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Comparison of marine sampling methods for organic contaminants: Passive samplers, water extractions, and live oyster deployment

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ABSTRACT

Laboratory and field trials evaluated the efficacy of three methods of detecting aquatic pesticide concentrations. Currently used pesticides: atrazine, metolachlor, and diazinon and legacy pesticide dieldrin were targeted. Pesticides were extracted using solid-phase extraction (SPE) of water samples, titanium plate passive samplers coated in ethylene vinyl acetate (EVA) and eastern oysters (*Crassostrea viginica*) as biosamplers. A laboratory study assessed the extraction efficiencies and precision of each method. Passive samplers yielded the highest precision of the three methods (RSD: 3–14% EVA plates; 19–60% oysters; and 25–56% water samples). Equilibrium partition coefficients were derived. A significant relationship was found between the concentration in oyster tissue and the ambient aquatic concentration. In the field (Housatonic River, CT (U.S.)) water sampling (n = 5) detected atrazine at 1.61–7.31 µg L^{-1}, oyster sampling (n = 2 × 15) detected dieldrin at n.d.–0.096 µg L^{-1} SW and the passive samplers (n = 5 × 3) detected atrazine at 0.97–3.78 µg L^{-1} SW and dieldrin at n.d.–0.68 µg L^{-1} SW.

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1. Introduction

Pesticides are frequently detected in rivers, streams, and other freshwater bodies, typically in the ng to µg per liter range (Hua et al., 2006). A study of 35 pesticides in rivers of the northeast US in the 1990's found surface water pesticide concentrations ranging between ng L^{-1} and µg L^{-1} (Garabedian et al., 1998). Similar studies have reported comparable ranges (Cernoch et al., 2011; Dalton et al., 2014; Hoffman et al., 2000; Lehotay et al., 1998). Pesticides pose a risk to long term water quality, human health, and ecosystem health making it necessary to have safe and effective sampling methods to monitor these compounds in aquatic systems (Vrana et al., 2005, 2006). In the past decade, passive sampling has increasingly been used as a substitute for traditional compound measurement via more labor intensive grab sampling and bio-sampling as it increases sampling efficiency and reduces sampling artifacts and costs (Cernoch et al., 2011; Dalton et al., 2014;

Lohmann and Muir, 2010; Scarapato et al., 2010; Smalling et al., 2013; St. George et al., 2011; Stuer-Lauridsen, 2005; Thromatou et al., 2011; Vrana et al., 2006). This study aims to test the efficacy of Ethylene Vinyl Acetate (EVA)-plate passive samplers as an alternative sampling method that is viable and cost-effective. These samplers are based on thin-film equilibrium sampling that can yield a quantitative measure of aqueous contaminant concentrations (St. George et al., 2011).

1.1. Target pesticides

A suite of four pesticides (dieldrin, diazinon, atrazine and metolachlor) was selected based on the work of Garabedian et al. (Garabedian et al., 1998). Dieldrin, an organochlorine pesticide, was the second most commonly used agricultural insecticide in the United States in the 1960s (after DDT) (Yang et al., 2012). Dieldrin has a propensity to bioaccumulate, particularly in animal fats, and human exposure through food consumption is of concern (Fox et al., 2010). Scientists estimate that dieldrin will persist in the environment until at least 2030, decades after its US phase out in 1987 (United States Environmental Protection Agency, 1980) and almost a century after its introduction in 1943 (Jorgenson, 2001). Today it is under restricted use in India, Mauritius, Togo,

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and the United Kingdom. Diazinon, an organophosphate insecticide, has been used widely in the United States for household and agricultural pest control (Aggarwal et al., 2013). In 2007, diazinon was the 8th most commonly used organophosphate insecticide active ingredient in all U.S. market sectors with approximately one million pounds produced annually (Grube et al., 2011). Diazinon was introduced in 1956 and was largely used for residential purposes until 2004 when it was banned from home use (United States Environmental Protection Agency, 2004). Diazinon is known to induce developmental abnormalities in amphibians (Lawrence and Isioma, 2010), it is highly toxic to honeybees (Centers for Disease Control and Prevention, 2014) and is a suspected endocrine disruptor (United States Environmental Protection Agency, 2007). Currently there are no set drinking water standards though the EPA has recommended a non-enforceable value of 0.001 mg L^{-1} (United States Environmental Protection Agency, 2006). Atrazine is currently the most heavily used s-triazine herbicide in the United States (United States Environmental Protection Agency, 2012) and the 2nd (to glyphosate) most commonly used active ingredient in conventional pesticides in the agricultural market sector in North America (Hua et al., 2006). In 2007, 73–78 million pounds were produced in the United States alone (Grube et al., 2011). Atrazine is an endocrine disruptor (United States Centers for Disease Control Agency for Toxic Substances and Disease Registry (ATSDR), 2003) and has been shown to impact sexual development in frogs (United States Centers for Disease Control Agency for Toxic Substances and Disease Registry (ATSDR), 1993; United States Environmental Protection Agency, 2003). An increased risk of pre-term delivery, intra-uterine growth retardation and low birth weight in humans were significantly correlated to atrazine concentrations in drinking water (Munger et al., 1997; Villanueva et al., 2005). Metolachlor, a broad spectrum herbicide, was first registered in the US in 1976 (United States Environmental Protection Agency, 1995). Metolachlor was the 4th most commonly used conventional pesticide active ingredient in the agricultural market sector in 2007 with 30–35 million pounds produced in the United States (Grube et al., 2011). Metolachlor toxicity is not well understood though it is classified as an Environmental Protection Agency group C carcinogen (suggestive carcinogenic effects) and has a World Health Organization type III toxicity classification (slightly hazardous) (World Health Organization, 2010).

1.2. Water spot sampling

Traditionally, pesticides are measured through spot, or grab, sampling (Vrana et al., 2005). Spot sampling entails filtration and extraction of large volumes of water and can be very costly and time consuming (El-Shenawy et al., 2009). Spot sampling is limited to a point measure of pollutant concentrations, which can be problematic as these concentrations may vary greatly over time and even over the course of a day (Stuer-Lauridsen, 2005). Point-in-time estimates often result in over- or underestimation of ambient concentrations, which makes it difficult to understand the overall impact to the aquatic system (Dalton et al., 2014). Increasing sampling frequency can overcome this variability but the volume of water needed to extract detectable levels of a pollutant can be large (1 to over 12 L) and can substantially increase the duration of extraction in the lab. Increasing the time to extraction can compromise the integrity of the original sample (Capel et al., 1995; Larson et al., 1995; Martin et al., 1992; Rabiet et al., 2010). Extraction efficiencies are of concern due to frequent losses to sampling containers, degradation between sampling and extraction times and other inefficiencies leading to low recoveries (Namiesnik et al., 2005). Typical percent recoveries for solid-phase extractions of

triazine herbicides range from 62 to 113% with relative standard deviations (RSDs) commonly below 15% (Dean et al., 1996). This recovery error is compounded with natural spatial and temporal variability in the water column and may lead to significant misrepresentations of pesticide concentrations.

1.3. Biosampling

Certain methods are able to deliver time integrated contaminant data through prolonged deployment of a single sampler, namely biosampling and passive samplers. Commonly used biosampling organisms include fish, bivalves, and macroalgae (Stuer-Lauridsen, 2005). Oysters are often used in biosampling due to their immobility, abundance, and wide range of distribution (Buisson et al., 2008; Smith et al., 1991). Additionally, oysters have the ability to concentrate, and a limited capacity to metabolize, both organometals and other organic contaminants (Buisson et al., 2008). Biosampling organisms can be naturally collected from an area of interest or they can be deliberately deployed into the aquatic environment for a regulated amount of time. They sample continuously during the length of deployment, which provides an integrated picture of contaminant concentration without multiple samples being taken. Biosampling is dynamic in that the organisms may be relocated to a new environment and reach a new steady state.

Biosampling has its own set of limitations. The organism must be alive and healthy to uptake any compound. Live organisms are limited in where they can be deployed, or collected, based on temperature, salinity, water quality, and various other factors essential to their survival. Species, therefore, have a limited geographic range in which they can be deployed which makes comparisons between regions a challenge (Lohmann and Muir, 2010). Rates of uptake have been shown to vary between members of the same species due to differences in age, sex (Namiesnik et al., 2005), lipid content, seasonal growth and reproduction, environmental factors, and experimental conditions such as length of exposure and deployment depth (Scarapato et al., 2010). Therefore, concentrations derived from biosampling have a wide range of standard deviations: 0.1–115% (Lehotay et al., 1998).

1.4. Passive sampling

Passive samplers are emerging as a useful method for monitoring contaminant levels without the limitations of biosampling or spot water samples. Passive sampling relies on the flow of compounds from the aquatic environment to a collecting media (Namiesnik et al., 2005). Various forms of passive samplers have been developed since they were introduced in the 1980s, many of which have been reviewed (Namiesnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005). Passive samplers can be deployed without consideration of water quality, and sample continuously over the length of deployment. There are two main sampling designs for passive samplers; the first provides a time-weighted average of contaminant concentrations. The second design reaches a dynamic equilibrium. There are many benefits of these systems: simple, robust design, low cost, minimal equipment, minimal labor hours during deployment, and accurate results (Namiesnik et al., 2005). Passive samplers still lack a clear comparison to traditional methods therefore more intercomparisons need to be established. The two most widely tested and used passive samplers are the Chemcatcher and Polar Organic Chemical Integrative Samplers (POCIS); both systems use a time-weighted average (Fox et al., 2010). A thin-filmed equilibrium sampler is currently not commercially available.

This study aims to test the efficacy of the EVA plate (a thin-film