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Technical basis for using passive sampling as a biomimetic extraction procedure to assess bioavailability and predict toxicity of petroleum substances

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HIGHLIGHTS

- Biomimetic extraction (BE) quantifies dissolved hydrocarbons in petroleum contaminated samples.
- BE hypothesized as surrogate measure of the molar sum of hydrocarbons in target lipid and resulting toxicity.
- BE-based toxic thresholds were consistent with target lipid model confirming predictive utility.

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ABSTRACT

Solid-phase microextraction fibers coated with polydimethylsiloxane (PDMS) provide a convenient passive sampling format to characterize bioavailability of petroleum substances. Hydrocarbons absorb onto PDMS in proportion to both freely dissolved concentrations and partitioning properties of the individual constituents, which parallels the mechanistic basis used to predict aquatic toxicity in the PETROTOX model. When deployed in a non-depletive manner, combining SPME with thermal desorption and quantification using gas chromatography-flame ionization creates a biomimetic extraction (BE) procedure that has the potential to simplify aquatic hazard assessments of petroleum substances since the total moles of all hydrocarbons sorbed to the fiber can be related to toxic thresholds in target lipid of aquatic organisms. The objective of this work is to describe the technical basis for applying BE measurements to predict toxicity of petroleum substances. Critical BE-based PDMS concentrations corresponding to adverse effects were empirically derived from toxicity tests on different petroleum substances with multiple test species. The resulting species sensitivity distribution (SSD) of PDMS effect concentrations was then compared and found consistent with the previously reported target lipid-based SSD. Further, BE data collected on samples of aqueous media dosed with a wide range of petroleum substances were highly correlated to predicted toxic units derived using the PETROTOX model. These findings provide justification for applying BE in environmental hazard and risk evaluations of petroleum substances and related mixtures.

1. Introduction

Environmental contaminants often occur as mixtures, which complicate risk and hazard assessments due to the variable toxicity and physicochemical properties of the individual constituents in the mixture. Petroleum substances are an important class of contaminants due to their wide-spread use in commercial products and chemical intermediates but also due to anthropogenic and natural releases of hydrocarbons through seeps or deposits and combustion (Board, 2005; Kvenvolden and Cooper, 2003). The hydrocarbon constituents in petroleum substances have a wide

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range in physicochemical properties including water solubility and vapor pressure (Arey et al., 2005; Mackay et al., 1997). These properties span several orders of magnitude for individual constituents even within the same petroleum substance. Further, the abundance of constituents within a substance can vary based on the source of crude oil, refinery processes (e.g., distillation), and natural weathering processes once substances are emitted into the environment.

One approach to address this complexity is to use coupled fate and effects models that account for the complex composition of a petroleum substance as well as the differential physicochemical properties of the individual constituents within the substance. The hydrocarbon block method is an example of this approach, which reduces the complexity of petroleum substances into more narrowly-defined blocks, or pseudoconstituents (King et al., 1996). The compositional data is used to determine the mole fraction of a given block and the dissolution is computed using Raoult's Law (Prausnitz et al., 1998). The toxicity of the dissolved pseudoconstituents is determined using critical body burden models, such as the Target Lipid Model (TLM) (Di Toro et al., 2000; Di Toro and McGrath, 2000; McGrath and Di Toro, 2009). The TLM simulates the accumulation of hydrocarbon into a hypothetical target lipid phase and toxicity occurs when the sum of all accumulated hydrocarbons exceed a critical threshold in this phase. This modeling approach has been formalized in the PETROTOX model which provides a predictive tool to estimate aquatic toxicity of petroleum substances based on substance composition (Redman et al., 2012, 2017b).

The complexity inherent in evaluating the toxicity of petroleum substances is one reason bulk exposure metrics, such as total polycyclic aromatic hydrocarbons (TPAH) or total petroleum hydrocarbon (TPH), serve as imprecise hazard assessment metrics (Redman and Parkerton, 2015). The practical challenge, however, is that detailed compositional analysis of dissolved hydrocarbon constituents is often not available to support an improved technical basis for quantitative risk assessment. Therefore, a need exists for a convenient analytical measurement that directly quantifies the bioavailability of all petroleum hydrocarbons that can contribute to toxicity. The growing application of passive sampling methods for environmental monitoring (Mayer et al., 2014) and hazard assessment of physically and chemically dispersed oils (Letinski et al., 2014) provides further motivation for evaluating the technical basis of this analytical approach. Solid phase microextraction (SPME) provides a convenient passive sampling format that can support hazard and risk assessment by providing measurements of freely dissolved contaminants (Mayer et al., 2014). Individual constituents partition to polydimethylsiloxane (PDMS) coated fibers in proportion to substance partitioning properties and abundance in the exposure media, which is analogous to the fundamental concepts (e.g., accumulation in target lipid) used in the PETROTOX model.

Most applications of SPME to environmental media characterize the concentrations of individual constituents (Mayer et al., 2014; Hawthorne et al., 2006). For exposures to petroleum substances, many unresolved constituents can contribute to aquatic toxicity (Scarlett et al., 2007), which are not captured in GC-MS analysis which quantifies only a limited set of individual hydrocarbon analytes. SPME-based methods that employ GC-FID provide a potential solution since the molar response of diverse hydrocarbons is similar based on quantification with flame ionization detection (Letinski et al., 2014). Thus, by measuring the total molar accumulation of hydrocarbons on fiber PDMS, a surrogate measurement of total petroleum hydrocarbon bioavailability is provided. The particular application of SPME in the present work is performed in a non-depletive manner by employing a low PDMS-water ratio so that the accumulation on the fiber does not significantly reduce exposure concentrations, a so-called biomimetic extraction (BE) (Letinski et al., 2014). This design is consistent with the intent of aquatic hazard testing, where uptake of chemicals by test organisms are not expected to deplete the exposure concentrations.

The goal of this work is to extend the validation of the BE method (Letinski et al., 2014; Leonards et al., 2011; Parkerton et al., 2000; Redman et al., 2014a, 2017a) for use in hazard assessments of petroleum substances through analysis of toxicity data sets including a broader diversity of test species and petroleum substances. Validation was done in successive steps. First, empirical BE-based critical effect concentrations were derived that correspond to observed acute and sublethal effects (e.g., LC50, EC50). The BE critical effect concentrations derived from paired toxicity test and BE data for different petroleum substances were then compared to target-lipid based effect concentrations obtained via application of the TLM. Second, BE measurements collected on samples of aqueous media dosed with a wide range of petroleum substances were compared for consistency with PETROTOX model predictions. Lastly, polyparameter linear free energy relationships (ppLFER) were then applied to gain further insights on the comparative partitioning behavior of different hydrocarbon classes between target lipid and the surrogate PDMS phase.

2. Materials and methods

A dataset of consistent, high quality ecotoxicity, BE, and substance compositional data are used as the basis for analysis in the present study. The BE method is based on more than 20 years of development and application (Letinski et al., 2014; Parkerton et al., 2000; Woods et al., 2007). The validation datasets include hundreds of individual BE measurements across 16 major classes of substances (Table 1) and for 11 test organisms including juvenile and fish embryos, marine and freshwater invertebrates, and algae. The present study builds on a prior toxicity modeling analysis (Redman et al., 2017b) by relating many of those same published data to corresponding BE measurements performed in one laboratory (e.g., ExxonMobil Biomedical Sciences, Inc, Annandale, New Jersey USA).

2.1. Passive sampling methods

Automated BE-SPME analysis was performed on a Perkin Elmer Autosystem gas chromatograph with flame ionization detector (GC-FID). The GC was equipped with a 15 m × 0.53 mm id capillary column with 1.5 μm Rtx-1 stationary phase (Restek) or equivalent and interfaced with a Gerstel (CTC Analytics) MultiPurpose Sampler (MPS) configured for automated SPME injections. The GC inlet was maintained at 280 °C and contained an empty 1 mm id (narrow bore) liner (no glass wool). Automated SPME fiber injections were made in the splitless mode with a split time of 3 min. The carrier gas was helium at a constant flow rate of 17 mL/min. The GC oven was temperature programed from 40 °C for 3 min up to 300 °C at a rate of 45 °C/minute. The FID temperature was 300 °C and the detector signal attenuation was −3.

Water samples were placed in ca. 20 mL glass vials with no headspace and sealed with Teflon® faced septum screw caps. Samples were automatically extracted with a 1 cm, 30 μm polydimethylsiloxane (0.132 μL PDMS) SPME fiber (Supelco) for 100 min at 30 °C with orbital agitation at 250 rpm prior to injection. The fiber was automatically thermally desorbed for 3 min directly in the GC injection port. The SPME fiber was thermally cleaned for at least