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The robustness of single-point Tenax extractions of pyrethroids: Effects of the Tenax to organic carbon mass ratio on exposure estimates

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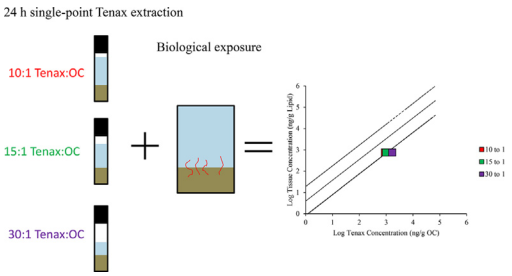
HIGHLIGHTS

- Variation in Tenax extraction methods may limit widespread use in risk assessments.
- Increasing Tenax:OC ratios had minimal impact on Tenax extractable concentrations.
- Tenax exposure estimates are as consistent as other extraction techniques.
- Using correct toxicological endpoints to model exposure is critical for success.
- Single-point Tenax extractions should use Tenax:OC ratios of at least 5:1.

GRAPHICAL ABSTRACT



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ABSTRACT

Use of Tenax extractable concentrations to estimate biological exposure to hydrophobic organic contaminants is well documented, yet method variation exists between studies, specifically in the ratio of Tenax mass to organic carbon mass in the sediment (Tenax:OC ratio) being extracted. The effects of this variation on exposure estimates are not well understood. As Tenax is theoretically in direct competition with organic carbon for freely dissolved chemical in sediment interstitial water, varying the Tenax:OC ratio could impact single-point Tenax extraction (SPTE) exposure estimates. Therefore, the effects of varying Tenax:OC ratios on SPTE pyrethroid concentrations from field-contaminated and laboratory-spiked sediments were compared to bioaccumulation by *Lumbriculus variegatus*. The Tenax:OC ratio had minimal effect on SPTE pyrethroid concentrations. The SPTE pyrethroid concentrations obtained using the highest and lowest Tenax:OC ratios ranged from 0.85- to 3.91-fold different, which is unlikely to contribute substantial error to bioaccessibility estimates. Comparisons to Tenax exposure endpoints from previous research reveal the variation in these endpoints is likely due to toxicokinetic and toxicodynamic differences; processes common to exposure estimates provided by any chemical extraction technique. As the pyrethroid concentrations in the experimental sediments caused toxicity to *L. variegatus*, thus affecting bioaccumulation, the SPTE concentrations overestimated bioaccumulation. However, SPTE concentrations strongly correlated with growth inhibition regardless of the Tenax:OC ratio, providing accurate estimates of the correct exposure endpoint. Tenax masses of 0.500–0.800 g

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should provide sufficient Tenax to achieve Tenax:OC ratios of at least 5:1, which will provide accurate exposure estimates while retaining the ease of conducting SPTEs.

1. Introduction

The success of evaluating risk of hydrophobic organic contaminants (HOCs) in aquatic sediments hinges on obtaining the most accurate estimates of the bioavailable compound present (DiToro et al., 1991; Simpson and Batley, 2016; USEPA, 1997). As such, substantial research within sediment toxicology has focused on finding accurate, reliable, and easy to use methods for evaluating HOC exposure. The most available form of chemical in sediment for uptake by biota is the chemical concentration freely dissolved in the interstitial water, which represents the chemical activity of the contaminant in sediment. While exposure can also occur through ingestion of contaminated sediment, the chemical concentration in the interstitial water can be used to estimate bioaccumulation and toxicity of HOCs in aquatic environments (DiToro et al., 1991; Lydy et al., 2014; Reichenberg and Mayer, 2006; Semple et al., 2004). Organic carbon normalization utilizes the principles of partitioning to account for the chemical fraction in sediment that will contribute to the freely dissolved interstitial water concentration by accounting for the fraction of sediment to which the contaminant is sorbed (DiToro et al., 1991). At equilibrium, the chemical activity of the contaminant on the organic carbon will equal that in the interstitial water, such that the partition coefficient between these two phases, the organic carbon water partition coefficient (K_{OC}), can be used to predict the chemical concentration in one phase or the other (DiToro et al., 1991). Use of organic carbon normalization to estimate exposure; however, does not always work well, as additional factors other than just organic carbon partitioning are responsible for the exposure concentration in sediments (Cornelissen et al., 2001; Morrison et al., 2000). Therefore, the development of other extraction techniques to more clearly represent exposure continues to be a major focus of environmental risk assessments.

The most common of these extraction techniques are passive samplers, such as solid-phase microextraction (SPME) fibers, which represent bioavailable sediment concentrations through equilibrium partitioning with the freely dissolved chemical in the environment (Lydy et al., 2014; OSWER, 2012; Parkerton and Maruya, 2014). The utility of passive samplers has been well documented and application of this technique in risk assessment is widely accepted (OSWER, 2012). Similarly, Tenax extractions, either sequential or single-point extractions, provide accurate measures of desorption of HOCs from sediment, and can be used to estimate both dermal and dietary exposure of HOCs to benthic invertebrates (Du et al., 2013, 2014; Harwood et al., 2012, Harwood et al. 2013a,b; Kraaij et al., 2001, Kraaij et al. 2002; Landrum et al., 2007; Mackenbach et al., 2012, 2014; Shor et al., 2003; ten Hulscher et al., 2003; You et al., 2006, 2008). Tenax extractions provide exposure estimates by measuring the bioaccessible chemical fraction, or the chemical fraction in the environment that may become available to cross a biological membrane in a given time frame (Du et al., 2013, 2014; Harwood et al., 2012, Harwood et al. 2013a,b; Kraaij et al., 2001, Kraaij et al. 2002; Landrum et al., 2007; Mackenbach et al., 2012, 2014; Semple et al., 2004; Shor et al., 2003; ten Hulscher et al., 2003; You et al., 2006, 2008). Since bioaccessibility is linked to the rapidly desorbing fraction (F_{rap}), which represents the labile chemical fraction available for uptake through both interstitial water and dietary release, improvements in Tenax extraction methods have been sought to provide accurate estimates of F_{rap} with the least laboratory effort and time (Cornelissen et al., 1998; Harwood et al., 2012; Kraaij et al., 2001, 2002; Kukkonen et al., 2004; Lydy et al., 2015; Sormunen et al., 2008; Trimble et al., 2008; You et al., 2007, 2009). While sequential Tenax extractions can be used to measure desorption of HOCs from sediment and offer the most comprehensive view of desorption, these experiments are time-consuming and labor intensive (Cornelissen et al., 1998, 2001). A simplification of this technique uses single-point Tenax extractions (SPTEs), generally lasting 6–30 h with 24 h extractions being most common (Cornelissen et al., 2001; Harwood et al., 2015; Lydy et al., 2015). Single-point Tenax extractable concentrations of HOCs correlate well with the chemical concentration in F_{rap} and thus, provide rapid estimates of exposure (Cornelissen et al., 1998, 2001; Kraaij et al., 2001, Kraaij et al. 2002; Kukkonen et al., 2004; Lydy et al., 2015; Sormunen et al., 2008; Trimble et al., 2008; Xu et al., 2008; Yang et al., 2008; You et al., 2007, 2009). Many studies exist demonstrating the utility of the SPTE as an estimate of bioaccessibility and exposure, but the methods used with this technique vary across studies (Lydy et al., 2015). A recent review of the Tenax literature revealed the largest variation in the application of the SPTE exists in the choice of Tenax mass used relative to the organic carbon mass in the Tenax extraction system (Lydy et al., 2015). Tenax to organic carbon mass (Tenax:OC) ratios have ranged between 0.132:1 to 109:1 to estimate exposure of different HOC classes across sediments, and only one study has briefly investigated the effects of this ratio on estimates provided by the Tenax method (White et al., 1999).

The success of Tenax extractions to estimate bioaccessibility of different compound classes across a wide range of environments depends on the ability of the Tenax to absorb all of the compound desorbed to the interstitial water from the sediment over the length of the extraction, without affecting the desorption kinetics of the compound (Cornelissen et al., 1998; Harwood et al., 2012; Kraaij et al., 2001, 2002; Kukkonen et al., 2004; Lydy et al., 2015; Sormunen et al., 2008; Trimble et al., 2008; You et al., 2007, 2009). The Tenax:OC ratio is important, because organic carbon is the sorbent in most sediments controlling sorption and desorption of HOCs and thus is in direct competition with the Tenax beads for freely dissolved chemical in the extraction system (DiToro et al., 1991; Pignatello and Xing, 1996). Thus in a Tenax extraction, both organic carbon and Tenax compete for the compound of interest through sorption of freely dissolved chemical in the interstitial water and the extent of sorption depends on the law of mass action and the relative affinities and capacities of organic carbon and Tenax. If this is true, then the relationship between organic carbon and Tenax should be governed by competitive sorption, and the Tenax:OC ratio would need to be large enough to prevent significant re-adsorption to the organic carbon after desorption. Too little Tenax relative to the organic carbon mass could underestimate bioaccessibility, while too much Tenax could result in an overestimate of bioaccessibility due to alterations of desorption kinetics of the residual fractions by creating an extremely large chemical activity gradient between the chemical in the organic carbon and on the Tenax during the extraction. Using different Tenax:OC ratios