



Occurrence of boscalid and other selected fungicides in surface water and groundwater in three targeted use areas in the United States

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ABSTRACT

To provide an assessment of the occurrence of fungicides in water resources, the US Geological Survey used a newly developed analytical method to measure 33 fungicides and an additional 57 current-use pesticides in water samples from streams, ponds, and shallow groundwater in areas of intense fungicide use within three geographic areas across the United States. Sampling sites were selected near or within farms using prophylactic fungicides at rates and types typical of their geographic location. At least one fungicide was detected in 75% of the surface waters and 58% of the groundwater wells sampled. Twelve fungicides were detected including boscalid (72%), azoxystrobin (51%), pyraclostrobin (40%), chlorothalonil (38%) and pyrimethanil (28%). Boscalid, a carboxamide fungicide registered for use in the US in 2003, was detected more frequently than atrazine and metolachlor, two herbicides that are typically the most frequently occurring pesticides in many large-scale water quality studies. Fungicide concentrations ranged from less than the method detection limit to approximately 2000 ng L⁻¹. Currently, limited toxicological data for non-target species exists and the environmental impacts are largely unknown. The results of this study indicate the importance of including fungicides in pesticide monitoring programs, particularly in areas where crops are grown that require frequent treatments to prevent fungal diseases.

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1. Introduction

Fungicides are employed to prevent the outbreak of persistent, historically significant plant diseases like late blight (caused by *Phytophthora infestans* and responsible for the Irish Potato famine of 1846) and newer plant diseases like Asian Soy Rust, both of which are potentially devastating if not controlled (Leadbeater and Gisi, 2009). Of the more than 67000 pesticide products currently registered for use in the United States, over 3600 are used to combat fungal diseases (USEPA, 2012). Even with the use of chemical-based crop protection measures, fungal pathogens were responsible for 7–24% of losses in yields to commodity crops such as potatoes worldwide in 2001–2003 (Oercke, 2006). Pesticide manufacturers are constantly developing new fungicides to find more effective treatments and to outpace the rate at which pathogens acquire resistance. For example, *Phytophthora infestans* rapidly developed strains resistant to widely used phenylamide fungicides leading to its classification as a high risk pathogen and necessitating co-application of other fungicides to provide the necessary crop protection (Brent and Hollomon, 2007). Depending upon the pathogen genome and the mode of fungicidal action

(ex. single versus multiple pathways), pathogens can develop resistance to newly introduced fungicides within a few years of exposure. For example, field and laboratory studies identified *Alternaria alternata* strains (responsible for Alternaria late blight of pistachio) resistant to boscalid within 2 years of registration (Avenot and Michailides, 2007) and azoxystrobin within 3–4 years of continuous application (Ma et al., 2003).

Although many studies have been conducted to evaluate efficacy and to determine toxicity to test organisms as part of the pesticide registration process, relatively little is known about the fate and effects of fungicides in the aquatic environment. Recent studies have documented the presence of some fungicides in runoff from greenhouse production (Roseth and Haarstad, 2010), golf courses (Larsbo et al., 2008) and commercial foliage plant nurseries (Wilson and Riiska, 2010), soil and water associated with banana production (Geissen et al., 2010), streams and bed sediment (Battaglin et al., 2010; Smalling and Orlando, 2011), and the atmosphere (Schummer et al., 2010). The occurrence of boscalid (first registered for use in the US in 2003) has only been documented in three studies: in streams (Smalling and Orlando, 2011), with field experiments to determine soil dissipation and residuals (Chen and Zhang, 2010) and in the atmosphere (Schummer et al., 2010). Unlike most other pesticides, fungicides are typically applied as a prophylactic crop protectant upwards of ten times per season (depending upon conditions and crop type), but typically at lower

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application rates than most herbicides or insecticides. This difference in usage increases the likelihood of chronic exposure of aquatic ecosystems to low concentrations of fungicides. Recent studies have documented the potential impacts of fungicides on amphibians (Belden et al., 2010), non-target fungi (Rasmussen et al., 2012) and macroinvertebrate communities (Liess and von der Ohe, 2005; Schäfer et al., 2011). The genotoxic, teratogenic and endocrine-disrupting properties of several fungicides have been established in field studies, mesocosms, *in vivo* (zebrafish and human lymphocytes) and *in vitro* studies (Bony et al., 2008; Taxvig et al., 2008; Şişman and Türkez, 2010; Orton et al., 2011).

The objective of this study was to determine the concentrations of understudied fungicides in small (first-order) surface water systems and shallow groundwaters draining agricultural areas of the United States with intense fungicide use. Twelve surface water and twelve groundwater sites were sampled in Maine, Idaho and Wisconsin for 33 fungicides and 57 other currently used pesticides throughout the growing season in 2009. Comparison of fungicide concentrations to other more frequently studied agricultural pesticides provided a context for interpreting the presence of these understudied compounds. Monitoring throughout the growing season allowed the observation of temporal changes in pesticide concentrations.

2. Materials and methods

2.1. Site Selection and sampling methods

Potential use of fungicides in the United States was evaluated using county-level GIS data on agricultural land (USDA, 2004) and chemical use (Gianessi and Reigner, 2002). Candidate counties were selected based upon the intensity of production for potatoes ($\geq 40 \text{ km}^2$ of harvested potatoes) (USDA, 2004) and the use of selected fungicides (for example, azoxystrobin usage $\geq 10 \text{ kg km}^{-2}$) (Gianessi and Reigner, 2002; USDA, 2004). Potatoes were selected as they are grown throughout the United States, receive frequent fungicide applications and favor well-drained soils. These candidate areas were further prioritized based upon the following factors to ensure the selection of a nationally-relevant group of sites: hydrologic and climatological setting, presence of shallow unconfined aquifers ($<10 \text{ m}$ to water), proximity to sensitive resources and environments, agricultural and irrigation practices and availability of pesticide application data (i.e. proximity to an agricultural research station conducting potato variety trials). Pesticide usage data from research farms within each study area were evaluated to ensure that the fungicides of interest were being applied. This provided assurances that the selected fungicides were applied to the fields overlying the shallow groundwater sampling locations and in proximity to surface waters draining the research farms. 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. Surface ($n = 12$) and groundwater ($n = 12$) sampling sites were selected in and around Presque Isle, Maine, Parma, Idaho and Hancock, Wisconsin (Fig. A.1). Sampled surface watershed sizes ranged from 7 to 20589 ha (Table A.1). Additional basin characteristics are given in the Supplemental material.

Surface water samples were collected every 3 weeks beginning after the first application of fungicides and ending after harvest (7 sampling events per site). Samples were collected on a set schedule regardless of flow conditions. Grab samples from surface waters were collected from the center of flow (in the case of the pond, vertically integrated from a point within 4 feet of the water's edge) and composited in methanol-rinsed Teflon churns. Selected

groundwater wells were sampled after the first application of fungicides. Shallow groundwater samples were collected from temporary wells installed within recently harvested potato fields on local agricultural extension farms (in Maine, an additional sample was collected from a nearby farm) using a Geoprobe® direct push system and a Geoprobe® SP-15 groundwater sampling system. The screened opening was set as near to the water table as possible. After sampling was completed, the temporary wells were removed and sealed with grout. Wells were pumped with a peristaltic pump and sampled using $\frac{1}{4}$ -in. acid-washed, methanol-rinsed Teflon tubing. At least three casing volumes of water were removed from wells prior to sampling, and field-measured properties (pH, specific conductance, water temperature, and turbidity) were monitored before sampling to ensure stable values prior to collecting water-quality samples (Wilde et al., 1998). Surface water and groundwater samples for pesticide analysis were passed through a 0.7 μm , baked, glass fiber filter in the field, split into pre-cleaned amber, glass bottles, chilled and shipped within 24 h for processing. For detailed information regarding well construction and groundwater sampling dates, see supplemental information (Table A.2).

2.2. Analytical methods

Filtered water samples were analyzed for a suite of 33 fungicides and 57 other currently used pesticides by extracting one liter of sample water onto Oasis HLB solid-phase extraction (SPE) cartridges (6 cc, 500 mg, 60 μm , Waters Corporation, Milford, Massachusetts). All samples were spiked with $^{13}\text{C}_3$ -atrazine, and diethyl- d_{10} diazinon (Cambridge Isotopes, Andover Massachusetts) as recovery surrogates. Following extraction, the SPE cartridges were dried, eluted with 12 mL of ethyl acetate, reduced under nitrogen. After extraction about 1 g of sodium sulfate (Na_2SO_4) was added to the sample bottles to remove any residual water and the bottles were rinsed three times with dichloromethane (DCM). The bottle rinses were reduced to under nitrogen, combined with the ethyl acetate fraction and reduced for analysis. A more detailed discussion of the extraction method can be found in Hladik et al. (2008).

Water sample extracts (1 μL injection volume) were analyzed for herbicides and insecticides on a Varian Saturn 3890 gas chromatograph coupled to a Varian 2000 ion trap (Walnut Creek, CA, USA) mass spectrometer (GC/IT-MS). Analyte separation on the gas chromatograph was achieved using a 30 m \times 0.25 mm i.d., 0.25 μm DB-5 ms fused silica column (Agilent Technologies, Folsom, California) with helium as the carrier gas at 1 mL min^{-1} . The temperature of the splitless injector was held constant at 275 °C. The temperature program was 80 °C (hold 0.5 min), increase to 120 °C at 10 °C min^{-1} , increase to 200 °C at 3 °C min^{-1} (hold 5 min), followed by a third increase to 219 °C at 3 °C min^{-1} , and a final increase to 300 °C at 10 °C min^{-1} (hold 10 min). The transfer line and ion trap temperatures were 280 °C and 220 °C, respectively. The mass spectrometer was operated in electron ionization (EI) mode with an emission current of 15 μA and no offset when run in full scan mode, and an emission current of 45 μA with a multiplier offset of 300 V when using selective ion storage (SIS) mode. Data was collected in full scan and SIS modes (Hladik et al., 2008).

Extracts (1 μL) were analyzed for fungicides on an Agilent 7890 gas chromatograph coupled to an Agilent 5975 (Folsom, CA) mass spectrometer operating in electron ionization mode (GC/EI-MS). Analyte separation was achieved using a 30 m \times 0.25 mm i.d., 0.25 μm DB-5 ms fused silica column (Agilent Technologies, Folsom, CA) with helium as the carrier gas at a flow rate of 1.2 mL min^{-1} . The temperature of the splitless injector was held constant at 275 °C. The temperature program was 80 °C (hold 0.5 min), increase to 180 °C at 10 °C min^{-1} , increase to 220 °C at

5 °C min⁻¹ (hold 1 min), increase to 280 °C at 4 °C min⁻¹ (hold 1 min), and a final increase to 300 °C at 10 °C min⁻¹ (hold 10 min). The transfer line, quadrupole and source temperatures were 280 °C, 150 °C and 230 °C, respectively. Data for all fungicides was collected in selective ion monitoring mode (SIM) with each compound having one quantifier ion and 1–2 qualifier ions.

All methods used either selective ion storage (SIS) or selective ion monitoring (SIM) for improved sensitivity, thus only the target compounds were reported with no attempt to report or quantify 'unknowns'. Positive identification of a compound required elution within the expected retention time window and ion abundance ratios were required to match that of the reference standard compounds. The base peak ion was used for quantitation and, one to two qualifier ions were used for confirmation (Table A.3). Compound concentrations were calculated from a 7–8 point standard curve (0.025–5 ng µL⁻¹) using internal standard quantitation. Method detection limits (MDLs) for all compounds excluding the fungicides were validated in a previous study (Hladik et al., 2008) using the USEPA procedure described in 40 CFR Part 136 (USEPA, 1992). Natural water was used for all MDL determination and was collected in 2005 from the Sacramento River at Miller Park (insecticides and herbicides) and in 2008 from the American River near the California State University Campus (fungicides). MDLs for all compounds in water ranged from 0.9 to 12.1 ng L⁻¹ (Table A.3). Analytes can be identified at concentrations less than the MDL with lower confidence in the actual value and are reported as estimates.

2.3. Quality assurance protocol

Pesticide concentrations in water samples were validated against a comprehensive set of performance based quality assurance/quality control (QA/QC) criteria including field and laboratory blanks, replicate samples (field and matrix spikes), matrix spikes and surrogate recovery.

Twenty-five field blanks generated from laboratory-grade organic free water were processed to test the cleanliness of the field procedures. Field blanks were subjected to the same sample processing, handling and equipment as the water samples and were collected during each sampling event. Eighteen of the twenty-five blanks processed had no detections. In the few cases where blank concentrations were above the MDLs (11 of 6552 analyses), sample concentrations were blank corrected by subtracting the blank concentration from the affected environmental samples. Twenty-eight sequential replicates were collected to test sample homogenization in the field and analytical reproducibility in the laboratory. Replicate samples were 100% in agreement for both detections and non-detections and results indicated 62 paired detections. Relative percent difference between replicate samples ranged from 0.04% to 33% with a median of 9.1%. Thirty samples were field spiked with the 90 target pesticides (spike concentration = 100 ng L⁻¹) and had average percent recoveries ranging from 85% to 104% with a median of 91% (Fig. A.2). Ring-¹³C₃-atrazine and diethyl-d₁₀ diazinon were used as recovery surrogates to assess the efficiency of sample extraction. Percent recovery of surrogates for all samples analyzed (including QC samples) ranged from 72% to 120% with a median of ring-¹³C₃-atrazine and diethyl-d₁₀ diazinon of 90% and 93%, respectively.

3. Results and discussion

3.1. Occurrence of fungicides

At least one fungicide was detected in 75% of the samples from surface water bodies and in 58% of the samples from groundwater wells. Twelve out of thirty-three fungicides were detected at least

once during this study, with boscalid and azoxystrobin being detected in more than 50% of the samples collected (Table 1). Of the surface water and groundwater samples with detectable fungicides, 53% of surface waters and 25% of groundwaters contained three or more fungicides. The median number of detected fungicides in surface water and groundwaters sampled was 3 and 2, respectively. A stream in Idaho, a stream Wisconsin and a shallow groundwater sample collected from beneath a potato field in Maine contained six fungicides each. Five fungicides (boscalid, azoxystrobin, chlorothalonil, pyraclostrobin and pyrimethanil) were detected in greater than 20% of the samples collected with concentrations ranging from less than the analytical method detection limit to 2120 ng L⁻¹ (Fig. 1, Table 1) with a median concentration for all fungicides detected of 33.2 ng L⁻¹. There were no significant differences in site to site or state to state variations in fungicide occurrence or concentration. This suggests that the observed fungicide occurrence pattern is characteristic of potato production. Field studies evaluating areas dominated by other crops have documented differing fungicide occurrence patterns. Azoxystrobin and propiconazole were the most frequently detected fungicides in streams draining soybean growing areas of the southern central US (Battaglin et al., 2010). Whereas, in the lettuce growing region of coastal California, boscalid, azoxystrobin and myclobutanil were the most frequently detected fungicides in surface water (Smalling and Orlando, 2011).

Boscalid, a carboxamide fungicide registered for use in the US in 2003, is a systemic fungicide used on a wide variety of food crops and turf and is applied to seeds and foliage at lower rates and has fewer approved uses than many other pesticides (including atrazine and metolachlor) (USEPA, 2003). Boscalid was the most frequently detected pesticide (72%) in this study with concentrations in surface water ranging from less than the MDL to 110 ng L⁻¹ with a median of 22.5 ng L⁻¹ (Table 1). Only one other study to date has reported consistent (85% detection frequency and median concentration of 74.5 ng L⁻¹) boscalid detections in surface waters (Smalling and Orlando, 2011). Boscalid was also detected frequently (62%) in the thirteen shallow groundwater wells with concentrations ranging from less than the MDL to 2120 ng L⁻¹ (nearly 20 times greater than the maximum concentration observed in samples from surface water bodies). The sample with the highest concentration was collected at the watertable beneath a potato field in Wisconsin 73 d after application. Boscalid was applied once that year (2009) at a rate of 178 g ha⁻¹ (consistent with recommended application rates (Boerboom et al., 2008)) and had not been applied for at least the 3 prior years. To our knowledge this is the first study that has reported boscalid detections in shallow groundwater. The groundwater ubiquity score (GUS) for boscalid is 2.5 (Table A.4) indicating that it has a marginal risk of leaching to groundwater (PPDB, 2012). Results from this study indicate that boscalid is present in surface water and has the potential to leach to groundwater. These findings are contrary to other studies which suggested that boscalid has low mobility in most soils and sediments and is unlikely to pose a risk to groundwater resources (USEPA, 2003; CADPR, 2003). A single study in Europe reported the detection of boscalid and other fungicides in air samples indicating its' potential for atmospheric transport (Schummer et al., 2010). Recent technological developments will facilitate increases in boscalid production capacity (Glasnov and Kappe, 2010). When combined with the increase in permitted uses in the US for application on an ever-growing list of crops, it is reasonable to suggest that more frequent detections of boscalid in surface and groundwater throughout a wider range of agricultural settings are likely to occur in the future.

3.2. Comparison to other pesticides

In addition to fungicides, water samples were also analyzed for a suite of 57 other current-use pesticides (21 herbicides, 27

Table 1

Summary of the pesticides detected, pesticide type, detection frequency, and median and maximum observed concentrations in surface water and groundwater samples. Results in parentheses are less than the method detection limit and are estimated. (F, fungicide, H, herbicide, I, insecticide, D, degradate).

	Type	Total (N = 72)	Groundwater (N = 12)			Surface water (N = 60)		
		Frequency (%)	Frequency (%)	Median (ng L ⁻¹)	Maximum (ng L ⁻¹)	Frequency (%)	Median (ng L ⁻¹)	Maximum (ng L ⁻¹)
Boscalid	F	72	58	16.0	2120	75	22.6	109
Metolachlor	H	57	33	68.3	120	62	37.0	1750
Atrazine	H	55	67	8.0	33.5	53	14.7	132
Azoxystrobin	F	51	17	(0.8)	(0.9)	58	30.6	59.8
Chlorothalonil	F	40	50	(0.5)	8.7	35	(1.1)	228
Pyraclostrobin	F	40	33	3.1	4.8	42	15.2	239
Pyrimethanil	F	28	8	na	6.0	32	(1.2)	(4.0)
Chlorpyrifos	I	21	0	nd	nd	25	3.3	65.0
Pendimethalin	H	17	0	nd	nd	20	32.7	57.4
Trifluralin	H	13	0	nd	nd	13	(0.8)	2.1
Ethalfuralin	H	10	0	nd	nd	12	4.0	34.4
Methylparathion	I	10	0	nd	nd	12	41.6	65.4
p p'-DDE	D	8	0	nd	nd	10	(1.4)	(3.2)
Bifenthrin	I	8	0	nd	nd	19	4.8	7.0
S-ethyl dipropylthiocarbamate (EPTC)	H	6	0	nd	nd	7	45.0	56.3
Cyprodinil	F	6	0	nd	nd	7	(4.0)	180
Zoxamide	F	4	0	nd	nd	5	23.8	493
Dacthal	H	3	0	nd	nd	3	6.1	6.5
Fludioxinil	F	3	0	nd	nd	3	(3.3)	(3.3)
Carbofuran	I	1	0	nd	nd	2	na	94.0
Simazine	H	1	8	na	140	0	nd	nd
Diazinon	I	1	0	nd	nd	2	na	1.7
Fipronil	I	1	8	na	(2.2)	0	nd	nd
Fenhexamid	F	1	8	na	116	0	nd	nd
Malathion	I	1	0	nd	nd	2	na	249
Triticonazole	F	1	0	nd	nd	2	na	66.8
Dimethomorph	F	1	8	na	33.3	0	nd	nd

na: median not calculated when the compound was only detected once during sampling.

nd: not detected.

insecticides, 8 degradates, and 1 synergist) to provide a basis of comparison for the detection frequency and concentrations of the 33 measured fungicides and to define the pesticide mixtures present in these systems. None of these pesticides were detected more frequently than boscalid (the most frequently detected fungicide). Three current-use pesticides (metolachlor, atrazine and chlorpyrifos) were detected in greater than 25% of the surface-water samples. Atrazine and metolachlor were detected in 67% and 33% of groundwater samples, respectively. Concentrations of atrazine and metolachlor ranged from less than the MDL to 1750 ng L⁻¹ (Table 1, Fig. 1) with a median concentration for all detected current-use pesticides of 13 ng L⁻¹. More than half of the surface water and groundwater with detectable current-use pesticides (including fungicides) contained five or more compounds; 10% of the samples contained ten or more current-use pesticides. In agricultural areas with high pesticide use, detection of a variety of compounds is not uncommon (Thurman et al., 1991; Gilliom et al., 2006; Kuivila and Hladik, 2008); however, the effects of these complex mixtures at an ecosystem level are not widely understood.

The median total pesticide concentration in a given sample during this study was 76 ng L⁻¹ and ranged from less than the analytical MDL to 2120 ng L⁻¹. On average, 44% of the pesticide concentration in a water sample was derived from a mixture of fungicides. Atrazine and metolachlor were detected in more than half of the samples (56% and 57% respectively) with median detected concentrations of 13.8 and 37.0 ng L⁻¹, respectively. These two pre-emergent herbicides are amongst the most commonly occurring pesticides in national-scale water quality studies as they are widely used for weed control throughout the US (Gilliom et al., 2006; Vecchia et al., 2009). Median concentrations of atrazine and

metolachlor from this study were an order of magnitude lower than those reported over the last two decades in the Midwestern United States (Thurman et al., 1991; Battaglin and Goolsby, 1998; Battaglin et al., 2002). Sampling in this study was scheduled coincident with fungicide application and was not optimized for herbicide applications. Pre-emergent herbicides are applied once during the growing season, typically in the spring, and are flushed from the fields during late spring and early summer rains (Thurman et al., 1991). As this study was designed to target fungicides, the initial sampling likely missed the herbicide peak in the late spring and early summer.

Fungicide occurrence and concentration patterns observed in streams during this study differ from those of the other current-use pesticides measured. Comparison of the concentrations of three representative pesticides: metolachlor (herbicide), methyl parathion (insecticide) and boscalid (fungicide) measured in Sand Run Gulch near Parma, ID illustrates this phenomenon (Fig. 2). This stream has a drainage area of 20589 ha comprised of 39% cultivated crops and 47% grassland. In Idaho, sampling began in the early summer (June, 2009) to coincide with the first fungicide applications of the season. Not surprising, and similar to other studies, metolachlor was detected frequently and had generally higher concentrations compared to fungicides and insecticides (Thurman et al., 1991). In this region, herbicides are flushed from the fields by return flow of irrigation waters rather than by rains typical of the Midwestern US "corn belt" (Thurman et al., 1991). Although, metolachlor was detected frequently, concentrations steadily decreased throughout the sampling period with time from initial pre-emergent application to crops early in the growing season. Methyl parathion, one of the most toxic organophosphate insecticides, was detected in mid July and early August of 2009.

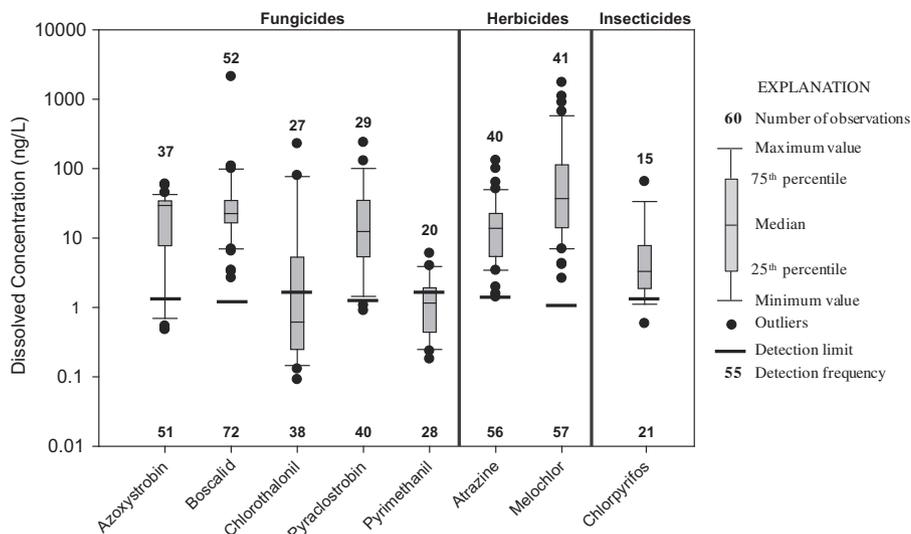


Fig. 1. Box plots of the dissolved concentrations of the seven most frequently detected pesticides in surface and groundwater samples collected between June and November 2009 in the study area. Results reported below the method detection limit are considered estimated values. Only detected concentrations are shown.

Insecticides are periodically applied during the growing season when necessary to combat the presence of crop-damaging insects. Unlike herbicides and insecticides, fungicides are applied at lower rates, but on a set schedule (dictated by factors including the relative humidity, stage of plant growth, and the presence of fungal disease in the region) to provide prophylactic crop protection from fungal diseases. The frequent application of fungicides (typically 5–10 applications per season) is reflected by the consistent presence of boscalid creating a relatively constant source of these chemicals to streams that receive drainage or irrigation return flow from treated fields. In most cases, fungicide applications are stopped several weeks before harvest (mid August to late October in Idaho). This is reflected by the lower boscalid detection during the last sample collection in September. This study demonstrates that, unlike most herbicides and insecticides, the practice of frequent fungicide applications throughout the growing season translates to more consistent concentrations in corresponding surface water systems. This practice creates the potential for chronic exposure of aquatic organisms to fungicides throughout the application period.

3.3. Potential environmental effects and implications

Based upon the current literature, impacts to aquatic communities from fungicides at the concentrations observed in this study are likely to sub-lethal or an indirect disruption of community structure by reducing fungal, phytoplankton and zooplankton populations. Non-disease (non-target) fungi are sensitive to antifungal substances (including synthetic fungicides) and changes to their community structure could impact key food web dynamics as well as critical nutrient and carbon cycling pathways (Barron, 2003; Gleason and Marano, 2010). Microcosm studies with azoxystrobin report altered zooplankton community structure, with copepod abundance significantly reduced and rotifer abundance increased after 12 d at nominal concentrations of 3000 ng L⁻¹ (Gustafsson et al., 2010). Chronic (21 d) exposure of the zooplankton, *Daphnia Magna*, to 26 ng L⁻¹ of azoxystrobin increased respiration, altered age at first reproduction, and either increased or decreased fecundity, depending on the clone used (Warming et al., 2009). Detrimental changes in the avoidance and stress response of amphipods (reduced swimming ability, longer righting times, and increased lipid content) have been observed in the presence of

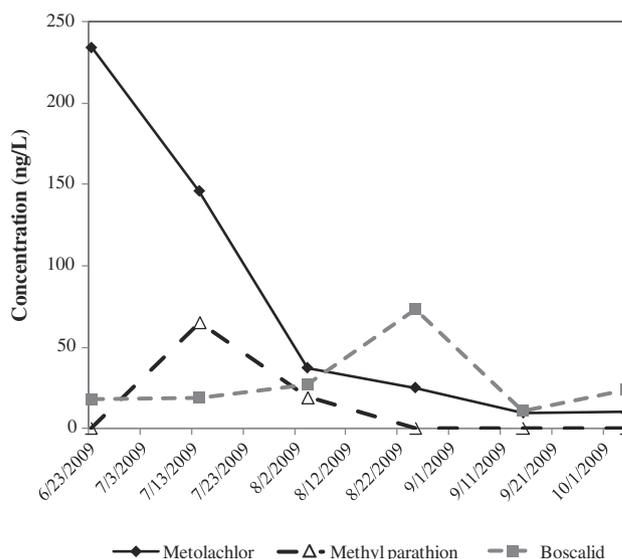


Fig. 2. Change in dissolved pesticide concentrations of metolachlor (herbicide), methyl parathion (insecticide) and boscalid (fungicide) over time in samples collected from Sand Run Gulch in Parma, ID.

1–10 ng L⁻¹ of chlorothalonil (Hellou et al., 2009). Median azoxystrobin and chlorothalonil concentrations observed in this study were 30.6 and 1.1 ng L⁻¹, respectively indicating the potential for sub-lethal effects to aquatic organisms in the studied water bodies.

4. Conclusion

The high detection frequency and relative concentration of fungicides, particularly newer chemicals like boscalid, illustrates the fact that while broad studies of high-use pesticides inform regulators about national trends, small scale, focused studies demonstrate that lower-use pesticides can be important at the local level. Consequently, a series of analytical methods developed for the purpose of determining the presence of pesticides at a national scale may not be appropriate for monitoring at smaller scales or in specialized crop-use settings. Monitoring programs must be

dynamic and strive to match their analytical capabilities with the chemical usage within the watersheds they sample. Regulators monitoring watersheds planted with crops that require intense fungicide use should consider including such compounds in their monitoring programs or risk missing the detection of these emerging contaminants in their surface water and groundwater systems. The high detection frequency of fungicides in this study is unlikely to be representative of all streams and groundwater influenced by agriculture, but underscores the importance of including these chemicals in pesticide monitoring programs were they are used. As fungicide use continues to increase (CADPR, 2012) and new compounds to combat plant diseases are introduced, studies are needed to target the fate and occurrence of these compounds in the environment and understand their effects on non-target, essential fungus as well as other aquatic organisms.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.04.023>.

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