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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_2 capture using monoethanolamine solvent. Two nitramines (DMNA and MEA-NO2) 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.

Keywords: Post combustion CO_2 capture, Nitrosamines, Nitramines, Hydrolysis, Photolysis, Environmental fate

1. Introduction

Recently there has been increased awareness regarding the emission of amine solvent or degradation products generated in post-combustion CO_2 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_x [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_2 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^3 for air [10]. This is based on a 10^{-6} 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_{OC} 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,