ACT 3 – Accelerating CCS Technologies

Sustainable OPEration of post-combustion Capture plants (SCOPE)

Assessment of the Impact of Various Amines on Micro- and Macro-organisms and their Potential Biodegradability in the Ecosystem

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ABBREVIATIONS

Abbreviation	Definition
AMP	2-Amino-2-methylpropanol
CO_2	Carbon dioxide
CCPM	Carbon dioxide Capture Plant Mongstad
CCP	Carbon Capture Plant
CCS	Carbon Capture and Storage
CHO	Chinese Hamster Ovary
CL	Critical Load
CL-20	Hexanitrohexaazaisowurtzitane
DIPNA	N,N-diisopropylethyl-N-ethylamine
DEA	Diethanolamine
DEEA	Diethylethanolamine
DGA	Di-glycolamine
DIPA	Di-isopropanolamine
DMNA	dimethylnitramine
DNA	Deoxy-ribonucleic acid
EA	Ethylamine
EC50	Effective Concentration causing 50 % inhibition of growth for an organism population
EIA	Environmental Impact Assessment
EPI Suite^{TM}	Estimation Program Interface Suite Trademark
GHGs	Green House Gases
GC-MS	Gas Chromatography-Mass Spectroscopy
IC50	Half maximal inhibitory concentration

HMX	Cyclotetramethylene Tetranitramine
HSE	Health, Safety and Environment
InhR	Inhalation Rate
IR	Ingestion Rate
IARC	International Agency for Research on Cancer
LC50	Median Lethal Concentration of a toxic substance, causing 50 % lethality for a tested organism population
LD50	Median Lethal Dose of a toxic substance causing 50 % lethality for animal population, after specified test duration
LC-MS	Liquid Chromatography - Mass Spectroscopy
LOEC	Lowest Observed Effect Concentration
MAPA	3-amino-1-methylaminopropane
MBBR	Moving bed biofilm reactor
MDEA	Methyldiethanolamine
MEA	Monoethylamine
MEA-NO_2	2- Nitroaminoethanol
MMA-nitramine	Monomethyl-nitramine
NAs	Nitramines
NDMA	dimethyl nitramine
NILU	Norwegian institute of air research
NDELA	N-nitrosodiethanolamine
NH_3	Ammonia
NSAs	Nitrosamines
NIPH	Norwegian Institute of Public Health
NMEA	N-Nitrosomethylethylamine

NOx	Nitrogen Oxides
NOEC	No-observed effect concentration
NPz	Nitrosopiperazine
NIVA	Norwegian Institute for Water Research
PCCC	Post Combustion CO_2 Capture
PEC	Predicted Environmental Concentration
PIPA	Py-Im- polyamide
NOM	Natural Organic Matter
PZ	Piperazine
$PZ-NO_2$	1-Nitropiperazine
QSAR	Quantitative Structure-Activity Relationship
RDX	Royal Demolition eXplosive, also known as cyclonite or hexogen (1,3,5-trinitro-1,3,5-triazine)
REACH	European Regulation for Registration, Evaluation, Authorization and restriction of Chemicals
SD	standard deviations
SO_2	Sulphur di-oxide
TD50	The median Toxic Dose of a drug or toxin is the dose at which toxicity occurs in 50% of cases
TCM	Technology Centre Mongstad
USEPA	United States Environmental Protection Agency

Executive Summary

An amine-based capture facility can contribute significantly to the environmental protection and climate action by reducing air pollution and associated carbon emissions. Pre-treatment of the flue gas not only removes 85 to 90% of the CO_2 from an amine-based capture plant, but also reduces by a considerable quantity other harmful flue gases component, including particulate matter, NOx, and SO_2. However, the use of amines for absorbing the carbon dioxide has been reported to raise health concerns although these are not fully understood. The available research indicates that various amines and their allied degradation products may have detrimental impacts on human health including irritation, sensitisation, carcinogenicity, and genotoxicity. These consequences indicated are, however, in the worst-case scenarios, and the potential repercussions depend largely upon the actual amount of amine emissions as well as the types of amines employed in the CO_2 capture. The amines once emitted in the air and deposited in soil, water, or vegetation may have some short- or long-term detrimental impacts on the ecosystem. Some of the amines may be readily degradable, while others are more persistent in the environment.

While the toxicity of the amines has been studied more in the context of human health hazards, there is lack of comprehensive and systematic studies on impacts of the amines and their derivatives on various types of living organisms and ecosystems. The available literature has been reviewed and is presented here. The reported impacts of amines/degradation products, especially nitramine and nitrosamine, on freshwater and marine water fish, aquatic invertebrates, algae, cyanobacteria, bacteria, and terrestrial plants are discussed in terms of acute and chronic toxicity effects. A few studies on biodegradation and biotransformation of amines under different conditions have indicated that certain environmental factors play a significant role, while others are not so important. It is suggested that there is a need to carry out systematic studies on the important amines and their degradation products, which are emitted from post-combustion capture plants under different conditions. The aim would be to understand the potential for toxic impacts and biotransformation in different regions, where ecological and environmental conditions may vary substantially.

Keywords: Amines, CO_2 capture, acute toxicity, chronic toxicity, ecotoxicology, nitramine, nitrosamine, biodegradability

1 Introduction and background

Climate change, a global effect caused by CO_2 emissions is a serious threat to the environment. Melting of the glaciers and warming of the oceans and increasing natural disasters throughout the world are considered key indicators of climate change. Such impacts may only be abridged by mitigating the global CO_2 emissions. The resulting demand for CO_2 capture and abatement has accelerated the research for CO_2 capture technologies. Carbon Capture and Storage (CCS) is an emerging technology with the potential to lessen greenhouse gases emissions, while facilitating controlled and sustainable use of fossil fuels. It is a process wherein CO_2 generated from the combustion of fossil fuels is separated, captured, transported, compressed, and lastly stored securely over a long period of time.

The CO_2 capture technologies are generally categorised as post-combustion, pre-combustion, oxyfuel CO_2 capture and calcium looping technologies. The post-combustion capture technique, which is the most mature of these technologies, comprises the separation of CO_2 from flue gas components through absorption in an aqueous amine solution. Use of amines for absorption in post-combustion CO_2 capture process may result in emissions of amines through the CO_2 stripped exhaust gas or accidental spills, or as degraded solvent, which may have some environmental impacts that need to be assessed.

The following paragraphs briefly discuss the post-combustion amine-based CCS technology and introduce the background with regards to amine emissions from such facilities and their characteristics as well as their fate, stability and general toxicity.

1.1 Post combustion amine-based CCS technology

Post-combustion CO_2 capture (PCCC) is a method for removing carbon dioxide (CO_2) from flue gas, which is the gas that is emitted from power plants and other industrial facilities that burn fossil fuels. The process involves exposing the flue gas to an aqueous solution of amines, which are organic compounds that contain nitrogen. The CO_2 in the flue gas reacts with the amines to form a soluble carbonate salt. The reaction is reversible, which means that the CO_2 can be recovered by boiling the solution and carbonate salt together in a different column, known as a stripping column. PCCC is an important technology for reducing greenhouse gas emissions, as it allows for the capture and storage of CO_2 that would otherwise be released into atmosphere. It is often used in conjunction with other technologies, such as carbon capture and storage (CCS), to reduce the overall carbon footprint of a facility. However, the release of amines in the environment can cause adverse effects not only on the life of humans but also on the life of plants and other organisms including algae and microbes in the regions where such facilities may operate (Gjernes et al., 2013).

1.2 Emissions monitoring in post-combustion capture plants

Emissions to air, in an amine-based carbon dioxide capture plant, are determined by the type of amine-solvent utilised along with operative settings of power plants. In order to recognise and measure nitramines and nitrosamines in emissions and process liquids, sampling and analytical methods are being established on quantifying amine and amine degradation products. This comprises the development of a sampling train that includes iso-kinetic sampling, sample management, conservation, storing and transportation, as well as the use of the analytical techniques (e.g. total nitrosamine analysis, chemiluminescence-based nitrosamine screening method, quantitative techniques for the investigation of specific and group of nitrosamines based on gas chromatography, and the study of nitramines based on liquid chromatography - mass spectrometry LC-MS). Analytical techniques for a wider range of amine compounds are anticipated to advance, as more specialised ones are discovered or manufactured for use in post-combustion capture facilities. The total amines analysis is useful for measuring unidentified amine compounds in emissions and in solvent samples collected.

1.2.1 Emission of amines from Post combustion CCS Plants

Recently, some new technologies have also been developed in which the solvents used for CO_2 capture are frequently a mixture of several different amines. This includes MDEA-piperazine blends, MEA-piperazine blends, triethylene tetramine and blends of N-methyldiethanolamine. For numerous new amine-based technologies in development, the amine mixture is not known because the solvent composition is considered intellectual property and, thus, company secret for respective manufacturers.

The amines used for CO_2 capture are recycled, but a minor portion of the amines are either degraded or emitted into the air. Through the atmospheric formation pathway, the amines and their transformation products are directly introduced to the nearby environment. This happens due to inevitable release of volatile amines along with flue gas, as is the case in CO_2 capture plants.

1.2.2 Nature and type of amines

Generally, amines are classified as primary, secondary, or tertiary amines, provisional on whether one, two or three of the hydrogen atoms in ammonia (NH_3) have been substituted via organic groups.

Amines can be manufactured artificially in factories for use in different industrial process or they can be found naturally in the environment. Alkaloids are a type of naturally occurring amine that are found in certain nature (plants) and have a variety of physiological effects. Some examples of alkaloids include caffeine, nicotine and morphine. Catecholamine neurotransmitters, such as dopamine, epinephrine, and norepinephrine, are also examples of amines that play important roles in human body. These neurotransmitters are involved in the regulation of various physiological processes, including mood and movement. Histamine is another example of a naturally occurring amine that is found in most animal tissues. It functions as a local chemical mediator and plays a role in immune system function, as well as in the regulation of cardiovascular and gastrointestinal functions.

Aniline and a number of other amines are important industrial chemicals which used in the manufacturing of fibres, rubbers, dyes and variety of products.

Monoethanolamine (MEA), methyldiethanolamine (MDEA), 2-Amino-2- methylpropanol (AMP), Piperazine (PIPA), diglycolamine (DGA), diethanolamine (DEA), and di-isopropanolamine (DIPA) are all examples of amines that are commonly used in carbon capture technologies (Figure 1). The specific properties of each amine, such as its chemical stability, CO_2 absorption capacity, and ability to regenerate can affect its suitability for use in different CO_2 capture applications. Monoethanolamine (MEA) is a commonly used amine in CO_2 absorption due to its high CO_2 cyclical capacity, high reactivity and low cost. However, amines like MEA can react and oxidise in the presence of sunlight to form by-products such as nitrosamines, nitramines, aldehydes and amides. These compounds are known to be toxic and carcinogenic to humans at very low concentrations, and exposure to them can have harmful effects on human health (Rusin & Stolecka, 2016).

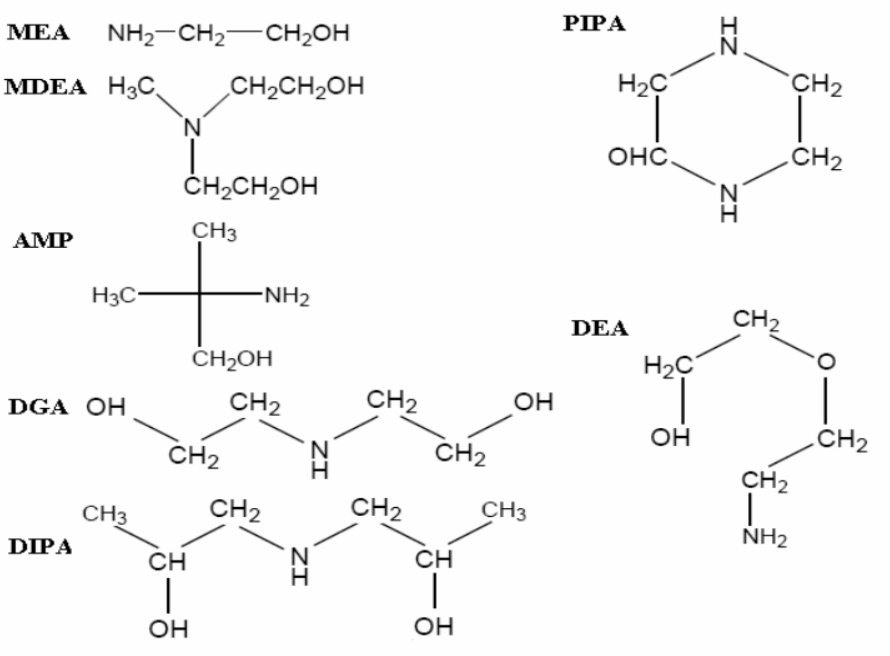

Figure 1. The chemical structures of the commonly used amines in CO_2 capture facilities.

1.2.3 Stability and decomposability of amines

Independent of the type of amine(s) used, degradation processes inside the capture plant may produce small and fugitive amines (Norling et al., 2022). Because of their high-water solubility and low soil sorption potential, nitrosamines (NAs) and nitramines (NSAs) are expected to be transported with local water flow regimes (e.g., overland flow, inter-land flow, rivers, etc) after deposition on the ground (Norling et al., 2022; Gundersen et al., 2017a; Gunnison et al., 2000). Nearby natural drinking water sources, such as lakes, rivers and groundwater, are thought to be at risk of receiving degradation products of amine emissions. When amines are released into the environment, they can undergo chemical reactions and degradation, resulting in the formation of various metabolites and other compounds. Some of these metabolites may be hazardous and potentially toxic and could pose a risk to human health (cancer), if ingested.

The degradation products of amines, including nitramines, nitrosamines, aldehydes, and amides can be harmful to human health, animals, plants and ecosystems (Figure 2, Table 1.1). For example, nitrosamines are a group of compounds that have been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC).

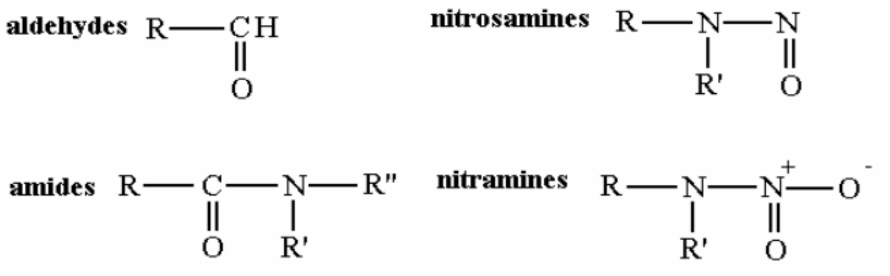

Figure 2. The chemical structures of degradation products of amines.

Table 1.1 Different types of stable primary and secondary amine compounds.

	COMPOUNDS	CAS No.
Amines		
	MEA (Monoethanolamine)	141-43-5
	MDEA (Methyldiethanolamine)	105-59-9
	AMP (2-amino-2-methyl-1-propanol)	124-68-5
	PIPA	110-85-0
	Piperidine	
	Pyrrolidine	
Amides		
	Acetamide	60-35-5
	Formamide	75-12-7
Nitrosamines	N-nitrosodi-n-propylamine	
	N-nitrosopyrrolidine	
	N-nitrosodimethylamine (NDMA)	62-75-9
	N-nitrosodiethanolamine (NDELA)	1116-54-7
	N-nitrosopiperazine (NPz)	5632-47-3
Nitramines		
	Dimethylnitramine (DMNA)	4164-28-7
	2-Nitroaminoethanol (MEA-NO2)	74386-82-6
	1-Nitropiperazine (PZ-NO2)	42499-41-2
	RDX	121-82-4
	HMX	2691-41-0

Amine-rich wastewater streams generated from the amine-based carbon capture plants can be considered as hazardous wastes due to their potential harmful effects on the environment and human health (Lepaumier et al., 2011; Nurrokhmah et al., 2013; Dong et al., 2019). These wastewater streams are often generated as a result of the degradation of amine-based absorbents used in the carbon capture process, and they may contain a variety of chemicals and contaminants, including carbamate polymers, nitramines, nitrosamines, heat-stable salts (HSS), ammonia and water (Nurrokhmah et al., 2013). These substances have been shown to have negative impacts on microbial, marine, plant and human health, and they may pose a risk to the environment if they are not properly managed and treated.

1.2.4 Atmospheric formation, degradation and dispersion of amines

There is limited experimental information on the atmospheric transformation of amines that are important for CO_2 capture plants. There is also minimal information available on the further degradation and lifetime of the generated hazardous components. The Atmospheric Degradation of Amine programme at the University of Oslo was launched in 2009 and included experimental research at the EUPHORE facility in Valencia, Spain. In the programme, which ran from 2009 to 2011, the potential for the following amines—like MEA, methyl, dimethyl, ethyl, diethyl, trimethyl, triethyl—to create nitrosamines and nitramines was studied. The programme also included the photolysis reaction of nitrosamines and lifespan of nitramines in atmosphere which are important factors to consider in the development of CO_2 capture technologies. In the context of CO_2 capture, QSAR models can be used to identify amines that are likely to be effective at capturing CO_2 from the atmosphere or industrial emissions. QSAR models can predict amine's ability to react with CO_2 and their stability under different conditions, which can help researchers to identify further study and development.

Other research exhibited that while primary amines do not produce nitrosamines, they could do so, in a process or in the environment. Among primary, secondary, and tertiary amines, it was found that the ability to create nitrosamines and nitramines grows in the order of primary amines < secondary amines < tertiary amines. The environmental permit for Technology Centre Mongstad (TCM) and technical qualification amine programme of CCM’s likely involve the study of the atmospheric transformation, destruction, and dispersion of these substances. This may include testing to determine how these substances react with other compounds in the atmosphere. For air and drinking water, these values must not be higher than 0.3 ng m^{-3} and 4 ng l^{-1}, respectively.

This is based on the nitrosamine NDMA's toxicity, for what the Norwegian Institute of Public Health (NIPH) advises the permissible limit. Modelling atmospheric chemistry, dispersion, deposition and degradation can help researchers understand how chemical compounds behave in environment and predict their potential impacts on ecosystem. The NILU (Norwegian Institute for Air Research) have developed a range of methods and tools for analysing these chemical compounds in air and drinking water.

1.2.5 Photodegradation and hydrolysis of some amines in the freshwater environment

A study by Sorensen et al. (2015) examined the hydrolytic and photolytic degradation of nine nitramines and nitrosamines recognised as probable degradation products of the solvents 2-monoethanolamine and piperazine. According to the study, NAs and NSAs are usually resistant to hydrolysis, whilst nitroso-piperazine and piperazine nitramine both experience degradation up to 50% at 50 °C temperature (pH 7). The study also found that although NAs are photolytically stable, NSAs are degraded quickly in aqueous solution when illuminated under sunlight. The study also found that NDELA (n-nitrosodiethylamine) may be persistent at environmentally relevant concentrations due to competition with natural organic matter (NOM) for photons. Photolysis is an specifically vital pathway for the degradation of nitrosamines as noted by Lee et al. (2005), whereas microbial degradation seems to be an imperative pathway for many nitramines, as reported by Douglas et al. (2009), Poste et al. (2014) and Schaefer et al. (2007). Primary amines, including methylamine, can be taken up by certain aquatic organisms, such as phytoplankton (Balch, 1985), which are tiny plants. Methylamine is also used as osmolytic solute in marine cartilaginous fishes which are a group of fish that includes sharks, rays etc (Hazon et al., 2003). Moreover, monoethanolamine, a common solvent used in CO_2 capture systems, can be used by bacteria and few phytoplankton species (Choi et al., 2012; Garsin, 2010), and has been shown to enhance cell growth in some cases; for example, the green alga named Scenedesmus sp. display at MEA concentrations up to 300 mg l^{-1}. The information is part of a larger investigation on how nitrosamines and nitramines behave in both terrestrial and aquatic settings.

1.2.6 Deposition, exposure and toxicity of amines

The majority of amines and amino acids utilised in carbon capture are very water soluble. The equivalent nitrosamines and nitramines are anticipated to behave similarly. Thus, it is expected that they will easily dissolve in rainwater and fog droplets before being precipitated and ending up in lakes, rivers, and other surface water bodies. Nitramines and nitrosamines in the environment were not detectable in the baseline studies carried out by the NIVA and NILU (Aarrestad et al., 2009). However, amines were found in the samples of soil, air moss and river water as a result of surveillance activities (Gundersen et al., 2017a; Gunnison et al., 2000).

According to surveys of the literature, 90 percent of the 300 nitrosamines that have been studied have either caused cancer in lab animals or bioassays. The confirmation of a genotoxic mechanism suggests a non-threshold method to risk assessment. IARC has reviewed the data on 23 nitrosamines that could occur in course of carbon capture and rated two of them as likely to be cancerous to human beings and seven of them as conceivably carcinogenic to human life (Nielsen et al., 2012; Angove et al., 2012; Lee et al., 1978). Substantially less information is available in literature on nitramines, although they are thought to be carcinogenic. None, however, are IARC-classified. Studies on the carcinogenicity of methyl nitramine and dimethyl nitramine in animals have been conducted (Buist et al., 2015). These findings suggest that nitroso dimethylamine, the equivalent nitrosamine, should be regarded as at least six times more toxic than dimethyl nitramine (NDMA).

2 Ecotoxicological effects of amines

Ecotoxicological studies are essential for regulatory agencies in assessing possible toxic effects of various chemicals on living organisms through direct exposure or accidental contact. Although the toxic effect of most of the compounds present in amine-based carbon capture plants are known, comprehensive assessment of their impact on ecosystem function, including surface and groundwater resources, have not been carried out methodically.

Nitrosamines (NSAs) and Nitramines (NAs) formed due to the reactions of flue gas nitrogen oxides (NOx) with the amines are apparently carcinogenic in nature and present likely risk for tainting surrounding air and drinking water resources making it necessary to set regulatory emission limits for them (Wagner et al., 2014). However, information on the toxicity of the nitramines is still very inadequate, particularly on plants and animals in various ecosystems (Norling et al., 2022). More comprehensive information is required on ecotoxicological impacts of NAs and NSAs on microbes (algae, cyanobacteria, bacteria) and eukaryotic organisms in terrestrial and aquatic habitats along with fate/biodegradation of NAs and NSAs and their derivatives. The information available in literature on effects of amines on living organisms is briefly reviewed in this section.

2.1 Acute and chronic toxicity of amines

Despite the recycling of the amine solvent throughout the capture process, degradation products, including aliphatic nitramines, whose environmental effects are not well known, are generated and discharged into the environment. The effects of these amines are likely to be different depending on whether exposure is acute or chronic in nature. The use of acute and chronic tests is a common approach for assessing the potential risks of chemicals to aquatic organisms. These tests are used by regulators and scientists to understand the probable impacts of chemicals on aquatic life and to inform decisions about the use and management of these chemicals. Acute toxicity tests measure the effects of a chemical on an organism following a short-term exposure to relatively high concentrations of a chemical. Chronic tests, on the other hand, measure the effects of a chemical on an organism following a long-term exposure to lower and more environmentally realistic concentrations of the chemical. These methods can also improve the trustworthiness of the environmental risk assessment (EIA) for an explicit chemical.

Toxicity tests, toxicological endpoints are generally determined as assessment- based or effect-based. In acute toxicity tests, endpoints are median lethal concentrations (LC50) or median effective concentration (EC50), an estimation of the acute no-observed effect concentration (NOEC), and behavioural observations. LC50 is the lethal concentration of the compound that kills 50% of the test population, whereas EC50 indicates immobilisation or an endpoint other than death. Studies conducted on acute and chronic impacts of various amines on different organisms have been reviewed here. By integrating, acute toxicity and chronic toxicity, a good quality interpretation of the potential toxicity of a vast range of chemicals can be attained. The NOEC is highest concentration at which there is no remarkable influence in comparison to control.

In chronic toxicity tests, partial life cycle of the test organism is considered, wherein the endpoints generally considered are percent egg hatchability, survival and growth. Aquatic toxicity tests for different countries vary and USEPA recommends that eight (8) dissimilar families must be tested for marine and freshwater species for the development of water quality criteria (Ecology Center US, 2022). This clearly shows that inadequacy of toxicological data of amines for aquatic organisms is a major constraint on development of regulatory water quality criteria.

2.2 Toxic effects on marine organisms

The initial environmental risk assessment (EIA) for the marine aquatic system was carried out in multi-trophic bioassays by Coutris et al. (2015) to investigate the acute and chronic toxicity of two nitramines, dimethylnitramine and ethanolnitramine, which were found to be significant degradation products of amine-based carbon capture emissions. Additionally, a comet assay was modified to include cells from experimentally treated fish in order to study the in-vivo genotoxicity of nitramines (NAs). Both nitramines showed minimal toxicity on using whole organism bioassays. Oysters showed more sensitive reaction to both substances, and in all bioassays, dimethylnitramine consistently exhibited higher toxicity than ethanol nitramine. Dimethylnitramine and ethanolnitramine had no toxic effects at concentrations of 0.08 and 0.18 mg l^{-1}, respectively. The findings of whole organism bioassays and the genotoxicity testing were incongruent; ethanolnitramine was found to be three orders of magnitude more genotoxic than dimethylnitramine. DNA damage was caused by a very low concentration of Ethanolnitramine (1 mg l^{-1}) whereas a much higher concentration of dimethylnitramine (100 mg l^{-1}) caused DNA damage. The mechanisms of genotoxicity for the two compounds were also shown to be different, with DNA strand breaks accounting for over 90% of the genotoxicity of ethanolnitramine and alkali-labile sites causing above 90% of the genotoxicity of dimethylnitramine. Red blood cells from fish subjected to >3 mg l^{-1} ethanolnitramine contained almost no DNA indicating acute genotoxicity.

2.3 Toxic effects on freshwater fish

Acute toxicity: A broad range of acute toxicity in freshwater fish were recorded to the four selected amines as shown in Table 2.1. Maximum sensitivity to MEA was shown by Zebra fish (*Danio rerio*) with the lowest 96h LC50 values (60.3 mg l^{-1}), whereas in adult rainbow trout (Salmo gairdneri) the LC50 value was 167 mg l^{-1}, and it was 375 mg l^{-1} in Western Mosquito fish. In case of AMP, only one study is available indicating toxicity at a concentration greater than 100 mg l^{-1}. Between all selected amines the lowest LC50 values (52 mg l^{-1}) were recorded for carp (Cyprinidae) on exposure to PIPA (Loeb & Kelly, 1963).

Following results of toxicity test on freshwater fish, the LC50 values for the adult carp and western mosquito fish exposed to the amides, formamides and acetamides were very high, ranging from 10,000 mg l^{-1} to 26,300 mg l^{-1} (Juhnke & Luedemann, 1978; Wallen et al., 1957). Blue gill (Lepomis macrochirus) was found to be very sensitive and on exposure to N-nitroso-diphenylamine, it showed 24h LC50 of 5.85 mg l^{-1} and even lower LC50 value of 3.6 mg l^{-1} on exposure to RDX (US EPA, 1978).
Based on the available studies, the acute toxicity of the amines and their degradation products for freshwater fish may be ordered as nitramines > nitrosamines > amines > amides (Table 2.1).

Table 2.1 Toxicity of various amines (indicated by LC50 values) to freshwater fish.

Compound	Fish name	EC/LC50 (mg l^{-1})					Reference
		NOEC	**24h**	**48h**	**72h**	**96h**	
Amines							
MEA	Goldfish (*Carassius auratus*)		190			170	Birdie et al., 1979
	Western mosquito fish (*Gambusia affinis*)		375	360	350	338	Verschueren, 2001
	Rainbow Trout (*Salmo gairdneri*)		175	150		167	Mayer et al., 1986
	Zebra fish (*Danio rerio*)	20				60.3	Groth et al. 1993
PIPA	Carp (Family Cyprinidae)				52-159		Loeb & Kelly, 1963
	Guppy (*Poecilia reticulata*)	100				>100	Web Link 1
Amides							
Acetamide	Western mosquito fish (*Gambusia affinis*)		26,300	26,300		13,300	Wallen et al. 1957
	Carp (Family Cyprinidae)			10,000			Juhnke & Luedemann, 1978
Formamide	Fathead minnow (*Pimephales promelas*)					5,000-10,000	EPA, 2004. doc: 201-15159A
Nitrosamines							
NDPA	Blue gill (*Lepomis macrochirus*)		5.85				US EPA, 1978
	Mummichog (*Fundulus heteroclitus*)		3,300				Ferraro et al., 1977
NDMA	Rainbow Trout (*Salmo gairdneri*)					1,770	Verschueren, 1996
	Fathead minnow					940	Draper & Brewer, 1979

	(Pimephales promelas)						
NDEA	Fathead minnow (Pimephales promelas)					775	Draper & Brewer, 1979
Nitramines							
RDX	Blue gill (Lepomis macrochirus)					3.6	Bentley et al., 1977
	Zebrafish (Danio rerio)		13-15			23-26	Mukhi et al., 2005
HMX	Fathead minnow (Pimephales promelas)					15-32	Bentley et al., 1977

Web link 1. http://www.ethyleneamines.com/NR/rdonlyres/0F711045-D7C1-4979-8286-032FF5C01636/0/PIP_Anh.pdf

Chronic Toxicity: In the case of amines, the chronic toxicity data was obtainable only for MDEA and PIPA. Bieniarz et al. (1996) observed that there was a decrease in egg hatching when exposed to 0.5 mg l^{-1} or higher concentration of MDEA. There was no influence on the activity of fish, named as Kuhlia sandvicensis, up to concentration 20 mg l^{-1}, when exposed to PIPA.

It is well known that exposure to certain chemicals can have negative effects on the health of aquatic organisms. A study on Oncorhynchus mykiss (rainbow trout) exposed to NDMA through diet, for a period of 1 year showed chronic toxicity. By the lowermost concentration of 200 mg kg^{-1} NDMA, increase in hepatocellular carcinomas was observed.

Similarly, chronic toxicity was observed in Fathead minnows (Pimephales promelas) exposed to concentrations of CL-20, a type of nitramine, with an IC50 (inhibition concentration) of 0.2-2.0 mg l^{-1} (Hayley et al., 2003; 2007). The growth of Fathead minnows was also affected when they were exposed to chronic concentrations of RDX, with LOEC (lowest observed-effect concentration) values of 5.8 mg l^{-1} (Burton et al., 1994 and Bentley et al., 1977). In addition, a 4-week exposure to RDX concentrations in zebra fish presented an adverse effect on their growth, at concentrations of 1mg l^{-1}. This information is summarised in Table 2.2.

Table 2.2 Chronic toxicity effects of some amines on freshwater fish.

Compound	Fish	Toxicological Endpoint	mg l^{-1} (*mg kg^{-1})	Reference
Amines				
MDEA	Carp (Cyprinidae)	Decrease in egg hatching - LOEC	0.5	Bieniarz et al., 1996
PIPA	Aholehole (*Kuhlia sandvicensis*)	Behavioural changes (schooling) - NOEC	20	Hiatt et al., 1953
Nitrosamine				
NDMA	Rainbow trout (*Oncorhynchus mykiss*)	52-week exposure – presence of hepatocellular carcinomas - LOEC	*200	Grieco et al., 1978
Nitramines				
CL-20	Fathead minnow (*Pimephales promelas*)	Growth IC50	0.2-2.0	Hayley et al., 2003; 2007
RDX	Fathead minnow (*Pimephales promelas*)	Growth effects - early development (LOEC)	5.8	Bentley et al., 1977
		Survival chronic exposure (LOEC)	4.9-6.3	Bentley et al., 1977
	Zebra fish (*Danio rerio*)	Effects on body weight after 4 weeks (LOEC)	1	Mukhi & Patiño, 2008

2.4 Toxic effects on aquatic invertebrates

Aquatic invertebrates, such as hydra and water fleas are often used as model organisms in basic biological research due to their ease of maintenance in the laboratory. They are also frequently used in ecotoxicological testing to assess the potential effects of chemical on aquatic ecosystems. In these studies, invertebrates are exposed to the test chemical and behavioural changes and mortality are commonly used as endpoint measures. In recent years, there has been an increasing trend towards using aquatic invertebrates in mechanistic and high-throughput screening studies in the fields of neurotoxicology, environmental toxicology, and genetic toxicology. However, very few studies of amine toxicity on aquatic invertebrates have been reported.

Acute effects: In a study on water flea (Daphnia magna), the LC50 concentrations were found to range between 10 -250 mg l^{-1} for three amine compounds (MEA, AMP, PIPA) with the most toxic effect being on exposure to PIPA. The acute toxicity data for selected amides indicated a broad range of LC50 values of 10,000 mg l^{-1} for acetamide (Bringmann & Kuhn, 1977) and 13 mg l^{-1} for formamide on D. magna (Le Blanc & Surprenant, 1983). The quickest response for nitrosamine was reported for an unidentified Cladoceran species, with a 48-hour median lethal concentration of 7.76 mg l^{-1} subsequent exposure to NDPA (USEPA,1978). For NDMA (nitrosodimethylamine), the 96-hour LC50 values varies from 300 mg l^{-1} in the amphipod Gammarus limnaeus to 2,250 mg l^{-1} in the Crayfish Austropotamobius pallipes (Draper & Brewer, 1979 and Alibaud et al., 1985). These values suggest that NDMA is less toxic to Gammus limnaeus than to Austropotamobius pallipes. For NDEA, the most sensitive species reported was A. pallipes with a LC50 value of 230 mg l^{-1} (Alibaud et al., 1985). As compared to others, the nitramines show distinctly higher acute toxicity to different species of invertebrates. Water flea (Ceriodaphnia dubia) with LOEC value of 6.01 mg l^{-1} was recorded as the most sensitive species on following exposure to RDX. The key information and sources are summarised in Table 2.3.

Chronic effects: The chronic toxicity of particular amines and their derivative products to marine invertebrates are shown Table 2.4. For formamide, the maximum allowable concentration for chronic testing was found to be 1.2-2.5 mg l^{-1} for D. magna. Exposure to nitrosodimethylamine (NDMA) has been shown to cause degeneration in the antennal gland of Crayfish (Procambarus clarkia) at 200 mg l^{-1} following exposure for approximately 6 months. At a lower concentration of 100 mg l^{-1}, NDMA caused hyperplasia of the tubular cells in the hepatopancreas (Harshbarger et al., 1971). In other studies, exposure to CL-20 and RDX caused different body growth and reproductive symptoms in the aquatic invertebrate Ceriodaphnia dubia at concentrations ranging from 0.4-2.0 mg l^{-1} and 4.68 mg l^{-1}, respectively. These findings suggest that these chemicals can have adverse effects on the growth and reproduction of aquatic invertebrates at relatively low concentrations (Hayley et al., 2003 and Peters et al., 1991).

Table 2.3 Toxicity effects of some amines on aquatic vertebrates.

Compound	Invertebrate	EC/LC50 (mg l^{-1})					Reference
		NOEC	LOEC	24h	48h	96h	
Amines							
MEA	Water flea (*Daphnia magna*)			83.6			Bringmann & Kuhn, 1977
	Brown shrimp (*Crangon crangon*)				100		Brooks, 2008
	Flagellate protozoan (*Entosiphon sulcatum*)				300		Bringmann & Kuhn, 1980
PIPA	Water flea (Daphnia magna)				10-100		Web Link 1
AMP	Water flea (*Daphnia magna*)	100			>100		Web Link 2
Amides							
Acetamide	Water flea (*Daphnia magna*)			10,000			Bringmann & Kuhn, 1977
Formamide	Water flea (*Daphnia magna*)				500		EPA, 2004. doc: 201-15159A
Nitrosamine							
NDPA	Cladoceran sp.				776		US EPA, 1978
NDMA	Amphipod (*Gammarus limnaeus*)					300	Draper & Brewer, 1979
	Crayfish (*Austropotamobius pallipes*)					2,250	Alibaud et al., 1985
	Flatworm (*Dugesia dorotocephala*)					1,365	Draper & Brewer, 1979
NDEA	Amphipod (*Gammarus limnaeus*)					500	Draper & Brewer, 1979
	Crayfish (*Austropotamobius pallipes*)					230	Alibaud et al., 1985
	Flatworm (*Dugesia dorotocephala*)					1,490	Draper & Brewer, 1979
Nitramines							
RDX	Mussel (*Mytilus galloprovincialis*)	28.4	>28.4				Brooks, 2008
	Water Flea (*Ceriodaphnia dubia*)	3.64	6.01				Peters et al., 1991
	Midge (*Chironomus tentans*)				15-100		Hovatter et al., 1997
HMX	Mussel (*Mytilus galloprovincialis*)	1.9	>1.9				Brooks, 2008

Web link 1. http://www.ethyleneamines.com/NR/rdonlyres/0F711045-D7C1-4979-8286-032FF5C01636/0/PIP_Anh.pdf
Web link 2. http://www.jtbaker.com/msds/englishhtml/a4572.h

Table 2.4 Chronic toxic effects of some amines on aquatic vertebrates.

Compound	Invertebrate	Toxicological Endpoint	Value	Reference
Amide				
Formamide	Daphnia magna	Maximum allowable concentration for chronic toxicity testing	1.2-2.5	Le Blanc & Surprenant, 1983
Nitrosamine				
NDMA	Crayfish (*Procambarus clarkii*)	Antennal gland degradation – 6 month exposure	200	Harshbarger et al., 1971
	Crayfish (*Procambarus clarkii*)	Hyperplasia of tubular cells in hepatopancreas-6 month exposure	100	Harshbarger et al., 1971
Nitramines				
CL-20	Water flea (*Ceriodaphnia dubia*)	LC50	0.4-2.0	Hayley et al., 2003; Hayley et al., 2007
RDX	Water flea (*Ceriodaphnia dubia*)	7d reproductive effects	4.68	Peters et al., 1991

Wagner et al. (2014) studied chronic cytotoxicity and acute genotoxicity of various N-nitrosamines and N-nitramines in Chinese hamster ovary (CHO) cells. The rank order of mutagenicity was found to be N-nitrosodimethylamine (NDMA)> N-nitrosomorpholine> N-nitrodimethylamine> 1,4-dinitrosopiperazine> N-nitromorpholine> 1,4-dinitropiperazine> N-nitromonoethanolamine> N-nitrosodiethanolamine> N-nitrodiethanolamine. 1-Nitrosopiperazine and 1-nitropiperazine were not mutagenic. Overall, N-nitrosamines were found to be approximately 15-fold more mutagenic than their N-nitramine analogues.

The research suggests that certain N-nitrosamines and N-nitramines may have the potential to cause genetic damage in cells, with N-nitrosamines being more potent than N-nitramines in this regard.

2.5 Toxic effects of aromatic amines on eukaryotic protists (Ciliates)

Amongst the protozoans, Ciliates are the largest and most complex group characterised by two nuclei, a variety of organelles, and a mouth like cytosome. A primary study (Sihtmäe et al., 2010) focussed on the toxicity of aniline and its derivatives on the test protozoan species Tetrahymena thermophila. The EC50 values were determined using Regtox software and the average EC50 values and were calculated based on 3–5 independent experiments as shown in Table 2.5. The study showed that the protozoa were less sensitive towards the anilines than the crustaceans, which makes them a better biosensor species to study the ecotoxicology assessment.

Table 2.5 Toxicity of some amines to the ciliate *Tetrahymena thermophila.*

Compound	EC50 (for 24h)
Aniline	358 ±1 80
2-Chloroaniline	252 ± 16
3-Chloroaniline	135 ± 9.0
4-Chloroaniline	36 ± 3.5
3,5-Dichloroaniline	29 ± 2.4

2.6 Effects of amines on terrestrial plants

There is hardly any literature on MEA toxicity on terrestrial plants probably because toxicity study for terrestrial plants has not been present-day problem in marketable use of MEA.

Monoethanolamine (MEA) is a chemical compound that is used in a variety of industrial and commercial applications, including as a supplement for the herbicides and insecticides. In fact, MEA has been reported to stimulate the growth of plants and improve the growth of seedlings (Kloppenburg & Hall 1990a, b). Some studies suggest that MEA is usually absorbed into the phospholipids and stabilises the bio-membranes of plant cells in adverse conditions. The exogenously applied MEA helps in stimulate protein synthesis, blossoming (flowering) and advances growth of the seedlings and hence performances as a plant bioregulator (Eckert et al. 1988a, b).

Studies have shown that application of MEA as a foliar spray can have positive effects on the growth and biomass formation of cereal crops such as rye, wheat and barley. In pot experiments, application of MEA at a concentration of 0.02 mol l^{-1} as a foliar spray increased biomass and grain yields by up to 14 % (Bergmann & Eckert 1990). MEA has also been shown to increase grain yields, particularly on nutrient deprived residual soils. In addition, MEA has been used as a component in foliar fertilizers in ground tests (Feckova et al., 2005)

Studies have revealed that the pre-treatment of sunflower seeds (Helianthus annus) with ethanolamine can enhance seedlings tolerance to surrounding conditions of saline stress during germination (Kogan et al., 2000). Similarly, spraying MEA (at a concentration of 0.5 mg plant^{-1}) on plants shown to decrease the oxidative stress in barley plants, which is caused by weedkillers, by stimulating the cell membranes studied by Mascher et al. (2005). It concludes that MEA and ethanolamine may have the potential to protect plants from stressors, such as high levels of salt or herbicides, and to promote plant growth and development.

Several studies indicated that RDX, a chemical compound, can be taken up by plants, resulting in increased concentrations in the stems and leaves (Harvey et al. 1991). Exposure to RDX has been found to reduce plant biomass and inadequately interrelated with decrease in plant height at concentrations of 100 and 200 mg kg^{-1} (Simini et al. 1995). Based on these findings, a screening scale for plants and soil at 100 mg kg^{-1} has been established. No studies have been found that have verified the toxicity of HMX

(Hexamethylenetetramine) to terrestrial plants. Thus, amines may play a stimulatory effect on plant growth.

2.7 Toxic effects on algae and cyanobacteria

Acute toxicity: The acute toxicity of the selected amines and their secondary products to freshwater and marine algae and cyanobacteria is shown in Table 2.6. The acute toxicity of acetamide showed large variations with lowest observed effect concentration (LOEC) was found to be 6,200 mg l^{-1} for the cyanobacterium (Microcystis aeruginosa) and 10,000 mg l^{-1} for the green algae (Scenedesmus quadricauda). Most sensitive species to acetamide was the Cryptomonad Chilomonas paramecium, with a 48-hour median lethal concentration (LC50) value of 49 mg l^{-1} as reported by Bringmann et al. (1980). As compared to other secondary products, nitramines showed significantly higher values of LC50 for algae. For example, the 96-hour LC50 value for the nitramine RDX was found around 3.2 to 10 mg l^{-1} in M. aeruginosa and S. quadricauda (Hovatter et al., 1997). No toxicity data was reported for nitrosamine compounds.

Chronic effects: For the selected amines and their degradation products, the chronic toxicity data for the algae and cyanobacteria are shown in Table 2.7. It appears that the utmost sensitive species to MEA was Scenedesmus quadricauda (green algae) and have LOEC value of 0.75 mg l^{-1} after 7-8 days of exposure (Bringmann & Kuhn, 1980; 1978). Other cyanobacteria, such as Anacystis aeruginosa and Microcystis aeruginosa, had similar LOEC values of 1.6 to 2.1 mg l^{-1} as reported by Bringmann & Kuhn (1978 & 1975). Acetamide had very low toxicity. Many changes were observed in the population and growth of A. aeruginosa and S. quadricauda for the 7 to 8 days exposure and recorded EC50 values of 6,600 mg l^{-1} and 10,000 mg l^{-1} for both (Bringmann & Kuhn, 1980; 1978). The highly sensitive species to nitrosamine was the marine green algae (Tetraselmis maculate) which displaying LOEC value of 0.025 mg l^{-1} and DNA damaged was reported following exposure.

A study by Gundersen et al. (2018) found that MMA- nitramine was more toxic to phytoplankton than the other two nitramines. The researchers tested the ecotoxicity of these compounds by exposing phytoplankton to different concentrations of the nitramines. They found that MMA-nitramine was highly ecotoxic of the three nitramines, with lethal concentrations (LC50 values) that were lower than other two nitramines. The concentration at which 50 % of the population is affected (EC50) for phytoplankton growth was 754 mg l^{-1} (Brakstad et al., 2011).

Table 2.6 Acute toxicity of selected amines on algae and cyanobacteria.

3 Compound	4 Algae/Bacteria	5	LOEC	6	EC10	7	EC/LC50 (mg l^{-1})		8 Reference
				15min	24h	48h	72h	96h	
Amines									
MEA	Marine algae (*Skeletonema costatum*)		83.1			198			Sintef Report, 2007
	Green algae (*Chlorococcales*)	31			70				Krebs, 1991
	Cryptomonad algae (*Chilomonas paramecium*)					733			Bringmann et. al., 1980
AMP	Marine algae (*Skeletonema costatum*)		64.8			118.6			Sintef Report, 2007
MDEA	Marine algae *(Skeletonema costatum*)		72.7			141.4			Sintef Report, 2007
PIPA	Green algae (*Selenastrum capricornutum*)						>1,000		Web Link 1
Amide									
Acetamide	Green algae (Chlorococcales)		1,000		1,000				Krebs, 1991
	Cryptomonad (*Chilomonas paramecium*)					49			Bringmann et al., 1980
	Blue-green algae (*Microcystis aeruginosa*)	6,200							Bringmann & Kuhn, 1978
	Green algae (*Scenedesmus quadricauda*)	10,000							Bringmann & Kuhn, 1978
Nitramine									
CL-20	Green algae (*Selenastrum capricornutum*)							>3.6	Gong et al., 2004
RDX	Blue-green algae (*Microcystis aeruginosa*)							3.2-10	Hovatter et al., 1997
	Green algae (*Selenastrum capricornutum)*							3.2-10	Hovatter et al., 1997
HMX	Blue-green algae (Microcystis aeruginosa)							>32	Hovatter et al., 1997
	Green algae (*Selenastrum capricornutum*)							>32	Hovatter et al., 1997

Web link 1. http://www.ethyleneamines.com/NR/rdonlyres/0F711045-D7C1-4979-8286-032FF5C01636/0/PIP_Anh.pdf

Table 2.7 Chronic toxic effects of some amines on algae and cyanobacteria.

Compound	Algae/cyanobacteria	Toxicological endpoint	Value (mg l^{-1})	Reference
Amines				
MEA	Blue-green algae (*Anacystis aeruginosa*)	8d growth effect (LOEC)	1.6-2.1	Bringmann & Kuhn, 1978
	Green algae (*Scenedesmus quadricauda*)	8d growth effect (LOEC)	0.75-0.97	Bringmann & Kuhn, 1978
	Blue-green algae (*Microcystis aeruginosa*)	8d growth effect (LOEC)	1.6-2.1	Bringmann & Kuhn, 1978
Amides				
Acetamide	Blue-green algae (*Anacystis aeruginosa*)	8d growth effect (EC50)	6,600	Bringmann & Kuhn, 1978
	Green algae (*Scenedesmus quadricauda*)	8d population changes (EC50)	10,000	Bringmann & Kuhn, 1980
Nitrosamine				
NDMA	Green algae (*Chlamydomonas reinhardtii*)	DNA damage (COMET)	1-10	Erbes et al., 1997
	Green algae (*Selenastrum capricornutum*)	8d growth effect (LOEC)	1-10	Draper & Brewer, 1979
NDEA	Green algae (*Selenastrum capricornutum*)	8d growth effect (LOEC)	1-10	Draper & Brewer, 1979

2.8 Bacterial response to amine exposure

It comes into view that bacterial response to acute exposure to the monoethanolnitramine (MEA-NO_2) and dimethylnitramine (DMA-NO_2) was evaluated by Gundersen et al. (2014). The study used a bacterial community (natural lake-water) and bacterial culture (pure) to measure the effects of the nitramines on aerobic respiration and metabolic profiling at community-level. It was done with the help of Ecoplates™ (BIOLOG) for 31-different ecological related carbon substrates. The results showed that MEA-NO_2 repressed the rate of oxygen consumption in the natural water resource (lake water) bacterial community at concentrations above 4 mg l^{-1}, but shown zero effect on the clean culture of Bacillus subtilis. Both nitramines were found to induce shifts in the metabolic profile of the natural lake-water bacterial community. Considering the highly dynamic nature of natural bacterial communities additional testing has been recommended by the authors to acquire a clearer image of bacterial response to the nitramines. The authors also noted that the levels of nitramines that affected bacteria in the study were 1,000 times higher than the estimated emissions from a PCC plant under worst-case situation conditions, and the ultimate environmental concentrations of the nitramines may be influenced by biogeochemical processes, such as soil sorption and biodegradation at any given site (Gundersen et al., 2014). It was suggested that additional testing may be needed to understand the full response of bacteria to these nitramines.

For MEA, the bacterium (Vibrio fischeri) was reported as very sensitive species with a LC50 concentration ranging between 6-39 mg l^{-1} (Table 9). Likewise, lethal concentrations (LC50 values) of 13 and 20 mg l^{-1} were recorded for bacteria Vibrio fischeri on exposure to AMP and PIPA discretely (Sintef report, 2007).

The results from these studies are summarised in Table 2.8.

Table 2.8 Acute toxicity of selected amines on bacteria.

Compound	Bacteria	LOEC	EC10	EC/LC50 (mg l^{-1})					Reference
				15min	24h	48h	72h	96h	
Amines									
MEA	Microtox (*Vibrio fischeri*)			6-39					Sintef Report, 2007 Libralto et al 2007
AMP	Microtox (*Vibrio fischeri*)			20					Sintef Report, 2007
	Microtox (*Vibrio fischeri*)			36					Sintef Report, 2007
PIPA	Microtox (*Vibrio fischeri*)			13					Sintef Report, 2007
Nitramines									
NDEA	Microtox (*Vibrio fischeri*)							>3.6	Gong et al., 2004

The research group of Gundersen et al. (2018) also investigated the impact of monomethyl, monoethanol and monoethanol – nitramines on the growth of bacterial strains such as Pseudomonas fluorescens and Rhodococcus sp. In this study, it was found that the growth of Rhodococcus sp. was sensitive to monomethyl nitramine (MMA-nitramine) and shown an EC50 value of 157 mg l^{-1}. This suggests that at concentrations above 157 mg l^{-1}, monomethyl nitramine is toxic to Rhodococcus sp. and can inhibit its growth. On the other hand, the growth of Pseudomonas fluorescens was found to be insensitive to any of the tested nitramines, indicating that these compounds have little or no effect on the growth of this particular bacterial strain. It is also worth mentioning that the tenacity of nitramines in the existence of these bacterial strains was determined in this study (Gundersen et al., 2018).

The growth of P. fluorescens was uninfluenced by exposure to MEA-, MMA-, and DMA-nitramine. Furthermore, during the course of the 33-hour trials, P. fluorescens was able to break down 8 -10% of the nitramines. The findings of this study shed light on critical bacterial nitramine response pathways that call for additional research in light of the continued use of CO_2 collection technologies.

A quantitative study by Wagner et al. (2014) used in vitro bioassays to assess the mutagenicity of certain N-nitrosamines and N-nitramines in Salmonella typhimurium, as well as the chronic cytotoxicity and acute genotoxicity of these compounds. The Salmonella assay is a commonly used method for testing the potential mutagenic effects of chemicals. S. typhimurium was found very sensitive to both N-nitrosamines and N-nitramines for Mutagenicity.

2.9 Potential Impact of amines on ecosystems

Since amines are nitrogenous compounds, their emissions and depositions near post-combustion capture plants have the potential to influence ecosystems by affecting growth and metabolism of living organisms in various ways depending particularly on the critical load (CL) and background levels of nitrogen in the environment, which varies from place to place. Habitats where the critical load is already increased or on the way to be surpassed, are likely to be largely affected by any emissions of amines. Even small concentrations of amines and their degradation products may, thus, be harmful to the ecosystem. Since nitrate may be formed by biological oxidation of ammonia (nitrification), and high input of ammonia may result in increased fertilisation, it may cause eutrophication of lakes. However, till now there is lack of data on this particular aspect, where nitrogen enrichment might cause ecosystem level impact. Thus, here is a necessity from an experimental perspective to test the impacts of various amines that are used for the CO_2 capture processes on soil and aquatic ecosystems, including changes in the composition and activity of microorganisms. It is essential to carefully evaluate the potential risks of amines to these ecosystems, in order to determine at what concentration they may be harmful (Brooks, 2008).

3 Biodegradation and biotransformation of nitrosamines and nitramines

In few studies, including Brakstad et al. (2018) and Brakstad and Zahlsen (2011), selected NSAs and NAs were subjected to aerobic and anaerobic biodegradation using natural lake and river water. At temperature 20°C, NSAs and NAs (20 g l^{-1}) having hydroxyl groups (alkanol) displayed aerobic biotransformation above 10 % after 28-days incubation, whereas 80% biotransformation was reported after a 56d biodegradation. Half-lives of the compounds were found to be 28.5-33.1 days. The biotransformation of N-nitrosodiethanolamine (NDELA) (20 °C; 56 days) at concentrations from 1 g l^{-1} to 100 g l^{-1} was not statistically different, but the water sources and temperatures (5-20ºC) significantly impacted biotransformation. Alkanol NSAs and NAs underwent anaerobic biotransformation quickly (20°C; 56 days) but not the alkyl compounds. At the same temperature, anaerobic biotransformation was almost similar and faster.

The hydroxyl substituent of alkanol nitrosamines and nitramines was predicted to be more degradable than nitroso- and nitro-substituents through bio-transformation routes. Half-lives were found to increase at low temperature (Brakstad and Zahlsen ,2011). Booth et al. (2014) found that biodegradation was increased for some of the compounds at lower concentrations and extended incubation period.

The study by Norling et al. (2022) aimed to investigate the potential impacts of nitrosamines and nitramines on a catchment-lake system, using a process-based simulation approach. The study focused on a full-scale CO_2 capture facility at the Oslo waste incineration plant in Norway and used previously modelled atmospheric deposition rates of nitrosamines and nitramines as input for the simulation. The study sought to quantify the effects of hydrological and biogeochemical processes and the fate and transport of these amines in the catchment-lake system, and to identify the processes along maximum sensitivity (such as NA biodegradation). The ambiguity in the results was addressed through the use of a probabilistic distribution (Monte Carlo analysis), which incorporated variability in the catchment, lake, and NA and NSA parameter values available in literature. This modelling tool allowed for a site-specific assessment of the potential risks associated with amine-based CO_2 capture and can inform risk assessment and management strategies.

Though biodegradation is identified to be the foremost removal process for nitramines in environment, biodegradation parameters are lightly constrained due to the absence of knowledge on exact chemicals biodegradability (Norling et al, 2022). Brakstad et al. (2018) noted that the biodegradability of nitramines is compound-specific, and that the hydroxyl group is more prone to biodegradation than the nitroso-and nitro-substituents. This means that different nitramines may have different rates of biodegradation, and this can affect their environmental fate and potential impacts. Hence, further research is needed to understand the biodegradation rates of nitramines under different environmental conditions, including different soil types, ground or lake water sideways assessment for the influence of bacterial communities and temperature are well-thought-out aspects of research. This information could be used to improve the accuracy of atmospheric dispersion modelling, which is used to predict the concentrations of nitramines in the environment.

Eide-Haugmo et al. (2009) tested the biodegradability of 42 compounds in the marine environment, including several solvents frequently used for carbon capture. They found that some of these solvents such as piperazine, N-methyldiethanolamine and 2-amino-2-methylpropanol showed low biodegradability. Tertiary amines and mixtures containing quaternary carbon did not breakdown readily, whereas the amino acids had low toxicity and high biodegradation potential. The EPI Suite^{TM} was used to envisage the biodegradability and ecotoxicity of the compounds tested. The predictions for biodegradability solitary showed agreement with the experimental results.

Hauser et al. (2013) demonstrated the effectiveness of a pre-denitrification biofilm system in removing nitrogen and organic matter from reclaimer waste of a monoethanolamine (MEA)-based CO_2 capture plant. The reclaimer waste in this study contained MEA and other contaminants, including N- (2- hydroxylethyl) glycine and 2-hydroxyethylformamide. In the biofilm system, the MEA was readily hydrolysed to ammonia and the organic intermediates were further oxidised, resulting int he removal of 98% MEA and 72% total nitrogen. The system had a hydraulic retention time of 7 hours. This study highlights the potential for using biofilm systems to treat the waste generated from CO_2 capture processes and remove contaminants that could potentially have negative impacts on the environment.

The feasibility of biological nitrogen removal of amines used in post-combustion capture plants has been tested in a moving bed biofilm reactor (MBBR) in pre-denitrification mode by Henry et al. (2017) in aerobic as well as anaerobic conditions. They tested nine different amine samples, including monoethanolamine (MEA) and reclaimer waste, using a new anoxic batch screening test in syringes. The results showed that amine, MEA, and reclaimer waste were slowly degradable under anoxic conditions. However, AMP, DEEA and MDEA remained undegraded under the current anoxic conditions. It seems that biodegradation was more effective in fresh water than in other conditions. This research may have implications for the treatment of wastewater containing these amines in post-combustion capture plants.

4 Knowledge gaps and research needs

It becomes quite evident from the above reviews and discussion that although PCCC plants offer a good option for CO_2 removal from atmospheric emissions, thus addressing the climate change problem to some extent, the associated amine emissions and their potential impacts on aquatic and terrestrial life and on the ecosystems as a whole require more rigorous studies and development of understanding. Most of the studies on amine toxicity have been carried out in temperate countries and little information is available for tropical countries. The studies have indicated that biodegradation is largely influenced by temperature, inoculum, water and soil environment, and the type of amine. Thus, more research on biodegradation rates under different environmental settings to signify soil, ground water and lake water conditions are required. Furthermore, the influence of native bacterial communities and temperature may prove key in affecting the fate of such emissions, and thus an important aspect of further research. Successful application of microbial biofilms for removal of amines will also be influenced by the bacterial communities harbouring different ecological habitats in different geographic locations. The inadequacy of toxicological data regarding amine and amine degradation products' impacts on aquatic organisms is a major constraint on the development of regulatory water quality criteria. In this context, future research needs include the following:

- Establish appropriate toxicity assays for nitramines and nitrosamines.
- Study the effect of amines on more groups of micro- and macro-organisms in order to understand the overall impact on ecosystems.
- Study the enzymatic activities or self defence mechanisms that are developed by various flora and fauna species against these derivatives of amines.
- Evaluate the effects on vegetation from direct and indirect exposures associated to nitrogen eutrophication from different amine solvents and find critical load concentrations at which they will affect the environment.
- Analyse the degradation rate and nutrient cycling for amines in the soil system in order to clarify the end-products accessible for vegetation and soil fauna.
- Assess direct detrimental effects on soil fauna by primary amine exposures and indirect effects owing to likely variations in vegetation and soil properties.
- Perform eco-toxicological tests on certain terrestrial fauna in precise laboratorial environments by using appropriate doses of amines and study degradation end-products.
- Further investigations to identify the metabolic products during biodegradation of nitrosamines like NDELA.
- Investigate the fate of nitrosamines precipitated in a catchment area and the subsequent impacts on its water systems.
- Compare photochemical degradation and biodegradation of nitrosamines in water during summer and winter periods.

5 Conclusions

An amine-based capture facility directly benefits the environment by reducing air pollution and carbon dioxide emissions. Several mixtures of amines used for absorbing the carbon dioxide, however, may have health repercussions and ecological impacts. Not enough is known about the environmental risks associated with using amines to extract CO_2. The research that is currently available demonstrates that various amines and their degradation products may have detrimental impacts on human health and surrounding biota.

Additionally, amines have been found to show toxic effects on some test animals and aquatic algae and microbes. Though sufficient systematic studies have not been carried out, amines have the potential for eutrophication and acidification of marine ecosystems.

To date, MEA is the amine most often utilised in CO_2 separation processes. MEA has a relatively high biodegradability, and MEA by itself will not have a negative impact on the health of people, animals, plants, or aquatic organisms. However, eutrophication and acidification can result from the nitrogen and ammonia that are released into the air because of amine breakdown. In comparison to MEA, other amines such as AMP, MDEA, and PIPA, are ecotoxicologically hazardous and have a low rate of biodegradation.

As soon as amines are released from a CO_2 capture plant, they begin to break down into other compounds. The different degradation products include amides, nitramines, and aldehydes, do not harm the environment. Nitrosamines are likely to be the breakdown products with the worst consequences on the environment since they may cause cancer, contaminate drinking water, and harm aquatic organisms.

To construct and run amine-based CO_2 capture facilities without posing any dangers to human health or the terrestrial and aquatic environment, more research must be conducted once the risks have been recognised. These studies must explain how the risks may be addressed. Furthermore, in order to better understand the toxicity of the different amine group of compounds, families of plant, animal and microbes species should be considered as test targets under diverse conditions.

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