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Multiple mitigation mechanisms: Effects of submerged plants on the toxicity of nine insecticides to aquatic animals[☆]

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ABSTRACT

Understanding the processes that regulate contaminant impacts in nature is an increasingly important challenge. For insecticides in surface waters, the ability of aquatic plants to sorb, or bind, hydrophobic compounds has been identified as a primary mechanism by which toxicity can be mitigated (i.e. the sorption-based model). However, recent research shows that submerged plants can also rapidly mitigate the toxicity of the less hydrophobic insecticide malathion via alkaline hydrolysis (i.e. the hydrolysis-based model) driven by increased water pH resulting from photosynthesis. However, it is still unknown how generalizable these mitigation mechanisms are across the wide variety of insecticides applied today, and whether any general rules can be ascertained about which types of chemicals may be mitigated by each mechanism. We quantified the degree to which the submerged plant *Elodea canadensis* mitigated acute (48-h) toxicity to *Daphnia magna* using nine commonly applied insecticides spanning three chemical classes (*carbamates*: aldicarb, carbaryl, carbofuran; *organophosphates*: malathion, diazinon, chlorpyrifos; *pyrethroids*: permethrin, bifenthrin, lambda-cyhalothrin). We found that insecticides possessing either high octanol-water partition coefficients (log K_{ow}) values (i.e. pyrethroids) or high susceptibility to alkaline hydrolysis (i.e. carbamates and malathion) were all mitigated to some degree by *E. canadensis,* while the plant had no effect on insecticides possessing intermediate log K_{ow} values and low susceptibility to hydrolysis (i.e. chlorpyrifos and diazinon). Our results provide the first general insights into which types of insecticides are likely to be mitigated by different mechanisms based on known chemical properties. We suggest that current models and mitigation strategies would be improved by the consideration of both mitigation models.

1. Introduction

Understanding how ecological factors can influence the effects of contaminants in aquatic ecosystems is a critical goal. For insecticides, a growing body of literature demonstrates that aquatic plants can dramatically reduce concentrations in surface waters (Cooper and Moore, 2003; Schulz, 2004; Reichenberger et al., 2007; Moore et al., 2011a,b). Indeed, the impact of aquatic plants on insecticides has been incorporated into environmental fate and effects models (e.g., CATS, AQUATOX, etc.) to better predict the ecological consequences of pesticide exposure (Park et al., 2008). Further, insecticide mitigation and remediation by aquatic plants is a key process considered in the design of agricultural best management practices (BMPs), which are designed to minimize the downstream ecological impacts of pesticide applications (Moore et al., 2011a,b). Given the important applications of insecticide mitigation by aquatic plants, understanding the mechanisms that drive this process is critical.

The traditional mechanism by which aquatic plants are thought to remove insecticides from the water is the sorption-based model, in which pesticides accumulate onto and into plant tissues. Although insecticide sorption rates by submerged plants can depend on many factors including the organic content and surface area of plants (Delle Site, 2001), a generally robust indicator of insecticide sorption potential is the octanol-water partition coefficient (i.e. K_{ow}; Gobas et al., 1991; Moore et al., 2011b). Insecticide sorption rates to aquatic plants scale approximately linearly with insecticide log K_{ow} (Gobas et al., 1991) and can differ by several orders of magnitude for insecticides possessing relatively low

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versus high octanol-water partition coefficients. For example (Gao et al., 2000a), demonstrated that for the relatively hydrophobic compound DDT (log $K_{ow} = 6.91$), 80% of the initial concentration (0.5 mg/L) was removed from the water column by the submerged plant *Elodea canadensis* within 1 h of applications. In contrast, using the same experimental setup, Gao et al. (2000b) showed that it took approximately 192 h for the same percent decrease to occur for the less hydrophobic insecticide malathion (log $K_{ow} = 2.75$). As a result of these studies, traditional toxicological models (e.g., AQUATOX) also rely heavily on this pathway, using insecticide octanol-water partition coefficients to predict sorption rates.

While studies examining sorption rates of different insecticides to plants are somewhat common in the literature (Crum et al., 1999; Hand et al., 2001; Karen et al., 1998; Thomas and Hand, 2011), they often utilize different experimental designs (e.g., lab versus field studies). With sorption rates being dependent on factors such as insecticide concentration, contact time with plants (Stehle et al., 2011), and plant species (Moore et al., 2009), it is difficult to draw cross-study comparisons about the relative ability of plants to mitigate different insecticides. Further, no studies to our knowledge have experimentally compared how aquatic plants mitigate the toxic effects on sensitive animal taxa using insecticides that span a wide range of log K_{ow} values. What is needed are studies comparing the ability of plants to mitigate the toxicity of different insecticides on sensitive species under identical environmental conditions in order to better predict the environmental effects of these contaminants in aquatic ecosystems.

Whereas most past studies have focused on plants mitigating insecticides via the sorption-based model, new evidence suggests that aquatic plants are also able to strongly mitigate the effects of some insecticides via other mechanisms. For example, Brogan and Relyea (2014) recently demonstrated a strong mitigating effect of submerged plants on malathion's toxicity driven entirely by alkaline hydrolysis caused by high pH levels; plant sorption played virtually no role. This newly discovered hydrolysis-based model of insecticide mitigation operates when plants photosynthesize and thereby increase the pH of the water. Because many insecticides such as malathion break down faster as pH increases, the presence of plants causes rapid break down of the insecticide and the water becomes less toxic to sensitive species. Given that many insecticides can break down via alkaline hydrolysis (Wolfe et al., 1977, 1978; Seaman and Riedl, 1986), one would predict that a wide variety of plant species should mitigate the lethal effects of hydrolysable insecticides. This prediction is supported by recent evidence that numerous species of submerged plants entirely negated malathion's toxicity to *Daphnia magna* less than 2 h after the insecticide was applied to the water at concentrations within ranges documented in surface waters (Brogan and Relyea, 2013). However, to date malathion is the only insecticide shown to be mitigated by the hydrolysis-based model. Despite the potential of the hydrolysis-based model to mitigate a variety of insecticides in aquatic ecosystems with elevated pH levels, such as those with high primary productivity (Talling, 1976; Ondok et al., 1984; Frodge et al., 1990; Toivonen and Huttenen, 1995), studies examining the generalizability of this mechanism to other hydrolysable insecticides are needed.

In this study, we expanded our current understanding of the mitigation potential of the sorption-based and hydrolysis-based mitigation models by comparing the ability of *E. canadensis* to mitigate the acute (48-h) toxicity of nine insecticides to *D. magna*. These animals are a common toxicological test organism due to their high sensitivity to most insecticides and an ecologically important member of aquatic food webs (Lathrop et al., 1999; Sarnelle, 2005). We tested two primary hypotheses: (1) *E. canadensis* will mitigate the acute toxicity of insecticides possessing high log K_{ow} values via the sorption-based mechanism (2) *E. canadensis* will mitigate the acute toxicity of insecticides possessing high susceptibility to rapid alkaline-hydrolysis via the hydrolysis-based mechanism, and (3) *E. canadensis* will not mitigate insecticides possessing low or intermediate log K_{ow} values and low susceptibility to alkaline-hydrolysis.

2. Materials and methods

2.1. Experimental design

We performed the experiment at the Donald S. Wood Field Laboratory at the University of Pittsburgh's Pymatuning Laboratory of Ecology in August 2012. Using a completely randomized design, we exposed *Daphnia magna* to five concentrations of each of nine insecticides, except aldicarb (3 concentrations tested) and permethrin (4 concentrations tested), in the absence and presence of the submerged plant *E. canadensis* (84 treatments). The insecticides spanned three widely used chemical classes (carbamates, organophosphates, and pyrethroids) and varied in physicochemical characteristics including log K_{ow} value and stability under alkaline conditions (Table 1). We replicated the 84 treatment combinations three times for a total of 252 experimental units. In addition, we performed three replicates of an ethanol vehicle control in the presence and absence of plants to serve as a baseline for comparing the toxicity of each concentration of each insecticide to *D. magna* (six additional experimental units).

2.2. Experimental setup

A goal of our study was to establish testing environments that would simulate some of the realism of natural wetlands, while simultaneously allowing us to minimize environmental variation between testing containers. With this in mind, we set up our testing containers on 2 August by adding 50 g of loamy terrestrial topsoil to 0.95-L glass jars to serve as sediment; we then added 700 mL of carbon-filtered, UV-irradiated well water. For jars that were randomly assigned the plant treatment, we added 5 g fresh mass of *E. canadensis* to each jar by cutting the plants into 15 cm fragments from each shoot's apical meristem. We obtained the plants from monocultures kept on site in 1200-L cattle tanks containing well water and terrestrial topsoil. The stock population of *E. canadensis* for these monocultures was collected and mixed from several local wetlands in Summer 2011 and we overwintered the plants in the tanks to ensure that they were not exposed to any contaminants prior to our experiment. Further, the wetlands from which the plants were collected had not received any pesticide applications for at least 5 y prior to our collection (*personal communication* Jerry Bish, Pennsylvania Game Commission).

After setting up the jars, we moved them outside to perform the experiment under semi-natural conditions where the test organisms would experience natural diel temperature and light cycles. To give the jars exposure to light and air while eliminating the possibility of rain entering the jars, we placed them in sideways-oriented glass aquaria (12 jars/aquaria). We randomly assigned each jar to an aquarium. The aquaria were located in 300-L pools (4 aquaria/pool) on top of 0.6 m-high wooden tables. Once the jars were all in place, we filled each pool with approximately 100 L of well water (~half of the height of each jar) to buffer the jars from reaching unnaturally high temperatures during the days.

Because pH and temperature can both affect the fate and toxicity of insecticides (Newman, 2010), we quantified water pH and temperature both 1 h prior to applying insecticides and 48 h afterwards. We measured pH using a calibrated pH meter (Oakton Instruments, Illinois, USA) and temperature using a calibrated YSI probe (YSI Inc., Ohio, USA). We measured temperature and pH by