An Ecological Risk Assessment of the Potential for Herbicide Impacts on Primary Productivity of the Lower Missouri River

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ABSTRACT

The Lower Missouri River Basin has been drastically altered due to impoundment, channelization, and conversion of the floodplain to agriculture. Agricultural practices have led to both ecological and human health concerns related to herbicide use. A study was conducted to perform an ecological risk assessment of the potential impacts of herbicides on aquatic plant communities of the Lower Missouri River Basin. Sixteen heribicides (atrazine, metribuzin, simazine, cyanazine, alachlor, metolachlor, chlorsulfuron, metsulfuron, triallate, EPTC, trifluralin, diquat, paraquat, dicamba, bromoxynil, and 2,4-D) were tested using one species of algae (*Selenastrum capricornutum*) and one floating macrophyte (*Lemna minor)*. These herbicides represented nine chemical classes and several modes of action and were chosen to represent major current uses in the U.S. The triazinone herbicide metribuzin and the sulfonylurea herbicides chlorsulfuron and metsulfuron were highly toxic but do not necessarily represent a large aquatic risk due to the low rates of application. Bromoxynil, dicamba, 2,4-D, and EPTC exhibited low toxicity. Diquat, paraquat, triallate, and trifluralin were relatively toxic but exhibit low environmental mobility. Cyanazine, alachlor, atrazine, and metolachlor pose the greatest risk to aquatic plants. However, a comparison of these toxicity data to published information concerning application rates, chemical fate, and measured environmental concentrations indicates that adverse impacts of herbicides on non-target aquatic plant communities of the Lower Missouri River are unlikely. However, human health concerns will continue to regulate the use of these chemicals.

INTRODUCTION

Minimum tillage practices have led to increased use of herbicides in agriculture. In 1994 over 97% of corn and soybean acreages were treated with one or more herbicides (over 192 million pounds total application) in the Midwestern states of Illinois, Indiana, Iowa, Minnesota, Missouri, Nebraska, and Ohio (USDA 1995). Herbicide runoff is known to be a major component of non-point source agricultural pollution in aquatic systems. Water quality monitoring programs have determined that herbicide contamination of surface waters (Richards and Baker 1993; Goolsby and Battaglin 1995; Coupe et al. 1995;), ground waters (Squillace and Thurman 1993; Mills and Thurman 1994) and rainfall (Nations and Hallberg 1992) are common and widespread. For example, the U.S. Geological Survey conducted a water quality survey of the Mississippi River Basin from 1989-1992 and measured detectable levels of herbicides in 98% of post-plant samples analyzed (Goolsby and Battaglin, 1995). Richards and Baker (1993) conducted a survey of Lake Erie tributaries from 1983 to 1991 and determined that herbicide contamination of rivers was widespread and especially common during the growing season of April to August.

The frequency and spatial extent of herbicide contamination of surface waters have led to numerous concerns about impacts on non-target aquatic organisms. Data indicates that the majority of herbicides exhibit low toxicity to fish and invertebrates (Mayer and Ellersieck 1986). However, herbicides are toxic to a variety of aquatic plants including submerged macrophytes and algae (Fairchild et al. 1997;1998) and have been suggested as potential causes for losses of aquatic plants in Midwestern streams (Menzel et al. 1984) and Chesapeake Bay (Forney and Davis 1981; Kemp et al. 1985). Primary production of facultative and obligate aquatic plants are the primary energy basis for aquatic ecosystems. Thus, herbicide impacts on primary producers are expected to have both direct and indirect impacts on the health of aquatic ecosystems.

The objective of this study was to conduct an ecological risk assessment for herbicides found in the Lower Missouri River Basin. Toxicity tests were conducted and interpreted in relation to application rates, chemical fate, and measured environmental concentrations to determine if herbicides represent an ecological risk to aquatic primary productivity of the river.

MATERIALS AND METHODS

Sixteen herbicides were tested using the standard test species of *Selenastrum capricornutum* and *Lemna minor*. Basic procedures and test conditions are presented in Fairchild et al. (1997). Herbicides were chosen to represent chemicals of current major agricultural use (Giannesi and Puffer 1991; USDA 1995) across a wide range of general classes and modes of action (Herbicide Handbook 1994) (Table 1). Physical/chemical characteristics of the herbicides are presented in Table 2. Herbicide application, transport, and exposure data was obtained from publications by the Water Resources Division, USGS (i.e. Goolsby et al. 1993; Goolsby and Battaglin 1995; Coupe et al. 1995). Additional exposure estimates were calculated based on extensive literature that indicates that !% is a proximate estimate of herbicide losses from agricultural fields (Baker et al. 1976; Wauchope 1978). For the purposes of pesticide registration it is often assumed that 1% of applied chemical in a 10 ha watershed could enter a 1 ha basin with water 1-m deep (Jenkins et al. 1989). This is accurate for herbicides that are relatively water soluble and have a K_{oc} value less than 1,000. However, the 1%

runoff factor overestimates dissolved losses of chemicals for many ionic (e.g. diquat and paraquat) or hydrophobic chemicals (e.g. trifluralin and triallate). However, these chemicals can be transported sorbed to eroded particals. Thus, for desktop purposes the 1% estimate was used. Risk was calculated by dividing the potential exposure concentration by the laboratory EC50 value for each chemical; numbers exceeding 0.1 are assumed to indicate risk.

RESULTS AND DISCUSSION

The toxicity of the sixteen herbicides are presented in Table 3 along with representative application rates, exposure estimates based on the 1% runoff calculation, and the desktop risk assessment.

The triazine (atrazine, cyanazine, metribuzin, and simazine), acetanilide (alachlor and metolachlor), sulfonylurea (chlorsulfuron and metsulfuron), dinitroanaline (trifluralin), and pyridine (diquat and paraquat) classes of herbicides exhibited high toxicity to one or both plant species, with toxicities ranging from 0.4 to 198 ug/L (96h EC-50) (Tables 3).

One of the thiocarbamate herbicides (triallate) was toxic to *Selenastrum* at 47 ug/L (96h EC50) but was non-toxic *Lemna*. In contrast four of the herbicides (bromoxynil, benzonitrile class; dicamba, benzoic acid class; 2,4-D, phenoxy class; and EPTC, thiocarbamate class) were relatively non-toxic and exhibited toxicity values greater than 6,000 ug/L (96-h EC50) for both species.

Neither *Selenastrum* nor *Lemna* was uniformly more sensitive to the list of herbicides tested. *Selenastrum* was most sensitive to half (eight) of the herbicides, whereas *Lemna* was more sensitive to the remaining chemicals (Table 3). Major departures in sensitivity of both *Selenastrum* and *Lemna* occurred between chemicals within individual classes of the triazine, acetanilide, and thiocarbamate herbicides (Table 3).

Estimated exposure concentrations (i.e. based on the 1% runoff of chemical from a 10 ha watershed into a 1 ha basin 1-m deep) vary in direct proportion to the application rate due to the use of spatial constants in the calculation. The results of the desktop risk assessment indicated that alachlor (2.2), cyanazine (0.85), triallate (0.30), diquat (0.28), metolachlor (0.27), paraquat (0.14), chlorsufuron (0.14), metribuzin (0.08), atrazine (0.07), and metsulfuon (0.07) pose the greatest risk to aquatic under the 1% runoff scenario (Table 3). However, these desktop risk estimates do not factor in the true degree of use, environmental mobility, and environmental half-life of the chemicals.

The risk assessment was refined by comparing plant sensitivity to measured herbicide concentrations from the Missouri River (Table 4). Major use chemicals such as atrazine, metolachlor, cyanazine, and alachlor are detected in over 95% of samples taken on an annual cycle (Table 4). However, neither average nor peak concentrations of herbicides in the Lower Missouri River exceed concentrations known to impact aquatic plants. Those chemicals that are most frequently detected are those that are widely applied, have low K_{oc} values, and high environmental persistence (Tables 2, 3, and 4). Cyanazine (actual risk 0.17) was the only heribicide found to exceed the 0.1 risk criterion. However, this was based on the maximum measured concentration which is extremely conservative.

Alachlor, atrazine, and metolachlor represent lower, yet measureable risk. The remainder of the chemicals are not assumed to be of any risk due to low use, mobility, and persistence. Metribuzin, triallate, chlorsulfuron, and metsulfuron, trifluralin, diquat, and paraquat are all highly toxic to aquatic plants. However, the relative ecological risk of these herbicides is reduced due to either lower application rates (e.g. metribuzin; chlorsufuron; metsulfuron), rapid dissipation rates (e.g. metribuzin and triallate), or sorption potential (e.g. triallate, trifluralin, diquat, and paraquat).

The data indicates that herbicides are unlikely to cause adverse impacts on primary productivity of the Lower Missouri River. Existing environmental data indicates that primary concerns for herbicides would occur in areas riparian areas receiving direct over-spray or excessive runoff (e.g. 1-10% of application) which may include ephemeral wetlands and farmed wetlands that exist in or near agricultural fields as temporary, seasonally-flooded habitats. These data are not reflected in the current USGS data at Herman which is intended to integrate exposures in the main river. Herbicide exposures and impacts in wetlands have not been widely studied and therefore represent a remaining data gap.

Although ecological risk for herbicides in the environment is low, the maximum recommended level of atrazine in drinking water (3 ug/L) is frequently exceeded. Thus, human health concerns may drive future changes in the uses of these herbicides.

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Table 1. Classification, mode of action, production, and use levels of herbicides tested with *Selenastrum* and *Lemna*.

Herbicide	Class	Mode of Action[1]	U.S. Annual Usage (#/yr X 10^3)[2]	Range of Use Rates (kg/ha)[1]	U.S. Annual Use Rank[2]
atrazine	triazine	inhibits photosynthesis	64,236	1.1 - 2.2	1
alachlor	acetanilide	inhibits protein synthesis	55,187	1.7 - 6.7	2
metolachlor	chloracetanilide	inhibits protein synthesis	49,713	1.4 - 4.5	3
EPTC	thiocarbamate	unknown	37,191	2.2 - 6.7	4
2,4,-d (salt)	phenoxy	auxin simulator	33,096	0.3 - 1.1	5
trifluralin	dinitroaniline	inhibits germination processes	27,119	0.6 - 2.2	6

cyanazine	triazine	inhibits photosynthesis	22,894	0.9 - 5.3	7
dicamba	benzoic acid	auxin simulator	11240	0.3 - 0.6	11
metribuzin	triazinone	inhibits photosynthesis	4,822	0.3 - 0.8	15
simazine	triazine	inhibits photosynthesis	3,964	2.2 - 4.5	20
triallate	thiocarbamate	inhibits cell elongation/division	3,509	1.1 - 1.7	22
paraquat (salt)	pyridine	free-radical formation	3,025	0.3 - 1.1	23
bromoxynil	benzonitrile	inhibits photosynthesis	2,627	0.2- 0.6	27
diquat	pyridine	free radical formation	166	0.4 - 0.6	77
chlorsulfuron	sulfonylurea	inhibits amino acid synthesis	77	.009 - .018	80
metsulfuron	sulfonylurea	inhibits amino acid synthesis	41	.004 - .012	87

[1] from Herbicide Handbook (1994).

[2] from Gianessi and Puffer (1991) and from USDA (1995) .

Table 2. Comparison of use rates, environmental behavior, runoff potential, and exposure potential based on runoff and aqueous half-life.

Herbicide	Use Rate (kg/ha)[1]	K_{oc}[2]	Soil $t_{1/2}$ (days)[2]	runoff potential[2]	Aqueous $t_{1/2}$ (days)[3]	exposure potential
Atrazine	1.1	160	60	high	47-193	high
Alachlor	2.2	190	14	medium	21	high
Metolachlor	2.1	200	20	high	75	high
EPTC	4.6	280	30	medium	no data	medium
2,4-D	0.4	20	10	high	1-7	low-medium
Trifluralin	0.9	1,400	60	medium	1-2	low
Cyanazine	2.3	168	20	high	103	high
Dicamba	0.4	2	14	high	30	high
Metribuzin	0.3	41	30	high	4	low
Simazine	0.7	138	75	high	30	high
Triallate	1.4	3,600	60	low	1	low
Paraquat	0.7	100,000	3,600	low	1-2	low
Bromoxynil	0.3	100	14	high	1-2	low
Diquat	0.5	100,000	3,600	low	1-2	low
Chlrosulfuron	0.01	1	30	high	no data	medium
Metsulfuron	0.003	61	61	high	29	medium

[1] from USDA (1995).

[2] From Wauchope, D.L.(1992), Interim Properties Database.

[3] Data sources: alachlor, 550 ha reservoir, Spalding et al. (1994)
atrazine, 0.1 ha ponds, Fairchild et al. (1994) and 550 ha reservoir, Spalding et al. (1994)
bromoxynil 0.01 ha pond, Muir et al. (1991) and 100 ml bacterial culture, Golovleva et al. (1988)
chlorsulfuron, no available data
cyanazine, 550 ha reservoir, Spalding et al. (1994)
dicamba, 0.1 ha ponds, Scifres et al. (1973)
diquat, variety ecosystems, Reinert and Rodgers (1987)
EPTC; no available data
metolachlor 550 ha reservoir, Spalding et al. (1994)
metribuzin, 0.1 ha pond, Fairchild et. al, 1996
metsulfuron, in-situ enclosures, Thompson et al. (1992)
paraquat, variety of habitats; Calderbank 1972 and 2 ha pond Way et al. (1970)
simazine, none given, Reinert and Rodgers (1987)
triallate, estimated based on K_{oc}
trifluralin, 30 L microcosm, Isensee et al. 1979 and 1 L microcosm, Huckins et al. (1986)
2,4-D, various reservoirs, Reinert and Rodgers (1987)

Table 3. Response of *Lemna* and *Selenastrum* to sixteen herbicides.

Herbicide	Use Rate (kg/ha)[1]	*Lemna* EC50 (ug/L)	*Selenastrum* EC50 (ug/L)	1% exposure estimate (ug/L)[2]	Desktop Risk Estimate[3]
atrazine	1.1	153	235	11	0.07
alachlor	2.2	198	10	22	2.20
metolachlor	2.1	343	77	21	0.27
EPTC	4.6	7,512	6,451	46	0.05
2,4-D salt	0.4	>100,000	41,772	4	0.01
trifluralin	0.9	170	673	9	0.05
cyanazine	2.3	705	27	23	0.85
dicamba	0.4	>100,000	36,375	4	0.00
metribuzin	0.3	37	43	3	0.08
simazine	0.7	166	1,240	7	0.04
triallate	1.4	>10,000	47	14	0.30
paraquat	0.7	51	559	7	0.14
bromoxynil	0.3	8,065	7,762	3	0.00
diquat	0.5	18	80	5	0.28
chlorsulfuron	0.01	0.7	135	0.1	0.14
metsulfuron	0.003	0.4	190	0.03	0.07

[1] from USDA (1995).

[2] 1% exposure estimate based on 1% of application rate entry into a 1-m deep wetland in a 10:1 land/water watershed.

[3] Risk rate calculated as !% exposure estimated divided by most sensitive plant EC50 (*Lemna* or *Selenatrum*).

Table 4. Actual risk of herbicides in Missouri River in relation to total use, percent transported, frequency of detections and peak concentrations of herbicides measured in water at Herman, MO and aquatic plant sensitivity. Actual risk values exceeding 0.1 indicate risk.

Herbicide	Herbicide Application Missouri Basin (metric tons)[1]	Total Herbicide Transported Missouri River (% applied)[1]	Frequency detection (n=44 samples)[1]	Measured concentration mean and range at Herman, MO (ug/L)[2]	Most sensitive plant EC50 (ug/L)[3]	Actual Risk[3]
Atrazine	6,280	1.1	100%	3.0 (0.4-5.7)	153	0.04
Alachlor	4,660	0.2	96%	0.4 (0.07-0.92)	10	0.09
EPTC	4,180	<0.1	13%	<0.05	6,451	0
Metolachlor	3,490	0.71	100%	1.0 (0.1-2.0)	77	0.03
Trifluralin	2,350	<0.1	47%	<0.05	170	0
Cyanazine	1,970	1.6	96%	1.6 (0.2-4.7)	27	0.17
Metribuzin	207	0.7	36%	0.07 (<.05-.19)	37	0
Simazine	52	2.1	86%	<0.05	166	0
Dicamba[4]	nm	nm	nm	nm	nm	0

[1] 1989 data from Goolsby and Battalgin (1993).
[2] Mean and range of 19 samples from April-June of 1991 from Coupe et al. (1995).
[3] Actual risk calculated as maximum measured concentration divided by most sensitive plant EC50.
[4] Dicamba not measured (nm) at Herman but categorized as no risk due to low toxicity (Table 3).