Review of amine emissions from carbon capture systems

Version 2.01

August 2015

Version 1.1 of this document (v1.1) was originally published on the SEPA website on 11 April 2013. Since that time further technical information on amine emissions from post-combustion carbon capture systems has been published and understanding on this issue has, and continues to, mature.

This version (v2.01) has been prepared following review of literature published up to July 2014.

This document has been updated with the conclusions of the additional literature and represents, what we believe, is an accurate summation of publicly available knowledge on this subject as at 31 July 2014.

Headline issues

Emissions of amines and associated reaction products

- Amine solvents will be used in some carbon capture processes. These compounds react to create new compounds both within the process itself and once emitted to the environment. The most significant emissions are likely to be to air in the flue gas or to waste water from pollution abatement processes.

- This report focuses primarily on emissions to air. Emissions to water and other potential waste streams are treated in less detail, reflecting the limited existing public domain information available. Emissions to water are nonetheless a potentially important source of amine emissions into the environment. Whilst emissions to air of the amine solvents themselves are unlikely to be of significant concern there is a higher degree of uncertainty associated with emissions of amine reaction (degradation) products such as nitrosamines.

- There is limited open source data available on emissions of such reaction products. Most available data is based on capture solvents that may not represent the mix of solvents that may be adopted in demonstration scale systems.

- Abatement systems to mitigate emissions of amines and amine reaction products to air are being developed. Such systems could generate additional waste water streams requiring additional treatment.

The potential impact of emissions on the environment and on human health

- Nitrosamines and nitramines are possible carcinogens. Whilst there is toxicity data available for a few of the more generally researched substances (e.g. the nitrosamine drinking water contaminant NDMA), the environmental toxicity of many of the other individual compounds is not well understood.

- Environmental Assessment Levels (EALs) or Environmental Quality Standards (EQS) have not been established in the UK or within the EU for most of the compounds of interest. Some other countries have proposed thresholds in air for grouped nitrosamines and nitramines in the absence of agreed EU standards. However, the proposed thresholds may be difficult to adopt formally in the UK as they were derived using an approach that is not compatible with that taken in the UK.

- Existing background levels of amines and their reaction products are unknown in the UK.

Measurement of amines and associated reaction compounds

- Amine compounds, in particular nitrosamines, are difficult to sample and analyse. There is no standardised technique for monitoring nitrosamines in stack emissions and there has been limited stack emission monitoring of amine compounds at carbon capture pilot plants.

- Measurement of nitrosamines in the ambient air at the levels expected around CCS processes appears possible but difficult (considering issues such as humidity and breakthrough) at the present time. Further work is required to develop a reliable method.

Next steps

- Operators applying for consent for carbon capture systems should be required to submit detailed emission and impact estimates for all relevant compounds. The source and basis for such emission estimates should be clearly stated.

- In the interim SEPA should apply the environmental thresholds proposed internationally but further work should be undertaken in the UK to develop fully derived and established standards in line with UK methodologies. SEPA will re-evaluate the Norwegian benchmark, the dose descriptor value on which the benchmark was derived and consider the use of a large assessment factor in deriving a human health standard that is more in line with UK methodology.

- Consideration should be given to understanding potential ambient levels of amine compounds within the UK. This should include an assessment of potential sources and monitoring techniques.

- Further work is required to understand atmospheric chemistry (in particular aerosol chemistry, formation and degradation mechanisms) aqueous chemistry and deposition effects.

- Further work is required to understand the degradation mechanisms and composition of degradation products in carbon capture systems.

- Further work is required to understand the composition of waste and waste water streams from carbon capture systems, including waste and waste water streams from abatement systems.

- Further work is required on stack emissions monitoring, including aerosol and gas phases, the issue of ‘fogging’ and the risk of formation/degradation of substances during monitoring.

- SEPA is field trialing an ambient air monitoring method developed by NILU for nitrosamines. The laboratory analysis of the samples is currently underway.

- Further work is required to develop a reliable method that can measure nitrosamines in the ambient air over a sufficient period to determine likely impacts of carbon capture processes. A reliable ambient air monitoring method is particularly needed to verify air dispersion models.

Executive summary

1. This paper is a review of literature published on emissions of amines (and related amine reaction products) from post-combustion carbon capture systems in power generation and their potential effects, the development of effective environmental standards and measurement techniques. This review does not consider carbon capture systems based on oxy-fuel combustion, pre-combustion technologies or post-combustion chilled ammonia scrubbing or absorption techniques based on amino acid salts or other solids. It does not cover other industries of possible relevance to the UK such as steel, cement or refineries.

2. This review (Version 2.01) is an update to Version 1.1 and reviews literature published until the end of July 2014. The structure of the review has generally been retained, with updates included throughout. The reviewed literature is, where possible, from peer reviewed sources, but some more recent non-peer reviewed reports and findings from international workshops are also considered. The literature search was undertaken using databases such as EBSCO and ScienceDirect (www.sciencedirect.com) and was designed to capture a wide range of publically available literature. Some research is not publicly available due to commercial confidentiality and there may be publicly available reports that have not been found by the literature search. This review is being made available to external bodies in the interests of transparency, despite the uncertainty noted in a number of areas. The review should not be used as guidance and does not necessarily express the opinions of SEPA.

3. There is an increasing amount of published research into amine degradation, emissions and impacts internationally, however it is recognised that some research is not published due to commercial confidentiality. Research from bench-scale and numerous pilot plants such as Ferrybridge (UK), Loy Yang (Australia), Maasvlakte (Netherlands) and Technology Centre Mongstad (Norway) has been published. The world's first commercial-scale (110MW) post-combustion carbon capture and storage project, a retrofit to the existing Boundary Dam power station in Canada, opened in October 2014. However development of full-scale carbon capture at Test Centre Mongstad was discontinued and the test centre has embarked on a new solvent testing phase.

4. The importance of research and knowledge sharing has recently been highlighted by, for example, the UK and Canadian Governments who have signed an agreement to work together on research and knowledge sharing for carbon capture and storage and the EU-US Energy Council whose recent Joint Statement (December 2014) emphasised the importance of intensifying and streamlining cooperation in this area, and undertook to explore further opportunities for further energy research collaboration (Joint Statement EU-US Energy Council, 2014).

5. The typical amine solvents used in carbon capture scrubbing systems tend to be the generic group of amines referred to as alkanolamines. Most reported work has concentrated on the use of monothanolamine (MEA), however a wide range of other alkanolamine and organic amine compounds have been proposed as carbon capture solvents. Proprietary solvents and solvent mixes are also being developed and information on the composition of these solvents is in some cases confidential.

6. The amine solvents degrade in the carbon capture process through oxidation, thermal degradation and acid gas reactions which can be promoted by metals. Loss can also be through evaporation of the solvent. Oxidation is considered to be the main degradation pathway for MEA however other amines are reported to be resistant to oxidation at absorber conditions. Thermal degradation is reported to account for 20-30% of total amine losses, hence the maximum operating temperature of the amine re-boiler and stripper

system is determined by thermal degradation. Acid gas reactions, in particular reaction with oxides of nitrogen, are of particular interest due to their potential to form nitrosamines. Secondary amines can react directly with nitrogen dioxide to form nitrosamines, however both primary and tertiary amines can also indirectly form nitrosamines. Concentrations of nitrosamines in the circulating/waste solvent are reported to range from 1.6mg/l to 215mg/l.

7. A wide range of amine degradation products are reported including ammonia, nitrosamines, nitramines, amides, aldehydes and volatile acids. Ammonia is reported to be the dominant emission, but nitrosamines and nitramines have been measured in stack emissions at concentrations up to 5µg/m^3 and 0.047µg/m^3 respectively. Emissions of amines through 'slip' have been measured at various pilot plants at concentrations up to 4.0mg/m^3.

8. Research is being carried out into the generation of aerosols from carbon capture plants and there remain uncertainties in the understanding of these. Significant amine emissions have been attributed to aerosols in measurements at Ferrybridge and Maasvlakte pilot plants.

9. Once emitted to the air, amines, nitrosamines and nitramines will undergo dispersion and complex chemical reactions. This involves multiphase chemistry, i.e. gas, aqueous (aerosols, cloud droplets, fog and rain) and particle phase (aerosol). Nitrosamines and nitramines are respectively formed by reaction with nitrogen monoxide and nitrogen dioxide. This reaction is complex and is generally initiated by the hydroxyl radical, but can also be as a result of reaction with chlorine atoms, nitrate radicals and ozone. Nitrosamines and nitramines can degrade in the atmosphere by photolysis, reactions with hydroxyl radical, chlorine atoms and nitrate radical. The significance of these mechanisms differs in gas, particles and clouds. Overall the steady state concentration of nitrosamines/nitramines can be calculated using reaction rate constants or percentage conversion rates measured through experimental studies. Reaction rate constants typically lead to conversion rates (i.e. amines emitted to nitrosamines in the ambient air) of <1% but can reach up to 8%. Percentage conversion rates reported from chamber experiments range between 0 and 10%. Due to the complexity of the chemical reactions there are uncertainties in both of these methods. An atmospheric dispersion model which includes a module simulating the simplified atmospheric chemistry of amines is now commercially available (ADMS). Other modelling tools are also being used for research purposes.

10. A brief review of amine emissions to water was undertaken. Some researchers report that the main amine loss (and thus emission to the environment) may actually occur in the waste water generated by the absorber scrubber systems. Measured total nitrosamines in wash water in a pilot plant have reached up to 6.79g/l. Nitrosamines and nitramines are generally resistant to hydrolytic degradation, while nitrosamines are highly susceptible to photodegradation. Biodegradation rate is reported to vary significantly between nitrosamines in the water environment, from around 30 days half-time for N-nitrosodiethanolamine to over 1500 days for nitrosopiperazine.

11. Emissions from other plant areas have been considered, including the volume and composition of wastes from thermal reclaiming systems. Treatment options for reclaimer wastes, by means of incineration and biological treatment, are briefly considered. Emissions are also considered from post-absorber waste systems, ion-exchange and electrodialysis, CO_2 compression and dehydration systems, direct contact coolers and activated carbon systems. Overall, it is recognised that more research on the quantity and composition of the waste containing amine compounds and degradation products from

capture plants is required in order to identify the most appropriate disposal/recovery options.

12. Techniques and technologies which may reduce emissions of amine compounds and their degradation products are considered, which fall within two general approaches: minimisation/removal of precursor species and/or post-generation removal from emissions to air and to water.

13. Thermal reclaiming is capable of removing all degradation products, heat stable salts and non-volatile impurities however the amine recovery rate for thermal reclaiming is less than that of ion-exchange and electrodialysis. On the other hand, ion-exchange and electrodialysis are only capable of removing ionic impurities. UV irradiation may offer another technique to reduce nitrosamine concentrations in solvent circuits, and reportedly can remove 90% of nitrosamines, and UV irradiation of wash water circuits may maximise removal by acid wash systems. The potential impact of corrosion on the system, such as increasing the rate of degradation of the solvent, has led to the use of solvent inhibitors. However these inhibitors can, in some cases, catalyse corrosion and may not be effective at the elevated temperatures in carbon capture systems. The addition of corrosion inhibitors is considered.

14. Water wash systems, reportedly capable of removing most amines and amine degradation products, are considered. Interest has increased recently in aerosols and the potential for these to pass through a water wash section. Additionally the removal of ammonia in the water wash section is considered as recent studies have suggested that ammonia removal is limited. Acid wash systems are reportedly effective at removing amine degradation products and base compounds although the possibility of nitrosamines and nitramines forming in the acid wash section has been identified. Pilot plant studies have attributed emissions to the presence of aerosols and post-absorber demister systems are now receiving more attention: whilst more research is required, post-absorber demisters are considered briefly in this review.

15. Monitoring for nitrosamines in the ambient air has not occurred around operational CCS plants, but has been done globally around other industrial sources of nitrosamines such as rubber processing, amines manufacture and chemical disposal sites. Concentrations have been measured up to 32µg/m^3 (in Baltimore, USA). A field trial of an ambient monitoring method developed by the Norwegian Institute for Air Research (NILU) is currently underway by SEPA.

16. In the UK, Environmental Assessment Levels (EALs) in air for some amines have been derived, but not for alkanolamines typically used in CCS such as MEA. UK Occupational Exposure Limits (OELs) exist for MEA and these can be used to derive a UK EAL of between 5µg/m^3 (long-term) and 15.2µg/m^3 (15 minute short-term). A number of health guideline values have been suggested globally for nitrosamines in the ambient air ranging from 0.07ng/m^3 to 10ng/m^3. These limits may be exceeded where releases from carbon capture plants take place where ambient (background) levels of nitrosamines are high. N-nitrosodimethylamine (NDMA) is typically monitored due to its toxicity (Group 2A Carcinogen) however recent research has suggested a lower derived minimal effect level (DMEL) for N-nitrosodiethylamine (NDEA).

17. For nitrosamines, a substantial amount of effort would be needed to apply a Toxic Equivalent (TEQ) approach to the large number of compounds involved (over 300) given the absence of toxicology data for many of the compounds concerned. Adopting a reference substance (NDMA) against which total nitrosamine emissions are assessed may be a more appropriate approach, similar to how benzo(a)pyrene has been used for

polyaromatic hydrocarbons. The EAL of 0.3ng/m^3 currently proposed by the Norwegian Institute of Public Health for total nitrosamines and nitramines (expressed as NDMA) cannot be adopted as a fully derived and established benchmark due to the differences in the way that the UK assesses carcinogenicity compared to other countries. There are also uncertainties associated with the approach of using an oral dose to derive inhalation concentration (route-to-route extrapolation). Setting standards for solvent mixtures may prove challenging due to limited knowledge of the behaviour of these mixtures.

18. Currently it is not possible to derive an EQS in the water environment for nitrosamines, due to the diverse nature of the group and lack of ecotoxicology data in water. A whole sample assessment approach such as Direct Toxicity Assessment (DTA) may be a suitable approach for assessing water discharges containing a complex mix of chemicals.

19. There has been limited stack emission monitoring of amine compounds from carbon capture pilot plants and no standard reference method exists for nitrosamines, nitramines or for the combination of substances anticipated in flue gas. Consideration needs to be paid to targeting both the aerosol and gas phases, the issue of ‘fogging’ and the risk of formation/degradation of substances during monitoring. Indeed, the variation in emissions measurements results between laboratories for the same analyte at the same sampling site of a facility has been shown to be significant. Numerous offline and online measurement methods have been used at pilot plants with varying success.

20. Various solvent and waste water monitoring techniques are reviewed.

21. Measurement of nitrosamines in the ambient air at the levels expected around CCS processes (sub ng/m^3) appears possible but with some limitations (humidity and breakthrough issues). Further work is required to develop a reliable method that can measure nitrosamines in the ambient air over a sufficient period to determine likely impacts of carbon capture processes. A reliable ambient air monitoring method is particularly needed to verify air dispersion models.

Table of contents

Tables and figures

Document status log

Version / date	Status	Comments / changes
V1 – 15 July 2011	Superseded by V1.01	Original manuscript submitted to the Environment Agency for England and Wales for review and comment and to Scottish Government and UK Government (Office of Carbon Capture and Storage (OCCS) for information
V1.01 – December 2011	Superseded by V1.1	Incorporates initial comments and updates assessment in light of additional available information at the end of October 2011. Minor typographical corrections addressed and structure revised.
V1.1 – February	Superseded	Final first draft version for publication incorporating

Version / date	Status	Comments / changes
2013	by V2.01	internal comments, additional references and peer review comments from the University of Edinburgh and the IEA Greenhouse Gas (IEAGHG) R&D Programme and comments from the Carbon Capture and Storage Association (CCSA).
V2.01 - April 2015		Draft for external peer review
V2.01 – August 2015	Live – this document	Final second draft version for publication incorporating internal comments, additional references and peer review comments from the University of Edinburgh, the IEAGHG, CCSA and University of Texas at Austin

1 Introduction, substances and properties

This paper is a review of available literature on emissions of amines and associated reaction products from post-combustion amine scrubbing carbon capture systems used in power generation. This review does not cover carbon capture systems based on oxy-fuel combustion, pre-combustion technologies or post-combustion chilled ammonia scrubbing or absorption techniques based on amino acid salts or other solids. Whilst amine-based carbon dioxide absorption systems can also be used in pre-combustion systems, in pre-combustion systems any amine-derived compounds escaping the gas processing plant will be abated in the syngas streams upon combustion and no direct release to air is expected.

Considerable international effort is being directed at the issue of the extent and impact of emissions of amine solvents and their reaction products from post-combustion carbon capture technologies. For instance, a number of multinational seminars and summary reports (IEAGHG 2013; IEAGHG, 2011a; IEAGHG 2010; Zero Emissions Platform, 2012; OCTAVIUS, 2014) have identified such emissions as a potential issue and noted that limited open source information is available. Others (Van Der Weijde and Van de Shouw, 2012; Henry et al 2011) have also recognised the key importance of addressing such emissions in an objective manner in order to reduce uncertainties in environmental permitting. Wherever possible, data on emissions and other releases in this review paper have been assessed on the basis of a 300MWe capacity carbon capture plant. This will aid reference to any large-scale UK demonstration projects which are expected to operate initially at this scale.

Initially most published data on this issue related to studies undertaken in Norway however more recently data has become available from other sources, including the UK, US, Australia and Holland, where pilot plants including Ferrybridge, Loy Yang and Maasvlakte have released data. This complements data available from bench-scale (laboratory) studies. Similarly, a significant amount of data relates to the use of solvents based on 2-aminoethanol (more usually referred to by its trivial name monoethanolamine or MEA). As such, the conclusions derived are likely to be subject to some uncertainty and may not be valid for capture systems based on solvents other than MEA, proprietary solvents and solvent mixes. The development of amine solvents is in some cases commercially confidential and therefore data on these solvents, and the expected emissions from their use, is not always publicly available.

The world's first commercial scale post-combustion amine scrubbing carbon capture and storage project at Boundary Dam, Canada was successfully commissioned in October 2014. Publication of process and emissions testing data at this site will help with our understanding of how scaling up affects emissions of amines and associated reaction products from these systems. Indeed, the Department of Energy and Climate Change (DECC) has recently signed an agreement to work with Canada's Department of Natural Resources on research and knowledge sharing surrounding CCS. Development of full-scale CCS at Mongstad has however been discontinued, but Test Centre Mongstad continues to act as a facility to test solvents. In the UK, DECC has recently announced £5million additional funding for CCS research, development and innovation in the UK.

It should also be recognised that this review is intended to inform technical assessments of post-combustion amine scrubbing carbon capture systems. This review is being made available to external bodies in the interests of transparency, despite the uncertainty noted in a number of areas. The report should not be used as guidance and does not necessarily express the opinions of SEPA. In line with the approach taken with Version 1.1 of this paper, and given the limited resources available for the review, independent peer review of

Version 2.01 of paper ‘Review of Amine Emissions from Carbon Capture Systems’ has been carried out.

The report is structured into four main sections. Section 1 outlines the general properties of the amine compounds likely to be emitted from carbon capture systems. Section 2 reviews the likely emissions of substances into the air, water and to land and also considers the atmospheric reactions that these substances can undergo. Section 3 reviews the likely environmental and health effects of substances focussing on the appropriate threshold values which may be applicable and against which the eventual environmental concentrations of emissions from carbon capture systems could be assessed. Section 4 considers the issues associated with the measurement of substances in stack emissions, solvents, wash waters and in ambient air.

1.1 Types of amines

There is a tendency for reference works to use non International Union of Pure and Applied Chemistry (IUPAC) or systematic nomenclature for various amine compounds. This has the potential for confusion. In this document, the first use of text naming a chemical is based on its full systematic (IUPAC) name together with any typical nomenclature and/or any typical abbreviation. Subsequent to this, the trivial name or abbreviation is used to identify the chemical. A full list of all the chemical compounds referred to in this paper is presented in a number of the supporting references (e.g. a Norwegian study on the extent of likely degradation products (Brakstad et al 2010a) that also details relevant abbreviations, acronyms and structure diagrams).

The group of chemicals known as organic amines are typified by substitution of one or more of the hydrogen atoms in ammonia (NH_3) by an organic group (Lawrence, 1994). This can be expressed in chemical notation as $N\text{-}(R_1,R_2,R_3)$. Primary amines are the group of compounds where one hydrogen atom has been substituted by one organic group, secondary amines have two hydrogen atoms substituted by two organic groups and so on. The typical amine solvents that have been used in carbon capture scrubbing systems tend to be the generic group of amines referred to as alkanolamines. These are primary or secondary amine compounds consisting of hydroxyl (alcohol) and amino functional groups on an alkane backbone. Most reported work has concentrated on the use of 2-aminoethanol (often referred to as monoethanol amine, MEA). This solvent is normally used as a baseline when comparing the performance of other types of amine solvents or mixtures of solvents.

Other alkanolamine compounds (either alone or in blended mixtures) have been proposed as carbon capture solvents include 2-(2-hydroxyethylamino)ethanol (often referred to as diethanolamine or DEA), 2-(2-hydroxyethyl(methyl)amino)ethanol (referred to as methyldiethanolamine or MDEA), 1-(2-hydroxypropylamino)propan-2-ol (referred to as di-isopropanolamine or DIPA) and 2-(methylamino)ethanol (referred to as monomethylethanolamine or MMEA). Other amine compounds have also been investigated as potential carbon capture solvents including cyclic and glycol amines such as 2-amino-2-methyl-propanol (referred to as aminomethylpropanol or AMP), the cyclic compound 1,4-diethylenediamine (universally referred to as piperazine or PIPA) and 2-(2-aminoethoxy)ethanol (referred to as di-glycolamine or DGA). A wide range of other, more highly substituted alkanolamines and polyamines are also being investigated at the laboratory scale (Lepaumier et al 2009). Proprietary solvents and solvent mixes are also being developed however information on the composition of these solvents is in some cases confidential.

Alkanolamine compounds are generally typified by having an odour of ammonia or rotten fish. They are strong bases and form alkaline solutions on dissolution. They are generally soluble or miscible in water and in solution can exhibit variable corrosive tendencies (Shao and Strangeland, 2009). These amine compounds can react with other compounds in the carbon capture system and the atmosphere to form a wide range of other compounds.

Solvent degradation is a complex phenomenon which is difficult to predict in new solvents and solvent blends and for this reason the importance of testing new solvents at pilot scale prior to large-scale use has been highlighted (Hoff et al, 2013). It is worth noting that in 2014 Technology Centre Mongstad (TCM) launched the world's first large-scale tests of current technology with the amine solvent MEA on a gas-fired turbine, the results of which will reportedly be shared with the global CCS community (Carbon Capture Journal, 2014).

1.2 Types of nitrosamines

The group of chemicals known as N-nitrosamines are typified by (R_1R_2)-N-N=O group where one or more of the hydrogen atoms on the non-oxygen bonded nitrogen atom is substituted by an organic group (IUPAC, 2012). A wide range of individual nitrosamines have been implicated in emissions from carbon capture systems although many studies are inconsistent on the extent of emissions. The specific compounds include nitroso compounds of the original alkanolamine solvents, nitroso compounds of short-chain aldehydes and of primary and secondary amines such as dimethylamine as well as cyclic compounds such as nitrosopiperazine. The most widely studied nitrosamine is N-methyl,N-nitroso-methanamine (usually referred to as N-nitrosodimethylamine or NDMA) due to its toxicity and potential environmental effects (see Section 3). Recent research has however suggested that N-ethyl,N-nitroso-ethanamine (commonly named N-nitrosodiethylamine or NDEA) may be more toxic than NDMA (Ravnum et al, 2014).

Most of the nitrosamines discussed above tend to be water soluble. For instance, NDMA is soluble in water (US EPA, 2012) and consequently aqueous scrubber systems, after the absorber column within the carbon capture system, may offer an effective way of abating such emissions to air. This is discussed further in section 2.5.

1.3 Types of nitramines

The group of chemicals known as nitramines are typified by (R_1R_2)-N-NO_2 group where one or more of the hydrogen atoms on the non oxygen-bonded amine nitrogen atom is substituted by an organic group (IUPAC, 2012). A wide range of nitramines have been implicated in the atmospheric reactions arising from emissions from carbon capture systems, however there is limited monitoring data. The specific compounds include nitro versions of many of the nitrosamines discussed above as well as nitro compounds of short-chain alcohols and of primary and secondary amines such as methanamime and N-methylmethanamine (referred to as dimethylamine or DMA) as well as cyclic compounds.

A range of studies have identified the potential nitramine compounds that may be of importance (see Section 2.1.5 below). Some studies (Knudsen et al, 2009b) have identified specific candidate nitramines for investigation such as N-nitro-N-methyl-methanamine (referred to as Dimethylnitramine or DMNA), N-nitromethanamine (referred to as methylnitramine) and 2-(N-nitroamino)-ethanol (referred to as ethanolnitramine) as being potential amine reaction products.

Some of the nitramine compounds identified are soluble in water (including DMNA) and aqueous scrubber systems may offer an effective way of abating such emissions to air. See section 2.5 for further review.

1.4 Types of other reaction products

The breakdown of amine compounds can result in a very wide range of other emissions. This includes ammonia as well as primary and secondary short-chain amines (such as methylamine). Other substances likely to be formed include amides (such as methanamide - common name formamide), as well as short-chain acids (ethanoic acid) and ketones. In addition, aldehyde compounds (such as ethanal), cyclic nitrogen compounds (such as morpholine) and peroxyacetylnitrate (PAN) type substances are likely to be emitted. These compounds generally have established and potentially significant environmental and health impacts (Attalla, 2010; Karl et al, 2011). The potential control methods for such emissions are discussed in Section 2.5 below.

2 Emissions

SEPA holds very limited data on amine emissions. Only two substances appear on the Scottish Pollutant Release Inventory (SPRI) database; diphenylamine and methylamine. These amines have not been reported as being released from a Scottish site either above or below the threshold (10 kilogrammes per annum (kg pa) and 1 kg pa respectively) since records began in 2002. In 2014 they were dropped from the SPRI pollutant list and are no longer reportable (however, substances can be reinstated or added as deemed necessary).

The Pollution Inventory (PI) for England and Wales does not include any nitrosamines.

2.1 Emissions to air

There is some available information on the expected emissions of amines and other pollutants from the published results of laboratory and pilot-scale tests, typically using MEA-based solvents. Several other amine solvents (either in isolation or as mixtures) are also potentially suitable for flue gas carbon dioxide capture, as discussed above in Section 1, as well as proprietary solvent mixtures containing undisclosed mixtures of amine solvents (Shao and Stangeland, 2009).

Most published work concentrates on the use of MEA. However, it should be noted that other solvent mixtures that could contain secondary or alkanolamines are likely to produce more extensive and wide-ranging potential reaction products (including nitrosamines). An increase in the type and quantity of the degradation products from such solvents over and above those produced from MEA alone is expected due to the reactivity of secondary amines in comparison to primary and tertiary amines (such as MEA and triethanolamine (TEA) respectively), that are unable to react directly with other substances to form stable nitrosamines (IEAGHG, 2011a; Pedersen et al, 2010; The Dow Chemical Company, 2010; Boot-Handford 2014). Solvent mixtures have been reported to maximise the desirable qualities of the individual amines (Adeosun et al, 2013) and incorporating secondary amines has been shown to enhance rates of absorption, reduce energy penalties and reduce corrosion problems (Aroonwilas and Veawab, 2007; Barzagli et al, 2009; Thitakamol, et al 2007). Solvent mixtures are therefore likely to be adopted in large-scale demonstration scale projects and specific testing of these mixtures may be required to demonstrate likely emissions.

It is likely that operators will have access to information generated from demonstration projects on emissions of many amine compounds and associated reaction products that has not been made available in the public domain. In light of the paucity of open source information available on such emissions, operators may need to provide detailed emission estimates for all relevant compounds, including the source and basis for such emission estimates, when seeking regulatory opinion of the approach used to quantify the emissions from the carbon capture process.

2.1.1 Amine 'slip' and emissions

During the carbon capture process, it is expected that a small proportion of amine solvent will escape from the absorber and be released to the atmosphere together with the cleaned flue gas (Shao and Stangeland, 2009). Amine emissions to the atmosphere will be as a gas, within moisture droplets and/or aerosols generated by the scrubber and in condensate formed after the flue gas exits the stack (Shao and Stangeland, 2009; IEAGHG, 2012a; da Silva et al, 2013a). The generation and impact from aerosols is particularly not well understood.

The extent of publicly reported amine concentrations in stack emissions are limited and vary significantly. Some of the available data are summarised in Table 2.1 below (expressed as a mass concentration value in milligrammes per normalised cubic metre mg/Nm^3). It is important to note that many of the reported emissions concentrations are based on pilot plant studies (on equipment that may have not been optimised for emission control and using specific fuels) and are a mix of theoretical and measured data.

Table 2.1: Reported amine concentrations in stack emissions

Source	Reported emission concentration (mg/Nm^3)	Comments
SINTEF SDR rig (OCTAVIUS-Session 4, 2014)	0.00065 to 0.0015	As DMA emissions in high oxygen, high stripper temp and high NOx
Niederaussem pilot plant (Moser et al, 2011a)	0.02 to 0.03	As MEA
Gassnova (OCTAVIUS-Session 1, 2014)	0.010-1	Total amine concentrations based on four different technology vendors after 3 000 hours testing in pilot or demo plants
CASTOR pilot plant (Ayrshire Power Ltd, 2010)	<0.1	-
CESAR pilot plant (da Silva and Aas, 2010) and theoretical studies (IEAGHG, 2012a)	<0.3	As MEA. Post-absorber wash sections in theoretical studies on coal-fired plant. Increased emissions from natural gas-fired plant (5.5 mg/Nm^3) may be expected if post-absorber cooling systems are not adopted
Overview studies (IEAGHG, 2006a)	0.5 to 3	As MEA (in isolation)
ENEL Pilot Plant (OCTAVIUS-Session 4, 2014)	1.2 to 1.5	As MEA emissions with WESP ON/OFF
Maasvlakte pilot plant, Holland (da Silva et al,	0.97 to 4.0	As MEA after demister unit. Aerosols found to be major contributor to

Source	Reported emission concentration (mg/Nm^3)	Comments
2013b)		emissions
Mobile test facility at Longannet (Graff, 2010)	1 to 4	-
Mongstad Test Centre, Norway (Berglen et al., 2010)	1.4 to 8.2	Estimated as MEA. Reference conditions not stated. 16.3 mg/m³ as a maximum possible emission scenario
Large-scale demonstration system estimates (Huizeling and van der Weijde, 2011; Scottish Power, 2010)	approx 2	Total amine emissions from absorber exit after wash systems with proprietary solvents
Loy Yang pilot plant, Australia (Azzi et al, 2014a)	2.4	As MEA
Mikawa Pilot Plant (Fujita et al, 2013)	2.7	Total amine emissions
Kårstø demonstration plant (Shao and Stangeland, 2009)	2.7 to 11	Estimated amine emissions
Anticipated emissions (Wen and Narula, 2009)	3.5 to 6.8	As amine, after absorber wash systems
Laboratory conditions (Thitakamol, et al 2007)	8.5	-

The emissions data in Table 2.1 generally shows that newer data tends to show lower emissions, indicating improved process control. Others report solvent loss in terms of tonnes per annum, for example amine emissions from the 420MW gas-powered facility at Karsto (Norway) were estimated to be in the range of 40-160 tonnes amine/year (da Silva et al, 2013a).

Some environmental permits (TCMDA Permit, 2011) for smaller demonstration scale carbon capture systems have suggested emission limit values of 6 ppm for total amine compounds (around $16mg/Nm^3$ expressed as MEA). Other environmental permits (ROAD Permit, 2012) for larger-scale demonstration carbon capture systems have suggested emission limit values for total organic hydrocarbon compounds (including amines) of $23mg/Nm^3$ (expressed as C). Other industrial processes, such as foundry and maggot farming activities have emission limit values for amines (Secretary of State’s Guidance 2004, 2005) ranging from 1 to 5 volumetric parts per million (ppmv) (5ppmv of equates to around 7mg/m3 of methylamine or 10mg/m3 of DMA) although it is recognised that this limit should only be applied where it is considered that there is potential for offensive odour beyond the site boundary.

The Ferrybridge Carbon Capture Pilot (CCPilot100+) permit variation (EPR/VP3337SR/V004) specifies a limit of 15 tonnes per annum for amines, (expressed as MEA) and the Environment Agency has developed an approach to the public reporting of total amine concentrations from carbon capture systems (Ferrybridge Permit, 2010). This can be adopted where commercial confidentiality issues associated with the disclosure of the precise amine solvents being used are apparent.

Emissions of amines in waste streams are discussed in Section 2.4. The abatement and control of amine emissions is discussed in Section 2.5 below.

2.1.2 Amine degradation mechanisms and reaction products

The main reaction pathways for amines within the carbon capture process are oxidation, thermal degradation and acid gas reactions. These mechanisms are complex and different solvents can act in different ways. However loss of MEA can also occur through evaporation from the absorber column (Reynolds et al., 2012). A summary of each mechanism is presented below.

2.1.2.1 Oxidative degradation

Oxidative degradation of amines is caused by the presence of oxygen and metals such as vanadium, iron and copper present in the flue gas (Shao and Stangeland, 2009; Gouedard et al., 2012; Boot-Handford et al., 2014). It is expected that this route will be the main degradation pathway although other reference studies (Berglen, et al., 2010) recognise that the mechanisms of oxidative degradation are not yet fully understood. The degradation products (Shao and Stangeland, 2009; IEAGHG, 2012a), Zero Emissions Platform, 2012) could comprise oxidised fragments of amines such as ammonia, organic acids, aldehydes (such as ethanal and methanal, etc.) and carboxylic acids (such as methanoic acid, hydroxyethanoic acid and ethandioic acid). Oxidation is reported to take place primarily in the absorber sump, absorber packing, and in the rich/lean solvent piping and heat exchanger (Artanto et al., 2012). Metals that encourage oxidation can be generated by corrosion of the pipework or can be intentionally added as salts for corrosion inhibition such as $CuCO_3$ or $NaVO_3$ (Gouedard et al., 2012).

It has been estimated that oxidation can consume 0.29−0.73kg MEA/tCO_2 captured (Goff and Rochelle, 2004). However some amines are reported to be resistant to oxidation at absorber conditions, including piperazine, tertiary amines, and hindered amines (Boot-Handford et al., 2014). When used in blends tertiary amines can themselves act as oxidation inhibitors (Boot-Handford et al., 2014). MDEA has also been reported as being effective in inhibiting the oxidation of MEA at absorber conditions (Voice et al., 2013). A variety of oxygen scavengers and corrosion inhibitors have also been investigated such as ethylenediaminetetraacetic acid (EDTA) and bicine (N,N-Bis(2-hydroxyethyl)glycene) which bind with the metal ions and act to limit such oxidation (Shao and Stangeland, 2009). Choosing the inhibitor is important as laboratory trials have found that many additives accelerate oxidative degradation or form heat stable salts with MEA (Reynolds et al., 2012). Addition of inhibitors is further considered in Section 2.5.1.6.
It is important to note that much of the literature on oxidative degradation is based on laboratory scale experiments which may not reflect the extent of the formation of degradation products in larger-scale systems (Berglen et al., 2010).

2.1.2.2 Thermal degradation

The capture mechanism of alkanolamines involves reaction with carbon dioxide and conversion of the alkanolamine to an amine carbonate salt. This capture of carbon dioxide can be reversed at elevated temperatures (in the amine re-boiler and stripper system) which can result in the degradation of the salt and amine (Eide-Haugmo et al., 2011). Thermal degradation is reported to primarily occur in the stripper packing (Gouedard et al., 2012), stripper sump, reboiler, solvent reclaimer and piping leading to the rich/lean heat exchanger (Artanto et al., 2012) and is reported to account for around 20-30% of total amine losses (Shao and Stangeland, 2009). A review of thermal degradation research found that primary and secondary ethanolamines degrade at 100-130^{0}C as they form cyclic oxazolidinones and ureas, whereas teritiary amines are more resistant to degradation if they do not include methyl and ethanol groups (Rochelle, 2012).

The maximum operating temperature of the amine re-boiler and stripper system is therefore determined by thermal degradation (Rochelle, 2012). Stripper operational temperatures are typically quoted at around 110ºC. This temperature is regarded (Davis and Rochelle, 2009) as being the optimum stripper temperature for MEA-based solvents representing the best compromise for minimising thermal degradation whilst maintaining the other parameters required for the best possible stripper operation. The main thermal degradation products of MEA are 1-(2-hydroxyethyl)-2-imidazolidone (HEIA) and 2-(2-aminoethyl)amino)ethanol (N-(2-hydroxyethyl)-ethylenediamine - HEEDA), Oxazolidin-2-one (OZD) and N,N-bis-(2-hydroxyethyl)urea along with other polymerisation products (IEAGHG 2012a; Davis and Rochelle, 2009). Recent monitoring at pilot plants (IFP Energies nouvelles and EDF R&D) using MEA has however found ten new degradation products; pyrazine and nine alkylpyrazines (Rey et al., 2013).

The thermal degradation rate of solvents based on compounds such as 2-amino-2-methylpropanol (AMP) is expected (Eide-Haugmo et al., 2011) to be less than MEA-based solvents. It has been reported that piperazine is most resistant to thermal degradation followed by AMP, a hindered amine, then MDEA, a tertiary amine and finally MEA, a primary amine (Artanto et al., 2012). Others however report piperazine as a reactive amine and state that mixtures containing piperazine will degrade more rapidly as the reactive amine participates in carbamate polymerisation (Rochelle, 2012). Results from a solvent degradation rig indicate that the degradation of nitrosamines and nitramine in the solvent is also highly temperature dependent, and that the levels of total nitrosamines and MEA-nitramine are significantly reduced by elevated stripper temperature (Einbu et al., 2013).

The study of combined oxidative and thermal degradation has lacked research attention (Artanto et al., 2012).

2.1.2.3 Acid gas reactions and formation of nitrosamines

These reactions concern the reaction of oxides of nitrogen and oxides of sulphur present in the flue gas entering the carbon capture system, with amines following the dissolution of these substances in the amine solvent. The reaction of each of these substances is considered below:

2.1.2.3.1 Oxides of nitrogen

Typical combustion flue gases from coal and gas-fired plants contain a mixture of nitrogen dioxide and nitrogen monoxide (together referred to as NO_x) with nitrogen monoxide (NO) forming the main component of between 90- and 95% (European IPPC Bureau, 2006). NO will not react with amines (Jansen et al., 2007), however it can be oxidised to nitrogen dioxide (NO_2) at the absorber inlet or flue gas desulphurisation system (IEAGHG, 2011a; Pedersen et al., 2010). The NO_2 can react with amines to form numerous degradation products including ammonia and nitrosamines (Berglen et al., 2010). Recent research has found the formation of N-nitrosomorpholine to increase linearly with the concentrations of NO and NO_2 up to concentrations of around 40mg/Nm^3 (Dai and Mitch, 2014). The NO_x to NO_2 conversion factor will be applicable when discussing atmospheric amine degradation.

Secondary amines can react directly with NO_2 (in a two phase reaction) to form nitrosamines. However both primary and tertiary amines can also form nitrosamines indirectly (Boot-Handford et al., 2014). It has been shown that MEA, a primary amine with low potential to form nitrosamines, degrades to the secondary amine DEA under influence of NO_x, with DEA then nitrosated to NDELA (Fostas et al., 2011).
NO_2 is the component of the NO_x emissions likely to enter the liquid phase in the absorber. NO_2 does not by itself react with amines to form nitrosamines but it can do so in a reaction catalysed by formaldehyde. This has been suggested to be the dominant mechanism for the formation of nitrosamine in carbon capture systems (da Silva et al., 2013a).

Measurements at some small scale demonstration sites (da Silva and Aas, 2010) appear to indicate that NO_x emissions will be reduced in the carbon capture system due to the reaction of NO_2 with amine compounds. Others suggest (E-on UK, 2011) that only minimal (<3%) NO_x absorption may occur in the absorber system. To minimise solvent degradation it is generally recognised (IEAGHG, 2007a; Harkin et al., 2010; IEAGHG 2006b) that NO_2 concentrations at the inlet to the carbon capture system should be kept below a threshold of between 2 and 40mg/Nm^3. This NO_2 concentration can usually be met by the use of the normal emission reduction systems associated with Best Available Techniques (BAT) (IEAGHG, 2007a; IEAGHG, 2007b). It is also recognised (IEAGHG, 2011a; Pedersen et al., 2010) that limiting NO_2 concentrations entering the capture system to levels as low as possible would minimise the formation of these unwanted degradation products.

For the newest and largest coal-fired and gas-fired plants, meeting the requirements of the European Union Industrial Emissions Directive (IED) (Directive 2010/75/EU), the worst case NO_2 concentration in the absorber inlet (assuming NO2 represents around 10% of total NO_x concentrations) would be around 15mg/Nm^3 for coal-fired plant. For gas-fired plant (assuming NO2 represents up to 50% of total NO_x concentrations) would be between 25 and 50mg/Nm^3. These expected concentrations could be reduced to below 5mg/Nm^3 if a pre-scrubber polishing unit or direct contact cooler system is adopted (IEAGHG 2011a; European IPPC Bureau, 2007).

2.1.2.3.2 Oxides of sulphur

Oxides of sulphur (SO_2, SO_3) can react with amine solvents to form heat-stable corrosive salts (Jansen et al., 2007; Knudsen et al 2009a). Concentrations at the inlet of the capture plant therefore need to be restricted to between 3 and 30mg/Nm^3 in order to minimise amine degradation and thus long-term solvent usage (Jansen et al., 2007; Smith et al., 2008; IEAGHG, 2007a). For solid fuel systems, these thresholds are typically achieved using an additional ‘polishing unit’ placed after the standard flue gas desulphurisation systems (Jansen et al., 2007) upstream of the absorber. It may be possible to adapt and enhance the efficiency of conventional flue gas desulphurization (FGD) systems to meet such values (Wu et al., 2010; IEAGHG, 2012b). This could reduce the need for a pre-scrubber system (Ayrshire Power Ltd, 2011) and the negative consequences of such systems in terms of plant cost, operability and chemical usage. However, careful design and operation of the enhanced conventional FGD system will be required to consistently meet the suggested threshold concentration values at the inlet of the carbon capture system. Due to the formation of heat stable salts and the use of pre-scrubber and post-absorber washes, total emissions of sulphur dioxide are expected to decrease to negligible concentrations after post-combustion carbon capture systems (IEAGHG 2012b; Ayrshire Power Ltd, 2010).

2.1.2.3.3 Other reaction pathways

It has been reported that concentrations of other substances in the carbon capture system, such as metals, particulate matter and carbon dioxide, can create other reaction pathways. Models have been developed to simulate the degradation processes occurring in the solvent (Thong et al., 2013). As with all models assumptions are made and a degree of uncertainty is expected.

Overall it is recognised that there is abundant public domain information on the degradation of amines. However, it is now being considered that pilot plant studies under real power plant operating conditions are showing that the possible degradation mechanisms of amine solvents and their kinetics may differ from those measured under laboratory conditions. For example, some organic compounds present in reclaimer wastes from a US coal-fired power station (Strazisar et al., 2003) have not been previously reported as MEA degradation products found in laboratory scale experiments. These findings imply that degradation products are likely to be, to some extent, specific to each plant and to the type of fuel used.

Consideration of other reaction pathways is given below.

2.1.2.3.3.1 Metals

Studies (Shao and Stangeland, 2009) have reported that the precise role of dissolved metals in amine degradation reactions are not fully understood although MEA degradation is reported (Knudsen et al., 2009a) to be catalysed in the presence of metals. It has also been reported that high metal concentrations lead to abnormally high ammonia emissions by promoting MEA degradation (Mertens et al., 2013). It has been reported that in the reaction of trace elements with amines, forming water soluble compounds, these compounds can be transported in the absorber/stripper systems by physical entrainment as aerosols (Azzi et al, 2013).

2.1.2.3.3.2 Particulate matter

Ensuring that particulate matter concentrations at the inlet of the capture system are reduced as far as possible is also important. Limiting the concentration of particulate matter to suggested (IEAGHG, 2007a) threshold values of <5 mg/Nm^3 will also reduce the input of other substances (such as metallic elements associated with particulate matter) into the capture plant.

2.1.2.3.3.3 Carbon dioxide

Recent research has indicated that CO_2 can itself act as both an inhibitor and catalyst in the formation of nitrosamines in DMA (Sun et al., 2011). CO_2 appears to act as a catalyst when a weak nitrosating agent, e.g. nitrite or nitrate is present, whereas CO_2 acts as an inhibitor if the nitrosation is induced by a strong nitrosating agent such as dinitrogen trioxide or nitrosyl chloride (Sun et al., 2011).

2.1.3 Emissions of nitrosamines

A review of available studies indicates that the breakdown products from amine solvent reactions (including nitrosamines) are varied (Shao and Stangeland, 2009; Pedersen et al., 2010; Ayrshire Power Limited, 2010; da Silva and Aas, 2010; Berglen et al., 2010; IEAGHG 2010; Brakstad et al., 2010a). It should be noted that some of the published data on emission concentrations relate to measurements made at or below the stated limit of detection (LOD) and thus the concentration values quoted will depend upon the chosen measurement technique. For example recent bench-scale experiments could not identify 42% of the nitrosamines formed (Einbu et al., 2013). The extent of the expected substances concerned and the reactions that lead to their occurrence in the process are discussed in section 1 and 2 above. The limited data on emissions from pilot plants, bench scale experiments and models that has been published are summarised in table 2.2.

Table 2.2: Reported emissions concentrations from pilot plants

Source	Reported nitrosamine emission µg/m^3	Comments
Ferrybridge Pilot Plant (Fitzgerald, 2014)	Total 20 NDINA 11 NDELA <0.1 to 1.8 NDIBA <0.1 to 3.1 NDINA <0.1 to 11 NDMA 0.1 to 0.2 NDBA <0.1 to 0.5	Nitrosamine emissions were inconsistent over two sampling campaigns. In October 2013, total nitrosamine was 20µg/m^3 with three different nitrosamines identified and the highest, N-nitrosodiisononylamine (NDINA) at 11µg/m^3. In December 2013, no nitrosamine was detected above 1µg/m^3 and of the three different types identified only NDELA was present in the October 2013 analyses
Loy Yang Pilot Plant (Azzi et al., 2014a)	NMOR 0.4 NDMA & NDEA <0.003	NMOR (4-nitrosomorpholine) concentration after wash water
Gassnova (OCTAVIUSSession 1, 2014)	0.1 to 5	Nitrosamine concentrations based on four different technology vendors after 3000 hours testing in pilot or demo plants NDEA, NDMA and NMOR analysed for.
Maasvlakte Pilot Plant (da Silva et al., 2013b)	0.005 to 0.047	Aerosols found to be major contributor to emissions
CSIRO Aspen-Plus simulation (Thong et al, 2012)	NMOR 0.003	Modelled emissions by Aspen-Plus. Concentration of maximum emission per m^3 CO_2
Mobile test facility at Longannet (IEAGHG, 2010; Graff, 2010)	<1	Nitrosamines were measured in four out of ten test runs

Mongstad Test Centre (Berglen et al., 2010)	5.0 to 9.9	Calculated data based on result from test facilities. Nitrosamine concentrations (expressed as NDMA) as a worst case scenario.

The possible measures to control nitrosamine emissions are discussed in Section 2.5 below.

Environmental permits for larger-scale capture demonstration plant (ROAD Permit, 2012) have imposed individual emission limits for nitrosamines and nitramines of 1mg/Nm^3.

2.1.4 Emissions of nitramines

Little dedicated work has yet been undertaken to quantify nitramine emissions from degraded amine solvents (Brakstad et al., 2010a). Published monitoring results of nitramines emissions are given in the Table 2.3. A list of typical nitramines that have been implicated in emissions from carbon capture systems is summarised in section 1.3 above. Table 2.3 presents the limited data reported on nitramine emissions from pilot plants.

Table 2.3: Reported nitramine emissions from pilot plants

Source	**Nitramine emission µg/m^3**	**Comments**
Maasvlakte Pilot Plant (da Silva et al., 2013b)	0.005 to 0.047	MEA-nitramine detected (in concs similar to nitrosamines) but no specific details
Gassnova (OCTAVIUS Session 1, 2014)	Not detected	Nitramine concentrations based on four different technology vendors after 3000 hours testing in pilot or demo plants
EPRI (OCTAVIUS Session 1, 2014)	0-40	Estimated nitramines emissions used to demonstrate detection limits for measurements. Concentration expressed as DMNA

2.1.5 Emissions of ammonia

The dominant emission produced from post-combustion carbon capture has been reported to be ammonia (IEAGHG, 2012a) and some regard ammonia and alkylamines as the most important degradation products due to their high volatility (Hoff et al., 2013). Trials at the Ferrybridge CCPilot100+ pilot plant reported ammonia stack emissions up to 305 mg/Nm^3, significantly higher than those predicted by process simulation modelling or those encountered during previous amine-based carbon capture pilot plant trials (Ferrybridge, 2014). At Ferrybridge ammonia concentrations at the absorber outlet were recorded at levels between 62 and 299mg/Nm^3 (Ferrybridge, 2014). In another case, high ammonia emissions of 20 to 70mg/Nm^3 were attributed to the higher concentration of oxygen in the flue gas (Kolderup et al., 2012). Some studies (Ayrshire Power Ltd, 2010) indicate that elevated emissions of ammonia may be expected from amine scrubber carbon capture systems that were not fitted with abatement equipment (in the order of 25 mg/Nm^3). These concentrations are lower than results from other studies (da Silva and Aas, 2010; Graff, 2010; Azzi et al., 2014a) that suggest ammonia releases in flue gases may reach up to 250mg/Nm^3. Other studies (EEA, 2011) indicate that unabated ammonia emissions could exceed even these values. However, other estimates (Huizeling and van der Weijde, 2011) of ammonia emissions from large-scale demonstration systems based on proprietary solvents fitted with absorber wash systems have been reported as being around 1mg/Nm^3.

The actual emissions of ammonia mainly depend on the absorber temperature. Ammonia arises from the oxidative degeneration of amines (Mertens et al, 2012). These emission concentrations would represent a high annual amine degradation rate which would increase with increasing NO_x concentration at the inlet of the scrubber system (Pedersen et al., 2010). Consequently, limiting NO_2 concentrations at the scrubber inlet is an important consideration. These high degradation rates are also expected to reduce with the adoption of proprietary amine mixtures.

While it is expected that elevated emissions of ammonia may be released from carbon capture systems it is not clear whether the quoted emissions estimates include the effect of aqueous abatement systems. A number of guidance notes (Secretary of State’s Guidance, 2004, 2005; European IPPC Bureau, 2006) suggest emission limit values for ammonia from various industrial process ranging from <1 to 5mg/Nm^3. Means to control ammonia emissions are discussed in section 2.5 below.

2.1.6 Emissions of other substances

A wide range of chemicals from the breakdown of amine compounds have been implicated in the emissions from carbon capture systems. The typical compounds are discussed in Section 1 above. Where emission concentrations of specific substances have been reported, results have been presented as less than the limit of detection (Zero Emissions Platform, 2012).

Some studies (Karl et al, 2011) suggest that emissions of amides, methanamide and ethanamide, may be of the order of 0.3ppm and 0.1ppm respectively. Methanal (formaldehyde) concentrations have been reported (da Silva and Aas, 2010; IEAGHG, 2012a) in emissions to air between 0.4 and 1.5mg/Nm^3.

Other volatile oxidative degradation products, such as volatile acids and aldehydes, have been detected in the gas streams exiting the absorber and desorber columns of both CASTOR and Niederaussem pilot plants (Reynolds et al., 2012). Over 20 degraded amines were identified after 3000 hours operation in a Toshiba solvent, TS-1, wash water scrubbing flue gas, and flue gas by using GC/MS and LC/MS at Toshiba 10 ton-CO_2/day pilot plant in coal-fired Mikawa Power Plant (Fujita et al., 2013).

It is worth noting the potential impact on NO_x emissions from power plant due to the addition of carbon capture systems. It has been reported that both reference data and models suggest that NO will not be removed by addition of post-combustion CCS and thus NO_x emissions are expected to increase slightly roughly in proportion to the increased fuel use (IEAGHG, 2012b) and temperature will also affect NO_x production.

The fate and behaviour of mercury compounds entering the carbon capture system has been assessed in some studies (IEAGHG 2012b). This work suggests that elemental mercury is not expected to be absorbed by MEA solvents to any great degree and that mercury oxidation is not expected to occur in amine solvents. Oxidised mercury is expected to be absorbed by aqueous amine solvents and is likely to be recovered in reclaimer sludge wastes.

It has been reported that in coal-fired power stations hydrogen halides decrease substantially when CO_2 capture is integrated due to acidic nature of these gases and the alkalinity of solvent (IEA GHG, 2012b). It has also been predicted that there will be a substantial reduction in the emissions of particulates and trace metal associated with particulates, such as iron, silicon and arsenic (IEA GHG, 2012b).

2.1.7 Emissions of aerosols

More research is being carried out into the generation and impact of aerosols in carbon capture systems. However there remain gaps and uncertainties in the understanding of the formation and release of aerosols.

Amines have shown a tendency to form aerosols and amine compounds can be a significant portion of the urban (and continental and marine air) submicron aerosol mass (Karl et al., 2010). In the urban environment these amine aerosols are typically generated by wastewater treatment, agriculture and possibly from vehicle emissions (Abalos et al., 1999; Angelino et al., 2001; Westerholm et al., 1993). Some studies have highlighted that the issue of ‘fogging’ (where spikes in amine emissions are caused as a result of amine vapour entrainment) on particulates/aerosols needs to be considered (Fitzgerald, 2014). In studies, it has been shown that tertiary amines form significant aerosol whereas secondary or primary amines do not (OCTAVIUS: Session 6-1, 2014; Murphy et al., 2007). And at the Ferrybridge pilot plant it was suggested that hydrogen chloride reacts with the absorber inlet water vapour to generate aerosols which in turn absorb/entrain the amines (Fitzgerald, 2014).

Aerosol precursors are reported to be ultrafine liquid or solid particles of sulphuric acid, salts or particulate matter (Mertens et al., 2013) and ammonia (vapour) and HCl (vapour) (Geotheer and da Silva., 2012) in the flue gas entering the system from the power plant. These precursors act as nucleation sites for water vapour within the process, and when formed, these mist droplets can absorb MEA (Mertens et al., 2013). Studies have found H_2SO_4 aerosols entering the absorber to be extremely small (<0.2μm) and remaining smaller than 1μm even with the uptake of water in the absorber. The same study found that most of the water (and thus amine) is found in aerosols between 0.5 and 2μm in size (Mertens et al., 2014).

In terms of gas-fired power plants, aerosol formed by reactions are not expected to be significant, however aerosol formed by condensation is something which could occur in gas-fired power plants (Geotheer and da Silva., 2012). Aerosols can also be formed by mechanical entrainment (Geotheer and da Silva., 2012).

During stable operating conditions on a mobile test unit, high MEA emissions were attributed to mist formation (Knudsen et al., 2013). Similarly, other pilot plants have reported that MEA emissions were attributed to mist formation in the system (Kolderup et al., 2012). Other studies at high NOx concentrations have reportedly found higher aerosol mass emissions (Azzi et al., 2014b). Elevated aerosol emissions have also been reported for coal-fired plant using MEA and piperazine (PZ) based solvents (Angove et al., 2013).

The formation of mists and aerosols can be reduced or their emissions abated by a number of methods: eliminating mist precursors upstream of the absorber (e.g. sulphuric acid, salts, particulates), avoiding large temperature gradients in the system through good design and operation, and removal of mist downstream (Mertens et al., 2013; Goetheer and da Silva, 2012).

Many studies on aerosols relate to the coal-fired case however tests have shown that besides flue gas quality, the absorber temperature profile and the presence of CO_2 in the flue gas are pre-requisite for aerosol emissions (Khakharia et al., 2013).
The presence of aerosols has potentially significant impacts for the efficiency of abatement systems (see section 2.5).

2.2 Atmospheric reactions

Emissions to the atmosphere of amines and their degradation products, namely nitrosamines and nitramines, can result in both the formation and destruction of many (~100) substances (IEAGHG, 2010; Shao and Strangeland, 2009). The focus of this section is on the degradation of the emitted amines, nitrosamines and nitramines from the carbon capture process, the further formation in the atmosphere of nitrosamines and nitramines and the consequent implications for determining the steady-state concentration of these substances.

The atmospheric chemistry is complex and involves gas phase, aqueous phase (aerosols, cloud droplets, fog and rain) and particle phase (aerosol) chemistry. Atmospheric reactions of the chemicals emitted can occur as a result of photolysis (reaction with light energy) and can also be initiated by reactions with oxidants and radicals. In addition, the chemistry and dispersion of the emissions need to be considered together as reactions may change as the plume dilutes. Understanding of the atmospheric chemistry of amines has improved recently. However it is acknowledged that there are still significant knowledge gaps, such as aerosol formation mechanisms and further work on these issues is required (Lee and Wexler, 2013; Ge et al., 2011b; Nielson et al., 2012; Karl et al., 2012a).

2.2.1 Formation of nitrosamines and nitramines

The key reaction leading to the formation of nitrosamines and nitramines from amines in the atmosphere is initiated as a result of oxidation, as shown in the simplified photo-oxidation scheme in figure 1.

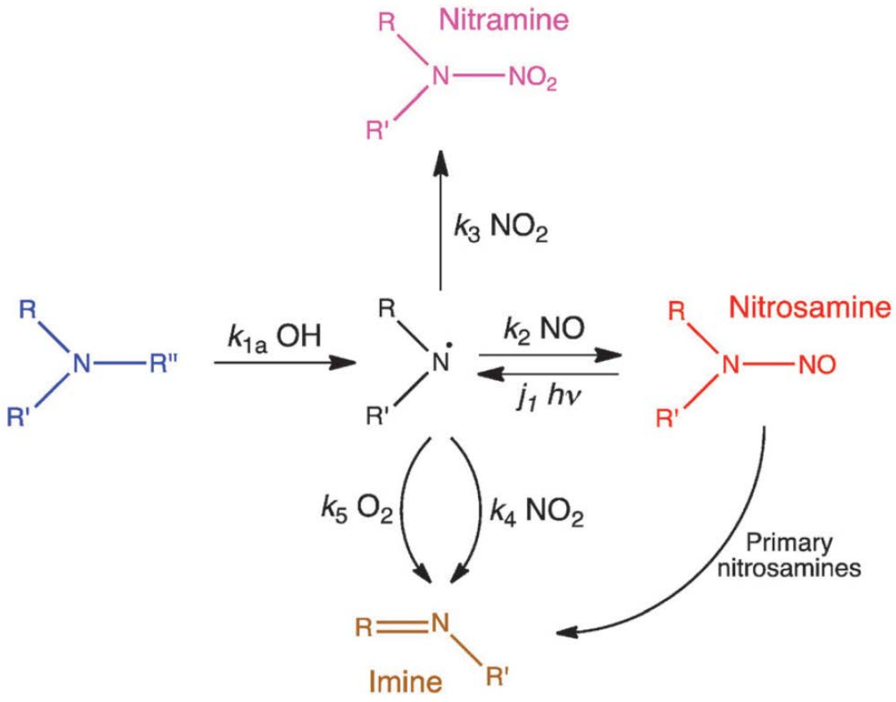

Figure 2.1: Atmospheric photo-oxidation scheme for amines taken from Nielson et al., 2012b.

The initial step in figure 2.1 shows the amine reacting with the OH radical to form an amine radical. This initiation step can also occur by reaction with chlorine, NO_3 radicals and ozone and is the rate-limiting step in the formation of nitrosamines and nitramines (Nielson et al., 2012b). Reaction with OH is the dominant gas phase loss process for amines (and indeed trace gases globally) and reaction rates between amines and OH are fast, however as OH radicals are produced photolytically this reaction will not occur at night-time (Nielson et al., 2012b). The upper limit of the atmospheric lifetime for MEA and piperazine by consideration of OH chemistry is estimated to be 2.4 hours and 1.2 hours respectively (Angove et al., 2013).

Reaction with chlorine atoms can be particularly important in coastal environments due to sea-spray and can contribute up to the equivalent of 10% of OH levels and react with amines extremely fast (Nielson et al., 2012b). However some lab experiments with Cl atoms have failed to produce nitrosamines (Feilberg 2011). NO_3 radicals, in contrast, have low concentrations during daylight hours as sunlight breaks NO_3 down into NO and O_2, but levels increase at night where it can be a dominant reactant. Ozone can be a significant removal process for tertiary amines (with approximately a four hours lifetime), but reactions are generally slow with primary and secondary amines (Nielson et al., 2012b). Reaction with bromine atoms may account for atmospheric loss of tertiary amines, but is not thought to be significant enough to be considered in dispersion modelling (Nielsen et al., 2012a).

The rates that these reactions occur have been determined through experiments and are characterised by rate coefficients or reaction rate constants.

The schematic in figure 2.1 represents a generic amine with three functional groups (typically H, alkyl or alcohol groups in various proportions). In primary and secondary amines where there are respectively two and one N-H bonds, the OH can abstract H to form the intermediary amine radical which can then react with NO or NO_2 to form nitrosamines and nitramines (or imines) respectively. The likelihood of the OH reacting with N-H rather than a C-H in the organic group is termed the branching ratio and is dependent on the C chain length and the number and the type of organic groups (e.g. alkyl or alcohol). Branching ratios for primary amines are reported to be 75C:25N in methylamine (Nielson et al., 2011a), $<10C_2:>81C_1:9N$ in ethylamine (Nielson et al., 2011a), and $8C_1:84C_2:8N$ (Nielson et al., 2011b), or $5C_1:80C_2:15N$ (Karl et al., 2012b) in monoethanolamine. Branching ratios in secondary amines are reported to be 63C:37N or 58C:42N in dimethylamine and $<10C_2:>30C_1:60N$ in diethylamine. In tertiary groups the H abstraction can only occur on the alkyl chain and formation of nitrosamine and nitramine requires further steps to break the C-N bond.

Unlike secondary amines, the primary amine MEA does not form a stable nitrosamine in air (Karl et al., 2012b). Primary amines cannot form nitrosamines as they degrade rapidly to release nitrogen gas and a positively charged carbon-based derivative (Ridd, 1961), but all amines can form nitramines (Tonnesen, 2011b). All amine solvents can form secondary amines through oxidative and thermal degradation (Fine et al., 2013).

Once the amine radical is formed it has the potential to react with NO to form nitrosamine or with NO_2 to form nitramine or imine, however the main products of photo-oxidation are amides, e.g. the major products (>80 %) in the photo-oxidation of MEA are methanamide and methanal (Nielson et al., 2011b). Through chamber experiments with MEA, only 8% of the initial MEA reaction with OH radicals results in the formation of amino radicals that may react with NO or NO_2, and therefore only a small fraction of the photo-oxidized MEA ends up as nitramine or nitrosamine (Nielson et al., 2011b).

It has been reported (but without published research) that directly downwind of power plant flue gases, limited formation of nitrosamines and nitramines is expected because the high NO concentration in the plume scavenges the OH radicals, which are necessary for amine degradation (Dautzenberg and Bruhn, 2013). Furthermore, it is reported that when MEA is present with limited NO, MEA or its reaction products act as an NO_2 sink, reducing reactivity by presumed removal of NO_2 (Azzi et al, 2014b).

Amines, nitrosamines and nitramines are all soluble in water and NDMA has been found in fogs and clouds at appreciable concentrations of 7.5-397 ng/l (Hutchings et al., 2010). Studies have shown that during fog episodes gas phase concentrations of DMA and DEA reduce by more than 80% and the nitrosamine NDELA fully partitions into the aqueous phase (Karl et al., 2012a). Due to its high volatility only a small fraction (0.1%) of NDMA will partition into the aqueous phase and the concentrations found in fogs are likely to be due to in-situ production in the droplets (Karl et al., 2012a). NDMA can therefore be considered as a pure gas phase compound with respect to estimating environmental effects (Karl et al., 2012a). Aqueous phase chemistry involves different reactions to those occurring in the gas phase and is generally initiated by radicals or ions; e.g. OH, NO_3 and SO_4^- (Nielson et al., 2012). Due to the acidic nature of rainwater (pH~5.6) (Karl et al, 2014), H-abstraction is less likely to take place at the N-H bond and will therefore not directly lead to nitrosamine formation. This consideration does not however apply to piperazine (Nielson et al., 2012). Furthermore reactions of amines with nitrite or nitrous acid are typically too slow to lead to nitrosamine formation and therefore partitioning into the aqueous phase can actually serve to prevent overall nitrosamine formation (Nielson et al., 2012).

2.2.2 Destruction of nitrosamines and nitramines

Nitrosamines and nitramines are destroyed in the atmosphere as well as formed.

Photolysis can be a major reaction leading to the destruction of nitrosamines in the gas, particle and aqueous phases (Nielson et al., 2012b). Photolysis on a timescale of five to thirty minutes has been suggested in full sunlight and 60 minutes in cloudier conditions (Hanst et al., 1977, Tuazon et al., 1984, Larsen 2011). In very low light, such as during the winter solstice, photolysis lifetime has been estimated to be 10 hours (Larsen, 2011). However in cloud droplets, nitrosamines are thought to be shielded against photolysis due to the screening effect of dissolved organic compounds (Hutchings et al., 2010. Karl et al, 2012a). This implies a longer lifetime of nitrosamines in clouds and fogs than in the gas phase. However others have found photolysis of nitrosamines in solution to be an effective destructive process (Hermann, 2011). This further highlights the uncertainty associated with liquid/aerosol chemistry.

It should also be noted that the photolysis rate constant has only been derived for NDMA (Tuazon et al., 1984). Reaction of nitrosamines with OH has been found to take 100 times longer than photolysis, around three days (Zabarnick et al., 1986) but reaction with OH is thought to be a major destructive process for both nitrosamines and nitramines in clouds (Nielson et al., 2012b). Reaction with Cl and NO_3 are not thought to constitute an important atmospheric sink for nitrosamines due to reactions being slow relative to photolysis (Nielson et al., 2012b). As shown in figure 1, it has been reported that primary nitrosamines isomerise and react with O_2 within seconds to give the corresponding imines (Nielson et al., 2012b), however more recent research appears to disprove this (da Silva et al., 2013c).

The atmospheric chemistry of imines is still unclear to a large extent.

Amines and nitramines do not absorb light in the wavelengths available in the lower troposphere and are therefore not photoreactive (Nielson et al., 2012b). Nitramines are therefore expected to be more stable in the atmosphere than nitrosamines and their half-life is thought to be around 2 days (Tuazon et al., 1984). Studies have been conducted on the reaction of nitramines with OH (Tuazon et al., 1984; Nielson et al., 2012), which is considered to be the major atmospheric sink. It is not thought that reactions with Cl and NO_3 constitute an important atmospheric sink for nitramines due to reactions being relatively slow (Nielson et al., 2012b).

It has been reported that in environments with very high NO_x concentrations, conversion of nitrosamines to nitramines might need to be considered (Larsen, 2011).

2.2.3 Steady state concentration

Research has been conducted through laboratory chamber experiments and modelling/calculations using reaction rate constants to estimate the conversion rate of amines to nitrosamines and nitramines in the atmosphere. Within all the studies, there are a number of uncertainties, such as the gas/particle/aqueous phase partioning and chemistry associated with these media (and the growing relevance of aerosol emissions), the formation and destruction processes and the speciation of nitrosamine and nitramines. Measurements in smog chambers can also be affected by the chamber walls as amines are notoriously prone to adhesion to such structures (Lee and Wexler, 2013).

It has been suggested that the steady state mixing ratio should be considered rather than the yield, which takes into account both the formation and destruction mechanisms (Nielson et al., 2012b). In some circumstances however, the predicted steady state may not have been reached by the time the plume reaches the ground impact area, such as that described around Mongstad (Tonnesen, 2011b). It is also worth repeating that nitrosamines (and nitramines) are a group of compounds and their chemical properties and toxicity differ, so studies focusing on the chemistry of a specific nitrosamine may not reflect that of the whole group.

There are two methods for estimating the resultant steady state concentrations of nitrosamine and nitramines in the ambient air, summarised below.

2.2.3.1 Percentage conversion rates

A percentage conversion rate directly measured through experimental studies, such as a photo-oxidation chamber. These studies use selected concentrations of amines, and reactants (such as NO_x, OH radical, photolysis) and therefore their transferability to environments with different ambient conditions must be considered. Some of these studies may not consider all formation and destruction mechanisms and therefore may not reflect the steady state concentrations. Conversion rates reported from chamber experiments are presented below and range between 0 and 10% (30% value disputed).

2.2.3.2 Reaction rate constants

Modelling using reaction rate constants such as those derived from Lindley et al (Lindley et al., 1979). These rate constants can be derived through Structure-Activity Relationship calculations or laboratory experiments and therefore the same experimental uncertainties apply, for example the rate constant for MEA with OH has been reported to range from 3.1×10^{-11} to 25.6×10^{-11} $cm^3 molecule^{-1} s^{-1}$ (Angove et al, 2013). The use of rate constant calculations are recommended by some as they can be tailored to different scenarios and are reported to take into account all formation and destructive mechanisms (Nielson et al., 2011c). Rate constants are incorporated into the Cambridge Environmental Research Consultants chemistry module (Atmospheric Dispersion Modelling System (ADMS amines). The total conversion rates of amines to nitrosamines reported using calculation from rate constant data and dispersion modelling are presented below and are typically <1% but can reach up to 8%.

A summary of the conversion rates and calculations to estimate the concentrations of nitrosamines and nitramines are given in tables 2.4 and 2.5.

Table 2.4: Amine to nitrosamine/nitramine conversion rates as measured directly through experimental studies

Source	Estimated conversion rate	Comments
Photooxidation chamber experiments (Pitts et al., 1978)	2.8% NDEA from DEA 0.8% NDEA from TEA	Chamber experiments undertaken in 0.08ppm NO and 0.17ppm NO_2 (0.16ppm NO_2 for TEA). DEA was destroyed in sunlight
Reaction chamber experiment (Hanst et al., 1977)	10-30% nitrosamine	Chamber experiments undertaken in high reactant concentrations (0.5ppm nitrous acid, 2ppm NO, 2ppm NO_2). Not representative of ambient conditions

Source	**Estimated conversion rate**	**Comments**
		where NO_x urban annual average concentrations are typically maximum 0.05ppm Conversion disputed and later reported to be as a result of surface reaction (Glasson, 1979)
EUPHORE MEA study (Nielson, 2011a)	0% nitrosamines 3-10% nitramines in typical European urban (up to 50ppbv NO_x) 0.05-3% nitramines in typical European rural (0.2-10ppbv NO_x)	European Photochemical Reactor (EUPHORE) study chamber
EUPHORE 1°,2°,3° amines (Nielson 2011b)	<2.3% nitrosamine from DMA in urban (up to 50ppbv NO_x) <4.2% nitrosamine from TMA in urban (up to 50ppbv NO_x) <0.4%-5% nitramines in rural (0.2-10ppbv NO_x) <1.5% - <15% nitramines in urban (up to 50ppbv NO_x)	EUPHORE study chamber

Source	Estimated conversion rate	Comments
TCM study (Berglen, 2010)	2-10% nitrosamines 0.4% nitramines from MMA 2.5% nitramines from DMA	Worst case conversion rates based on literature. These were disputed (Nielson, 2011c). See text below for further discussion

Table 2.5: Amine to nitrosamine/nitramine conversion rates as derived using reaction rate constants

Source	Estimated conversion rate	Comments
Modelling study (Karl, 2012b)	0.87% nitramines yield	Modelled concentrations using WRF-EMEP model. Reaction between nitramine and OH radicals was not considered in the model
Calculated steady state concentrations (Nielson, 2011c)	1% NDMA from DMA (worst case) 0.2% NDMA from DMA (most likely) Agree with nitramines concs in TCM modelling study	Rebuttal of TCM study above. Estimated annual average steady state concentration 0.1%
Calculated concentrations at TCM (Tonnesen, 2011b)	~0.2% to ~4.2%	Response to rebuttal by Nielson above. Steady state concentrations were reported not to be setup in the 40 minutes the plume took to reach main ground impact area.
Calculations using rate constants (Nielson et al., 2012b)	8% nitramines 2% nitrosamines	Calculations based on 4ppbV NO and 16ppb NO_2

As part of the air dispersion modelling for Mongstad, conversion factors between 2% and 10% were assigned to substances with the potential to form nitrosamines. For example primary amines have little potential to form nitrosamines, tertiary amines have higher potential and secondary amines have the highest potential to form nitrosamines. Also cyclic amines like piperazine have high potential to form nitrosamines (Berlen et al, 2010). However this approach was disputed both in terms of the percentage values used and as it only considers yield, thereby overlooking destruction of nitrosamines (Nielson, 2011c). Instead, rate constants were recommended which take into account formation and destruction mechanisms. Using these it was calculated that steady-state NDMA concentration would be less than 0.1% of the DMA present in the air mass. For modelling purposes at TCM the maximum nitrosamine concentration for NDMA was recommended to be ten times the estimated annual average steady-state concentration; 1% of DMA.

Due to photolysis it has been reported that amine photo-oxidation in an (expanding) air parcel will be far less than indicated by the yield of nitrosamine in the amine photo-oxidation (Nielson, 2011c). For a nitrosamine photolysis lifetime of 2 hours a 2% nitrosamine yield in the amine photo-oxidation only results in around 0.3% nitrosamine in the air parcel – all due to photolysis of the nitrosamine (Nielson, 2011c).

Taking on board the comments from Nielson (Nielson, 2011c), NILU updated their dispersion calculations to consider the nitrosamine concentration with lapsed time rather than using the 2 to 10% conversion rates (Tonnesen, 2011b). The percentage conversion rates given in the report are shown in the figure 2.2.

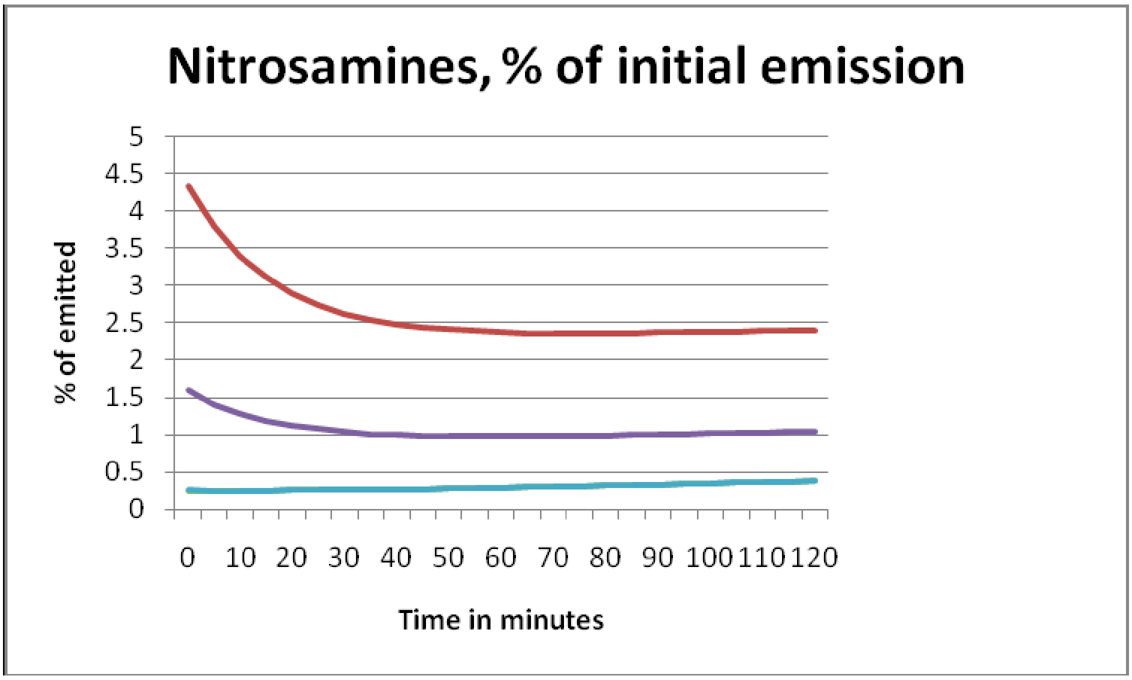

Figure 2.2: Showing % conversion over time of two solvents from two processes at TCM taken from Tonnesen, 2011b.

An atmospheric dispersion model which includes a module simulating the simplified atmospheric chemistry of amines is now commercially available from Cambridge Environmental Research Consultants (ADMS amines). Other modelling tools currently being used for research purposes include WRF-EMEP (Karl et al., 2014), WRF-Chem (Gjernes et al, 2013), COSMO-MUSCAT (Gjernes et al, 2013), Calpuff by DNV (Gjernes, 2013), and TAPM (Azzi et al, 2014b). By introducing chemistry into dispersion models it has been suggested that the maximum ambient air concentration of the sum of nitrosamines/nitramines can be reduced by a factor of 10 relative to the assumption of instant formation at the outlet of the stack (Gjernes et al, 2013). This is due to simultaneous dispersion and chemical transformation considerably slowing down the formation rate of nitrosamines and nitramines (Gjernes et al, 2013).

As with all models, assumptions are made based on available research and literature and therefore both the inputs and outputs of any model need to be updated and scrutinised, and model uncertainty allowed for. As understanding of the presence of aerosols in carbon capture systems has developed, it has also been reported that more work is needed to integrate aerosol formation into amine chemistry models. However, understanding of aerosol formation is still not advanced, and recent research such as the CLOUD experiment at CERN has studied the role that amines play, i.e. significance of reaction with sulphuric ad, in aerosol particle formation (Charley, 2013).

2.3 Emissions to water

Two separate pathways for emissions to water from post-combustion carbon capture systems are considered:

- Emissions of liquid waste from the carbon capture system to surface waters.
- Emissions to air that are followed by wet deposition either directly to surface waters or to land with subsequent transport to surface waters.

Wet deposition to surface waters is considered in section 3.2.

2.3.1 Waste water emissions to surface waters

There appears to be little published evidence on the extent of liquid wastes that may be generated by carbon capture systems (such as waste amine solvent, wash water and acid wash water, condensate recovery system wastes or liquid wastes from cleaning). Some of these liquid waste streams might not be suitable for discharge into surface water.

The aqueous scrubber wastes will contain soluble non-volatile degradation products such as short-chain organic acids (Brakstad et al., 2010a). The limited published data available (Pedersen et al., 2010; da Silva and Aas, 2010) suggests that NDELA and methylamine have been detected in waste waters from test rigs at concentrations of 0.01 mg/l and 0.3 mg/l respectively. This is consistent with other reports that cite unsourced data (Zero Emissions Platform, 2012) that suggest nitrosamine concentrations in the aqueous solvents themselves will be many orders of magnitude lower than the concentration of the amine solvent. Some studies (Reynolds et al., 2012) note that dissolved nitrites and nitrates in process make-up water may react with amine compounds to form nitrosamine and nitramines. Measured total nitrosamines in wash water in a pilot facility reached 54mg/l (assuming NDMA) from a MEA-based solvent and 6790mg/l (assuming nitrosopiperazine)from a mixed AMP/PZ solvent (Dai et al., 2012). In addition, NO has been found to play a particularly important role in driving N-nitrosomorpholine formation in wash water which is suggested to be a consequences of partial oxidation to NO_2 by O_2 (Dai and Mitch, 2014).

The accumulation of nitrosamines in wash water is influenced by the structural characteristics of the amine solvent employed. Primary amines are reported to lead to the lowest nitrosamine accumulation for diamines and amino acids, while order (primary, secondary or tertiary) does not have an effect on nitrosamine accumulation for alkanolamines (Dai and Mitch, 2013b).

2.3.2 Fate of amines and amine degradation products in surface waters

Nitrosamines and nitramines are generally resistant to hydrolytic degradation, while nitrosamines are highly susceptible to photodegradation (Sørensen et al., 2013). Based on atmospheric studies, it has been assumed that nitrosamines would degrade rapidly in the aquatic environment due to exposure to light (Tuazon et al., 1984) however a number of environmental factors, such as the concentration of suspended solids in the aqueous phase (which will impact on the extent of penetration of light into the water) will affect the photodegration rate of nitrosamines (Sørensen et al., 2013). Furthermore, aquatic mixing that could transport nitrosamines to the depth of the receiving waters where light energy cannot penetrate may reduce the photodegradation rate (Sørensen et al., 2013).

The biodegradation rate of different nitrosamines varies significantly in the water environment with half-lives of around 30 days for NDELA to over 1500 days for NPZ (Brakstad and Zahlsen, 2011). Studies of the biodegradability of 20 alkanolamines in seawater indicated that ultimate degradation half-lives ranged from eight days to more than 700 days, and were influenced by the structural characteristics of each individual compound (Brakstad et al., 2012). The degradation of NDMA in lake water was found to be slow, of first-order kinetics and depending on concentration, with degradation rates increasing with decreasing initial NDMA concentration (Kaplan and Kaplan, 1985). Furthermore, rates of degradation were reduced when supplemental carbon was available in aqueous systems, while unaffected in soil systems (Kaplan and Kaplan, 1985). More research on the prevalence and toxicity of amines, nitrosamines and nitramines in natural waters is necessary before the environmental impact of new point sources from carbon capture facilities can be adequately quantified (Poste et al., 2014).

Techniques and technologies to reduce emissions, including the concentration of amines and their degradation products within emissions to water, are considered in Section 2.5 below.

2.4 Emissions from other plant areas

A review of potential waste streams, their predicted quantities and their disposal requirements indicated that very little information on such issues had been published at the time of the first review and limited new information has been published on these issues since.

Waste water or solid wastes from post-combustion carbon capture systems are not commonly quantified and reported during pilot plant trials (Moser et al 2011b). More work on this area is required to determine the exact composition of these wastes and the appropriate treatment or disposal routes. Some wastes are likely to be classed as hazardous wastes IEAGHG, 2012b; Veltman and Hertwich, 2009). A description and summary of available data for each potential waste stream is given below (the additional wastes from abatement technologies are considered in Section 2.5).

2.4.1 Reclaimer system wastes

The application of thermal reclaiming in carbon capture systems is considered in Section 2.5 below. Due to a lack of accumulation of impurities in the solvent in pilot plants as a result of relatively short operating times, the reclamation of solvent has not always been necessary (Reynolds et al., 2012) and as a result available data is limited. In the study of toxicity to aquatic organisms (fish, invertebrates and algae), MEA reclaimer waste (from coal-fired plant) is reported to contain additional toxic substances other than MEA (Wang et al., 2013).

The composition of reclaimer waste will vary depending on, for example, the flue gas composition and the corrosion products accumulated in the solvent. Available data (Thikakamol et al., 2007; Kingsnorth 2011a; Kingsnorth,, 2011b) suggests that batch reclaimer system wastes may have high pH values and appreciable sulphur contents and comprise a mixture of organic material, particulate matter and salts such as sodium nitrate as well as methanoic, ethanoic and ethandioic acid salts, thiosulphates, thiocyanates and sodium sulphate. The wastes may also contain (IEAGHG, 2006a) trace elements in ppm quantities such as chromium, copper, iron and nickel. Selenium has been identified at hazardous concentration in reclaiming waste from at least two full scale post-combustion carbon capture systems (coal-fired) (IEAGHG, 2014). Oxidised mercury is also expected to be absorbed by aqueous amine solvents and is likely to be recovered in reclaimer sludge wastes (IEAGHG, 2012c). These wastes will also contain amine compounds and a proportion of any corrosion inhibitors added to the solvent. Monitoring of the concentration of these substances in the amine recirculation system is an important consideration and some threshold values for the above substances have been derived (Thikakamol et al., 2007; IEAGHG, 2012c; Kingsnorth, 2011c; Scottish Power, 2010) (contaminant levels of 1.2 to 10% by weight) to determine when batch reclaimer systems should be operated.

Estimates of the production rate of amine reclaimer sludges vary considerably (Shao and Stangeland, 2009; IEAGHG, 2006a; Thikakamol et al., 2007; IEAGHG 2012c; Ayrshire Power Ltd, 2011b; Kingsnorth, 2011d; Wen and Narula, 2009; EEA, 2011) and it is not easy to determine the exact magnitude for a typically expected rate of waste production. Specific generation rates range between 0.02 to 15.9kg/tonne CO_2 captured. Some other sources indicate volumes of reclaimer waste may be 3.2kg waste/tonne CO_2 for MEA based systems (EEA, 2011). The range in values may reflect the theoretical nature of some of the estimates derived and published.

It has been reported that dilution with water by as much as 50% may be needed to recover sludge from the reclaimer (IEAGHG, 2014) with consequent impact on volumes requiring treatment and/or disposal. In terms of treatment options for reclaimer waste, incineration has been identified as a potential option however the high water content in the waste may mean that this option is not cost effective (Botheju et al., 2011).

Biological treatment has also been considered. However, it has been reported that nitrate levels may be too high for effective biological treatment and so an initial cleaning step may be required (IEAGHG, 2014). A very low carbon to nitrogen ratio is typically found in amine wastes and it may be necessary to take steps to increase the carbon – nitrogen ratio and to prevent ammonia and pH inhibition of the degradation process (Botheju et al., 2011; Wang et al., 2013). Consequently the nature of the wastes may require long residence times for biological treatment and as such may present a limitation to this treatment option (Geotheer and da Silva., 2012). Similarly, experimental and theoretical studies on amine/amine wastes have shown that both aerobic and anaerobic biodegradation is possible and that a combination of these can be the most efficient solution. However the experiments in this case identified a non-biodegradable fraction of the amine waste of unknown composition (Botheju et al., 2011). The toxicity to aquatic organisms (fish, invertebrates and algae) of effluent from treated waste from anaerobic digestion of MEA reclaimer waste (from a coal-fired plant), when combined with a co-substrate was largely attributed to total ammonia nitrogen (NH_4^+ and NH_3) and free ammonia generated from degradation of the waste. However other toxic constituents may survive anaerobic digestion and unidentified toxic organics in the effluent were observed in this case (Wang et al., 2013).

2.4.2 Post-absorber wash system wastes

The limited data on the composition of post-absorber wash system wastes is considered in Section 2.3.1 above and the application of water and acid wash systems to post-combustion carbon capture plants is considered in Section 2.5 below.

2.4.3 Other wastes

There is limited data on the composition of wastes from Ion Exchange (IE) and Electrodialysis (ED). These abatement technologies are considered in Section 2.5. There is also limited information on amine containing wastes from CO_2 compression and dehydration systems, or mechanical filtration systems, and from direct contact cooler systems (pre-treatment scrubbers) (IEAGHG, 2011c) on post-combustion carbon capture plants.

Some studies (Jansen et al., 2007; Ayrshire Power Ltd, 2011c; Rao and Rubin, 2002; Feron et al., 2007) have suggested that spent activated carbon waste could be generated at rates of between 0.03 to 3.2kg/tonne captured. Adopting a central case estimate of these ranges (0.8kg/tonne CO_2) indicates that around 2000 tonnes per annum of activated carbon waste would be generated by a 300MWe demonstration scale carbon capture system.

Overall, it is recognised that more research on the quantity and composition of the waste containing amine compounds and degradation products from capture plants is required in order to identify the most appropriate disposal/recovery options.

2.5 Techniques and technologies to reduce emissions

The reduction in emissions of amine compounds and their degradation products can be achieved by two general approaches: minimisation/removal of precursor species and/or post-generation removal from emissions to air and to water. Minimisation of precursor species is discussed above in Section 2.1.2.

Some argue that emissions of parent amines to below 3mg/m^3 can be achieved by careful design of a combination of, for example, UV-light, water wash, acid wash and demisters (Hoff et al., 2013). Systems for the treatment of solvent/wash system circuits, post-absorber abatement systems and waste water treatment systems are considered in the sections below.

2.5.1 Treatment of solvent/wash system circuits

The build-up of, for example, corrosion products and amine degradation products within the solvent can alter the solvent's properties and increase degradation of the solvent (IEAGHG, 2014). Some studies (Thikakamol et al., 2007) indicate that filtering of a slipstream of the main amine solvent cycle (to remove degradation products from the amine solvent) at a rate of 0.5 to 2.0% of the total inventory may be required. Measurements at Loy Yang pilot plant found the nitrosamines NMOR and NDELA to be present within the solvent at concentrations of 16µg/l and 2.8mg/l respectively (Azzi et al., 2014a). Measurements at 'Pilot Plant 2' in Texas found nitrosopiperazine concentrations of 0.115g/l in the solvent (Nielsen et al., 2013) and nitrosamines with concentrations of 2.91µmol/ml (~0.215g/l assuming NDMA) in MEA in a pilot plant in Trona, California (Strazisar et al., 2003). These nitrosopiperazine concentrations were found to be in a steady state, being formed by high NO_2 and destroyed at stripper temperatures of 150^{0}C.

This section considers the treatment of solvent/wash system circuits by thermal reclaiming, ion-exchange, electrodialysis, ultraviolet radiation and the addition of inhibitors.

2.5.1.1 Thermal reclaiming

Different methods for thermal reclaiming exist (Idem et al., 2013) which are not considered in this paper. At present thermal reclamation, which can remove all degradation products, heat stable salts (HSS) and non-volatile impurities, is unique in this treatment capability (Idem et al., 2013). Amine reclaimer systems are only expected to operate intermittently in batch cycles (IEAGHG 2012a; Thikakamol et al., 2007) although low volume continuous systems may also be adopted. A recent study assumed an amine recovery rate of 85-95% for thermal reclaiming (IEAGHG, 2014). However, it has also been reported that some corrosion inhibitors degrade or are ineffective when used in systems with the elevated temperatures such as in thermal reclaiming systems (Boot-Handford et al., 2014).

2.5.1.2 Ion exchange

Ion exchange can only remove ionic impurities and ionic degradation products and so non-ionic species, such as nitrosamines, can accumulate in the amine system (IEAGHG, 2014). Therefore ion exchange alone may not be sufficient for CO_2 capture applications (Idem et al., 2013). Additionally, transition metals are minimally removed and those that are removed are likely to foul the exchange resin (IEAGHG, 2014). Ion exchange, which does not degrade the amine solvent and is most effective with high concentrations of heat stable salts, has been reported as capable of removing 90% of heat stable salts and recovering up to 99% of amines from a slipstream of amine (IEAGHG, 2014). Continuous operation has been proven to be more efficient than batch treatment (Idem et al., 2013).

2.5.1.3 Electrodialysis

Electrodialysis is limited to the removal of salts, allowing non-ionic impurities (e.g. nitrosamines) and most transition metals to accumulate in the system, where metals have the potential to foul membranes and the anode and cathode plates (IEAGHG, 2014) and can act as catalysts for nitrosamine formation (Knudsen et al., 2009a). Electrodialysis is reported to require filtration pre-treatment of amine feed down to 1 µm to avoid fouling (Idem et al., 2013) and a literature review by IEAGHG found that electrodialysis can lead to 1-2% amine loss (2014). It is reported that 86% - 97% removal of heat stable salts can be achieved by ED (IEA GHG 2014).

An evaluation of reclaiming technologies for solvents based on MEA alone, a MDEMA and PZ mixture and PZ alone, indicated that thermal reclaiming is likely to achieve the lowest amine recovery rates of 85-95% amine recovery whereas electrodialysis techniques can achieve 96-98% amine recovery and a 99% recovery rate for ion exchange. Electrodialysis and ion exchange systems were considered most effective when high concentrations of HSS were present (IEAGHG 2014).

Where ion-exchange and electrodialysis technologies are employed, the waste streams associated with these are reported to contain up to 95% water and so it is reported that they may be suitable for treatment in waste water treatment plants however in this case there was assumed to be no metals content in the waste streams (IEAGHG, 2014). ED waste is likely to contain high levels of salts and chemicals and may therefore be considered hazardous (Idem et al., 2013).

2.5.1.4 Ultraviolet (UV) irradiation

Nitrosamine concentrations in solvent circuits have also been found to reduce with UV irradiation (from an artificial UV source) within the absorber solvent (IEAGHG, 2011a). This was reported to offer an additional means to abate nitrosamine emissions without the use of extensive aqueous scrubber systems (IEAGHG, 2012a). Similarly, when using wash water with a recycle of wash water to the absorber, the level of nitrosamine in the wash water can increase, and UV irradiation may provide a method for reducing the nitrosamine concentration in the wash water (Goetheer and da Silva, 2012). NDMA appears to be photolysed in aqueous phases (Stefan and Bolton, 2002) and treatment with UV sources have been reported (IEAGHG, 2012a; Xu et al., 2008; Plumlee et al., 2008) to eliminate nitrosamine concentrations in some effluents.

However UV treatment for reducing nitrosamine concentrations has been reported to be difficult in amine solutions due to their colour that limits UV penetration (Geotheer and da Silva., 2012) and increased amine concentration leads to a decrease in the decay of nitrosamines by UV-light (Knuutila et al., 2013). These authors also reported that NDELA decomposed faster than NDMA

Others report that reductions in the UV-light NDELA degradation rates have been attributed to the absorption of UV by impurities, such as degradation products and/or dissolved metals (Mercader et al., 2013). Such studies also suggest that UV light may also accelerate the degradation of the solvent. Conversely, others report that photolysis is not destructive towards the solvent and the presence of nitrite ions in the irradiated solvent does not lead to the formation of nitrosamines (Jackson and Attalla, 2013).

Some studies suggest UV treatment could potentially achieve up to 90% removal of N-nitrosamines and have indicated that amines do not absorb UV light significantly and are thus unlikely to degrade (Shah et al 2013).

2.5.1.5 Ozone

There is limited information on ozone as a treatment technique for the solvent/wash system circuits, however it has been identified as possible treatment technique after UV radiation which may reduce amine and acetaldehyde concentrations in wash waters (Shah et al, 2013).

2.5.1.6 Addition of inhibitors to limit corrosion

Corrosion is a serious concern associated with thermal reclaiming (IEAGHG, 2014). Corrosion rates have been reported to be more related to temperature than other factors such as solvent loadings (Kittel et al., 2009) however, it has also been reported that every process parameter can have an impact on corrosion and most corrosion rates tend to increase with increasing amine concentration (Saiwan et al., 2013). The addition of inhibitors can reduce the rate of solvent degradation and nitrosamine formation. Corrosion of normal carbon steel can be controlled using stainless steels. Acceptable carbon steel corrosion rates with MEA/piperazine mixtures below 0.25mm/year are expected (Shao and Stangeland, 2009) with the use of corrosion inhibiters (such as sodium metavanadate and copper carbonate). However, continuous injection of corrosion inhibitors could lead to a build-up of chemicals in the amine solution, causing changes in the solution’s physical properties.

Some researchers have looked at low toxic corrosion inhibitors (Srinivasan et al., 2013) due to the content of toxic heavy metals in traditional corrosion inhibitors which can catalyse corrosion and work has been undertaken to identify corrosion inhibitors which prevent carbon steel corrosion and also inhibit MEA oxidation (Wattanaphan, 2012). The effect of NO_x on corrosion requires further work (Saiwan et al., 2013).

2.5.2 Post-absorber abatement systems

This section considers post-absorber water wash systems, acid wash systems, demisters and other scrubbing systems.

2.5.2.1 Water wash systems

Most amine solvents (and mixtures) and their associated degradation compounds tend to be water soluble (Shao and Stangeland, 2009; US EPA, 2012) and consequently adoption of aqueous scrubber systems, after the absorber column within the carbon capture system has been regarded as one method available for abating any unwanted emissions.

Many of the abatement technologies for emissions to air of amines and their degradation products only effectively transfer the pollutants from the gaseous phase to the aqueous phase and do not actually destroy the pollutants themselves. In fact, some researchers report that the main amine loss may actually occur in the waste waters generated by the capture plant (Shao and Stangeland, 2009). Any aqueous scrubber systems after the absorber are expected to remove non-volatile and medium volatile solvent degradation products from the gas phase, in addition to the solvents themselves although recent research has highlighted that the presence of aerosols may impact upon the efficiency of any aqueous scrubber system.

The impact on plant costs and operability with the addition of extensive, multistage scrubber systems may be significant due to the scale of the equipment that may be required for larger-scale capture plant. It is noted that other solvents (not based on MEA) may be more difficult to remove from emissions by aqueous scrubbing systems due to volatility and solubility considerations.

Studies on a coal-fired plant indicated that 99.9% removal of amine (with an inlet MEA concentration of 300mg/Nm^3) by a water wash system, which incorporated a demister (Azzi et al., 2013). In another test rig, online Fourier transform infrared spectroscopy (FTIR) analysis indicated a 99% MEA removal efficiency (from an inlet concentration of 270 mg/m^3) with no nitrosamines detected in the gas (Fostas et al., 2011).

However, other studies have shown that average MEA removal rates of only 60% (from an inlet concentration of 370mg/Nm^3) within water wash and demister systems (Kolderup et al., 2012). Others have found significant MEA emissions at the exit of a single water wash stage, ranging from 85-180mg/Nm^3 (dry) which were higher than predicted by process modelling (Goetheer and da Silva, 2012).

Recent research has found that a single stage water wash may not be sufficient to reduce MEA emissions to low levels. This is reportedly due to the presence of MEA in the form of aerosols, which a traditional water wash is not able to remove (Mertens et al., 2013). One study found solvent degradation products methylamine, ethylamine and dimethylamine present at measurable levels in both the before and after water wash gas streams (at low ppbv levels). However these compounds were not detected in the solvent or water wash liquor, suggesting that they are not retained in the circulating solvent and penetrate through the water wash section (Azzi et al., 2014a).

Multi-stage aqueous scrubber systems with demisters were expected (da Silva and Aas, 2010; IEAGHG, 2012a; Mertens et al., 2012) to be able to reduce amine emissions to levels of < ~0.5mg/Nm^3. However due to the small size of MEA aerosols, it has been reported that general demisters are not capable of removing these small aerosol emissions (Mertens et al., 2013).

It has been reported that wash water units may serve as a source, rather than a sink of N-nitrosamines to the atmosphere due to reactions of residual NO_x with amines accumulating in the wash water (Shah et al 2013). Other work has suggested that NO_x scavengers added to the water wash may present a potential option to prevent formation/reformation of nitrosamines and nitramines (Goetheer and da Silva., 2012).

Elevated emissions of ammonia may be released from carbon capture systems although it is not clear whether the quoted emission estimates include the effect of aqueous abatement systems. It has been reported that the anticipated emission concentrations should be easily abated (IEAGHG, 2012a; Zero Emissions Platform, 2012) in multi-stage aqueous scrubber systems (including acid wash stages) at the exit of absorber due to the high aqueous solubility of ammonia. However it has been reported that a water wash provided negligible reduction in ammonia emissions (Azzi et al., 2014a) and elevated ammonia emissions were reported at Ferrybridge pilot plant which operated with a single-stage water wash (Ferrybridge, 2014). In another case the water wash was reported to have no effect on NH_3 emissions (Mertens et al., 2013).

Pilot plant data has suggested that emissions of acetaldehyde (around 1mg/Nm^3) may penetrate through the water wash section or be formed in the water wash section (Azzi et al., 2014a).

2.5.2.2 Acid wash systems

An aqueous acid scrubber is expected to be efficient at removing base compounds. However, it is less certain how effective this will be in abating other amine degradation products from the gaseous phase and little data exists on expected abatement efficiencies although some studies (IEAGHGa, 2012/07) suggest that acid wash sections will be effective at removing unwanted amine degradation products. UV treatment of water/acid wash water circuits are considered to an effective way of maximising the removal that can be achieved by wash systems (IEAGHG 2012a).

Some studies (IEAGHG, 2012a) suggest that acid wash sections are effective at removing unwanted amine degradation products. In fact scrubbing with acid is reported to be seen as proven and currently state-of-the-art and is being used in some large-scale units (IEAGHG, 2012a). Ammonia emissions of below 5mg/Nm3 at a pH of 6 were obtained during tests of an acid wash scrubber at TNO's capture plant at Maasvlaakte (Khakharia et al, 2014).

There is reported to be the possibility that nitrosamines and nitramines may form in the acid wash which will most likely be a function of amine concentration, build-up of nitrate and nitrite (and other species in equilibrium with NO_X) and increased pH (Kolderup et al, 2014).

2.5.2.3 Post-absorber demisters

It has been reported that MEA appears to be an example of a component that might easily promote fog formation and mist emissions (Jansen et al 2007). Different components will have different susceptibility to mist emissions and it is reported to be most significant for hydrophilic components with a significant vapour-pressure at absorber conditions (da Silva et al., 2013b). Whilst flue gas from natural gas is expected to be less likely to form mist (and aerosols) due to reduced concentrations of particulate matter compared to coal systems, these aerosols are not removed by typical internal contacting surfaces in the absorber or water wash (Knudsen et al., 2013).

During trials at Maasvlakte pilot plant ammonia emissions were unaffected by the demister, which is consistent with ammonia emissions being in gaseous state, and aerosols were found to be a major contributor to overall emissions (da Silva et al., 2013b).

Anti-mist techniques have reportedly been successful during testing on coal-fired flue gas on a mobile test unit (Knudsen et al., 2013). The advantages and disadvantages of different types of demister systems have been reviewed (IEAGHG 2012a). These include Swirl-mist eliminators, vane demisters, wire mesh demisters, muticyclones and Brownian Demisters. Swirl-mist eliminators were identified as the preferred choice due to high efficiency of separation and low pressure drop. In other work Brownian Demister Units have been found to be effective at removing emissions of MEA in the range 67-92% but ineffective at removing ammonia emissions as they are present in the vapour phase (Kolderup et al., 2012). Scaling up can be an issue with demisters due to the pressure increase created (Geotheer and da Silva., 2012).

Other authors have identified the potential to remove aerosols by the use of electrostatic precipitators however more research is required on the application of this technique in the carbon capture sector (Geotheer and da Silva., 2012).

2.5.3 Waste water treatment

The treatment of drinking water by UV radiation, free radicals, ozone or ozone-hydrogen peroxide following the formation of nitrogenous disinfection by-products, including nitrosamines, after chloramination, has been reported (Nawrowocki and Andrezejewski, 2011). Furthermore, ozone treatment of reverse-osmosis concentrate containing nitrosamines has been investigated (Fujioka et al., 2014). The presence of nitrosamine precursors was found to be critical in the efficiency of removal, as some treatments lead to the formation of nitrosamines if precursors are present (Nawrowocki and Andrezejewski, 2011). UV radiation has been found to be almost as efficient as the combination of UV and ozone treatment; ozone and hydrogen peroxide together also show high efficiency (Nawrowocki and Andrezejewski, 2011).Whether these treatment options are feasible for the treatment of waste waters from post-combustion carbon capture systems requires further research.

The investigation of the removal rates for eight nitrosamines in full-scale sewage treatment plants in Switzerland (Krauss et al., 2009) found aqueous removal efficiencies between 43% (NMOR) and 89% (NPIP) during activated sludge treatment. Large variability of these rates was found not only between plants, but also within the same plant over a period of time (Krauss et al., 2009).

3 Environmental effects

The environmental concentrations of amines and the various amine reaction products (in terms of protection of human health and the environment) requires careful consideration (IEAGHG, 2011a; IEAGHG 2007b; Carbon Capture Journal, 2009).

3.1 Emissions to air

3.1.1 Ambient air (background) levels

Globally, monitoring of nitrosamines in ambient air has been primarily undertaken in industrial areas around potential sources of nitrosamine precursors, e.g. rubber processing, amine manufacturing, leather tanning, metal casting and food processing. The analytical methods used to produce these results generally have a low maturity and have not been adopted as national standards and there is no evidence of successful method validation as shown in Section 4 below. However a field trial of the method developed by NILU is being undertaken by SEPA. Table 3.1 below summarises the data available.

Table 3.1: Ambient nitrosamine concentrations

Compound and citation	Reported concentration (ng/m^3)	Comments
NDMA in ambient air (Pellizari et al., 1977)	400 to 32,000	Around various industrial sites that manufacture secondary amines in Baltimore, USA
NDMA in ambient air (Gordon, 1978)	30 to 1000	A study of fifteen sites in the Los Angeles area in the USA around various industrial sites that manufacture secondary amines
NDMA concentrations in air (Khesina et al., 1996)	30 to 60	Monitoring of N-nitrosamines undertaken in Moscow. Concentrations of NDMA of “several hundred ng/m^3” were reported in an industrial emissions area and >100ng/m^3 in a “heavy traffic area”
Ambient nitrosamines in particulates (Akyuz and Ata, 2013)	3.1 to 160	Study in seasonal variations of nitrosamines in airborne particles in Zonguldak, Turkey
Ambient concentrations in air of piperazine (Graedel et al., 2011)	10 to 60	-
Ambient air levels of NDMA (US National Library of Medicine; TOXNET, 2011)	10 to 46	2010 summary of other ambient measurements. The lower concentrations were measured in rural environments and the higher in urban.
Total N-nitrosamines in air Austria (Spiegelhalder and Preussmann, 1987)	10 to 40	16 sites around an industrial area of Linz, Austria. In this study, 363 ambient air samples were taken and NDMA was detected in 54 samples, N-ethyl-N-nitros-ethanamine (N-nitrosodiethylamine or NDEA) in 45 samples and 4-nitrosomorpholine (NMOR) in 2 samples. 6% of the samples contained >0.01$\mu g/m^3$ total N-nitrosamines

Compound and citation	Reported concentration (ng/m^3)	Comments
NDMA in ambient air(Hutchings et al., 2010)	8.4	California, USA
Ambient nitrosamines in particulates (Ozel, 2011)	0.62 to 22	Study of urban particulate matter in Birmingham. NDEA (nitrosodiethylamine) $0.62ng/m^3$ NDBA (nitrosodibutylamine) $3.5ng/m^3$ NPIP (nitrosopiperidine) $22ng/m^3$
Ambient nitrosamines in workplace dust (HSE, 2010)	0 to 2.0	Study of worker's exposure in rubber manufacturing by HSE, UK
Estimated ambient nitrosamines and nitramines from Loy Yang pilot plant (Azzi et al, 2014b)	10^{-10}–10^{-9} nitrosamines 10^{-8}–10^{-7} nitramines	Modelled from emissions from Loy Yang pilot plant by CSIRO
NDMA in ambient air (Pellizari, 1977)	None detected	Around a chemical disposal site in New Jersey
9 nitrosamine and 5 nitramine compounds in ambient air (Tonnesen, 2011)	None detected	Baseline study of air quality around the Mongstad refinery, Norway prior to operation of the carbon capture pilot plant (limit of detection 0.01 to $0.09ng/m^3$)
Nitrosamines in fogs and clouds (Hutchings et al., 2010)	7.5-400ng/l	Combination of field and laboratory studies

The above table suggests that industrial sources could contribute significantly to ambient levels of nitrosamines and nitramines.

NDMA, as well as a range of other nitrosamines, have been shown to be present in tobacco smoke and considerable research has been done on the extent and concentrations of such compounds in relation to tobacco smoking (Brunnemann et al, 1992).

3.1.2 Environmental standards for amines

A number of potential environmental quality limits (in air) for specific amines have been proposed (Shao and Stangeland, 2009). For example, some initial Norwegian work (Brakstad et al., 2010a) proposed a long-term EAL for MEA of $3\mu g/m^3$. This appears to have been derived from a long-term occupational exposure limit (OEL) of $0.3mg/m^3$ whilst a UK long-term OEL for MEA is $2.5\ mg/m^3$ (HSE, 2007. ECHA, 2010). A more recent Norwegian review (Lag et al., 2011) concluded that a long- term exposure guideline value for MEA of $10\mu g/m^3$ should be adopted which was consistent with the range of values adopted in the environmental permitting of a larger-scale demonstration project in the Netherlands (ROAD Permit, 2012). The UK have both long-term OEL and short-term (15 minute average) OEL for MEA of 7.6 mg/m^3 (HSE, 2007). If the UK occupational exposure levels are used to derive EALs for MEA, by applying a factor of 500 (due to carcinogenic effects) (HSE, 2007) EALs for MEA can be proposed at levels of between 5μg/m^3 (long-term) and 15.2μg/m^3 (15 minute short-term).

Further, a number of potential environmental quality limits (in air) for total amine compounds have been proposed (Shao and Stangeland, 2009; Brakstad et al., 2010a). The values quoted vary from 3 to 120μg/m^3. A short-term EAL of 3μg/m^3 for grouped amines can be derived by applying a safety factor 100 to the strictest occupational exposure limit quoted of 0.3mg/m^3. Other commonly used amines for carbon capture (e.g. AMP, MDEA and piperazine) do not have UK Work Exposure Limits (WELs). Other countries have differing occupational exposure limits for different amine compounds. For example, for piperazine, Norway and Denmark have only long-term occupational exposure limits (0.3mg/m^3 and 0.1mg/m^3 respectively) whilst Finland (Arcos Organics, 2010) has both a long-term OEL of 0.1mg/m^3 and a short-term OEL of 0.3mg/m^3. Since the EAL for a specific substance may vary, depending on the occupational exposure limit used and the safety factor applied, it would be inconsistent to develop UK EALs in the absence of any UK occupational exposure limits.

Horizontal Guidance Note H1: Assessment and Appraisal of BAT (EA/SEPA/NIEA, 2003/EA, 2010) contains a list of long-term and short-term EALs for some amines that are derived from British Occupational Exposure Standards (OESs) and Maximum Exposure Limits (MELs). In 2011, new and revised Workplace Exposure Levels (WELs) were introduced and the UK Health and Safety Executive (HSE) reviewed their approach to deriving occupational exposure standards, in line with the European Commission's third Directive on Indicative Occupational Exposure Limit Values (IOELV) (2009/161/EU). The IOELV are health-based limits set under the Chemical Agents Directive (98/24/EC). In most cases, the British WELs will be identical or very close to the EU IOELV. The HSE has carried out extensive work on MEA in the past but has confirmed that there is no current work on toxicological or human exposure research on other amines and degradation products arising from carbon capture systems. Where amines have no EALs or health guideline values, advice from UK independent scientific committees (e.g. Committee on Carcinogenicity, Committee on Mutagenicity and Committee on Toxicity) may need to be sought.

It should be noted that most health studies are based on the use of a single amine solvent; e.g. MEA, however there may be a commercial preference for solvent mixtures (mixed amines) to maximise the effectiveness of capture rate (see Section 1.1). Solvent mixtures are likely to produce more extensive reaction products than single amine solvents. Setting regulatory emission limit values and standards for amine mixtures and the degradation products that will result from their use may prove challenging due to limited knowledge of the behaviour of these mixtures.

The REACH regulation requires manufacturers and importers in the EU to register chemical substances with the European Chemicals Agency (ECHA). The ECHA has now registered MEA under the provisions of REACH (ECHA, 2010) and has assigned the substance an EC number of 205-483-3.

3.1.3 Environmental standards for nitrosamines and nitramines

Nitrosamines pose a potential environmental and health threat because they have a demonstrated environmental toxicity (US EPA, 2011; Brooks, 2008). NDMA and NDEA are potential chemical mutagenic carcinogens and are listed by the International Agency on

Cancer Research (IARC) as a group 2A carcinogen classified as “probably carcinogenic to humans” (IARC, 2012).

A number of health and environmental guideline values have been suggested globally for nitrosamines in the ambient air ranging from 0.07ng/m^3 to 10ng/m^3 and 10ng/m^3 for nitramines (Shao and Stangeland, 2009; Berglen et al., 2010; Brakstad et al., 2010a; Knudsen et al., 2009b). These limits may be exceeded where releases from carbon capture plants take place where ambient (background) levels of nitrosamines are high, especially where there are other sources as noted in Section 3.1.1 of this report. Some UK EALs for amines and nitrosamines have also been suggested by UK Front End Engineering (FEED) studies (Kingsnorth, 2011d). Other works have assessed and reviewed a range of international guidelines and regulations that may apply to nitrosamines and nitramines as groups (Selin, 2011; Selin, 2012). The statistical basis for these proposed standards (e.g. annual average, eight hour 95%ile average, etc.) are often not stated although it is assumed that these relate to longer-term averages.

A commonly quoted value (NIPH, 2011) for total (grouped) nitrosamines and nitramines, initially proposed by the Norwegian Institute of Public Health (NIPH), is 0.3ng/m^3. The environmental permit for Technology Centre Mongstad (TCM) uses this EAL, stating that the combined emissions to air at the absorber exit and the estimated annual average of background concentrations of nitrosamines and nitramines (i.e. predicted environmental contribution) should not exceed 0.3ng/m^3 for ambient air (Gjernes et al., 2013).

However, in a recent study (Ravnum et al., 2014) the Derived Minimal Effect Level (DMEL) of five nitrosamines (including NDMA and NDEA) and two nitramines (including Methyl—nitramine (NTMA) and Dimethyl-nitramine (NDTMA) were calculated from available dose descriptors and from raw data for animal studies. By applying a linearized modelling instead of the “large assessment factor” that was used in deriving 0.3ng/m^3 assessment limit for NDMA, a higher concentration for genotoxicity of NDMA (0.86 ng/m^3) was determined and a lower concentration for genotoxicity of NDEA (0.45 ng/m^3). Based on the results, they recommend a DMEL of 0.45ng/m^3 to be an acceptable level for the estimation of genotoxicity for nitrosamines and nitramines released by a carbon capture system. Even though the levels (i.e. 0.3ng/m^3 and 0.45 ng/m^3) are not considerably different, it suggests that subtle differences in data and data analysis can produce different results, which could further increase the uncertainties in risk assessment.

The toxic equivalent (TEQ) approach is used for the environmental assessment of dioxins and furans which consist of a broad class of compounds (about 210) with varying potencies. This approach relies on applying a toxicity factor assigned to each congener, relative to the most toxic compound. The TEQ approach has been applied (Wagner et al., 2014) by calculating the mutagenic potency of NDMA and comparing the relative genotoxicity of each congener of nitrosamines and nitramines to the potency of NDMA. The TEQ approach is applied to dioxins and furans but more studies on nitrosamines and amines are needed to determine whether the same approach can be applied to these groups of compounds. Dioxins/furans are considered as having thresholds (and their exposures are not linked to risk values) but NDMA is a well-established non-threshold mutagenic compound and because it poses risk at any level, its exposure is linked to an acceptable risk value.

Recent studies note that it is essential that the toxicities of the individual compounds add up to represent the ‘toxicity’ of the mixture of compounds in flue gases (an approach called ‘additive toxicity’). But where there are no data for toxicities of the individual compounds contained in the mixture and where the individual compounds has not been fully identified, comparison cannot be realistic. The lack of available toxicology data has recently been highlighted in an international workshop (Octavius: Session 2, 2014). Toxicity interactions between individual compounds in a mixture may either be synergistic or additive and may require the development of a matrix to match every substance present. *In vivo* reactions, like metabolic activation, will also render the comparison between a single substance and overall toxicity difficult.

Similarly, UK guidance (Horizontal Guidance Note H1, EA/SEPA/NIEA, 2003/EA, 2010) recommends a general approach for dealing with groups of similar compounds “where full characterisation and composition is not known” and recommends that a surrogate substance be used to represent the entire released mass. In this case, a substantial amount of effort would be needed to apply a TEQ approach to a group of compounds such as nitrosamines and nitramines because of the large number of compounds involved (over 300) and the absence of any relevant toxicology data for many of the compounds concerned. However, nitrosamines and nitramines may be assessed en masse for monitoring and assessment following the “grouped approach” and adopting a precautionary approach that assumes that the entire composition is expressed as the most harmful compound in the group. This approach does not require the assignment of toxic equivalent factors (TEFs) to single compounds in the group.The robustness of this approach depends on the extent of established evidence for the toxicity of the surrogate compound selected (IGHRC, 2009). In this regard, the NIPH has recommended NDMA as the most toxic nitrosamine based on extensive drinking water toxicity data for the compound (Lag et al., 2011). This work recognises that NDMA may be more potent when exposure occurs via inhalation rather than by oral intake (based on a 1991 study by Klein and co-workers) and recommends an assessment level of 0.3ng/m^3 for the inhalation exposure route.

Chemical mutagenic or genotoxic carcinogens are assessed for cancer risks where an estimate of risk for a number of individuals in a population is determined based on a given exposure level. Amine compounds are mostly non-mutagenic (Lag et al., 2011). However, in assessing the risk of exposure to the reaction products of amine compounds a precautionary approach is taken and this assumes that these substances are mutagenic carcinogens and therefore are assessed for cancer risks. The work undertaken in Norway (Lag et al 2011) estimates a risk of people developing cancer for an excess lifetime inhalation exposure to 0.3ng/m^3 of NDMA and describes this as a negligible risk level for cancer of 1 in a million (i.e. 1 in 10^6) after lifelong exposure associated with this air concentration. The Norwegian approach for deriving the cancer risk level for NDMA is based on the US EPA quantitative risk assessment approach. In contrast, in the UK, genotoxic carcinogens are categorically assigned a risk level with a typical risk level of 10^{-5} (a risk of 10 in a million) recommended by the UK Committee on Carcinogenicity (CoC). Because NDMA is considered genotoxic, the use of threshold techniques in deriving the EAL does not apply. Genotoxic carcinogens (referred to as non-threshold substances) are not considered to have thresholds.

The assessment level of 0.3ng/m^3 for NDMA developed by NIPH was derived from established drinking water dose-response modelling and linear extrapolation. There are uncertainties associated with the approach of using an oral dose to derive inhalation concentration (route-to-route extrapolation). Route-to-route extrapolation increases toxicological uncertainty in two ways (the uncertainty in applying animal data to human exposure and the link between oral and inhalation exposures) resulting in reduced confidence in the risk assessment. The UK approach for deriving health guidelines for non-threshold mutagenic carcinogens is based on categorical risk level (as opposed to the NIPH quantitative risk assessment). There is therefore continuing effort in research for dose-response inhalation toxicity data from which to derive more realistic levels that are protective of human health. These studies (Wagner et al., 2014; Gjernes et al., 2013) have investigated issues such as Quantity Structure Activity Relation (QSAR) modelling (the prediction of chemical toxicity based on their intrinsic physical-chemical properties) and the use of prokaryotic cells at different levels of toxicity testing. These studies also recognise that most of the alternative toxicity tests are not adequate if used in isolation and that a combination of one or more tests may be required. This approach is also reflected in the REACH programme that has developed Integrated Testing Strategies (ITS) for different toxicological aspects.

As a result of the differences in deriving the NIPH benchmark environmental concentration and due to the associated technical considerations relating to the basis for deriving the stated cancer risk, the proposed value cannot be adopted as a fully derived and established benchmark in the UK. However, it should be noted that the methodology used in Norway is in line not only with the methodology used in the US and Canada but also in line with the approach used within the EU. This approach for deriving cancer risk levels is also already in use within the UK under REACH and, as such, is an accepted risk assessment approach.

In summary therefore, adopting a reference substance (NDMA) against which total nitrosamine emissions are assessed may be an appropriate way to proceed. The currently proposed guideline EAL for total nitrosamines and nitramines (0.3ng/m^3) cannot be adopted as a fully derived and established benchmark due to the differences in the way that the UK assesses carcinogenicity compared to other countries. However the proposed thresholds were developed in line with the methodology used within Europe under the EU regulation on registration, evaluation, authorisation and restriction of chemicals (REACH). In the absence of other data, the guideline EAL of 0.3ng/m^3 could be adopted as an initial benchmark against which emissions and the ultimate environmental concentration of such substances from carbon capture plant could be assessed.

3.1.4 Environmental standards for other substances

In addition to nitrosamines, nitramines and amines other degradation products need to be considered such as aldehydes (e.g. methanal and ethanal) and amides (mainly methanamide) (Shao and Stangeland, 2009). Current UK guidance (EA/SEPA/NIEA, 2003/EA, 2010) contains the EALs for ethanal (long-term 370µg/m^3, short-term 9,200µg/m^3) and methanal (long-term 5µg/m^3; short-term 100µg/m^3). The EALs are derived from UK Occupational Exposure Limits (OELs) except the short-term EAL for methanal which is derived from the WHO (World Health Organisation) air quality guideline (WHO, 2000).

3.2 Emissions to water

3.2.1 Background levels

It has been suggested that more research on the prevalence and toxicity of amines, nitrosamines and nitramines in surface waters is necessary before the environmental impact of new point sources from carbon capture facilities can be adequately quantified (Poste et al., 2014).

Baseline studies in Norway were not able to show detectable amounts of nitrosamines or nitramines in the environment, while detecting amines in air, soil, moss and water (Grung et al., 2012; Tonnesen, 2011b). The levels of amines ranged from low ng/g to almost µg/g in plant and soil samples, while the levels in water were from 10ng/l to 50µg/l. The amine observed in highest levels in all samples (DMA) is a natural constituent of many plants (Grung et al., 2012, Tonnesen, 2011b).

Some research has shown NDMA to be the most prevalent nitrosamine in treated drinking water, but making up only about 5% of the total nitrosamine pool (Dai & Mitch, 2013a). Sampling of chlorinated recreational waters suggested that NDMA only accounted for about 10% of the total nitrosamine pool, with the other nitrosamines rarely detected (Shah and Mitch, 2012).

3.2.2 Environmental standards for amines

Alkanolamines are generally water soluble and are thus more likely to biodegrade than persist in the environment; however, biodegradation rates are also governed by other factors. While some research postulated rapid degradation of alkanolamines, nitramines and nitrosamines, it has been shown that nitrosamine precursors produced during the destruction of nitrosamines can recombine in natural waters, causing nitrosamine concentrations to increase again away from the treatment plant (Nawrowocki and Andrezejewski, 2011).

Seawater degradation rates have been found to be heavily affected by the structural characteristics of the amine with half-life times ranging from 8 days to over 700 days (Brakstad et al., 2012; Brakstad & Zahlsen, 2011; Sorensen et al., 2013) (see Section 2.3). Ideally solvents should be chemically and thermally stable during the process but biodegradable when released into water. A recent review of the chemical stability and biodegradability in the marine environment of new solvents for CO_2 capture (Eide-Haugmo et al., 2011) found that more chemically stable compounds were generally less biodegradable. N,N-dimethylethanolamine (DMMEA) and 3-amini-1-methylaminopropane (MAPA) were the most biodegradable and stable substances tested however none of the chemicals tested were considered to have the desired combination of stability in the process and biodegradability in water.

The ecotoxicity and biodegradability of a wide range of solvents has been tested in the marine environment (Eide-Haugmo et al., 2009a; Eide-Haugmo et al., 2012). The results were compared to models used to predict the environmental properties of substances based on their chemical structure. A range of amine solvents were tested including alkanolamines, polyamines, cyclic amines, amino acids, volatile amines and organo-compounds. The toxicity of the majority of compounds tested was generally low however there was a large variation in the biodegradability in the marine environment. The large variation can be explained by the differences in the environment and abundance. Sterically hindered compounds, tertiary alkanolamines and man-made cyclic compounds were the least biodegradable. The models were not good predictors of the environmental fate of the chemicals tested so these studies recommended that new solvents should be evaluated for environmental impact before use.

3.2.3 Environmental standards for nitrosamines and nitramines

In 2008, the Department for Environment Food and Rural Affairs (DEFRA) commissioned a study into NDMA concentrations in drinking water following its detection at significant levels in US drinking water. The study (Dillon et al., 2008) found concentrations below the US drinking water standard in samples collected from UK water treatment works. There are a range of proposed drinking water standards although some 2011 Norwegian work (Lag et al., 2011) has suggested a value of 4ng/l of total nitrosamines and nitramines (expressed as NDMA) as an acceptable environmental threshold.

Other studies have confirmed that environmental information on emissions to water of nitrosamines is limited (Brakstad et al., 2010a). The data that are available on ecotoxicity for the likely substances to be emitted from carbon capture systems varies considerably. This reflects different toxicity levels, but also that tests have been performed by different laboratories, by different methods, and with different species within each trophic level (fish and algal species). Variations between tests were higher for volatile than for medium volatile (e.g. N,N-bis(2-hydroxyethyl)nitrous amide) and non-volatile products (such as methanoic acid). The combination of expected low emission, water-solubility (low bioaccumulation potentials), biodegradability and low to moderate acute ecotoxicity for most amine degradation products indicates that the environmental risk associated with these products may be moderate or low. However, some of the degradation products (such as 2-(2-aminoethyl-amino) ethanol–HEED) as well as MDEA and DETA (Eide-Haugmo et al., 2009b) may persist in the environment due to poor biodegradability. Considerable differences may exist in the degradation rates between freshwater and marine waters (Shao and Stangeland, 2009; Brakstad et al, 2010b). This may pose a possible risk if accumulated in the environment. It has been reported (US National Library of Medicine: TOXNET) that piperazine is not expected to adsorb onto suspended solids and sediment. Nitrate may be formed by biological oxidation of ammonia, which may result in increased fertilization effects in the local catchment area.

Most general toxicity studies (not related to carbon capture system) have concentrated on NDMA. The USEPA has set a maximum admissible concentration in drinking water of 7ng/l for NDMA. Oral exposure (mainly via drinking water) for amines is well documented based on an extensive 1991 drinking water study by the WHO (Lag et al., 2011). There is very little information on nitrosamines detected in aqueous wastes from carbon capture plants (such as N-nitrosodiethanolamine-NDELA) and no EQSs or EALs have been set. However, while NDMA was found to be the most prevalent nitrosamine of those determined by EPA method 521 in treated drinking water, it made up only about 5% of the total nitrosamine pool (Dai and Mitch, 2013a). Thus, most of the nitrosamine pool remains uncharacterised.

There is limited information on the biodegradability and toxicity of amine breakdown products in the water environment (Shao and Stangeland, 2009; 2007; Brakstad et al, 2010b). Amine compounds emitted to the marine environment will often undergo biodegradation although there is significant variation in the biodegradability of different substances. Several of the amines solvents that may be used in carbon capture, like MDEA, AMP and piperazine have very low degradability and are likely to have a significant residence time in marine environments. The ecotoxicity of these amines is also relatively high (EC-50 <10mg/l). Conversely, most alkanolamines have low toxicity levels (EC-50 between 10 and 1000mg/l) and readily degrade (BOD level at around 25 percent). Some other preliminary works have derived a threshold for ‘nitrosamines’ in water based on a predicted no effect concentration (PNEC) value of 0.025µg/l. However, on review this PNEC was derived for the specific nitrosamine chemical NDMA and based on an ecotox endpoint for a species of salt-water algae (Brooks, 2008) and would only be applicable to marine environments.

At present in the UK it is not possible to derive and set an EQS in the water environment for the general chemical group known as nitrosamines.The impediments to this include the diverse nature of the chemical (with individual chemicals within the group having widely different toxicities to aquatic organisms). Similarly there is no suitable available method to measure ‘total nitrosamines’ in water and there is no ecotoxicity data for total nitrosamines in water. Therefore, any UK EQS for nitrosamines would have to relate to specific nitrosamine chemicals. If this compound was identified and accepted as the individual nitrosamine of greatest concern it may be possible to propose this as a potential representative chemical to the Water Framework Directive UK Technical Advisory Group for consideration for development of a specific EQS. The feasibility of this would depend on the availability of sufficient usable ecotox data.

3.2.4 Ecotoxicological standards

Any effluents from carbon capture systems are likely to contain a complex mixture of chemicals of varying toxicity. Consequently, consideration of the toxicity of individual components may not be appropriate. A ‘whole sample’ assessment approach such as Direct Toxicity Assessment (DTA) may be a suitable approach for assessing discharges containing a complex mix of chemicals (such as by following SEPAs position (SEPA, 2012) outlined in WAT-SG-57, see Section 4.2.3 below). A standardised test for genotoxicity could also be used, considering the genotoxic/carcinogenic nature of some chemicals potentially in the discharge.

3.3 Environmental standards for emission to land and ecosystems

Nitrosamines such as NDMA are expected to have a very high mobility in soils (Eide-Haugmo et al., 2009; US National Library of Medicine; TOXNET, 2011). However, little data is available on the extent of deposition to land that can be expected from emissions of amines and their reaction products from carbon capture systems, although wet deposition is reported to likely be a major removal process from the atmosphere (da Silva et al., 2013a).

Models have been used to make predictions of wet and dry deposition of nitrosamines and nitramines from the Test Centre Mongstad, Norway (Karl et al, 2014). Results from this modelling exercise suggest that maximum deposition fluxes are likely to be up to 120 times lower than previously estimated, as they were able to treat MEA-nitramine production in more detail and used a reduced estimate of rainfall amount and frequency. However it was also discovered that dry deposition was more important than previously thought, being predicted to account for 40% of all nitramine and nitrosamine deposition (Karl et al., 2014). It was noted that due to the Mongstad project, atmospheric deposition of nitramine and nitrosamine in the surrounding area could be three times greater than background levels reported.

Release of amines to the atmosphere could have consequences in terms of acid and nitrogen deposition and contribute to the eutrophication of ecological habitats. Amine degradation products may have similar impacts. It is noted that direct effects on terrestrial plants and vegetation arising from the emissions of such substances is likely to be less significant than from emissions of acid gases that are likely to be emitted at significantly greater concentrations than amine compounds. However, the direct impacts of amine deposition on terrestrial ecology are not well known. While the amount of amines being deposited on their own may not be thought to be harmful to ecosystems, if they are being deposited on ecosystems already under pressure from acid and nutrient nitrogen (N) deposition and above or close to their critical load, then the additional deposition from carbon capture processes could be harmful to sensitive ecosystems. The acid and nitrogen deposition effects of amine emissions may therefore also need to be addressed if carbon capture systems are installed widely in the future. Some studies (Ge et al., 2011a) recognise the role that amines may play as atmospheric bases and the potential for neutralisation of acids which form in the atmosphere. Other studies (Shao and Stangeland, 2009) note that amines may also cause corrosive damage themselves. However, more research is required into the multiple and complex effects of amines and their reaction products on the environment.

Some studies (Grung et al., 2012) note that deposition of amine and nitrosamine compounds from carbon capture plants is likely to be less significant in causing eutrophication and acidification than the deposition arising from other nitrogen compounds. However it is possible that critical loads could be exceeded as a result of increased nitramine and nitrosamine deposition if background deposition is already close to critical load thresholds (Grung et al., 2012). It was also noted that the impact of extra N deposition from nitramine and nitrosamine on surface vegetation is unlikely to be significant unless deposition rates are towards the top end of the expected range, which is a possibility that seems to have been ruled out by during more recent modelling (Karl et al., 2014).

The biodegradation rate of amines in soil will contribute to the availability of nitrogen for plant use. This is likely to vary extensively, depending on the soil type and which amines are present. Previous studies (Zero Emissions Platform, 2012) reported that the half-life of NDMA in soils can range from 4 to 23 days depending on the soil type and that degradation decreases significantly as contamination levels increase. Similar soil half-life of 1 - 22 days for nitramines and nitrosamines has been reported, with most degradation occurring due to microbial activity (Karl et al., 2014). With regard to the effect of soil condition on degradation of nitramines/nitrosamines it has been reported that C-content of the soil had little effect, but that degradation increased with soil depth (Karl et al., 2014). In light of this, it has been suggested that soils in the Mongstad area would tend not to effectively degrade nitramines and nitrosamines entering via atmospheric deposition and passing through them due to their shallow depth, low organic matter content and sparse vegetation cover, all of which would tend to result in reduced microbial activity (Karl et al., 2014). It was speculated that this would lead to leaching of nitramines and nitrosamines to surface waters, although not to concentrations where levels would exceed permitted maxima. As noted above, a significant proportion of amine compounds are soluble and thus are expected to impact mainly on the water environment.

It has been suggested that nitramine and nitrosamine levels in soils and the impact of atmospheric deposition on these in areas around CCS plants may be resolved when sampling sites visited around TCM in 2011 are revisited in 2016 (Grung et al., 2012). This would allow comparison of nitramine and nitrosamine levels before and after operation of the Mongstad CCS facility. However TCM is now only used periodically as a solvent testing facility and not as a full time operational CCS plant and as such any change to the environmental concentration of amine or nitrosamine compounds detected may underestimate the true impacts of a major CCS plant.

4 Measurement techniques and issues

This section considers the monitoring techniques for amines, nitrosamines and other degradation products in stack emissions, waste waters, solvents and in ambient air.

4.1 Stack emission monitoring

There has been limited stack emission monitoring of amine compounds from carbon capture processes. While more common substances such as ammonia and alkylamines can be measured using standard reference methods, standard reference methods for nitrosamines, nitramines and for the combination of substances anticipated in flue gas from a carbon capture plant do not currently exist. However, the European Committee for Standardisation (CEN) are in the preliminary stages of developing a Draft European Standard Reference Method for amine monitoring in carbon capture plants. International collaborations such as the Electric Power Research Institute (EPRI) working group are also working to develop standards for emission measurements (EPRI, 2012).

The methods available for nitrosamines and nitramines have primarily been developed for occupational exposure monitoring and would require adapting and validating to allow monitoring of the flue gas from a carbon capture plant. As many of the target compounds are likely to be contained within both the aerosol and the gas phase, sample media would need to target both aerosol and gas phases. The issue of ‘fogging’, where spikes in amine emissions are caused as a result of amine vapour entrainment on particulates/aerosols, needs to be considered (Fitzgerald, 2014). Stripper ‘foaming’ can also contribute to amine spikes (Fitzgerald, 2014).

Consideration also needs to be given to the risk of false detection and potential issues relating to formation or degradation of nitrosamines and MEA (Brakstad, 2010a; Wittgens et al, 2010a; Azzi et al, 2014a). For example, sampling probes/equipment should be coated in inert material; samples should not be exposed to light or nitrogen oxides and should be stabilised once collected (Azzi et al, 2014a, Wittgens 2011b). Heated lines may not be appropriate when sampling for thermally unstable compounds. The addition of a microfilter to allow sampling of <1µm aerosols has been suggested (Zahlsen et al., 2012). In their review of state-of-the-science on emissions from amine-based CO_2 capture plants, the European Technology Platform for Zero Emission Fossil Fuel Power Plants noted that the variation in the emissions measurements results of various solvent amines and degradation products between laboratories for the same analyte at the same sampling site of a facility can be significant (Zero Emissions Platform, 2012).

The monitoring techniques which potentially could be used to detect these substances can be divided into online and offline monitoring and are discussed in the following sections.

Due to the wide range of physical/chemical properties (in particular the volatilities) of the nitrosamines group there is unlikely to be one sampling approach that works for all nitrosamines.

4.1.1 Offline measurements

4.1.1.1 Offline measurement using solid sorbent media and liquid impingers

A European and British Standard exists for the sampling of organic compounds, which can be modified for the sampling of amines (BS EN 13649:2002). Subsequent analysis can be carried out using US National Institute for Occupational Safety and Health (NIOSH), or US Occupational Safety and Health Association (OSHA) methods depending on the specific substances required. There are several UK Accreditation Service (UKAS) and Monitoring Certification Scheme (MCERTS) accredited test laboratories for both methods. A BGI (German Work Safety Association) method has also been used in a UK pilot plant (Fitzgerald, 2014)

The use of solid sorbent media and liquid impingers are both included in standard methods for periodic sampling of flue gas. Cold-trapping of the condensate followed by absorbing onto these media has also been proposed (Wittgens 2011a, Zahlsen et al., 2012, Järvinen 2010). Multiple sample trains or multi-component trains are likely to be required for the diverse range of target substances (EPRI, 2012).

The most common occupational health methods for sampling nitrosamines involve extracting a sample onto solid sorbent media such as silica gel, XAD resins, proprietary substances based on magnesium silicates or charcoal-tube absorption, followed by solvent extraction and analysis by GC-FID, GC-TEA (Thermal Energy Analyser) or GC-NCD (Nitrogen Chemiluminescence Detector). However, choosing the right type of absorbent is important and evidence in relevant literature (Rounbehler, 1980) shows that recovery rates can vary from very high to zero, depending on the medium selected. Some sorbents have been shown to generate nitrosamines by retained amines reacting with NO_x. Thermosorb/N sorbent tubes do not tolerate moisture well and therefore would not be appropriate in wet flue gas without pre-drying of the sample (Zahlsen, 2010). The effect of carbon dioxide on some sorbent tubes is also not fully understood (Järvinen, 2010).

Liquid impingers can effectively absorb substances present in the aerosol phase as well as in the gas phase. This is not possible for some solid sorbent media. Results from recent pilot plant studies show the importance of nitrosamines in the aerosol phase (Silva et al, 2013). The impinger solution must however be carefully chosen to efficiently absorb the target compound (e.g. aqueous phosphate-citrate solution or sulfamic acid when sampling for nitrosamines) (Azzi et al, 2010) and inhibitors may need to be added to prevent reactions occurring in solution, particularly nitrosation (Järvinen 2010).

Cold trapping of a stack sample to form a condensate and dried gas phase has been proposed due to the ability of this technique to stop degradation of the sample. Other benefits of this method also include only needing to take one bulk sample and the method's ability to cope with the high moisture content of the flue gas (Azzi et al, 2010. Järvinen, 2010. Wittgens et al, 2010a). This approach would allow detailed analysis on the condensate to be undertaken in order to allow more targeted analysis of individual chemical species.

As these offline sampling methods have had only limited (or no) field testing in carbon capture processes, even though the procedures are in some cases well documented, they would require full validation. Standardised analytical methods available for nitrosamines and alkanolamine compounds (with limits of detection) are given in Table 4.1. These methods are primarily for occupational health monitoring and have not been specifically accredited for flue gas monitoring (e.g. not tested for interactions with CCS effluent components, moisture and temperature).

Table 4.1: NIOSH and OSHA analytical methods for nitrosamines and aminoethanol compounds in stack emissions

Group	Substance	Analytical method	Limit of detection ($\mu g/m^3$)
Nitrosamines	NDMA, NDEA, N-Nitroso-N-propyl-1-propanamine (or N,N-Dipropylnitrous amide -NDPA), NDBA), NPIP, 1-nitrosopyrrolidine (NPYR), and NMOR	NIOSH 2522	0.05
Nitrosamines Mixture I	NDMA, NDEA, NDPA, NDBA, NPIP, NPYR and NMOR	OSHA 27	0.13 (NDMA) 0.13 (NDEA)

Group	Substance	Analytical method	Limit of detection (µg/m^3)
			0.13 (NDPA) 0.12 (NDBA) 0.12 (NPIP) 0.13 (NPYR) 0.20 (NMOR)
Nitrosamines Mixture II	N-Methyl-N-nitrosoethanamine (referred to as nitrosomethylethylamine or NMEA), NDiPA, N-Methyl-N-nitroso-butanamine (referred to as Nitrosomethylbutylamine or NMBA), N-ethyl-N-nitroso-butanamine (referred to as Nitrosoethylbutylamine or NEBA), N-nitroso-N-propyl-butanamine (referred to as Nitrosopropylbutylamine or NPBA) N-nitroso-N-pentyl-pentanamine (referred to as nitrosodiamylamine or NDAmA)	OSHA 38	0.13 (NMEA) 0.15 (NDiPA) 0.13 (NMBA) 0.15 (NEBA) 0.13 (NPBA) 0.20 (NDAmA)
Aminoethanol compounds	2-dibutylaminoethanol	NIOSH 2007	200
	2-diethylaminoethanol		

4.1.2 Online / continuous emissions monitoring

To provide increased confidence for both regulatory purposes and process control continuous emissions monitoring systems may be necessary. These have the benefit of providing real-time continuous output of emissions data but compared to offline measurements have a relatively low sensitivity. Due to the wide range of substances, their wide physiochemical properties and in some cases their carcinogenity (i.e. toxicity inhibiting research) there are limited spectroscopic libraries for online measurements (Octavius Session 3, 2014). On-site calibrations of continuous monitors can also be difficult as it is not possible to produce accurate gas mixtures in cylinders for substances such as MEA (Fitzgerald, 2014), however a gas with a similar response can be used in its place.

Some of the more common instrumental techniques are discussed below.

4.1.2.1 Continuous emissions monitoring – FTIR

Fourier transform infrared spectroscopy (FTIR) has been used for monitoring amine based substances at various bench and pilot scale plants such as Ferrybridge (Fitzgerald, 2014), the Pilot-scale Advanced Capture Technology at UKCCSRC (PACT, 2013), Loy Yang in Australia (Azzi et al, 2014a), EUPHORE, Spain (Nielsen et al, 2011b), Oslo photo-chemistry reactor, Norway (Nielsen, 2011d), Maasvlakte, Netherlands (Silva et al, 2013), mobile carbon capture facilities in Norway and Longannet and the Esbjerg pilot plant in Denmark (Graf, 2010; Mertens, 2012; Da Silva and Aas, 2010). Such instruments are multicomponent analysers that can monitor stack emissions in real time with an approximate one-minute resolution. FTIR uses infra-red spectroscopy to create a molecular fingerprint of the sample, which is compared to an internal library to allow identification and quantification of the substances in the sample. The libraries of some FTIR manufacturers currently contain a number of amine-based compounds including MEA, DEA and ammonia, but not nitrosamines or nitramines. One study suggested the non-isokinetic nature of FTIR meant that large water droplets bypassed the sample probe and therefore underestimated MEA concentrations (Fitzgerald, 2014). This study found the presence of droplets and aerosols may interfere with detection, creating noisy readings for MEA (Fitzgerald, 2014). The ‘stickiness’ of amines means that they can be retained by the FTIR instrument and therefore the system needs to be thoroughly flushed (Fitzgerald, 2014).

In the UK, FTIR measurements should be undertaken in-line with the established guidance (Environment Agency, 2012) and there are several test laboratories which use FTIR in the UK, with at least one being UKAS accredited for monitoring amines.

4.1.2.2 Other measurement/analytical techniques

Numerous continuous emissions monitoring systems are available and accepted as appropriate for in-situ and extractive ammonia monitoring (Environment Agency, 2013). A Tunable Diode Laser (TDL) analyser was used at the Ferrybridge pilot plant to follow trends in solvent deterioration (Fitzgerald, 2014). It was noted that signal deterioration can occur through lens obscuration of the analyser. This analyser was MCERTS accredited to BS EN 15267-3. It has been reported that gaseous ammonia measurement in the off-gas stream cannot be used alone as a representative measurement of the degradation rate of amine used in carbon capture systems. Rather a combination of gaseous ammonia and liquid concentrations of ammonium species should be used to produce more accurate degradation rate information.

On-line Mass Spectrometry (OLMS) was trialled at Ferrybridge pilot plant, but demonstrated to be labour intensive and found to have poor calibration capability (Fitzgerald, 2014). Despite numerous attempts, the use of OLMS was discontinued as it was not deemed robust, accurate and reliable enough to meet the Environment Agency’s requirements.

Proton Transfer-Reaction Time of Flight Spectroscopy (PTR-ToF-MS) was used at Test Centre Mongstad to continuously monitor the gas emissions from degradation of MEA (Zhu et al, 2013). Due to interferences from humidity, ammonia and CO_2 the method requires pre-dilution with zero air of 1:10 to 1:20. No nitrosamines or nitramines were detected, but new products including pyrazine and nitromethane were detected. Limits of detection for PTR-ToF-MS are in the region of 30 ng/m^3 (Nielsen, 2011d).

Liquid Chromatography Mass Spectrometry (LCMS), Gas Chromatography Mass Spectrometry (GCMS) and Ion Chromatography have been used in some projects for the measurement of degradation products including nitrosamines and nitramines (Azzi et al, 2014a. Brakstad, 2010a, Järvinen 2010). Choosing LCMS or GCMS depends on the volatility of the substance; GC is preferable for analysis of NDMA, NDEA and NMOR, while LC is better for analysis of NDELA, and is also suitable for NMOR (Azzi et al, 2014a). A LCMS scan gives a qualitative assessment of degradation products formed and can detect most ionisable degradation products with molecular weight higher than 70 although for lighter components such techniques are less reliable and the analytical methods must be tuned to search for specific components (Brakstad, 2010a). Limits of detection for LCMS are in the region of 3 ug/m^3 (Azzi et al, 2014a, Keränen 2012). Limits of detection for GCMS are lower, in the region of 3 ng/m^3 (Azzi et al, 2014a).

Chemiluminescence analysers are conventionally used for detecting oxides of nitrogen but can also be applied to other nitrogen based compounds (Environment Agency, 2013). A Thermal Energy Analyser combined with Gas Chromatography uses a similar technique and has good selectivity for nitrogen based compounds. Both these analysers require extraction of the flue gas which may cause stability issues. Methods for screening analysis based on GC-MS-NCD (Nitrogen Chemiluminesence Detector) and group specific analysis based on denitrosation using CuCl/HCl with analysis by GC-MS-NCD have been developed (Zahlsen et al., 2011).

Quantitative analysis for nitrosamines has been proposed based on LC-MS-MS-QQQ (Triple Quad) (Zahlsen et al., 2011). This method has sensitivity for nitrosamines in the low or sub-microgram per litre level.

Differential Optical Absorption Spectroscopy (DOAS) is a conventional continuous emissions monitoring method for analyzing a wide range of substances and analyses in situ so there is no requirement for a heated line which can cause thermal degradation of certain substances (Environment Agency, 2013). There’s no evidence that DOAS has been used at carbon capture sites and the sensitivity to nitrosamines is unknown.

Raman spectroscopy is currently used for monitoring some amine processes which are used to remove acid gases from hydrocarbons (Järvinen, 2010b). It has the benefit of not requiring sample conditioning but it is not a conventional method for stack testing.

Due to the increasing relevance of aerosol emissions Phase Doppler Interferometer (PDI) has been trialled at the National Centre for Carbon Capture (NCCC) in the US which can measure particle size, concentration and velocity (Octavius Session 4, 2014). A multicomponent approach using High Resolution Time of Flight Aerosol Mass Spectrometer (HR-TOF-AMS) combined with Electrospray Ionization Mass Spectrometry (ESI-MS) for aerosol composition found both expected and new degradation products of common amines in a bench-scale experiment (Ge, 2014).

Numerous other less conventional techniques are available such as semi-continuous thermal desorption, colormetric analysers, ion molecule reaction, ion mobility spectrometry and UV sensitivity spectrometry but there is no evidence that they’ve been used to measure amine degradation products in carbon capture processes (Järvinen, 2010b, EPRI, 2012). All techniques would require full validation prior to being used.

The reduction of CO_2, NO_x and particulates from the flue gas, combined with the removal of amines and amine degradation products, prior to discharge, will alter the composition of the final flue gas discharged to atmosphere. This may have implications for the most appropriate reference conditions for analysis of the flue gas as well as the concentration of other components in the flue gas (CCSNetwork.eu, 2011).

4.2 Waste water monitoring

4.2.1 Nitrosamines

As part of the pilot scale project at the Mongstad Test Centre specific procedures were developed for the monitoring of total N-nitrosamines, NDELA, N-nitrosopiperazine and individual N-nitrosamines in process wash waters and solvents (Azzi et al, 2011. Ramboll, 2011). Some methods were found not to be robust due to matrix interferences and require further work and other methods developed would require full validation before they can be implemented. The high levels of amines, aldehydes and nitrite in wash-water could also lead to artifactual formation of nitrosamines (Dai et al, 2012). To counteract this it has been suggested that a 30-fold molar excess of sulfamic acid to nitrite should be maintained in the sampling impinge train.

Standard methods for the determination of nitrosamines in water which could be used for wash water analysis include USEPA Method 521 and USEPA Method 607. USEPA Method 521 for the determination of nitrosamines in drinking water uses solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry. It has a detection limit ranging from 0.26 to 0.66ng/l. USEPA Method 607 for the determination of nitrosamines in wastewaters has a method detection limit of 0.15 to 0.81µg/l. However, use of US EPA method 521 to determine six nitrosamines in treated drinking water, showed NDMA to be the most prevalent, but it made up only about 5% of the total nitrosamine pool (Dai & Mitch, 2013a). Use of this method on chlorinated recreational waters suggested that NDMA only accounted for about 10% of the total nitrosamine pool, with the other method 521 nitrosamines rarely detected (Shah & Mitch, 2012). Thus, most of the nitrosamine pool remains uncharacterised.

The use of gas chromatography with low resolution mass spectrometry (GC/LRMS) has been proposed as a simple, more affordable tool for surface water screening (Kim and Han, 2011). Other non-standard methods are available that use chemiluminesence detectors or liquid chromatography mass spectrometry (LCMS). LCMS was used at the Loy Yang pilot plant to analyse extracted wash water samples with a detection limit of 1µg/l for NMor and NDELA (Azzi et al, 2014a). LCMS has also been used to analyse nitramines in synthesised washwater with detection limits in the range 0.5-40µg/l (Dye et al, 2011).

4.2.2 Nitramines

A review of available analytical technologies for the measurements of nitramines in water concluded that currently no comprehensive method is available (Lindahl et al., 2014). The lowest concentration limits of quantification for the aliphatic and cyclic nitramines in the methods reviewed were in the ng/l range; however, most methods are in the µg/l range (Lindahl et al., 2014).

4.2.3 Direct toxicity assessment

As mentioned in Section 3.2 above, any effluents from carbon capture systems are likely to contain a complex mixture of chemicals of varying toxicity and consequently, Direct Toxicity Assessment (DTA) is likely to be adopted as one approach for assessing and permitting discharges containing such a complex mix of chemicals (such as following the current SEPA position outlined in WAT-SG-57 (SEPA, 2012). For this, testing of the effluent using an algae test and an invertebrate test (see table 4.2) will be required.

Table 4.2 – Algae and invertebrate test

Freshwater receiving environment	Marine receiving environment
Freshwater Algal Growth Inhibition Test	Marine Algal Growth Inhibition Test
Daphnia magna Immobilisation Test	Oyster Embryo Larval Development Test, or *Tisbe battagliai* Mortality Test

A standardised test for genotoxicity could also be used, considering the genotoxic/carcinogenic nature of some chemicals potentially in the discharge.

4.3 Solvent monitoring techniques

Analysis of trace compounds, such as nitrosamines, in the amine solvent can be complicated by interference from the solvent itself (Zahlsen, 2010). Extraction of the target compound or solvent dilution can be carried out to overcome this. Two analytical techniques have been used to detect nitrosamines in circulation in the solvent system. These are gas chromatography mass spectrometry nitrogen chemiluminescence detector (GC-MS-NCD) which has a LOD of 100µg/l and liquid chromatography mass spectrometry (LCMS) which has a LOD of between 1µg/l and 10µg/l (IEAGHG, 2011a, Azzi et al, 2014a).

Other more specific methods have been developed for solvent process monitoring (Ramboll, 2011; Azzi et al, 2011) although these methods require full validation before being implemented. Headspace Solid Phase Microextraction (HS-SPME) has reportedly been developed for volatile products with a reduced matrix effect which allow detection of minor products (Octavius Session 5, 2014). Several new pyrazine and alkylpyrazines compounds have been identified in MEA in the liquid phase using HS-SPME at IFPEN & EDF pilot plants (Octavius Session 5, 2014).

4.4 Ambient air monitoring

In order to measure nitrosamines at the levels predicted in the ambient air a method is required with a sub ng/m^3 limit of detection.

One technique for the determination of NDMA is based on US Environment Protection Agency (USEPA) method T0-7 and involves drawing ambient air through a Thermosorb/N sorbent tube followed by analysis using GCMS and has a reported LOD of 1µg/m^3. Institut National de Reserche et de Securite (INRS) method 031 also has a reported LOD of 1µg/m^3. The NIOSH and OSHA methods shown in the table in Section 4.1 can be adapted for ambient air monitoring of nitrosamines and have LODs down to 0.05 µg/m^3. These LODs are too high for use as ambient monitoring techniques given the expected levels of nitrosamines in the environment.

As part of the baseline study for Test Center Mongstad, nitrosamines were sampled using an in-house method based on OSHA method 27 (Tonnesen et al, 2011). This method used a multi-line sampling device to collect large volume samples and has a reported LOD of 0.01ng/m^3. Each sample comprises 10 Thermosorb/N sorbent tubes with an open interface allowing both gases and ultrafine particles to be collected in the sampling process. The extracts from the tubes are pooled and analysed using GC/HRMS and UHPLC/MS. This technique was also used to sample for nitramines with a detection limit of 0.1ng/m^3. However, Thermosorb/N sorbent tubes are validated for humidity of less than 80% which is likely to be exceeded in coastal environments, particularly when sample durations of up to one week are required. Breakthrough studies (OSHA Method 27, 1981) also show limitations on effective nitrosamine sampling due to flow rate and volume sampled.

SEPA trialled this method as part of a research project around Peterhead in September 2014. The samples collected are currently being analysed and will be reported when available.

Monitoring under pseudo-natural conditions was undertaken of the photo-oxidation of MEA in Spain in the European photoreactor (EUPHORE) (Nielson, 2010). Both manual sampling methods and instrumental methods were used. Nitrosamines were sampled onto Thermosorb/N absorbent tubes and then analysed by HPLC with high resolution mass spectrometry. Nitramines were sampled onto 2,4-dinitrophenylhydrazine (2,4-DNPH)-coated silica packed in a polyethylene tube and then analysed by reversed phase liquid chromatography (HPLC) combined with serial connected diode array detector (UV) and high resolution mass spectrometry (HRMS). Amines were sampled onto a filter and also analysed by HPLC and HRMS. The limit of detection for nitramines was approximately 4.7µg/m^3 and the limit of detection for nitrosamines was 0.033µg/m^3. These LODs are greater than the benchmark Environmental Assessment Levels (EALs) for nitrosamines and nitramines. The limit of detection for amines was not stated.

In-situ instrumental techniques used at EUPHORE (Nielson, 2010) included Proton Transfer Reaction - Mass Spectrometry (PTR-TOF-MS) with LOD ~18ng/m^3, and the Aerosol Mass Spectrometer (AMS) which allows analysis of fine particles and FTIR. No LODs were given for AMS or FTIR.

Other ambient air studies have used Thermosorb/N tubes for sampling nitrosamines and either Gas Chromatography Thermal Energy Analysis (GC-TEA), Gas Chromatography Nitrogen Chemiluminescence Detector (GC-NCD) or GCMS for analysis (Marano, 1982). The limit of detection for nitrosamines by chemiluminescence detector appears to be the lowest at approximately 0.005 µg/m^3 which is above the benchmark EAL for grouped nitrosamines.

Due to the increased relevance of aerosols, methods have also been developed for monitoring nitrosamines and nitramines in the aerosol/particle phase (Ozel, 2011. Akyuz and Ata, 2013). Samples are typically collected by pumping ambient air through quartz filters and analysed by GCxGC-NCD (Ozel, 2011) or GCMS (Akyuz and Ata, 2013). LOD were reported to be in the range 0.16-0.27pgN (Ozel, 2011) and 4-22pg/m^3 (Akyuz and Ata, 2013). Samples taken of fogs/clouds were analysed using GC-Chemical Ionisation-Mass Spectrometry for detection of NDMA that appear to have an LOD down to 7ng/l.

Other ambient air studies for monitoring amines (not specifically nitrosamines) have used weak cation exchange resin followed by extraction and analysis using ion chromatography. This has allowed ng/m^3 detection limits (Dawson et al, 2014)
For workplace exposure measurements of nitrosamines the Health and Safety Laboratory (HSL) have traditionally sampled onto Thermosorb/N cartridges and analysed using Gas Chromatography Thermal Energy Analysis (GC-TEA) (Pengelly, 2011). This is essentially the same method as NIOSH 2522 and OSHA 38 detailed in Table 4.1. The Thermal Energy Analyser is very specific to nitrosamines and for occupational samples of 4 - 5

hours duration the HSL is able to reach detection limits of around 0.1µg/m^3. One nitrosamine that cannot be detected by this method is N-nitrosodiphenylamine because this compound undergoes thermal degradation in the GC injector. In more recent studies including a study of workplace exposure to nitrosamines at rubber processing sites personal samplers containing Thermosorb-N cartridges were used and then analysed by GCMS (HSE, 2010). Unlike the Thermal Energy Analyser, the mass spectrometry detector is not specific to nitrosamines and so the presence of other volatile organic carbons (VOCs) can cause significant interferences.

The methods adapted from US occupational-safety methods (USEPA method T0-7 and INRS method 031) do not usually meet the required limit of detection. The detection levels achievable for all nationally adopted ambient air analytical methods appear greater than the environmental threshold benchmark values suggested for total nitrosamines, etc. However, there is evidence that methods have been developed for analysing amines in clean rooms, as these compounds can adversely affect the production of electronic components. Other industries may have developed a method for assessing amines in ambient air using pre-concentration onto synthetic media, followed by liquid chromatography and analysis by GC-MS with sensitivities down to the ng/m^3 levels (Aygün, 2004).

As shown in Section 3.1.1, nitrosamines have been measured in ambient air in Austria and the US with concentrations of <10ng/m^3. However, the analytical methods used to produce these results have a low maturity, have not been adopted as national standards and there is no evidence of successful method validation.

To summarise, measurement of nitrosamines in the ambient air at the levels expected around CCS processes (sub ng/m^3) appears possible but difficult (considering issues such as humidity and breakthrough) at the present time. Further work is required to develop a reliable method that can measure nitrosamines in the ambient air over a sufficient period to determine likely impacts of carbon capture processes. A reliable ambient air monitoring method is particularly needed to verify air dispersion models.

5 Glossary

ADMS	Atmospheric Dispersion Modelling System
AMP	2-amino-2-methyl-propanol (or aminomethylpropanol)
AMS	Aerosol Mass Spectrometer
As	Arsenic
BAT	Best Available Technique
BGI	German Work Safety Association
BOD	Biochemical Oxygen Demand
C	Carbon
CASTOR	CO_2, Capture to Storage Project
CCPilot100+	Ferrybridge Pilot Plant
CEM	Continuous Emissions Monitoring
CEN	European Committee for Standardisation
CERN	European Organization for Nuclear Research
Cl	Chlorine
CLOUD	Cosmics Leaving Outdoor Droplets experiment
CCS	Carbon capture and storage
CCSA	Carbon capture and Storage Association
CO_2	Carbon dioxide
COSMO-MUSCAT	Chemistry-Transport Model System
CoC	Committee on Carcinogenicity
CoM	Committee on Mutagenicity
CoT	Committee on Toxicity
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CuCl	Copper chloride
DGA	2-(2-aminoethoxy)ethanol (or di-glycolamine)
DIPA	1-(2-hydroxypropylamino)propan-2-ol (or di-isopropanolamine)
DEA	2-(2-hydroxyethylamino)ethanol (or diethanolamine)
DECC	Department of Energy and Climate Change
DEFRA	Department for Environment Food and Rural Affairs

DETA	Diethylenetriamine
DMA	N-methylmethanamine (or dimethylamine)
DMMEA	N,N-dimethylethanolamine
DMNA	N-nitro-N-methyl-methanamine (or Dimethylnitramine)
DMEL	Derived Minimal Effect Level
DNV	Det Norske Veritas
DOAS	Differential Optical Absorption Spectroscopy
DTA	Direct Toxicity Assessment
EA	Environment Agency
EAL	Environmental Assessment Level
ECHA	European Chemicals Agency
ED	Electrodialysis
EDF	Électricité de France
EDTA	Ethylenediaminetetraacetic acid
EEA	European Environment Agency
EPRI	Electric Power Research Institute
EQS	Environmental Quality Standards
ESI-MS	Electrospray Ionization Mass Spectrometry
EUPHORE	European Photochemical Reactor
Fe	Iron
FEED	Front End Engineering
FGD	Flue Gas Desulphurisation
FTIR	Fourier Transform Infrared spectroscopy
GCCSI	Global Carbon Capture and Storage Institute
GC-FID	Gas Chromatography Flame Ionisation Detector
GCxGC-NCD	Gas Chromatography Nitrogen Chemiluminescence Detector
GC/HRMS	Gas Chromatography with High Resolution Mass Spectrometry
GC/LRMS	Gas chromatography with Low Resolution Mass Spectrometry
GC-TEA	Gas Chromatography Thermal Energy Analysis
GC-NCD	Gas Chromatography Nitrogen Chemiluminescence Detector

GC-MS	Gas Chromatography Mass Spectrometry
GC-MS-NCD	Gas Chromatography Mass Spectrometry Nitrogen Chemiluminesence Detector
H	Hydrogen
H_2SO_4	Sulphuric Acid
HCl	Hydrogen chloride
HEEDA	2-(2-aminoethyl)amino)ethanol (N-(2-hydroxyethyl)-ethylenediamine)
HEIA	1-(2-hydroxyethyl)-2-imidazolidone (HEIA)
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
HR-TOF-AMS	High Resolution Time of Flight Aerosol Mass Spectrometer
HS-SPME	Headspace Solid Phase Microextraction
HSE	Health and Safety Executive
HSL	Health and Safety Laboratory
HSS	Heat stable salts
IARC	International Agency on Cancer Research
IE	Ion Exchange
IEAGHG	IEA Greenhouse Gas
IED	European Union Industrial Emissions Directive (IED) (Directive 2010/75/EU)
IFPEN	IFP Energies nouvelles
INRS	Institut National de Reserche et de Securite
IOELV	Indicative Occupational Exposure Limit Values
ITS	Integrated Testing Strategies
IUPAC	International Union of Pure and Applied Chemistry
Kg pa	kilogrammes per annum
LC-MS	Liquid Chromatography Mass Spectrometry
LC-MS-MS-QQQ	Liquid Chromatography Mass Spectrometry Triple Quad
LOD	Limit of detection
MAPA	3-amini-1-methylaminopropane
MCERTS	Monitoring Certification Scheme
MEA	2-aminoethanol (or monoethanol)

MEL	Maximum Exposure Limits
MDEA	2-(2-hydroxyethyl(methyl)amino)ethanol (or methyldiethanolamine)
MMA	Monomethylamine
MMEA	2-(methylamino)ethanol (or monomethylethanolamine)
MWe	megawatt electrical
N	Nitrogen
NCCC	National Centre for Carbon Capture
NDEA	N-ethyl,N-nitroso-ethanamine (or N-nitrosodiethylamine)
NDELA	N-nitrosodiethanolamine
NDAmA	N-nitroso-N-pentyl-pentanamine (or nitrosodiamylamine)
NDBA	Nitrosodibutylamine
NDMA	N-methyl,N-nitroso-methanamine (or N-nitrosodimethylamine)
NDPA	N-Nitroso-N-propyl-1-propanamine (or N,N-Dipropylnitrous amide)
NDINA	N-nitrosodiisononylamine
NDiPA	Nitroso-diisopropylamine
NDTMA	Dimethyl-nitramine
NEBA	N-Ethyl-N-nitroso-butanamine (or Nitrosoethylbutylamine)
NILU	Norwegian Institute for Air Research
NIOSHUS	National Institute for Occupational Safety and Health
NPIP	Nitrosopiperidine
NPYR	1-nitrosopyrrolidine
NTMA	Methyl-nitramine
NH_3	Ammonia
NH_4	Ammonium
NIEA	Northern Ireland Environment Agency
NIPH	Norwegian Institute of Public Health
NMBA	N-Methyl-N-nitroso-butanamine (or Nitrosomethylbutylamine)
NMEA	N-Methyl-N-nitrosoethanamine (referred to as nitrosomethylethylamine)
NPBA	N-Nitroso-N-propyl-butanamine (or Nitrosopropylbutylamine)
NMOR	4-nitrosomorpholine

NO	Nitrogen monoxide
N_2O_3	Dinitrogen trioxide
NO_2	Nitrogen dioxide
NO_x	Combination of nitrogen dioxide and nitrogen monoxide NO3
NPZ	N-nitrosopiperazine
O2	Oxygen
OCCS	Office of Carbon Capture and Storage
OCTAVIUS	Optimisation of CO_2 Capture Technology Allowing Verification and Implementation at Utility Scale
OEL	Occupational Exposure Limits
OES	Occupational Exposure Standards
$OH^{\cdot}$	Hydroxyl radical
OLMS	On-line Mass Spectrometry
OSHA	US Occupational Safety and Health Association
OZD	Oxazolidin-2-one
PAN	Peroxyacetylnitrate
PDI	Phase Doppler Interferometer
PEC	Predicted Environmental Contribution
PI	Pollution Inventory (for England and Wales)
PIPA	1,4-diethylenediamine (or piperazine)
PM	Particulate matter
PNEC	Predicted No Effect Concentration
Ppmv	Parts per million volume
Ppbv	Parts per billion volume
PTR-ToF-MS	Proton Transfer-Reaction Time of Flight Mass Spectroscopy
PZ	Piperazine
QSAR	Quantity Structure Activity Relation
REACH	Registration, Evaluation, Authorisation & Restriction of Chemicals
ROAD	Rotterdam Opslag en Afvang Demonstratie project
SEPA	Scottish Environment Protection Agency
Si	Silicon

SINTEF	Stiftelsen for industriell og teknisk forskning
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SO_4^-	Sulphate
SPRI	Scottish Pollutant Release Inventory
TAPM	The Air Pollution Model
TCMDA	Technology Centre Mongstad
TCM	Technology Centre Mongstad
TDL	Tunable Diode Laser
TEA	Triethanolamine
TEF	Toxic Equivalent Factors
TEQ	Toxic Equivalent
UHPLC/MS	Ultra High Performance Liquid Chromatography Mass Spectrometry
UKAS	UK Accreditation Service
UKCCSRC	UK Carbon Capture and Storage Research Centre
US EPA	United States Environment Protection Agency
UV	Ultraviolet
VOC	Volatile Organic Compounds
WEL	Workplace Exposure Limits
WESP	Wet Electrostatic Precipitator
WHO	World Health Organisation
WRF-Chem	Weather Research and Forecasting (WRF) model coupled with Chemistry
WRF-EMEP	Weather Research and Forecasting (WRF) model coupled with European Monitoring and Evaluation Programme model
XAD	Polyaromatic adsorbent resin
ZEP	Zero Emissions Platform

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