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The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005–2006

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Abstract Vernal pools are sensitive environments that provide critical habitat for many species, including amphibians. These small water bodies are not always protected by pesticide label requirements for no-spray buffer zones, and the occurrence of pesticides in them is poorly documented. In this study, we investigated the occurrence of glyphosate, its primary degradation product aminomethylphosphonic acid, and additional pesticides in vernal pools and adjacent flowing waters. Most sampling sites were chosen to be in areas where glyphosate was being used either in production agriculture or for nonindigenous plant control. The four site locations were in otherwise protected areas (e.g., in a National Park). When possible, water samples were collected both before and after glyphosate application in 2005 and 2006. Twenty-eight pesticides or pesticide degradation products were detected in the study, and as many as 11 were identified in individual samples. Atrazine was detected most frequently and concentrations exceeded the freshwater aquatic life standard of 1.8 micrograms per liter (μg/l) in samples from Rands Ditch and Browns Ditch in DeSoto National Wildlife Refuge. Glyphosate was measured at the highest concentration (328 μg/l) in a sample from Riley Spring Pond in Rock Creek National Park. This concentration exceeded the freshwater aquatic life standard for glyphosate of 65 μg/l. Aminomethylphosphonic acid, triclopyr, and nicosulfuron also were detected at concentrations greater than 3.0 μg/l.

Keywords Atrazine · Glyphosate · Nonindigenous plants · Pesticides · Vernal pools

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Introduction

Vernal pools are sensitive environments that provide critical habitat for many aquatic species, including amphibians (Colburn 2004). Vernal pools are defined as ephemeral wetlands that reliably contain standing water during cooler wetter times of the year, but which dry up during warmer dryer times of the year, or during droughts. Some vernal pools may only fill with runoff from precipitation, whereas others may receive shallow groundwater inputs (Zedler 2003). Vernal pools are often sensitive to small changes in hydrologic conditions.

The general water quality (Whigham and Jordan 2003) and in particular the occurrence of pesticides (Relyea 2006) in vernal pools is poorly documented; moreover, these types of water bodies are not always protected by label requirements for no-spray buffer zones (Mann et al. 2003; Thompson et al. 2004). A few studies have indicated the presence of pesticides in vernal pools even when they are relatively distant from the areas of pesticide use (Frank et al. 1990; Du Preez et al. 2005). Recent studies indicate that some pesticides, pesticide degradation products, or pesticide adjuvants may have adverse effects on the development and survival of amphibians (Tavera-Mendoza et al. 2002; Osano et al. 2002; Gilbertson et al. 2003; Goulet and Hontela 2003; Hayes et al. 2002a, b; 2003; Christin et al. 2004; Howe et al. 2004; Mann et al. 2003; Relyea 2004, 2005b). Whether such effects actually occur under environmental conditions, however, is less well understood because the exposure concentrations in surface waters such as vernal pools has not been well documented.

Many of these studies investigated the potential effects of two herbicide active ingredients: glyphosate and atrazine. The potential impacts these two herbicides have on amphibians is controversial, with several studies (Wojtaszek et al. 2004; Thompson et al. 2004; Edginton et al. 2003; Chen et al. 2004) and general reviews (Solomon et al. 1996; Giesy et al. 2000; US Environmental Protection Agency 1993, 2006) concluding that deleterious effects on amphibians or other aquatic organisms are unlikely under realistic environmental exposures or normal-use scenarios

Glyphosate is a nonselective contact herbicide that kills plants by inhibiting the synthesis of aromatic amino acids needed for protein formation. Glyphosate was first registered for use in the USA in 1974 in Roundup® (the use of trade names does not imply endorsement by the US Geological Survey), and is among the most commonly used herbicides for agricultural, silvicultural, and nonagricultural weed control in the world (Woodburn 2000). Glyphosate use in the USA has increased dramatically from 7,700 metric tons of active ingredient in 1992 to 46,300 metric tons in 2002 (Gianessi and Reigner 2006; Aspelin 2003). The majority of this increase is the result of glyphosate use on soybean, cotton, and corn crops that have been genetically modified to tolerate it. Glyphosate is typically (but not always) applied "post-emergence" or after crops and weeds have emerged from the ground. Some studies indicate that the planting of glyphosate-tolerant crops in US agriculture has saved farmers money, reduced the total pounds of herbicides applied (Gianessi and Sankula 2003; Gianessi and Reigner 2006), and reduced the occurrence of herbicide concentrations in runoff exceeding drinking water standards (Shipitalo et al. 2008). The spatial pattern of glyphosate use on agricultural land in the conterminous USA (circa 2002) is shown on Fig. 1.

Within National Parks and National Wildlife Refuges, glyphosate is recommended for control of some noxious or nonindigenous plant species (T. Cacek, US National Park Service; and T. Parson, US Fish and Wildlife Service, April 2004, personal communication). Little if any information is available on the extent to which glyphosate contaminates the water of National Parks or Wildlife Refuges. It is a commonly stated in the marketing materials for these products that glyphosate is non-toxic to wildlife, and that once applied, glyphosate is absorbed by plants or adsorbed by soils, is immobilized, and is degraded within a few weeks (Monsanto 2005). Numerous studies, however, have demonstrated that some glyphosate is transported from fields or urban areas to groundwater, streams, and other water bodies (Newton et al. 1994; Smith et al. 1996; Wood 2001; Augustin and Seibel 2002; Scribner et al. 2003; Thompson et al. 2004; Battaglin et al. 2005; Kjaer et al. 2005; Kolpin et al. 2006; Shipitalo et al. 2008).

Glyphosate is of low oral and dermal acute toxicity to humans and is no more than slightly toxic to birds, fish, and aquatic invertebrates (US Environmental Protection Agency 1993; Giesy et al. 2000). Several studies indicate that commercial glyphosate formulations can be more toxic than pure glyphosate due to the toxicity or action

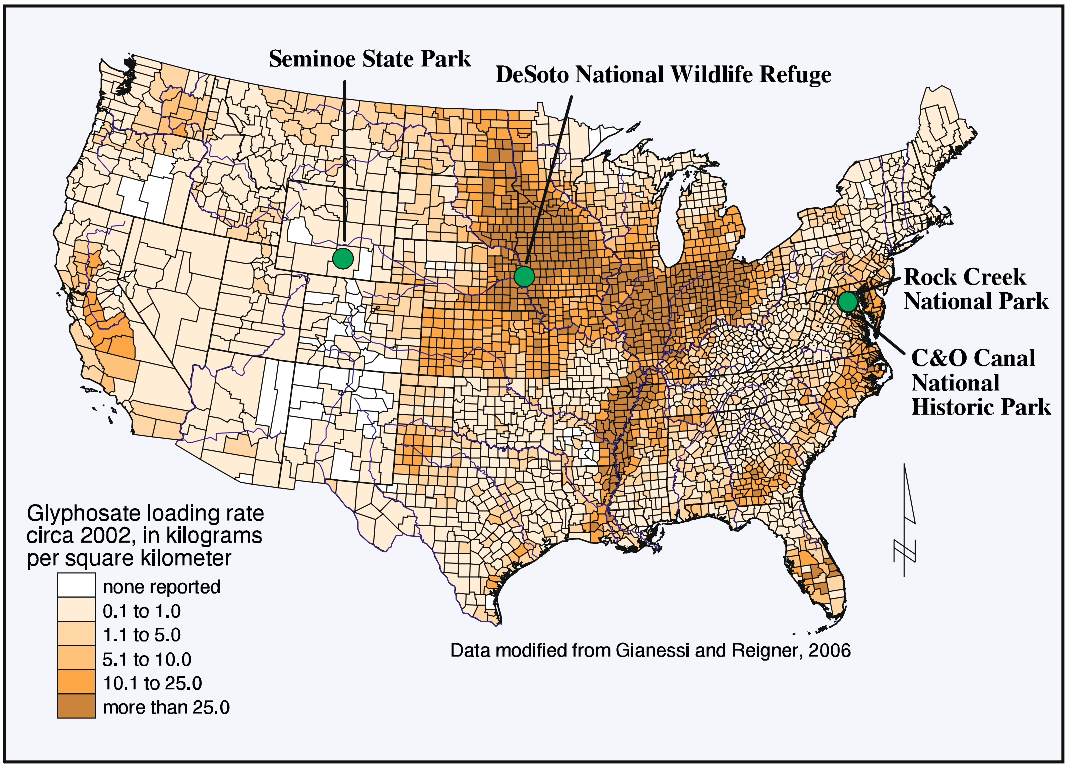

Fig. 1 Study site locations and county-level estimates of glyphosate loading from use on agricultural land, circa 2002

of the surfactants used (Giesy et al. 2000; Bringolf et al. 2007). Other studies indicate that the polyethoxylated tallowamine (POEA) surfactant (MON0818), used in some glyphosate formulations, is the principal toxicant responsible for effects on fish and amphibians (Edginton et al. 2004; Folmar et al. 1979; Perkins et al. 2000; Thompson et al. 2004). However, MON0818 concentrations were not actually measured in any of these studies. In some cases, effects on the development and survival of amphibians have been observed at glyphosate concentrations of 1,000 μg/l or less (Cauble and Wagner 2005; Edginton et al. 2004; Howe et al. 2004; Relyea 2004, 2005a, b, c; Relyea et al. 2005).

A cytotoxic effect on human embryonic cells of both Roundup® and glyphosate has been demonstrated (Richard et al. 2005; Benachour et al. 2007), as has endocrine disruption, specifically inhibition of estrogen synthesis (Benachour et al. 2007). In these two studies, the increased activity of Roundup® relative to glyphosate was attributed to the adjuvants allowing better stabilization and cell penetration of the glyphosate.

Glyphosate degrades to aminomethylphosphonic acid (AMPA) primarily by microbial processes (Vereecken 2005), though abiotic degradation also occurs (Barrett and McBride 2005). AMPA retains the phosphate group and many of the source herbicide properties. AMPA degrades slower than glyphosate in most soils, perhaps due to greater adsorption to soil particles, and hence may be more persistent than glyphosate. Both glyphosate and AMPA are water soluble and can persist in aquatic environments for several weeks (Giesy et al. 2000). Few toxicity studies dealing with AMPA are available, however, it is generally considered to be less toxic than glyphosate (Carlisle and Trevors 1988; Giesy et al. 2000). Environmentally detected AMPA also can form by the degradation of phosphonic acid in some detergents (Skark et al. 1998).

Atrazine is a triazine herbicide that is used primarily on corn, sorghum, and sugar cane crops.

Atrazine was first registered for use in the USA in 1958 (US Environmental Protection Agency 2006). The agricultural use of atrazine in the USA has exceeded 32,000 metric tons per year for at least the past 15 years (Gianessi and Reigner 2006; Donaldson et al. 2002; Aspelin 2003; US Department of Agriculture 2006). Atrazine typically (but not always) is applied "pre-emergence" or before crops or weeds have emerged from the ground. Atrazine and its degradation products are mobile in the environment and among the most commonly detected pesticides in US streams, reservoirs, groundwater, and precipitation (Kolpin et al. 1995; Battaglin et al. 2003; Scribner et al. 2005).

Atrazine is practically non-toxic to mammals and birds but moderately-to-highly toxic to fish and aquatic invertebrates (US Environmental Protection Agency 2006). Atrazine can be toxic to terrestrial and aquatic plants at concentrations as low as 20 μg/l (Fairchild et al. 1998; Solomon et al. 1996) and can result in aquatic community- and population-level risk at concentrations of 10 to 20 μg/l (US Environmental Protection Agency 2006). Atrazine can be directly toxic to amphibians with LC_{50} concentrations ranging from 200 to 127,000 μg/l (Birge et al. 2000). Recent studies indicate that atrazine can induce developmental abnormalities in amphibians, reptiles, and fish at concentrations as low as 0.1 μg/l (Hayes et al. 2002a, b, 2003; Hayes 2004; Sullivan and Spence 2003; Tavera-Mendoza et al. 2002). Others, however, have refuted these findings (Coady et al. 2004; Jooste et al. 2005). A study by Brodkin et al. (2007) indicates that exposure to atrazine at a concentration of 21 μg/l can result in immune disruption in adult northern leopard frogs.

Objective

The objective of the study described in this paper was to document occurrence of glyphosate, its primary degradation product aminomethylphosphonic acid (AMPA), atrazine, and additional pesticides and pesticide degradation products in water samples collected from amphibian habitats in four protected areas (Fig. 1), hereafter referred to as "the parks." At three of these locations, water sample collection was coordinated with glyphosate application in order to get samples that represent the maximum potential for exposure to aquatic plants and animals. The fourth location represents a control for the study where no glyphosate was applied in the year prior to or during the time of sample collection. The local use of atrazine was not considered in site selection, but atrazine is frequently used on corn and has been detected in precipitation at locations that are distant from its point of use (Majewski et al. 2008).

For this study, we tested the following hypotheses:

1. Can aquatic habitats within the parks be contaminated by application of glyphosate used to control noxious or nonindigenous plants, or weeds within the parks?
2. Can aquatic habitats in the parks be contaminated by application of herbicides or other pesticides to urban/suburban/agricultural areas adjacent to the parks' boundaries?
3. Do pesticide concentrations in aquatic habitats in the parks have the potential to affect populations or health of native amphibian species?

The purpose of this study is to provide baseline of information on the occurrence of glyphosate, atrazine and several other pesticides in the selected National Parks and Wildlife Refuges that is relevant to studies of ecology, hydrology, and biology of water-related habitats at those sites. The results also may help managers of other Parks and Refuges determine how to best use herbicides to control noxious or nonindigenous plants, and to identify the potential for contamination of small water bodies from external sources. Our ability to address the third hypothesis is limited by both the number of water samples we collected and the availability of relevant toxicity information.

Methods

Study sites

All of the vernal pools or small ponds sampled in this study are used by amphibians for breeding habitat (Rice and Jung 2004; Hayes et al.

2003; Robert Barry, US Fish and Wildlife Service, March 2005, personal communication). The sites are located in (1) Rock Creek National Park (NP) in Washington, DC, which is a largely forested urban park surrounded by suburban development; (2) Chesapeake & Ohio (C&O) Canal National Historic Park (NHP) in Maryland, which also is a largely forested urban park, bordered on one side by the Potomac River and on the other by suburban development (near the study sites); (3) DeSoto National Wildlife Refuge (NWR) in Missouri Valley, Iowa, which is a mixture of forests, meadows, wetlands, and agricultural land along the Missouri River, and is surrounded by intensive row-crop agricultural production; and (4) Seminoe State Park (SP) near Sinclair, Wyoming, which is arid rangeland with a few cottonwood trees along the North Platte River, that is surrounded by even more arid rangeland (near the study sites).

The first three parks were selected because there was planned use of glyphosate directly adjacent to a vernal pool, the presence of a nearby vernal pool where glyphosate was not being used directly adjacent, and the availability of information on the timing of past pesticide use and the expected timing of future pesticide use. There is moderate use of glyphosate in the counties surrounding the parks in Washington, DC and Maryland, and heavy use of glyphosate in the counties surrounding the park in Iowa (Fig. 1). The park in Wyoming was selected as the control for the study because no glyphosate was applied in the park in the year prior to or during the time of sample collection and little glyphosate was used in the counties surrounding the park.

In Rock Creek NP, the primary study site is a vernal pool named Riley Spring Pond (Table 1). The background/control site is the Weir Pond, and samples also were collected from Rock Creek just downstream from Riley Spring Pond. Stream discharge data are from Rock Creek at Sherrill Drive, Washington, DC (USGS gaging station number 01648000). In C&O Canal NHP, the primary study site is the Lock 7 Vernal Pool (Table 1). The background/control site is the Carderock Vernal Pool, and samples also were collected from the C&O Canal at Lock 7, adjacent to the Lock 7 Vernal Pool.

Table 1 Study site names, locations, elevations, types, and drainage areas

Site ID	Site name	State	Latitude	Longitude	Land surface altitude (m)	Site type	Drainage area (km^2)
RC1	Weir Pond	DC	38°59′06″	77°02′57″	54	Control	NA
RC3	Riley Spring Pond	DC	38°58′42″	77°02′33″	49	Treatment	NA
RC4	Rock Creek at Riley Spring	DC	38°58′40″	77°02′30″	48	Stream	161
CO1	Carderock Vernal Pool	MD	38°58′36″	77°12′22″	55	Control	NA
CO2	Lock 7 Vernal Pool	MD	38°57′46″	77°08′13″	23	Treatment	NA
CO3	C&O Canal at Lock 7	MD	38°57′47″	77°08′13″	22	Stream	NA
DS1	Field-side wetland	IA	41°32′09″	96°02′29″	303	Treatment	NA
DS2	Rands Ditch	IA	41°32′30″	96°02′09″	305	Stream	12.9
DS3	Browns Ditch	IA	41°31′20″	95°59′24″	303	Stream	5.2
DS4	Browns Pond	IA	41°31′19″	95°59′20″	304	Control	NA
SM1	Dugway Campground Pond	WY	41°51′41″	107°03′20″	1,954	Control	NA
SM2	N. Platte River at Dugway Campground	WY	41°51′42″	107°03′19″	1,951	Stream	10,810

Altitude is referenced to the North American Vertical Datum of 1988

NA not applicable, ° degrees, ′ minutes, ″ seconds

In DeSoto NWR, the primary study site is the Field-Side Wetland vernal pool (Table 1), which is adjacent to privately managed cropped land. The Rands Ditch site is adjacent to the Field-Side Wetland, but the ditch does not flow directly into the wetlands. The control site at DeSoto NWR is the Browns Pond vernal pool, which is not adjacent to cropped fields. The Browns Ditch site is adjacent to Browns Pond, but the ditch does not flow directly into the pond. Both ditches drain predominantly cropped land and flow into DeSoto Lake (Buske 1991).

Although each park had both treatment and control sites, often these sites were in close proximity to each other and could be influenced similarly by atmospheric deposition of pesticides. Hence, sites in Seminoe State Park, near Sinclair, Wyoming, were selected as study control sites. This park is more distant from substantial pesticide use than are the other three parks. The site in Seminoe State Park is the Dugway Campground Pond, a vernal pool at the Dugway Campground near Sinclair, Wyoming. Samples also were collected from the North Platte River adjacent to the pond site, just upstream from a USGS gaging station on the North Platte River above Seminoe Reservoir, near Sinclair, Wyoming (USGS station 06630000; Table 1).

Sampling procedures

The water temperature, pH, and specific conductance of most samples were measured in the field using a YSI Model 63 handheld meter (when available), and discharge (when reported) was obtained from a nearby USGS gaging station. In some cases, the YSI meter was not available and water temperature, pH, and specific conductance were not measured.

Samples were collected and processed using standard US Geological Survey (USGS) protocols (Wilde et al. 1999) unless otherwise noted, and analyzed using state-of-the-art techniques at the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas (ORGL), and the USGS National Water Quality Laboratory in Lakewood, Colorado (NWQL). All water samples were collected as single-point dip samples, near the center of flow (for streams) and near the edge (for vernal pools). Approximately 3 l of raw water were collected, kept on ice, and shipped within a day of collection to the USGS Colorado Water Science Center Laboratory. Upon receipt, samples were filtered through a 0.7-μm pore-size baked glass-fiber filter using an aluminum plate filter holder and a ceramic piston fluid metering pump with all Teflon tubing into pre-cleaned 125-ml or 1-l amber glass bottles. Three 125-ml amber glass bottles from each sample were sent to the ORGL and one 1-l amber glass bottle from each sample was sent to the NWQL.

Analytical methods

Water samples were analyzed at two laboratories. At the ORGL, a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method was used (Lee et al. 2002a, b) to determine glyphosate, AMPA, and glufosinate concentrations with a laboratory reporting level (LRL) of 0.02 μg/l (Scribner et al. 2007). At the NWQL, a high-performance liquid chromatography/mass spectrometry method (Furlong et al. 2001) was used to determine concentrations of 62 additional pesticides, pesticide degradation products, and caffeine with LRLs between 0.008 and 0.08 μg/l (Table 2; Childress et al. 1999). This method was selected because it quantified concentrations of other pesticides that could be used in or near the parks including: 2,4-D, atrazine, dicamba, triclopyr, and oryzalin. Data coded with an "E" indicate an estimated concentration. Estimated concentrations include those that are below or above the calibration curve, concentrations for analytes with average recoveries of less than 60%, or concentrations of analytes routinely detected in laboratory blanks (Furlong et al. 2001; Kolpin et al. 2002).

Quality-assurance samples

Both the ORGL and NWQL are NELAC (National Environmental Laboratory Accreditation Conference) certified and operate under extensive quality-management requirements (Maloney 2005). For this study, field quality-assurance samples consisted of one field blank collected from DeSoto NWR, one field duplicate

Table 2 Compounds analyzed, laboratory reporting limits (LRLs), common uses (Meisterpro 2004) and aquatic life guidelines (Environment Canada 2002)

Compound	Laboratory reporting limit (μg/l)	Compound type	Common uses	Freshwater aquatic life guideline (μg/l)	Detected in this study
2,4-D	0.038	Herbicide	Many crops	4	Yes
2,4-D Methyl ester	0.016	Herbicide degradate	NA	–	Yes
2,4-DB	0.02	Herbicide	Alfalfa, peanut, soybean	–	No
2-Chloro-4-isopropylamino-6-amino-s-triazine (CIAT)	0.028	Herbicide degradate	NA	–	Yes
2-Chloro-6-ethylamino-4-amino-s-triazine (CEAT)	0.08	Herbicide degradate	NA	–	Yes
2-Hydroxy-4-isopropylamino-6-Ethylamino-s-triazine (OIET)	0.032	Herbicide degradate	NA	–	Yes
3(4-Chlorophenyl)-1-methyl urea	0.036	Algaecide degradate	NA	–	No
3-Hydroxycarbofuran	0.008	Insecticide degradate	NA	–	No
3-Keto-carbofuran	0.02	Insecticide degradate	NA	–	No
Acifluorfen	0.028	Herbicide	Soybean, peanut, rice	–	No
Aldicarb	0.04	Insecticide	Cotton, potato, citrus	1.0	No
Aldicarb sulfone	0.018	Insecticide degradate	NA	–	No
Aldicarb sulfoxide	0.022	Insecticide degradate	NA	–	No
Aminomethylphosphonic acid (AMPA)	0.10	Herbicide degradate	NA	–	Yes
Atrazine	0.008	Herbicide	Corn, sugarcane	1.8	Yes
Bendiocarb	0.02	Insecticide	Many crops	–	No
Benomyl	0.022	Fungicide	Many crops, turf	–	Yes
Bensulfuron-methyl	0.018	Herbicide	Rice	–	No
Bentazon	0.012	Herbicide	Many crops, turf	–	Yes
Bromacil	0.018	Herbicide	Noncrop weed control	5.0	Yes
Bromoxynil	0.028	Herbicide	Wheat, corn, barley	5.0	No
Caffeine	0.018	Pharmaceutical	Coffee, tea, soda	–	Yes
Carbaryl	0.018	Insecticide	Many crops, turf	0.2	Yes
Carbofuran	0.016	Insecticide	Many crops	1.8	No
Chloramben methyl ester	0.024	Herbicide degradate	NA	–	No
Chlordiamino-s-triazine (CAAT)	0.04	Herbicide degradate	NA	–	Yes
Chlorimuron-ethyl	0.032	Herbicide	Soybean, peanut	–	No
Chlorothalonil	0.035	Fungicide	Many crops	0.18	No
Clopyralid	0.024	Herbicide	Wheat, corn, pasture	–	No
Cycloate	0.014	Herbicide	Spinach, sugar beets	–	No
Dactal monoacid	0.028	Herbicide degradate	NA	–	No
Dicamba	0.036	Herbicide	Corn, wheat, noncrop	10	Yes

Table 2 (continued)

Compound	Laboratory reporting limit (μg/l)	Compound type	Common uses	Freshwater aquatic life guideline (μg/l)	Detected in this study
Dichlorprop	0.028	Herbicide	Corn, noncrop	–	No
Dinoseb	0.038	Herbicide	US use cancelled in 1986	0.05	No
Diphenamid	0.01	Herbicide	US use cancelled in 1986	–	No
Diuron	0.014	Algaecide	Cotton, fruit	–	Yes
Fenuron	0.018	Herbicide	Noncrop	–	No
Flumetsulam	0.04	Herbicide	Corn, soybean	–	No
Fluometuron	0.016	Herbicide	Cotton, sugarcane	–	Yes
Glufosinate	0.10	Herbicide	Corn, noncrop	–	No
Glyphosate	0.10	Herbicide	Soybean, corn, noncrop	65	Yes
Imazaquin	0.036	Herbicide	Soybean	–	Yes
Imazethapyr	0.038	Herbicide	Corn, soybean, peanut	–	Yes
Imidacloprid	0.02	Insecticide	Cotton, fruit, vegetables	–	Yes
Linuron	0.014	Herbicide	Many crops	7.0	No
MCPA	0.03	Herbicide	Wheat, corn, noncrop	2.6	No
MCPB	0.01	Herbicide	Peas, pasture	–	No
Metalaxyl	0.012	Fungicide	Many crops	–	Yes
Methiocarb	0.01	Molluscicide	Ornamentals	–	No
Methomyl	0.02	Insecticide	Many crops	–	No
Metsulfuron-methyl	0.025	Herbicide	Wheat	–	No
Neburon	0.012	Herbicide	Not registered for use in US	–	No
Nicosulfuron	0.04	Herbicide	Corn	–	Yes
Norflurazon	0.02	Herbicide	Cotton, fruit, noncrop	–	No
Oryzalin	0.012	Herbicide	Fruit, turf	–	Yes
Oxamyl	0.03	Insecticide	Many crops	–	Yes
Picloram	0.032	Herbicide	Noncrop brush control	29	No
Propham	0.03	Herbicide	Not registered for use in US	–	No
Propiconazole	0.01	Fungicide	Wheat, peanuts, corn	–	Yes
Propoxur	0.008	Insecticide	Noncrop, fruit, other crops	–	No
Siduron	0.02	Herbicide	Turf	–	Yes
Sulfometuron-methyl	0.038	Herbicide	Noncrop weed control	–	Yes
Tebuthiuron	0.026	Herbicide	Noncrop weed control	1.6	No
Terbacil	0.016	Herbicide	Fruit, berries, hay	–	No
Triclopyr	0.026	Herbicide	Noncrop weed control, turf	–	Yes

NA not applicable, – not available, μ*g/l* micrograms per liter

Table 3 Sample collection dates, sample types, and field properties

Site ID	Site name	State	Sample type	Date	Water temperature (°C)	pH	Specific conductance (μS/cm)	Discharge (m^3/s)
RC1	Weir Pond	DC	Prior	3/14/05	8.0	6.45	14	–
RC1	Weir Pond	DC	Post	3/24/05	6.2	6.21	470	–
RC1	Weir Pond	DC	Prior	3/8/06	7.5	6.32	546	–
RC1	Weir Pond	DC	Post	4/5/06	16.4	6.96	0	–
RC3	Riley Spring Pond	DC	Prior	3/14/05	9.4	7.56	10	–
RC3	Riley Spring Pond	DC	Post	3/24/05	6.5	6.66	56	–
RC3	Riley Spring Pond	DC	Prior	3/8/06	D	D	D	–
RC3	Riley Spring Pond	DC	Post	4/5/06	D	D	D	–
RC4	Rock Creek at Riley Spring	DC	Prior	3/14/05	7.8	7.45	753	0.95
RC4	Rock Creek at Riley Spring	DC	Post	3/24/05	7.1	7.25	661	9.97
RC4	Rock Creek at Riley Spring	DC	Prior	3/8/06	6.8	8.02	474	0.88
RC4	Rock Creek at Riley Spring	DC	Post	4/5/06	13.9	7.26	224	1.05
CO1	Carderock Vernal Pool	MD	Prior	3/8/06	8.7	6.05	75	–
CO1	Carderock Vernal Pool	MD	Post	4/5/06	13.7	5.85	97.2	–
CO2	Lock 7 Vernal Pool	MD	Prior	3/8/06	7.3	7.02	479	–
CO2	Lock 7 Vernal Pool	MD	Post	4/5/06	14.8	7.01	524	–
CO3	C & O Canal at Lock 7	MD	Prior	3/8/06	9.2	7.47	379	–
CO3	C & O Canal at Lock 7	MD	Post	4/5/06	14.9	7.16	312	–
DS1	Field-side wetland	IA	Prior	4/13/05	13.8	7.15	285	–
DS1	Field-side wetland	IA	Post	6/8/05	21.3	6.94	66.6	–
DS1	Field-side wetland	IA	Prior	5/24/06	D	D	D	–
DS1	Field-side wetland	IA	Post	7/5/06	D	D	D	–
DS2	Rands Ditch	IA	Prior	4/13/05	13.6	7.53	850	–
DS2	Rands Ditch	IA	Post	6/8/05	20	7.46	285	–
DS2	Rands Ditch	IA	Prior	5/24/06	19.0	7.40	135	–
DS2	Rands Ditch	IA	Post	7/5/06	D	D	D	–
DS3	Browns Ditch	IA	Prior	4/13/05	15	7.12	385	–
DS3	Browns Ditch	IA	Post	6/8/05	21.9	7.31	320	–
DS3	Browns Ditch	IA	Prior	5/24/06	20.9	7.52	1090	–
DS3	Browns Ditch	IA	Post	7/5/06	D	D	D	–

Table 3 (continued)

Site ID	Site name	State	Sample type	Date	Water temperature (°C)	pH	Specific conductance (μS/cm)	Discharge (m^3/s)
DS4	Browns Pond	IA	Prior	4/13/05	13.6	7.19	542	–
DS4	Browns Pond	IA	Post	6/8/05	23.5	7.04	541	–
DS4	Browns Pond	IA	Prior	5/24/06	D	D	D	–
DS4	Browns Pond	IA	Post	7/5/06	D	D	D	–
SM1	Dugway Campground Pond	WY	Prior	4/19/05	–	–	450	–
SM1	Dugway Campground Pond	WY	Post	5/5/05	16.3	8.65	437	–
SM1	Dugway Campground Pond	WY	Prior	4/21/06	9.9	8.23	466	–
SM1	Dugway Campground Pond	WY	Post	6/26/06	–	–	–	–
SM2	N. Platte River at Dugway Campground	WY	Prior	4/19/05	–	–	244	54.5
SM2	N. Platte River at Dugway Campground	WY	Post	5/5/05	12.7	8.77	335	39.6
SM2	N. Platte River at Dugway Campground	WY	Prior	4/21/06	7.2	8.04	221	55.5
SM2	N. Platte River at Dugway Campground	WY	Post	6/26/06	–	–	–	26.8

– not measured, *D* no measurement because site was dry, *°C* degrees Celsius, *μS/cm* microsiemens per centimeter at 25°Celsius, *m^3/s* cubic meters per second

collected from Rock Creek NP, one field duplicate collected from C&O Canal NHP. In addition there were seven laboratory duplicates, but only glyphosate and AMPA were analyzed in these quality-assurance samples. As a standard procedure for each of the analytical methods used in this study, a duplicate sample, a spiked environmental sample, and a blank (distilled water) sample were analyzed after every 10 environmental samples, and a distilled-water spiked sample was analyzed after every 20 environmental samples. Results from these QA samples are utilized by the laboratory for quality management and are not reported here.

Herbicide use and the timing of sample collection

At all sites in Rock Creek NP, C&O NHP, and DeSoto NWR, water samples were collected just prior to the planned use of glyphosate ("prior" in Table 2), and just after the first precipitation event after glyphosate was applied in the parks ("post" in Table 2). Hence, the period of time between samples at a site, and the period of time between glyphosate application and the collection of the second sample varied by park and year (Table 3).

Rock Creek National Park

Glyphosate is used periodically in Rock Creek NP to control lesser celandine (*Ranunculus ficaria*). In general, herbicides are applied when weather allows in February, March, and early April, before the native wildflowers emerge in great numbers. Glyphosate also is used in summer months to control Japanese stiltgrass (*Microstegium vimineum*). Current application activities are scheduled to avoid initial bird and amphibian breeding, but spotted salamanders and wood frogs are active during this time period (Rice and Jung 2004; Sue Salmons, National Park Service, March 2005, personal communication).

In 2005, samples were collected from sites in Rock Creek NP on March 14, prior to the application of herbicides. During the week of March 16, the floodplain areas adjacent to Riley Spring Pond were hand sprayed with Accord® (same as Rodeo®) to which the Timberland® 90 brand surfactant was added, to control the lesser celandine

(Sue Salmons, National Park Service, March 2005, personal communication). On March 23, approximately 3 cm of rain fell at the site, and the second set of samples was collected the morning of March 24 (Table 3).

In 2006 drought conditions persisted in the study area and Riley Spring Pond was dry. Samples were collected from the other sites in Rock Creek NP on March 8, 2006, prior to the application of herbicides. Between March 20 and April 2, the floodplain areas adjacent to Riley Spring Pond were hand sprayed with AquaNeat® or Rodeo®, and Garlon4® was applied as a stump treatment (Sue Salmons, National Park Service, March 2006, personal communication). On April 3, approximately 1 cm of rain fell in the region, and the second set of samples was collected on April 5, 2006 (Table 3).

C&O Canal National Historic Park

Due to the drought conditions that persisted in the study area in 2006, samples were collected from sites in C&O Canal NHP that still contained water. Glyphosate is used periodically in C&O Canal NHP to control lesser celandine (*Ranunculus ficaria*). As at Rock Creek NP, herbicides are applied when weather allows in February, March, and early April, before the native wildflowers emerge in great numbers. In 2006, samples were collected from sites in C&O Canal NHP on March 8, 2006, prior to the application of herbicides. During the week of March 12, the floodplain areas adjacent to Lock 7 Vernal Pool were hand sprayed with Rodeo® to which the Timberland® 90 brand surfactant was added, with a follow-up treatment on March 27 (Ron Dean, National Park Service, March 2006, personal communication). On April 3, approximately 1 cm of rain fell in the region, and the second set of samples was collected on April 5, 2006 (Table 3).

DeSoto National Wildlife Refuge

Glyphosate is applied to soybeans and genetically modified corn that is grown within the refuge. In 2005, samples were collected on April 13, prior to the application of herbicides. The field adjacent to the Field-Side Wetland site was planted in Roundup® Ready Corn, and Roundup® was applied to that field on June 6 (Robert Barry, US Fish and Wildlife Service, June 2005, personal communication). On the morning of June 8 approximately 3 cm of rain fell at the site, and the second set of samples was collected in the afternoon on June 8, 2005 (Table 3).

In 2006, samples were collected from sites in DeSoto NWR on May 24, prior to the application of glyphosate on adjacent fields. In spring 2006, drought conditions persisted in this part of Iowa, and the Field-Side Wetland and Browns Pond sites were dry. The field adjacent to the Field-Side Wetland site was planted in Roundup® Ready soybeans, and Roundup was applied to that field during the week of June 12 (Robert Barry, USFWS, June 2006, personal communication). Little rain fell at the study site over the next 4 weeks and by July 7 both pond sites and both ditch sites were dry (Table 3).

Within DeSoto NWR the following other herbicides were approved for use in 2005 and 2006 (Robert Barry, USFWS, February, 2006, personal communication): bromoxynil, carfentrazone ethyl, clethodim, dicamba, dimethenamid, fluazifop-P-butyl, flumiclorac pentyl, flumioxazin, fluridone, fosamine ammonium, glufosinate ammonium, lactofen, mesotrione, rimsulfuron, sethoxydim, thifensulfuron, tribenuron, triclopyr, and 2,4-D (amine and ester).

Seminoe State Park

No herbicides were applied in the vicinity of the Dugway Campground Pond in 2005 or 2006 (Susan Foley, BLM, May 2006, personal communication). Various products containing 2,4-D, clopyralid, metsulfuron methyl, and picloram were used to control Russian knapweed, leafy spurge, and wild licorice at the site in 2003 and also may have been applied in 2004 using either backpack sprayers or truck-mounted sprayers (Susan Foley, Bureau of Land Management, May 2005, personal communication).

In 2005, samples were collected on April 19 and on May 5 (Table 3). The Dugway Campground Pond was spiked with atrazine on May 23 to an estimated concentration of 100 μg/l as part of a study (T. Hayes, University of California at Berkeley, May 2005, personal communication) designed to determine the effect of atrazine exposure on the sexual development of native amphibians. In 2006, samples were collected on April 21 and on June 26.

Results

Of the 65 pesticides or pesticide degradation products (Table 2), 28 were detected in the 34 samples obtained for this study, and as many as 11 pesticides or pesticide degradation products were identified in individual samples. Thirteen of 18 pre-application samples and 11 of 16 post-application samples (71% of all 34 samples) contained one or more of the pesticides or pesticide degradation products. None of the 65 pesticides or pesticide degradation products was detected in the four samples collected for this study from the North Platte River in Wyoming, or from the two samples collected in 2005 from the Dugway Campground Pond. Atrazine was detected most frequently (53% of samples), followed by CIAT (47%), caffeine and OIET (44%), glyphosate (32%), 2,4-D and CEAT (29%), and AMPA (26%). Glyphosate was measured at the highest concentration (328 and 12 μg/l), followed by AMPA (41 and 3.2 μg/l), atrazine (26.2, 14.7, and 13.6 μg/l), triclopyr (9.83 μg/l), OIET (6.02 μg/l), CIAT (3.64 μg/l), and nicosulfuron (3.29 μg/l) (Fig. 2; Table 4). At the parks in Washington, D.C., Maryland, and Iowa, selected water samples were collected during or just after the first substantial rainfall that occurred after the use of glyphosate adjacent to the study sites. Without additional samples, it is not known if the concentrations of glyphosate or other pesticides in

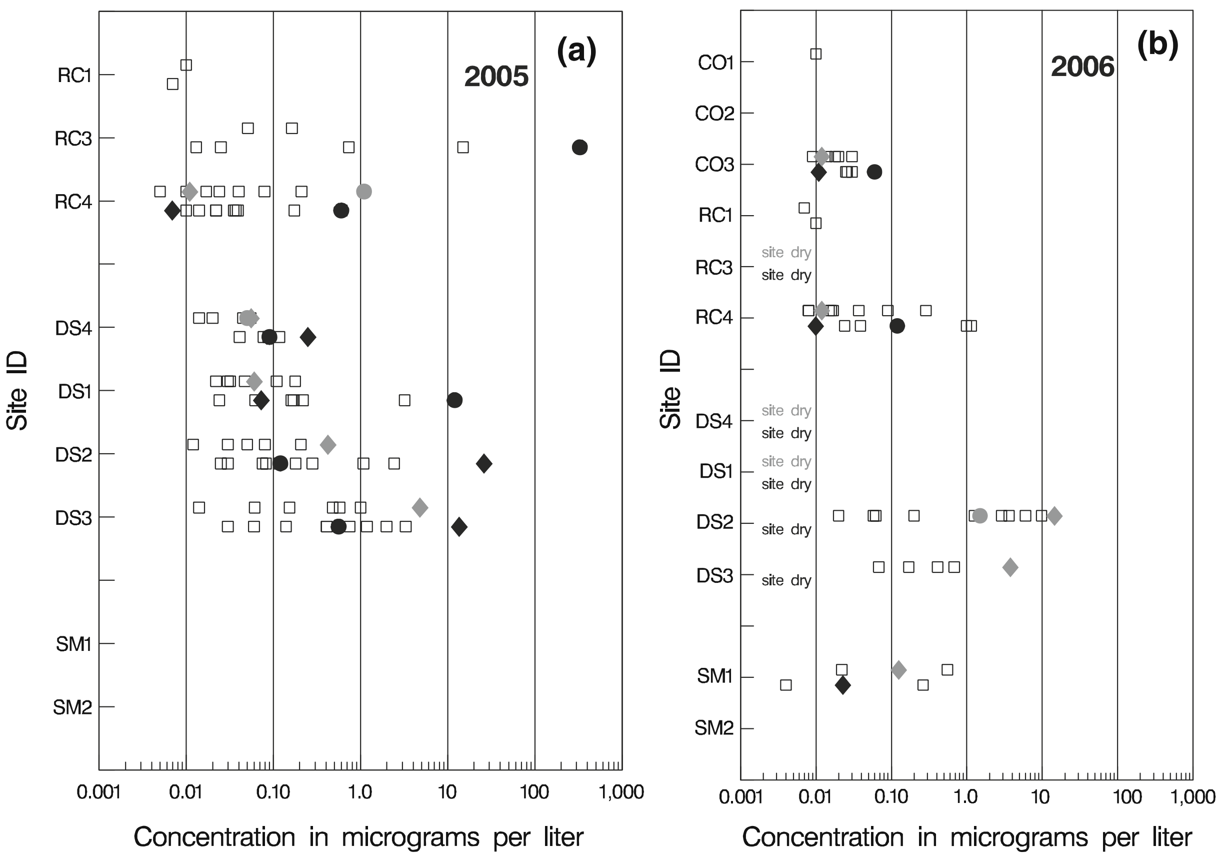

Fig. 2 Pesticide concentrations in micrograms per liter, by site, in samples collected prior to (*grey symbols*) and just after (*black symbols*) the adjacent application of glyphosate in: **a** 2005 and **b** 2006; *solid circles* represent glyphosate concentrations, *solid diamonds* represent atrazine concentrations, and *squares* represent all other detected pesticides

Table 4 Concentrations of detected pesticides and pesticide degradation products

Site name	Sample type	Date	2,4-D	2,4-D methyl ester	CIAT	CEAT	OIET	AMPA	Atrazine	Benomyl	Bentazon	Bromacil
Weir Pond	Prior	3/14/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Weir Pond	Post	3/24/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Weir Pond	Prior	3/8/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Weir Pond	Post	4/5/06	0.77	E 0.123	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Riley Spring Pond	Prior	3/14/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Riley Spring Pond	LD	3/14/05	*	*	*	*	*	< 0.02				
Riley Spring Pond	Post	3/24/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	15	< 0.008	< 0.022	E.025	< 0.018
Riley Spring Pond	FD	3/24/05	*	*	*	*	*	41	*	*	*	*
Rock Creek at Riley Spring	Prior	3/14/05	E.017	< 0.016	.04	< 0.08	< 0.032	.21	.011	< 0.022	< 0.012	E.010
Rock Creek at Riley Spring	Post	3/24/05	E.609	< 0.016	E.022	< 0.08	< 0.032	< 0.02	E.007	< 0.022	< 0.012	E.014
Rock Creek at Riley Spring	Prior	3/8/06	< 0.038	< 0.016	0.037	E 0.008	E 0.008	0.09	0.012	E 0.016	< 0.012	< 0.018
Rock Creek at Riley Spring	Post	4/5/06	E 1.15	< 0.016	< 0.030	< 0.08	< 0.032	0.12	0.01	< 0.022	< 0.012	< 0.018
Carderock Vernal Pool	Prior	3/8/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Carderock Vernal Pool	LD	3/8/06	*	*	*	*	*	< 0.02	*	*	*	*
Carderock Vernal Pool	Post	4/5/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Lock 7 Vernal Pool	Prior	3/8/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Lock 7 Vernal Pool	Post	4/5/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Lock 7 Vernal Pool	FD	4/5/06	*	*	*	*	*	< 0.02	*	*	*	*
C & O Canal at Lock 7	Prior	3/8/06	< 0.038	< 0.016	0.03	E.009	E.02	< 0.02	0.012	< 0.022	< 0.012	< 0.018
C & O Canal at Lock 7	Post	4/5/06	< 0.038	< 0.016	0.03	< 0.08	E.025	< 0.02	0.011	< 0.022	< 0.012	< 0.018
Field-side wetland	Prior	4/13/05	E.047	< 0.016	E.022	E.03	.109	< 0.02	.061	< 0.022	< 0.012	< 0.018
Field-side wetland	LD	4/13/05	*	*	*	*	*	< 0.02	*	*	*	*
Field-side wetland	Post	6/8/05	< 0.070	< 0.016	E.171	E.16	E.219	3.2	E.073	< 0.022	< 0.012	< 0.018
Rands Ditch	Prior	4/13/05	< 0.038	< 0.016	.08	E.03	.206	< 0.02	.424	< 0.022	< 0.012	< 0.018
Rands Ditch	Post	6/8/05	E.082	< 0.016	E 1.08	E.28	E 2.43	.18	E 26.2	0.115	< 0.012	< 0.018
Rands Ditch	LD	6/8/05	*	*	*	*	*	.17	*	*	*	*
Rands Ditch	Prior	5/24/06	< 0.038	< 0.19	E 3.64	E 1.26	E 6.02	2.9	E 14.7	< 0.022	< 0.024	< 0.018
Rands Ditch	LD	5/24/06	*	*	*	*	*	2.9	*	*	*	*

Table 4 (continued)

Site name	Sample type	Date	2,4-D	2,4-D methyl ester	CIAT	CEAT	OIET	AMPA	Atrazine	Benomyl	Bentazon	Bromacil
Browns Ditch	Prior	4/13/05	< 0.038	< 0.016	E.153	< 0.08	E.577	1.0	E 4.81	< 0.022	< 0.012	< 0.018
Browns Ditch	Post	6/8/05	.041	< 0.016	E 1.18	E.41	E 1.99	.75	E 13.6	< 0.022	< 0.012	< 0.018
Browns Ditch	Prior	5/24/06	E.068	< 0.19	.411	.17	.682	< 0.02	E 3.84	< 0.022	< 0.024	< 0.018
Browns Pond	Prior	4/13/05	E.045	< 0.016	< 0.028	E.02	.055	< 0.02	.056	< 0.022	< 0.012	< 0.018
Browns Pond	Post	6/8/05	E.087	< 0.016	E.077	< 0.08	E.041	< 0.02	E.249	< 0.022	< 0.012	< 0.018
Browns Pond	FB	6/8/05	*	*	*	*	*	< 0.02	*	*	*	*
Dugway Campground Pond	Prior	4/19/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Dugway Campground Pond	LD	4/19/05	*	*	*	*	*	< 0.02	*	*	*	*
Dugway Campground Pond	Post	5/5/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Dugway Campground Pond	LD	5/5/05	*	*	*	*	*	< 0.02	*	*	*	*
Dugway Campground Pond	Prior	4/21/06	< 0.038	< 0.016	0.022	< 0.08	E 0.555	< 0.02	0.126	< 0.022	< 0.012	< 0.018
Dugway Campground Pond	Post	6/26/06	< 0.038	< 0.19	E 0.004	< 0.08	0.263	< 0.02	0.023	< 0.022	< 0.024	< 0.018
N. Platte River at Dugway Campground	Prior	4/19/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
N. Platte River at Dugway Campground	Post	5/5/05	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
N. Platte River at Dugway Campground	Prior	4/21/06	< 0.038	< 0.016	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
N. Platte River at Dugway Campground	Post	6/26/06	< 0.038	< 0.19	< 0.028	< 0.08	< 0.032	< 0.02	< 0.008	< 0.022	< 0.012	< 0.018
Percent detections in all but QA samples			29	3	47	29	44	27	53	6	3	6
Site name	**Sample type**	**Date**	**Caffeine**	**Carbaryl**	**CAAT**	**Dicamba**	**Diuron**	**Fluometuron**	**Glyphosate**	**Imazaquin**	**Imazethapyr**	
Weir Pond	Prior	3/14/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	E.007	< 0.038	
Weir Pond	Post	3/24/05	E.010	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038	
Weir Pond	Prior	3/8/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038	
Weir Pond	Post	4/5/06	0.019	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038	
Riley Spring Pond	Prior	3/14/05	E.051	< 0.018	< 0.04	< 0.036	< 0.014	E.163	< 0.02	< 0.036	< 0.038	
Riley Spring Pond	LD	3/14/05	*	*	*	*	*	*	< 0.02	*	*	

Riley Spring Pond	Post	3/24/05	< 0.026	< 0.018	< 0.04	< 0.036	< 0.014	E.013	328	< 0.036	< 0.038
Riley Spring Pond	FD	3/24/05	*	*	*	*	*	*	301	*	*
Rock Creek at Riley Spring	Prior	3/14/05	.079	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	1.1	< 0.036	< 0.038
Rock Creek at Riley Spring	Post	3/24/05	.174	E.01	< 0.04	< 0.036	E.039	< 0.016	.60	< 0.036	< 0.038
Rock Creek at Riley Spring	Prior	3/8/06	0.287	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
Rock Creek at Riley Spring	Post	4/5/06	E 0.991	< 0.018	E 0.024	< 0.036	< 0.030	< 0.016	0.12	< 0.036	< 0.038
Carderock Vernal Pool	Prior	3/8/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Carderock Vernal Pool	LD	3/8/06	*	*	*	*	*	*	< 0.02	*	*
Carderock Vernal Pool	Post	4/5/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Lock 7 Vernal Pool	Prior	3/8/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Lock 7 Vernal Pool	Post	4/5/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Lock 7 Vernal Pool	FD	4/5/06	*	*	*	*	*	*	< 0.02	*	*
C & O Canal at Lock 7	Prior	3/8/06	0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
C & O Canal at Lock 7	Post	4/5/06	0.026	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	.06	< 0.036	< 0.038
Field-side wetland	Prior	4/13/05	.032	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Field-side wetland	LD	4/13/05	*	*	*	*	*	*	< 0.02	*	*
Field-side wetland	Post	6/8/05	E.062	< 0.018	E.024	< 0.036	< 0.014	< 0.016	12	< 0.036	< 0.038
Rands Ditch	Prior	4/13/05	E.012	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Rands Ditch	Post	6/8/05	E.075	< 0.018	E.025	< 0.036	< 0.014	< 0.016	.12	< 0.036	< 0.038
Rands Ditch	LD	6/8/05	*	*	*	*	*	*	.10	*	*
Rands Ditch	Prior	5/24/06	< 0.018	< 0.018	0.062	E 0.058	0.02	< 0.016	1.5	< 0.036	< 0.038
Rands Ditch	LD	5/24/06	*	*	*	*	*	*	1.4	*	*
Browns Ditch	Prior	4/13/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	E.061
Browns Ditch	Post	6/8/05	E.030	< 0.018	E.06	< 0.036	.014	< 0.016	.56	< 0.036	< 0.038
Browns Ditch	Prior	5/24/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
Browns Pond	Prior	4/13/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	.05	< 0.036	< 0.038
Browns Pond	Post	6/8/05	E.117	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	.09	< 0.036	< 0.038
Browns Pond	FB	6/8/05	*	*	*	*	*	*	< 0.02	*	*
Dugway Campground Pond	Prior	4/19/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Dugway Campground Pond	LD	4/19/05	*	*	*	*	*	*	< 0.02	*	*

Table 4 (continued)

Site name	Sample type	Date	Caffeine	Carbaryl	CAAT	Dicamba	Diuron	Fluometuron	Glyphosate	Imazaquin	Imazethapyr
Dugway Campground Pond	Post	5/5/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
Dugway Campground Pond	LD	5/5/05	*	*	*	*	*	*	< 0.02	*	*
Dugway Campground Pond	Prior	4/21/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
Dugway Campground Pond	Post	6/26/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
N. Platte River at Dugway Campground	Prior	4/19/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
N. Platte River at Dugway Campground	Post	5/5/05	< 0.018	< 0.018	< 0.04	< 0.036	< 0.014	< 0.016	< 0.02	< 0.036	< 0.038
N. Platte River at Dugway Campground	Prior	4/21/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
N. Platte River at Dugway Campground	Post	6/26/06	< 0.018	< 0.018	< 0.04	< 0.036	< 0.016	< 0.016	< 0.02	< 0.036	< 0.038
Percent detections for all but QA samples			44	3	15	3	9	6	32	3	3

Site name	Sample type	Date	Imidacloprid	Metalaxyl	Nicosulfuron	Oryzalin	Oxamyl	Propiconazole	Siduron	Sulfometuronmethyl	Triclopyr	Number of pesticides detected
Weir Pond	Prior	3/14/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	1
Weir Pond	Post	3/24/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	1
Weir Pond	Prior	3/8/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Weir Pond	Post	4/5/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	3
Riley Spring Pond	Prior	3/14/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	2
Riley Spring Pond	LD	3/14/05	*	*	*	*	*	*	*	*	*	0
Riley Spring Pond	Post	3/24/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	.731	5
Riley Spring Pond	FD	3/24/05	*	*	*	*	*	*	*	*	*	2
Rock Creek at Riley Spring	Prior	3/14/05	.024	E.005	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	9

Rock Creek at Riley Spring	Post	3/24/05	E 0.035	.022	< 0.04	< 0.012	< 0.03	< 0.01	.037	< 0.038	< 0.026	11
Rock Creek at Riley Spring	Prior	3/8/06	E 0.015	< 0.012	< 0.04	< 0.012	< 0.03	0.017	< 0.02	< 0.038	< 0.026	9
Rock Creek at Riley Spring	Post	4/5/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	0.039	< 0.038	< 0.026	7
Carderock Vernal Pool	Prior	3/8/06	< 0.02	< 0.012	E.01	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	1
Carderock Vernal Pool	LD	3/8/06	*	*	*	*	*	*	*	*	*	0
Carderock Vernal Pool	Post	4/5/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Lock 7 Vernal Pool	Prior	3/8/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Lock 7 Vernal Pool	Post	4/5/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Lock 7 Vernal Pool	FD	4/5/06	*	*	*	*	*	*	*	*	*	0
C & O Canal at Lock 7	Prior	3/8/06	E.014	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	6
C & O Canal at Lock 7	Post	4/5/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	5
Field-side wetland	Prior	4/13/05	< 0.02	< 0.012	< 0.04	.178	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	7
Field-side wetland	LD	4/13/05	*	*	*	*	*	*	*	*	*	0
Field-side wetland	Post	6/8/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	8
Rands Ditch	Prior	4/13/05	< 0.02	< 0.012	E.05	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	6
Rands Ditch	Post	6/8/05	< 0.02	< 0.044	E.03	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	11
Rands Ditch	LD	6/8/05	*	*	*	*	*	*	*	*	*	1
Rands Ditch	Prior	5/24/06	< 0.02	< 0.03	< 0.04	< 0.023	< 0.05	< 0.01	< 0.02	0.20	E 9.83	11
Rands Ditch	LD	5/24/06	*	*	*	*	*	*	*	*	*	2
Browns Ditch	Prior	4/13/05	< 0.02	< 0.012	E.48	< 0.012	E.014	< 0.01	< 0.02	< 0.038	< 0.026	7
Browns Ditch	Post	6/8/05	< 0.02	< 0.012	E 3.29	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	11
Browns Ditch	Prior	5/24/06	< 0.02	< 0.03	< 0.04	< 0.023	< 0.05	< 0.01	< 0.02	< 0.09	< 0.026	5
Browns Pond	Prior	4/13/05	< 0.02	.014	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	6
Browns Pond	Post	6/8/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	6
Browns Pond	FB	6/8/05	*	*	*	*	*	*	*	*	*	0
Dugway Campground Pond	Prior	4/19/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Dugway Campground Pond	LD	4/19/05	*	*	*	*	*	*	*	*	*	0
Dugway Campground Pond	Post	5/5/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
Dugway Campground Pond	LD	5/5/05	*	*	*	*	*	*	*	*	*	0

Table 4 (continued)

Site name	Sample type	Date	Imida-cloprid	Metalaxyl	Nico-sulfuron	Oryza-lin	Oxamyl	Propico-nazole	Siduron	Sulfometu-ronmethyl	Tri-clopyr	Number of pesticides detected
Dugway Campground Pond	Prior	4/21/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.091	< 0.026	3
Dugway Campground Pond	Post	6/26/06	< 0.02	< 0.012	< 0.04	< 0.023	< 0.05	< 0.01	< 0.02	< 0.090	< 0.026	3
N. Platte River at Dugway Campground	Prior	4/19/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
N. Platte River at Dugway Campground	Post	5/5/05	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.038	< 0.026	0
N. Platte River at Dugway Campground	Prior	4/21/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.091	< 0.026	0
N. Platte River at Dugway Campground	Post	6/26/06	< 0.02	< 0.012	< 0.04	< 0.012	< 0.03	< 0.01	< 0.02	< 0.091	< 0.026	0
Percent detections all but QA samples			12	9	15	3	3	3	6	3	6	71

All concentration in micrograms per liter

∗ not analyzed, *LD* laboratory duplicate, *FD* field duplicate, *FB* field blank, *CIAT* 2-chloro-4-isopropylamino-6-amino-s-triazine, *CEAT* 2-chloro-6-ethylamino-4-amino-s-triazine, *OIET* 2-hydroxy-4-isopropylamino-6-ethylamino-s-triazine, *AMPA* aminomethylphosphonic acid, *CAAT* chlordiamino-s-triazine these samples represent the maximum potential for exposure to aquatic plants and animals.

Rock Creek National Park

Glyphosate and AMPA

In 2005, neither glyphosate nor AMPA were detected in the pre-application samples from the Weir Pond (control) or Riley Spring Pond (treatment). Neither glyphosate nor AMPA were detected in the post-application sample from the Weir pond. Both glyphosate (328 μg/l) and AMPA (15 μg/l), however, were detected in the post-application sample from Riley Spring Pond. The elevated concentrations of these two compounds were confirmed by a duplicate sample (Fig. 2; Table 4). Both glyphosate and AMPA were detected at low concentrations in the pre-application sample from Rock Creek, and glyphosate was detected in the post-application sample (Fig. 2a).

In 2006, glyphosate was applied adjacent to the treatment site in late-March, and the first rainfall was approximately 6 days later. Riley Spring Pond was dry at the time of sample collection both before and after treatment. Neither glyphosate nor AMPA were detected in the pre- or post-application samples from the Weir Pond. AMPA was detected in the pre-application sample from Rock Creek, and both glyphosate and AMPA were detected in the post-application sample (Fig. 2b).

Atrazine and other pesticides

In 2005, in the Weir Pond, one pesticide (imazaquin) was detected in the pre-application sample, and caffeine was detected in the post-application sample. In Riley Spring Pond, fluometuron and caffeine were detected in the pre-application sample, and bentazon, fluometuron, and triclopyr (0.731 μg/l) were detected in the post-application sample. In Rock Creek, 2,4-D; atrazine; one atrazine degradation product; bromacil; caffeine; imidacloprid; and metalaxyl were detected in the pre-application sample. In the post-application sample 2,4-D; atrazine; one atrazine degradation product; bromacil; caffeine; carbaryl; diuron; imidacloprid; metalaxyl; and siduron were detected (Fig. 2a).

In 2006, Riley Spring Pond was dry at the time of sample collection both before and after treatment. No pesticides or pesticide degradates were detected in the pre-application sample from the Weir Pond, in the post-application sample, 2,4-D, 2,4-D methyl ester, and caffeine were detected. In Rock Creek, atrazine; three atrazine degradation products; benomyl; caffeine; imidacloprid; and propiconazole were detected in the pre-application sample. In the post-application sample 2,4-D; atrazine; one atrazine degradation product; caffeine; and siduron were detected (Fig. 2b; Table 4).

The differences in pesticide content and concentrations between the two ponds, and Rock Creek, indicate that there was little hydrologic connection between these water bodies when the samples were collected. The pesticide concentrations in the Riley Spring Pond indicate that glyphosate, AMPA, and triclopyr originated from use within the park and were transported to the site by surface runoff or shallow groundwater flow. The other pesticides detected in Riley Spring Pond (fluometuron and bentazon) likely originated from a source outside the park and may have been introduced into the pond by atmospheric deposition. Because fluometuron was detected in both the pre- and post-application samples from Riley Spring Pond, but not in either sample from the adjacent Weir Pond, the role of atmospheric deposition is unclear. The pesticide concentrations in the Weir Pond indicate that imazaquin and 2,4-D originated from a source outside the park. The herbicide 2,4-D is used on a variety of crops in Maryland (Gianessi and Reigner 2006), but its detection at this site in association with caffeine indicates that urban or home use and subsequent runoff could be the source.

C&O Canal National Historic Park

Glyphosate and AMPA

In 2006, neither glyphosate nor AMPA were detected in the pre- or post-application samples from the Carderock Vernal Pool (control) or Lock 7

Vernal Pool (treatment) sites. Neither glyphosate nor AMPA were detected in the pre-application sample from the C&O Canal site, but glyphosate was detected in the post-application sample.

Atrazine and other pesticides

In 2006, one pesticide, nicosulfuron, was detected in the pre-application sample from the Carderock Vernal Pool, and none were detected in the post-application sample. No pesticides, pesticide degradation products, or caffeine were detected in either the pre- or post-application sample from the Lock 7 Vernal Pool. In the C&O Canal at Lock 7, atrazine, three atrazine degradation products, caffeine, and imidacloprid were detected in the pre-application sample. In the post-application sample, atrazine, two atrazine degradation products, and caffeine were detected (Fig. 2b).

The differences in pesticide content and concentrations between the two vernal pools and the C&O Canal indicate that there was little hydrologic connection between these water bodies when the samples were collected.

DeSoto National Wildlife Refuge

Glyphosate and AMPA

In 2005, glyphosate was detected in both the pre- and post-application samples from the Browns Pond (control), but AMPA was not detected in either sample. Neither glyphosate nor AMPA were detected in the pre-application sample from the Field-Side Wetland (treatment) site. Both glyphosate (12 μg/l) and AMPA (3.2 μg/l) were detected in the post-application sample from the Field-Side Wetland site. AMPA was detected in the pre-application sample from Browns Ditch, and glyphosate and AMPA were detected in the post-application sample. Neither glyphosate nor AMPA were detected in the pre-application sample from Rands Ditch. Glyphosate and AMPA were detected in the post-application sample (Fig. 2a).

In 2006, the two pond sites were dry for both the pre- and post-application samples, and the two ditch sites were dry for the post-application sample. Glyphosate and AMPA were detected in the pre-application sample from Rands Ditch, whereas neither were detected in the pre-application sample from Browns Ditch (Fig. 2b).

Atrazine and other pesticides

In 2005, in the Field-Side Wetland, atrazine; three atrazine degradation products; 2,4-D; caffeine; and oryzalin were detected in the pre-application sample. In the post-application sample, atrazine, four atrazine degradation products, and caffeine were detected. In Rands Ditch, atrazine, three atrazine degradation products, caffeine, and nicosulfuron were detected in the pre-application sample. In the post-application sample, 2,4-D; atrazine; four atrazine degradation products; benomyl; caffeine; and nicosulfuron were detected. In Browns Pond, 2,4-D; atrazine; two atrazine degradation products; and metalaxyl were detected in the pre-application sample. In the post-application sample, 2,4-D; atrazine; two atrazine degradation products; and caffeine were detected. In Browns Ditch, atrazine; two atrazine degradation products; imazethapyr; nicosulfuron; and oxamyl were detected in the pre-application sample. In the post-application sample, 2,4-D; atrazine; four atrazine degradation products; caffeine; diuron; and nicosulfuron were detected (Fig. 2a).

In 2006, in Rands Ditch, atrazine, four atrazine degradation products; dicamba; diuron; sulfometuron-methyl; and triclopyr were detected in the pre-application sample. In Browns Ditch 2,4-D; atrazine; and three atrazine degradation products were detected (Fig. 2b).

The differences in pesticide content and concentrations between the two ponds, and two ditches, indicate that there was little hydrologic connection between these water bodies at the times the samples were collected. The pesticide concentrations measured at the Field-Side Wetlands indicate that glyphosate and AMPA originated within the park and were transported to the wetlands by runoff, whereas the other pesticides (2,4-D, atrazine, caffeine, and oryzalin) may have originated from a groundwater source inside or outside the park (Buske 1991) or were deposited by atmospheric deposition. Of the detected compounds, only glyphosate, 2,4-D, dicamba, and triclopyr were approved for use within the park. The relatively high concentrations of atrazine, nicosulfuron, and triclopyr in ditch samples could adversely affect water quality in DeSoto Lake.

Seminoe State Park

In 2005, no pesticides were detected in the four samples collected from Seminoe State Park. In 2006, no pesticides were detected in the two samples collected from the North Platte River. Atrazine and two atrazine degradation products were detected in the pre-application sample from the pond. Atrazine and two atrazine degradation products also were detected in the post-application sample (Fig. 2). The presence of atrazine and atrazine degradation products in this pond is most likely the result of the addition of atrazine to the pond in May 2005.

The two sites in Seminoe SP were sampled more frequently than twice per year in 2004–2006 as part of another study. In July 2004, both glyphosate (0.04 μg/l) and AMPA (0.66 μg/l) were detected in a sample from the river. Glyphosate (0.02 μg/l) and AMPA (0.27 μg/l) also were both detected in the pond sample from that date. In August 2005, both glyphosate (0.07 μg/l) and AMPA (0.05 μg/l) were detected in a sample from the river. Glyphosate (0.06 μg/l) and AMPA (0.04 μg/l) also were both detected in the pond sample from that date. Flumetsulam was detected in the pond in a sample from June 2004, and picloram and caffeine were detected in the river in a sample from July 2004 (W. Battaglin, USGS, unpublished data 2005).

The similarities in pesticide content and concentrations between the pond and river indicate that there could be hydrologic connection between these water bodies during or just prior to the times the samples were collected.

Discussion

The results of this study indicate that sensitive aquatic habitats such as vernal pools can be contaminated by the use of herbicides to control weeds in cropped areas or noxious or nonindigenous plants within parks. Contamination is more likely when herbicides are used adjacent to these water bodies. Herbicides were more common and detected at higher concentrations in samples collected from vernal pools after local use than in samples collected prior to use. However, this pattern was less distinct for stream and ditch samples, which can contain herbicide or other pesticide contamination that originated from outside the parks or refuges. The concentrations of pesticides in vernal pools also were related to the timing of application and subsequent rainfall. A longer time period between pesticide application and rainfall seemed to result in lower concentrations of pesticides in receiving water bodies.

The concentration of glyphosate exceeded the freshwater aquatic life standard (Environment Canada 2002) of 65 μg/l in one sample from the Riley Spring Pond in Rock Creek NP adjacent to where it was used for nonindigenous plant control. The glyphosate product applied near this site (Accord®) is designed and labeled for use adjacent to water bodies and is considerably less toxic than Roundup® (Howe et al. 2004). Accord® does not contain the MON0818 surfactant but the Timberline® 90 surfactant was added prior to application. No studies on the toxicity of the Timberline® 90 surfactant were found. Other nonionic surfactants have been shown to cause narcosis in amphibian tadpoles at concentrations ranging from 1,100 to 25,400 μg/l, although the mode of toxicity remains unclear (Mann and Bidwell 2001). Atrazine concentrations exceeded the freshwater aquatic life standard of 1.8 μg/l in samples from Rands Ditch and Browns Ditch in DeSoto NWR. Triclopyr occurred at relatively high concentration in Rock Creek NP (0.731 μg/l) and DeSoto NWR (9.83 μg/l). The ester form of triclopyr can be toxic to some species of fish, aquatic invertebrates, and amphibians, but typically at higher concentrations (LC_{50} 100–10,000 μg/l; Tatum 2004). No other pesticide or pesticide degradate exceeded its freshwater aquatic life standard, but such standards are available for only 6 of the 28 detected compounds (Table 2). Also, standards based on individual compound toxicity may not provide sufficient protection, because organisms are most often exposed to mixtures of compounds that can have additive or synergistic effects (Hayes et al. 2006). In this study, 24 of 34 samples had at least one compound detected and 21 samples had two or more compounds detected. None of the analyzed compounds (Table 2) were detected in 10 of the samples.

Potential sources of pesticides and caffeine

The most likely source for atrazine, glyphosate, their degradation products, and most other detected pesticides is runoff from application to adjacent areas upstream or up-gradient from the sampling location. Atmospheric deposition, ground-water discharge, and point-source discharges also are possible sources for some chemicals that are not or have not been used adjacent to the sampled sites. For example, low concentrations of caffeine may result from the presence of wastewater or possibly from atmospheric deposition. A few of the detected pesticides (for example, fluometuron) are used in locations that are quite distant (more than 80 km on cotton fields in Virginia) from the study sites (Gianessi and Reigner 2006) making it difficult to explain their detection in study samples. In other cases, pesticide occurrence may have resulted from use long before the samples were collected. Triclopyr was applied (as a cut-stump treatment) in the area immediately around the Riley Spring Pond site in February 2004, about 13 months prior to its detection in a sample from this site (Sue Salmons, National Park Service, October 2005, personal communication). Triclopyr also is used on pastureland in Maryland (Gianessi and Reigner 2006). Triclopyr degrades rapidly by photolysis in surface water, but may persist in groundwater (Ganapathy 1997; Getsinger et al. 2000).

Outside of the park boundaries, potential sources of pesticides vary due to differences in the surrounding landscapes. In Rock Creek NP and C&O Canal NHP potential sources include use in agriculture in the upstream watersheds, use in the urban areas that surround the parks, and deposition by precipitation. Most of the pesticides detected in samples from these two parks including 2,4-D, atrazine, benomyl, bentazon, carbaryl, diuron, nicosulfuron, metalaxyl, propiconazole, imazaquin, and imidacloprid; are used on crops in Maryland (Gianessi and Reigner 2006; US Department of Agriculture 2006). Bromacil and siduron are herbicides that are contained in products registered for use on residential turf. Fluometuron is registered for use only on cotton; the nearest likely point of use is in North Carolina or Virginia.

The potential sources of pesticides to the drainage ditches and wetlands in DeSoto NWR include use in agriculture in the ditch drainage areas, discharge with groundwater, and atmospheric deposition. Many of the detected pesticides including 2,4-D, atrazine, benomyl, glyphosate, imazethapyr, metalaxyl, nicosulfuron, oryzalin, and oxamyl are used on crops in Iowa (Gianessi and Reigner 2006). Three of these pesticides, benomyl, oryzalin, and oxamyl are used almost exclusively on apples in Iowa. Triclopyr is not used on cropland in Iowa, but is recommended for use on pastures, non-cropland, and turf (Iowa State University 2003).

There are few potential sources of pesticides to the two sites in Seminoe SP other than the direct addition of atrazine to the pond site. Atrazine is used on corn and fallow land in Wyoming, glyphosate is used on a variety of crops, and flumetsulam may be used on corn in Wyoming (Gianessi and Reigner 2006), but no corn is grown in the watershed upstream from the sampling sites. Other potential sources of pesticides to the North Platte River include limited agricultural use in the upstream drainage area (approximately 50 km away), and their occurrence in atmospheric deposition (Mast et al. 2003; Hageman et al. 2006).

Caffeine was detected in one or more samples from nine of the 12 sites sampled in this study. The presence of caffeine in water at some of these sites likely resulted from runoff from urban land or discharge from wastewater-treatment facilities. However, the detection of caffeine in the water of several of the vernal pools indicates a source of either deposition with precipitation, a very direct input of human waste, or possibly sample contamination. Caffeine in very high doses (~100 times the level in cola) is lethal to some frogs (Kraus and Campbell 2002), but would not be expected to cause a problem at the concentrations detected in this study.

Management implications

Vernal pools typically form annually in the spring and early summer months and provide essential temporary breeding habitat for amphibians. The timing of herbicide applications often coincides with the pool formation and use by native species for breeding or feeding, making these habitats particularly sensitive to contamination.

The results of this study provide a baseline of information on the occurrence of glyphosate in the selected National Parks and Wildlife Refuges that is relevant to studies of ecology, hydrology, and biology of water-related habitats at those sites. It should be noted that the study design attempted to select some sites where the likelihood of glyphosate detection was high, and these sites may not be representative of vernal pools in other parks or wildlife refuges where glyphosate is not extensively used. The information on the occurrence of glyphosate, atrazine, other pesticides, and degradates in selected National Parks and Wildlife Refuges should provide the impetus for future studies of pesticide sources and occurrence. Such studies should help land managers determine how to best control nonindigenous plants and other pests and to better understand the fate and transport of pesticides used within US Parks and Refuges.

Although the ecological effects of these findings were not assessed, it is clear that vernal pools are vulnerable to contamination from herbicide applications during spring and early summer months. Spring in the Eastern and Central United States is associated with high baseflows, aquifer recharge, and episodic rainfall-runoff events that fill vernal pools and potentially hasten the transport of herbicides during critical time periods in the natural history of many amphibian species.

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