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Identifying the cause of sediment toxicity in agricultural sediments: The role of pyrethroids and nine seldom-measured hydrophobic pesticides

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HIGHLIGHTS

- Monitoring fails to test for many agricultural pesticides used in any given area.
- Nine seldom-analyzed pesticides (e.g., abamectin) were tested for in sediments.
- One-quarter of the sediment samples were toxic to the amphipod, *Hyalella azteca*.
- The seldom-analyzed pesticides may have contributed to toxicity in a few samples.
- Pyrethroid insecticides were responsible for the vast majority of toxicity.

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ABSTRACT

Few currently used agricultural pesticides are routinely monitored for in the environment. Even if concentrations are known, sediment LC_{50} values are often lacking for common sediment toxicity testing species. To help fill this data gap, sediments in California's Central Valley were tested for nine hydrophobic pesticides seldom analyzed: abamectin, diazinon, dicofol, fenpropathrin, indoxacarb, methyl parathion, oxyfluorfen, propargite, and pyraclostrobin. Most were detected, but rarely at concentrations acutely toxic to *Hyalella azteca* or *Chironomus dilutus*. Only abamectin, fenpropathrin, and methyl parathion were found at concentrations of potential concern, and only in one or two samples. One-quarter of over 100 samples from agriculture-affected waterways exhibited toxicity, and in three-fourths of the toxic samples, pyrethroids exceeded concentrations expected to cause toxicity. The pyrethroid Bi-fen-thrin in particular, as well as lambda-cyhalothrin, cypermethrin, esfenvalerate, permethrin, and the organophosphate chlorpyrifos, were primarily responsible for the observed toxicity, rather than the more novel analytes, despite the fact that much of the sampling targeted areas of greatest use of the novel pesticides.

1. Introduction

California's Central Valley has an extensive network of natural and manmade watercourses returning irrigation runoff to the rivers. Sampling in 2002–2006 found 27% of 200 sediment samples caused toxicity to the amphipod, *Hyalella azteca* (Weston et al., 2008). Based on pyrethroid concentrations, these insecticides were likely responsible for mortality in 61% of the toxic samples. The organophosphate, chlorpyrifos, was a secondary contributor. Organochlorine pesticides never attained concentrations of concern. After considering these three pesticide classes, toxicity in 33% of the instances were of undetermined cause. Finding toxicity of unknown cause is not surprising. Over 160 pesticides are applied in the Central Valley (Kuivila and Hladik, 2008) and few are routinely analyzed in environmental samples. Even if analyses are done, concentrations causing sediment toxicity are generally unknown, as are the potential interactions between pesticides.

This study was designed to determine if seldom-analyzed, hydrophobic insecticides, fungicides and herbicides were present in sediments and contributing to toxicity. We describe three approaches to determine if these compounds cause sediment toxicity. Sediments were collected from areas where these pesticides were most heavily used, and tested for their presence and toxicity. Archived sediments previously found to be toxic were also tested for these pesticides. Finally, toxic sediments were evaluated with toxicity identification evaluation (TIE) procedures to identify substances responsible.

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2. Materials and methods

2.1. Pesticide selection

We have typically analyzed sediment for chlorpyrifos and seven pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, and permethrin). Risk ranking of current-use Central Valley pesticides (Lu and Davis, 2009) was used to identify other pesticides of potential concern, focusing on those with high toxicity (based on water exposures since sediment toxicity data were lacking) and with a K_{oc} > 1000, since they would be most likely to be found in sediment. We added fenpropathrin, which was not in the risk-ranking document, but we had observed it in Central Valley sediments. We deleted compounds with major analytical difficulties, very low expected environmental persistence, or extremely low toxicity to *H. azteca* or the midge, *Chironomus dilutus* in preliminary testing. The final list included insecticides (abamectin, diazinon, fenpropathrin, indoxacarb, methyl parathion), acaricides (dicofol, propargite), a fungicide (pyraclostrobin), and a herbicide (oxyfluorofen). We refer to these pesticides as "novel", reflecting their absence in past sediment monitoring. Diazinon has been widely monitored in water, but rarely in sediment.

2.2. Sediment collection

Agricultural pesticide use in California is reported to the Department of Pesticide Regulation's Pesticide Use Reports (PUR) database. In the first phase, referred to as "targeted sampling", the PUR database was used to identify areas of greatest use for each pesticide of interest and to establish months of peak use. Waterways draining those areas were sampled at the end of the peak use period. Oxyfluorfen and diazinon were sampled in February, pyraclostrobin in June, and all others in July to September (all in 2007–2008). Five to 16 sites were identified for each pesticide, with 69 total samples collected. Collection sites were in creeks (56% of sites), agricultural drains (35%), and rivers (9%). The upper 1–2 cm of sediment were collected, and subsampled for toxicity testing, grain size, pesticides, and organic carbon (oc) analyses. Samples were analyzed for the pesticide(s) for which the site had been selected, and the traditional analytes of chlorpyrifos and pyrethroids. Targeting peak use locations and times would yield "worst-case" conditions if off-site transport occurs during or soon after application. For growing season applications, summer irrigation runoff would often be the primary transport mechanism, but in some locations and with some crops, there is little irrigation runoff, and winter rains provide the first opportunity for runoff. While winter rains could be important for some compounds, 4 months elapse between summer application and the first appreciable rain (usually December), providing opportunity for degradation of many pesticides in farm soils.

An additional 12 samples, referred to as "archived samples", were previously collected sediments toxic to *H. azteca*, but with insufficient pyrethroids or chlorpyrifos to explain the cause. They had been collected without regard to the intensity of use of any pesticide, and had been archived in a frozen state for 1–3 years. They were analyzed for all the novel pesticides.

In a third "TIE sampling" phase, sites found to be toxic in various monitoring programs were reported to us, and revisited to collect sediment as described above. Forty samples were tested, with 14 used for TIE procedures. These 14 were analyzed for pyrethroids and chlorpyrifos, with additional analysis for the novel pesticides should TIEs indicate other causes of toxicity. Most sites were in the Central Valley, but two were near Salinas, California.

2.3. Analytical chemistry

The traditional pyrethroids and chlorpyrifos were extracted by accelerated solvent extraction (ASE) followed by solid phase extraction (SPE) clean-up (You et al., 2008). Diazinon, dicofol, fenpropathrin, indoxacarb, methyl parathion, oxyfluorfen, and pyraclostrobin, were extracted by the ASE-SPE method of Wang et al. (2010). Analyses were performed using an Agilent 6890 series gas chromatography (GC) with a micro-electron capture detector (μECD) and a nitrogen phosphate detector (NPD) (Agilent Technologies, Palo Alto, CA, USA). An HP-5MS and a DB-608 column were used. Diazinon and methyl parathion were detected by NPD and all other pesticides by μECD. Two surrogates, 4,4′-dibromooctafluorobiphenyl (DBOFB) and decachlorobiphenyl (DCBP), were added prior to the ASE extraction, with recoveries of 80–113% and 88–121%, respectively. Propargite was extracted using a sonication extraction method modified from EPA method 3550B, and analyzed by GC/mass spectrometry (Ding et al., 2011). Abamectin was quantified using high-performance liquid chromatography with fluorescence detection after sonication extraction and derivatization (Ding et al., 2011). Matrix spikes, matrix spike duplicates and blanks (clean sand) were run every 20 samples. Some data are presented in toxic units (TUs), calculated as actual concentration divided by the *H. azteca* or *C. dilutus* 10-d sediment LC_{50}, with all values oc-normalized.

2.4. Toxicity testing

Sediments were tested with *H. azteca* following standard protocols (USEPA, 2000). Approximately 75 mL of sediment was placed in five replicate 400-mL beakers, and the beakers filled with 250 mL water made moderately hard by adding salts to Milli-Q purified water (Millipore, Billerica, MA, USA). Ten 7–14-d old *H. azteca* were added to each beaker, held at 23 °C with a 16 h:8 h light:dark cycle, and fed daily with 1 mL yeast/cerophyll/trout chow. An automated system delivered 500 mL water to each beaker daily. After 10 d, survivors were recovered on a 425 μm screen. All tests included a 2% organic carbon control sediment collected from a drinking water reservoir. This sediment was collected far from any agricultural influence, but was screened for pyrethroids that could also be of urban origin, and none were found.

Three TIE procedures developed for pyrethroids were used. First, addition of piperonyl butoxide (PBO) inhibits enzymatic detoxification of pyrethroids, increasing toxicity if they are responsible. The PBO was added to overlying water at 25 μg L^{-1} (Amweg and Weston, 2007). About 80% of water was removed daily and replaced with fresh PBO solution. Second, tests were done at 18 °C, roughly doubling pyrethroid toxicity compared to the standard 23 °C test (Weston et al., 2009). Third, samples were treated with engineered enzymes, developed to hydrolyze specific pesticides. Enzyme OpdA degrades chlorpyrifos and other organophosphates (Sutherland et al., 2004). Enzyme E3-013 degrades bifenthrin, permethrin, and possibly other pyrethroids (Weston and Jackson, 2009). Both enzymes reduce toxicity of contaminated sediments (Weston and Jackson, 2009), though it is not clear if they hydrolyze adsorbed pesticides or only those in interstitial and overlying water. The enzymes were obtained through research collaboration with Orica Ltd., Melbourne, Australia. Enzyme was added to the overlying water daily (10 mg L^{-1}) with the water change. To establish if toxicity reduction was due to enzymatic activity, or simply complexation of toxicant with dissolved organic matter (DOM) contributed by the enzyme, trials included a DOM control. Bovine serum albumin (BSA) at 10 mg L^{-1} was initially used, but later OpdA enzyme was used as a DOM control for E3-013, and vice versa.