also been suggested that high aqueous solubility (a function of the octanol/water partition coefficient; K_{ow}) of nitrosamines means they are not expected to adsorb strongly to soils and may leach out before they have time to biodegrade (Yang et al, 2005). Gunnison et al., (2000) examined the biodegradability of NDMA in soils under aerobic and anaerobic conditions using native microbial consortia. Results indicated a high level of NDMA mineralisation under both aerobic and anaerobic incubations when measured using bench-scale microcosms.

Tate and Alexander (1975) reported that N-nitrosodimethylamine, N-nitrosodiethylamine, and N-nitrosodi-n-propylamine were resistant to degradation in soil and lake water. No degradation of these nitrosamines was observed in lake water during a 3.5-month period. A lag of nearly 30 days occurred before their slow disappearance from soil. Tate and Alexander (1976) studied the microbial degradation of a suite of nitrosamine compounds. *N*-Nitrosodimethylamine was not degraded in flooded soil or in microbial enrichments from bog sediments. In addition, enrichment cultures inoculated with soil and sewage did not yield microorganisms capable of metabolizing *N*-nitrosodimethylamine, *N*-nitrosodiethylamine, or *N*-nitrosodi-*n*-propylamine. The data suggested that the nitrosamines persist in samples of natural environments because of the resistance of the nitrogen-nitrogen bond in nitrosamines.

Drewes et al., (2006) studied the biodegradability of seven N-nitroamine compounds at environmental concentrations and under conditions relevant to groundwater recharge operations. The study used a combination of controlled laboratory-scale soil-column experiments and groundwater monitoring at a full-scale riverbank filtration facility. The results suggested that N-nitrosodimethylamine and six other N-nitrosamines (N-nitrosodiethylamine, N-nitrosomethylethylamine, N-nitroso-n-propylamine, N-nitrosodi-n-butylamine, N-nitrosopiperidine, and N-nitrosopyrrolidine) are biodegradable under oxic and anoxic oxidation-reduction conditions. Half lives determined for these compounds varied between 1.3 and 7 days, indicating removal to below detection limits (<2 ng/L) within short travel times in groundwater recharge systems. The findings suggest that complete removal of N-nitrosamines requires the presence of an adapted biocommunity.

Soil Adsorption:

Gunnison et al., (2000) examined the soil adsorption and desorption properties of NDMA, observing that the sorptive capacity of the soils tested was insignificant for NDMA. Furthermore, the adsorption of the NDMA by the soil was almost completely reversible. Similarly, Gan et al., (2006) report that NDMA is miscible in water and negligibly adsorbed to soil, and therefore may pose a threat to groundwater. A field study to evaluate the leaching potential of NDMA in turfgrass soils was completed. NDMA was detected infrequently in the leachate regardless of the soil type. NDMA was relatively persistent in the turfgrass soils during laboratory incubation, indicating that mechanisms other biotransformation, likely volatilization and/or plant uptake, contributed to the rapid dissipation.

2.11.3 Summary

The literature review work conducted as part of this project is based upon the assumption that nitrosamines are present in terrestrial and aquatic environmental compartment. It does not consider their release to the atmosphere and any atmospheric processes (e.g. degradation) which may occur. Such information and data was not readily available in the literature. The data and information present in the literature review above suggests that the main form of environmental risk associated with nitrosamines is that of water pollution. This conclusion is largely based on the fact that nitrosamines exhibit high aqueous solubilities and low adsorption affinity to soils. Given that likely nitrosamine and nitramine process degradation products will be hydrophilic species, it is expected that natural waters (lakes, groundwater and marine systems) will be the ultimate sink for such chemicals.

No data in the literature suggests bioaccumulation nitrosamine and nitramine is unlikely owing to their inherent hydrophilic properties, however literature data on this topic is extremely scarce. The same properties also indicate that these types of compound are unlikely to undergo long-range transport and therefore cause widespread pollution effects.

This information would suggest that the main risk from nitrosamines and nitramines formed either inside a post-combustion CO_2 capture plant or in the localised atmospheric environment is the contamination of water and groundwater around the plant. Therefore, sampling and monitoring of the nitrosamine and nitramine content in waters around the plant is perhaps the easiest way to determine if the plant operation is resulting in nitrosamine emissions at detectable levels.

2.12 Assessment of the QSAR-based predictions used in the study

An assessment and evaluation of the accuracy and limitations of the different QSAR-based models used in the project will be conducted. The assessment is divided into two parts; QSAR models used for assessing the environmental fate of the process degradation products (2.12.1) and QSAR models used for predicting the hydroxyl radical reaction rate constants of the atmospheric degradation products (2.12.2).

2.12.1 QSAR-based models to predict the environmental fate of the process degradation products

EPI Suite™ (2009a) was used extensively in this work as a QSAR-based tool for predicting the environmental fate of the parent amines and their process degradation products. This approach was used as it offers both a rapid method from environmental screening of chemicals and is able to predict values for which data do not currently exist. The US EPA (2009a) states that this QSAR approach cannot be used for all chemical substances as insufficient experimental data is available for accurately predicting values. Furthermore, estimated values should not be used if experimental (measured) data is available. The EPI Suite™ calculators are based primarily on a fragment constant approach that has been validated with an independent set of chemicals. The number of chemicals in each database varies between the different programmes within EPI Suite™. However, in general EPISUITE predicts physicochemical data within an order of magnitude, which is normally sufficient for regulatory screening purposes (European Commission JRC, 2010).

In the case of the present study we suggest that EPI Suite™ is more reliable for some chemical types than for others. As is the case for all QSAR based approaches, the data generated by the model is only as good as the data the model is based on. This means that for well known environmental pollutants (e.g. polycyclic aromatic hydrocarbons; PAHs) there is a depth of experimental data from which the estimated values are derived. These estimated values are therefore typically reliable. In contrast, estimated values generated for new environmental pollutant chemicals, which have not previously been studied and which deviate significantly (e.g. compound size, structure and chemical/functional groups) from well known compounds, are often extremely unreliable.

One advantage of EPI Suite™ is that where experimental data exists in the database it utilises then this data is also returned together with the predicted value for the parameter in question. Comparison of the experimental and predicted values can give an insight into the reliability/accuracy of the EPI Suite™ model(s). In many cases there is reasonably good correlation between the experimental and predicted values. However, this is somewhat to be expected as the QSAR model is based upon experimental values. As there tends only to be extensive experimental for specific groups of compounds (e.g. PAHs) and little available for more uncommon chemical groups the predicted data can be expected to be more accurate for the common groups of compounds.

Taking into account these limitations, it is suggested that the EPI Suite™ method still represents the best tool for estimating the environmental fate of the parent amines and their process degradation products. The nitrosamines, nitramines and alkylamines are of prime concern. However, there are few experimental data available for any of the parameters studied.

Therefore, it is suggested that any experimental data generated in Phase II of this project is input into, or made available for use in QSAR models so that they can be improved in the future for the types of compounds associated with CO_2 capture.

2.12.2 QSAR-based models to predict hydroxyl radical reaction rate constants of the predicted atmospheric degradation products

Hydroxyl radical reaction rate constants (*k*(OH)) for the reaction of parent amines and predicted atmospheric reaction products of amines were predicted in this project with the help of structure-activity relationship (SAR) methodology developed by Dr. Roger Atkinson and co-workers (Atkinson 1985, 1986, 1987, 1988, 1989, 1991), commonly referred to as the Atkinson method. The Atkinson method is often used for OH radical rate estimation (Kwok & Atkinson, 1995, Meylan & Howard, 2000). This structure-activity relationship (SAR) methodology is based on observations that gas-phase OH radical reactions with organic compounds proceed by the following four pathways: H-atom abstraction from aliphatic C-H and O-H bonds, OH-radical addition to olefinic (>C=C<) and acetylenic (>C≡C<) bonds, OH radical addition to aromatic bonds and OH radical reaction with selected nitrogen (N), sulphur (S) and phosphorous (P) atom units. It is assumed that the OH radical reactivity can be estimated by the additive group contribution approach and the overall OH reaction rate is a sum of all possible individual reaction rates. The group contribution method is based on chemical experience and statistical arguments (fitting to known data). With the exception of the electrophilic substituent constants for aromatic rings the group contribution method has no mechanistic background (Güsten, 1999).

The Atkinson method is implemented in the program EPI Suite™ through the module AOPWIN (US EPA, 2009). EPI Suite™ is a screening-level tool and should not be used if acceptable measured values are available. The AOPWIN software is used to estimate half-life values in air and is based upon estimated hydroxyl radical and ozone rate constants. AOPWIN incorporates updated fragment and reaction values as cited in Kwok and Atkinson (1995). In addition, Syracuse Research Corporation has derived some additional fragment and reaction values from more recent experimental data. Appendix I in AOPWIN lists all fragment and reaction values used by AOPWIN. EPI Suite™ has undergone detailed review by a panel of EPA's independent Science Advisory Board (http://yosemite.epa.gov/sab/sabpeople.nsf/WebCommittees/BOARD), and results were published (http://www.epa.gov/sab/panels/epi_suite_review_panel.htm).

The accuracy of the Atkinson method in AOPWIN has been tested by the use of 720 chemicals with experimental OH rate values (Meylan & Howard, 2000). With respect to the non-logarithmic *k*(OH) values, 90 % of the predicted values were within a factor 2 of experimental data and 95 % within a factor 3. In a recent ongoing study (Schüürmann et al 2007) 886 compounds with experimental log *k*(OH) values from -15.7 to -9.1 were compared with estimated AOPWIN values. The Atkinson method yielded r^2=0.92 and rms 0.35 for the whole dataset. For the subset of 40 compounds with N, S and P atom units decreased the r2 (0.87) and rms (0.31). The authors conclude that at present the Atkinson method provides good *k*(OH) estimated for most compounds and is the current method of choice. The drawback with AOPWIN is that it has been explicitly stated that extrapolation outside of the database used for its development results in lack of assurance and reliability and is not recommended (Kwok and Atkinson, 1995; Atkinson, 2000; Meylan and Howard, 2000). However, the applicability domain has only been defined in qualitative terms and the AOPWIN software does not provide any additional tools to identify compounds outside of this domain (Öberg, 2005). Unfortunately, Atkinson's method has shown larger deviations for several important classes of chemical compounds: organic compounds with 3 halogens on the same carbon atom as in DDT, chemicals with NOx groups as in nitroalkanes, phosphates, often used in herbicides, and small heterocyclic rings (Güsten, 1999).

Taking into account all these limitations, the Atkinson method still is at present the best tool for estimating the atmospheric lifetimes of the degradation products of amines (Bråten et al., 2008). The nitrosamines and nitramines are of prime concern. There are few experimental data available and a bold estimate of the reactivity of nitrosamine and nitramines, but according to the data available the –NNO and -NNO_2 groups actually enhance the reactivity of the neighbouring C-H bonds by a factor of ~10 compared to an alkyl group, see *Table 15*.

Table 15: *Predicted and rate constants for the reaction of nitrosamines and nitramines with the atmospheric hydroxyl radical (from Bråten et al., 2008).*

Rate constant	**k(OH) molecule^{-1} cm^3 s^{-1}**	**τ_{OH}**
$k_{(OH + OxNN\text{-}CH3)}$	1.3E-12	9 days
$k_{(OH + OxNN\text{-}CH2\text{-})}$	8.9E-12	1 day
$k_{(OH + OxNN\text{-}CH<)}$	18.0E-12	15 hr

Until experimental data are available the best estimate of the OH reaction rate constants indicates that OH radical reactions with nitrosamines and nitramines of the general formulas OxNN-CH2- and OxNN-CH< are relevant under atmospheric conditions. Experimental evaluation of rate constants for the reaction of nitrosamines and nitramines with the OH radical should have a high priority.

2.13 Revised ranking of the parent amines

Ranking of the parent amines based on the risk of exposing humans and the natural environment to the predicted harmful compounds.

2.13.1 Ranking with respect to process degradation products

The factors used to complete the environmental fate assessment (Section T9) and hazard assessment (T10) will be used to determine a ranking of the parent amines. This is based upon the risk of exposing humans and the natural environment when the predicted process degradation products are the focus of interest:

1. Octanol/water partition coefficient (K_{ow})
2. Water solubility
3. Biodegradation
4. Soil adsorption coefficient (K_{oc})
5. Aqueous hydrolysis
6. Bioaccumulation and bioconcentration
7. Ecotoxicity

For the parent amines and process degradation products studied, all of the log K_{ow} values were below 1 indicating that the chemicals involved with CO_2 capture would be highly hydrophilic. Therefore, no ranking can be made using this parameter. Similarly, the water solubility values were returned by EPI Suite™ for the parent amines and process degradation products studied ranged between 10^{+4} mg/L to >10^{+6} mg/L, indicating that all of the chemicals are highly water soluble. Therefore, no ranking can be made using this parameter. The log K_{oc} values for the parent amines and their associated process degradation products indicated that all chemicals studied exhibit a low adsorption affinity to soils. Again, no ranking can be made using this parameter as there is no obvious difference between the different parent amines. Only a very small number of the parent amines and their predicted process degradation products were members of the chemical classes suited for calculation of aqueous hydrolysis. As a result, no aqueous hydrolysis values were returned for most of the study compounds. However, of the few compounds which did return a value, the estimated half-lives were significantly above these thresholds >1 year. Therefore, no ranking can be made using this parameter as there is no obvious difference between the different parent amines. All of the process degradation products and parent amines studied had calculated log BCF values indicating low bioaccumulation concern and therefore a low hazard. Again, no ranking can be made using this parameter as there is no obvious difference between the different parent amines.

Only biodegradation and ecotoxicity data provided any differences between the parent amines and their process degradation products. These have been used to rank the parent amines according to the level of hazard, with 1 being the most hazardous and 4 being the least hazardous.

All of the parent amines were classed as being readily biodegradable, indicating that these compounds represent less of a hazard in the environment. However, differences were observed between the process degradation products from each parent amine. Based on these results it was possible to calculate the percentage of the process degradation products for each of the parent amines which were classed as readily biodegradable and therefore representing the least environmental risk:

1. MEA = 76%
2. MDEA = 50%
3. AMP = 33%
4. Piperazine = 0%

These data indicate that MEA represents the least hazardous of the parent amines as it produces the fewest number of environmentally persistent process degradation products. In contrast, piperazine appears to be the most hazardous as all of its process degradation products are not readily biodegradable.

Differences in toxicity were observed between the process degradation products from each of the parent amines. Based on these results it was possible to calculate the percentage of the process degradation products for each of the parent amines which were classed as being of moderate concern and therefore representing the least environmental risk:

1. Piperazine = 25%
2. MDEA = 33%
3. MEA = 40%
4. AMP = 100%

These data indicate that piperazine represents the least hazardous of the parent amines as it produces the fewest number of process degradation products classed as being of moderate concern. In contrast, AMP appears to be the most hazardous, as all of its process degradation products are considered of moderate concern.

It should be noted that the available data sets for piperazine, AMP and MDEA contained only a very small number of process degradation products compared to the data set for MEA. As a result, the percentage values presented above should not be considered definitive.

2.13.2 Ranking with respect to atmospheric degradation products

Three factors determine the ranking of the parent amines based on the risk of exposing humans and the natural environment, when the predicted atmospheric degradation products are in the focus of interest:

1. Reactivity of parent amines with OH radicals,
2. Probability of parent amines to produce harmful products in the OH-reaction,
3. Reactivity of harmful atmospheric degradation products with OH radicals.

The assumptions inherent to this approach are that 1) no process degradation products form and 2) parent amines are not toxic themselves. The reactivity of parent amines with the OH radical will determine how fast it degrades in the atmosphere. Together with the probability to form harmful products in the atmosphere through reaction with OH radicals this determines the production rate of harmful degradation products. A parent amine that reacts fast with OH and at the same time forms harmful products with a high fractional yield involves a high risk of exposure. The third factor influencing the exposure risk is the reactivity of the harmful products towards atmospheric OH radicals. Harmful products that degrade fast with OH radicals to form less harmful products are a lower risk than slowly degrading compounds. Slowly degrading compounds tend to accumulate in the atmosphere and might undergo transport to distant locations (long-range transport).

Among the predicted harmful atmospheric degradation products are aldehydes, amides, nitrosamines, and nitramines. Some aldehydes and amides are known to be very toxic compounds and have a high carcinogenic potential such as formaldehyde and acetamide (Låg et al., 2009). Expected atmospheric concentrations of aldehydes and amides forming in the oxidation of parent amines are however below critical exposure levels (Karl et al., 2008) and the two compound groups were for this reason not considered in the present risk evaluation. Nitrosamines and nitramines are of primary concern (Knudsen et al., 2009). Nitrosamines are predicted to form in the OH-initiated oxidation of amines (Bråten et al., 2008). Nitrosamines are rapidly removed from the atmosphere due to their photolysis in sunlight (Chow, 1973) and their reaction with OH radicals is probably of minor importance. In contrast to nitrosamines, it is expected that nitramines accumulate in the atmosphere due to their relatively low reactivity towards OH radicals (Grosjean, 1991). The reactivity of the respective nitramine forming in the OH-initiated oxidation of the parent amine will therefore largely determine the risk associated to with parent amines.

In the following the ranking in terms of each of the three factors above is estimated. The highest rank for a parent amine is associated with the highest risk of exposing humans and the natural environment. A final ranking of the parent amines is established taking into account all three factors with equal weight.

A ranking of the parent amines according to their OH-reactivity (Table 16) shows that piperazine reacts fastest with OH radicals and has an estimated atmospheric lifetime of less than one hour. Piperazine is 6-7 times more reactive than AMP, which is the least reactive among the four suggested solvent amines.

Table 16*: Ranking based on the reactivity of parent amines with OH radicals based on predicted rate constants using EPI Suite™.*

Ranking	**Parent amine**	***k*(OH) molecule^{-1} cm^3 s^{-1}**	**τ_{OH} (hours)***	**f_{E1}**
1	Piperazine	169E-12	0.8	6.9
2	MDEA	97.0E-12	1.4	3.9
3	MEA	35.8E-12	3.9	1.4
4	AMP	25.5E-12	5.5	1

* Lifetime calculated for [OH] = 2E6 molecules cm^{-3}.

Table 17 shows the ranking of parent amines according to their probability to form nitrosamines and nitramines. Only few experimental data exists on the product yields of nitrosamines and nitramines in the atmospheric oxidation of amines with the OH radical. For MEA, no indication for the formation of nitrosamines was found in chamber experiments (Nielsen et al., 2010). For AMP, a primary amine, the ozone formation potential has been studied in experiments (Carter et al., 2000). Carter et al. (2000) suggest that hydrogen abstraction occurs at the amino group while it is inhibited for the carbon atoms next to the amino group. An attack of OH at the amino group would favour the formation of nitrosamines or nitramines. It is estimated here that AMP forms three times more nitramines than MEA, but no nitrosamines. MDEA, a tertiary amine, is treated as triethylamine for which product yields of nitrosamines and nitramines are known experimentally. Piperazine, a secondary heterocyclic amine with two amino groups, is treated as diethylamine for which product yields are known. Based on these assumptions, piperazine has a ~20 times higher probability to form nitramines than MEA:

Table 17*: Ranking based on the probability of parent amines to produce nitrosamines and nitramines in the reaction with OH radicals based on experimental product yields and best guess estimates.*

Ranking	**Parent amine**	**y(R-NNO) (in %)**	**y(R-NNO$_2$) (in %)**	**Reference**	**f_{E2}**
1	Piperazine	2.8	32	as diethylamine. Pitts et al. (1978)	21
2	MDEA	1.8	7.4	as triethylamine, Pitts et al. (1978)	5
3	AMP	0.0	<4.50	3 x nitramine yield of MEA. Carter et al. (2000); this project	3
4	MEA	0.0	<1.5	Nielsen et al. (2010)	1

The third ranking of parent amines is done based on the reactivity of nitramines, that are predicted to form primarily in the atmospheric amine degradation, towards OH radicals. The faster an nitramine reacts with OH radicals the faster it is removed from the atmosphere, reducing the toxic impact of the corresponding amine. Surprisingly the predicted nitramine from piperazine was found to react rapidly with OH and has a predicted lifetime of only 1.2 hours in the atmosphere (Table 18). The predicted nitramine from AMP reacts 25 times slower and has a lifetime of 28 hours. The AMP nitramine thus has the highest potential to accumulate in the atmospheric environment.

Table 18*: Ranking based on the reactivity of predicted nitramines with OH radicals based on predicted rate constants using EPI Suite™.*

Ranking	**Parent amine**	***Nitramine (predicted)***	***k*(OH) molecule^{-1} cm^3 s^{-1}**	**τ_{OH} (hours)***	**f_{E3}**
1	AMP	O2N-NH-C-(CH3)2-CH2-OH	4.5E-12	28.0	23.3
2	MEA	Ethanol, 2-(nitroamino)-	14.8E-12	9.4	7.8
3	MDEA	Etanamine, N-Etyl-N-Nitro-	19.0E-12	7.3	6.1
4	Piperazine	O2N-NH-CH2-CH2-NH-CH2-CH=O	111.6E-12	1.2	1

* Lifetime calculated for [OH] = 2E6 molecules cm^{-3}.

To arrive at an objective ranking for the four amines with respect to their atmospheric degradation products, an environmental impact factor f_E was assigned to each amine in the three different ranking categories. The factor is obtained by normalizing the lifetime or yield in each categories by the value associated to the fourth rank (i.e. f_E of the fourth rank is set to unity). An overall environmental impact factor F_E was obtained by multiplication of the 3 category-specific values ($F_E = f_{E1} \cdot f_{E2} \cdot f_{E3}$).

Table 19*: Ranking of parent amines with respect to predicted atmospheric degradation products.*

Ranking	**Parent amine**	**F_E**
1	Piperazine	145
2	MDEA	119
3	AMP	70
4	MEA	11

Table 19 shows the result from the evaluation of the four generic amines. Piperazine is first in the ranking which means that it should be considered the most harmful for environment and health with respect to its atmospheric degradation products. MEA is fourth in the ranking and should be considered the least harmful of the four amines. It is emphasized that the toxicity of the parent amine was not considered in this ranking. The highest uncertainties are associated with the possible formation yield of nitramines in the atmospheric degradation of these amines. Experiments in a photochemical reactor using varying levels of NO_x should be performed to determine the production yield of nitramines. The evaluation implies that the toxicity of all nitramines is the same. Toxicity studies are needed to assess ecoxoticity and human toxicity of individual nitramines.

It is suggested that 'dark reactions' could be just as important as 'light reactions' in assessing atmospheric fate and processes. Although theoretical calculations of 'dark reactions' are not within the scope/timeframe of this project, they may be important for the risk evaluation. Reaction rate constant of selected amines with the NO_3 radical are estimated to range between

0.5 and 3.5×10^{-13} molecules cm^3 s^{-1} using Atkinson SAR (Carter et al., 2000). The average concentration of NO_3 radicals at night is typically ~2.5×10^8 molecules cm^{-3}, resulting in chemical atmospheric lifetimes of the amines between 3 and 22 hours. For MEA and AMP the atmospheric degradation at night is predicted to be a factor of two and three slower, respectively, than by the OH radical at daytime (average OH concentration of 2.0×10^6 molecules cm^{-3}). Reactions with the NO_3 radical could be relevant in terms of formation of harmful products and in terms of particle formation. In general, the attack by the NO_3 radical is followed by hydrogen abstraction in analogy to the OH-initiated H-abstraction. Theoretically, the formation of nitrosamines and nitramines should be comparable to the daytime reaction with OH, since their formation occurs via addition of NO or NO_2 to the radical $R_2N^{\cdot}$, respectively, that form after initial H-abstraction (Reactions R3-R5, section 2.5).

Experiments on the NO_3-initiated oxidation of amines with regard to the development of gas-phase chemistry mechanisms are lacking.

References

Angelino, S., Suess, D. T., Prather, K. A. (2001). Formation of aerosol particles from reactions of secondary and tertiary alkylamines: Characterization by aerosol time-of-flight mass spectrometry. *Environmental Science & Technology*, *35*, 3130-38.

Atkinson, R. (1985). Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.*, 85, 69-201.

Atkinson, R. (1986). Estimations of OH radical rate constants from H-atom abstraction from C-H and O-H bonds over the temperature range 250-1000 K. *Intern. J. Chem. Kinet.*, 18, 555-568.

Atkinson, R. (1987). A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *Intern. J. Chem. Kinet.*, 19, 799-828.

Atkinson, R. (1988). Estimation of gas-phase hydroxyl radical rate constants for organic chemicals. *Environ. Toxicol. Chem.*, 7, 435-442.

Atkinson, R. (1989). Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. *J. Phys. Chem. Ref. Data Monograph* No. 1. N.Y., Amer. Inst. Physics & Amer. Chem Soc.

Atkinson, R. (1991). Kinetics of the gas-phase reactions of a series of organosilicon compounds with OH and NO_3 radicals and O_3 at 297±2 K. *Environmental Science & Technology*, 25, 863-866.

Atkinson, R. (2000). Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.*, 34, 2063-2101.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Rossi, M. J., Troe, J. (1997). Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. *J. Phys. Chem. Ref. Data*, 26, 521-1011.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Jr., Kerr, J.A., Rossi, M. J., Troe, J. (2001). Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry Web Version December 2001, 1-56.

Atkinson, R. D. B., R. Cox, J. Crowley, R. Hampson, R. Hynes, M. Jenkin, M. Rossi, J. Troe, and T. Wallington (2008). "Evaluated Kinetic and Photochemical data for Atmospheric Chemistry:Volume I-IV." Atmos. Chem. Phys. **8**: 4141-4496.

Bamford, C. H. (1939). "A study of the photolysis of organic nitrogen compounds - Part I Dimethyl- and diethyl-nitrosoamines." Journal of the Chemical Society: 12-17.

Boethling, R.S., Howard, P.H., Meylan, W., Stiteler, W., Beaumann, J. Tirado, N. (1994). Group contribution method for predicting probability and rate of aerobic biodegradation. *Environ. Sci. Technol.*, 28, 459-65.

Boethling, R.S., Lynch. D.G., Thom, G.C. (2003). Predicting Ready Biodegradability of Premanufacture Notice Chemicals. *Environ. Toxicol. Chem*, 22, 837-844.

Boethling, R.S., Lynch, D.G., Jaworska, J.S., Tunkel, J.L., Thom, G.C., Webb, S. (2004). Using BIOWIN, Bayes, and batteries to predict ready biodegradability. *Environ. Toxicol. Chem.*, 23, 911-920.

Bråten, H. B., Bunkan, A. J., Bache-Andreassen, L., Solimannejad, M., Nielsen, C. J. (2008). Final report on a theoretical study on the atmospheric degradation of selected amines. Oslo, Norway (NILU OR 77/2008).

Carter, W. P. L. (2008). Reactivity estimates for selected consumer product compounds. Final Report, Contract No. 06-408. Center for Environmental Research and Technology, College of Engineering, University of California, Riverside, California, USA.

Charrois, J.W.A., Arend, M.W., Froese, K.L., Hrudey, S.E. (2004). Detecting N-nitrosamines in drinking water at nanogram per liter levels using ammonia positive chemical ionization. *Environmental Science & Technology*, 38, 4835-4841.

Chow, Y. L. (1973). Nitrosamine chemistry: reactions of aminium radicals. *Acc. Chem. Res.*, 6, 354-360.

Christiansen, O., J. Gauss, et al. (1999). "The electronic spectrum of pyrrole." Journal of Chemical Physics **111**(2): 525-537.

Christiansen, O. and P. Jorgensen (1998). "The electronic spectrum of furan." Journal of the American Chemical Society **120**(14): 3423-3430.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., Fall, R. (2007). Measurement of Volatile Organic Compounds in the Earth's Atmosphere using Proton-Transfer-Reaction Mass Spectrometry. *Mass Spectrometry Reviews*, 26, 223-257.

Drewes, J.E., Hoppe, C., Jennings, T. (2006). Fate and transport of N-nitrosamines under conditions simulating full-scale groundwater recharge operations. *Water Environment Research*, 78, 2466-2473.

Dye, C., Schmidbauer, N., Schlabach, M. (2008). Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air. Kjeller/Oslo (NILU OR 80/2008).

Freeman, S. A., R. Dugas, et al. (2010). "Carbon dioxide capture with concentrated, aqueous piperazine." International Journal of Greenhouse Gas Control **4**(2): 119-124.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A.,, J. R. Cheeseman, Montgomery, J. A., Jr., Vreven, T., Kudin, K. N., Burant,, et al. (2003). Gaussian 03, Revision B.03. Pittsburgh, PA., Gaussian Inc.

Gan, J., Bondarenko, S., Ernst, F., Yang, W., Ries, S.B., Sedlak, D.L. (2006). Leaching of N-nitrosodimethylamine (NDMA) in turfgrass soils during wastewater irrigation. *Journal of Environmental Quality*, 35, 277-284.

Grosjean, D. (1991). Atmospheric chemistry of toxic contaminants: 6. Nitrosamines: Dialkyl nitrosamines and nitrosomorpholine. *J. Air Waste Manage. Assoc.*, 41, 306-311.

Gunnison, D., Zappi, M.E., Teeter, C., Pennington, J.C., Bajpai, R. (2000). Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. *Journal of Hazardous Materials*, 73, 179-197.

Güsten, H. (1999). Predicting the abiotic degradability of organic pollutants in the troposphere. *Chemosphere*, 38, 1361–1370.

Harris, G. W. and J. N. Pitts (1983). "RATES OF REACTION OF HYDROXYL RADICALS WITH 2-(DIMETHYLAMINO)ETHANOL AND 2-AMINO-2-METHYL-1-PROPANOL IN THE GAS-PHASE AT 300 +- 2 K." Environmental Science & Technology **17**(1): 50-51.

Hill, M.J. (1988). Nitrosamines—toxicology and microbiology. , Ellis Horwood, Int. Publ. in Science and Technology, New York, Basel, Weinheim, Chichester, Cambridge.Geiger, G. and J. R. Huber (1981). "PHOTOLYSIS OF DIMETHYLNITROSAMINE IN THE GAS-PHASE." Helvetica Chimica Acta **64**(4): 989-995.

Howard, P.H., Boethling, R.S., Stiteler, W.M., Meylan, W.M., Hueber, A.E., Beauman, J.A., Larosche, M.E. (1992). Predictive model for aerobic biodegradability developed from a file of evaluated biodegradation data. *Environ. Toxicol. Chem*., 11, 593-603.

Kaplan, D.L. Kaplan, A.M. (1985). Biodegradation of N-Nitrosodimethylamine in Aqueous and Soil Systems. *Appl. Environ. Microbiol*., 50, 1077-1086.

Karl, M., Brooks, S., Wright, R., Knudsen, S. (2008) Worst case studies on amine emissions from CO_2 capture plants (Task 6). Kjeller/Oslo (NILU OR 78/2008).

Karl, M., Gross, A., Leck, C., Pirjola, L. (2010a). New particle formation in the High Arctic: Observations and model simulations. *Geophys. Res. Abstracts*, 12, EGU2010-8393.

Karl, M., Gross, A., Leck, C., Pirjola, L. (2010b). A new flexible multicomponent aerosol dynamic model to study the marine boundary layer. I. Model development and evaluation, manuscript in preparation.

Koch, R., Palm, W. U., Zetzsch, C. (1997). First rate constants for reactions of OH radicals with amides. *Int. J. Chem. Kinet.*, 29, 81-87.

Knudsen, S., Karl, M., & Randall, S., (2009). NILU Technical Report, TR 04/2009, Kjeller, Norway.

Kwok, E. S. C. and Atkinson, R. (1995). Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update. *Atmos. Environ.*, 29, 1685-95.

Lane, J. R. and H. G. Kjaergaard (2008). "Calculated electronic transitions in sulfuric acid and implications for its photodissociation in the atmosphere." Journal of Physical Chemistry A **112**(22): 4958-4964.

Lindley, C. R. C., J. G. Calvert, et al. (1979). "RATE STUDIES OF THE REACTIONS OF THE (CH3)2N RADICAL WITH O2, NO, AND NO2." Chemical Physics Letters **67**(1): 57-62.

Lyman, W.J. (1990). Chapter 4. Adsorption coefficient for soils and sediments. In: *Handbook of Chemical Property Estimation Methods*. Lyman, W.J. *et al*., editors. Washington, DC: American Chemical Society.

Låg, M., Andreassen, Å., Instanes, C., Lindemann, B. (2009). Health effects of different amines and possible degradation products relevant for CO_2 capture. Oslo, Norway (FHI Report 2009:3), available at http://www.fhi.no/dav/de810a615a.pdf.

Meylan, W. and Howard, P.H. (2000). User’s Guide for APOWIN, Version 1.9. Syracuse Research Corporation. North Syracuse, N.Y., March, 2000.

Mitch, W.A., Sedlak, D.L. (2002). Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environmental Science & Technology*, 36, 588-595.

Mitch, W.A., Sedlak, D.L. (2004). Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environmental Science & Technology*, 38, 1445-1454.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C., Seinfeld, J. H. (2007). Secondary aerosol formation from atmospheric reactions of aliphatic amines. *Atmospheric Chemistry and Physics*, *7*, 2313-37.

NCAR. "Tropospheric Ultraviolet and Visible (TUV) Radiation Model (http://cprm.acd.ucar.edu/Models/TUV/)." from http://cprm.acd.ucar.edu/Models/TUV/.

Nielsen, C.J., D'Anna, B., Dye, C., George, C., Graus, M., Hansel, A., Karl, M., King, S., Musabila, M., Müller, M., Schmidbauer, N., Stenstrøm, Y., & Wisthaler, A. (2010). CLIMIT project no. 193438, Kjeller, NILU OR 8/2010.

Öberg, T. (2005). A QSAR for the hydroxyl radical reaction rate constant: validation, domain of application, and prediction. *Atmos. Environ.*, 39, 2189-2200.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, T., Flagan, R. C., Seinfeld, J. H. (1996). Gas-particle partitioning and secondary organic aerosol yields. *Environmental Science & Technology*, 30, 2580-2585.

Pitts, J. N., Grosjean, D., Vanmcauwenberghe, K., Schmidt, J. P., Fitz, D. R. (1978). *Environmental Science & Technology*, 12, 946-953.

Pratt, K. A., Hatch, L. E., Prather, K. A. (2009). Seasonal Volatility Dependence of Ambient Particle Phase Amines. *Environmental Science & Technology*, *43*, 5276-81.

Preussman, R. (1983). Das nitrosaminproblem. VerlangChemie, Weinheim.

Rywotycki, R. (2003). The influence of environment, mode of nutrition and animal species on level of nitrosamine contamination in venison. *Meat Science*, 65, 1045-1053.Sander, S. P., R. R. F., D.M. Golden, M.J. Kurylo, G.K. Moortgat, H. Keller-Rudek, P.H. Wine, A.R. Ravishankara, C.E. Kolb, M.J. Molina, B.J. Finlayson-Pitts, R.E. Huie, V.L. Orkin (2006). Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation Number 15, JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena.

Schüürmann, G., Ebert, R.-U., Nnedza, M., Dearden, J. C., Paschke, A., Kühne, R. (2007). Chapter 9. Predicting fate-related physicochemical properties. In: *Risk assessment of chemicals. An introduction*. Van Leeuwen, C. J., Vermeire, T., Vermeire, T. G.. Springer, ISBN 978-1-4020-6101-1, Dordrecht, NL.

Seinfeld, J. H. and S. N. Pandis (2006). Atmospheric chemistry and physics: from air pollution to climate change. Hoboken, John Wiley & Sons, Inc.

Smyk, B., Różycki, E., Barabasz, W. (1990). Nitrosamines—biological effects on the application of mineral nitrogen fertilization in agriculture. *Geodesy and Environment, PAN*, 35, 131–144.

Solignac, G., Mellouki, A., Le Bras, G., Barnes, I., Benter, T. (2005). Kinetics of the OH and Cl reactions with N-methylformamide, N,N-dimethylformamide and N,N-dimethylacetamide, *J. Photochem. Photobiol. A Chem.*, 176, 136-142.

Tate, R.L., Alexander, M. (1975). Stability of nitrosamines in samples of lake water, soil, and sewage. *Journal of the National Cancer Institute*, 54, 327-330.

Tate, R.L., Alexander, M. (1976). Resistance of nitorsamines to microbial attack. *Journal of Environmental Quality*, 5, 131-133.

Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market (2003). This can be viewed and downloaded from the web site of the European Chemicals Bureau: http://ecb.jrc.ec.europa.eu/tgd/

Tuazon, E. C., Carter, W. P. L., Atkinson, R., Winer, A. M., Pitts, J. N., Jr. (1984). Atmospheric reactions of N-nitrosodimethylamine and dimethylnitramine. *Environmental Science & Technology*, 18, 49-54.

Tunkel, J., Howard, P.H., Boethling, R.S., Stiteler, W., Loonen, H. (2000). Predicting Ready Biodegradability in the Japanese Ministry of International Trade and Industry Test. *Environ. Toxicol. Chem*., 19, 2478-2485.

TOXNET (2008). Hazardous Substances Data Bank. United States National Library of Medicine. http://toxnet.nlm.nih.gov.

U.S. EPA (2005). Pollution Prevention (P2) Framework Manual, US Environmental Protection Agency, OPPT, EPA-748-B-04-001. June 2005. United States Environmental Protection Agency, Washington, DC, USA. May be obtained through the link ‘P2 Framework Manual June 2005 (PDF)’ found at http://www.epa.gov/oppt/sf/pubs/index.htm.

U.S. EPA (2006a). EPI Suite™ Estimation Methods: Physical/Chemical Properties. Presentation. May be downloaded at http://www.epa.gov/oppt/sf/presentations/sf/pchem-epi.pdf.

U.S. EPA (2006b). EPI Suite™ Estimation Methods: Environmental Fate. Presentation. United States Environmental Protection Agency, Washington, DC, USA. May be downloaded at http://www.epa.gov/oppt/sf/presentations/sf/envfate-epi.pdf.

U.S. EPA (2006c). Performing an Aquatic Toxicity Assessment Under the Sustainable Futures Initiative. Presentation. United States Environmental Protection Agency, Washington, DC, USA. May be downloaded at http://www.epa.gov/oppt/sf/presentations/sf/aqtox-ecosar.pdf.

U.S. EPA (2009a). Estimation Programs Interface (EPI) Suite™ for Microsoft Windows, v 4.00. United States Environmental Protection Agency, Washington, DC, USA. Available online http://www.epa.gov/oppt/exposure/pubs/episuite.htm.

U.S. EPA (2009b). User’s Guide for the ECOSAR Class Program. United States Environmental Protection Agency, Washington, DC, USA. May be obtained through the link ‘ECOSAR User's Guide (PDF)’ found at http://www.epa.gov/oppt/newchems/tools/21ecosar.htm.

Wyllie, T., Morehouse, L. G., (1990–1991). Mycotoxic fungi, mycotoxins, mycotoxicoses. New York and Basel: Marcel Dekker.

Yang, W.C., Gan, J., Liu, W.P., Green, R. (2005). Degradation of N-Nitrosodimethylamine (NDMA) in Landscape Soils. *Journal of Environmental Quality*, 34, 336-341.

Yekutiel, M., J. R. Lane, et al. (2010). "Calculated Spectroscopy and Atmospheric Photodissociation of Phosphoric Acid." Journal of Physical Chemistry A **114**(28): 7544-7552.

Zhao, Y.Y., Boyd, J., Hrudey, S.E., Li, X.F. (2006). Characterization of new nitrosamines in drinking water using liquid chromatography tandem mass spectrometry. *Environmental Science & Technology*, 40, 7636-7641.

3 WP3 Proposed test protocol for use in the evaluation of amine-based solvents

3.1 Test protocol

The test protocol (“H&ETQP Test protocol”) is prepared and submitted as a independent document.

3.2 Pre-execution and validation of solvent test protocol

The process test protocol has been designed so that it should be executable within a 6 month time frame for a number of solvent technology providers. However it would a significant advantage if a number of pre-execution and validation experiments could be executed for 1 (or more) generic solvent system (e.g. MEA) prior to this 6 month period. As a result a Pre-execution Protocol has also been submitted as an appendix to the main Test protocol Document.

3.3 Post test-protocol work

At some point it would be useful to measure concentrations of emitted compounds at a full scale or pilot scale CO2 capture plant.