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Preface

CO_2 capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO_2 emissions to the atmosphere. A leading technology for CO_2 capture is through the use of amines. The *CO_2 and Amines Screening Study Project* began with *Phase I* in May 2008. The project was initiated by the Norwegian Institute for Air Research (NILU) based on the results of an expert meeting in October 2007, and discussions with the Norwegian Pollution Control Authority (SFT). The expert meeting and the following Phase I project is based upon the concern that the emissions from CO_2 capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC) Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric degradation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 1, 2, 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.

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1 Introduction

Capturing carbon dioxide from a fossil fuel burning power plant has become a commercial process worldwide, and CO_2 capturing is also planned for Norwegian power plants. One of the few methods that have been proven to work on an industrial scale is chemical absorption using amines, especially monoethanolamine (MEA). However methyldiethanolamine (MDEA), aminomethylpropanol (AMP) and piperazine are also considered to be relevant amine components for CO_2 removal.

Minor amounts of amines used in the absorption process and degradation products, such as amides, aldehydes, nitrosamines and nitramines (Bråten et al. 2009), will probably be omitted and deposited in the vicinity of the power plant stations and have the possibility to affect the ecosystem. Amines are generally a part of central life processes and are essential components in amino acids, cell membranes and proteins. However, the effects of the relevant amines and their degradation products on terrestrial vegetation and free-living fauna are poorly understood. The main knowledge comes from laboratory experiments with animals related to impacts on human health, and several amines and degradation products are found to be toxic to humans (Låg et al. 2009a,b). Amines are nitrogen-rich compounds and might also affect eutrophication processes within the ecosystems, resulting in increased plant nutrient availability and increased plant growth which further might influence the free-living fauna.

This report tries to sum up what is known in literature on the effects of external influence of MEA, MDEA, AMP and Piperazine and some of the degradation products on terrestrial vegetation and fauna. This is done by use of available biological and ecological databases. Based on the literature review and general ecological knowledge on how nitrogen affects terrestrial ecosystems, we conclude on what might be the most important effects on vegetation and fauna from amines used in the capture of carbon dioxide. Finally we present recommendations regarding gaps in knowledge and possible experimental research on this topic.

2 Effects of relevant amines used in CO_2 removal

2.1 Monoethanolamine (MEA)

MEA is an organic chemical compound and an aliphatic primary amine. It is a toxic, flammable, corrosive, colourless, viscous liquid with a smell similar to ammonia. In addition to be used commercially for removing CO_2 from flue gas, MEA is also used in metalworking fluids to neutralize acidic components in lubricants and prevent corrosion and rusting. In aquatic solutions it is used as a component in detergents for laundry and dishwashing, degreasers, disinfectants, personal care products such as hand lotions, cosmetic creams and shampoos. It is also a raw material in production of many pharmaceutical products (http://www.dow.com/amine). In agriculture it is used in chemical herbicides and pesticides, especially as an organic chelating agent used to reduce activity of elevated antioxidant enzyme levels in bi-pyridylium resistant plant species biotypes to overcome herbicide resistance (Koschnik & Haller 2006). MEA is also used in wood treating for wood preservatives (Shah & Lee 1992).

Though MEA is commercially produced for industrial purposes, it is also a natural component in plants and animals. It is the second most abundant head group for phospholipids in cell membranes and is thus one of the most important building blocks in nature. Leaf beetles sequester alkaloids from plants and secrete MEA as a defence medium (Pasteels et al. 1988).

2.1.1 Effects on vegetation and soil

We have found no information on MEA toxicity on terrestrial plants in available literature. However, this does not mean that it is not toxic to plants at higher concentrations. The lack of information in literature is probably related to the fact that toxicity to terrestrial plants has not been the current problem in commercial use of MEA. The main result from the literature research is found in connection with the use of MEA in agriculture.

Plant growth
In general MEA is incorporated into the phospolipids and stabilizes the biomembranes of plant cells in unfavourable environments, and exogenous applied MEA promotes protein synthesis, stimulates flowering and improves growth seedlings and thus acts as a plant bioregulator (Eckert et al. 1988a,b; Bergmann & Eckert 1990). Used as a supplement to herbicides and pesticides MEA has been found stimulating to plant growth (Kloppenburg & Hall 1990a,b,c). However, Koschnik & Haller (2006) found MEA, used as a copper chelating agent, to slightly increase the ion leakage from the water plant dotted duckweed (*Landolita punctata*) at doses of 1-10 mg/L, and significant effects on leakage were found at 100 mg/L.

Several pot experiments have been performed on the effect of MEA on growth and biomass formation of rye, wheat and barley. MEA applied in aqueous solution as a foliar spray (0.02 mol/L, 10 mg MEA/pot, each pot containing 16 plants) increased the biomass and grain yields formation of tillers (up to 14%), and promoted the growth of basal stem parts (Bergmann & Eckert 1990). The increased production of tillers and the stimulated growth of basal internodes were associated with higher nitrogen content in the plants. 10 mg MEA per pot increased the grain yield of spring barley from 5% to 9% (Bergmann et al. 1991).

Muller et al. (1991) showed that application of MEA to barley increased the natural amount of MEA in barley from 200 mg/kg dry weight to about 450 mg/kg dry weight. Field trials and large scale experiments were conducted by Weber et al. (1990) using an application of 1.5 kg/ha. The application increased the grain yield on nutrient poor residual soils. MEA has also been used in field experiments as a component in foliar fertilizer (Avit 35) and sprayed on sugar beet leaves, resulting in increased root yield and foliar digestion (Feckova et al. 2005). The basic organic substance in Avit 35 is MEA which intervenes into the polyamines biosynthesis by ornithine decarboxylase inhibition and also by inhibition of enzymatic processes at the ethylene biosynthesis, which is influenced by ureasalicylate in mixture with urea. No concentration of applied MEA was given in the paper of Feckova et al. (2005).

2.1.2 Stress to plants,

Pot experiments run for several years showed that MEA, sprayed on plants in water solution of 0.01 M (0.3-0.5 mg MEA per plant), improved the drought tolerance of barley, reduced the plant stress and increased the yield grain proteins and the yield of lucine, isoleucine and other essential amino acids (Roth & Bergmann 1988; Bergmann et al. 1990, 2002; Mascher et al. 2005a). MEA sprayed on plants (0.5 mg/plant) also decreased the oxidative stress in barley, caused by herbicides, by stimulation of the cell membranes (Mascher et al. 2005b). Saline stress is crucial to seed germination and development stages of seedlings and may affect plant growth (Delagdo et al. 1996). Pre-treatment of seeds soaked in 0.01mol/L MEA for six hours exerts a protective effect against saline stress in corn and barley (Leinhos et al. 1996; Lippmann & Bergmann 1995). Similar experiments by Kogan et al. (2000) have shown that pre-treatment of seeds of sunflower (*Helianthus annus*) with ethanolamine (in 100mM solution for six hours) led to enhanced seedlings tolerance to conditions of saline stress during germination.

2.1.3 Soil and soil water

The release of alkanoamines (e.g. MEA) from industrial use into the subsurface soils may be potential hazard to the environment. After the release, alkanoamines may migrate into the subsurface soil and ground water due to their high density and high water solubility (Gallagher et al. 1995; Wrubleski et al. 1997; Soerensen et al. 1999; Mrklas et al. 2004).

MEA can persist for decades on soils with high concentrations. Hawthorne et al. (2005) showed that after an accidental release of MEA at a site of a former chemical processing plant up to 400 to 3000 mg MEA/kg were still detected after 10 years. However, several studies have shown that amines biodegrades (by microorganisms) to ammonia, acetaldehyde, acetate, nitrite, nitrate and nitrogen gas under both aerobic and anaerobic conditions, involving processes of nitrification and denitrification (Lee & Portier 1999; Mrklas et al. 2003, 2004, 2006; Ndegwa et al. 2004; Wong et al. 2004; Hawthorne et al. 2005).

Amines biodegrades more easily in non-polluted soils compared with heavily polluted soils. Bacterial degradation studies on MEA was performed with soils that were contaminated 10 years ago and on uncontaminated soils from the same site that had been spiked with 1320 mg MEA/kg dry wt (Hawthorne et al. 2005). The polluted sites showed slow biodegradation while MEA was completely degraded within 3 days of incubation at the spiked soil. Ndegwa et al. (2004) showed that contaminated clay-rich soil biodegraded additional MEA of 2000 mg/kg completely within 10 days under aerobic conditions and within 12 days under anaerobic conditions.

Sorensen et al. (1997) demonstrated that MEA concentrations exceeding 1500 mg/kg inhibited in-situ biodegradation. On the other hand, Mrklas et al. (2004) showed a successful biodegradation even at concentrations of 31.000 mg/kg in bioreactors. Biodegradation is also very dependant on temperature. Cold temperatures (below 6 °C) have shown to reduce the biodegradation rates significantly (Ndegwa et al. 2004).

2.1.4 Effects on fauna

We have found almost no information on the effects on terrestrial free-living fauna. The acute oral toxicity of MEA, however, has been studied in several laboratory animal species and it appears to be relatively low. The oral dose, after which 50% of the animals died (LD50) in rats was 1.1-2.7 g/kg body weight (Knaak et al. 1997). Dermal exposure of pregnant rats to 225 mg/kg/day and rabbits to 75 mg/kg/day of MEA resulted in significant increase in the incidence of skin irritation/lesions and maternal body weight effects. Despite maternal effects observed in rats and rabbits, no evidence of developmental or fetal toxicity was observed at any dose level tested. Thus, it was concluded that MEA was not developmentally toxic following dermal application at exposure levels up to and including 225 mg/kg/day for rats and 75 mg/kg/day for rabbits (Liberacki et al. 1996). Skin and eye irritation in rabbits were rated as severe (Dutertre-Catella et al. 1982).

Giving a dose of 450 mg MEA/kg/day to pregnant rats resulted in maternal toxicity as evidenced by statistical significant decreases in feed consumption and significant decreases in mean maternal body weight. No significant fetal effects were observed at any dose level tested, nor were there any indication of a treatment-related effect on postnatal growth or on the viability of offspring (Hellwig & Liberacki 1997). MEA did not induce chromosome damage in rat liver epithelial type cells (Knaak et al. 1997). No data on carcinogenicity have been located. The literature review performed by Brooks (2009) shows that MEA is toxic to fish and aquatic invertebrates at high concentrations (96 h LC50 for fish eggs was 60.3 mg/l and for adult fish 167-375 mg/l, and 24 h LC50 for water flea (*Daphnia magna*) was 83.6-165 mg/l). It is difficult to compare sensitivities on fish and mammals because exposure doses are given in mg/kg body weight in the mammal studies, whereas it is given as mg/l in the water with fish.

2.2 Methyldiethanolamine (MDEA)

MDEA is a clear, water-white, hygroscopic liquid in room temperature with an ammonia-like odour. It is a tertiary alkanoamine which absorb carbon dioxide at lower temperatures and releases the acid gas at higher temperatures. This is the basis process which separates carbon dioxide from gas streams (Huntsman technical Bulletin, http://www.huntsman.com). It is commonly used for the removal of CO_2 from gas mixtures or in gas sweetening processes for the extraction of CO_2 and H_2S.

2.2.1 Effects on vegetation and soil

We have found no information in literature on effects of MDEA on terrestrial vegetation. However, uptake of MDEA by the vegetation from polluted groundwater and wetlands has been discussed by Headly et al. (2002) in connection with analytical methods to determine alkanoamines in environmental studies.

The aerobic biodegradability of MDEA in waste water from a gas sweetening process was investigated by Fürhacker et al. (2003) in a standardised ISO-batch test by analysis of dissolved organic carbon (DOC) and in a separate continuous flow experiment in an activated sludge treatment system, where MDEA was added directly into the aeration tank. Additional features of the treatment system were a sludge loading ratio of 0.11 kg BOD_5/(kg TS*d), equivalent to a volume charge of 0.50 kg $BOD_5/(m^3$ d). The result of the batch test indicated that the MDEA-solution was non-biodegradable during the test period of 28 days. In contrast to the findings in the batch tests, the continuous experiments showed a total organic carbon (TOC) removal in the treatment plant of up to 96% TOC. Thus the authors concluded that MDEA-solution added to the waste water of the gas sweetening plant was readily biodegradable.

MDEA is an alkanoamine similar to MEA and will probably as MEA biodegrade in soil to nitrogen components available to plants and act as a growth stimulating medium.

2.2.2 Effects on fauna

We have found no information on the effects on terrestrial free-living fauna. MDEA has been found acute toxic to rats with oral LD50 at 1.9 g/kg body weight. However, MDEA did not induce reproducible significant or dose-related increases in the frequencies of mutations, sister chromatid exchanges or micronuclei, which indicate that MDEA is not genotoxic (Ballantyne & Leung 1996; Leung & Ballantyne 1997). On the other hand MDEA has been found to induce severely skin irritation to rats, characterized by necrosis, ecchymoses, exfoliation, crusting, excoriation, erythema, and edema at doses of 1000 mg/kg/day (Leung & Ballantyne 1998). No local irritation was seen at a dosage of 250 mg/kg/day. No carcinogenicity or chronic toxicity studies with MDEA have been found.

2.3 Aminomethylpropanol (AMP)

AMP is either a colourless liquid or a white crystalline solid. In liquid form AMP has an amine-like odour. It is widely used in cosmetics, as an emulsifier and a buffering agent to keep the pH of a mixture neutral.

2.3.1 Effects on vegetation and soil

We have found no information in literature on effects of AMP on terrestrial vegetation and soil. However this is an amine with carbon and nitrogen components, and will probably as the other amines biodegrade in soil to nitrogen components available to plants and thus act as a growth stimulating medium.

2.3.2 Effects on fauna

We have found no information on the effects on terrestrial free-living fauna. The LD50 for rats and mice were 2.9 and 2.15 g/kg body weight respectively (Anon 2007, CIR 1990, IUCLID 2000). The LD50 for rabbits was found to be > 2g/kg body weight (IUCLID 2000). AMP was tested in one year study with dogs where no evidence of any preneoplastic lesions was found. The data suggest that AMP is not carcinogenic (Anon 2007). AMP was non-mutagenic, both with and without metabolic activation in *Salmonella typhimurium* and *Saccharomyces cerevisiae* strains (CIR 1990).

2.4 Piperazine

Piperazine is a secondary amine that consists of a six-membered carbon ring containing two nitrogen atoms. It exists as small alkaline crystals with a saline taste (http://en.wikipedia.org/wiki/piperazine). The piperazines are a broad class of chemical compounds which contain a core piperazine functional group, many with pharmacological properties. Besides used as an anthelmintic, it is also used in the manufacture of plastics, resins, pesticides, break fluid and other industrial materials. Piperazine easily absorbs water and carbon dioxide and is commonly used as an activator to an aqueous solution of the tertiary methyldiathanolamine (MDEA) in the bulk removal of carbon dioxide from gas streams (Derks 2006).

2.4.1 Effects on vegetation and soil

Very little is known on the effect of piperazine on vegetation and soil. However, piperazine, used as a buffer component, has shown to greatly promote adventitious root formation in cuttings of sunflower (*Helianthus annus*), pea (*Pisum sativum*), mung bean (*Vigna radiata*) and to a lesser extent in bean (*Phaseolus vulgaris*), especially at lower pH (Liu et al. 1995). Cuttings were placed in different concentrations of piperazine, ranging from 1 to 10 mM at different pH for 5 hours and then placed in deionised water for three to seven days (depending on the species analysed) before analyses of adventitious roots formation.

The biodegradability of the secondary amines pyrrolidine, piperidine, piperazine, morpholine and thiomorpholine (1.0 mM), has been studied under denitrifying, sulphate reducing and methanogenic anaerobic conditions by Bae et al. (2002). Pyrrolidine and piperadine were completely degraded within 15 days, however only under denitrifying conditions and required nitrate to utilize the amines as carbon, nitrogen and energy source for their anaerobic growth. Piperazine, morpholine and thiomorpholine did not degrade even under denitrifying conditions. This suggests that piperazine is resistant to degradation under anaerobic conditions.

On the other hand, Chen et al. (1997) found that piperazine rings, in a synthetic antibacterial agent (danoflaxin) used in veterinary medicine, were completely degraded by soil organisms, such as bacteria, fungi and yeast. Occurrence of piperazine-degrading microorganisms in nature has also been reported by Emtiazi & Knapp (1994). Thus piperazine, composed of carbon and nitrogen, will probably biodegrade in soil to nitrogen components available to plants and act as a growth stimulating medium.

2.4.2 Effects on fauna

We have found no information on the effects on terrestrial free-living fauna. However, piperazine has been found highly toxic for dung beetles. The residues or metabolites of piperazine had deleterious effects on the dung beetle *Onthophagus gazella*, in the developmental stages of the beetle (few eggs, larvae and pupae). It gave 48.6% inhibition of development in the beetle larvae after 48 hours with concentration 55.65 mg/kg (Blume et al. 1976; Lumaret & Errouissi 2002). Piperazine is also found to be toxic to water flee (*Daphnia magna*) Brooks (2009), and invertebrates might thus be sensitive to piperazine. Piperazine has demonstrated a relatively low acute toxicity (LD50 1-5 g/kg body weight) by oral, dermal, and subcutaneous route of administration to rodents (Swedish Chemicals Inspectorate 2005). However, Lijinsky & Kovatch (1993) showed that piperazine could interact with nitrosating agents in vivo to form nitrosamines with possible carcinogenic risk in rats.

3 Effects of possible degradation products

The screening process of atmospheric degradation of MEA, AMP, MDEA, and Piperazine showed that the main degradation products are different amides, nitrosamines and nitramines (Bråten et al. 2009). Aldehydes such as formaldehyde and acetaldehyde are intermediate products with life times less than 3 days and will not be considered here.

3.1 Amides

Formamide and acetamide have been highlighted as end products of atmospheric degradation of amines. Formamide, also known as methanamide, is an amide derived from formic acid. It is a clear liquid which is miscible with water and has an ammonia-like odour. It is used primarily for manufacturing sulfa drugs and synthesising vitamins and a softener for paper and fiber (http://en.wikipedia.org/wiki/Formamide. Acetamide, also known as ethanamide, is a white crystalline solid in pure form. It is produced by dehydrating ammonium acetate and use as a plasticizer and in the synthesis of many organic compounds. However, amides are also a part of chemical processes in nature, e.g. in hormones (Defur 2004).

3.1.1 Effects on vegetation

We found no information on effects of formamide on vegetation. However, acetamide and several other amides and amide-derivates are used as components in herbicides to control undesired vegetation especially in agriculture (Zhao et al. 2005; Buhler et al. 1994; Belinelo et al. 2001). Acetamide applied to centipedegrass (*Eremochloa ophiuroides*) leads to seedhead depressions (Johnson 1993), and Ikuenobe et al. (1994) found that an acetamide containing product ("metolachor") significantly reduced both the number of regenerating weeds and weed biomass of cowpea (*Vigna unguiculata*). In nature, allelopatic plants, such as black nightshade (*Solanum nigrum*) produce amides that inhibit the growth of nearby plants (Henriques et al. 2006). Thus it seems like amides act as a negative plant growth regulator. The amount of amides in plants is also affected by the supply of nitrogen to the ecosystem (Sahulka 1962).

3.1.2 Effects on fauna

We found no information on effects of formamide on terrestrial fauna. However, different types of acetamides are toxic to rats, hamsters and humans, including carcinogenicity, reproductive and developmental toxicity (Pienta 1980; Lundberg 1992; Kegley et al. 2008). Acetamide gave a weak mutagenic effect in *Drosophila* flies (Batiste-Alentorn et al. 1995). Historically invertebrates have been excellent models for testing toxic chemicals (Defur 2004), and several amides are known as insecticides affecting the larval stage (Miranda et al. 2003; Vanin et al. 2008).

3.2 Nitrosamines

Nitrosamines are chemical compounds of the chemical structure (R1)(R2)N-N=O, where R1 and R2 can be an alkyl or aryl group. Nitrosamines are produced from nitrites and secondary amines and are found in many foodstuffs, in tobacco smoke and latex products. Harmful effects are mainly related to animals and humans (see also Låg et al. 2009b).

3.2.1 Effects on vegetation

We did not find any information in literature on effects of nitrosamines on terrestrial plants and vegetation.

3.2.2 Effects on fauna

Nitrosodimethylamine (NDMA) is the simplest dialkylnitrosamine. It does not bio-accumulate. Based upon laboratory studies in which tumours have been induced in all species examined at relatively low doses, NDMA is clearly carcinogenic. There is an overwhelming evidence that NDMA is mutagenic and clastogenic. The lowest tumorigenic dose for the development of hepatic tumours in male and female rats exposed to NDMA in the critical study was 34 µg/kg body weight per day for the development of biliary cystadenomas in female animals. This equates to a unit risk of 1.5×10^{-3} per µg/kg body weight (Liteplo et al. 2002). Frogs (*Rana temporaria*) were exposed to 5 mg NDMA/litre in water for 63 days and 203 days. In both studies, the frogs developed hepatocellular carcinomas as well as adenomas and tumours of the haematopoietic system (Khudoley 1977). Khudoley & Picard (1980) believed that amphibians were more sensitive (shorter latency period and higher tumor incidence) than fish to the carcinogenic effects of the nitrosamine.

Comparable experiments in 20 species of mammals, reptiles, birds, amphibians and fish treated with nitrosodiethylamine (NDEA) were performed by Lijinsky (1993). The animals received approximately 1000 mg/kg body weight (400-2500 mg/kg) lifetime dose. Animals with lifespan varying from 3 years (mouse) to > 50 years (snake) developed tumors with latent periods of roughly 1 year, showing no relationship to lifespan. Carcinogenic effects have also been reported from experiments with rats (Lijinsky & Kovatch 1993). Here nitrosamines (derived from piperazine) with doses of 5.2 mg twice a week for 36 weeks resulted in tumors in the bladder. Rats treated with 40 mg twice a week, all died by week 59.

3.3 Nitramines

Effects of nitramines from explosives have been studied in connection with release to the environment from U.S. Army Ammunition Plants and other military facilities, reviewed by Talmage et al. (1999). This concerns nitroaromatic compounds such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5-tetrazocine (HMX) and associated by-products and degradation products.

RDX is a crystalline high explosive used extensively by the military in shells, bombs and demoliation charges. HMX is a colourless, crystalline solid and is a component of plastic explosives, solid fuel rocket propellants and military munitions.

3.3.1 Effects on vegetation and soil

Data from several studies indicate that RDX can be taken up by plants, increasing the concentration in stems and leaves (e.g. Harvey et al. 1991; Simini et al. 1992; Cataldo et al. 1993). Biomass of plants exposed to 100 and 200 mg/kg was significantly reduced, and plant height was found weakly correlated with a decrease in plant height (Simini et al. 1992, 1995). From this study the screening benchmark for plants and soil were set to 100 mg/kg. No studies were found that tested the toxicity of HMX to terrestrial plants.

RDX and HMX contamination of soils results from spills, wastes in land fills and open burning/dentonation operations. The biodegradation of RDX has been studied under both aerobic and anarerobic conditions. The data suggest that RDX is resistant to aerobic biodegradation while biodegradation take place under anaerobic conditions (McCormick et al. 1981; Osmon & Klausmeier 1972; Spanggord et al. 1980, 1983). In water HMX biodegrades under both aerobic and anaerobic condition (Spanggord et al. 1983).

3.3.2 Effects on fauna

RDX is known to have an effect on the central nervous system of mammals (USEPA 1989). In addition to neurotoxicity, effects on the blood, kidney, liver, eyes have been observed. However, most evidence indicates that RDX is not teratogenic or carcinogenic. The chronic NOAEL (no-observed-adverse-effect level) of wildlife species varies between 1.1 and 8.7 mg/kg/d (Talmage et al.

1999). The review of Talmage (1999) found no studies on toxicity of RDX to birds. However, earthworms were found slightly affected by RDX (Simini et al. 1995; Phillips et al. 1993).

HMX is toxic to some terrestrial organisms including mice and rats (Everett et al. 1985; Everett & Maddock 1985), and the chronic NOAEL for wildlife species varies between 0.3 and 3.3 mg/kg/d (Talmage et al. 1999). A large data gap however exists in the terrestrial ecotoxicology for HMX. Although HMX toxicity to soil invertebrates such as earthworms, enchytraeid and collembolan is relatively well-documented (Philips et al. 1993; Robidoux et al. 2001, 2004; Schäfer & Achazi 1999), no studies have been found so far that tested its toxicity to avian species, terrestrial plants and microorganisms (cf. Talmage et al. 1999). HMX hardly influenced soil microorganisms, whereas RDX only showed slightly significant effects (Gong et al. 2001, 2002).

The polycyclic nitramine CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) was not found lethal to the earthworm *Eisenia andrei* at 90.7 mg/kg in sandy loam soil with pH 5.1. However, low concentrations of CL-20 (0.1 mg/kg) were found to reduce fertility of earthworms (Robidoux et al. 2004).

Carcinogenic action of dimethylnitramine (DMNO) , diethylnitramine (DENO) and dibuthylnitramine (DBNO) has been found on various animal species studied. DMNO dissolved in aquarium water at a dose of 5 ppm induced tumors in 18 out of 40 and 6 out of 18 frogs respectively. Another amphibian species, *Xenopus*, showed similar sensitivity of DMNO action. 200 ppm of DBNO in tap water induced hyperplastic lesions on the urinary bladder and DENO produced liver tumors in 2 of 5 rats (Pliss et al. 1982).

Rats were treated with 1 mmol/kg x week and 0.5 mmol/kg x week of N-nitrodimethylamine (NTDMA) or N-nitromethylamine (NTMA). It induced mainly tumors of the nasal cavity, neurinoma of the spine, spinal nerves and peripheral nerves. NTMA was slightly less potent than the dimethyl compound, and females were less susceptible than males to the carcinogenic action of the nitramines (Scherf et al. 1989).

4 Main effects of amines on ecosystems - eutrophication of habitats

4.1 Eutrophication – a negative effect on ecosystems

Based on the literature review the amines and their degradation products will most likely enter the nitrogen cycle of the ecosystems. The additional nitrogen will increase the availability of inorganic nitrogen in the top-soil and will be taken up by the vegetation and finally lead to increased plant growth and loss of biodiversity. This eutrophication process caused by airborne nitrogen is recognized as one of the most important threats to European biodiversity (EEA 2003) and expert opinions consider that nitrogen deposition will be the third greatest driver of biodiversity loss at global scale (after land use and climate) over the coming century (Sala et al. 2000).

Nitrogen is the limiting nutrient for plant growth in many terrestrial ecosystems and has the potential to increase net primary productivity which in turn leads to reduced diversity of terrestrial ecosystems (Stevens et al. 2006). Effects can be related to changes in plant species composition, plant growth (especially increased grass and herb dominance, decrease in mosses and lichens), biomass productivity, litter production, nitrogen availability, soil nutrients, soil acidification and mycorrhiza infection, which again might affect the soil fauna (e.g. Bobbink et al. 1988). Increased grass/herb dominance will probably favour grazers of invertebrates, birds and mammals, and altered competition may lead to changes in animal populations and species composition. Change in prey populations may also lead to changes in the populations of birds of prey and carnivores.

4.2 Critical loads of nitrogen (levels where N might be harmful to ecosystems)

Effects on the ecosystems depend on the total amount on nitrogen deposited as wet and dry deposition. The effects on ecosystems are described under the "critical load" concept. It states that the critical load of a pollutant (CL) is the deposition load an ecosystem can endure without significant harmful effects, according to present knowledge (Nilsson & Grennfelt 1988). CLs for nitrogen on terrestrial ecosystems have been developed as a step towards a sustainable air pollutant control policy where conservation of ecosystems is highlighted. The CLs for nitrogen are assessed under the Convention on Long-range Transboundary Air Pollution (LRTAP/UNECE) and described for European habitats in Achermann & Bobbink (2003).

CLs for Norwegian habitats are given as a range of values dependent on precipitation, temperature, soil richness and management (Table 1). However, these loads are mainly based on empirical studies carried out in United Kingdom, middle Europe and Sweden under different environmental conditions to those in the Norwegian habitats. Thus the Norwegian critical loads may vary from the international agreed values. The lowest critical values in Norway are set to 5 kg/ha/yr, e.g. for alpine- and arctic heathlands, bogs and oligotrophic softwater lakes, probably also boreal forests.

Table 1: Empirical critical loads for nitrogen deposition (kg N/ha per year) to Norwegian habitats. Possible effects of exceedance, based on Achermann & Bobbink (2003). Classification of habitats according to EUNIS habitat classification for Europe. ## reliable, # quite reliable, (#) expert judgement.

Ecosystem	Habitat	kg N/ha per year	Effects
Forest* (G)	G1 Broad leaved deciduous woodland G3 Coniferous woodland G4 Mixed deciduous and coniferous woodlands	10-20 #	Changes in soil processes, ground vegetation, mycorrhiza, increased risk of nutrient imbalances and susceptibility to parasites.
Mire (D)	D1 Raised bogs and blanket bogs	5-10 ##	Changes in species composition, N saturation of *Sphagnum*
	D2.2 Poor fens	10-20 #	Increased sedges and vascular plants, negative effect on peat mosses
	D4.1 Rich fens	15-35 (#)	Increased tall graminoids, decreased diversity
Culture landscape	E Grassland and tall forb habitats	10-30 (#)	Increased tall grasses, decline in diversity, increased mineralization, N leaching, decreased bryophytes and lichens
	Coastal heathland (F4.11 Northern wet heaths, F2 Dry heaths)	10-20 ##	Decrease in heather dominance, decline in lichens and mosses, transition of heather to grassland
Alpine and arctic vegetation (F, E)	F2 Arctic, alpine and subalpine scrub habitats, E4.2 Moss and lichen dominated mountain summits	5-15 (#)	Decline in lichens, mosses and evergreen shrubs
	E4.3, E4.4 Alpine and subalpine grasslands	10-15 (#)	Increase in nitrophilous graminoids, biodiversity change
Inland surface water (C)	C1.1 Permanent oligotrophic waters	5-10 ##	Isoetid-species negatively effected, increased biomass and and rate of succession
Coastal and marine habitats (A, B)	B1 Coastal dune and sand habitats	10-20 (#)	Increased plant production, increase N leaching, increase of tall grasses, accelerated succession
	A2.6 Coastal salt marshes and saline reedbeds	30-40 (#)	Increase late-successional species, increased productivity

* New research from Sweden has shown that nutrient poor boreal forests might have a critical load as low as 500 mg N/m^2 per year (Strengbom et al. 2003; Nordin et al. 2005). This load is also proposed as the lower critical load for forests in Scandinavia by a work group under ECE (Economic commision for Europe). Effects of amines depend on the background N-deposition

The major source of airborne nutrients to Norwegian terrestrial ecosystems is long-range transboundary atmospheric nitrogen from fossil fuel combustion and agriculture, shown by a decreasing N deposition from south (21 kg/ha/yr) to the north of Norway (2 kg/ha/yr) (Hole & Tørseth 2002). However, local emissions e.g. from Norwegian oil industry and shipping also contribute to the current background deposition along the Norwegian coast. The deposition of nitrogen has been relatively constant during the last 30 years with a decline of 4 % from 1997 to 2001, compared with the period from 1978 to 1982. However, new models points towards a substantial increase of 30% or more in nitrogen deposition over western Norway as a consequence of increasing precipitation related to climatic change, and oxidised nitrogen increases more than the deposition of reduced nitrogen (Hole & Engardt 2008).

Combining the background deposition and the CLs for nitrogen of habitats, there is to day an exceedance of the CL for several habitats in the southern and middle parts of Norway, and several areas are at risk for entering eutrophication processes. Enhanced nitrogen deposition from amine emission from a CO_2 capturing plant will probably affect habitats where the CL is already exceeded or on the way to be exceeded. Thus the effects from additional nitrogen from amines and their degradation products used in the CO_2 capturing process depend on the background deposition at the sites, and even small concentrations of amines may thus be harmful to the ecosystem.

5 Main conclusions

5.1 Effects of the main amines on vegetation

We found no information on direct toxicity of MEA, MDEA, AMP and Piperazine to terrestrial plants and vegetation. However, sprayed onto plants amines act as a plant bio-regulator, increasing plant growth and seed yield and reduces plant stress. Amines biodegrades in soil and soil water into nitrogen components available for plant growth. Thus the main affect of amines is probably related to eutrophication of plant communities. Based on the available literature we can not range the amines with regard to the eutrophication potential. However, if the amines are completely degraded, it is possible that the eutrophication potential is equal to the number of nitrogen deposited.

In areas with high nitrogen background deposition habitats sensitive to nitrogen enrichment might be affected. Effects can be related to changes in plant species composition, plant diversity, plant growth, biomass productivity, litter production, nitrogen availability, soil nutrients, soil acidification and mycorrhiza infection, which indirectly might affect the fauna.

5.2 Effects of degradation products on vegetation

Very little is known on effects on terrestrial vegetation of the degradation products amides, nitrosamines and nitramines. However, amides are known to be growth restrictive and are widely used in herbicides.

5.3 Effects of the main amines on fauna

There is also very little information on effects of relevant amines used for CO_2 removal on terrestrial free-living fauna. Laboratory experiments on animals, related to human health risks, show that all relevant amines are irritating to skin and also toxic at high concentrations with almost the same oral LD50. However, none of the amines have been reported to be carcinogenic or gentoxic. These experimental results may also apply for free-living terrestrial animals. Based on the data available it is difficult to range the amine's toxicity effect on free-living fauna. However, piperazine has been found highly toxic to dung beetle and partly to water invertebrates. It can also interact with nitrosating agents in vivo to form nitrosamines with possible carcinogenic risk. Thus piperazine might be the most unfavourable amine to fauna.

5.4 Effects of degradation products on fauna

The degradation products amides, nitrosamines and nitramines are known to be toxic to mammals and soil invertebrates, and they might also affect soil microorganisms. Especially nitrosamines and nitramines are found carcinogenic to mammals.

5.5 Needs for new knowledge on effects on the ecosystem

In lack of relevant data in the literature there is a need for an experimental approach to test the effects of amines used for the CO_2 capturing process on the soil ecosystem and to find at what concentration they might be harmful. This should be carried out as an amine spraying experiment in a selected habitat known to be sensitive to nitrogen enrichment. One should focus on the effects of eutrophication of the main amines to be used in the CO_2 capturing process (one or more of the amines MEA, MDEA, AMP and Piperazine) on vegetation, soil processes and soil fauna.

Specifically one should address three sub-goals:

- Assess the effects on vegetation from direct exposures and indirect effects related to nitrogen eutrophication from different amines, and to find at what concentrations they will affect the ecosystem (the critical load concept)
- Analyse the degradation and nutrient cycling of one or more amines in soil in order to clarify the end products available for plants and soil fauna
- Assess direct harmful effects on soil fauna by primary amine exposures and indirect effects from possible changes in vegetation and soil properties

It would also be important to carry out eco-toxicological tests on selected terrestrial fauna in controlled laboratorial environments, using relevant doses of amines and their degradation products.

Such projects will produce new knowledge important for the sustainable use and management of habitats and species that are vulnerable to airborne nitrogen pollution. It will stimulate Norwegian environmental research and strengthen the international collaboration on issues related to effects of air pollution on ecosystems. The main output will be better understanding of the effects of amines and their degradation products on northern species and ecosystems, and the actions that need to be taken by stakeholders to preserve the important component of the biodiversity of northern Europe.

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TITLE Effects on terrestrial vegetation, soil and fauna of amines and possible degradation products relevant for CO2 capture A review	PROJECT LEADER Svein Knudsen NILU PROJECT NO. N-108068
AUTHOR(S) Per Arild Aarrestad and Jan Ove Gjershaug	CLASSIFICATION * A CONTRACT REF. Erik Gjernes, Gassnova SF Merethe Sjøvoll, StatoilHydro ASA, Rehan Naqvi, Shell Technology Norway AS

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ABSTRACT
This report gives an overview of the minor knowledge that exists on effects of amines, used in capturing carbon dioxide, and their main degradation products on terrestrial vegetation and fauna. Amines such as MEA, MDEA, AMP and Piperazine and several of their degradation products act as growth stimulating medium for plants, and most biodegrade easily in soils to plant available nitrogen. Deposited in the environment they might contribute to eutrophication of terrestrial ecosystems, leading to increased growth of grasses, reduced plant diversity and changes in soil nutrients and soil fauna. Amines are skin-irritating and toxic to animals at high concentrations, and several of their degradation products, such as nitrosamines and nitramines, are known to be carcinogenic to mammals, reptiles and amphibians, probably also toxic to soil fauna and soil microorganisms. Piperazine is probably the most unfavourable amine. There is a great need for new research on environmental effects of relevant amines and their degradation products in order to run carbon dioxide capture plants with minor negative effects on the environment.

NORWEGIAN TITLE
Effekter fra aminer på terrestrisk vegetasjon, jord og fauna og mulige nedbrytningsprodukter som er relevante for CO_2-fangst.

KEYWORDS

CO_2 capture	Amines	Ecotoxicology

ABSTRACT (in Norwegian)
Denne rapporten gir en oversikt over den kunnskap som fins om effekter av aminer benyttet ved rensing av karbondioksid og av deres nedbrytningsprodukter på terrestrisk vegetasjon og fauna. Aminer som MEA, MDEA, AMP og Piperazine og flere av deres nedbrytningsprodukter virker vekststimulerende på planter. De fleste omdannes i jordsmonnet gjennom biologiske prosesser til plantetilgjengelig nitrogen. Avsatt i naturen vil aminer således kunne føre til eutrofiering av økosystemer med økt grasvekst, redusert plantediversitet og endringer i jordsmonn og jordfauna. Aminer virker irriterende på hud og er giftige for dyr ved høye konsentrasjoner. Flere av deres nedbrytningsprodukter, som nitrosaminer og nitraminer, er kjent for å være kreftfremkallende for pattedyr, krypdyr og amfibier, og muligens også giftige for jordfauna og mikroorganismer. Av de vurderte aminene er Piperazine trolig den som er mest ugunstig for fauna. Kunnskapen er imidlertid liten, og det er behov for mer forskning på effekter av aminer og deres nedbrytningsprodukter med tanke på en miljøvennlig rensing av karbondioksid.

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