Monitoring DEET in Water: Fundamental Study to Evaluate the Plausibility of Mimics

Sylvain Merel¹, Andrey Nikiforov², Shane Snyder¹

¹Department of Chemical and Environmental Engineering, University of Arizona, Tucson (AZ)
²Toxicology Regulatory Services, Charlottesville (VA)

Corresponding author: smerel@email.arizona.edu

Quick Facts on DEET History

- DEET (N,N-Diethyltoluamide, Fig. 1) was initially used by the US Army in the mid-1940s to protect soldiers from mosquitoes during jungle warfare.
- Nowadays DEET is widely used as an insect repellent incorporated in more than 140 commercially available repellent products.

Occurrence of DEET in the Environment

- DEET is washed from the skin when swimming or during showering. Consequently DEET is expected to occur in surface water connected to recreational water bodies or receiving treated wastewater.

Hypothesis

There are compounds that yield a false positive or result in elevated concentration for DEET using existing analytical methodologies.

Objective

Perform theoretical and preliminary research to test the plausibility of a DEET mimic occurring in the environment.

Approach

Step 1: Select and procure potential DEET mimics
- With chromatography and mass spectrometry detection, a mimic should have a mass and structure similar to DEET. Potential mimics were primarily identified through the NIST library, searching for the molecular mass of DEET ± 0.5 Da.
- Mimics were also further selected based on availability from commercial chemical suppliers.

Step 2: Analyze DEET and potential mimics
- As DEET has been reported in the environment using GC-MS and LC-MS/MS methods, authentic standards and selected mimics were analyzed and compared.
- GC-MS method was reproduced from Köpfl et al. (2002) while LC-MS/MS method was reproduced from Trenholm et al. (2006).
- Compounds were analyzed in full scan mode in order to compare the mass spectrum and in MRM mode in order to compare the fragmentation pattern.

Step 3: Collect and analyze wastewater effluents for DEET and mimics
- Wastewater effluents were collected from five locations in four different states, including humid and dry areas expected to have dissimilar DEET concentrations.
- Samples were spiked with a DEET 68 surrogate then split to perform both Liquid-Liquid Extraction (LLE) and Solid Phase Extraction (SPE) for GC-MS and LC-MS/MS analysis, respectively. Duplicate analysis was also performed on samples spiked with mimics (250 ng/L).
- In order to improve the identification of mimics, extracts were also analyzed by high resolution mass spectrometry (LC-QTOF).

Materials

- Solvent and standards
  - HPLC grade water, dichloromethane and methanol were procured from Fisher
- Standards of DEET were procured from Sigma-Aldrich, Alfa Aesar, Accustandard, Vertellus and Clariant
- Selected mimics were procured from Sigma-Aldrich

Chromatography

- LC was performed using an Agilent 1290 UHPLC with a C12 column (Phenomenex Synergy MAX-RP 250 x 4.60 mm; 80 A; 4u particle size)
- GC was performed using an Agilent 7890A with a DB-5MS UU column (Length: 15 m; Diameter: 0.25 mm; Film: 0.25 µm)

Mass spectrometry

- SPE extracts were analyzed using an Agilent 6460 triple quadrupole mass spectrometer and an Agilent 6540 quadrupole time of flight mass spectrometer.
- LLE extracts were analyzed using an Agilent 7000 triple quadrupole mass spectrometer.

Results

Selection of potential DEET mimics
- More than 180 compounds were identified as potential mimics using the NIST library.
- Discrimination based on elemental composition, potential to give similar product ions as DEET, and commercial availability prioritized six potential mimics (Fig. 2). For instance, carbendazim, a fungicide, has a similar transition to DEET and potential to occur in surface water.

Conclusions

- GC-MS and LC-MS/MS analysis can report substantially different values showing a potential matrix effect.
- The mimics selected may overestimate the concentration of DEET reported.
- Other potential mimics known to occur in wastewater have recently been identified and may be evaluated in future studies.

Acknowledgement

The authors thank the DEET Task Force for funding the present study as well as Agilent Technologies for providing analytical instruments and supplies.

References