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Dissipation of a commercial mixture of polyoxyethylene amine surfactants in aquatic outdoor microcosms: Effect of water depth and sediment organic carbon

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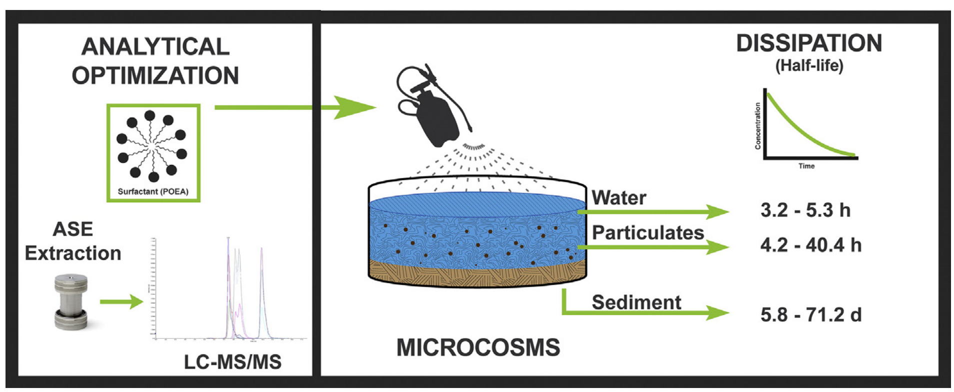
HIGHLIGHTS

- POEA half-life was monitored in microcosm water, sediment and suspended solids.
- Sediment extraction methods were optimized for the quantification of POEA.
- POEA showed very short (<6 h) water-column dissipation half-life.
- POEA showed high affinity for sediment materials.
- High affinity for sediment resulted in low recovery from spiked samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This study optimized existing analytical approaches and characterized the effect of sediment total organic carbon (0.05–2.05% TOC), and water depth (15, 30, and 90 cm) on the fate of MON 0818, a commercial mixture of polyoxyethylene amine surfactants (POEAs), in outdoor microcosms. Mixtures of POEAs are commonly used as adjuvants in commercial herbicide formulations containing glyphosate. Until recently, analytical methods sensitive enough to monitor environmental concentrations of POEAs in aquatic systems were not available. After optimizing recently developed analytical methods, we found that the combined use of accelerated solvent extraction (ASE) and liquid chromatography–tandem mass spectrometry provided a reliable approach for determining the concentration of sediment-adsorbed POEAs. The surfactant showed strong affinity for sediment materials, with low maximum recoveries by ASE of 52%. Under microcosm conditions, water depth or sediment characteristics did not significantly affect the water-column half-life of POEA, which ranged from 3.2 to 5.3 h. Binding of POEAs to suspended solids was observed, which dissipated via one- or two-phase exponential decay; when two-phase decay occurred, fast phase half-life values ranged from 0.71 to 1.3 h and slow-phase values ranged from 18 to 44 h. Concentrations of POEA increased in sediment shortly after application and decreased over the study period with a half-life of 5.8 to 71 d. The concentrations of POEAs in the sediment of the shallow (15 cm) ponds dissipated following a two-phase exponential decay model with an initial fast-

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phase half-life of 1.1 to 8.9 d and a slower second-phase half-life of 21 d. Our results suggest that aquatic organisms are unlikely to be exposed to POEAs in aqueous phase for periods of more than a few hours following an over-water application, and that sediment is a significant sink for POEAs in aquatic systems.

1. Introduction

Mixtures of polyoxyethylene tallow amines (POEA), a group of non-ionic/cationic surfactants belonging to the larger class of alkylamine ethoxylates (ANEOs), are commonly used formulants in glyphosate herbicide formulations, such as Roundup® brand herbicides and Vision® (Giesy et al., 2000; Riechers et al., 1994). The available data on the toxicological effects of POEAs to aquatic organisms (Brausch et al., 2007; Brausch and Smith, 2007; Bringolf et al., 2007; Folmar et al., 1979; Frontera et al., 2011; Guilherme et al., 2012; Moore et al., 2012; Moore et al., 1986; Servizi et al., 1987; Tsui and Chu, 2003; Wan et al., 1989) strongly support the hypothesis that POEA is the main driver of toxicity from glyphosate herbicide formulations to non-target aquatic organisms. Results of these laboratory studies suggest the potential for effects (e.g., laboratory EC_{10} and EC_{50} values for mortality and growth inhibition) at concentrations close to those estimated to occur in the environment. The concern over POEA-mediated toxicity, especially the potential effects on amphibians (NRA, 1996), has resulted in regulatory authorities prohibiting direct application of formulations containing POEA to lakes, rivers, and streams in countries such as Australia, Canada, and the United States (Giesy et al., 2000; PMRA, 2015). However, the potential exists for input to aquatic systems through drift, movement through runoff of surface waters, or through aerial overspray of shallow ephemeral wetlands, for example, during aerial applications in forestry. Additionally, in recent years, a number of use-label expansions have been submitted by state and provincial conservation authorities requesting permission to use the POEA-containing formulations, for the control of the invasive reed species *Phragmites australis* in the north east of the US and Canada (Bickerton, 2007; Crowe et al., 2011). Taken together, there is a potential for POEA to enter surface waters, underscoring the need for a more comprehensive characterization of its fate and behaviour.

Over the last two decades, a number of studies have attempted to characterize the composition of these surfactant mixtures, both in the original herbicide formulations and in environmental samples (Corbera et al., 2010; Krogh et al., 2003; Krogh et al., 2002; Lang et al., 1999; Mesnage et al., 2013; Oskarsson and Holmberg, 2006; Schreuder et al., 1986; Tush et al., 2013). While a few of these studies present quantitative methodologies (Corbera et al., 2010; Schreuder et al., 1986), these have been usually aimed at greater concentrations, such as those typically found in the commercial herbicide formulations themselves. The number of easily accessible and reliable analytical methods for the quantification of these surfactants at environmentally and/or toxicologically relevant concentrations is; however, much more limited. Krogh et al. (2002) and Krogh et al. (2003) were, until recently, the only available studies providing methods able to measure commonly used mixtures of ANEOs in both water and soil matrices at environmentally relevant concentrations (limit of detection: 0.3–6 μg l^{-1} in water and 24–43 μg kg^{-1} in soil). Wang et al. (2005) were able to quantify MON 0818, the commercial mixture of POEAs often present as a component in the Roundup® family of herbicides, in fortified well water samples with a limit of quantitation (LOQ) of 50 ng ml^{-1}. This study, however, followed the manufacturer's own analytical protocols and the method, which is only briefly described in the study, and not available in the open literature.

As part of a large-scale collaborative project involving the present study, Ross and Liao (2015) recently developed a sensitive, reliable, and simple analytical method for the analysis of POEA at environmentally relevant concentrations in natural waters and sediments. The LOQ of this method is 0.5 ng ml^{-1} for water and 2.5 ng g^{-1} for sediment extracts, which is an order of magnitude below the LOQ achieved in soil extracts (24–43 ng g^{-1}) by Krogh et al. (2002).

The previous lack of adequate analytical methods has made it difficult to evaluate the fate of ANEOs, particularly POEAs, in the aquatic environment as well as the estimation of field dissipation data as described in the US EPA Fate, Transport and Transformation Test Guidelines (US EPA, 2008b). Using conservative estimates based on an unpublished suspended sediment-water biodegradation study with ^{14}C-labelled POEA presented as part of the glyphosate registration submission (summarized in NRA (1996)), Giesy et al. (2000) applied a water column half-life of 21–42 d for their risk assessment of Roundup®. Wang et al. (2005), measured the changes on water concentrations of MON 0818 in laboratory-based microcosms (72 l) containing sediments with different levels of total organic carbon (TOC). The authors observed shorter water column half-lives in aquaria containing sediment with higher TOC (18 and 13 h for 1.5 and 3% TOC, respectively), while no significant changes in concentration in water were observed in the aquaria with no sediment over the duration of the study (96 h). The half-life values calculated by Wang et al. (2005) are considerably shorter than those estimated by Giesy et al. (2000).

Given the limited aquatic field dissipation data available for POEA and incomplete understanding of its role in the toxicity of formulated glyphosate products, the aims of this study were 1) to optimize the existing analytical methodologies for their use on large numbers of environmental samples, with special attention to the sediment extraction step (improved extraction, and application of high-throughput methods), and 2) to evaluate the effect of water depth and sediment organic carbon on the fate of POEA in outdoor aquatic microcosms.

2. Materials and methods

2.1. Test substance and reagents

The commercial surfactant mixture MON 0818 was used in this study. MON 0818 is the main surfactant used in traditional glyphosate formulations such as Roundup Original® and its forestry-use equivalent Vision®. MON 0818 contributes approximately 15% of the total weight of these formulations (Edginton et al., 2004). The product consists mainly of polyoxyethylene-(15)-tallow-amine (POEA) (CAS no. 61791-26-2), a tallow-based mixture of alkylamine ethoxylates (ANEOs) with varying length on their alkyl/alkene chain, R, (14–18 C) and ethoxylate chains (average of 15) (Fig. 1) Pure (99%) POEA was used to prepare all analytical standards. A technical solution of MON 0818 was used for the microcosm fate studies. Analysis of the particular solution used in this study showed it contained 68% POEA. Both the technical solution and the pure standard were supplied by the Monsanto Company (St. Louis, Missouri, US).

Additional information on reagents, artificial soils materials and glassware cleaning and preparation are provided in Section 1.1 of the SI.

2.2. Sample preparation

Water samples were prepared by following, with slight modifications, the steps described in Ross and Liao (2015). Briefly, refrigerated samples of water diluted 1:1 v/v with methanol were brought to room temperature for 30 min, and vortexed for 10 s. One millilitre of each sample was transferred to a 1.5-ml Eppendorf vial and centrifuged at 14,000 × g (MiniSpin® plus, Eppendorf, Mississauga, ON) for 5 min. A