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Environmental fate of fungicides and other current-use pesticides in a central California estuary

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ABSTRACT

The current study documents the fate of current-use pesticides in an agriculturally-dominated central California coastal estuary by focusing on the occurrence in water, sediment and tissue of resident aquatic organisms. Three fungicides (azoxystrobin, boscalid, and pyraclostrobin), one herbicide (propyzamide) and two organophosphate insecticides (chlorpyrifos and diazinon) were detected frequently. Dissolved pesticide concentrations in the estuary corresponded to the timing of application while bed sediment pesticide concentrations correlated with the distance from potential sources. Fungicides and insecticides were detected frequently in fish and invertebrates collected near the mouth of the estuary and the contaminant profiles differed from the sediment and water collected. This is the first study to document the occurrence of many current-use pesticides, including fungicides, in tissue. Limited information is available on the uptake, accumulation and effects of current-use pesticides on non-target organisms. Additional data are needed to understand the impacts of pesticides, especially in small agriculturally-dominated estuaries.

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1. Introduction

Coastal estuaries are among the most ecologically important and critically threatened habitats in California and worldwide (Sheehan and Tasto, 2001; Barbier et al., 2011). Less than 20% of California's coastal wetlands remain, and these are impacted by serious water-quality degradation (Dahl, 1990; Sheehan and Tasto, 2001; California Natural Resources Agency, 2010). Rain and irrigation water that drain from agricultural and urban areas transports pesticides and other contaminants into surface waters and aquatic habitats (De Vlaming et al., 2000). Several previous studies have documented the occurrence and biological effects of current-use pesticides in three major central coast rivers/estuaries (Hunt et al., 1999; Anderson et al., 2003, 2006). The Santa Maria watershed along the central California coast contains year-round, intensively-cultivated agricultural land that supports an approximately $500 million/year industry, producing much of the Nation's lettuce, berries and crucifer crops (California Department of Pesticide Regulation, 2013). This estuary and lagoon provide critical nursery and foraging habitat for numerous marine and estuarine fish and invertebrate species, including the threatened tidewater goby. Pesticide-specific monitoring in the Santa Maria estuary has been limited; however, several studies have begun to address the fate and subsequent toxicity of current-use pesticides in the estuary (Anderson et al., 2006, 2010; Phillips et al., 2006, 2010).

Many studies in agricultural areas throughout California have documented the occurrence of a wide variety of current-use pesticides (CUPs) in water and sediment (Sapozhnikova et al., 2004; Kuivila and Hladik, 2008; Hladik et al., 2009) but only a few studies have assessed the uptake and accumulation of CUPs in aquatic organisms. For example, studies have documented the environmental occurrence of CUPs in clams (Pereira et al., 1996), in crabs and crab embryos (Mortimer, 2000; Dugan et al., 2005; Smalling et al., 2010) and fish (Sapozhnikova et al., 2004; Hoai et al., 2011). Limited information on the occurrence of CUPs in aquatic organisms is available because CUPs are considered less environmentally persistent and less bioaccumulative compared to legacy organochlorine pesticides such as *p,p′*-DDT. However, due to high use in agricultural watersheds, there is concern over the wide application of CUPs and their possible impacts on aquatic ecosystems.

Little is known about the effects of some CUPs on non-target organisms. Fish, invertebrates, and other non-target organisms in agricultural watersheds are exposed to a wide variety of pesticides

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throughout their life cycles. Fungicide application typically occurs throughout the growing season, which increases the likelihood of chronic exposure to low concentrations potentially impacting macroinvertebrate communities (Schäfer et al., 2011). The effects of the fungicide, azoxystrobin, on larval salmon have also been documented (Olsvik et al., 2010). Herbicides may directly impact phytoplankton communities due to their similarity in structure to target plant species. For example, the sub-lethal effects of herbicides on phytoplankton growth and cell density were more pronounced at increased salinities (DeLorenzo et al., 2011). Insecticides such as pyrethroids and organophosphates (OPs) are highly toxic to marine and freshwater fish and invertebrates (US Environmental Protection Agency, 2013) and have the potential to alter benthic community structure in agricultural estuaries (Anderson et al., 2010). Pyrethroid and OP insecticides may also directly affect salmon and other fish species through disruption of olfactory sensory neurons necessary in predator avoidance behaviors (Scholz et al., 2000; Moore and Waring, 2001; Sandahl et al., 2004). Although non-target organisms are exposed to complex mixtures of pesticides in most agricultural watersheds, little information is currently available on the effects of these mixtures particularly those containing fungicides. Tierney et al. (2008) noted that mixtures of both herbicides and insecticides elicited a greater response in salmon than individual compounds.

The overall objective of the study was to document the concentrations of pesticides in water, bed sediment, fish and sand crabs in the Santa Maria estuary. The occurrence of pesticides was evaluated relative to toxicity and benthic macroinvertebrate community impacts in a separate report describing results of a larger study (Anderson et al., 2010). This information on pesticide concentrations and exposure of biota to bioavailable contaminants is intended to provide a baseline for future evaluations of watershed-scale effectiveness of agricultural management practices that are slated for implementation.

2. Materials and methods

2.1. Study area and sample collection

The Santa Maria River watershed comprises approximately 486,840 hectares along California's central coast. Orcutt Creek drains approximately 20,230 hectares of land southeast of the Santa Maria River estuary (Smalling and Orlando, 2011) (Fig. 1). Inputs to the Santa Maria estuary are dominated by Orcutt Creek and a much smaller drainage ditch that enters the river near the entrance to the Rancho Guadalupe Dunes Preserve. Together, the flows from these two sources comprise 92% of the total input of water into the estuary (Anderson et al., 2010). River flows are frequently blocked by a littoral berm, and water collects behind the berm to form a large semicircular lagoon (approximate area of 15 hectares) which fills until the water level overtops the beach dune barrier. Flow then erodes the beach dune barrier and the estuary drains over a period of hours to a few days. This filling/draining cycle occurred repeatedly during the course of the study (Smalling and Orlando, 2011). Water samples were collected from Orcutt Creek and at two sites in the Santa Maria Estuary (Fig. 1). The upper estuary sampling site (Santa Maria upper) was located one kilometer downstream of the confluence of Orcutt Creek, but the precise location varied slightly with changes in estuary size during the study. The lower estuary sampling site (Santa Maria lower) was located as close to the beach dune barrier as possible but also varied slightly in location with changes in estuary size. The upper estuary site was selected to represent direct inputs into the estuary from Orcutt Creek while the lower site was selected as an integrator of the entire estuary.

Water samples for the analysis of dissolved pesticides were collected from the upper and lower estuary sites approximately monthly between February and October 2008 (1 storm and 7 dry season events). At each site, a grab sample was collected at a single depth in 1-L pre-cleaned amber bottles. Water samples from Orcutt Creek were collected three times (1 storm and 2 dry season events) in 2008 using a depth-integrating, isokinetic sampler following standard USGS sampling protocols (Wilde et al., 1998).

Bed sediments were collected from eight randomly selected sites throughout the estuary during October 2008 using a small, solvent rinsed hand core or a petite ponar sampler (Anderson et al., 2010). Bed sediment samples were also collected from active depositional areas at the Orcutt Creek site in October 2008 in clean, amber glass jars using a solvent rinsed, stainless steel spoon. All sediment samples were sieved through a 2 mm (stainless steel) sieve in the field and shipped on ice to the laboratory where they were stored frozen at −20 °C prior to extraction and analysis.

Fish were collected in the lower estuary in October of 2008 using a 100-foot beach seine. Targeted species included the starry flounder (*Platichthys stellatus*) and staghorn sculpin (*Leptocottus armatus*). The species and size of each fish (Table 1) were recorded after collection, and all samples were wrapped in solvent rinsed aluminum foil, packed on ice and transported to the laboratory for processing, extraction and analysis. Four individual flounder were dissected in the laboratory and homogenized muscle tissue was placed in 250 mL pre-cleaned clear glass jars and stored at −20 °C. Muscle tissue from two of the samples (fish ID # 20 and 21) were mistakenly composited and homogenized so the final number of flounder samples analyzed was three. Due to their small size, whole-body sculpin samples were analyzed. Three whole body samples were cut into smaller pieces using solvent-rinsed, stainless steel shears, and then homogenized in a solvent-rinsed stainless steel blender. The single whole-body homogenate was placed in a 250 mL pre-cleaned clear glass jar and stored at −20 °C.

Approximately 50 sand crabs (*Emerita analoga*) were collected in the surf zone at three sites in August 2008 using dip nets and gloved hands and placed in 500 mL pre-cleaned, clear glass jars and transported on ice to the laboratory. Both males and females were collected. Due to the timing of collection, many of the females were gravid. Sand crab samples were collected from the mouth of the estuary (mouth), 50 m north of the mouth (north), and 50 m south of the mouth (south), similar to the methods described in Dugan et al. (2005). Samples from each site were homogenized crudely in a clean, stainless steel blender in the laboratory and the homogenates were stored frozen at −20 °C prior to extraction and analysis.

2.2. Sample extraction

2.2.1. Water and bed sediment

Filtered water samples were analyzed for a suite of 68 pesticides by extracting one liter of sample water onto an Oasis HLB solid-phase extraction (SPE) cartridges (Smalling and Orlando, 2011). Prior to extraction, all water samples were filtered using either a continuous-flow centrifuge (Smalling and Orlando, 2011) or a 0.7 μm glass fiber filter and were spiked with ^{13}C-atrazine, and diethyl d_{10}-diazinon as recovery surrogates. Following extraction, the SPE cartridges were dried under carbon dioxide, eluted with ethyl acetate, reduced and deuterated internal standards were added (Hladik et al., 2008).

Bed sediment samples were extracted for 34 fungicides and 57 other currently-used pesticides based on methods described previously (Smalling and Kuivila, 2008; Smalling et al., 2013). Briefly, sediment samples were extracted three times using a Dionex 200 Accelerated Solvent Extractor (ASE) with dichloromethane at 100 °C and 1500 psi. Sulfur was removed using a gel-permeation/