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Marine ecotoxicity of nitramines, transformation products of amine-based carbon capture technology

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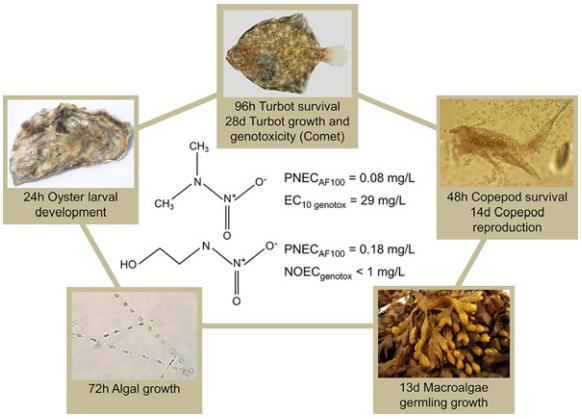
HIGHLIGHTS

- The environmental risk posed by nitramines, CO_2 capture by-products, was unknown.
- A multi-trophic suite of bioassays was used to assess ecotoxicity and genotoxicity.
- Nitramine toxicity through necrosis was considered low.
- The first risk assessment for dimethylnitramine and ethanolnitramine was produced.
- Ethanolnitramine induced massive DNA damage in turbot.

GRAPHICAL ABSTRACT



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ABSTRACT

In the context of reducing CO_2 emissions to the atmosphere, chemical absorption with amines is emerging as the most advanced technology for post-combustion CO_2 capture from exhaust gases of fossil fuel power plants. Despite amine solvent recycling during the capture process, degradation products are formed and released into the environment, among them aliphatic nitramines, for which the environmental impact is unknown. In this study, we determined the acute and chronic toxicity of two nitramines identified as important transformation products of amine-based carbon capture, dimethylnitramine and ethanolnitramine, using a multi-trophic suite of bioassays. The results were then used to produce the first environmental risk assessment for the marine ecosystem. In addition, the in vivo genotoxicity of nitramines was studied by adapting the comet assay to cells from experimentally exposed fish. Overall, based on the whole organism bioassays, the toxicity of both nitramines was considered to be low. The most sensitive response to both compounds was found in oysters, and dimethylnitramine was consistently more toxic than ethanolnitramine in all bioassays. The Predicted No Effect Concentrations for dimethylnitramine and ethanolnitramine were 0.08 and 0.18 mg/L, respectively. The genotoxicity assessment revealed contrasting results to the whole organism bioassays, with ethanolnitramine found to be more genotoxic than dimethylnitramine by three orders of magnitude. At the lowest ethanolnitramine concentration (1 mg/L), 84% DNA damage was observed, whereas 100 mg/L dimethylnitramine was required to cause 37% DNA damage. The mechanisms of genotoxicity were also shown to differ between the two compounds, with oxidation of the

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DNA bases responsible for over 90% of the genotoxicity of dimethylnitramine, whereas DNA strand breaks and alkali-labile sites were responsible for over 90% of the genotoxicity of ethanolnitramine. Fish exposed to >3 mg/L ethanolnitramine had virtually no DNA left in their red blood cells.

1. Introduction

The capture and storage of carbon dioxide (CO_2) from the exhaust gases of fossil fuel power stations is an important technology for reducing CO_2 emissions to the atmosphere. Approximately 43% of the global CO_2 emissions in 2011 were attributed to the generation of electricity from fossil fuel power stations (IEA, 2013). Chemical absorption with amines is emerging as the most advanced mitigation technology for post-combustion capture of CO_2 from fossil fuel power stations (Reynolds et al., 2012). The exhaust gas from the power station is bubbled through an amine solution in the absorber unit, producing a CO_2-saturated amine solution. In the stripper unit, heat separates CO_2 and amines, resulting in pure CO_2 ready to be stored on one side, and amine solution, recycled and sent back to the absorber unit, on the other side. The main advantage of post-combustion CO_2 capture is that the technology can be incorporated into existing power plants, avoiding the need to build new facilities. In addition, the technology benefits from almost two decades of full-scale experience for removal of CO_2 from natural gas (Lackner, 2009; Reynolds et al., 2012). However, the environmental impacts of replacing CO_2 emissions with the discharge of amine solvents and their chemical transformation products, as by-products of the capturing process, are largely unknown.

There is increasing public and environmental concern with regard to two main groups of amine transformation products, nitrosamine and nitramine contamination in air and drinking water supplies downstream of amine-based CO_2 capture plants (Reynolds et al., 2012). A few in vitro studies showed that nitramines could be carcinogenic and mutagenic (Fjellsbø et al., 2014; Wagner et al., 2014). Recent theoretical modeling and controlled laboratory experiments reported the occurrence of nitramines as transformation products of amines in the carbon capture process within the discharge effluent (Bråten et al., 2008; Nielsen et al., 2009). Two of the nitramine compounds that were identified included dimethylnitramine (CAS No. 4164-28-7) and ethanolnitramine (CAS No. 74386-82-6). However, despite the likelihood of these compounds increasing in the environment, with the potential to cause environmental harm, no environmental toxicity data for these compounds currently exist. Due to the location of some CO_2 capture and storage plants along the coastline, as well as their tendency to partition to the water phase, amines and their transformation products are likely to end up in the marine environment. Therefore, an ecotoxicity assessment performed on marine organisms is needed in order to provide an appropriate assessment of the environmental risk.

In addition to organismal toxicity, there is a real concern that nitrosamines and nitramines can cause genotoxic effects (Fjellsbø et al., 2014; Frei et al., 1984, 1986; Wagner et al., 2012). However, although nitramines are considered not as potent as nitrosamines in terms of their genotoxic potential, the greater persistence of nitramines in the environment increases their likelihood to cause environmental harm (Låg et al., 2011). In the present study, the comet assay was used in fish exposed to sub-lethal concentrations of the two nitramine compounds to assess their potential in vivo genotoxicity. The comet assay detects DNA strand breaks and alkali-labile sites (i.e. apurinic and apyrimidinic sites or AP sites), which arise from the loss of a damaged base. In normal cells, strands breaks and AP sites are not the only kind of damage. Oxidized bases are present in at least as great a number and can be readily detected with the comet assay, by incorporating an additional step involving formamidopyrimidine DNA glycosylase (FPG, Collins et al., 2008).

The first aim of the study was to determine the acute and chronic ecotoxicity of dimethylnitramine and ethanolnitramine using a suite of standardized and non-standardized tests on marine species belonging to several trophic groups. The ecotoxicity data were then used to assess the environmental risk of the two nitramine compounds in the marine environment. The second aim was to determine the potential in vivo genotoxicity of these two compounds by measuring the frequency of DNA damage in fish blood.

2. Materials and methods

2.1. Nitramines

Dimethylnitramine (CAS No. 4164-28-7, purity >98%) and ethanolnitramine (CAS No. 74386-82-6, purity 98%) were purchased from Chiron AS (Norway). Stock solutions at 5 g/L were prepared in ultrapure water (Milli-Q, Millipore, USA) and stored at 4 °C until use. Aged filtered (0.45 μm) seawater collected from a depth of 60 m from the Outer Oslo fjord, Norway, was used as a negative control and for the preparation of dilution series. In all bioassays, test solutions were prepared on the first day of testing (and, in chronic tests, on days where exposure media had to be renewed), by diluting stock solutions with appropriate amounts of filtered seawater to produce the required concentration series.

2.2. Bioassays

A bioassay battery consisting of three acute toxicity tests (24 h oyster larval development, 48 h copepod mortality and 96 h turbot mortality), a sub-chronic toxicity test (72 h algal growth), and three chronic toxicity tests (13 days macroalgae germling growth, 14 days copepod reproduction and 28 days turbot growth) was applied for both nitramines.

2.2.1. Oyster larval development

The toxicity of nitramines to the developing embryos of the Pacific oyster *Crassostrea gigas* was assessed based on the standard protocol ASTM E724 (ASTM, 1994). For both nitramines, the concentration series tested was 0, 2, 4, 9, 21, 45 and 100 mg/L. Zinc sulfate ($ZnSO_4 \cdot 7H_2O$, CAS No. 7446-20-0) was used as a positive control.

Oysters were obtained in spawning condition from Guernsey Sea Farms Ltd, Guernsey, UK. Separate male and female gamete suspensions were made by stripping the gonads and placing them in filtered seawater. Prior to fertilization, egg density was adjusted to 3000 ± 300 eggs/mL and sperm mobility was confirmed by microscopic examination at ×400 magnification. For fertilization, 10 mL of the sperm suspension was added to 1 L of the egg suspension. The fertilized embryos were allowed to develop into trocophore larvae (2 h after fertilization) before they were placed in the test vessels. The test was performed in 12 well microplates with four replicate vessels for each test concentration and eight replicate vessels for controls. The number of fertilized embryos added to each replicate vessel was approximately 50 per mL. The vessels were incubated in the dark for 24 ± 2 h at 24 ± 1 °C. The test was terminated and the embryos fixed with the addition of 200 μL of neutral buffered formalin. Dissolved oxygen, salinity and pH were measured in the high, medium and low concentration test solutions at the start and the end of the exposure period and were within accepted validity criteria (ASTM, 1994). Samples of the lowest and highest test concentration solutions were taken at the start and the end of the exposure period for analytical determination of nitramine concentrations.

The number of normal D-larvae (normally developed embryos) was counted in 1 mL of test solution for each test vessel after 24 ± 2 h using