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Potential analytical interferences and seasonal variability in diethyltoluamide environmental monitoring programs

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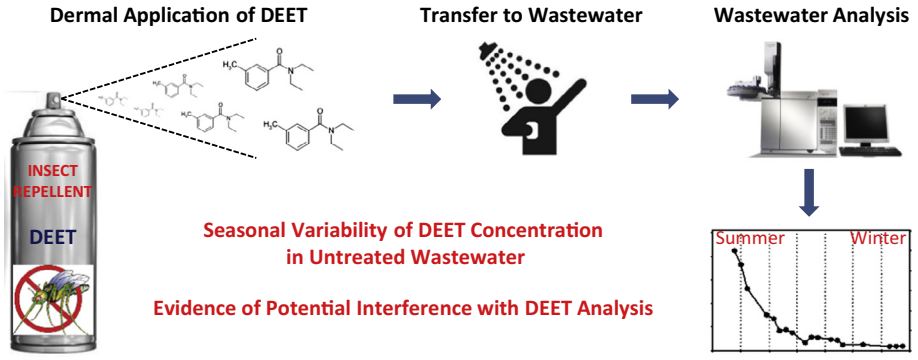
HIGHLIGHTS

- Seasonal variation of DEET concentration in primary wastewater influent.
- Discrepancies in DEET concentration reported by different analytical methods.
- Some compounds can mimic DEET and induce overestimation of its concentration.
- Interference or DEET contamination in solvents used for sample preparation and analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

N,N-diethyl-m-toluamide (DEET), the active component of many insect repellents, is among the most frequently detected compounds in aqueous environments with concentrations reported in the ng L^{-1} to μg L^{-1} range. However, DEET is often detected in blanks and reported concentrations differ significantly depending on the analytical technique employed. In addition, relatively sparse data are available regarding the seasonal variability of DEET concentrations in water and there are apparent inconsistencies with expected use patterns. Therefore, the present study investigates potential interferences affecting the detection and quantification of DEET then the geographical and seasonal variations of DEET concentrations. To examine potential analytical interferences, DEET was analyzed in five geographically-diverse wastewater effluents using both gas chromatography and liquid chromatography coupled to mass spectrometric detectors. At times, the concentrations quantified by the employed analytical methods varied significantly. Five compounds with similar molecular weights and structures as DEET were investigated as potential mimics and some were shown to induce an overestimation of DEET. Further experimentation suggested that the solvents used in sample preparation and HPLC analysis are another possible source of interference. Besides potential interferences, the seven-month weekly monitoring of DEET in the primary effluent of a wastewater treatment plant demonstrated a clear seasonal trend with decreasing concentration from summer to winter. These data collectively demonstrate that there are many challenges in the quantification of DEET in complex environmental samples and that co-occurrence of similarly structured substances present in the water sample and/or the solvents used for the analysis could induce analytical bias.

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1. Introduction

Over the last two decades, with the constant progress in analytical science, monitoring trace organic contaminants (TOrCs) such as pharmaceuticals and personal care products (PPCPs) in complex matrices such as surface water or wastewater have become increasingly popular and routine. Analytical methods have become increasingly more reliable and sensitive, allowing the simultaneous quantification of a broad range of TOrCs with reporting limits in aqueous samples often at ng L^{-1} level or lower. Among the TOrCs commonly monitored in environmental water matrices, N,N-diethyl-m-toluamide (diethyltoluamide or DEET – Fig. 1) is one of the most frequently detected compounds (Kolpin et al., 2002; Knepper, 2004; Loraine and Pettigrove, 2006; Anumol et al., 2013).

The United States Environmental Protection Agency (US EPA) estimated the nationwide usage of DEET to be approximately 1810 ton per year in 1998 (US EPA, 1998; Chen et al., 2012). It was later reported that approximately one third of the US population was expected to use at least one DEET-containing products (US EPA, 2007) from the 524 commercial names referenced (US EPA, 2014).

After product uses by dermal application, DEET is typically washed from the skin when bathing, so its occurrence in municipal wastewater is ensured. In fact, DEET has been previously reported in USA (Trenholm et al., 2008; Anumol et al., 2013), Europe (Terzic et al., 2008; Rodil et al., 2012), Asia (Nakada et al., 2006; Sui et al., 2011) and Australia (Costanzo et al., 2007) wastewaters. Several studies have examined the attenuation of DEET by water treatment processes, including membranes and membrane bioreactors (Alturki et al., 2010), activated sludge (Bernhard et al., 2006; Nakada et al., 2006), sand filtration (Nakada et al., 2007), activated carbon (Snyder et al., 2007; Gerrity et al., 2011), UV irradiation (Kim and Tanaka, 2009; Kim et al., 2009) and chemical oxidation (Snyder et al., 2006; Peller et al., 2011).

Despite attenuation during wastewater treatment, residual DEET is present in the effluent discharged to the environment (Trenholm et al., 2006; Anumol et al., 2013) and has been measured in drinking water (Benotti et al., 2009; Rodil et al., 2012). For instance, a survey of wastewater contaminants in US streams reported DEET as one of the most frequently detected anthropogenic compounds with a frequency of 74% and a maximum concentration of 1.1 μg L^{-1} (Kolpin et al., 2002). Likewise, DEET was one of the most consistently detected and persistent TOrCs evaluated (Benotti et al., 2009) in US drinking waters. In addition, DEET has been reported in surface water from Europe (Quednow and Püttmann, 2009), Asia (Heeb et al., 2012) and Australia (Costanzo et al., 2007) at concentrations up to 4 μg L^{-1} (Dsikowitzky et al., 2011). DEET has also been reported in landfill leachate (Eggen et al., 2010) and groundwater (Barnes et al., 2008). Thus, DEET appears to be a ubiquitous environmental contaminant; however, seasonal and geographic patters do not appear to provide consistent or expected trends.

While DEET is expected to be used primarily in summer within regions with warm humid climates, which favor the proliferation of mosquitos, unusually high DEET concentrations have been reported in dry regions such as the Mojave Desert (Trenholm et al., 2006) and the Sonoran Desert (Anumol et al., 2013). These findings contradict the expected geographical pattern for the use of DEET. Data regarding the seasonal variation of DEET concentration are usually too limited to draw any conclusion. Indeed some studies reported concentrations slightly higher in summer than winter but without statistical comparison due to a data set too limited (Nakada et al., 2006; Sui et al., 2011; Yang et al., 2011; Calza et al., 2013; Loos et al., 2013a). Moreover, discrepancies among measured DEET concentrations can be observed depending on the analytical method used (Trenholm et al., 2008). Also, in addition to unusually high concentrations (up to 15 μg L^{-1}) reported in treated wastewater (Loos et al., 2013b), the frequent and practically ubiquitous detection of DEET in blanks (Nakada et al., 2007; Trenholm et al., 2008; Anumol et al., 2013; Kolpin et al., 2013) has in some cases come to the exclusion of DEET from environmental studies (Ferguson et al., 2013). This suggests the influence of a potential unexpected source of DEET and/or the possibility of analytical artifacts that impact the identification and quantification of DEET in complex environmental matrices. In fact, a previous study mentioned the existence of an unknown interference co-eluting with DEET, preventing its quantification (Weigel et al., 2004). It is therefore important to evaluate the degree to which analytical methods can accurately and precisely measure DEET and whether the possibility exists for structural analogs (i.e., mimics) to result in the over-quantification of DEET detected in routinely tested aqueous environmental matrices.

The present study aims to evaluate potential analytical bias (potential mimics, solvent impurities, etc.) susceptible to cause an overestimation of DEET concentration in the aqueous environment

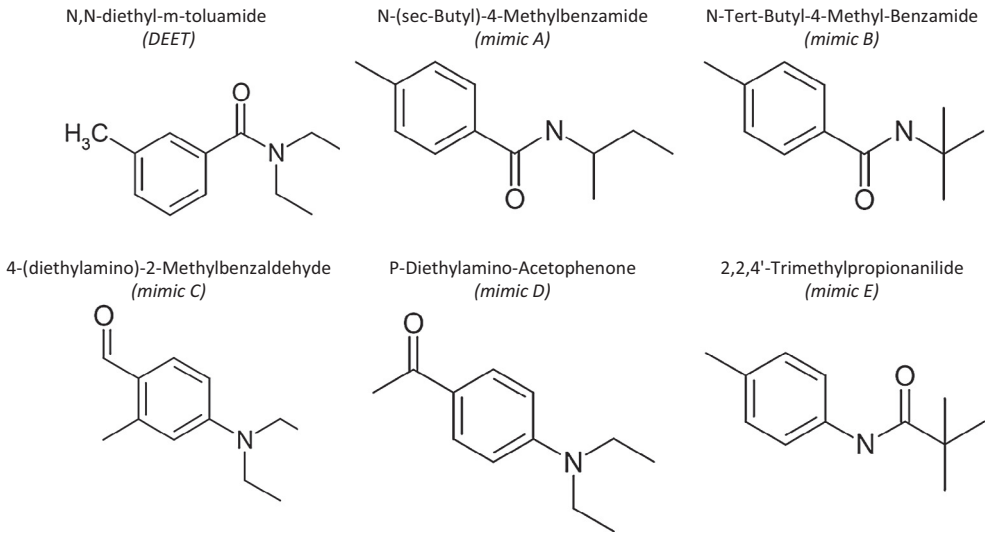

Fig. 1. Structure of DEET and selected mimics.