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Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California

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HIGHLIGHTS

- Suisun Marsh, in California, provides habitat to several imperiled fish species.
- Pesticides were sampled in creek waters flowing to the marsh after a winter storm.
- Urban creeks were toxic to invertebrates due to bifenthrin and fipronil.
- No toxicity was seen in agriculture-affected creeks, at least during the winter.
- Fipronil was measurable in the marsh, but not toxic due in part to dilution.

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ABSTRACT

Suisun Marsh, in northern San Francisco Bay, is the largest brackish marsh in California, and provides critical habitat for many fish species. Storm runoff enters the marsh through many creeks that drain agricultural uplands and the urban areas of Fairfield and Suisun City. Five creeks were sampled throughout a major storm event in February 2014, and analyzed for representatives of several major insecticide classes. Concentrations were greatest in creeks with urban influence, though sampling was done outside of the primary season for agricultural pesticide use. Urban creek waters reached maximum concentrations of 9.9 ng/l bifenthrin, 27.4 ng/l fipronil, 11.9 ng/l fipronil sulfone, 1462 ng/l imidacloprid, and 4.0 ng/l chlorpyrifos. Water samples were tested for toxicity to *Hyalella azteca* and *Chironomus dilutus*, and while few samples caused mortality, 70% of the urban creek samples caused paralysis of either or both species. Toxic unit analysis indicated that bifenthrin was likely responsible for effects to *H. azteca*, and fipronil and its sulfone degradate were responsible for effects to *C. dilutus*. These results demonstrate the potential for co-occurrence of multiple insecticides in urban runoff, each with the potential for toxicity to particular species, and the value of toxicity monitoring using multiple species. In the channels of Suisun Marsh farther downstream, insecticide concentrations and toxicity diminished as creek waters mixed with brackish waters entering from San Francisco Bay. Only fipronil and its degradates remained measurable at 1–10 ng/l. These concentrations are not known to present a risk based on existing data, but toxicity data for estuarine and marine invertebrates, particularly for fipronil's degradates, are extremely limited.

1. Introduction

Insecticide residues entering aquatic habitats via runoff have been shown to have effects ranging from selection for pesticide-resistant genotypes (Weston et al., 2013), to mortality of indicator species (Bailey et al., 2009), to changes in community composition (Schulz and Liess, 1999). Organophosphate insecticides, such as diazinon and chlorpyrifos, have long been associated with aquatic toxicity following rain-related transport of residues into waterways (Bailey et al., 2009; Kuivila and Foe, 1995). Pyrethroids have been an increasingly important insecticide class for the past decade as organophosphate use has declined. They have been shown to enter creeks at toxic concentrations after rain events, even traveling downstream more than 20 km from their source while retaining their toxicity to aquatic life (Weston et al., 2014). In recent years, use of phenylpyrazole insecticides, especially fipronil, has become more common, and it is now commonly detected in urban creeks at concentrations acutely toxic to a variety of invertebrates (Weston and Lydy, 2014). Neonicotinoids, such as imidacloprid, are an

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emerging class of insecticides with potential for aquatic toxicity (Smit et al., 2015), though the research focus has largely been on their toxicity to pollinators (Cresswell, 2011).

The present study examined the potential for insecticide-related aquatic toxicity in agriculture and urban-influenced creeks flowing into Suisun Marsh, and in the sloughs of the marsh itself. Suisun Marsh is the largest brackish marsh in California, and is located near the confluence of the Sacramento and San Joaquin Rivers in northern San Francisco Bay. Freshwater enters the marsh through several upland creeks that flow through agricultural or urban lands before becoming sloughs as they enter the marsh, where they broaden and their flow becomes tidally influenced. Thus, there is the potential for these creeks to transport a variety of agricultural and/or urban contaminants into Suisun Marsh.

Intensive sampling was conducted during the largest storm event of the 2013/2014 winter rainy season. Sampling was done to quantify water concentrations of representatives from several insecticide classes (the organophosphate chlorpyrifos, the phenylpyrazole fipronil and its degradates, the neonicotinoid imidacloprid, and eight pyrethroids). The compounds were selected based on high use, prior linkage with aquatic toxicity in the region, or emerging use with little previous monitoring (imidacloprid). Since insecticide effects on fish within the marsh could be indirect through toxicity to their invertebrate prey, toxicity testing of water samples was conducted with the amphipod, *Hyalella azteca*, and the chironomid, *Chironomus dilutus*. While the study was focused on the Suisun Marsh watershed, findings should be internationally relevant, as many estuarine areas receive runoff from mixed-use urban and agricultural watersheds, and the insecticides investigated are used worldwide.

2. Material and methods

2.1. Description of study area

Suisun Marsh contains 470 km^2 of marsh, much of it diked and seasonally flooded to support waterfowl hunting. Among the diked wetlands is a network of tidal sloughs, with salinities temporally varying from 0 to 17 psu depending on the volume of river flow entering the Bay (Meng et al., 1994). Given that most of the wetlands surrounding San Francisco Bay have been lost to agriculture or urban development, the wetlands of Suisun Marsh are considered critical spawning and rearing habitat for a diverse assemblage of native and introduced fish species (Meng et al., 1994; Meng and Matern, 2001; O'Rear and Moyle, 2014). Of particular significance is the use of the marsh by several native species whose numbers have dramatically declined throughout the estuary in recent decades (Sommer et al., 2007), such as Sacramento splittail (*Pogonichthys macrolepidotus*), longfin smelt (*Spirinchus thaleichthys*), and delta smelt (*Hypomesus transpacificus*). The marsh and adjacent Suisun Bay provides summer and fall habitat for subadult and adult delta smelt (Sommer and Mejia, 2013), and there is evidence that it provides spawning habitat for delta smelt in winter and spring months as well (Bennett, 2005; Murphy and Hamilton, 2013).

2.2. Field sampling

Sampling addressed impacts of runoff following winter storms, as these events have been shown to result in both urban and agricultural pesticide inputs to estuarine waters in environments similar to the study site (Weston et al., 2014). We recognize that this focus does not address conditions during the summer growing season, when most agricultural pesticide application occurs. However, pesticide inputs at that time would be inherently unpredictable, as they depend on application and irrigation practices of individual growers, and the volume of pesticide-contaminated runoff from irrigation return flows is likely to be much smaller than the volume of runoff accompanying storm events. All sampling was conducted in response to a single major rain event, with light rain beginning 6 February 2014, and heavier rains from the night of 7 February until 9 February. Rainfall accumulations at Cordelia, California (gauge location = 38.172, −122.129) were 1.4 cm on the 6th, 2.7 cm on the 7th, 4.8 cm on the 8th, and 3.1 cm on the 9th. In this region of California, most rainfall occurs from November through March, but the 2013/2014 wet season had exceptionally little rainfall, and accumulation never exceeded 1 cm in any day of the entire wet season up until the February storm sampled for the present study. Thus, the sampled rain event can be considered a “first flush”, the first major rain event of the season, often accompanied by high suspended sediment loads entering the San Francisco Bay estuary and with pesticides associated with those particles (Goodwin and Denton, 1991; Bergamaschi et al., 2001).

There were two types of sampling sites: creek samples and slough samples (Fig. 1). The former were collected from most of the major creeks that flow to Suisun Marsh, at the last vehicle-accessible location prior to their entry to the marsh. Creek sites were sampled in both morning and afternoon of 8 February, and in the morning of 9 February. Suisun Creek was the only sampled creek for which pesticide sources in the watershed were primarily agricultural (87% of developed land agricultural, 9% urban or residential; Fairfield-Suisun Sewer District, 2004). Laurel Creek and McCoy Creek watersheds were largely urban (3% agricultural, 95% urban/residential, and 14% agricultural, 68% urban/residential, respectively). Green Valley and Ledgewood Creek watersheds had mixed land uses (50% agricultural, 45% urban/residential, and 74% agricultural, 24% urban/residential, respectively). All the urban areas in the study area are served by storm drain systems that divert untreated runoff from the streets to nearby creeks. The region's municipal wastewater treatment plant discharges into Suisun Marsh, approximately midway between sites LLC and SSV, thus the discharge would not affect water quality at the creek sites, but could influence some of the slough sites, especially SSV and SSO.

Flow at the Laurel Creek sampling site (LLC) was weak compared to the other waterways because it only received runoff from urban storm drains in the immediate vicinity. The main flow from the upper reaches of Laurel Creek is diverted eastward, joining with flow from McCoy Creek, and their combined flow was characterized at site MCC.

As the creeks enter Suisun Marsh, velocities decrease, conductivity increases, and tidal action becomes significant. Five slough sites were sampled within the marsh daily from 8 to 10 February, and a sixth site (site SSO) was sampled 10 February near the outfall of the slough system into Grizzly Bay, an embayment of northern San Francisco Bay. In order to best represent freshwater flowing seaward from the sloughs, rather than tidally-driven brackish waters flowing into the marsh from Grizzly Bay, slough sites were sampled within the 3-h period preceding the lowest tide each day. Nightfall prevented sampling at low tide or shortly thereafter.

Water samples were collected just below the surface either from the bank or using a stainless steel bailer from bridges, depending on access at each site. The only exception was site SSO, which required boat access. Samples were collected in glassware certified clean for pesticide analysis (I-Chem 200 series, Fisher Scientific, Waltham, MA), using 4-l bottles for toxicity testing samples and 1-l bottles for chemistry samples. Hexane (10 ml) was added as a keeper solvent to samples intended for pyrethroid, chlorpyrifos, and fipronil analysis. Samples were kept at 4 °C, with toxicity testing done within 48 h and pesticide extractions done within 96 h. Total suspended solid (TSS) samples were collected in 250-ml glass bottles.

2.3. Analytical procedure

For those samples intended for analysis of pyrethroids, chlorpyrifos, fipronil, or fipronil degradates, the analytical surrogates 4,4′-dibromooctafluorobiphenyl (DBOFB) and decachlorobiphenyl (DCBP) (Supelco, Bellefonte, PA) were added to the samples, and approximately 850 ml of water was liquid:liquid extracted using U.S. Environmental Protection Agency Method 3510C (USEPA, 2013). Three sequential