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Pesticide Residues in Water, Sediment, and Fish at the Sparta, IL, USA, National Guard Armory

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The Sparta National Guard Armory is located in Randolph County, a rural area of southern Illinois. Recently acquired property added 15 lakes situated on 2800 acres consisting of fallow fields and interspersed strips of timber. The primary use of the private land surrounding the site is agricultural. Surface area and depth varies among the lakes; maximum depth ranges between three to 29 meters depending on the lake. Many of the lakes are connected via shallow wetlands and drainage ditches. The combined area of the lakes is approximately 650 acres. The lakes at the Sparta site are a product of closed coal strip-mines that have filled with rainwater, seasonal creek flooding, and groundwater seepage. Coal mining and agriculture historically supported the southern Illinois economy. As a result of the Clean Air Act of 1970 and the 1977 amendment, industry use of high-sulfur coal decreased and caused many coal-mines to close. Reclamation of strip-mines for natural areas and recreational purposes has become common practice. These strip-mines have been completely filled for many years and a variety of aquatic life is present within the lakes. Few studies have been conducted on the water quality of reclaimed strip-mines. Published papers generally deal with the effects of acid mine drainage containing high metal concentrations on water quality and resident species by past and active mining operations (Grippo and Dunson 1996; Roark and Brown 1996; Diamond et al. 2002). However, these lakes are pH neutral (7-8) and the greatest likelihood for impact is due to the surrounding agricultural operations.

Agriculture, specifically corn, is a major income source for Midwestern states. Pesticide use is widespread and has improved crop yields. However, adverse environmental effects to non-target organisms are often a byproduct. The land surrounding the lakes and creeks were planted with corn, soybeans, and hay during 2003. In 2002, 6.4 million kilograms of atrazine were applied to corn crops in Illinois alone (Illinois Agricultural Statistics Survey 2003). Simazine is often applied in the same areas as atrazine with 120,500 kg applied in Illinois in 2002 (Illinois Agricultural Statistics Survey 2003). Metolachlor ranks second after atrazine in frequency of herbicides used in agriculture in the United States. Metolachlor is used in conjunction with atrazine, to control broadleaf and grassy weeds in corn, soybean, and potato crops.

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The Illinois National Guard proposed a preliminary evaluation of the newly acquired land. The proposed land usage includes off-road vehicle driving training and a vehicle-washing facility, both of which may impact the aquatic resources. A preliminary survey was requested so that potential future use impacts could be monitored. Because of the site's proximity to agricultural land use, there is potential for water quality degradation due to historic and current pesticide use. In the present study, samples collected from 15 lakes and two creeks on the Sparta, IL National Guard Armory were analyzed. Surface water was analyzed for current-use (aromatic fungicides, carbamate, organophosphate, pyrethroid, triazine, and urea) and sediment and fish for historic (organochlorine) and some current-use (pyrethroid, organophosphate) pesticides to determine present contamination levels.

MATERIALS AND METHODS

Fifteen lakes, three large (L1-L3) and twelve small (S1-S12), and two creeks were included in our survey of potential pesticide contamination at the Sparta, IL site. Each small lake contained two sample sites and each large lake contained three sample sites. Plum Creek (PC) had six sample sites and Dog Creek (DC) had one sample site. Surface water samples were collected in 1-L glass jars from each lake and creek site during four seasonal collecting periods (winter, spring, summer and fall 2003) for pesticide analysis. Sediment samples were collected with an acetone rinsed metal spade in spring 2003 from the littoral zone of each lake and stored in 1-L glass jars. All water and sediment samples were placed in ice-filled coolers for transport to Southern Illinois University-Carbondale (SIUC) where they were kept refrigerated at 4°C until analysis.

Fish collected by electrofishing and seining for pesticide analysis included largemouth bass (*Micropterus salmoides*), channel catfish (*Ictalurus punctatus*), freshwater drum (*Aplodinotus grunniens*), bowfin (*Amia calva*), yellow bullhead catfish (*Ameriurus natalis*), spotted sucker (*Minytrema melanops*), common carp (*Cyprinus carpio*), smallmouth buffalo (*Ictiobus bubalus*), and bluegill (*Lepomis machrochirus*). Fish were euthanized with a tricaine methanesulfonate (MS-222, Argent Chemical Laboratories, Inc., Redmond, WA, USA) overdose and placed on ice in coolers for transport to SIUC, where they were stored at -20°C until analysis.

Current-use pesticide methods were adapted from a procedure previously described (Belden et al. 2000). Briefly, pesticides were extracted from 1 L water on C_{18} SPE cartridges (Accubond, Agilent Technologies, Palo Alto, CA, USA), eluted with 1:1 acetone:hexane, and analyzed using an Agilent 6890 gas chromatograph equipped with a nitrogen-phosphorous detector (Palo Alto, CA, USA). Water samples were extracted within 48 h of collection, and analyzed for the presence of atrazine, carbaryl, chlorpyrifos, chlorothalonil, diazinon, dylox, metolachlor, oxadiazon, parathion, pendimethalin, and simazine. Contaminant identification was confirmed by a dual-column method. Quantification was based on peak area utilizing external standards (ND $\leq$1ng/g) obtained from Protocol (Middlesex, NJ, USA).

Fish and sediment analysis methods are described in detail elsewhere (You and Lydy 2004; You et al. 2004). Briefly, frozen fish fillets were homogenized, mixed with anhydrous $MgSO_4$, sonicated with an extraction solvent (acetonitrile, acetone, methanol or 10% methanol in acetonitrile) using a Sonica and Materials Incorporated Model VCX 400 Ultrasonic Processor (Newtown, CT, USA), centrifuged, and diluted with distilled water to a final volume of 200 mL. Next, the extract was passed through a C_{18} SPE cartridge followed by a Florisil cartridge and finally a Na_2SO_4 SPE cartridge to remove residual water from the system. Frozen sediment samples were thawed, mixed with anhydrous $MgSO_4$, and sonicated with 50 mL of 1:1 acetone:methyl chloride. A deactivated florisil column was used to clean-up the final extract. Both fish and sediment SPE extracts were analyzed using an Agilent 6890 Series GC equipped with an electron-capture detector (Palo Alto, CA, USA). Contaminants quantified included aldrin, bifenthrin, α-BHC, β-BHC, γ-BHC, α-chlordane, γ-chlordane, chlorpyrifos, λ-cyhalothrin, dieldrin, DDE, DDD, DDT, endosulfan II, endrin, endrin aldehyde, endrin ketone, esfenvalerate, heptachlor, heptachlor epoxide, methoxychlor, and both cis- and trans-permethrin. Sediment spike (5 ppb) recoveries ranged from 85.8 – 115 % (You et al. 2004). Fish spike (50 ppb) recoveries ranged from 77.2 - 103.8 %, with the exception of esfenvalerate (40 %) (You and Lydy 2004).

RESULTS AND DISCUSSION

Current-use pesticides were detected in all surface water samples. Seasonal water sampling results are presented in Table 1. Six current-use pesticides were detected in winter 2002-03 samples, with atrazine and simazine being most frequently detected. Parathion was detected at four locations in winter 2002-03; all concentrations detected above detections limits were greater than the Illinois chronic water quality criteria (WQC) (http:www.epa.state.il.us/water/water-quality-standards/). However, parathion was not detected in any spring, summer, or fall samples confirming seasonal use and the need for improved management practices to decrease winter concentrations. There were no exceedences of WQC for the three pesticides detected in either spring or fall 2003 samples, however atrazine and simazine were still detected in the majority of samples. Summer 2003 samples had four pesticides present above detection limits (1 ng/L); atrazine concentrations exceeded the chronic WQC and diazinon concentrations exceeded the acute WQC, suggesting that local agricultural use could be affecting these lakes. Atrazine concentrations as low as 1 μg/L have been shown to have potential for disrupting gonadal development in *Xenopus laevis* (Hayes et al. 2002). Populations of amphibians in these lakes and creek may be impacted due to the continuous exposure to atrazine. Although acute (mortality) effects to non-target crustacean and insects due to diazinon have been reported as low as 0.9 μg/L, sublethal effects such as decreased 5-h EC50 for *Daphnia magna* filtration

Table 1. Detected surface water pesticide concentrations (ng/L, frequency, geometric mean of detects and range) by season, collected from Sparta, IL National Guard Armory and Illinois acute and chronic water quality criteria.

	Winter 2002-03		*Spring 2003*		*Summer 2003*		*Fall 2003*			
Chemical	Frequency	Mean (Min – Max)	Frequency	Mean (Min – Max)	Frequency	Mean (Min – Max)	Frequency	Mean (Min – Max)	Acute WQC[a]	Chronic WQC[b]
Atrazine	39/39	63 (23-1200)	42/42	240 (47-1900)	41/41	1400 (120-15000)	33/33	520 (53-3300)	280000	12000
Carbaryl	3/39	33 (ND-52)	0/42	ND	2/41	35 (ND-36)	0/33	ND	NA	NA
Chlorpyrifos	1/39	5.7 (ND-5.7)	0/42	ND	0/41	ND	0/33	ND	110	NA
Diazinon	0/39	ND	0/42	ND	2/41	53 (ND-73)	0/33	ND	50	NA
Dylox	0/39	ND	0/42	ND	0/41	ND	1/33	100 (ND-100)	NA	NA
Metolachlor	10/39	121 (ND-190)	11/42	140 (ND-180)	0/41	ND	0/33	ND	1700000	130000
Parathion	4/39	17 (ND-23)	0/42	ND	0/41	ND	0/33	ND	65	13
Simazine	24/39	63 (ND-1200)	37/42	71 (ND-280)	28/41	150 (ND-1300)	33/33	91 (20-450)	1000000	50000

[a] - Acute Aquatic Life Criteria in Illinois (www.epa.state.il.us/water/water-quality-standards/)
[b] - Chronic Aquatic Life Criteria in Illinois (www.epa.state.il.us/water/water-quality-standards/)
ND – Not detected at concentration greater than 1 ng/L
NA - No water quality criteria available

rates have been reported at 0.47 μg/L (Stuijfzand et al. 2000). Sublethal effects may not immediately result in death in these laboratory tests, but survival will decrease when these effects occur in the field. Seasonal emergence of non-target invertebrates may occur at the same time as diazinon application, leading to exposure of younger organisms that are likely more sensitive (Stuijfzand et al. 2000). Simazine was frequently detected, but concentrations were 38 times less than the chronic WQC.

There were seven pesticides detected in the sediment samples from the creeks (Table 2), but only heptachlor concentrations exceeded a US EPA Region 5 ecological screening level. Ecological screening levels are chemical concentrations of contaminants in sediment that are associated with potential adverse effects. Lake sediment samples had a total of 19 detected chemicals. Most chemicals were only detected in one to five of the 45 sediment samples. A notable exception was DDT, which was detected in 22 of 45 samples. Dieldrin, endrin, gamma-chlordane, and heptachlor were detected at concentrations greater than their US EPA Region 5 ecological screening level. The exceedences indicate a potential for the aquatic ecosystem to have been impacted by past pesticide use, but the frequency of detection was low, so there may only be a few selected "hot spots" or lakes where additional sampling would be useful to determine the extent of the contamination.

Frequency of historic organochlorine and current-use pesticide detection in fish fillets was generally low (Table 3). However, DDT and endrin were detected in 15 and 17 of 85 samples, respectively. Endrin concentration in one largemouth bass sample from S2 was extremely high (3000 ng/g). Two other samples, one common carp from S11 and one largemouth bass from S10 had elevated endrin concentrations (110 and 190 ng/g, respectively). These concentrations are close to the US FDA action level of 300 ng/g for maximum permissibility in the edible portion of fish (USEPA 1980). Chemicals found at high levels in the sediment such as dieldrin and heptachlor were detected in one and three of the 85 fish that were analyzed, respectively. Endrin was detected in two lake sediments (S2, S5), but 17 fish samples had detectable (>1 ng/g) concentrations. All fish collected from S2 were largemouth bass and had endrin detected. Four of five fish from S10 also had detectable endrin. The elevated concentrations of endrin and DDT in fish fillets versus that found in the sediment is not unexpected, since organochlorine pesticides biomagnify. Three currently used pyrethroid pesticides, esfenvalerate, cis- and trans-permethrin, were detected in fish fillets. These compounds were designed to replace the organophosphate pesticides, but the presence of them in fish fillets suggest that these chemicals may also bioaccumulate and have potential for adverse ecological effects.

Pesticide use has affected the water, sediment, and fish quality of the Sparta National Guard Armory. Surface water samples in 2003 had atrazine, diazinon and parathion concentrations that exceeded WQC. Sediment and fish in the majority of the lakes and creeks sampled had evidence of historic nearby

Table 2. Concentration of organochlorine and pyrethroid pesticides (μg/kg, frequency, range, and location) in sediment samples collected from the Sparta National Guard Armory, IL in 2003 and sediment quality criteria (SQC, μg/kg).

Chemical	Frequency	Range Min	Range Max	Location of Maximum	SQC
Creeks					
DDD	3/9	1.0	1.3	PC6	4.88
DDE	1/9	1.3	1.3	PC6	3.16
DDT	5/9	1.2	2.0	PC1	4.16
dieldrin	1/9	1.9	1.9	PC6	1.9
γ-chlordane	2/9	1.4	1.8	PC6	3.24
heptachlor	3/9	1.0	3.2	PC6	0.6
permethrin (cis)	3/9	1.0	3.8	PC1	NA
permethrin (trans)	3/9	1.1	1.2	PC1	NA
Lakes					
aldrin	2/45	1.1	1.1	L1	2.0
α-BHC	1/45	1.0	1.0	S5	6.0
β-BHC	2/45	1.6	1.7	S5	5.0
bifenthrin	2/45	1.0	1.0	S2	NA
α-chlordane	2/45	1.1	1.1	L1	3.24
DDD	5/45	1.1	4.1	S7	4.88
DDE	4/45	1.1	1.5	S5	3.16
DDT	22/45	1.0	2.7	S12	4.16
dieldrin	6/45	1.0	6.5	L1	1.9
endosulfan II	1/45	1.5	1.5	S5	1.94
endrin	2/45	1.4	2.3	S5	2.22
endrin aldehyde	2/45	1.4	2.1	L3	480
endrin ketone	3/45	1.2	2.7	S5	NA
esfenvalerate	3/45	1.0	2.5	S2	NA
γ-chlordane	5/45	1.1	3.6	L1	3.24
heptachlor	3/45	1.3	7.2	S5	0.6
λ-cyhalothrin	3/45	1.2	2.1	S11	NA
methoxychlor	2/45	1.3	1.9	S5	13.6
permethrin (cis)	9/45	1.0	71	S12	NA
permethrin (trans)	9/45	1.0	24	S12	NA

NA - No water quality criteria available

Table 3. Concentration of organochlorine, organophosphate, and pyrethroid pesticides (ng/g, frequency, range, and location of detection) in fish fillets collected from the Sparta National Guard Armory, IL during 2003.

Chemical	Frequency	Range Min	Range Max	Location of Maximum	Species[a]
Lakes					
β-BHC	1/85	5.7	5.7	S8	CCP
chlorpyrifos	3/85	9.6	15	L3	CCP
DDE	1/85	5.0	5.0	S9	LMB
DDT	15/85	5.0	9.1	S10	LMB
dieldrin	1/85	7.6	7.6	L3	SBU
endosulfan II	1/85	13	13	S10	LMB
endrin	17/85	5.3	3000	S2	LMB
endrin aldehyde	1/85	40	40	S2	LMB
endrin ketone	3/85	15	550	S2	LMB
esfenvalerate	1/85	9.9	9.9	S2	LMB
heptachlor epoxide	2/85	6.4	19	S8	CCP
permethrin, cis-	2/85	5.7	11	S5	SBU
permethrin, trans-	1/85	5.8	5.8	L3	SBU
Creek					
endrin	3/15	5.3	6.2	PC5	SPS

[a]Maximum detected concentration was found in this species, other species may have detectable concentrations. Species abbreviations are: CCP – common carp, LMB – largemouth bass, SBU – smallmouth buffalo, SPS – spotted sucker, YBH – yellow bullhead catfish.

agricultural activities. Four sediment pesticide concentrations exceeded sediment quality criteria (SQC), so there may be current adverse ecological effects present at these locations. Several fish had detectable concentrations of currently used pyrethroid pesticides, which are the replacement group for organophosphates.

Local agricultural activities are likely the source for the pesticide contamination that appears to influence all the waters of the acquired land. Recommendations will be made to the Illinois National Guard to work with local farmers to implement improved pesticide management practices (e.g., instituting buffer strips, timing applications when heavy rain is not forecast) to minimize future impacts.

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