Screening for Pesticides in High Elevation Lakes in Federal Lands

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Introduction

According to a study released by the Western Airborne Contaminants Assessment Project (WACAP) contaminants such pesticides, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) were detected in fish in Rocky Mountain and Glacier national parks, and other western national parks (Landers et al., 2008). Some concentrations of historic-use pesticides such as dieldrin and DDT in these remote areas exceeded wildlife and human health thresholds for fish consumption. Current-use pesticides (trifluralin, triallate, chlorpyrifos, dacthal) were detected in lichen and conifer needles from Glacier, Rocky Mountain, and Grand Teton national parks, and Great Sand Dunes National Park & Preserve.

Elevated concentrations of contaminants in remote mountainous regions could be the result of atmospheric transport, precipitation, and the process of "cold condensation" when chemicals volatilize in warm locations and condense once they reach colder areas characteristic of high elevations (Blais et al., 1998). Upslope wind patterns during the day in concert with increased deposition and precipitation rates at high altitude caused by colder temperatures make mid-latitude mountainous areas convergence zones for the accumulation of organic pollutants (Daly and Wania, 2005). Semivolatile organic contaminants including polychlorinated biphenyls, organophosphate pesticides, and polycyclic aromatic hydrocarbons were detected in the European Alps and Canadian Rockies (Weiss et al., 2000; Blais et al., 1998). The Rocky Mountains tend to receive high levels of precipitation and are relatively close to sources of pollution from agriculture, oil and gas development, and high population densities. Therefore, mountainous areas within the U.S. Environmental Protection Agency (EPA) Region 8, including the states of Colorado, Wyoming, and Montana, may be particularly prone to the deposition and accumulation of pesticides and other contaminants.

Additionally, local sources of contaminants may exist from the use of pesticides by land managers to control invasive weeds, insects, or other pests. Pesticides (i.e., herbicides) are sometimes used in national parks to control or eradicate invasive species, taking into account environmental effects and other alternatives (NPS 2002).

National parks, national forests, and wilderness areas preserve America's natural resource heritage and are often considered to be among the most pristine ecosystems in the nation. For many scientists, managers, and regulators, remote federally managed areas within Region 8 are often considered to be the baseline or reference sites used to assess the condition of other waters. Therefore, it is important to assess if contaminants are present in areas thought to be pristine. This project represents a screening assessment to measure a suite of pesticides in waters within remote high elevation areas.

Study Design

Samples were collected at Great Sand Dunes National Park & Preserve, Rocky Mountain National Park, Grand Teton National Park, and Glacier National Park, and the Shoshone National Forest/ Bridger-Teton Wilderness during the summer of 2009 in lakes and streams selected by each park unit. Study locations and sample sites are identified in Table 1.Grab water samples were collected by park personnel and shipped to the EPA Region 8 Laboratory for analysis within a seven day hold time using Liquid Chromatography Mass Spectrometry (EPA Method 8321A). A schedule of all analytes is provided in the Appendix.

Table 1. Summary of National Park Service (NPS) and US Forest Service (USFS) sites sampled for the pesticide screening study in high elevation lakes in EPA Region 8.

NPS or USFS site	Abbreviation	State	Lake(s) Sampled
Glacier National Park	GLAC	Montana	Hidden (HI) Upper Two Medicine (UTM)
Grand Teton National Park	GRTE	Wyoming	Death Canyon (DC) Solitude (S) Grizzly Bear (GB)
Great Sand Dunes National Park & Preserve	GRSA	Colorado	Sand Creek (SC) Medano Creek (MC) (*)
Rocky Mountain National Park	ROMO	Colorado	Ypsilon (Y) Poudre (P) Bear (B) Lone Pine (LP)
Shoshone National Forest/ Bridger-Teton Wilderness	SNF	Wyoming	Hobbs (H) Deep (D) Upper Frozen (UF) Black Joe (BJ)

(*) Creeks, not lakes, sampled at GRSA.

Results

Herbicides, an insecticide, a fungicide, and a rodenticide were detected at low levels in the National Park Service units and US Forest Service areas sampled during this study (Figure 1, Tables 2 & 3). The rodenticide, bromodiolone, was detected at an average concentration of 72.4 ng/L in Hobbs, Black Joe, and Upper Frozen lakes, Shoshone National Forest. Imidacloprid, an insecticide, was detected at Glacier National Park (NP) at a concentration of 29.5 ng/L in Hidden Lake and at a concentration of 28.8 ng/L in Deep Lake, Shoshone National Forest (NF). The fungicide, Azoxystrobin, was detected at concentration of 54.5 ng/L in Death Canyon Lake at Grand Teton NP. Two imadazole selective herbicides, Imzaethapyr and Imazaquin were detected in four park units: Glacier NP, Grand Teton NP, Rocky Mountain NP, and Grand Sand Dunes National Park & Preserve (NP & Pres.). Imazethapyr was detected in Glacier NP (Upper Two Medicine Lake) and Grand Teton NP (Solitude, Grizzly Bear, and Death Canyon lakes) at a concentration of 11.2 and average concentration of 11.5 ng/L, respectively. Imazaquin was detected in Rocky Mountain NP (Bear and Lone Pine lakes) and Great Sand Dunes NP & Pres. (Medano Creek) at an average concentration of 13.8 and concentration of 33.9 ng/L, respectively. Although the parent compound of the herbicide dimethenamid was not detected in any of the samples, the breakdown product dimethenamid ESA was detected at a concentration of 14.9 ng/L in Medano Creek, Great Sand Dunes NP & Pres.

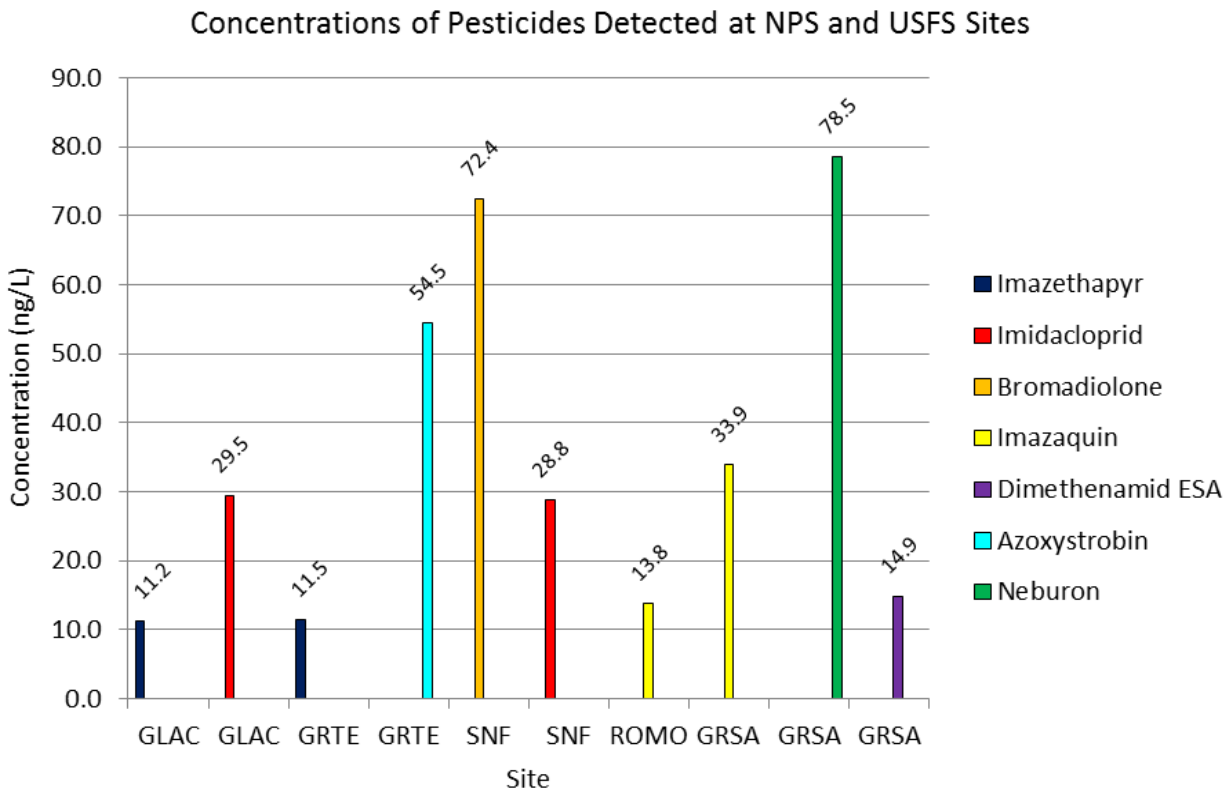

Figure 1. Concentrations of pesticides detected in National Park Service units and a National Forest. Water samples were collected from Shoshone National Forest (SNF)/Bridger-Teton Wilderness, Glacier National Park (GLAC), Grand Teton National Park (GRTE), Rocky Mountain National Park (ROMO), and Great Sand Dunes National Park & Preserve (GRSA), and analyzed for pesticides using LCMS (EPA Method 8321A).

The concentrations of pesticides at the sites listed below are the result of multiple detects (n=) of the pesticide in different lakes; the graph presents the average concentration for that site: GRTE/ Imazethapyr (n=4); SNF/ Bromadiolone (n=3); ROMO/ Imazaquin (n=2). The same method is applied in the data displayed by Table 3 (i.e., average pesticide concentration over n= detects); however, Table 2 includes the pesticide concentration per individual lake. The remaining pesticide concentrations presented both in Figure 1 and Table 3 at the other sites are a result of n=1 detect per site.

Table 2 (following page). Data summary of pesticide detections and concentrations in lakes at NPS and USFS sites in the Rocky Mountains.

Analyte	No. of Analyses	No. of Detections	Sample Conc. (ng/L)	Site	Lake	Average Conc. (ng/L)	Max Conc. (ng/L)	Detection Freq.
Imazethapyr	26	5	11.2	GLAC	UTM	11.4	11.7	19.2%
			11.4	GRTE	S			
			11.7	GRTE	GB			
			11.4	GRTE	S			
			11.4	GRTE	DC			
Bromadiolone	26	3	59.9	SNF	BJ	72.4	78.7	11.5%
			78.7	SNF	H			
			78.5	SNF	UF			
Imazaquin	26	3	10.6	ROMO	B	20.5	33.9	11.5%
			16.9	ROMO	LP			
			33.9	GRSA	MC			
Imidacloprid	26	2	28.8	SNF	D	29.2	29.5	7.7%
			29.5	GLAC	HI			
Dimethenamid ESA	25	1	14.9	GRSA	MC	14.9	14.9	4.0%
Azoxystrobin	26	1	54.5	GRTE	DC	54.5	54.5	3.8%
Neburon	26	1	78.5	GRSA	MC	78.5	78.5	3.8%

Table 3. Summary of pesticide detections at National Park Service units and a US Forest Service unit in EPA Region 8. Benchmarks, when available, are from U.S. EPA Office of Pesticide Programs (2011).

NPS/ USFS Site (Lake-s)	Analyte, Concentration (ng/L)	Use	OPP Acute Aquatic Life Benchmarks (µg/L)	OPP Chronic Benchmarks (µg/L)
GLAC (UTM)	Imazethapyr, 11.2 (0.0112 µg/L)	Herbicide	>50,0000 Fish 50,000 invertebrate 11,500 nonvascular plants 18 vascular plants	43,100 fish 97,000 invertebrate
GLAC (HI)	Imidacloprid, 29.5 (0.0295 µg/L)	Insecticide	>41,500 fish 35 invertebrate >10,000 nonvascular plants	1,200 fish 1.05 invertebrate
GRTE (S) (GB) (DC)	Imazethapyr, 11.5 (0.0115 µg/L)	Herbicide	>50,0000 Fish 50,000 invertebrate 11,500 nonvascular 18 vascular plants	43,100 fish 97,000 invertebrate
GRTE (DC)	Azoxystrobin, 54.5 (0.0545 µg/L)	Fungicide	235 fish 130 invertebrate 49 nonvascular plants 3,400 vascular plants	147 fish 44 invertebrate
GRSA (MC)	Imazaquin, 33.9	Herbicide	NA	NA
GRSA (MC)	Dimethenamid ESA*, 14.9 (0.0149 µg/L)	Herbicide (breakdown product)	3,150 fish 6,000 invertebrates 14 nonvascular plants 8.9 vascular plants	300 fish 1,020 invertebrates
GRSA (MC)	Neburon, 78.5	Herbicide (cancelled)	NA	NA
ROMO (B) (LP)	Imazaquin, 13.8	Herbicide	NA	NA
SNF (H) (UF) (BJ)	Bromodiolone, 72.4	Rodenticide	NA	NA
SNF (D)	Imidacloprid, 28.8 (0.0288 µg/L)	Insecticide	>41,500 fish 35 invertebrate >10,000 nonvascular plant	1,200 fish 1.05 invertebrate

*Breakdown product, benchmarks are based upon parent compound.

Discussion

Concentrations detected in this screening study were compared to the EPA Office of Pesticide Programs' (OPP) aquatic life benchmarks for freshwater species to determine any potential adverse effects to aquatic life. The OPP aquatic life benchmarks are based on toxicity values reviewed by EPA and are based on the most sensitive and scientifically acceptable toxicity endpoint (EPA, 2011). EPA OPP relies on studies required under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), as well as a wide range of environmental laboratory and field studies available in the public scientific literature to determine these benchmarks. When EPA OPP benchmarks were not available, the measured concentrations were compared with toxicity values obtained from The Extension Toxicology Network (EXTOXNET) or the Pesticide Action Network (PAN) (Kegley *et al.*, 2011).

Bromodialone is an anticoagulant rodenticide for use against mice and rats and is applied using bait boxes or at bait stations. There are no EPA OPP aquatic life benchmarks for bromodialone. For trout, the 96 hour LC50 (Lethal Concentration) is 1,400 µg/L and the 96 hour NOAEC (No Observable Adverse Effects Concentration) is 460 µg/L (EXTOXNET, ND). The 96 hour LC50 for Daphnia (water flea) is 8,800 µg/L and the Daphnia 96 hour NOAEC is 88 µg/L. The average concentration of 72.4 ng/L (0.0724 µg/L) detected at Hobbs, Black Joe, and Upper Frozen lakes Shoshone National Forest is well below the Daphnia NOAEC (Table 3, Figure 1). Therefore, no adverse impacts are expected from the bromodiolone detected in surface water.

Imidacloprid is an insecticide that works by interfering with the insect nervous system and is very toxic to aquatic invertebrates (EXTOXNET, 1996). However, the toxicity to fish is moderately low. The EPA OPP acute and chronic aquatic life benchmarks for fish are >41,500 µg/L and 1,200 µg/L, respectively (2011). The EPA OPP acute and chronic aquatic life benchmarks for invertebrates are 35 and 1.05 µg/L, respectively. The levels detected in Glacier National Park (29.5 ng/L (0.0295 µg/L) at Hidden Lake) and Shoshone National Forest (28.8 ng/L (0.0288 µg/L) at Deep Lake) are well below the acute and chronic (Table 3). Therefore, the levels detected in Glacier National Park and in Shoshone National Forest will likely not have an impact on aquatic life.

Azoxystrobin is a broad spectrum fungicide and generally degrades rapidly in the environment (half life less than two weeks) (EXTOXNET, 1997). The acute and chronic aquatic life benchmarks for fish are 235 and 147 µg/L, respectively (EPA, 2011). Azoxystrobin is more toxic to invertebrates with a chronic benchmark of 130 µg/L and a chronic benchmark of 44 µg/L. Azoxystrobin is also toxic to nonvascular plants including phytoplankton and macroalgae. The acute benchmark for nonvascular plants is 49 µg/L. The concentration of Azoxystrobin (54.5 ng/L, or 0.0545 µg/L) detected in Grand Teton National Park (Death Canyon Lake) will likely not affect aquatic life (Table 3, Figure 1).

Imazaquin and Imazethapyr are both selective herbicides and are practically nontoxic to fish and aquatic invertebrates (EXTOXNET, 1996). The EPA OPP acute aquatic life benchmarks for fish and invertebrates are 50,000 µg/L. The chronic aquatic life benchmarks are 43,100 µg/L and 97,100 µg/L for fish and invertebrates, respectively (EPA, 2011). EPA OPP does not have aquatic life benchmarks for imazaquin, but LC50 values for imazaquin are >280,000 µg/L for both rainbow trout and *Daphia magna* (EXTOXNET, 1996). Therefore, the concentration of imazethapyr detected at Upper Two Medicine Lake Glacier National Park (0.0112 µg/L), and the average concentration of imazethapyr at Solitude, Grizzly Bear, and Death Canyon lakes Grand Teton National Park (0.0115 µg/L) as well as the concentrations of imazaquin at Bear and Lone Pine lakes Rocky Mountain National Park (0.0138

µg/L) and Medano Creek Great Sand Dunes National Park & Preserve (0.0339 µg/L) are far below any level of concern (Figure 1, Table 3).

The herbicide dimethenamid was not detected in any of the sites sampled. However, the breakdown product, dimethenamid ethanesulfonic acid (ESA), was detected at creek Great Sand Dunes National Park at a concentration of 14.9 ng/L (0.0149 µg/L) (Figure 1). There are no toxicity data available for dimethenamid ESA. However, the parent compound, dimethenamid, is not toxic to invertebrates and fish (Kegley *et al.*, 2011). The EPA OPP chronic aquatic life benchmarks for fish and invertebrates are 300 and 1,020 µg/L respectively. Dimethenamid is, however, toxic to nonvascular plants and vascular plants. The EPA OPP acute aquatic life benchmarks are 14 µg/L and 8.9 µg/L, for nonvascular and vascular plants, respectively (Table 3). It is still unlikely that the concentration of dimethenamid ESA measured at Great Sand Dunes National Park & Preserve would have an effect on aquatic plants.

Neburon is a selective herbicide and is cancelled for production in the U.S. When a pesticide registration is cancelled, manufacturing of the products containing the active ingredient cease, but existing stocks can still be used. There are no aquatic benchmarks for neburon and there is a paucity of toxicity data for fish and invertebrates. As an herbicide, neburon is toxic to plants including phytoplankton and macroalgae. Toxic doses of neburon for phytoplankton range from 4 to 200 µg/L (Kegley *et al*., 2011). The concentration of 78.5 ng/L (0.0785 µg/L) detected in Medano Creek, Great Sand Dunes National Park & Preserve, likely will not affect macrophytes and microalgae (Table 3).

In summary, the concentrations of pesticides detected in this screening survey at a national forest and national parks in high elevation waterbodies of the Rocky Mountain west were low and far below the aquatic life benchmarks. Future work could expand the analytes to hydrophobic compounds in sediment/fish, as the current analysis was limited to hydrophilic compounds; determine the source of pesticides detected in parks and national forests; and collaborate on additional studies to determine occurrence and ecological impacts of contaminants.

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Appendix

USEPA Region 8 Laboratory GC-MS Pesticides in Water Analyte Listing - 13/April/2009
Analyte count = 87

USEPA Region 8 Laboratory LCMS Pesticides in Water Analyte Listing - 13/April/2009
Analyte count = 68

Compound Name	Compound Name
4,4'-DDD	2,4-D
4,4'-DDE	2,4-DB
4,4'-DDT	3-Hydroxycarbofuran
Acetochlor	Acetochlor & Alachlor ESA
Alachlor	Acetochlor OA
Aldrin	Alachlor OA
alpha-Chlordane	Aldicarb
alpha-Lindane	Aldicarb sulfone
Ametryn	Aldicarb sulfoxide
Atraton	Atrazine
Atrazine	Atrazine de-ethyl
Azinphos-methyl	Atrazine de-ethyl de-isopropyl
Benfluralin	Atrazine de-isopropyl
beta-Lindane	Azinphos methyl
Bromacil	Azoxystrobin
Butachlor	Bendiocarb
Butylate	Bensulfuron methyl
Carbaryl	Bentazon
Carbofuran	Bromacil
Carboxin	Bromadiolone
Chlordane	Bromoxynil
Chlorpropham	Butachlor ESA
Chlorpyrifos	Carbaryl
cis-Permethrin	Carbofuran
Cyanazine	Chlorimuron ethyl
Cycloate	Clopyralid
DCPA (Dacthall)	Dicamba
deethyl-Atrazine	Dimethachlor ESA
delta-Lindane	Dimethenamid ESA
Diazinon	Dimethenamid OA
Dichlorvos	Diuron
Dieldrin	Fluometuron
Diphenamid	Hexaflumuron
Disulfoton	Imazaquin
Disulfoton sulfone	Imazethapyr
Endosulfan I	Imidacloprid
Endosulfan II	Linuron
Endosulfan sulfate	Lufenuron
Endrin	Malathion

Endrin aldehyde	MCPA
Endrin ketone	MCPB
EPTC	Mesotrione
Ethalfluralin	Metalaxyl
Ethoprophos	Methiocarb
Etridiazole	Methomyl
Fenamiphos	Metolachlor ESA
Fenarimol	Metolachlor OA
Fipronil	Metsulfuron methyl
Fluridone	Monuron
Heptachlor	Neburon
Heptachlor epoxide	Nicosulfuron
Hexazinone	Oxamyl
Lindane	Picloram
Linuron	Propachlor OA
Malathion	Propazine
Merphos	Propiconazole
Methoxychlor	Propoxur
Metolachlor	Siduron
Metribuzin	Simazine
Mevinphos	Spinosyn D
MGK-264 (a)	Sulfometuron methyl
MGK-264 (b)	Tebuthiuron
Molinate	Terbacil
Napropamide	Terbuthylazine
Norflurazon	Thiamethoxam
Parathion	Thiamethoxam
Pebulate	Tralkoxydim
Phorate	Triclopyr
Prometon	
Prometryne	
Pronamide	
Propachlor	
Propanil	
Propazine	
Simazine	
Simetryn	
Stirofos	
Tebufos	
Tebuthiuron	
Terbacil	
Terbuthryn	
Thiobencarb	
Triadamefon	
Triallate	
Tricyclazole	
Trifluralin	
Vernolate	