Review of Amine Emissions from Carbon Capture Systems

Version v1.1

Scottish Environment Protection Agency

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This document was originally prepared in the latter half of 2011 and developed through to the end of 2012. We are aware that further detailed technical information on emissions of amine compounds from carbon capture systems has been, or is now in the process of, being published. This information comes from sources such as the IEAGHG research programme and from the work undertaken in relation to the Mongstad Technology Centre in Norway. We are currently reviewing this additional information and aim to update this report with the conclusions of these studies as required in 2013.

Executive summary

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 little 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 compounds to air are being developed. Such systems could generate additional waste water that may require additional treatment. Measures to abate emissions to water are under consideration.

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. Despite this, the proposed thresholds were developed in line with the methodology used within the Europe under the EU regulation on registration, evaluation, authorisation & restriction of chemicals (REACH). Consequently, the thresholds proposed can be adopted as useful benchmarks.

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

Measurement of amines and associated reaction compounds

- Amine compounds are difficult to sample and analyse. There has been limited stack emission monitoring of amine compounds at carbon capture pilot plants.

- Current standard techniques for measuring the ambient air concentration of many of the compounds of interest have limits of detection greater than the proposed threshold levels.

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 standards in line with UK methodologies.

- 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.

0 Executive Summary

0.1 Purpose and Scope

0.1.1 This paper reviews the emission of amines (and related amine reaction products) from post combustion carbon capture systems, their potential effects and considers the development of effective environmental standards. The paper considers four main aspects: emissions of amines and associated reaction products; the potential impact of such emissions on the environment and on human health; the extent of relevant environmental quality standards; and issues associated with measurement of such compounds at low concentrations in emissions and in the environment. The assessment does not cover carbon capture systems based on oxy-fuel combustion, pre-combustion technologies or post combustion chilled ammonia scrubbing, amino acid salt or solid absorption techniques. Whilst amine-based carbon absorption systems can be used in pre-combustion systems, in this situation any amine-derived compounds escaping the gas processing plant as emissions will be abated in the syngas streams upon combustion and no direct release is expected.

0.1.2 There is a significant amount of work underway internationally within the public and private sectors on the issues raised within this paper. Many of the knowledge gaps identified may have already been addressed in the private sector. It is expected that data from the current UK small scale pilot plant projects and the Technology Centre Mongstad project in Norway, should provide information that will assist UK Environment Agencies in developing standards and approaches to regulating carbon capture plant.

0.1.3 In mid-2011, SEPA began to consider the emissions and potential impacts of amines (and related amine reaction products) from post-combustion amine scrubber carbon capture systems. SEPA undertook to develop this paper as a result of concerns raised over the potential health effects of such compounds at the proposed CCS project at Mongstad in Norway. In addition, it was intended that this review would help inform any SEPA assessment of applications for carbon capture systems using such technologies within Scotland.

0.1.4 It should be recognised that the majority of published data on amines and their associated reaction products relates to studies undertaken in Norway. There are limited other data available to cross reference or confirm these studies. However, the data available are generally based on the results of laboratory scale or small scale pilot plant studies. Similarly, most available data relate to the use of solvents based on 2-aminoethanol (more usually referred to by its trivial name monoethanolamine or MEA). It is likely that demonstration scale carbon scrubbing systems will adopt other solvents not based solely on MEA. As such, the conclusions derived are likely to be subject to some uncertainty and may not be valid for capture systems based on other solvents.

0.2 Amine Solvents

0.2.1 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 amine compounds consisting of hydroxyl (alcohol) and amino functional groups on an alkane backbone. Most reported work has concentrated on the use of aqueous solutions of MEA. This solvent is normally used as a baseline when comparing the performance of other types of amine solvents or mixtures of solvents. A wide range of other alkanolamine compounds have been proposed as carbon capture solvents. Alkanolamine compounds are generally odorous, are strong bases and are generally highly soluble or miscible in water forming alkaline solutions on dissolution. Some alkanolamine solutions can be corrosive. Alkanolamine compounds can react and degrade in the carbon capture system itself and in the atmosphere to form a wide range of other compounds which in turn can also form further compounds such as nitrosamines as well as other organic substances.

0.3 Amines: Associated Reaction Products

0.3.1 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 amine nitrogen atom are substituted by an organic group. A wide range (many dozens) of individual nitrosamines have been implicated in emissions from carbon capture systems although many works are inconsistent on the extent of emissions. The most widely studied nitrosamine is N-methyl,N-nitroso-methanamine (often referred to as N-nitrosodimethylamine or NDMA) due to its toxicity and potential environmental effects. N-Nitrosamines have been identified as being significant in terms of emissions from rubber production processes and are present in tobacco smoke, foodstuffs and in drinking water. N-Nitrosamines can also form in the atmosphere as reaction products of amine precursor species. N-Nitrosamines pose a potential environmental and health threat because they have a demonstrated environmental toxicity and are known carcinogens. The properties of individual compounds vary. The efficiency of aqueous scrubber systems for removing nitrosamines is not understood or widely reported. NDMA can be measured in the aquatic environment as it is formed by the chlorination of organic compounds in drinking water. NDMA is known to be persistent but does not bioaccumulate and is degraded by UV light.

0.3.2 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 are substituted by an organic group. A range of nitramines have been implicated in the resultant atmospheric reactions of other degradation products arising from carbon capture systems. Some of the compounds identified are considered carcinogenic. There is generally less information available on such compounds and no clear indication of which key substances are of concern. It is also not clear how efficiently aqueous scrubber systems will be at removing any nitramines that may be present. They are expected to be toxic in the aquatic environment but less so than nitrosamines.

0.3.3 Reaction of the amine solvents with oxides of sulphur and oxides of nitrogen (following the dissolution of these substances in the aqueous amine solution) is of environmental relevance. Oxides of sulphur react with amine solvents to form heat stable corrosive salts. Sulphur oxide concentrations therefore need to be restricted to between 3 and 30 mg/Nm^3 at the inlet of the carbon capture system in order to minimise amine degradation and thus long term solvent usage. This will require the adoption of additional abatement systems (or high efficiency FGD systems) for coal fired systems prior to any carbon capture system. In terms of oxides of nitrogen, only nitrogen dioxide reacts with amines to form degradation products including nitrosamines. To minimise solvent degradation it is generally recognised that nitrogen dioxide concentrations should be kept below a threshold of 20 to 40 mg/Nm^3. It is also reported that limiting NO_2 concentrations entering the capture system to levels as low as possible will minimise the formation of unwanted degradation products such as nitrosamines. As a precautionary stance

SEPA should consider requiring Operators to limit nitrogen dioxide concentrations entering amine based carbon capture systems to levels as low as possible and significantly below the stated thresholds in order to minimise the formation of nitrosamines etc. The negative consequences of the additional abatement equipment and chemical use that may be required to achieve this should be considered.

0.3.4 It is recognised that there is abundant public domain information on the degradation of amines. However, it is now considered that pilot plant studies under real power plant operating conditions have shown that the possible degradation mechanisms of amine solvents and their kinetics may differ from those measured under laboratory conditions. Limiting the input of particulate matter (and the associated metallic elements contained therein) into capture systems may help reduce such degradation reactions. This also implies that the actual degradation rates and mechanisms for amine solvents may be a plant and fuel specific issue.

0.4 Emissions to Air

04.1 There is some available information on the expected emissions to air of amines and alkanolamines. Emissions to the atmosphere will be in the gaseous form and also partly contained within moisture droplets. Emissions of alkanolamines have been reported in a wide range from <0.1 mg/Nm^3 up to 16 mg/m^3. It is excepted that emissions will lie at the lower end of this range and some proprietary systems under development claim to be able to reduce amine slip to <0.3 mg/Nm^3. Due to the solubility and basic nature of these compounds, the adoption of aqueous scrubber systems after the absorber column within the carbon capture system may offer an effective way of abating such emissions. However, the impact on plant costs and operability of the addition of extensive, multistage scrubber systems should not be underestimated due to the scale of the equipment that may be required.

0.4.2 Very limited information on the emissions to air of nitrosamines and nitramines is available. The limited data identified to date show a wide of emissions concentrations of nitrosamines. Due to their solubility, adoption of aqueous scrubber systems after the absorber column within the carbon capture system may offer a way of abating such emissions but there is little data available on the expected effectiveness. In terms of nitramines it is difficult to draw any firm conclusions on the likely extent of nitramine formation in the conditions of typical carbon capture systems. The potential for the formation of nitramines in the atmosphere is widely reported although there is less certainty about the extent of direct emissions. The breakdown of amine compounds can result in a very wide range of other chemicals. Where emission concentrations of other specific substances have been reported the results have been presented at less then the limit of detection or in the range of a few ppm. Emissions of ammonia may be significant (at concentrations over 25 mg/Nm^3) but could be easily abated by multi-stage aqueous scrubber systems. 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 on such emissions, Operators applying for consent for carbon capture systems should be required to submit detailed emission estimates for all relevant compounds. The source and basis for such emission estimates should be clearly stated.

0.4.3 Emissions of amines and their reaction products to the atmosphere can result in other compounds being formed, including nitrosamines, nitramines and others. The atmospheric chemistry involved is complex and can involve other pollutants and sunlight as well as gas phase, aerosol phase and aerosol chemistry. At present, dispersion models are being developed which include a module simulating the atmospheric chemistry of amines. However, it is possible to make assumptions on the rate of conversion of amines in the atmosphere to compounds such as nitrosamines, based on the literature available. It is considered that applying a nominal 10% conversion rate of all precursor species (expressed as total amines) to derive a value for the total concentration of nitrosamines and nitramines that would be generated in the atmosphere is appropriate. This value appears to represent a reasonable approach to addressing the effect of atmospheric chemical reactions on such substances. However, given the uncertainty in the processes, the indeterminate effect of climatic (solar) conditions and the sparse nature of available data, SEPA should require that modelling predictions of various conversion ratios are undertaken. These results can be compared with available data to gauge the level of risk due to potentially varying rates of conversion. This subject is currently being researched further by a number of academic institutions.

0.5 Waste Streams

0.5.1 There appears to be little published evidence of the extent of liquid wastes that may be generated from carbon capture systems. 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. Treatment with UV sources have been reported to eliminate nitrosamine concentrations in some effluents. Dissolved nitrate and nitrites in process make-up water has been reported to react with organic amines to form nitrosamines and nitramines although more work is required to further quantify such degradation.

0.5.2 A review of potential waste streams, their predicted quantities, their recovery/disposal requirements and their environmental consequences indicates that very little information on such issues has been published. Production of solvent reclaimer waste may total around 2,500 tonnes per annum for a 300MWe scale carbon capture plant together with around 200 tonnes per annum of activated carbon waste. No information appears to be available on amine containing wastes from the CO_2 compression and dehydration systems, mechanical filtration systems or from water treatment systems. It is recognised that more research on the quantity and composition of the waste containing amine compounds from capture plants is required in order to assess the most appropriate disposal/recovery options and the likely releases from waste recovery sites. Further review of literature on this subject will be required as data become available from demonstration projects. Although the disposal costs of wastes from carbon capture systems will be significant, in the interim sufficient UK capacity is likely to exist for appropriate disposal.

0.6 Ambient Monitoring

0.6.1 No monitoring has been undertaken by SEPA or the Environment Agency for background concentrations of nitrosamines in ambient air. Ambient concentrations in air of amine solvents (piperazine) of 10-60 ng/m^3 have been reported in the US. Globally, monitoring of nitrosamines in ambient air has been primarily undertaken in industrial areas around potential sources of nitrosamine precursors. Ambient monitoring in Austria, the US and Russia at such locations suggest total N-nitrosamine concentrations may range from 4 to 40 ng/m^3 and other studies have reported concentrations of the individual nitrosamine compound NDMA ranging from 3 ng/m^3 to 32µg/m^3. However, in other studies no NDMA was detected. Work undertaken in relation to tobacco smoking has indicated that concentrations of some nitrosamines can reach appreciable levels in enclosed areas where smoking was permitted with NDMA measured at concentrations of between 7.9 to 45.0 ng/m^3. Total nitrosamine concentrations in industrial rubber processing workplaces have been reported up to 2.0 µg/m^3 (mean value 560 ng/m^3).

0.7 Emission Limits and Standards

0.7.1 In the UK, Environmental Assessment Levels (EALs) have not been established for MEA or the other likely amine solvent species. However, UK Occupational Exposure Limits (OELs) do exist for MEA and these can be used to derive a UK EAL of between 5 µg/m^3 (long term) and 15.2 µg/m^3 (15 minute short term). For other substances (such as methanal) there are some established UK EALs. There are no UK OELs for the other amines and so Occupational Exposure Standards (OESs) adopted by some other European countries could be adopted (with caution) to derive relevant EALs. 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 any relevant toxicology data for many of the compounds concerned. Therefore, adopting a reference substance (NDMA) against which total nitrosamine emissions are assessed is a more appropriate approach. The EAL of 0.3 ng/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. However, in the absence of other data, this value 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. In the longer term SEPA should consider progressing the formulation of standards for such compounds suitable for use in the UK using the current procedures in place. SEPA should also adopt Direct Toxicity Assessment (DTA) as an approach for assessing and permitting discharges to water containing the complex mix of chemicals that are expected from carbon capture systems.

0.8 Emissions to Water

0.8.1 A review of relevant literature has confirmed that environmental information on emissions to water of amines and other amine reaction products such as nitrosamines is limited. The data that are available on ecotoxicity vary considerably. Most general toxicity studies have concentrated on NDMA. At present it is not possible to derive and set an Environmental Quality Standard (EQS) in the water environment for nitrosamines. Any UK EQS for nitrosamines would have to relate to specific nitrosamine chemicals (such as NDMA) and this is a potential representative chemical that could be considered by the Water

Framework Directive (WFD) UK Technical Advisory Group for consideration for development of a specific EQS. This issue will be considered further within SEPA science functions. Alternatively, Direct Toxicity Assessment (DTA) is likely to be considered as an approach for assessing and permitting discharges containing such a complex mix of chemicals.

0.9 Monitoring and Measurement

0.9.1 There has been limited emission monitoring of amine compounds from carbon capture pilot plants. Amine compounds are difficult to sample and analyse and monitoring may be further complicated by the risk of false detection as well the formation or destruction of nitrosamines during sampling. A number of monitoring techniques could be used to detect these substances in stack emissions. Laser systems that can monitor ammonia (that can be used as an indicator compound for amine emissions) are being investigated. In terms of ambient air measurements, the levels of detection of all direct measurement methods (in the order of 0.1 $\mu g/m^3$) may lie above the expected ambient concentrations. These detection limits are also significantly greater than the proposed environmental quality benchmarks that may be applicable. Given this issue, amine reaction products should be monitored at source using stack emissions testing and could also be characterised by regular analysis of a variety of contaminants in liquid solvent and waste water samples. Further studies could assist in providing clarity on the UK aspect of emissions of amine and associated reaction products. This could include further review and assessment of other amine producing industries in the UK, their locations, assessment of background levels of amine compounds and amine compound emissions.

0.10 Next Steps

0.10.1 This paper will be updated as further information becomes available. Further review of literature on this subject will be required as data become available from various UK and international demonstration projects. SEPA will continue to work with the Environment Agency for England and Wales to address the knowledge gaps identified in this report, thereby avoiding duplication of effort and ensuring a common set of standards across the UK.

0.10.2 The data and conclusions arising from this assessment may set a precedent for use by others and act as a reference document. This is despite the uncertainty noted in a number of areas. As such, and given the limited resources available for this assessment it was considered that independent peer review of this work was required. This was completed by the University of Edinburgh and the IEAGHG R&D Programme in early 2012.

0.10.3 SEPA will also specifically update and advise the other environment agencies within the Network of the Heads of European Environment Agencies (EPA Network) Carbon Capture and Storage Interest Group (CCS IG) and industry representatives through the Carbon Capture and Storage Association (CCSA) regarding the content of this paper. This should allow all available information and resources to be pooled and aid the development of the regulatory understanding of this issue which should help address some the uncertainties noted.

Scope of Report

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 (OCCS) for information
V1.01 – December 2011	Superseded by V1.1	Incorporates initial comments and updates assessment in light of additional available at the end of October 2011. Minor typographical corrections addressed and structure revised.
V1.1 – January 2013	Live – this document	Final draft version for publication incorporating internal comments, additional references and peer review comments from the University of Edinburgh and the IEAGHG R&D Programme and comments from the CCSA.

1 Introduction, Substances and Properties

This paper is a technical assessment of data available on emissions of amines and associated reaction products from post combustion amine scrubbing carbon capture systems. This assessment 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 absorption systems can be used in pre-combustion systems, in this situation 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[1,2,104] have identified such emissions as a potential issue and noted that limited open source information is available. Wherever possible, data on emissions and other releases have been assessed on the basis of a 300 MWe capacity carbon capture plant. This will aid reference to any large scale UK demonstration projects which are expected to operate initially at this scale.

It should be recognised that most published data on this issue relates to studies undertaken in Norway. There are limited other data available to cross reference or confirm these studies. However, in all cases, the data available are generally based on the results of laboratory scale or small scale pilot plant studies. Similarly, most available data relate to the use of solvents based on 2-aminoethanol (more usually referred to by its trivial name monoethanolamine or MEA). It is likely that demonstration scale carbon scrubbing systems in the UK will use solvents not solely based on 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. Consequently, this review is updated as further information becomes available on the emissions of amine based substances arising from capture systems not based solely on the use of MEA. It should also be recognised that the data and conclusions arising from this assessment may set a precedent for use by others and act as a reference document. This is despite the uncertainty noted in a number of areas. As such, and given the limited resources available for this assessment it was considered that independent peer review of this work was required. This was completed in March 2012 by the University of Edinburgh[3] and the International Energy Agency Greenhouse Gas Research and Development (IEAGHG R&D) Programme.

The report is structured into 4 main sections. The first section outlines the general properties of the amine compounds likely to be emitted from carbon capture systems. Section 2 addresses the likely emissions of these substances into the air, water and to land and also considers the atmospheric reactions that these substances can undergo. Section 3 examines the environmental effects of these substances concentrating on the appropriate environmental threshold values which may be applicable and against which the eventual environmental concentrations of emissions from carbon capture systems

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[1] IEAGHG *Control of Nitrosamine Formation in CO_2 Capture Plants: Report on Meeting, 2 February, Essen, Germany.* IEA Greenhouse Gases R&D Programme Report 2011/5. June 2011. www.ieaghg.org

[2] IEAGHG *Environmental Impacts of Amine Emissions during Post Combustion Capture. Report on Meeting, February 2010, Oslo, Norway*. IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org.

[3] The peer review was undertaken by Dr Mathieu Lucquiaud, School of Engineering and Dr Mathew Heal, School of Chemistry both at the University of Edinburgh (referred to in summary as the University of Edinburgh).

could be assessed. Section 4 address the issues associated with the measurement of these substances in gaseous releases and in ambient air.

1.1 Types of Amines

There is still 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[47] 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[4]. 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 aqueous solutions of 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 including 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[5].

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[6]. These amine compounds can also react in the carbon capture system and the atmosphere to form a wide range of other compounds.

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[4] Lawrence, S.A, *Amines: Synthesis, Properties and Applications* Cambridge: Cambridge University Press; 1994. ISBN 0 521 78284 8.

[5] Lepaumier *et al*. Degradation Study of New Solvents for CO_2 Capture in Post-combustion. In: *Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), 16–20 November 2008, Washington DC, USA* Energy Procedia 2009;1(1):893-900.

[6] Shao, R. and Stangeland, A. *Amines used in CO_2 Capture – Health and Environmental Impacts*, The Bellona Foundation. 15 September 2009 available at www.bellona.org.

Some Norwegian studies[47] have identified possible health hazards from long term exposure to amines by inhalation including carcinogenic, mutagenic and reproductive health effects. However, not all amine compounds can be classified as having such effects due to an absence of toxicological data for some substances. Such effects are usually assumed for all amine compounds as a precautionary approach and this seems appropriate. Dermal absorption and oral exposure can contribute substantially to the total body burden of such compounds. Adoption of aqueous scrubber systems after the absorber column within the carbon capture system may offer an effective way of abating such emissions. However, the impact on plant costs and operability of the addition of extensive, multistage scrubber systems should not be underestimated due to the scale of the equipment that may be required.

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[7]. A wide range (many dozens) of individual nitrosamines have been implicated in emissions from carbon capture systems although many works 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 methanamine (usually referred to as methylamine) as well as cyclic compounds. The most widely studied nitrosamine is N-methyl,N-nitroso-methanamine (usually referred to as N-nitrosodimethylamine or NDMA, CAS 62-75-9) due to its toxicity and potential environmental effects (see section 3.1 below).

Nitrosamines can also be significant in terms of emissions from rubber processes[8]. Similarly, 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[9]. Nitrosamines also occur in foodstuffs and in drinking water, arising in the latter as by-products of water chlorination and/or chloramination[10]. Nitrosamines are not expected[1] to be formed in the manufacturing process of amine solvents used for carbon capture. NDMA has been detected in a range of foodstuff at levels ranging from 1 to 100 μg/kg (typically 1 to 10 μg/kg)[87]. Nitrosamines can also form in the atmosphere as reaction products of amine precursor species. Nitrosamines pose a potential environmental and health threat because they have a demonstrated environmental toxicity[11,12]. NDMA is a chemical mutagenic carcinogen and is listed by the International Agency on Cancer Research

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[7] *IUPAC Nomenclature Gold Book*. International Union of Pure and Applied Chemistry; 2012 http://goldbook.iupac.org/PDF/goldbook.pdf (accessed June 2012)

[8] Keen, C. *A Small Survey of Exposure to Rubber, Process Dust, Rubber Fume and N-nitrosamines*. Health and Safety Executive publication RR810 Section 1.3. www.hse.gov.uk 2010.

[9] Brunnemann, K et al. Analysis of Tobacco-specific N-nitrosamines in Indoor Air. *Carinogeneesis.* 1992;13 (12): 2415 – 2418. http://carcin.oxfordjournals.org (abstract) (accessed June 2011).

[10] Kim, H. and Han, K. Ingestion Exposure to Nitrosamines in Chlorinated Drinking Water. *Environmental Health and Toxicology* 2011:26, e2011003. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3214982/pdf/eht-26-e2011003.pdf?tool=pmcentrez (accessed 25 July 2012)

[11] United States Environmental Protection Agency (US EPA) *Integrated Risk Information System (IRIS) Dossier for Chemical N-Nitrosodimethylamine* www.epa.gov/iris/subst/0045.htm (CASRN 62-75-9) (accessed June 2011)

[12] Brooks, S *Task 9 Report: The Toxicity of Selected Primary Amines and Secondary Products to Aquatic Organisms: A review. Phase I: CO_2 and Amines Screening Study for Environmental Risks*. Norwegian Institute for Water Research 2008.

(IARC) as a group 2A carcinogen classified as “probably carcinogenic to humans”[13]. Most of the nitrosamines discussed above tend to be water soluble. For instance, NDMA is miscible in water[14] and consequently, adoption of aqueous scrubber systems, after the absorber column within the carbon capture system may offer an effective way of abating such emissions.

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[7]. A wide range of nitramines (a few dozen) have been implicated in the atmospheric reactions arising from emissions from carbon capture systems. 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. There is very limited information available on the specific nitramine compounds likely to be present in emissions from carbon capture system and some reports[104] indicate that no nitramines have been measured in emissions from pilot plants.

A wide range of studies have identified the potential nitramine compounds that may be of importance(see section 2.1.3 below). Some studies[98] have identified specific candidate nitramines for investigation such as N-nitro-N-methyl-methanamine (referred to as Dimethylnitramine or DMNA CAS 4164-28-7), N-Nitromethanamine (referred to as Methylnitramine CAS 598-57-2) and 2-(N-nitroamino)-ethanol (referred to as Ethanolnitramine CAS 74386-82-6) as being potential amine reaction products. Some of the compounds identified are considered carcinogenic[15]. Some of the nitramine compounds identified are soluble in water (including DMNA) and adoption of aqueous scrubber systems after the absorber column within the carbon capture system may offer an effective way of abating any emissions.

1.4 Types of Other Reaction Products

The breakdown of amine compounds can result in a very wide range of other emissions. As for nitrosamines, a wide range of individual compounds have been implicated in direct emissions from carbon capture systems. This includes primary and secondary short chain amines (such as methylamine). Other substances likely to be formed include amides (such as methanamide - common name formamide) that has known developmental toxicity effects and is a suspected carcinogen and irritant) as well as short chain acids (ethanoic acid) and ketones. In addition, aldehyde compounds (such as methanal, cyclic nitrogen compounds (such as Morpholine) and PAN type substances (1-(nitroperoxy)-ethanone or peroxyactylnitrates) are likely to be emitted. These compounds generally have established and potentially significant environmental and health impacts[16,17].

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[13] International Agency for Research on Cancer *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans.* Volumes 1–102 http://monographs.iarc.fr/ENG/Classification/index.php (accessed 24 June 2012)

[14] US Environment Protection Agency National Service Center for Environmental Publications. *Emerging Contaminant - N-nitrosodemethylamine (NDMA*) EPA Fact Sheet, 505-F-07-006. http://nepis.epa.gov/Exe/ZyNET.exe/ (accessed June 2012)

[15] Dusinska, M et al. *Nitramine Analysis Procedural Development* Norwegian Institute for Air Research (NILU) Report OR15/2011. http://co2.nilu.no (accessed June 2012)

[16] “Environmental Impacts of Emissions from Post-combustion CO_2 Capture”. Attalla, M. www.ieaghg.org/index.php?/environmental-impacts-of-amine-emission-during-post-combustion-capture.html.

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. Neither of these substances has so far been reported above the reporting threshold in any industry sector regulated by SEPA (10 kilogrammes per annum (kg pa) and 1 kg pa respectively). The Pollution Inventory (PI) for England and Wales provides information on emissions of chemical pollutants from industrial sites regulated Environment Agency. Review of this data indicates that 29 amine compounds are included in the database (including MEA, DEA and methylamine but no nitrosamine compounds). However, only 6 substances have been recorded above the reporting threshold values and the vast majority of such emissions relate to emissions to water of benzeneamine (aniline) from the sewage treatment and chemical sectors. No emissions of MEA or other amine compounds likely to be relevant to carbon capture systems have been recorded. SEPA will continue to work with the Environment Agency to explore such issues further and investigate the monitoring or calculation methods used to estimate such emissions.

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 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[6]. Most published work concentrates on the use of MEA. However, it should be noted that primary amines (such as MEA) cannot directly react with other substances to become stable nitrosamines[1,18,19]. As such, the range of potential reaction products (including as nitrosamines) produced directly from other solvent mixtures that could contain secondary or tertiary alkanolamines is likely to be more extensive and wide ranging than those produced from the use of MEA alone[104]. Other solvent mixtures incorporating secondary amines have been shown to enhance carbon capture rates, reduce energy penalties and reduce corrosion problems[20,25] and these types of solvent mixtures are likely to be adopted in large scale demonstration scale projects.

2.1.1 Amine "Slip" and Emissions

During the carbon dioxide 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[6]. Amine emissions to the atmosphere will be in the gaseous form

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[17] Matthias, K. et al. "Worst Case Study Method to Assess the Environmental Impact of Amine Emissions from a CO_2 Capture Plant*". International Journal of Greenhouse Gas Control* 2011;5(3): 439-447

[18] Pedersen ,S. et al. IEAGHG *"Flue Gas Degradation of Amines*". Report on Meeting February 2010, Oslo, Norway. IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org.

[19] The Dow Chemical Company *"DOW Product Safety Assessment: Mono-ethanolamine"* 23 March 2010. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0459/0901b80380459c23.pdf?filepath=productsafety/pdfs/noreg/233-00265.pdf&fromPage=GetDoc accessed September 2012

[20] Aroonwilas, A. and Veawab, A. Integration of CO_2 Capture Unit Using Single and Blended Amines into Supercritical Coal-fired Power Plants: Implications for Emissions and Energy Management*. International Journal of Greenhouse Gas Control* 2007;1(2):143-150.

and also partly contained within moisture droplets generated by the scrubber and in condensate formed after the flue gas exits the stack[6,23]. The extent of publically reported amine concentrations in stack emission are limited and vary significantly. Some of the available data are summarised in the table below. 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 are a mix of theoretical and measured data.

Citation	**Reported Emission Concentration (mg/Nm^3)**	**Comments**
CASTOR pilot plant[21]	<0.1	-
Niederaussem pilot plant [44]	0.02 to 0.03	As MEA
CESAR pilot plant[22] and theoretical studies[23]	<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[24]	0.5 to 3	As MEA (in isolation)
Mobile test facility at Longannet[48]	1 to 4	-
Anticipated emissions[74]	3.5 to 6.8	As amine, after absorber wash systems
Laboratory conditions[25]	8.5	-
Mongstad Test Centre, Norway[26]	1.4 to 8.2	Estimated as MEA. Reference conditions not stated. 16.3 mg/m^3 as a maximum possible emission scenario
Kårstø demonstration plant[6]	2.7 to 10.9	Estimated amine emissions

There is ongoing research to reduce amine slip using abatement systems such as aqueous scrubbers and some proprietary systems under development claim[22] to be able to reduce amine slip to <0.3 milligrammes per normalised cubic metre (mg/Nm^3). Multi-stage aqueous scrubber systems with de-misters are expected[23,50] to be able to

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[21] Ayrshire Power ltd. Section 36 Application. *Post Application Clarification Report.* September 2010. http://www.scotland.gov.uk/Topics/Business-Industry/Energy/Infrastructure/Energy-Consents/Applications-Database/Hunterston-Index/Correspondence. Accessed July 2012

[22] Da Silva, E and Aas, N. *Emission Measurements at Dong's Pilot Plant for CO_2 Capture in Esbjerg* Report on Meeting February 2010, Oslo, Norway. IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org.

[23] IEAGHG *Gaseous Emissions from Amine Based Post-combustion CO_2 Capture Processes and Their Deep Removal.* IEAGHG Report 2012/07. www.ieaghg.org.uk

[24] *IEAGHG Environmental Impact of Solvent Scrubbing of CO_2* IEA Greenhouse Gases R&D Programme. Report 2006/14. October 2006. www.ieaghg.org.

[25] Thitakamol B, Veawab A, Aroonwilas A. Environmental Impacts of Absorbtion-based CO_2 Capture Unit for Post Combustion Treatment of Flue Gas from Coal-fired Power Plant. *International Journal of Greenhouse Gas Control* 2007;1(3):318-342.

[26] Berglen, TF et al. *CO_2 TCM updated Air Dispersion Calculations*. Norwegian Institute for Air Research – NILU Report OR 41/2010 (Update of report OR12/2008). http://www.klif.no/nyheter/dokumenter/tcm_soknad_vedlegg8.pdf accessed September 2012

reduce amine emissions to very low levels. Emissions of alkanolamines are excepted to lie at the lower end of the range of results reported.

A number of guidance notes[27] suggest emission limit values for amines from various industrial processes ranging from 1 to 5 volumetric parts per million (vppm) 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 Environment Agency has developed an approach to the public reporting of total amine concentrations from carbon capture systems[28]. 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.

2.1.2 Emissions of Amine Reaction Products

The main reaction pathways for amines within the carbon capture system include oxidation, thermal degradation and acid gas reactions. A summary of each reaction route is presented below:

- Oxidation: Oxidative degradation of amines is caused by the presence of oxygen and metals such as vanadium, iron and copper present in the flue gas[6]. It is expected that this route will be the main degradation pathway although other reference studies[26] recognise that the mechanisms of oxidative degradation are not yet fully understood. The degradation products[6,23,104] can be oxidised fragments of amines including compounds such as ammonia, organic acids, oxidants, aldehydes (such as ethanal and methanal etc.) and carboxylic acids (such as methanoic acid, hydroxyethanoic acid and ethandioic acid). Avoiding radical formation will limit oxidative degradation and it is possible to add oxidation inhibitors such as ethylenediaminetetraacetic acid (EDTA) and bicine (N,N-Bis(2-hydroxyethyl)glycene) to the solvent, which will bind with the metal ions and act to limit such oxidation[6]. 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[26].

- 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 which can result in the degradation of the salt and amine[29]. Formation of heat stable salts occurs when these carboxylic acids react with MEA or with other degradation products. Stripper operational temperatures are typically quoted at around 110ºC. This temperature is regarded[30] as being the optimum stripper temperature for MEA-

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[27] Secretary of State's Guidance for Iron, Steel and Non-Ferrous Metal Foundry Processes, Process Guidance Note 2/4, Issue 1.0, Published October 2004 and Secretary of State's Guidance for Maggot Breeding Processes, Process Guidance Note 6/5, Issue 1.0, Published July 2005 and Secretary of State's Guidance for Fish Meal and Fish Oil Processes, Process Guidance Note 6/19, Issue 1.0, Published July 2005.

[28] Reporting Amine Releases CCS Plants. V5, 4 November 2010. As noted in Table S4.4 footnote 2 of permit variation EPR /VP3337SR/V004 for Ferrybridge Power Station.

[29] Haugmo *et al* Chemical Stability and Biodegradability of New Solvents for CO_2 Capture *Energy Procedia* 2011;4:1631-1636.

[30] Davis, J and Rochelle, G. Thermal Degradation of Monoethanolamine at Stripper Conditions *Energy Procedia* 2009;1:327-333.

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) along with other polymerisation products[23]. Thermal degradation of MEA is reported to account for around 20-30% of total amine losses[6]. Degradation by reaction with CO_2 itself at elevated temperatures evident in stripper systems is also reported[104] to be a degradation route leading to the formation of long chain non-volatile substances.

- Acid gas reactions: These reactions concern the interaction of oxides of sulphur and oxides of nitrogen (present in the flue gas entering the carbon capture system) with amines following the dissolution of these substances in the aqueous amine solution. The reaction of each of these substances is addressed in turn as follows:

  - Oxides of sulphur (SO_2, SO_3) can react with amine solvents to form heat stable corrosive salts[31]. Sulphur oxide concentrations therefore need to be restricted to between 3 and 30 mg/Nm^3 in order to minimise amine degradation and thus long term solvent usage[31,32,33]. The source literature do not specify the normalised reference conditions although this is assumed to be the standard reference conditions of dry, STP and 3% oxygen for gas fired systems, 6% oxygen for coal systems and 15% oxygen for gas turbines. For solid fuel systems, these thresholds are typically achieved using an additional ‘polishing unit’ placed after the standard flue gas desulphurisation systems[31] upstream of the absorber. It may be possible to adapt and enhance the efficiency of conventional flue gas desulphurisation (FGD) systems to meet such values[34,36]. This could do away with the need for a pre-scrubber system[35] 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[36].

  - A typical combustion flue gas from coal fired plants contains mixture of nitrogen dioxide and nitrogen monoxide (referred to as NO_x) with nitrogen monoxide (NO) forming the main component of between 90% and 95%[37]. Nitrogen monoxide will not react with amines[31], however it can be oxidised to nitrogen dioxide at the absorber inlet or flue gas desulphurisation system[1,18]. Nitrogen dioxide will

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[31] Jansen, D. *et al*. *EOS-CAPTECH – Integration of CO_2 Capture Technologies in Existing Plants in the Netherlands* CAPTECH 2007 www.CO2-captech.nl/

[32] Smith, K et al. *Evaluation of Wet FGD Technologies to Meet Requirements for Post CO_2 Removal of Flue Gas Streams* Dravo Technologies 2008. http://www.mass.gov/dep/air/priorities/hazeapd25.pdf accessed September 2012

[33] IEAGHG *CO_2 Capture Ready Plants* International Energy Agency Greenhouse Gas R&D Programme Technical Study. Report 2007/4. Section 7.2.

[34] Wu, S et al. Technology Options for Clean Coal Power Generation with CO_2 Capture In: *XXI World Energy Congress*, 12 – 16 September 2010, Montreal, Canada

[35] Ayrshire Power Ltd. *Addendum to Section 36 Application.* Annex D. www.ayrshirepower.co.uk/environment accessed September 2012

[36] IEAGHG *Emissions of Substances Other than CO_2 from Power Plants with CCS* IEA Greenhouse Gases R&D Programme Report 2012/03 www.ieaghg.org

[37] European IPPC Bureau *Reference Document on Best Available Techniques for Large Combustion Plant* (the Combustion BREF Note for Integrated Pollution Prevention and Control (IPPC)) 2005 Section 3.4. http://eippcb.jrc.es. Accessed September 2012

partially react with amines and amine degradation products to form numerous other degradation products including ammonia and nitrosamines[26]. Measurements at some small scale demonstration sites[22] appear to indicate that NO_x emissions will be reduced in the carbon capture system due to the reaction of nitrogen dioxide (NO_2) with amine compounds. To minimise solvent degradation it is generally recognised[33,38,39] that nitrogen dioxide concentrations at the inlet to the carbon capture system should be kept below a threshold of between 2 and 40 mg/Nm^3. This nitrogen dioxide concentration can usually be met by the use of the normal emission reduction systems associated with Best Available Technology (BAT)[33,40]. It is also recognised[1,18] that limiting nitrogen dioxide 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 plant meeting the requirements of the European Union Industrial Emissions Directive (IED) (Directive 2010/75/EU), the worst case nitrogen dioxide concentration in the absorber would be around 15 mg/Nm^3. This concentration could be reduced to below 5 mg/Nm^3 if a pre-scrubber polishing unit or direct contact cooler system is adopted[1,41].

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 have shown that the possible degradation mechanisms of amine solvents and their kinetics may differ from those measured under laboratory conditions. This reflects the already established position for oxidative degradation noted above. For example, some organic compounds present in reclaimer wastes from a US coal-fired power station[42] have not been previously reported as MEA degradation products found in laboratory scale experiments. This is attributed to degradation mechanisms catalysed by transition metals not present in laboratory scale experiments. However, it should be recognised that the compounds measured in this study arose from the reclaimer wastes that are subject to higher temperatures than the general amine circulation system. Other studies[6] have reported that the precise role of dissolved metals in amine degradation reactions are unknown although MEA degradation is reported[43] to be catalysed in the presence of metals. This is supported by others[44,45] who have confirmed that the consumption and measured losses of MEA may differ between different plants. These findings imply that degradation products are

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[38] Harkin, T et al. Reducing the Energy Penalty of CO_2 Capture and Storage Using Pinch Analysis Chemical Engineering Transactions 18:255-260 http://www.aidic.it/pres09/webpapers/10Harkin.pdf accessed September 2012

[39] IEAGHG *CO_2 Capture as a Factor in Power Station Developments* IEA Greenhouse Gases R&D Programme Report 2006/8. May 2006. www.ieaghg.org

[40] IEA GHG *Capturing CO_2* IEA Greenhouse Gases R&D Programme Report, May 2007. ISBN 978-898373-41-4. www.ieaghg.org

[41] European IPPC Bureau *Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers* (the large volume chemical BREF Note for Integrated Pollution Prevention and Control (IPPC)). 2007 http://eippcb.jrc.es. accessed September 2012

[42] Strazisar *et al* Degradation Pathways for Monoethanolamine in a CO_2 Capture Facility *Energy & Fuels* 2003;17(1):1034-1039.

[43] Knudsen, J., Jensen, J., Vilhelmsen, P.-J., Biede, O. Experience with CO_2 Capture from Coal Flue Gas in Pilot-scale: Testing of Different Amine Solvents *Energy Procedia* 2009; 1(1):783–790

[44] Moser, P.; Schmidt, S.; Stahl, K. Investigation of Trace Elements in the Inlet and Outlet Streams of a MEA-based Post-combustion Capture Process: Results from the Test Programme at the Niederaussem Pilot Plant *Energy Procedia* 2011;4(1):473-479 London: Elsevier; 2011

[45] Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T. Performance of MEA in a Long-term Test at the Post-combustion Capture Pilot Plant in Niederaussem *International Journal of Greenhouse Gas Control* 2011; 5(4):620–627

likely to be, to some extent, specific to each plant and to the type of fuel used. This aspect will need to be considered further in any subsequent updates to this paper. However, 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[33] 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.

2.1.3 Emissions of Nitrosamines

A review of available studies indicates that the breakdown products from amine solvent reactions (including nitrosamines) are varied and variable[6,18,21,22,26,46,47]. 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. The extent of the expected substances concerned are summarised above in section 1. The limited data on emissions that have been published are summarised on the table below.

Citation	Reported Emission Concentration	Comments
Mobile test facility at Longannet[2,48].	'sub µg/m^3' range	Nitrosamines were measured in four out of ten test runs
Mongstad Test Centre [26].	0.0015ppmv (5.0µg/m^3) to 0.003ppmv (9.9µg/m^3)	Calculated data based on result from test facilities. Nitrosamine concentrations (expressed as NDMA) as a worst case scenario.

Other sources report[49] that N,N-bis(2-hydroxyethyl)nitrous amide (N-nitrosodiethanolamine or NDELA) was the main nitrosamine observed in studies of amine degradation by flue gases at higher concentrations than other studies[18] that indicate that up to 0.5 ppm NDELA may be present in solvent samples exposed to NOx. Similarly, no nitrosamines were detected in samples not exposed to NOx. Theoretical studies[23] using these solvent concentrations suggest that the corresponding emissions to air of total nitrosamines could reach 2 to 6 mg/Nm^3. However, these studies stress that such results are based on theoretical equilibrium/kinetic calculations and do not represent actual measurements from operating plants and are likely to overestimate emissions to air.

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[46] Attalla M and Azzi M. *Environmental Impacts of Atmospheric Emissions from Amine based Post-Combustion CO_2 Capture* (Report on Meeting at Oslo, Norway in February 2010) IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org.

[47] Brakstad et al. *Support on Input to Environmental Discharges - Evaluation of Degradation Products* Technology Centre Mongstad: Aker Clean Carbon 2010. http://www.tcmda.com/Global/Aminrapporter/EVALUATION%20OF%20DEGRADATION.pdf accessed September 2012

[48] Graff, O.F. *Emission Measurement and Analysis from Mobile Carbon Capture Test Facility* (Report on Meeting at Oslo, Norway in February 2010) IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org.

[49] Fostas *et al.* Effects of NOx in the Flue Gas Degradation of MEA *Energy Procedia* 2011;4(1):1566-1573 London: Elsevier; 2011

The formation of stable nitrosamines is not expected directly from primary amines (such as MEA), however in a solvent system based on primary amines there will be formation of degradation products with secondary and tertiary amine functionality[47]. The formation of the secondary amine DEA from MEA has been found to increase with increased oxygen and nitrogen dioxide concentrations[1]. Stable nitrosamine formation is mainly associated with secondary amines but may also be formed from systems with tertiary amines (such as tris(2-hydroxyethyl)amine or triethanolamine - TEA)[26]. The pH and temperature and types of solvents likely to be used in full scale carbon capture systems are likely to be different from the conditions where nitrosamine chemistry has been studied in detail to date[47]. However, it is reported[47] that the concentration of species formed by reaction with nitrogen oxide can be influenced by pH. Nitrosamine concentrations have also been found to reduce with ultraviolet (UV) irradiation (from an artificial UV source) within the absorber solvent[1]. This could offer a means to abate nitrosamine emissions without the use of extensive aqueous scrubber systems[23].

2.1.4 Emissions of Nitramines

Nitramines are also formed as a result of reactions between amine solvents, amine degradation products and nitrogen dioxide in the atmosphere. The potential for the formation of nitramines in the atmosphere is widely reported[2,6] although other reports cite unsourced data[104] that indicate that direct emissions of nitramines have not been reported from pilot plant studies or have been measured in liquid streams. However little dedicated work has yet been undertaken to identify nitramine emissions from degraded amine solvents[47]. Where emission concentrations are reported, the expected nitramine concentrations have been calculated from amine emission concentrations and a factor reflecting the expected atmospheric degradation of amines to nitramines[17]. A list of typical nitramines that have been implicated in emissions from carbon capture systems is summarised in section 1.3 above.

2.1.5 Emissions of Ammonia

Some studies[21] 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[22,48] that suggest ammonia releases in flue gases may reach ~50 mg/Nm^3. The actual emissions of ammonia mainly depend on the absorber temperature. Ammonia arises from the oxidative degeneration of amines[50]. These emission concentrations would represent a high annual amine degradation rate which would increase with increasing NOx concentration at the inlet of the scrubber system[18]. 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. In summary, it is expected that elevated emission of ammonia may be released from carbon capture systems although it is not clear whether the quoted emissions estimates include the effect of aqueous abatement systems. A number of guidance notes[27,37] suggest emission limit values for ammonia from various industrial process ranging from <1 to 5 mg/Nm^3. However, the anticipated emission concentrations would be easily abated[23,104] in multi-stage aqueous scrubber systems at the exit of absorber.

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[50] Mertens, J., Knudsen, J., Thielens, M-L, Andersen, J. On-line Monitoring and Controlling Emissions in Amine Post-combustion Carbon Capture: A Field Test *International Journal of Greenhouse Gas Control* 2012;6(1):2–11

2.1.6 Emissions of Other Substances

The breakdown of amine compounds can result in a very wide range of other chemicals that have been implicated in the emissions from carbon capture systems. A list of typical compounds that have been implicated in emissions from carbon capture systems is discussed in section 1.4 above. Where emission concentrations of specific substances have been reported (such as DMA) results have been presented as less then the limit of detection[104]. Other studies[17] suggest that emissions of methanamide and ethanamide may be on the order of 0.3 ppm and 0.1 ppm respectively. Methanal concentrations have been reported[22,23] in emissions to air between 0.4 and 1.5 mg/Nm^3.

The fate and behaviour of mercury compounds entering the carbon capture system has been assessed in some studies[36]. 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 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 applying for consent for carbon capture systems should be required to submit detailed emission estimates for all relevant compounds. The source and basis for such emission estimates should be clearly stated.

2.2 Atmospheric Reactions

Emissions of amines and their reaction products to the atmosphere can result in other compounds being formed, including nitrosamines, nitramines and methanamide (amongst others). The atmospheric chemistry involved is complex and can involve other pollutants and sunlight as well as gas phase, aerosol phase and aerosol chemistry. There are, however, many unknowns in the atmospheric chemistry of amines and many possible (~100) products can be formed from amine precursor species[26]. Only a few studies on the atmospheric chemistry of amines have been carried out although further work on this issue is being undertaken[60,62]. At present, atmospheric dispersion models which include a module simulating the atmospheric chemistry of amines are being developed.

However, it is possible to make assumptions on the rate of conversion of amines in the atmosphere to other compounds, such as nitrosamines, based on the literature available. These data can then be used to model the dispersion of amines and their degradation products either dynamically or as inert compounds. Work that has investigated amine reactions in the atmosphere has been carried out in the US[51,57] and more recently in Europe[60,62]. Both US studies studied ethylamines, whereas as alkanolamines are most typically used in carbon capture processes[6]. However, given the solubility of most amine compounds, some researchers[62] have reported adopting wet deposition parameters (akin to those used for SO_2 deposition estimates) in the modelling studies of a carbon capture plant. However, the atmospheric lifetime of amine compounds and their derivatives will range considerably from minutes (due to photolysis) to much longer periods, particularly in relation to the photo-oxidative products. This would allow for atmospheric transport to occur over longer distances. The occurrence, properties and

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[51] Pitts, J.N. Jr., et al. Photooxidation of Aliphatic Amines Under Simulated Atmospheric Condition: Formation of Nitrosamines, Nitramines, Amides and Photochemical Oxidant. Environmental *Science & Technology* 1978;12(8):946-953.

fate of amine compounds in the atmosphere has recently been subject to further detailed reviews[52,53]. However, nitramine and nitrosamine compounds are not addressed in any detail.

Nitrosamines can be formed in the atmosphere in the gas-phase from reaction of an amine with a nitrosating agent, such as the nitrosyl cation (NO+) from nitrous acid[26,54]. Nitrosamines have the potential to degrade either through sunlight photolysis or by reacting with other oxidising atmospheric pollutants. Although some reports suggest that both ozone and oxidised nitrogen compounds could play a role in amine oxidation during the night, the degradation products of amines can also act as a sink for oxidising compounds. As such, the reduction of such oxidising compounds from reaction with amines during the day could contribute to the photo-driven reactions that directly result in the formation of tropospheric ozone. However, the nitrosating pathway for amines will be minor compared with other gas-phase reaction of amines and the actual half-life of such compounds during daylight hours is expected to be short due to such photolysis. For instance; photolysis on a timescale of minutes to tens of minutes has been reported for NDMA[55]. Others[51] suggest that nitrosamine compounds can have half-lives of 30 minutes in full sunlight and 60 minutes in cloudier conditions (although such rates will be location specific and depend on the strength of solar radiation). In the case of tertiary amines, it was found that tertiary nitrosamine concentrations increase when initially exposed to sunlight. It was also found[51] that in sunlight, amines act as a catalyst for rapid conversion of NO to NO_2. Other studies[56] have investigated the aqueous photolysis of a number of alkyl nitrosamines in a solar simulator. Direct photolysis at high irradiation levels (representing southern California midsummer, midday sun) suggested that NDMA would have a half-life of 16 minutes in such conditions with lower values for other nitrosamines. Quantified products of NDMA photolysis included methylamine, DMA, nitrite, nitrate, and ionic methanoic acid. The study concluded that photolysis is likely to be the dominant loss process for NDMA in aqueous effluents (timescales of hours) even for fairly low levels of irradiation.

In the US, it is reported that 3% of secondary amines and 1.8% of tertiary amines are converted to nitrosamines in laboratory chamber studies[51]. Other US overview studies[57] (which include data from several studies) have suggested a conversion ratio of amines to nitrosamines of between 10 and 30%, although this may be an overestimate due to high nitrous acid concentrations in this particular experiment. Some studies[58] have reported worst case conversion rates of tertiary amines to nitrosamines of 2%. More recent Norwegian reaction chamber studies have found that less than 0.6% of DMA

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[52] Ge, X., Wexler, A. S. and Clegg, S. L. Atmospheric Amines - Part I. A Review *Atmospheric Environment* 2011;45(3):524-546.

[53] Ge, X., Wexler, A. S. and Clegg, S. L. Atmospheric Amines - Part II. Thermodynamic Properties and Gas/particle Partitioning. *Atmospheric Environment* 2011;45(3):561-577.

[54] Hanst, P. L., Spence, J. W. and Miller, M. Atmospheric Chemistry of N-Nitroso Dimethylamine *Environmental Science & Technology* 1977;11(1):403-405.

[55] Tuazon, E. C., Carter, W. P. L., Atkinson, R., Winer, A. M. and Pitts, J. N. Atmospheric Reactions of N-nitrosodimethylamine and Dimethylnitramine *Environmental Science & Technology* 1984;18(1):49-54

[56] Plumlee, M. H. and Reinhard, M. Photochemical Attenuation of N-nitrosodimethylamine (NDMA) and Other Nitrosamines in Surface Water *Environmental Science & Technology* 2007;41(17):6170-6176.

[57] Grosjean, D. Atmospheric Chemistry of Toxic Contaminants. 6. Nitrosamines: Dialkyl Nitrosamines and Nitrosmorpholine *Journal of the Air and Waste Management Asscoiation* 1991;41(5):306-311

[58] Matthias, K et al. *Amines Worst Case Studies Worst Case Studies on Amine Emissions from CO_2 Capture Plants (Task 6)* Norwegian Institute for Air Research Report OR 78/2008http://co2.nilu.no/LinkClick.aspx?fileticket=qNhKgZGUHjM%3D&tabid=2549&mid=5547&language=en-GB accessed September 2012

and 1.1% of N,N-Dimethylmethanamine (trimethylamine – TMA) were converted to nitrosamine[60].

Nitramines are formed through the oxidation of primary, secondary and tertiary amines and can be stable in sunlight. These compounds are therefore expected to be more stable in the atmosphere than nitrosamines and their half life is thought to be around 2 days[59]. However, this half life will depend on location and the strength of solar radiation. Some studies suggest that the main process which removes nitramines from the atmosphere is reaction with hydroxide[57]. Other work[58,60] suggests that worst case amine to nitramine yields may reach 7-8% (less than 5% from TMA, less than 2.5% from DMA and less than 0.4% from methylamine). Nitramines therefore have the potential to be present in the atmosphere for longer periods of time than nitrosamines resulting in different exposure profiles.

Within all the studies, there are a number of uncertainties in the assumptions made, and some reports note that gas to aerosol conversion and aerosol chemistry is not included in current yield factors[26]. This may impact on the quoted rates of conversion. More recent experiments[60] have been carried out to examine the photo-oxidation of amines, and confirm that gas to particle conversion is a significant factor which needs to be accounted for. A box model[61] has been developed to simulate the photo-oxidation of amines from an existing model and this work also confirmed the production of ozone[62].

The overall conclusion that can be reached from the limited number of studies relevant to the investigation of ambient concentrations of nitrosamines in the atmosphere is that nitrosamines are destroyed by photolysis and are water soluble. These two factors imply that nitrosamines may have fairly short atmospheric lifetimes and consequently relatively small spatial scales of influence from their emission source. Although it is not known how far amines travel from their source it is expected that different amine compounds will travel different distances[98] .

Consequently, it is considered that applying a nominal 10% conversion factor (representing a very conservative/worst case approach) of the highest instantaneous predicted environmental concentration of all precursor species (expressed as total amines) to derive a value for the total nitrosamine and nitramine concentration that would be generated in the atmosphere. This value appears to represent a reasonable (but highly conservative) approach to addressing the effect of atmospheric chemical reactions on such substances. Given the uncertainty in the processes, the indeterminate effect of climatic (solar) conditions and the sparse nature of available data, SEPA should require that modelling predictions of various conversion ratios are undertaken. These results can be compared with available data to gauge the level of risk due to potentially varying rates of conversion.

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[59] Nielsen, C. *Health Aspects of Amine Capture Solvents - Overview from On-going Norwegian Research Projects* (University of Oslo) CO2NET Seminar and Networking Event 2011, London, May 2011. www.co2net.eu.

[60] Nielsen, C., et al. Atmospheric Degradation of Amines (ADA) Summary Report: Photo-Oxidation of Methylamine, Dimethylamine and Trimethylamine Norwegian Institute for Air Research CLIMIT project no. 201604 Report OR 2/2011 http://www.nilu.no/Publikasjoner/tabid/62/ctl/PublicationDetails/mid/764/publicationid/25756/language/en-GB/Default.aspx accessed September 2012

[61] A box model is a model which has no transport or dispersion of pollutants included in it; it will generally assume that complete mixing has occurred within the 'box'.

[62] Nielsen, C et al . Atmospheric Degradation of Amines (ADA), Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA) Norwegian Institute for Air Research CLIMIT project no. 193438, Report OR 8/2010 http://ada.nilu.no/Reports/tabid/3191/language/en-GB/Default.aspx accessed September 2012

2.3 Emissions to Water

There appears to be little published evidence of the extent of liquid wastes that may be generated by carbon capture systems (such as waste amine solvent, water treatment plant effluents, condensate recovery system wastes or liquid wastes from cleaning). Some researchers report that the main amine loss may actually occur in the waste waters generated by the capture plant[6]. 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. The aqueous scrubber wastes will also contain soluble non-volatile degradation products such as short chain organic acids[47]. The limited published data available[18,22] suggests that NDELA and methylamine has been detected in waste waters from test rigs at concentrations of 10 parts per billion (ppb(w)) and 0.3 milligramme/litre (mg/l) respectively. This is consistent with other reports that cite unsourced data[104] that suggest nitrosamine concentrations in the aqueous solvents themselves will be many orders of magnitude lower than the concentration of the amine solvent. 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[23] suggest that acid wash sections will be effective at removing unwanted amine degradation products. NDMA appears to be photolysed in aqueous phases[63] and treatment with UV sources have been reported[23,64,65] to eliminate nitrosamine concentrations in some effluents. Some studies[66] note that dissolved nitrites and nitrates in process make-up water may react with amine compounds to form nitrosamine and nitramines. Further work is needed in this area. For any nitrosamine-contaminated waste water, simple dilution of process effluents before discharge may offer a way of achieving the desired concentration limits. However, such dilution will not reduce the total mass emissions of such substances and may still not be able to achieve the required threshold concentrations due to the low level of proposed environmental benchmarks for such substances discussed in section 3.2 below.

2.4 Emissions from Other Plant Areas

A review of potential waste streams, their predicted quantities and disposal requirements indicates that very little information on such issues has been published. There are a number of waste streams that will be generated by a capture plant. This waste is likely to be present as sludge from the water treatment plants and amine reclaimer systems and from the amine filtration systems. More work on this area is required to determine the exact composition of these sludges and wastes (and the available recovery/disposal routes either on site or off-site). Such wastes are likely to be classed as hazardous wastes[36,67]. Available data for each potential waste stream can be summarised as follows:

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[63] Stefan, M. I. and Bolton, J. R. UV Direct Photolysis of N-nitrosodimethylamine (NDMA): Kinetic and Product Study *Helvetica Chimica Acta* 2002;85(5):1416-1426.

[64] Xu, B. *et al*. Efficiency of Photodecomposition of Trace NDMA in Water by UV Irradiation School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090. Huan Jing Ke Xue 2008, July; 29(7).

[65] Plumlee, H. *et al*. N-nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV treatment and Analysis via LC-MS/MS Water Res. 2008;42(1-2):347-55.

[66] Reynolds, A., Verheyen, T., Adeloju, S., Meuleman, E., Feron, P. Towards Commercial Scale Post-combustion Capture of CO_2 with Monoethanolamine Solvent: Key Considerations for Solvent Management and Environmental Impacts *Environmental Science and Technology* 2012;46 (7):3643–3654

[67] Veltman, K. *Human and Environmental Impact Assessment of Post-combustion CO_2 of a Natural Gas Fired Power Plant* Presentation to 5th Trondheim Conference on CO2 Capture,

- Reclaimer system wastes (a mixture of water, organic and inorganic substances). Amine reclaimer systems are only expected to operate intermittently in batch cycles[23,25] although low volume continuous systems may also be adopted. The likely composition of batch reclaimer system wastes (a mixture of water, organic and inorganic substances) has not been addressed by many studies. Available data[25,68,69] suggests that such 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[24] trace elements in ppm quantities such as chromium (Cr), copper (Cu), iron (Fe) and nickel (Ni). 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[25,36,70,71] (contaminant levels of 1.2 to 10% by weight) to determine when reclaimer systems should be operated. Estimates of the production rate of amine reclaimer sludges vary considerably[6,24,25,36,72,73,74,75] with specific generation rates ranging between 0.02 to 15.9 kg/tonne CO_2 captured. Adopting the central case mid range of these estimates of 0.5 to 1.1 kg/tonne CO_2 abated suggests that between 1,000 and 2,500 tonnes per annum of reclaimer waste can be expected from a 300MWe scale carbon capture plant.

- Little information appears to be available on amine containing wastes from the CO_2 compression and dehydration systems or from mechanical filtration systems. Little information on water or water treatment wastes[76] from direct contact cooler systems

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Transport and Storage 16-17 June, 2009 http://www.energy.sintef.no/arr/CO2_2009 accessed September 2012

[68] *Feasibility of CCS Sludge Co-firing in Power Plant* UK Department for Energy and Climate Change Report KCP-ENT-CAP-REP-0001, Section 2 and section 4.2.2. Kingsnorth Carbon Capture and Storage Project FEED Study report. October 2011. http://www.decc.gov.uk/assets/decc/11/ccs/chapter4/4.32-sludge-co-firing-report.pdf accessed September 2012

[69] Kingsnorth EP Application Form KCP-ENT-CON-APL-0001. Kingsnorth Carbon Capture and Storage Project. October 2011. www.decc.gov.uk/en/content/cms/emissions/ccs/demo_prog/feed/feed.aspx accessed September 2012

[70] “Design Basis for CO_2 Recovery Plant”. Report KCP-FWM-CAP-SPC-0001, Section 4.4. Kingsnorth Carbon Capture and Storage Project FEED Study Report. October 2011. http://www.decc.gov.uk/assets/decc/11/ccs/chapter5/5.4-design-basis-for-co2-recovery-plant.pdf accessed September 2012

[71] “PFD and Mass Balance (Flue Gas)”. Scottish Power UKCCS Demonstration FEED Study Report ukccs-kt-s7.10-acc-001-acc-hmb. www.decc.gov.uk/en/content/cms/emissions/ccs/demo_prog/feed/feed.aspx

[72] Ayrshire Power Ltd. *Application for S36 Consent. CCS design concept report* Section 4.1.5 www.ayrshirepower.co.uk/environment

[73] “Kingsnorth Environmental Statement”. Report KCP-ENT-CON-REP-0001, Section 3.2.4.2. Kingsnorth Carbon Capture and Storage Project FEED Study Report. October 2011. http://www.decc.gov.uk/assets/decc/11/ccs/chapter9/9.4-kingsnorth-environmental-statement.pdf accessed September 2012-09-10.10

[74] Wen, H. and Narula, R. *Impacts of Carbon Capture on Power Plant Emissions*. Presentation to 12th Meeting of the International Post Combustion Capture Network. September 29 - October 1, 2009 Regina, Canada

[75] Air Pollution Impacts from Carbon Capture and Storage (CCS) EEA Technical Report No. 14/2011. European Environment Agency, Copenhagen 2011. ISBN 978-92-9213-235-4. http://www.eea.europa.eu/publications/carbon-capture-and-storage accessed September 2012

[76] IEAGHG Evaluation and Analysis of Water Usage of Power Plants with CO_2 Capture IEA Greenhouse Gases R&D Programme. Report 2010/05. March 2011. www.ieaghg.org.

(pre-treatment scrubbers) on post combustion amine scrubbing capture plants has been identified.

- Activated carbon. Some studies[25] 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. Others[31,77,78,79] suggest that spent activated carbon waste could be generated at rates of between 0.03 to 3.2 kg/tonne captured. Adopting a central case estimate of these ranges (0.8 kg/tonne CO_2) indicates that around 200 tonnes per annum of activated carbon waste would be generated by a 300 MWe demonstration scale carbon capture system.

- Corrosion of plant areas exposed to amine compounds are expected and such corrosion may be significant for plant manufactured from normal carbon steels. This could lead to a loss of containment of solvent. This corrosion is expected to be controlled using stainless steels. Acceptable carbon steel corrosion rates with MEA/piperazine mixtures below 0.25mm/year are expected[6] with the use of corrosion inhibiters (such as sodium metavanadate ($NaVO_3$) and copper carbonate ($CuCO_3$)). Corrosion rates appear to be more related to temperature than other factors such as solvent loadings[80].

Overall, it is recognised that more research on the quantity and composition of the waste containing amine compounds from capture plants is required in order to assess the most appropriate disposal/recovery options. However, in the near term relatively significant amounts of wastes are likely to be generated from a 300 MWe demonstration scale carbon capture plant. Although the disposal costs of these wastes will be significant, sufficient UK capacity is likely to exist for its appropriate disposal. SEPA should ensure that appropriate treatment or destruction of any off gases arising from processes regenerating amine contaminated activated carbon is undertaken.

3 Environmental Effects

Emissions to the environment may occur through the cleaned exhaust gas, as degraded solvent and as accidental spills. The environmental concentrations that would be acceptable in terms of protection of human health and the environment of amine solvents and the various amine reaction products requires careful consideration[1,40,81].

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[77] Application for S36 Consent. Ayrshire Power Ltd. Appendix 4.7 to Chapter 4 (Table 2.1) www.ayrshirepower.co.uk/environment accessed September 2012

[78] Rao, A. and Rubin, E. A Technical, Economic and Environmental Assessment of Amine-based CO_2 Capture Technology for Power Plant Greenhouse Gas Control *Environmental Science and Technology* 2002;36(20):4467-4475

[79] Mohammad, R.M. *et al.* CO_2 Capture from Power Plants: Part 1: A Parametric Study of the Technical Performance Based on Monoethanolamine. *International Journal of Greenhouse Gas Control* 2007;1(1):37-46

[80] Kittel, J *et al*. Corrosion in MEA Units for CO_2 Capture: Pilot Plant Studies. *Energy Procedia* 2009;1(1):791-797. doi:10.1016/j.egypro.2009.01.09

[81] CO_2 Capture by Amines is Safe. Carbon Capture Journal, 25 September 2009. http://www.carboncapturejournal.com/displaynews.php?NewsID=448 accessed September 2012

3.1 Emissions to Air

3.1.1 Ambient Levels

Emissions of amine and amine reaction products can be present in the form of gases and aerosols. No monitoring has been undertaken by SEPA or the Environment Agency for background concentrations of nitrosamines in ambient air. Globally, monitoring of nitrosamines in ambient air has been primarily undertaken in industrial areas around potential sources of nitrosamine precursors. The analytical methods used to produce these results however have a low maturity and have not been adopted as national standards and there is no evidence of successful method validation. See section 4 below. The table below summarises the data available.

Compound and citation	Reported Emission Concentration (ng/Nm^3)	Comments
Total N-nitrosamines in air Austria[82]	10 ng/m^3 to 40 ng/m^3	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
NDMA in ambient air [83]	30 to 1000 ng/m^3	A study of fifteen sites in the Los Angeles area in the USA around various industrial sites that manufacture secondary amines
NDMA in ambient air [84]	None detected	Around a chemical disposal site in New Jersey
NDMA in ambient air [85]	400 ng/m^3 and 32,000 ng/m^3	Around various industrial sites that manufacture secondary amines in Baltimore, USA
NDMA in ambient air[92]	8.4 ng/m^3	California, USA
NDMA concentrations in air[86]	30 to 60 ng/m^3 (city centre)	Monitoring of N-nitrosamines undertaken in Moscow. Concentrations of NDMA of "several hundred ng/m^3" were reported in an industrial emissions area and >100 ng/m^3 in a "heavy traffic area"
Ambient air levels of NDMA[87]	10 ng/m^3 (rural) ~ 46 ng/m^3 (urban)	2010 summary of other ambient measurements
9 nitrosamine and 5 nitramine compounds in ambient air[127]	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 0.09 ng/m^3)
Ambient concentrations of amine compounds[127]	ND to 31 ng/m^3	Baseline study of air quality around the Mongstad refinery, Norway prior to operation of the carbon capture pilot plant (methylamine, Dimethylamine and Diethylamaine)
Ambient concentrations in air of piperazine[88]	10-60 ng/m^3	-

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[82] Spiegelhalder B, Preussmann R Nitrosamine Measurements in Ambient Air of an Industrial Area in Austria *International Agency for Research on Cancer (IARC) Scientific Publication* 1987;(84):411-4.

[83] Gordon R. J. *Survey for Airborne Nitrosamines* Prepared by University of California, School of Medicine, for the California Air Resources Board. Contract No. A6-096-30, 1978. http://nepis.epa.gov/EPA/ accessed September 2012

[84] Pellizari E D *Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectrometry*. US Environmental Protection Agency. EPA-600/2-77-100, 1977 (NTIS: PB 269U654)

[85] Pellizzari et al. Estimation of N-nitrosodimethylamine Levels in Ambient Air by Capillary Gas Liquid Chromatography Mass Spectrometry *Analytical Letters* 1976; 9(6):579-594.

[86] Khesina AIa, Krivosheeva LV, Sokol'skaia NN, Koliadich MN Urban Air Pollution by Carcinogenic N-nitrosamines (abstract only). *Vestn Ross Akad Med Nauk* 1996;(3):25-8.

[87] http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+62-75-9

[88] Graedel, T.E *Chemical Compounds in the Atmosphere*. New York: Academic Press, p.301; 1978.

Other UK studies[89] on samples of urban particulate matter collected in Birmingham, identified the presence of 3 nitrosamines: NDEA at concentrations not exceeding 0.62 ng/m^3; N-Butyl-N-nitroso-1-butanamine (usually referred to as N-nitrosodibutylamine or NDBA) at concentrations not exceeding 3.5 ng/m^3; and N-nitrosopiperidine at concentrations not exceeding 22 ng/m^3.

Baseline monitoring of a wide range of amine and nitrosamine/nitramines has been undertaken around the Mongstad refinery in Norway (prior to the operation of the pilot scale carbon capture plant). This study[90] found appreciable existent concentrations of MEA, Methylamine and Dimethylamine (DMA) and to a less extent Diethylamine (DEA) in soil, moss and lake waters around the refinery. For instance MEA was found in concentrations of up to 534 ng/g in moss, 292 ng/g in soil and 650 ng/litre in lake waters. Natural sources such as animal waste and direct anthropogenic emissions (not related to carbon capture systems) were attributed as the sources of the measured concentrations. No nitrosamines and nitramines were detected above the limits of detection in any of the samples taken (LOD water 0.7 to 1.5 ng/litre and LOD for soil/moss 1 to 2 ng/g).

Nitrosamines can also form by reaction between amines and nitrosating agent in the aqueous phase such as in cloud/fog/rain droplets in the air[91,92]. Nitrosamines have been detected[52,92,93] at concentrations of up to 240 ng/litre in water in fogs and at concentrations between 7.5 to 397 ng/litre in water in fogs and clouds. However, the evidence of rapid aqueous-phase photolysis of NDMA discussed in section 2.2 above appears to be slightly at odds with the reported concentrations in fog/cloud water. Some studies[92] conclude that aqueous-phase reactions do not have sufficient yield to account for the measured aqueous-phase NDMA concentrations and that the dominant route for NDMA in fog/cloud water is formation of NDMA in the gas-phase followed by partitioning into the fog/cloud water.

Work undertaken in relation to tobacco smoking[9,94] has indicated that concentrations of some nitrosamines can reach appreciable levels in the indoor environment (for example NDMA has been measured at concentrations of between 7.9 to 45.0 ng/m^3 in enclosed public areas where smoking was permitted). Others[8] have measured total nitrosamines concentrations in industrial rubber processing workplaces of up to 2,001 ng/m^3 (mean value 560 ng/m^3).

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[89] Özel, M. Z., Hamilton, J. F. and Lewis, A. C. New Sensitive and Quantitative Analysis Method for Organic Nitrogen Compounds in Urban Aerosol Samples". *Environmental Science & Technology* 2011;45(4):1497-1505.

[90] Norwegian Institute for Water Research Report SNO 6311-2012. Terrestrial and Aquatic Baseline Study and Monitoring Programme for CO_2 Technology Centre Mongstad. http://www.tcmda.com/Global/Aminrapporter/6311_2012%20Mongstad%20baseline%20terrestrial%20and%20aquatic%20final%20report.pdf accessed December 2012.

[91] Mirvish, S. S. Formation of N-Nitroso Compounds - Chemistry, Kinetics, and Invivo Occurrence. *Toxicology and Applied Pharmacology* 1975;31(3):325-351.

[92] Hutchings, J. W., Ervens, B., Straub, D. and Herckes, P. N-Nitrosodimethylamine Occurrence, Formation and Cycling in Clouds and Fogs. *Environmental Science & Technology* 2010;44(21):8128-8133.

[93] Herckes, P., Leenheer, J. A. and Collett, J. L Comprehensive Characterization of Atmospheric Organic Matter in Fresno, California Fog Water. *Environmental Science & Technology* 2007;41(2):393-399.

[94] Klus, H et al. Tobacco-specific and Volatile N-nitrosamines in Environmental Tobacco Smoke of Offices. *Indoor Environment* 1992;1(1):348-350 http://ibe.sagepub.com (abstract) http://legacy.library.ucsf.edu/tid/xen56e00/pdf accessed September 2012

3.1.2 Environmental Standards for Amines

Alkanolamines such as MEA, DEA and MDEA are the most commonly used amine solvents in carbon capture. Some estimates[24] suggest that a ten-fold increase in the production of alkanolamines may be required when amine scrubbing carbon capture systems are deployed more widely up to 2050 (based on current production estimates). The European Chemicals Agency (ECHA) has now registered MEA under the provisions of REACH[96] and has assigned the substance an EC number of 205-483-3. A number of potential environmental quality limits (in air) for amines have been proposed[6]. For example, some initial Norwegian work[47] proposed a long-term EAL for MEA of 3 µg/m^3. This appears to have been derived from a long-term occupational exposure limit (OEL) of 0.3 mg/m^3 whilst a UK long-term OEL for MEA is 2.5 mg/m^3 [95,96]. A more recent Norwegian review[110] concluded that a long term exposure limit for MEA of 10 µg/m^3 should be adopted. The UK, in addition to having a long-term OEL[95], has a short-term (15 minute average) OEL for MEA of 7.6 mg/m^3. If the UK occupational exposure levels are used to derive EALs for MEA, by applying a factor of 500 (due to carcinogenic effects)[95] EALs for MEA can be proposed at levels of between 5 µg/m^3 (long-term) and 15.2 µg/m^3 (15 minute short term).

A number of potential environmental quality limits (in air) for total amine compounds have been proposed[6,47]. The values quoted vary from 3 to 120 µg/m^3. A short term EAL of 3 µg/m^3 for grouped amines can be derived by applying a safety factor 100 to the strictest occupational exposure limit quoted of 0.3 mg/m^3. Other commonly used amines for carbon capture (e.g. AMP, MDEA and piperazine) do not have UK 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 (0.3 mg/m^3 and 0.1 mg/m^3 respectively) whilst Finland[97] has both a long-term OEL of 0.1 mg/m^3 and a short-term OEL of 0.3 mg/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.

Some studies[24] provide an analysis of the environmental impacts of releases of amine solvents (both from use and production). Life cycle assessment (LCA) methodology was used to estimate the cost of impacts on human toxicity as well as ten other environmental issues (such as abiotic depletion, global warming, ozone layer depletion, freshwater ecotox, etc). Even though there is a net benefit on all environmental impacts, human toxicity seems to be the most likely to be negatively impacted from the use and production of amine solvents.

3.1.3 Environmental Standards for Nitrosamines and Nitramines

Several potential standards have been proposed for (grouped) nitrosamines and nitramines[6,26,47,98] in air. These range from 0.07 ng/m^3 to 10 ng/m^3 for nitrosamines

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[95] EH40/2005 Workplace exposure limits. Health and Safety Executive 2007. www.hse.gov.uk/pubns/priced/eh40.pdf.

[96] The European Chemicals Agency. http://apps.echa.europa.eu/registered/registered-sub.aspx R.8 Version 2. December 2010

[97] Arcos Organics (2010). Material Safety Data Sheet for Piperaizine. Revision Date 24-Nov-2010.

[98] Knudsen, S et al *Summary Report: Amine Emissions to Air During Carbon Capture. Phase 1: CO_2 and Amines Screening Study for Effects to the Environment* Norwegian Institute for Air Research. Report Reference OR 8 2009, N-108068. March 2009. www.CO_2.nilu.no accessed September 2012

and 10 ng/m^3 for nitramines. The latest and most quoted proposed value[99] for total grouped nitrosamines and nitramines is 0.3 ng/m^3. The statistical basis for these proposed standards (e.g. annual average, 8 hour 95%ile average etc) are often not stated although it is assumed that these relate to longer term averages. The UK Health and Safety Executive (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.

The toxic equivalent (TEQ) approach is used for the environmental assessment of dioxins and furans which consist of a broad class of chemicals (about 210) with varying potencies. This approach relies on applying a toxicity factor assigned to each congener relative to the most toxic compound. Similarly, UK guidance[102] 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[100]. In this regard, the Norwegian Institute of Public Health (NIPH) has recommended NDMA as the most toxic nitrosamine based on extensive drinking water toxicity data for the compound[110]. 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 0.3 ng/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[110]. 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[110] estimates a risk of people developing cancer for an excess lifetime inhalation exposure to 0.3 ng/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 UK approach for deriving guidelines for non threshold carcinogens is based on categorical risk level (as opposed to the US EPA quantitative risk assessment). As a result of these differences and other detailed

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[99] The Norwegian Institute of Public Health (NIPH) Press Release. 4 April 2011 Published at http://www.eurekalert.org/pub_releases/2011-04/niop-cch040411.php accessed Sept 2012

[100] Interdepartmental Group on Health Risks from Chemicals *Chemical Mixtures: A Framework for Assessing Risk to Human Health (CR14)* IGHRC (2009). Institute of Environment and Health, Cranfield University, UK.

technical considerations[101] relating to the basis for deriving the stated cancer risk associated with the proposed benchmark environmental concentration, 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 the EU regulation on registration, evaluation, authorisation & restriction of chemicals (REACH) and, as such, is an accepted risk assessment approach. Whilst the advice from the CoC is not a legislative requirement SEPA should have regard to this advice. Consequently, SEPA will consult further with relevant bodies to assess the most appropriate approach for assessing environmental pollutants given the variation in the data used to derive such thresholds. However, in the absence of other data, this value 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.

There are no reliable exposure data on the annual human intakes (intakes assume a body burden) of nitrosamines from various sources. However, exposure to concentrations from external sources is provided below.

Human exposure to nitrosamines from various sources can be compared to exposure to ambient air at the proposed benchmark EAL of 0.3 ng/m^3[110] as follows:

- NDMA has been measured at concentrations 7.9 to 45.0 ng/m^3 in a poorly ventilated indoor air in an office where extensive smoking took place[94].

- NDMA is considered a disinfection byproduct in drinking water and the WHO maximum acceptable level is 100 ng/l[108]. A lifelong exposure to concentration of 4 ng/l NDMA in drinking water is associated with a negligible excess cancer risk level of 1 in 10^{-6}[110].

- DEA is found in cosmetics but reliable concentration data are not given.; and

- From food intake, major sources of exposure are from tobacco smoke and food products. Some studies[104] note that nitrosamines can form in the body “from nitrosable amino compounds (in food, drugs and personal care products) and nitrosating agents (e.g. nitrite)” suggesting that environmental exposure (i.e. air and water) may make little contribution to total burden.

3.1.4 Environmental Standards for Other substances

In addition to nitrosamines and nitramines, other degradation products of amines also include substances such as aldehydes (such as methanal, and ethanal) and amides (mainly methanamide)[6]. Current UK guidance[102] contains the EALs for ethanal (long term 370 µg/m^3; short term 9,200 µg/m^3) and methanal (long term 5 µg/m^3; short term 100 µg/m^3). The EALs are derived from UK Occupational Exposure Limits (OELs) except

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[101] Environment Agency (England and Wales) *Human health toxicological assessment of contaminants in soil.* Science Report Final SC050021/SR1. www.environment-agency.gov.uk/research/planning/64000.aspx]. Accessed September 2012

[102] Scottish Environmental Protection Agency, Environment Agency, Environment and Heritage Service *The Horizontal Guidance Note H1 – Environmental Risk Assessment for Permits*. August 2010 Annex (f). www.sepa.org.uk

the short term EAL for methanal which is derived from the WHO air quality guideline[103]. Current guidance does not contain EALs for any of the identified potential amine solvents or any of the other possible degradation products of such compounds.

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 N deposition and above or close to their critical load, then the additional deposition from carbon capture plant 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[52] recognise the role that amines may play as atmospheric bases and the potential for neutralisation of acids which form in the atmosphere. Other studies[6] note that amines may also cause corrosive damage themselves. However, more research is required into the multiple and complex effects of amines on the environment.

In summary therefore, UK EALs in air have not been established for MEA or the other likely amine solvent species (DEA, piperazine etc). However, UK OELs exist for MEA which can be used to derive a UK EAL in air of between 5 $\mu g/m^3$ (long term) and 15.2 $\mu g/m^3$ (15 minute short term) for this substance. Because there are no UK OELs for other amine compounds likely to be used in carbon capture systems, the OES adopted by some other European countries could be adopted (with caution) to derive relevant EALs. For other substances (such as methanal etc) there are some established UK EALs. For nitrosamines, adopting a reference substance (NDMA) against which total nitrosamine emissions are assessed is an appropriate way to proceed. The currently proposed EAL of 0.3ng/m^3 for total nitrosamines and nitramines 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. Notwithstanding the different UK approach on carcinogenicity assessment, this is an acceptable methodology in the UK for regulatory purposes and is the methodology behind regimes implemented in the UK such as REACH. As such, in the absence of other data, this value 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.

3.2 Environmental Standards for Emissions to Water

A range of amine solvents can be used for CO_2 capture and should be registered for use and their toxicity established as part of the registration process[104]. The most common solvents currently in use are alkanolamines such as MEA, DEA and MDEA. Alkanolamines are generally water soluble and are thus more likely to biodegrade than persist in the environment. Ideally solvents should be chemically and thermally stable during the process but biodegradable when released into water. A recent review of the

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[103] World Health Organisation Regional Office for Europe, Copenhagen Air Quality Guidelines for Europe". WHO Regional Publications, European Series, No. 91 (2000). Second Edition. http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf

[104] Zero Emissions Platform Status Review. *The formation, Control and Environmental Fate of Emissions from Amine –based CO_2 Capture Plants*. Zero Emissions Platform report. January 2012. www.zeroemissionsplatform.eu/library/publication/187-zep-amines-report.html accessed September 2012

chemical stability and biodegradability in the marine environment of new solvents for CO_2 capture[105] 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[106,107]. The results were compared to models used to predict the environmental properties of substances based on their chemical structure. The 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 median biodegradability of naturally occurring compounds was higher than the median of all compounds although it ranged from <1-100%. 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.

In 2008, DEFRA commissioned a study into NDMA concentrations in drinking water following its detection at significant levels in US drinking water. The study[108] found concentrations below the US drinking water standard in samples collected from UK water treatment works. Other information[87] from 2010, summarising available data, suggests that NDMA concentrations in seawater in the US can vary from 35 to 940 ng/litre and may be less than 600 μg/litre in freshwater. Recent Norwegian work[110] has suggested a value of 4ng/litre 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[47]. 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) may persist in the environment due to poor biodegradability, and this may pose a possible risk if accumulated in the environment. Conversely, it has been reported[109] that piperazine is not expected to adsorb to 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.

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[105] Eide-Haugmo *et al*.Chemical Stability and Biodegradability of New Solvents for CO_2 Capture. *Energy Procedia* 2011;4(1) :1631-1636

[106] Eide-Haugmo *et al*. Environmental Impact of Amines. *Energy Procedia* 2009;1(1):1297-1304

[107] Eide-Haugmo *et al.* Marine Biodegradability and Ecotoxicity of Solvent for CO_2- Capture of Natural Gas. *International journal of Greenhouse Gas Control* 2012;9(1):184 - 192

[108] DEFRA NDMA *Concentrations in Drinking water and Factors Affecting its Formation*. DEFRA Report 7348. March 2008. (CSA 7240 / Wt02049 / DWI70/2/210). http://dwi.defra.gov.uk/research/completed-research/reports/DWI70_2_210.pdf accessed September 2012

[109] http://toxnet.nlm.nih.gov

Most general toxicity studies (not related to carbon capture system) have concentrated on NDMA. The US EPA has set a maximum admissible concentration in drinking water of 7 ng/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[110]. 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.

There is limited information on the biodegradability and toxicity of amine breakdown products in the water environment[6,29,111]. 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 1000 mg/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 0.025 µg/litre. 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[12] 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 (e.g. NDMA). 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 WFD 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. This issue should be considered further within SEPA science functions.

Alternatively, 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. As such, Direct Toxicity Assessment (DTA) is likely to be adopted as one approach for assessing and permitting discharges containing such a complex mix of chemicals (following the current SEPA position[112] outlined in WAT-SG-57). The 'Green Screen' toxicity test could also be used to assess the cytotoxicty and genotoxicity of the effluent. The effluent should meet the SEPA standards following dilution and dispersion as outlined relevant SEPA guidance[113].

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[110] Lag M. et al.*Health Effects of Amines and Derivatives Associated with CO_2 Capture*. Norwegian Institute for Public Health (2011) http://www.klif.no/publikasjoner/2806/ta2806.pdf accessed September 2012

[111] Brakstad et al. *Quality Check of Data Sheets for Alternative Solvents. Supporting report to application for environmental permit for the TCM facility.* June 2010. http://www.tcmda.com/Global/Aminrapporter/QUALITY%20CHECK%20OF%20DATA%20SHEETS%20FOR%20ALTERNATIVE%20SOLVENTS.pdf accessed September 2012

[112] SEPA *Toxicity Screening for Discharges*. WAT-SG-57. www.sepa.org.uk/water/water_regulatyion/guidance/pollution_control.aspx.

[113] SEPA *Modelling Discharges to Coastal and Transitional Waters*. WAT-SG-11. www.sepa.org.uk/water/water_regulatyion/guidance/pollution_control.aspx.

3.3 Environmental Standards for Emission to Land

Nitrosamines such as NDMA are expected to have a very high mobility in soils[87]. However, little data is again available on the extent of deposition to land that can be expected from emissions of amines and their reaction products from carbon capture systems. Some studies[90] note that deposition of amine and nitrosamine compounds from carbon capture plant (in terms of eutrophication and acidification) is likely to be less significant than the deposition arising from other nitrogen compounds. The biodegradation of amines in the soil will also contribute to the availability of nitrogen for plant use. The impact of amines on soil quality will also be affected by their rate of degradation. This is likely to vary extensively, depending on the soil type and which amines are present. Some studies report[104] that previous work suggested that the half life of NDMA in soils, due to biodegradation, can range from 4 to 23 days depending on the soil type and that degradation decreases significantly as contamination levels increase. As noted above, a significant proportion of amine compounds are soluble and thus are expected to impact mainly on the water environment. However, in all cases, Operators will need to establish the extent of emissions and the expected environmental impacts.

4 Measurement Techniques and Issues

4.1 Stack Emission Monitoring

There has been limited stack emission monitoring of amine compounds at carbon capture pilot plants and amine compounds are notoriously difficult to sample and analyse. There is also the risk of false detection as well as potential issues related to formation or destruction of nitrosamines during sampling[47]. However, there is some experience of monitoring for such substances in the field of occupational exposure and health. The monitoring techniques which potentially could be used to detect these substances in stack emissions are discussed below.

4.1.1 Continuous Emissions Monitoring - FTIR

FTIR has been used for monitoring amine based substances (exact substances not specified) at a mobile carbon capture facility in Risavika, Norway and Longannet and the Esbjerg pilot plant in Denmark[48,50]. Such instruments are multicomponent analysers that can monitor stack emissions in real time with an approximate 1-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. The lowest detection limit (LDL) for MEA is 0.3ppm compared to the estimated expected emission concentration of ~0.5ppm[26]. The LDL for DEA is 0.15ppm compared to the estimated expected emission concentration of perhaps 0.0005ppm[26]. A FTIR unit can in theory be calibrated to measure nitrosamines however there is no evidence that this has been undertaken. In the UK, FTIR measurements should be undertaken in-line with the established guidance[114] and there are several test laboratories which use FTIR in the UK, with at least one being accredited (MCERTS) for monitoring amines. Ion-mobility spectrometry (IMS) and on-line mass-spectrometry (OLMS) have also been proposed as

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[114] Environment Agency *Technical Guidance Note (Monitoring) M22. Measuring Stack Gas Emissions Using FTIR Instruments*. Environment Agency. Version 2. March 2011. (http://publications.environment-agency.gov.uk/pdf/GEHO0311BTPY-E-E.pdf)

suitable techniques. Such systems have been used for process monitoring and in some research applications for stack monitoring.

4.1.2 Continuous Emissions Monitoring - Tunable Diode Laser and Industrial Mass Spectrometer

Numerous continuous emissions monitoring systems are available and accepted as appropriate for in-situ and extractive ammonia monitoring[115]. The $5MW_e$ (100 tonne per day) pilot carbon capture plant at Ferrybridge Power Station, Yorkshire plan to monitor ammonia as an indicator compound for amine degradation emissions using a Tunable Diode Laser which has a limit of detection of 1ppmv. The site will also continually monitor for MEA using an Industrial Mass Spectrometer with a limit of detection of 0.5ppmv. Nitrosamines will also be measured, however, at this stage the technique and limit of detection are not yet defined.

4.1.3 Periodic Measurement using Tedlar Bags

There is evidence[116] that tedlar bags have been used for sampling amine compounds in stack emissions, which have then been analysed using GC-ToF-MS (Gas chromatography time of flight mass spectrometry). Tedlar bags are commonly used for sampling odour in stack emissions, however they are not conventionally used for other substances as they are prone to leakage and dilution. Analysis using GC-ToF-MS is also not common.

4.1.4 Periodic Measurement using Sorbent Tubes

There is currently no evidence that sorbent tubes have been used for monitoring amine based substances in emissions from carbon capture systems, however a European and a British standard does exist[117] for the sampling of organic compounds, which can be modified for the measurement 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. The commonest methods involve extracting a sample onto various 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 or GC-TEA (Thermal Energy Analyser). However, choosing the right type of absorbent is important and evidence in relevant literature[118] shows that recovery rates can vary from very high to zero, depending on the medium selected. There are several MCERTS-accredited test laboratories for both methods. The analytical methods available for nitrosamines and alkanolamine compounds (with limits of detection) are given in the table below. These methods have not been specifically accredited for flue gas monitoring.

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[115] Environment Agency *Technical Guidance Note (Monitoring) M2. Monitoring of Stack Emissions to Air*. Environment Agency. Version 7. March 2010. (http://publications.environment-agency.gov.uk/PDF/GEHO0710BSXF-E-E.pdf).

[116] Trap,H. *Comparison of Emission Profile Between Conventional Amine and Amino Acid Based Systems.* Report on Meeting at Oslo, Norway in February 2010. IEA Greenhouse Gases R&D Programme. Report 2010/11. June 2010. www.ieaghg.org. accessed September 2012

[117] BS EN 13649:2002 Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Activated carbon and solvent desorption method.

[118] Rounbehler D. P., Reisch J. W., Coombs J. R., Fine D. H. Nitrosamine Air Sampling Sorbents Compared for Quantitative Collection and Artefact Formation. *Analytic Chemistry* 1980;52(2):273–276.

Analytical methods for nitrosamines and aminoethanol compounds in stack emissions

Group	Substance	Analytical Method	Limit of Detection (LOD)
Nitrosamines	NDMA, NDEA, N-Nitroso-N-propyl-1-propanamine (or N,N-Dipropylnitrous amide -NDPA), NDBA), NPIP, 1-nitrosopyrrolidine (NPYR), and NMOR	NIOSH 2522	0.05µg/m3
Nitrosamines Mixture I	NDMA, NDEA, NDPA, NDBA, NPIP, NPYR and NMOR	OSHA 27	0.13µg/m3 (NDMA) 0.13µg/m3 (NDEA) 0.13µg/m3 (NDPA) 0.12µg/m3 (NDBA) 0.12µg/m3 (NPIP) 0.13µg/m3 (NPYR) 0.20µg/m3 (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	0.13µg/m3 (NMEA) 0.15µg/m3 (NDiPA) 0.13µg/m3 (NMBA) 0.15µg/m3 (NEBA) 0.13µg/m3 (NPBA) 0.20µg/m3 (NDAmA)
Aminoethanol compounds	2-dibutylaminoethanol 2-diethylaminoethanol	NIOSH 2007	200µg/m³

4.1.5 Other Measurement Techniques

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[47]. 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[47]. 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 100ng/ml and liquid chromatography mass spectrometry triple quad (LC-MS-QQQ) which has a LOD of 10ng/ml[1].

Other studies[119,120] for the determination of a number of nitrosamines in water have

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[119] Llop, A., Borrull, F. and Pocurull, E. Fully Automated Determination of N-nitrosamines in Environmental Waters by Headspace Solid-phase Microextraction Followed by GC-MS-MS. *Journal of Separation Science* 2010;33(23):3692-3700.

[120] Munch, J. W. and Bassett, M. V. Method Development for the Analysis of N-nitrosodimethylamine and Other N-Nitrosamines in Drinking Water at Low Nanogram/liter

used fully automated methods based on a headspace solid-phase microextraction onto PDMS / PEG fibres or coconut charcoal with a dichloromethane solute followed by GC-MS-MS using chemical ionization or by gas chromatography-chemical ionization tandem mass spectrometry using large-volume injection. Similar studies[121] report a solid-phase extraction method using Ambersorb 572 and LiChrolut EN with detection levels for all N-nitrosamines down to 0.4 to 1.6 ng/litre.

4.2 Ambient Air Monitoring

US Environment Protection Agency (USEPA) method T0-7 for the determination of NDMA in ambient air involves drawing ambient air through a Thermosorb/N sorbent tube followed by analysis using GCMS and has a reported LOD of 1 µg/m^3. Institut National de Reserche et de Securite (INRS) method 031 also has a reported LOD of 1 µg/m^3. The occupational health methods shown in the table in Section 4.1.4 can be adapted for ambient air monitoring of nitrosamines and have a LOD down to 0.05 µg/m^3. Monitoring under pseudo-natural conditions has been undertaken of the atmospheric gas phase photo-oxidation of MEA in Spain[122]. 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 0.033 µg/m^3. These LODs are greater than the benchmark EALs for nitrosamines and nitramines. The limit of detection for amines was not stated.

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 [82,123]. The limit of detection for nitrosamines by chemiluminescence detector appears to be the lowest at approximately 0.005µg/m^3 which is above the benchmark EAL for grouped nitrosamines[82]. Other studies[92] have used GC-Chemical Ionisation-Mass Spectrometry for detection of NDMA in fog/cloud water samples followed by preparative and pre-concentration steps that appear to have an LOD down to 7 ng/litre. Others[124] describe a method for determination of six volatile nitrosamines in extractions of meat products using two-dimensional GCxGC with a N-specific nitrogen chemiluminescence detector. The LODs reported are not directly applicable to ambient atmospheric concentration analysis.

For workplace exposure measurements of nitrosamines the Health and Safety Laboratory (HSL) have traditionally sampled onto Thermosorb/N cartridges and analysed using Gas

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Concentrations Using Solid-phase Extraction and Gas Chromatography with Chemical Ionization Tandem Mass Spectrometry. *Journal of AOAC International* 2006;89(2):486-497

[121] Charrois, J. W. A., Arend, M. W., Froese, K. L. and Hrudey, S. E. Detecting N-nitrosamines in Drinking Water at Nanogram per liter Levels Using Ammonia Positive Chemical Ionization. *Environmental Science & Technology* 2004;38(18):4835-4841.

[122] Nielson CJ et al. *Atmospheric Degradation of Amines. Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA).* 2010 CLIMIT project no. 193438. http://ada.nilu.**no**/ accessed September 2012

[123] Marano R, et al, Determination of Trace Levels of Nitrosamines in Air by Gas Chromatography / Low-Resolution Mass Spectrometry. *Analytic Chemistry* 1982;54(12): 1947-1951.

[124] Özel, M. Z., Gogus, F., Yagci, S., Hamilton, J. F. and Lewis, A. C. Determination of Volatile Nitrosamines in Various Meat Products Using Comprehensive Gas Chromatography-nitrogen Chemiluminescence Detection. *Food and Chemical Toxicology* 2010;48(12):3268-3273.

Chromatography Thermal Energy Analysis (GC-TEA)[125]. This is essentially the same method as NIOSH 2522 and OSHA 38 detailed in the Table above. The Thermal Energy Analyser is very specific to nitrosamines and for occupational samples of 4 - 5 hours duration the HSL[125] is able to reach detection limits of around 0.1 µg/m³. The only 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[8]. Unlike the Thermal Energy Analyser, the mass spectrometry detector is not specific to nitrosamines and so the presence of other VOCs can cause significant interferences.

The methods adapted from US occupational-safety methods (USEPA method T0-7 and INRS method 031) do not usually have 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 effect 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 ppt levels[126].

Some studies[127] report ambient nitrosamine measurements using an in-house validated method and the principles found in OSHA method 27. This method used a multi-line sampling device to collect large volume samples which resulted in detection limits as low as 0.01 ng/m^3. Analysis of the samples was divided into aliquots with analysis by liquid chromatography (HPLC) combined with high resolution mass spectrometry and the other by high sensitivity and selectivity gas chromatography combined with the Thermal Energy Analyzer (TEA).

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

Consequently accurate measurement of these substances in the environment at the low levels identified (in order to assess the potential impacts of carbon capture systems) appears unrealistic at the present time. Given this issue, amine reaction products could be characterised by stack emission monitoring and regular analysis of a variety of contaminants in liquid solvent and waste water samples.

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[125] Ian Pengelly (Ian.Pengelly@hsl.gov.uk) *Measurement techniques for nitrosamines* Email to: Jackson B.(ben.jackson@sepa.org.uk) 14 June 2011

[126] Sekar Fatma Aygün, Ahmet Uyanık and Bekir Batı. Adsorption of N-Nitrosodiethylamine and N-Nitrosodimethylamine on Activated Carbon: A Pre-Concentration Procedure for Gas Chromatographic Analysis. *Microchimica Acta* 2004;146(3-4):279-283.

[127] Tønnesen, D et al. *Baseline Study for Air and Precipitation Quality for CO_2 Technology Centre Mongstad*. Norwegian Institute for Air research Report OR 73/2011. http://www.tcmda.com/Global/Aminrapporter/TCM%20NILU%20Baseline-final.pdf accessed September 2012