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## Preliminary studies into the environmental fate of nitrosamine and nitramine compounds in aquatic systems

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### Abstract

Preliminary hydrolysis and photolysis data are presented for a suite of nitramines and nitrosamines relevant to post combustion CO<sub>2</sub> capture using monoethanolamine solvent. Two nitramines (DMNA and MEA-NO<sub>2</sub>) and the nitrosamine NDELA were resistant to hydrolytic degradation at pH 4, 7 and 9. The nitrosamine NPz was hydrolytically stable at pH 4 and 9, but exhibited ~30% degradation at pH 7. Nitrosamines appear highly susceptible to photolytic degradation, while nitramines are photolytically stable. The data form part of an ongoing study investigating the fate of nitrosamines and nitramines in terrestrial and aquatic environments.

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### 1. Introduction

Recently there has been increased awareness regarding the emission of amine solvent or degradation products generated in post-combustion CO<sub>2</sub> capture (PCCC) plants. Amine solvent degradation products include nitrosamines and nitramines which may present human health or environmental issues. Monoethanolamine (MEA) is the most commonly studied solvent. Although stable nitrosamines cannot be formed directly from primary amines such as MEA, they can be formed from degradation products with secondary or tertiary amine functionalities. Nitramines can form from primary, secondary or tertiary amines. Nitrosamines and nitramines may also be formed in the atmosphere through reactions of the amine and other degradation products with NO<sub>x</sub> [1, 2]. Nielsen et al. [3] report that atmospheric degradation of MEA did not yield nitrosamines, but the nitramine form was observed. This is consistent for a primary amine. Nitrosamines are susceptible to photodegradation and therefore generally short-lived

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in the atmosphere (~5 min). In contrast, nitramines are more stable and will have longer atmospheric residence times (2 days) [4, 5]. The stability of nitramines indicates a higher potential for atmospheric accumulation than for nitrosamines. The hydrophilic nature of CO<sub>2</sub> capture solvents and their degradation products suggests wet deposition is the most likely removal process from the atmosphere to terrestrial and aquatic matrices [6].

Existing toxicological data indicates that most nitrosamines are highly carcinogenic. Less is known about nitramines, but they appear mutagenic and carcinogenic although typically less potent than nitrosamines [7, 8]. Reviews of existing toxicity data and recommended exposure limits for nitrosamines and nitramines have recently been reported [8-10]. The Norwegian Public Health Institute proposes acceptable exposure levels for all nitrosamines and nitramines of 4 ng/L for drinking water and 0.3 ng/m<sup>3</sup> for air [10]. This is based on a 10<sup>-6</sup> lifetime risk of cancer following exposure to the nitrosamine, N-nitrosodimethylamine (NDMA). The USA, Canada and several European countries have, or are in the process of, establishing regulations for acceptable levels of the nitrosamine NDMA in water [8].

To assess the risk of human exposure to nitrosamines and nitramines an understanding of their environmental fate is required. A range of natural processes, including hydrolysis, photolysis, soil adsorption and biodegradation determine environmental persistence and accumulation. To date, there has been relatively little peer-reviewed data published on nitrosamine and nitramine environmental fate. Previous studies of nitrosamine and nitramine hydrolysis have indicated that both compound classes are stable and unaffected by pH or concentration [11, 12]. Based on atmospheric studies, rapid degradation of nitrosamines in aquatic environments can be expected whilst nitramines are likely to be persistent [4, 5]. Laboratory studies have shown that nitrosamines typically have half-lives less than 30 minutes when exposed to simulated sunlight [12, 13]. No data is available for nitramine compounds. The biodegradation of nitrosamines and nitramines has been investigated in a number of recent studies [12, 14-16]. In all cases, the nitrosamines and nitramines studied were generally stable except for nitrosodimethylamine (NDMA) and nitrosomethylethylamine (NMEA) at 10 µg/L [12] and nitrosodiethanolamine (NDELA) at 2 mg/L [16]. The biodegradation of nitrosamines may be dependent upon the concentration of the chemicals [12, 14]. Mohr et al. [17] suggest that low log *K*<sub>OC</sub> values for the nitramines indicate they will preferentially partition to water if available, but adsorption to organic rich soil was observed.

In the present study, we report preliminary hydrolysis and photolysis data for a suite of nitrosamines and nitramines relevant to the use of MEA solvent in a PCCC plant. These preliminary data are part of a larger ongoing study investigating the fate of nitrosamines and nitramines in terrestrial and aquatic environments. The findings of these preliminary experiments are discussed within the context of other available environmental fate data for the nitramines and nitrosamines studied.

## 2. Experimental methods

### 2.1. Materials

The nitramines and nitrosamines used in the study were supplied by Chiron AS, Trondheim, Norway. The studied chemicals are presented in Table 1. For preparation of the buffer solutions, analytical grade (p.a.) potassium chloride, sodium hydroxide and boric acid were supplied by Merck KGaA, Darmstadt, Germany. Analytical grade potassium dihydrogen phosphate was supplied by Riedel-deHaën AG, Seelze,

Germany and analytical grade potassium biphthalate was supplied by Fluka Analytical, Steinheim, Germany.

Table 1. Summary of the nitramines and nitrosamines selected for use in this study

<b>Chemicals</b>	<b>Abbreviation</b>	<b>CAS No.</b>
<i>Nitramines</i>		
<b>2-Nitroaminoethanol</b>	MEA-NO <sub>2</sub>	74386-82-6
<b>1-Nitropiperazine</b>	PZ-NO <sub>2</sub>	42499-41-2
<b>Dimethyl nitramine</b>	DMNA	4164-28-7
<i>Nitrosamines</i>		
<b>n-Nitrosodimethylamine</b>	NDMA	62-75-9
<b>n-Nitrosopiperazine</b>	NPz	5632-47-3
<b>n-Nitrosodiethanolamine</b>	NDELA	1116-54-7
<b>n-Nitrosomorpholine</b>	NMOR	59-89-2

## 2.2. Hydrolysis study

The hydrolytic stability of four nitrosamines and three nitramines at pH 4, 7 and 9 has been assessed using Tier 1 of OECD Guideline 111, "Hydrolysis as a Function of pH". The test, which acts as a preliminary screen, was conducted at 50°C for 5 days to assess the possible degradation over 1 year at 25°C. Reagent grade potassium biphthalate (pH 4), monopotassium phosphate (pH 7) and boric acid (pH 9) were used to make buffers at the required pH values. The buffers were sterilized by autoclaving for 20 minutes at 121 using a TOMY Autoclave SS-325 (Nerliens Kemisk Tekniske AS, Oslo, Norway) and a PHM82 Standard pH-meter (Radiometer A/S, Copenhagen, Denmark) with a glass electrode (GK 2401B, 103 mm) was used to confirm the pH of the buffer solutions.

Stock solutions of each compound was prepared (200 mg/L) in sterilized deionised water. 5 or 50 µL aliquots of these stock solutions were spiked into 100 mL of the buffer solutions to create sample concentrations of 10 and 100 µg/L (depending on the analytical limit of detection). The sample solutions were divided into three aliquots of 30 mL and transferred to 40 mL glass vials. After removing day 0 samples, the solutions were purged with N<sub>2</sub> for 30 seconds and sealed with lids. The samples were incubated at 50 °C for 5 days (120 h), and sampled at the end of this period. Prior to analysis all samples were stored at -20°C.

## 2.3. Photolysis study

The photolytic stability of four nitrosamines and three nitramines in water was estimated using Tier 1 of OECD Guideline 316, "Phototransformation of Chemicals in Water – Direct Photolysis". Sample solutions of each test chemical were prepared at a concentration of 100 mg/L (~10<sup>-3</sup> mol/L) by diluting stock solutions (200 mg/L) into a buffer solution at pH 7 (monopotassium phosphate). Two aliquots of each sample solution were then transferred to separate Quartz SUPRASIL® cuvettes (Hellma Analytics

100-QS, 10 mm path length). The UV-Vis absorption spectra of the sample solutions were measured using a Hitachi U-2000 UV/VIS Spectrophotometer, scanning the wavelength range 250-800 nm. The two parallels of each compound were each analysed twice, and an average absorption value was calculated at each wavelength.

According to OECD Guideline 316, compounds with absorption maxima above 290 nm (wavelength representing the lower cut-off value for solar irradiation at the earth's surface) will be susceptible to photolytic degradation. The maximum possible direct photolysis rate constant,  $k_{d(\max)}$ , can be estimated using Equation 1. The term  $\varepsilon_\lambda$  is the molar decadic absorption coefficient [ $\text{L mol}^{-1} \text{cm}^{-1}$ ] at wavelength  $\lambda$ ;  $L_\lambda$  is the average daily solar photon irradiance on amount basis [ $\text{mmol cm}^{-2} \text{d}^{-1}$ ] over wavelength interval  $\Delta\lambda$ , centred at wavelength  $\lambda$ . Values for  $L_\lambda$  for both summer and winter conditions at 50° latitude were obtained from the US EPA Guideline OPPTS 835.2210, "Direct Photolysis Rate in Water By Sunlight" [18]. The half-life of each compound was then estimated by substituting  $k_{d(\max)}$  into Equation 2.

$$k_{d(\max)} = \sum_{\lambda=290}^{\lambda=800} \varepsilon_\lambda \cdot L_\lambda \quad (1)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

#### 2.4. Analytical chemistry

All compounds were analysed by liquid chromatography – triple quadrupole mass spectrometry (LC-MS-MS-QQQ). Chromatography was performed on an Agilent 1290 LC system and mass spectrometric detection was performed on an Agilent 6490 QQQ system. The following analytes were determined: MEA-NO<sub>2</sub>, Pz-NO<sub>2</sub> and DMNA, NPz, NDELA, NMOR and NDMA. The analytes were separated by reverse phase chromatography on various columns. The mobile phases were based on methanol and acetonitrile as solvents, and formic acid and ammonium acetate buffers. The analytes were ionized with APCI or jet-stream ESI. All analytes were detected at their optimal transitions with target and qualifier fragment ions. Retention times were within the range of 1 to 10 minutes. For all analytes, the limits of quantification were within the range of 0.1 to 1 ng/mL. For all analytes deuterated internal standards were used. The precision (repeatability) was better than 5% RSD for all analytes.

### 3. Results and discussion

#### 3.1. Hydrolysis study

At the time of preparing this manuscript hydrolysis data was only available for two nitramines (DMNA and MEA-NO<sub>2</sub>) and two nitrosamines (NDELA and NPz). The results from the preliminary hydrolysis study of the selected nitramines and nitrosamines are shown in Figure 1a and Figure 1b respectively. Hydrolytic stability after 5 days (n=3) was calculated as a percentage of the test compound concentrations determined at Day 0 (n=3). No significant hydrolytic degradation was observed for any of the compounds

tested at pH 4 and 9. Furthermore, all of the compounds are also stable at pH 7, with the exception of NPz. The data for NPz indicate ~30% loss due to hydrolysis over 1 year at 25 °C. The results are in accordance with those reported in the studies by Williams et al. [12] and Mohr et al. [15] which show that nitrosamines and nitramines are generally resistance to hydrolytic degradation. To the author's knowledge, no previous studies have examined the hydrolysis rate of NPz, and it is unclear why it undergoes hydrolytic degradation at pH 7. Further work, including repetition of the Tier 1 hydrolysis test, will be conducted to confirm the results observed for NPz in this preliminary study.

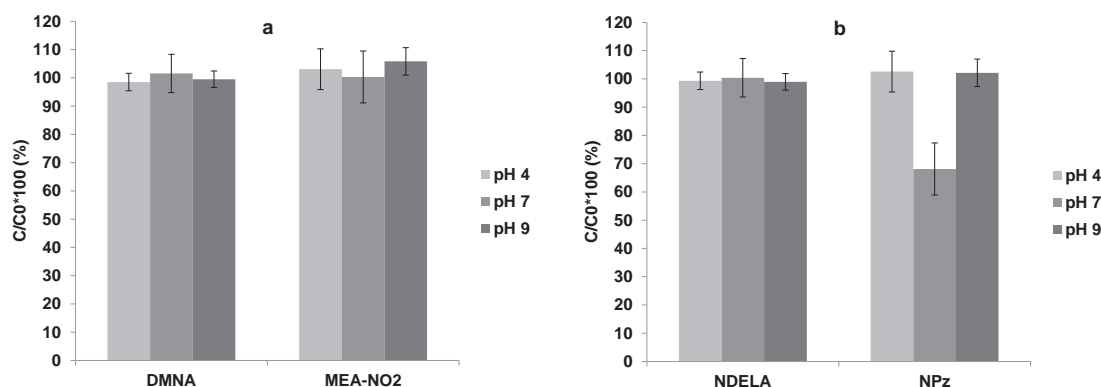


Figure 1. Bar plot showing the degree of hydrolytic degradation of the nitramines DMNA and MEA-NO<sub>2</sub> (a) and nitrosamines NDELA and NPz (b) at 50 °C and at three different pH values. Data are expressed as the percentage ratio of concentration at day 5 over day 0. Error bars represent one standard deviation (n=3)

### 3.2. Photolysis study

The results from the preliminary Tier 1 assessment of photolytic stability of the selected nitramines and nitrosamines are summarised in Figure 2a and Figure 2b respectively. The data clearly show that a difference exists between the absorbance spectra of the nitramine compounds (a) and the nitrosamine compounds (b). None of the nitramines show absorbance maxima in the wavelength range 290-800 nm, whilst all of the nitrosamines studied have a clear absorbance peak at approximately 340 nm. The absorbance peak at ~340 nm is within the wavelength range corresponding to solar irradiation at the earth's surface. Based on this data, it can be assumed that nitrosamines in water are highly susceptible to photodegradation. The preliminary data reported here for the selected nitrosamines are in accordance with rapid photodegradation observed for nitrosamines in laboratory studies by Williams et al. [12] and Plumlee and Reinhard [13]. As the nitramine compounds studied did not show absorbance maxima in the wavelength range 290-800 nm, it is unlikely that these compounds would undergo significant photodegradation in water. Whilst there are no reports of the photodegradability of PCCC-related nitramines, the preliminary results in this study are consistent with the observations of nitramine stability in the atmosphere [5].

As the nitrosamines exhibit an absorbance peak at ~340 nm an estimation of their maximum possible direct photolysis rate constant and corresponding half-life can be calculated. The half-lives of the test compounds under summer and winter conditions at 50° latitude are presented in Table 2. The half-lives

are estimated to be less than 20 minutes under summer conditions and less than 2 hours under winter conditions. Therefore, further investigation on the photolytic degradation rate of the nitrosamines used in this study is necessary. The nitrosamine compounds will be studied further according to the OECD Guideline 316 Tier 2 test to determine more accurate photodegradation rates.

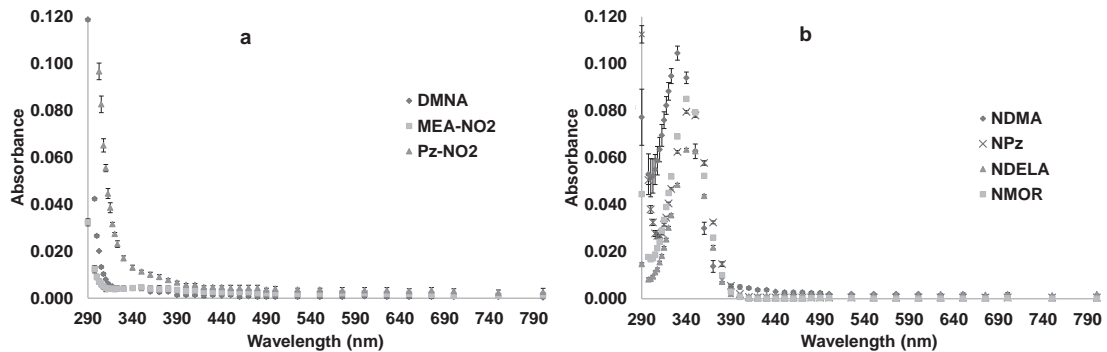


Figure 2. Comparison of absorbance spectra in 100 mg/L solutions of nitramines (a) and nitrosamines (b) in the wavelength range 290 – 800 nm. Error bars represent one standard deviation ( $n=4$ , except for Pz-NO<sub>2</sub>, where  $n=3$ ).

Table 2. Estimated photolytic half-lives (min) of nitrosamines in water using UV/VIS spectrophotometric data and values of average daily solar photon irradiance at 50° latitude under summer and winter conditions

Chemical	$t_{1/2}$ (min) 50° latitude, summer	$t_{1/2}$ (min) 50° latitude, winter
NDMA	15	92
NPz	15	90
NDELA	11	61
NMOR	17	111

### 3.3. Environmental fate of nitrosamines and nitramines

The preliminary data reported here permit an initial assessment of the environmental fate of some nitramine and nitrosamine degradation products related to PCCC plants operating with MEA. Nitramines released to surface or ground waters will neither photodegrade nor hydrolyse, indicating they are quite persistent in these environments. Whilst nitrosamines also appear to be resistant to hydrolysis, it is indicated that they will rapidly photodegrade when released to surface waters. A number of other environmental factors, such as concentration and type of natural organic material and the amount of particulate material present in surface waters will have a significant impact on the level of nitrosamine photodegradation. Furthermore, nitrosamines which are present below the photic zone will not be subject to photodegradation, indicating aquatic mixing times could also have an effect.

An overview of the fate of nitramine and nitrosamine compounds in environment will also need to consider other relevant processes such as adsorption to soil and biodegradation. Existing reports indicate that of the four nitrosamines relevant to this study, only NDELA is both readily biodegradable (OECD Guideline 301) and also degradable at low concentrations in lake water [14, 16]. The concentrations of nitrosamines and nitramines in aquatic systems may have a significant influence on their biodegradability. Preliminary soil adsorption studies for the nitramines DMNA and MEA-NO<sub>2</sub> indicate these compounds will preferentially partition to water if available, but that some adsorption to organic rich soils will occur [17].

The preliminary data available suggest that for both nitramines and nitrosamines the most likely environmental sink will be ground waters. However, their persistence and potential for accumulation would be dependent upon their susceptibility to biodegradation. The data presented here form part of an ongoing study to evaluate the relevance of all of these environmental parameters on the fate of PCCC-related nitrosamines and nitramines.

#### 4. Conclusions and further work

In the current study, preliminary data regarding the hydrolysis and photolysis of a suite of nitrosamines and nitramines identified as relevant degradation products for the commonly used PCCC solvent MEA are presented. Reliable analytical methodologies were developed for the analysis and quantification of the selected nitramines and nitrosamines. Two nitramine compounds (DMNA and MEA-NO<sub>2</sub>) and the nitrosamine NDELA were resistant to hydrolytic degradation at the three different pH conditions tested. Whilst the nitrosamine NPz was hydrolytically stable at pH 4 and pH 9, a ~30% degradation in the OECD Guideline 111 Tier 1 test was observed at pH 7. A further, more detailed, study of the hydrolysis of NPz is required at pH 7, investigating the effect of different temperatures and longer periods of time. Hydrolysis data will also be determined for Pz-NO<sub>2</sub>, NDMA and NMOR. The preliminary Tier 1 photolysis data confirm that nitrosamines are highly susceptible to photolytic degradation, while nitramines appear to be photolytically stable. The photodegradation of the selected nitrosamines will be further studied in more detail according to the OECD Guideline 316 Tier 2 test.

The preliminary data reported herein represent the current status of a larger ongoing study investigating the fate of nitrosamines and nitramines in terrestrial and aquatic environments. Methylnitramine (MNA) will also be included in the full study. These selected nitrosamines and nitramines will also be subjected to soil adsorption and biodegradation studies in order to form a clear understanding of the environmental fate of these compounds.

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