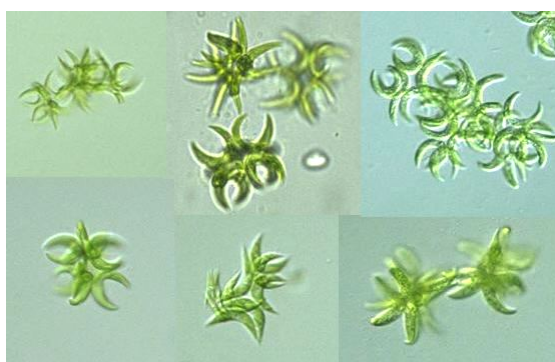




The toxicity of selected primary amines and secondary products to aquatic organisms:
A review



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Abstract

This is a review of the current available literature on the ecotoxicity of selected primary amines and secondary products to freshwater animals and plants. This review is not a comprehensive list of amine toxicity, but focuses on the toxicity of compounds that will be potentially emitted to the environment by the process of CO₂ capture using selected amine compounds (MEA, MDEA, AMP, PIPA). The main secondary products include amides (formamide and acetamide), nitrosamines and nitramines. In some cases ecotoxicity data on the specific chemicals are limited or unavailable. Of the data that are available the most sensitive response to amine exposure was found in chronic studies with fish and algae with a LOEC of 0.5 mg/L MDEA and 0.75 mg/L MEA respectively. For nitrosamines, the most toxic effect was found in algae with a LOEC of 0.025 mg/L NDMA, which was the lowest effect concentration found for all compounds and test species. The highest toxicity of nitramines was found at 0.2 mg/L and 0.4 mg/L CL-20 in fish and invertebrates, respectively. Due to the limited data available for many of the chemicals, high assessment factors were applied based on the EU technical guidance document on risk assessment (ECB, 2003). Using the simple risk assessment equation (PEC/PNEC = RF), it was estimated that environmental concentrations that exceed the following threshold concentrations could potentially cause environmental harm (i.e. 7.5 µg/L MEA, 20 µg/L AMP, 5 µg/L MDEA, 100 µg/L PIPA, 24 µg/L amides, 0.025 µg/L nitrosamine, 0.2 µg/L nitramine). Nitrosamines and nitramines were the most toxic with the highest risk for causing environmental harm. However, most of the toxicity data for these two groups was not for the specific chemicals calculated in Task 3, but rather inferred toxicity from related compounds. Therefore, future ecotoxicity work should focus on these specific, potentially high risk chemicals for which there are no ecotoxicity data currently available.

4 keywords, Norwegian	4 keywords, English
1. CO ₂ fangst	1. CO ₂ capture
2. Risiko analyse	2. Risk assessment
3. aminer	3. amine
4. nitrosaminer	4. nitrosamine


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CO₂ and Amines

**The toxicity of selected primary amines and
secondary products to aquatic organisms**

A review

Preface

CO₂ capture and storage has been proposed for the two Norwegian gas-fired power plants as a means of reducing CO₂ emissions to the atmosphere and thus reducing the main driver of global warming. A leading technology for CO₂ capture uses amines. In this process a small fraction of the amines is lost in the stack gas and emitted to the atmosphere. Secondary products such as amides, nitrosamines and nitramines may be formed in the CO₂ capture process, the stack gases and in the atmosphere. A consortium of Norwegian research institutes led by the Norwegian Institute for Air Research (NILU) has conducted a literature study of the possible adverse environmental impacts of these emissions to air. The work was supported by StatoilHydro, Shell Technology Norway, Gassnova A/S and the Research Council of Norway (CLIMIT programme). This report is a review of the current available literature on the ecotoxicity of selected primary amines and secondary products to freshwater animals and plants. In cases where no data for freshwater organisms were found, equivalent data for marine organisms were included where available.

Oslo, November 2008

Richard F. Wright

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Summary

The following report is a review of the current available literature on the ecotoxicity of selected primary amines and secondary products to freshwater animals and plants. In cases where no data for freshwater organisms were found, equivalent data for marine organisms were included. This review is not a comprehensive list of amine toxicity, but focuses on the toxicity of compounds that will be potentially emitted to the environment by the process of CO₂ capturing using selected amine compounds (MEA, MDEA, AMP, PIPA). The main secondary products include amides (formamide and acetamide), nitrosamines and nitramines. This report has highlighted some areas where ecotoxicity data on the specific chemicals are limited or unavailable. Of the data that are available the most sensitive response to amine exposure was found in chronic studies with fish and algae with a LOEC of 0.5 mg/L MDEA and 0.75 mg/L MEA respectively. For nitrosamines, the most toxic effect was found in algae with a LOEC of 0.025 mg/L NDMA, which was the lowest effect concentration found for all compounds and test species. The highest toxicity of nitramines was found at 0.2 mg/L and 0.4 mg/L CL-20 in fish and invertebrates respectively. Due to the limited data available for many of the chemicals, an uncertainty factor of 1000 was applied. Using the simple risk assessment equation ($PEC/PNEC = RF$), it was estimated that environmental concentrations that exceed the following threshold concentrations could potentially cause environmental harm (i.e. 500 ng/L amines; 1200 ng/L amides, 200 ng/L nitramine, 25 ng/L nitrosamine). It was concluded that nitramines and nitrosamines were the most toxic with the highest risk for causing environmental harm. However, most of the toxicity data for these two groups was not for the specific chemicals calculated in Task 3, but rather inferred toxicity from related compounds. Therefore, it is suggested that future ecotoxicity work should focus on these specific, potentially high risk chemicals for which there are no ecotoxicity data currently available.

1. Glossary

AMP	2-amino-2methylpropanol
CL-20	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
EC50	Effect concentration at which 50% of the population are effected
FW	Fresh water
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
IC50	Inhibition concentration at 50% inhibition
LC50	Lethal concentration at which 50% of the population are killed
LOEC	Lowest observable effect concentration
MDEA	Methyldiethanolamine
MEA	Ethanolamine
NDEA	N-nitrosdiethylamine
NDMA	N-nitrosodimethylamine
NDPA	N-nitroso-diphenylamine
NOEC	No observable effect concentration
NPYR	N-nitrosopyrrolidine
PEC	Predicted environmental concentration
PIPA	Piperazine
PNEC	Predicted no effect concentration
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RF	Risk factor
SW	Sea water

2. Scope of work

The following is a review of the current literature on the toxicity of selected primary amines and secondary products to freshwater organisms. In cases where no data for freshwater organisms were found, equivalent data for marine organisms were included. This review is not intended to be a comprehensive list, but focuses on the primary amine compounds that will be considered for use in carbon dioxide (CO₂) sequestration. These amine compounds include:

CAS number:

- | | |
|----------------------------------|----------|
| 1) Ethanolamine (MEA) | 141-43-5 |
| 2) 2-amino-2methylpropanol (AMP) | 124-68-5 |

- 3) Methyldiethanolamine (MDEA) 105-59-5
 4) Piperazine (PIPA) 110-85-0

In addition, the atmospheric degradation of these compounds following their use in the CO₂ capturing process within a gas fuelled power station was calculated by the University of Oslo in Task 3. The stable compounds following atmospheric degradation of the main amines are listed in table 1. These compounds include acetamide(s), formamide(s), nitrosamines and nitramines.

Table 1. List of the stable compounds following atmospheric degradation of the four selected amines (i.e. MEA, AMP, MDEA, PIPA) (Information from Task 3).

Compound	Formula	CAS number
Acetamide	C ₂ H ₅ N O	60-35-5
Formamide	C H ₃ N O	75-12-7
Ethyl, 2-hydroxy-1-oxo-	C ₂ H ₄ O ₂	107031-65-2
N-methylene-Methanamine	C ₂ H ₅ N	1761-67-7
Formamide, N-Formyl-N-Methyl-	C H ₃ N O	75-12-7
Formamide, N,N-Dimethyl-	C ₃ H ₇ N O	68-12-2
Acetamide, N-Methyl-	C ₂ H ₇ N O	79-16-3
Acetamide, N,N-Dimethyl-	C ₄ H ₉ N O	127-19-5
Formamide, N,N-Diethyl-	C ₅ H ₁₁ N O	617-84-5
Acetamide, N,N-Diethyl-	C ₆ H ₁₃ N O	685-91-6
Nitramines & Nitrosamines		
Methanamine, N-Nitroso-	C H ₄ N ₂ O	64768-29-2
Methanamine, N-nitro-	C H ₄ N ₂ O ₂	598-57-2
Methanamine, N-Methyl-N-nitroso-	C ₂ H ₆ N ₂ O	62-75-9
Methanamine, N-Methyl-N-nitro-	C ₂ H ₆ N ₂ O ₂	4164-28-7
Methanol., (methylnitroamino)-	C ₂ H ₆ N ₂ O ₃	32818-80-7
Ethanamine, N-ethyl-N-Nitroso-	C ₄ H ₁₀ N ₂ O	55-18-5
Ethanamine, N-ethyl-N-Nitro-	C ₄ H ₁₀ N ₂ O ₂	7119-92-8

A literature search of the known ecotoxicological effects of these compounds to freshwater organisms has been carried out and data presented where available. However, for many of the compounds listed in **Table 1** no toxicity data were available. In these instances data have been included for the model compounds within each of the main groups in order to infer toxicity from similar related compounds. For example, nitramine toxicity data were available for the monocyclic nitramines RDX and HMX, and polycyclic nitramine CL-20, all of which are used by the military as explosives.

3. Concentrations of selected amines and nitrosamines in freshwater

Data on the concentrations of amine and nitrosamine compounds in freshwater are limited. Due to the hydrophilic nature of these compounds there will be a tendency for them to remain in solution rather than partition into other phases such as animal tissues or sediments. However, due to the short half-life of amines in water (days to weeks); the concentrations of these compounds in freshwaters are often low or undetected. The data that were available have been compiled in **Table 2**. For the four selected amines no environmental data were found. Data were found for two other amine compounds (piperidine & pyrrolidine) with maximum river water concentrations of 9 µg/L (Neurath et al. 1977).

Table 2. Amines and nitrosamine concentrations in the aquatic environment

	Compound	Concentration	Reference
Amines	MEA, MDEA, AMP, PIPA	No data available	
	Piperidine	Up to 9 µg/L in (river water)	Neurath et al., 1977
	Pyrrolidine	0.9–2.5 µg/L (river water) 14 µg/L (primary effluent) 6 µg/kg (Cod eggs)	Neurath et al; 1977 Scully et al., 1987 Hamano et al; 1981
Amide	Acetamide	31 µg/L (landfill leachate)	Yasuhara et al., 1993
	Formamide	2 mg/L (effluent water)	US EPA, 1981
Nitrosamines	N-nitrosodi-n-propylamine	0.12-2.8 µg/L (waste water)	IARC, 1978
	N-nitrosopyrrolidine	0-3 µg/kg (UK fish) 2-37 µg/kg (HK fish) 0.09-0.02 µg/L (effluent water) 1.3-4.2 µg/L (sewage sludge)	IARC, 1978 IARC, 1978 IARC, 1978 Mumma et al., 1984
	N-nitrosodimethylamine (NDMA)	10 ng/L (US drinking water)	(Najm & Trussel, 2001, Mitch et al. 2003a)
Nitramine	RDX	Ground water: 9-100 µg/L US Army ammunition plant (AAP) 20-780 µg/L Milan AAP 1.9 mg/L Milan AAP Surface water: 0.1-0.15 mg/L US APP Up to 109 mg/L near Milan APP	Spalding et al., 1988 Ryon et al., 1984 Best et al., 1999 Small & Rosenblatt, 1974 Ryon et al., 1984
	HMX	Ground water: up to 208 µg/L	Lewin et al., 1997

For nitrosamines, river water concentrations of N-nitrosopyrrolidine were found up to 0.02 µg/L, and they have been found as high as 37 µg/kg in fish tissues from Hong Kong (IARC, 1978). N-nitrosodimethylamine (NDMA) has been detected in drinking water in California, USA at a concentration of 10 ng/L (Najm & Trussel, 2001; Mitch et al., 2003a). This concentration was found downstream from a highly treated municipal waste effluent and was above the regulatory guidelines on NDMA concentrations in drinking water in the State of California (i.e. 8 ng/L, Najm & Trussel, 2001, Mitch et al. 2003a).

High environmental concentrations of nitramines (RDX and HMX) have been found in both ground and surface waters near to army ammunition plants. Concentrations as high as 109 mg/L and 208 µg/L have been reported for RDX and HMX respectively (Ryon et al., 1984; Lewin et al., 1997). This is due to the frequent use of both RDX and HMX as an important ingredient in explosives.

4. Acute toxicity of primary amines and secondary products to aquatic species

The application of both acute and chronic toxicity tests is an effective tool commonly used by regulators and scientists for assessing the potential risk of environmental chemicals to aquatic organisms. Acute effects tend to measure the organism's response following short term exposure to relatively high concentrations, whereas chronic effects measure an organism's response to longer term exposures at lower and more-environmentally realistic concentrations. By combining both acute and chronic toxicity data, a better understanding of the potential toxicity of a wide range of compounds can be achieved. This approach can also improve the reliability of the environmental risk assessment for a particular chemical. In the current review, chronic toxicity data were taken from tests that reported exposure durations of greater than six days.

An important consideration when evaluating the data is that toxicity tests are often carried out in controlled laboratory environments with single compounds. Consequently, such measurements can only provide information on the environmental risk of a specific compound, since environmental interactions including synergistic and/or antagonistic effects with other naturally occurring and/or anthropogenic compounds can not be accounted for.

The selected compounds within this review have been classified into the four main compound groups including; amines, amides, nitrosamines, and nitramines. However, it is important to note that the

physico-chemical properties of the compounds within these groups can differ markedly from each other, which in turn can have significant effects on the compounds toxicity. For example, differences in the partition coefficients between compounds can influence the bioavailability and toxicity to aquatic organisms. The absence of physico-chemical data for the compounds, particularly for nitrosamines and nitramines, prevents the chemicals from being grouped in this way. It is suggested that the chemical toxicity value generated for each group should only be taken as a guideline in cases where the toxicity data for the specific compound(s) is not available.

The main emphasis of the review is targeted towards freshwater species, although data are also presented on marine species, particularly in cases where data for freshwater organisms were not available. The ecotoxicity data are separated into the main organism groups including fish, invertebrates and algae/bacteria. The difference in toxicity between these groups has been evaluated. The absence of ecotoxicological data from the following tables can be used to highlight knowledge gaps and to identify potential areas for further work for an improved risk assessment.

4.1 Fish – Acute toxicity

The acute toxicity of amines to freshwater fish is shown in **Table 3**. A wide range of toxicity values were recorded for the four selected amine compounds. For MEA, the early life stage (eggs) of the Zebra fish (*Danio danio*) were the most sensitive with a 96h LC50 of 60.3 mg/L MEA. For adult fish, the LC50 concentrations ranged from 167 mg/L in the rainbow trout (*Salmo gairdneri*) to 375 mg/L in Western Mosquito fish (*Gambusia affinis*). Only one data point was available for AMP toxicity to fish with an estimated EC50 concentration >100 mg/L. For MDEA, high 96h LC50 values were reported in the Orfe (*Leuciscus idus*) ranging from 100 to 2200 mg/L. The lowest LC50 concentration for all amines was reported in Carp (Cyprinidae) following exposure to PIPA, with an LC50 of 52 mg/L (Loeb & Kelly, 1963).

The acute toxicity of the amides, formamide and acetamide to freshwater fish revealed extremely high LC50 values. The LC50 of formamide ranged between 10,000 to 26,300 mg/L in the adult carp and Western mosquito fish (Juhnke & Luedemann, 1978; Wallen et al. 1957).

The available toxicity data of nitrosamine to freshwater fish showed a large range of LC50 concentrations. The most sensitive response was shown in the Blue gill (*Lepomis macrochirus*) with a 24h LC50 of 5.85 mg/L following exposure to N-nitroso-diphenylamine (NDPA, US EPA, 1978). However, the LC50 values of nitrosamines taken from other studies were markedly higher ranging between 775 to 3300 mg/L (Ferraro et al., 1977; Draper & Brewer, 1979).

Due to the absence of toxicity data for the nitramines listed in **Table 1**, model nitramine compounds HMX and RDX were chosen to represent the chemical group. These nitramines are used regularly by the military as an explosive; as a result a reasonably large amount of aquatic toxicity data were available.

The toxicity of RDX to three freshwater fish species ranged between an LC50 of 3.6 to 26 mg/L (Mukhi et al., 2005, Hovatter et al., 1997, Bentley et al., 1977). Similar levels of toxicity (16-32 mg/L) were also reported in the Fathead minnow (*Pimephales promelas*) following exposure to HMX (Bentley et al., 1977).

Overall, from the data collected, the acute toxicity of the primary amines and secondary products to the freshwater fish were ranked as nitramines>nitrosamines>amines>amides, with the lowest lethal concentration (96h LC50) recorded at 3.6 mg/L RDX in the Blue gill (*Lepomis macrochirus*).

4.2 Invertebrates – Acute toxicity

The acute toxicity of amines to freshwater invertebrates is shown in **Table 4**. For the four amine compounds the LC50 concentrations ranged between 10 and 250 mg/L, with the most toxic effect found in the water flea (*Daphnia magna*) when exposed to PIPA.

The acute toxicity of the amides (formamide and acetamide), revealed a wide range of LC50 values. The LC50 of acetamide for *D. magna* was 10,000 mg/L (Bringmann & Kuhn, 1977). For formamide a 48h LC50 concentration of 13 mg/L for *D. magna* was reported (Le Blanc & Surprenant, 1983), although a separate study found a 48h LC50 of 500 mg/L in the same species (EPA, 2004).

The available toxicity data for nitrosamines to freshwater invertebrates demonstrated a large range of LC50 concentrations. The most sensitive response was found in an unspecified Cladoceran species with a 48h LC50 of 7.76 mg/L following exposure to NDPA (US EPA, 1978). The 96h LC50 values for NDMA ranged from 300 mg/L in the amphipod, *Gammarus limnaeus* (Draper & Brewer, 1979) to 2250 mg/L in the Crayfish, *Austropotamobius pallipes* (Alibaud et al., 1985). For NDEA, 96h LC50 values ranged from 203 mg/L to 1490 mg/L with *A. pallipes* being the most sensitive invertebrate species measured (Alibaud et al., 1985).

The toxicity of nitramines to invertebrates was distinctly higher than for the other chemical groups. For the nitramine RDX, the most sensitive species measured was the water flea, (*Ceriodaphnia dubia*)

with a lowest observable effect concentration (LOEC) of 6.01 mg/L (Peters et al., 1991). The midge, (*Chironomus tentans*) had a 48h LC50 concentration of 15 mg/L (Hovatter et al., 1997).

4.3 Algae/bacteria – Acute toxicity

The acute toxicity of the selected amines to freshwater and marine algae and bacteria is shown in **Table 5**. For MEA, the LC50 concentrations ranged between 6 and 733 mg/L, with the bacteria (*Vibrio fischeri*) the most sensitive species (Sintef report, 2007; Libralto et al., 2007). This LC50 value of 6 mg/L MEA was the lowest effect concentration found for all four amine compounds, although similarly low LC50 values of 13 and 20 mg/L were found in *V. fischeri* as a response to PIPA and AMP exposure respectively (Sintef report, 2007).

The toxicity data for acetamide showed large variations in effect concentrations. The most sensitive toxicity value was reported in the Cryptomonad species (*Chilomonas paramecium*), with a 48h LC50 concentration of 49 mg/L (Bringmann et al., 1980). However, most other acetamide toxicity values were significantly higher with a LOEC value of 6,200 mg/L and 10,000 mg/L for the blue-green algae, *Microcystis aeruginosa*, and the green algae, *Scenedesmus quadricauda*, respectively.

Acute toxicity data for freshwater or marine algae/bacteria were not available for nitrosamine compounds and are thus not reported. The toxicity of the nitramines to the algae was higher than for the other chemical groups. For the nitramine RDX, a 96h LC50 value of 3.2-10 mg/L was measured in *M. aeruginosa*, and *S. quadricauda* respectively (Hovatter et al., 1997).

Table 3. Acute toxicity of selected primary amines and secondary products to freshwater fish. Data obtained from PAN and TOXNET databases, peer reviewed journals and web links.

Compound	Fish	EC/LC50 (mg/L)				LC100 24h	Source
		NOEC	24h	48 h	72h		
Amines							
MEA	Goldfish (<i>Carassius auratus</i>)		190			170	Birdie et al., 1979
	Western mosquito fish (<i>Gambusia affinis</i>)		375	360	350	338	Verschueren, 2001
	Blue gill (<i>Lepomis macrochirus</i>)		338	366	346	300-329	Verschueren, 2001
	Rainbow Trout (<i>Salmo gairdneri</i>)		175	150		167	Mayer et al., 1986
	Zebra fish - eggs (<i>Danio rerio</i>)	20				60.3	100 Groth et al. 1993
AMP	Fish sp, (not specified)	100				>100	Web Link 1
MDEA	Fathead minnow (<i>Pimephales promelas</i>)					1200	Web Link 2
	Fathead minnow (<i>Pimephales promelas</i>)					1000	Web Link 3
	Orfe (<i>Leuciscus idus</i>)					100-2200	Web Link 3
PIPA	Carp (<i>Cyprinidae</i>)				52-159		Loeb & Kelly, 1963
	Guppy (<i>Poecilia reticulata</i>)	100				>100	Web Link 4
Amides							
Acetamide	Western mosquito fish (<i>Gambusia affinis</i>)		26,300	26,300		13,300	Wallen et al. 1957
	Carp (<i>Cyprinidae</i>)			10,000			Juhnke & Luedemann, 1978
Formamide	Fathead minnow (<i>Pimephales promelas</i>)					5,000-10,000	EPA, 2004. doc: 201-15159A
Nitrosamines							
NDPA	Blue gill (<i>Lepomis macrochirus</i>)		5.85				US EPA, 1978
	Mummichog (<i>Fundulus heteroclitus</i>)		3,300*				Ferraro et al., 1977
NDMA	Rainbow Trout (<i>Salmo gairdneri</i>)					1770	Verschueren, 1996
	Fathead minnow (<i>Pimephales promelas</i>)					940	Draper & Brewer, 1979
NDEA	Fathead minnow (<i>Pimephales promelas</i>)					775	Draper & Brewer, 1979
Nitramines							
RDX	Blue gill (<i>Lepomis macrochirus</i>)					3.6	Bentley et al., 1977
	Zebra fish (<i>Danio rerio</i>)	13-15				23-26	Mukhi et al., 2005
	Rainbow Trout (<i>Salmo gairdneri</i>)					3.6-13	Hovatter et al., 1997
HMX	Fathead minnow (<i>Pimephales promelas</i>)					15-32	Bentley et al., 1977

Web Link (WL) 1. <http://www.jtbaker.com/msds/englishhtml/a4572.h>

* seawater species

WL 2. http://www.optimal.com.my/pdf/Gas_Treating_Ethanolamines/MDE01_MDEA.pdfWL 3. <http://www.elementis-specialties.com/index.asp?fuseaction=Industries.getwercs&ProductCode=10898&Lang=EN&SubFormat=ANSI>WL 4. http://www.ethyleneamines.com/NR/rdonlyres/0F711045-D7C1-4979-8286-032FF5C01636/0/PIP_Anh.pdf

Table 4. Acute toxicity of selected primary amines and secondary products to aquatic invertebrates. Data obtained from PAN and TOXNET databases, peer reviewed journals and web links.

Compound	Invertebrate	SW/		EC10/		EC/LC50 (mg/L)		Source
		FW	NOEC	LOEC	24h	48 h	96h	
Amines								
MEA	Water flea (<i>Daphnia magna</i>)	FW			83.6-165			Bringmann & Kuhn, 1977
	Brown shrimp (<i>Crangon crangon</i>)	SW				100		MAFF, 1971
AMP	Water flea (<i>Daphnia magna</i>)	FW	100			>100		Web link 1
MDEA	Water flea (<i>Daphnia magna</i>)	FW				250		Web link 2
	Water flea (<i>Daphnia magna</i>)	FW				230		Web link 3
PIPA	Water flea (<i>Daphnia magna</i>)	FW				10-100		Web link 4
Amides								
Acetamide	Water flea (<i>Daphnia magna</i>)	FW			10,000			Bringmann & Kuhn, 1977
Formamide	Water flea (<i>Daphnia magna</i>)	FW				13		Le Blanc & Surprenant, 1983
						500		EPA, 2004. doc: 201-15159A
Nitrosamine								
NDPA	Cladoceran sp.	FW				7.76		US EPA, 1978
NDMA	Amphipod (<i>Gammarus limnaeus</i>)	FW					300	Draper & Brewer, 1979
	Crayfish (<i>Austropotamobius pallipes</i>)	FW					2250	Alibaud et al., 1985
	Flatworm (<i>Dugesia dorotocephala</i>)	FW					1365	Draper & Brewer, 1979
NDEA	Amphipod (<i>Gammarus limnaeus</i>)	FW					500	Draper & Brewer, 1979
	Crayfish (<i>Austropotamobius pallipes</i>)	FW					230	Alibaud et al., 1985
	Flatworm (<i>Dugesia dorotocephala</i>)	FW					1490	Draper & Brewer, 1979
Nitramines								
RDX	Mussel (<i>Mytilus galloprovincialis</i>)	SW						
	Adult survival (96h)		28.4	>28.4				Rosena & Lotufo, 2007
	Adult byssus (48h)		28.4	>28.4				Rosena & Lotufo, 2007
	Mussel embryo development (48h)		31	>31				Rosena & Lotufo, 2007
	Water Flea (<i>Ceriodaphnia dubia</i>)	FW	3.64	6.01				Peters et al., 1991
	Midge (<i>Chironomus tentans</i>)	FW				15-100		Hovatter et al., 1997
HMX	Mussel (<i>Mytilus galloprovincialis</i>)	SW						
	Adult survival (96h)		1.9	>1.9				Rosena & Lotufo, 2007
	Adult byssus (48h)		1.9	>1.9				Rosena & Lotufo, 2007
	Mussel embryo development (48h)		1.97	>1.97				Rosena & Lotufo, 2007

Web link (WL) 1. <http://www.jtbaker.com/msds/englishhtml/a4572.h>

WL 2. http://www.optimal.com.my/pdf/Gas_Treating_Ethanolamines/MDE01_MDEA.pdf

WL 3. <http://www.elementis-specialties.com/index.asp?fuseaction=Industries.getweracs&ProductCode=10898&Lang=EN&SubFormat=ANSI>

WL 4. http://www.ethyleneamines.com/NR/rdonlyres/OF711045-D7C1-4979-8286-032FF5C01636/0/PIP_AnH.pdf

Table 5. Acute toxicity of selected primary amines and secondary products to aquatic algae and bacteria. Data obtained from PAN and TOXNET databases, peer reviewed journals and web links.

Amines	Algae/Bacteria	SW FW	LOEC	EC10	EC/LC50 (mg/L)					Source
					15min	24h	48 h	72h	96h	
MEA	Marine algae (<i>Skeletonema costatum</i>)	SW		83.1			198			Sintef Report, 2007
	Microtox (<i>Vibrio fischeri</i>)	SW			6-39					Sintef Report, 2007 Libralto et al 2007
	Haptophyte (<i>Isochrysis galbana</i>)	SW					80-160		80	Roseth et al., 1996;
	Green algae (<i>Chlorococcales</i>)	FW	31			70				Krebs, 1991
	Cryptomonad (<i>Chilomonas paramecium</i>)	SW					733			Bringmann et al 1980
	Flagellate (<i>Entosiphon sulcatum</i>)	FW						300		Bringmann & Kuhn 1980
AMP	Marine algase (<i>Skeletonema costatum</i>)	SW		64.8			118.6			Sintef Report, 2007
	Microtox (<i>Vibrio fischeri</i>)	SW			20					Sintef Report, 2007
MDEA	Marine algae (<i>Skeletonema costatum</i>)	SW		72.7			141.4			Sintef Report, 2007
	Microtox (<i>Vibrio fischeri</i>)	SW			36					Sintef Report, 2007
	Green algae (<i>Scenedesmus subspicatus</i>)	FW							20	Web link3
PIPA	Skeletonema	SW		315.8			472.2			Sintef Report, 2007
	Microtox, <i>Vibrio fischeri</i>	SW			13					Sintef Report, 2007
	Green algae (<i>Selenastrum capricornutum</i>)	FW						>1000		Web link4
Amide										
Acetamide	Green algae (<i>Chlorococcales</i>)	FW		1,000		1,000				Krebs, 1991
	Cryptomonad (<i>Chilomonas paramecium</i>)	SW					49			Bringmann et al., 1980
	Flagellate (<i>Entosiphon sulcatum</i>)	FW						99		Bringmann & Kuhn, 1980
	Blue-green algae (<i>Microcystis aeruginosa</i>)	FW	6,200							Bringmann & Kuhn, 1978
	Green algae (<i>Scenedesmus quadricauda</i>)	FW	10,000							Bringmann & Kuhn, 1978
Formamide	Green algae	FW						8000		EPA, 2004. doc: 201- 15159A
Nitramines										
CL-20	Green algae <i>Selenastrum capricornutum</i>	FW							> 3.6 ¹	Gong et al., 2004
	Microtox (<i>Vibrio fischeri</i>)	SW							> 3.6 ¹	Gong et al., 2004
RDX	Blue-green algae (<i>Microcystis aeruginosa</i>)	FW							3.2-10	Hovatter et al., 1997
	Green algae (<i>Selenastrum capricornutum</i>)	FW							3.2-10	Hovatter et al., 1997
HMX	Blue-green algae (<i>Microcystis aeruginosa</i>)	FW							>32	Hovatter et al., 1997
	FW green algae <i>Selenastrum capricornutum</i>	FW							>32	Hovatter et al., 1997

WL 3. <http://www.elementis-specialties.com/index.asp?fuseaction=Industries.getwercs&ProductCode=10898&Lang=EN&SubFormat=ANSI>

WL 4. http://www.ethyleneamines.com/NR/rdonlyres/0F711045-D7C1-4979-8286-032FF5C01636/0/PIP_Anh.pdf

5. Chronic toxicity of primary amines and secondary products to aquatic species

The chronic effects of the selected primary amines and their secondary products to aquatic organisms have been poorly studied when compared to the acute effects. The chronic toxicity of these compounds to freshwater fish, invertebrates and algae/bacteria are shown in **Table 6**, **Table 7**, and **Table 8**. Chronic effects were considered as those effects that would result following exposure to the test compound for greater than six days.

5.1 Fish – Chronic toxicity

For the amines, chronic exposure data was only available for MDEA and PIPA. A decrease in egg hatching was observed in Carp exposed to 0.5 mg/L MDEA and greater (Bieniarz et al., 1996). No effect on the schooling behaviour of the fish, *Kuhlia sandvicensis* was reported when exposed to PIPA concentrations up to 20 mg/L (Hiatt et al., 1953).

Table 6. Chronic toxicity of primary amines and secondary products to aquatic fish spp.

Compound	Fish	Endpoint	mg/L (*mg/kg)	Reference
Amines				
MDEA	Carp (<i>Cyprinidae</i>)	Decrease in egg hatching - LOEC	0.5	Bieniarz et al., 1996
PIPA	Aholehole (<i>Kuhlia sandvicensis</i>)	Behavioural changes (schooling) - NOEC	20	Hiatt et al., 1953
Nitrosamine				
NDMA	Rainbow trout (<i>Oncorhynchus mykiss</i>)	52 week exposure - presence of hepatocellular carcinomas - LOEC	*200	Grieco et al., 1978
Nitramines				
CL-20	Fathead minnow (<i>Pimephales promelas</i>)	Growth IC50	0.2-2.0	Hayley et al., 2002; 2003
RDX	Fathead minnow (<i>Pimephales promelas</i>)	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 (<i>Danio rerio</i>)	Growth effects after 28 days (LOEC)	2.4	Burton et al., 1994
		Effects on body weight after 4 weeks (LOEC)	1	Mukhi & Patiño, 2008
		Significant increase in mortality (LOEC)	9.6	Mukhi & Patiño, 2008

Only one study was found that provides toxicity data on the chronic effects of nitrosamines to aquatic fish. In this case, rainbow trout (*Oncorhynchus mykiss*) were exposed to NDMA, via the diet, for a 52 week period. After this time an increase in the presence of hepatocellular carcinomas was observed at the lowest exposure concentration of 200 mg/kg.

The chronic toxicity values for nitramines, CL-20 and RDX were reported in selected freshwater fish. Growth effects were observed in Fathead minnows (*Pimephales promelas*) exposed to concentrations of CL-20 with an IC50 concentration of 0.2-2.0 mg/L (Hayley et al., 2002; 2003).

Growth effects were also found in *P. promelas* when exposed to chronic concentrations of RDX with LOEC values of 2.4 and 5.8 mg/L (Burton et al., 1994 and Bentley et al., 1977). In addition, a four week chronic exposure of the zebra fish (*Danio danio*) to RDX concentrations resulted in adverse effects on body weight (LOEC of 1 mg/L) and an increase in mortality (LOEC- 9.6 mg/L, Mukhi & Patiño, 2008).

5.2 Invertebrates – Chronic effects

The chronic toxicity data for the selected primary amines and secondary products to the aquatic invertebrate species are limited to a few compounds (**Table 7**). For formamide, the maximum allowable concentration for use as a carrier in chronic toxicity test was estimated at 1.2 to 2.5 mg/L (LeBlanc & Suprenant, 1983), i.e. this concentration and below would have no adverse chronic effects to *D. magna*.

Table 7. Chronic toxicity of primary amines and secondary products to aquatic invertebrates

Compound	Crustacea	endpoint	value	Reference
Amide				
Formamide	<i>Daphnia magna</i>	Maximum allowable concentration for chronic toxicity testing	1.2-2.5	Le Blanc & Surprenant, 1983
Nitrosamine				
NDMA	Crayfish (<i>Procambarus clarkii</i>)	Antennal gland degradation - 6mth exposure	200	Harshbarger, et al. (1971)
	Crayfish (<i>Procambarus clarkii</i>)	Hyperplasia of tubular cells in hepatopancreas- 6mth exposure	100	Harshbarger, et al. (1971)
Nitramines				
CL-20	Water Flea (<i>Ceriodaphnia dubia</i>)	Growth, IC50	0.4-2.0	Hayley et al., 2002; 2003
RDX	Water Flea (<i>Ceriodaphnia dubia</i>)	7d reproductive effects	4.68	Peters et al 1991

Six month exposure of the crayfish, *Procambarus clarkii*, to NDMA caused extensive degeneration in all parts of the antennal gland at 200 mg/L and hyperplasia of the tubular cells in the hepatopancreas at 100 mg/L (Harshbarger et al., 1971). For the nitramines, CL-20 and RDX growth and reproductive effects were reported in *C. dubia* at 0.4-2.0 mg/L (Hayley et al., 2003; 2002) and 4.68 mg/L (Peters et al., 1991) respectively.

5.3 Algae/bacteria – Chronic effects

The available chronic toxicity data for the selected primary amines and secondary products to the algae and bacteria are listed in **Table 8**. MEA is the only amine represented. The most sensitive species to MEA measured as growth effects following 7 and/or 8 day exposure was the green algae (*Scenedesmus quadricauda*) with a LOEC concentration of 0.75 mg/L (Bringmann & Kuhn, 1980; 1978). Similar LOEC values were reported for the blue green algae, *Anacystis aeruginosa* and *Microcystis aeruginosa* (i.e. 1.6 to 2.1 mg/L MEA respectively, Bringmann & Kuhn, 1978; 1975).

Table 8. Chronic toxicity of primary amines and secondary products to algae and bacteria

Compound	Algae/Bacteria	SW FW	endpoint	(mg/L) value	Reference
Amines					
MEA	Blue-green algae (<i>Anacystis aeruginosa</i>)	FW	8d growth effect (LOEC)	1.6-2.1	Bringmann & Kuhn, 1978.
	Blue-green algae (<i>Anacystis aeruginosa</i>)	FW	8d growth effect (LOEC)	1.6-2.1	Bringmann, 1975
	Green algae (<i>Scenedesmus quadricauda</i>)	FW	8d growth effect (LOEC)	0.75-0.97	Bringmann & Kuhn, 1978.
			7d growth effect (LOEC)	0.75	Bringmann & Kuhn, 1980
	Blue-green algae (<i>Microcystis aeruginosa</i>)	FW	8d growth effect (LOEC)	1.6-2.1	Bringmann & Kuhn, 1978.
Amides					
Acetamide	Blue-green algae (<i>Anacystis aeruginosa</i>)	FW	8d growth effects (EC50)	6,600	Bringmann & Kuhn, 1978
	Green algae (<i>Scenedesmus quadricauda</i>)	FW	7d population changes (EC50)	10,000	Bringmann & Kuhn, 1980
	Green algae (<i>Scenedesmus quadricauda</i>)	FW	8 d population changes (EC50)	10,000	Bringmann & Kuhn, 1978
Nitrosamine					
NDMA	Green algae (<i>Chlamydomonas reinhardtii</i>)	FW	DNA damage (COMET)	1-10	Erbes et al., 1997
	Green algae (<i>Selenastrum capricornutum</i>)	FW	growth effect (LOEC)	1-10	Draper & Brewer, 1979
	Green algae <i>Tetraselmis maculata</i>	SW	Growth effects (7d) - LOEC	0.025	Aubert et al. 1982
NDEA	Green algae (<i>Selenastrum capricornutum</i>)	FW	growth effect LOEC	1-10	Draper & Brewer, 1979

Extremely low levels of toxicity were found for acetamide with growth and population changes in *A. aeruginosa* and *S. quadricauda* following 7-8 day exposure with EC50 values of 6,600 mg/L and 10,000 mg/L respectively (Bringmann & Kuhn, 1980; 1978).

The chronic toxicity data for nitrosamines on algal growth and DNA damage revealed a relatively high level of toxicity. The most sensitive species tested was the marine green algae *Tetraselmis maculate*, with a LOEC value of 0.025 mg/L from tests on growth effects following 7 days exposure (Aubert et al., 1982).

6. Summary of toxicity data

A list of the most sensitive responses for each taxonomic and compound group has been included in **Table 9**. For amines, the most sensitive response was found in the chronic exposure of MDEA to fish (0.5 mg/L), followed closely by chronic exposure of algae to MEA (0.75 mg/L). Chronic exposures of amines to invertebrates were not available for any of the four amine compounds.

For the amides, the highest level of toxicity was found in selected invertebrates with the most sensitive effect found at a chronic exposure at 1.2 mg/L Formamide. Amide toxicity to fish and algae was often three fold higher than the lowest effect in invertebrates.

Table 9. Summary of the most sensitive responses for the four main groups of compounds. (Data expressed as mg/L; — data not available)

Group	Test	MEA	AMP	MDEA	PIPA	Amides (Formamide/ Acetamide)	Nitrosamine	Nitramine
Fish	Acute	20 (NOEC)	100 (LC50)	100 (LC50)	52 (LC50)	5000 (Formamide)	5.85 (NDPA)	3.6 (RDX)
	Chronic	—	—	0.5	20	—	200 (NDMA)	0.2 (CL-20)
Invertebrate	Acute	83.6 (LC50)	100 (NOEC)	230 (LC50)	10 (LC50)	13 (Formamide)	7.76 (NDPA)	6.01 (RDX)
	Chronic	—	—	—	—	1.2 (Formamide)	100 (NDMA)	0.4 (CL-20)
Algae/ Bacteria	Acute	6 (LC50)	20 (LC50)	20 (LC50)	13 (LC50)	49 (Acetamide)	—	3.2 (RDX)
	Chronic	0.75 (LOEC)	—	—	—	6600 (Acetamide)	0.025 (NDMA)	—

The most toxicity effect for the nitrosamines was found in algae/bacteria exposed to NDMA, with a LOEC of 0.025 mg/L. This was by far the lowest effect concentration found for any of the compounds

included in this review. For the fish and invertebrates, the acute toxicity concentration was lower than the chronic effect concentration. This is contrary to expected data and suggests a shortage of sensitive chronic toxicity tests for nitrosamine compounds.

The lowest effect concentrations reported for nitramines were found at 0.2 mg/L and 0.4 mg/L for chronic exposure to nitramine CL-20 in fish and invertebrates respectively. Although nitramine chronic exposure data was not available for algae, comparison of the lowest effect concentration data available suggests that the toxicity of the nitramines does not differ greatly between the organism groups with lowest effects ranging between 0.2 and 6.01 mg/L.

7. Risk Assessment of amines and nitrosamines

The assessment of contaminant risk in the environment is often carried out using the simple equation.

$$\frac{\text{Predicted Environmental concentration (PEC)}}{\text{Predicted No Effect Concentration (PNEC)}} = \text{Risk Quotient (RQ)}$$

If the PEC is greater than the PNEC then the RQ will be greater than one. In this case there would be potential for environmental harm and the need for further investigations to take place. Conversely, an $RQ < 1$ would suggest little or no risk of environmental harm.

The critical values for the assessment of chemical risk have been listed in table 10. The LOEC has been taken from the data tables previously described in this review. The PNEC value has been calculated by dividing the LOEC by the appropriate assessment factor listed in table 10. Determining the appropriate assessment factor was based on the European Union Technical guidance document on risk assessment (ECB, 2003).

Knowledge of the PNEC value and the transformation of equation 1 will provide information of the required PEC value that will produce an RQ of greater than 1. Therefore, inputs from the CO₂ capturing operation into the environment that results in water concentrations greater than the PEC shown in **Table 10** will have the potential to cause environmental harm. For the amines, a water concentration of >7.5µg/L MEA, >20µg/L AMP, >5µg/L MDEA and >100 µg/L PIPA has the potential to cause environmental harm. For the secondary products a concentration of >24 µg/L amide, 0.025 µg/L nitrosamine and >0.2 µg/L nitramine has the potential to cause environmental harm.

An assessment factor of 1000 has been applied for nitramines and nitrosamines due to the limited ecotoxicological information available on the specific chemicals. For these compounds the toxicity data was inferred from similar related compounds due to the absence of toxicological data on the actual compounds that would be produced from the CO₂ capture process using the model amine compounds. As more ecotoxicological information on the actual compounds becomes available then the reliability of the toxicity endpoints will increase, and the uncertainty factor can be reduced.

Table 10. Critical values for the determination of risk for each of the main chemical groups based on the most sensitive environmental effect measured.

Compound	LOEC (mg/L)	Assessment factor	Calculated PNEC (µg/L)	Required PEC for an RQ >1 (µg/L)
MEA	0.75	100	7.5	>7.5
AMP	20	1000	20	>20
MDEA	0.5	100	5	>5
PIPA	10	100	100	>100
Amides	1.2	50	24	>24
Nitrosamines	0.025	1000	0.025	>0.025
Nitramines	0.2	1000	0.2	>0.2

8. Gaps in our understanding and further research requirements

The following review has highlighted several areas where ecotoxicity data are sparse or unavailable. These often relate to the chronic effects of many of the compounds tested such as the chronic effect of amines on invertebrates and fish.

From the data presented in this review it is clear that the most potentially toxic compounds are nitrosamines and nitramines. However, for both of these chemical groups the toxicity data available are not specific to the actual compounds that have been calculated to occur from the CO₂ capture process (Task 3). Therefore, there is a great deal of uncertainty about the aquatic toxicity of these specific nitramine and nitrosamine compounds. It is suggested that future ecotoxicity work focuses on the acute and chronic toxicity of these specific compounds for a better evaluation of the potential impact of the CO₂ capturing plant.

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