Science of the Total Environment 447 (2013) 179–185

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Occurrence and persistence of fungicides in bed sediments and suspended solids from three targeted use areas in the United States

Kelly L. Smalling [a,*], Timothy J. Reilly [b], Mark W. Sandstrom [c], Kathryn M. Kuivila [a]

[a] U.S. Geological Survey, 6000 J St., Placer Hall, Sacramento, CA 95819, USA
[b] U.S. Geological Survey, 810 Bear Tavern Rd, Suite 206, West Trenton, NJ 08628, USA
[c] U.S. Geological Survey, PO Box 25585, Denver Federal Center, Mail Stop 407, Lakewood, CO 80225, USA

HIGHLIGHTS

► 34 fungicides were measured in bed and suspended solids from areas of intense fungicide use.
► 2 fungicides were detected in 55 % of the bed sediment and 83 % of the suspended solid samples collected.
► Pyraclostrobin, a strobilurin fungicide, was the most frequently detected pesticide in sediment.
► The study represents the first detection of pyraclostrobin in suspended solids and zoxamide in sediments.
► Fungicides persist in the environment and concentrations in sediments varied both temporally and spatially.

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form 17 December 2012
Accepted 7 January 2013
Available online 4 February 2013

Keywords:
Fungicides
Pyraclostrobin
Bed sediment
Suspended solids
Persistence

ABSTRACT

To document the environmental occurrence and persistence of fungicides, a robust and sensitive analytical method was used to measure 34 fungicides and an additional 57 current-use pesticides in bed sediments and suspended solids collected from areas of intense fungicide use within three geographic areas across the United States. Sampling sites were selected near or within agricultural research farms using prophylactic fungicides at rates and types typical of their geographic location. At least two fungicides were detected in 55% of the bed and 83% of the suspended solid samples and were detected in conjunction with herbicides and insecticides. Six fungicides were detected in all samples including pyraclostrobin (75%), boscalid (53%), chlorothalonil (41%) and zoxamide (22%). Pyraclostrobin, a strobilurin fungicide, used frequently in the United States on a variety of crops, was detected more frequently than *p,p′*-DDE, the primary degradate of *p,p′*-DDT, which is typically one of the most frequently occurring pesticides in sediments collected within highly agricultural areas. Maximum fungicide concentrations in bed sediments and suspended solids were 198 and 56.7 μg/kg dry weight, respectively. There is limited information on the occurrence, fate, and persistence of many fungicides in sediment and the environmental impacts are largely unknown. The results of this study indicate the importance of documenting the persistence of fungicides in the environment and the need for a better understanding of off-site transport mechanisms, particularly in areas where crops are grown that require frequent treatments to prevent fungal diseases.

Published by Elsevier B.V.

1. Introduction

Fungicides are pesticides designed to control fungal diseases, but few studies have documented their environmental occurrence and persistence in aquatic sediments. The registration and use of fungicides have changed dramatically in the United States over the last 8 years in response to the potential threat of recently-introduced fungal diseases such as Asian soybean rust and increased resistance of fungal diseases. Fungicides are used on a wide variety of crops and are typically applied repetitively throughout the growing season (up to 12 times) but at lower application rates compared to insecticides and herbicides. They are also used for professional landscape and turf maintenance and by homeowners. Most currently used fungicides are moderately hydrophobic (log K_{ow} 3–4), have the potential to sorb to sediment organic matter, and are thought to present a low risk for groundwater contamination (Arias-Estevez et al., 2008; Pesticide Properties Database, 2012). The persistence and mobility of pesticides are governed by different processes occurring in sediments including, sorption/desorption kinetics, volatilization, degradation (chemical and/or biological), uptake by plants and leaching (Arias-Estevez et al., 2008).

Investigations on the occurrence of fungicides in the environment have generally been focused on surface waters, with few studies documenting the presence of fungicides in sediments. For example,

* Corresponding author. Tel.: +1 916 278 3052; fax: +1 916 278 3013.
E-mail address: ksmall@usgs.gov (K.L. Smalling).

0048-9697/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.scitotenv.2013.01.021

Table 1
Sampling site names, watershed area and percent of the watershed in agricultural for bed sediment and suspended solids sampling sites in Idaho, Maine and Wisconsin.

USGS station name	Common station name	Samples collected	Watershed area (hectare)	Percent of watershed in agriculture
Sand Run Gulch at Hwy 95 Xing nr Parma, ID	Sand Run Gulch	Suspended solids, bed sediment	20,589	39%
Ditch near Wanstad Road nr Parma, ID	Wanstad Rd Ditch	Bed sediment	308	86%
U of I Farm Ditch at Hwy 95 nr Parma, ID	U of I Farm Ditch	Bed sediment	23	92%
Hardwood Brook below Glidden Brk nr Caribou, ME	Hardwood Brook	Bed sediment	1478	54%
Glidden Brook near Caribou, ME	Glidden Brook	Suspended solids, bed sediment	1134	54%
Unnamed Trib to Aroostook Pond nr Presque Isle ME	Aroostook Farm Trib	Bed sediment	6.9	50%
Aroostook Pond near Aroostook Farm nr Presque Isle, ME	Aroostook Farm Pond	Bed sediment	NA	NA
Ditch #4 on Lake Road nr Kellner, WI	Ditch #4	Suspended solids, bed sediment	12,981	63%
Unnamed Ditch at Beaver Ave nr Hancock, WI	Beaver Ave Ditch	Bed sediment	1703	79%
Unnamed Ditch At Apache and 4th Ave nr Plainfield, WI	Apache Rd Ditch	Bed sediment	378	89%

NA = not applicable.

recent studies have documented the presence of some fungicides in runoff from greenhouse production (Roseth and Haarstad, 2010) and commercial foliage plant nurseries (Wilson and Riiska, 2010), soils (Bermudez-Couso et al., 2007; Geissen et al., 2010), streams and bed sediment (Battaglin et al., 2010; Reilly et al., 2012; Smalling and Orlando, 2011; Smalling and Kuivila, 2008; Wang et al., 2011), and the atmosphere (Schummer et al., 2010). The limited numbers of other studies that have investigated fungicides in agricultural soils have detected residues of some fungicides in a relatively high percentage of samples (Vanni et al., 2003; Bending et al., 2006, 2007; Chen and Zang, 2010). For example, in vineyards, repeated use of copper-based fungicides increases the copper levels in soils up to 8 times which has the potential to degrade these soils over time making them less productive (Fernández-Calviño et al., 2008). Fungicides also have the potential to move off-site but only a few studies to date have measured fungicide in sediments near agricultural areas (Bermudez-Couso et al., 2007; Hladik et al., 2009; Karaouzas et al., 2011; Wightwick et al., 2012).

Little is known about the effects of fungicides on non-target organisms. Fungicide application typically occurs throughout the growing season which increases the likelihood of chronic exposure of non-target organisms to low concentrations of fungicides. Changes in soil microbial enzyme activity and subsequently reducing microbial diversity after exposure to fungicides have been demonstrated (Niemi et al., 2009; Johnsen et al., 2001) which have the potential to decrease soil fertility. Fungicides are also considered ecotoxicologically relevant to macroinveterbrate communities in sediments (Schäfer et al., 2011). The mode of action for many fungicides is less selective than those of other currently applied insecticides and herbicides and therefore has the potential to negatively impact a wide range of non-target organisms (Maltby et al., 2009). Schäfer et al. (2011) suggested that fungicides may be more toxic to freshwater communities than previously expected and should be considered in risk based assessments. Understanding the occurrence of fungicides in sediments is an important first step in determining the effects on stream ecosystems.

The objective of this study was to determine the concentrations of fungicides associated with bed sediments and suspended solids in small watersheds draining agricultural areas of the United States with intense fungicide use. Twenty bed sediment samples were collected prior to fungicide application in the early summer and after harvest in the late fall from sites in Idaho, Maine and Wisconsin in 2009. Concurrently, passive sediment samplers were deployed in one stream in each study area during the growing season (up to five deployments for a three week interval each time) to capture suspended solids. The comparison of fungicide concentrations to other, more frequently studied agricultural pesticides will provide a context for interpreting the occurrence of these understudied compounds in the environment.

2. Materials and methods

2.1. Site descriptions and sample collection

Fungicide use potential in the United States was evaluated using county-level Geographic Information System (GIS) data on agricultural land (USDA, 2004) and chemical use (Gianessi and Reigner, 2006). Potatoes were selected as the crop of interest because a variety of fungicides are used throughout the growing season and they are grown across the United States in different geographic regions and climatologic settings. Candidate counties were selected based upon the intensity of production for potatoes and the use of selected fungicides. Counties with high fungicide use potential were further prioritized based upon the following factors to ensure the selection of a nationally-relevant group of sites: hydrologic and climatological setting, proximity to sensitive resources and environments, agricultural and irrigation practices and availability of pesticide application data. Pesticide usage data from research farms within each study area were evaluated to ensure that the fungicides of interest were being applied. While sites were selected as close to the research farms as possible, other crops and pesticide application practices within the watersheds could not be included in this selection process as 2009 pesticide usage data was not (and is not currently) available. Sampling sites were selected in and around Parma (Idaho), Aroostook (Maine) and Hancock (Wisconsin) (Table 1, Fig. A1).

Bed sediment samples were collected from active depositional zones at three to four sites in each state twice during the growing season (pre-fungicide application and post-harvest). Samples were collected in clean, amber glass jars using a solvent rinsed, stainless steel spoon. All sediment samples were sieved through a 2 mm sieve in the field and shipped on ice to the laboratory for extraction and analysis. For detailed information on bed sediment sampling sites see Supplemental Material and Table 1.

Passive sediment samplers were used to collect suspended solids from the streams (Phillips et al., 2000). Each sampler consists of a narrow (4-mm) inlet and outlet tube, attached to a larger sample collection tube (98-mm diameter by 1-m long). This assembly is installed horizontally in the stream with the inlet tube orientated directly into the flow. Water enters the inlet tube proportionally to ambient flow velocity, but the water and sediment within the sample collection tube drastically reduces flow and causes sedimentation of suspended material. The sample collection tube is made of aluminum, end caps of HDPE, and the inlet and outlet tubes of stainless steel to minimize potential contamination by plasticizers and other organic compounds. Passive sediment samplers were installed in the middle of the channel at approximately 0.6 of the mean water depth by attaching them to two steel bars hammered into the streambed in one stream per state. The samplers were deployed in one stream