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Preliminary assessment of the Fate of Nitramines in soil and freshwater

Executive Summary Report

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1 OBJECTIVES AND SCOPE OF SERVICES

1.1 Objectives

The main objective of this work is to assess the fate of nitramines in soil and soil water. The sub goals are:

1. Literature study to assess state-of-art knowledge regarding the fate of nitramine in the environment, focusing on the identification of governing factors for mobility and microbial degradation, to illustrate in a box model key parameters important for formation and decay of nitramines based on best available knowledge.
2. To conduct a screening laboratory study assessing partitioning coefficients or adsorption isotherms on eight soil samples, with focus on organic horizons, from the region around TCM, to assess transport and mobility of nitramines with water through the terrestrial environment.
3. To conduct a pilot study of hydrolysis of nitramines in water over a broad pH range to study their pH dependent stability
4. To conduct a small factorial designed biodegradation of nitramines assessing the effect of temperature, DOC and phosphorous.

1.2 Scope of Service

Sorption of nitramines to soil. This task concerns the partitioning of nitramines between water and soil after the deposition to soil. The following activities are included:

- Assess partitioning coefficient or adsorption isotherms of nitramines to soils
- Estimate mobility and theoretical likelihood of nitramines to reach fresh water

Hydrolysis of nitramines. Hydrolysis of nitramines in acidic, neutral and basic water is studied over a 4-week period under abiotic conditions.

Biodegradation of nitramines. Biodegradation of nitramines is tested using a factorial, experimental design at two temperatures and along gradients of P and DOC. A pilot study of potentially harmful effects on biota was performed on key test organisms in aquatic toxicology surveys: the crustacean Daphnia and the green algae Selenastrum.

2 HEALTH, SAFETY AND ENVIRONMENT

The project involved handling of hazardous chemicals and was carried out as required by statutes and regulations. The Standard Operational Procedure (SOP) in the UiO laboratory is that all compounds under study, including possible degradation products, are treated as potentially carcinogenic unless other information is available. A Safe Job Analysis has been conducted.

The University of Oslo is a Governmental institution that follows HSE rules and regulations according to Norwegian Law. UiO is not required to produce HSE data

sheets for compounds synthesized for research purpose. The HSE-manual can be found here:

http://www.mn.uio.no/kjemi/english/about/hse/hse-manual/HSE-manual-department-of-chemistry-english-2011.pdf

Work at the National Environment Research Institute (NERI) in Denmark, were conducted in accordance with the SOP operative at NERI, which meets the required regulations according to Danish Law.

No accidents or near accidents have occurred during the project lifetime.

3 ACTIVITIES

The project *Evaluation of Fate of Nitramines in soil and freshwater* comprised 3 activities. The results from these 3 activities are summarized in the following sections.

3.1 Activity 1: Sorption of nitramines

The study of the nitramine sorption to soil is reported in the report: *Sorption of Nitramines to Soil, Final Report December 2011*.

This nitramine sorption test shows that the bulk of monoethanolnitramine and dimethynitramine are sorbed to the organic rich soils, but that a significant amount remain in the aqueous phase. The test also show clearly that the studied nitramines have a greater sorption to organic rich soil than to mineral soils. This agrees with the general concept that sorption of organic pollutants to soil is greatly influenced by the organic content in the soil.
The average distribution coefficient at equilibrium, K_d, for organic soils was found to be 16 and 47 for monoethanolnitramine and dimethynitramine, respectively. For the mineral soils, K_d was found to be 2.0 and 3 for monoethanolnitramine and dimethynitramine, respectively. The organic carbon partition coefficient, log K_{oc}, was calculated to be approx. 1.6 and 2.0 for monoethanolnitramine and dimethynitramine, respectively.
Compared with other organic pollutants of environmental concern the studied Nitramines are nevertheless to be considered as highly water-soluble and exhibit a relatively low sorption to soil. Based on this pilot test we can conclude that a significant fraction of the nitramines will likely eventually pass through the terrestrial environment and be leached out into surface waters. Further research is therefore required in order to assess the fate and transport of the nitramines in the environment.

3.2 Activity 2: Hydrolysis of nitramines

A thorough study to evaluate nitramine hydrolysis is documented in the report: *Hydrolysis of Nitramines, Final Report October 2011*.

The hydrolysis of dimethylnitramine, $(CH_3)_2NNO_2$, and 2-(nitroamino)-ethanol, $HOCH_2CH_2NHNO_2$, was studied at pH= 5, 7 and 9 over a period of more than 40

days. The lifetime of the two nitramines with respect to hydrolysis is more than 1 year and is independent on pH in the region 5-9. The effect of salt was studied in 2.5 wt% NaCl solutions at pH = 5; no significant decrease in hydrolysis lifetime was observed. It was concluded that primary and secondary nitramines do not undergo hydrolysis to any significant degree under relevant environmental conditions.

3.3 Activity 3: Biodegradation of nitramines

Microbial activity in water is generally dependant on temperature and substrates, where the access to phosphorus (P) and dissolved organic carbon (DOC) are the key parameters. This test was therefore run under a factorial, experimental design at two temperatures and along gradients of P and DOC. The rate of microbial degradation of DMA seems to be slow, yet following-up experiments with better analytical resolution and more species of DMA should be performed before arriving at final conclusions. We also strongly recommend sampling from natural aquatic localities in the vicinity of CO_2-treatment plants to reveal the levels and concentrations that could be anticipated. Following-up toxicological tests should be more sophisticated than those conducted in this pilot study, and also then relate to concentrations measured *in situ*.

Since nitramines also could have potentially harmful effects on biota, we also performed additional pilot studies on key test organisms in aquatic toxicology surveys, the crustacean Daphnia and the green algae Selenastrum. These initial screenings should be seen as rather preliminary, yet with a possible exception for *Daphnia magna*, they suggest no harmful, short-term impact of DMA-concentrations < 5000 µg L^{-1} (i.e. the range of concentrations that can be anticipated under natural conditions).

4 CONCLUSIONS AND RECOMMENDATIONS

The *Evaluation of fate of nitramines in soil and freshwater* project has supplied scientifically sound data as the basis for addressing severe knowledge gaps relating to the fate and impact of nitramines in the Mongstad region.

Nitramine sorption:

Both nitramines are sorbed to organic soils, but a significant amount is likely to be transported with the soil-water. To what extent is inconclusive.

Recommendation:	*Further research is required to determine the fate and transport of the nitramines.*

Nitramine hydrolysis:
There is now a high-quality experimental data set available for nitramine hydrolysis under relevant environmental conditions (pH and salt content). All results point to a very slow hydrolysis.

Recommendation:	*No need for further studies. Nitramines do not hydrolyse in the aquatic environment.*

Nitramine biodegradation:
The rate of microbial degradation of DMA seems to be slow.

Recommendation:	*Experiments with better analytical resolution and more species of DMA should be performed on indigenous water quality before arriving at final conclusions.*

4.1 Overall conclusion

The overall conclusion of the three pilot experiments indicates that the nitramines are potential persistent compounds which may accumulate in the soil and partly be transported to surface waters.

Recommendation:	*More research is required to accurately determine the extent of the accumulation/transport and thereby the fate of the nitramines in the environment.*