

**Comments to State Water Resources Control Board on Proposed Amendment to the
Recycled Water Policy to Incorporate Monitoring Requirements for
Constituents of Emerging Concern**



To Whom It May Concern:

In response to the Draft Amendment to the Recycled Water Policy dated 10 May 2012, the DEET Task Force (DTF) has prepared the following comments. Several recent reports, including the “Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water – Recommendations of a Scientific Advisory Panel Report”, have indicated that DEET occurs in the aqueous environment with large prevalence and magnitude. However, some occurrence data for DEET is questionable considering lack of correlation with geographical usage patterns, lack of seasonal trends, and potential analytical interferences. Specifically, the DTF is completing a yearlong study with the University of Arizona, Department of Chemical and Environmental Engineering, which indicates that some organic chemicals may act as mimics resulting in false positive detections for DEET using current and formerly applied analytical techniques. These DEET mimics have the potential to cause erroneous analytical results. We suggest that the State Water Board should not mandate DEET monitoring before a suitable analytical method that is uniquely-specific for DEET in environmental matrices is developed and fully validated. Using current analytical methodologies, data from water monitoring programs for DEET will likely lead to false conclusions that will simply confound interpretation of results from the monitoring program for Constituents of Emerging Concern.

Two abstracts for posters on the University of Arizona research program to be presented at the 2012 SETAC North America Annual Meeting are enclosed as supporting information for the comments above.

Sincerely,

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Presentation Type:

Poster Preferred

Track:

Environmental or Analytical Chemistry

Session:

CECs in Wastewater and Receiving Water: Analysis and Perspectives

Abstract Title:

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

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Abstract:

The recent advances in analytical chemistry allow trace levels (ng/L or lower) of organic chemicals (TORCs) to be easily detected in environmental matrices. Consequently, punctual and routine analysis of wastewater and receiving water reveal the occurrence of more and more contaminants, most of them being classified under the term Contaminants of Emerging Concern (CECs). Among these CECs, the insect repellent DEET is one of the most frequently reported. However, the concentrations reported in several studies are relatively high (reaching hundreds ng/L) and not really consistent with the usage of DEET, which is expected to be limited to the mosquito season and localized to humid areas affected by mosquitoes. A potential explanation for these unexpected values could be the occurrence of one or more chemical mimics in the environment that would lead to an overestimation of DEET concentration in water. Therefore, we performed a fundamental study to evaluate the plausibility of such a hypothesis utilizing both GC-MS and LC-MS methods. A mimic would have the same retention time and transitions as DEET, which implies similar structure and mass. Based on these criteria, the compounds most readily available were researched through the websites of common chemical suppliers. Six potential mimics were identified for this study and analyzed through LC-MS, LC-MS/MS, GC-MS and GC-MS/MS. While 4 of the 6 potential mimics could be easily discarded because of an inappropriate retention time, the other 2 could not be resolved from DEET by LC-MS analysis. In addition, LC-MS/MS analysis showed similar transitions between these two compounds and DEET. Even though the relative abundances of each transition might be slightly different, detecting an anomaly or not only depends on the operator of the instrument and the level of tolerance accepted in each laboratory. In conclusion, the present study does not confirm a specific DEET mimic in the environment but clearly demonstrates the plausibility of such a hypothesis. Future work will extend the research on potential mimics to other compounds structurally similar to DEET and confirm whether or not the tangible mimics identified in the laboratory could actually occur in environmental samples.

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Poster Preferred

Track:

Environmental or Analytical Chemistry

Session:

CECs in Wastewater and Receiving Water: Analysis and Perspectives

Abstract Title:

Monitoring DEET in Water: Potential Interference from Solvents During LC-MS/MS Analysis

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Abstract:

The tremendous improvement of analytical capabilities over the last decade has made it relatively easy to measure trace levels of organic contaminants (TORCs) in a wide range of matrices. Consequently, emerging contaminants are now frequently monitored in the environment, particularly in wastewater and receiving water. Among TORCs, the insect repellent DEET has been frequently detected in US waters. DEET is even considered as a relevant indicator to assess the contribution of wastewater effluent in the receiving water. Recent papers have monitored DEET through sample concentration by solid phase extraction followed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) analysis. While LC-MS/MS provides relatively high specificity, the concentration of DEET reported can reach several hundred ng/L, which seems unusually high for a chemical used only during the mosquito season. In addition, DEET often has been detected in laboratory blanks. Therefore, in this study we search for a potential interference from the mobile phase itself. Two mobile phase (water/methanol and water/acetonitrile) and two brands of organic solvents were tested on three different columns. The mobile phase was allowed to flow through the columns at 5% organic for 0; 5; 10; 20; 30 and 60 minutes before performing the analysis for DEET on a 0 μ L injection (no sample injected and no contact between the needle and the vial). The results showed the signal of DEET (4 transitions monitored) increases with the flow time, which sustains the postulate of an interference in the mobile phase. To further confirm this hypothesis, HPLC water, methanol and acetonitrile (two brands of each) were concentrated through evaporation below nitrogen stream and then analyzed for DEET by LC-MS/MS. All the concentrated samples exhibited a higher signal for DEET. In addition, the relative abundances of the four transitions monitored were similar to those observed when analyzing the analytical standard of the insect repellent. Such findings suggest a potential interference originated from the solvents during the analysis of DEET, which might lead to an overestimation of the actual concentration of this compound in the environment. Further research will be conducted to characterize this interference and determine to what extent it could influence the concentrations of DEET reported.