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DISTRIBUTION AND ENVIRONMENTAL FATE OF PESTICIDES IN PRAIRIE WETLANDS

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Abstract. *There is abundant, albeit fragmentary, evidence that prairie wetlands are being contaminated extensively by agricultural pesticides (primarily herbicides and insecticides) and other anthropogenic contaminants. Such inputs can affect fundamental ecosystem properties such as primary production which, in turn, affects habitat and resource supply for wetland fauna. We review data on the use of pesticides, off-site transport of residues from treated land, and the frequency with which these residues are subsequently detected in receiving streams and wetlands on the prairies. As the environmental distribution of a pesticide is affected by its chemical and physical properties, and the abiotic and biotic characteristics of the receiving wetland, greater insight into its ecological impacts will be obtained from considering the underlying partitioning and degradative processes that determine distribution rather than from case-by-case studies of persistence. Future research on chemical contamination of prairie wetlands should include the development and testing of dissipation and fate models under conditions typical of prairie wetlands using a process-oriented approach, emphasizing the roles of adsorption and photolysis in a shallow, high area to volume environment. Output from a computer model based on the fugacity concept (QWASFI: Quantitative Water, Air, Soil, Film Interactions) indicates the potential to predict the environmental behavior of specific chemicals in wetlands.*

Concern regarding the introduction of anthropogenic chemicals to prairie wetlands is increasing (e.g., Sheehan et al. 1987; Grue et al. 1989)

TABLE 1
 FREQUENCY OF DETECTION OF TOXIC CHEMICALS IN SURFACE
 WATERS (LAKES, PONDS, FARM DUGOUTS) OF SOUTHERN
 MANITOBA, BASED ON ANALYSIS OF 160 SAMPLES
 COLLECTED IN 1995 (GURNEY AND JONES 1997)

Chemical	Chemical type	Frequency of detection (n = 160)
microcystin LR	cyanobacterial toxin	70.0%
2,4-D	herbicide	17.5%
bromoxynil	herbicide	2.5%
dicamba	herbicide	8.8%
atrazine	herbicide	1.3%
MCPA	herbicide	0.6%
trifluralin	herbicide	0.6%

because such inputs are known to negatively affect plant and animal populations in the terrestrial environment. The Great Plains is an area of chemically intensive agriculture in which pothole wetlands bordering cropland are numerous. These wetlands are important as the breeding ground for over 50% of North American waterfowl (e.g., Batt et al. 1989); however, effects of contaminants on wildlife are largely unknown. Prairie wetlands may intermittently recharge groundwater (e.g., LaBaugh et al. 1987; van der Kamp and Hayashi 1998), so the resource on which humans ultimately depend may become contaminated. Although this review focuses on agricultural pesticides, they are not the only anthropogenic chemicals found in prairie wetlands. Adjuvants contained in pesticide formulations, as well as petroleum products from storage tanks and machinery, and fertilizers may also contaminate wetlands. Furthermore, toxic chemicals arising from natural sources, but exacerbated by agricultural inputs, may complicate the cumulative effect of human activities on prairie wetlands. For example, while pesticides were found in surface waters in Manitoba (Gurney and Jones 1997), the most commonly encountered toxicant was microcystin LR, a potent neurotoxin that is a metabolic by-product of blue-green algae (cyanobacteria) that flourish on nutrients from sewage and fertilizer (Table 1).

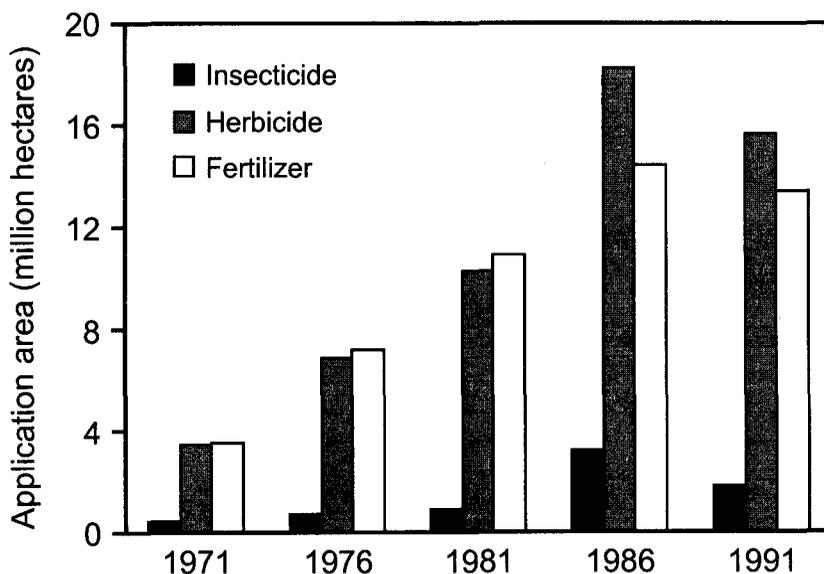


Figure 1. Use of agricultural chemicals (insecticide, herbicide, fertilizer) in the three Canadian prairie provinces from 1971 to 1991. Data are from Environment Canada (1996).

Use of Pesticides on the Prairies

Pesticides refer to chemicals which are toxic to the growth of living organisms, and include chemicals targeted at plants (herbicides), fungi (fungicides), insects (insecticides), and others. Definitive data on the proportionate importance of these groups in prairie agriculture are lacking; however, it is generally assumed that herbicides primarily and fungicides secondarily comprise the majority of use. Pesticide use has increased in Canada by roughly 500% over the past 25 years (Fig. 1) and a corresponding trend has occurred on the American Great Plains (Grue et al. 1989). By one recent estimate, 99% of the acres planted to corn and soybeans in Iowa are treated with herbicides and 31% of the corn acres are treated with insecticides (Hartzler et al. 1997). Data for specific chemicals illustrate both the increase in quantity of use and the diversification in the chemicals applied. Phenoxy herbicides, including 2,4-D and MCPA, were introduced to the Canadian prairies soon after World War II (Fig. 2). Use increased dramatically until

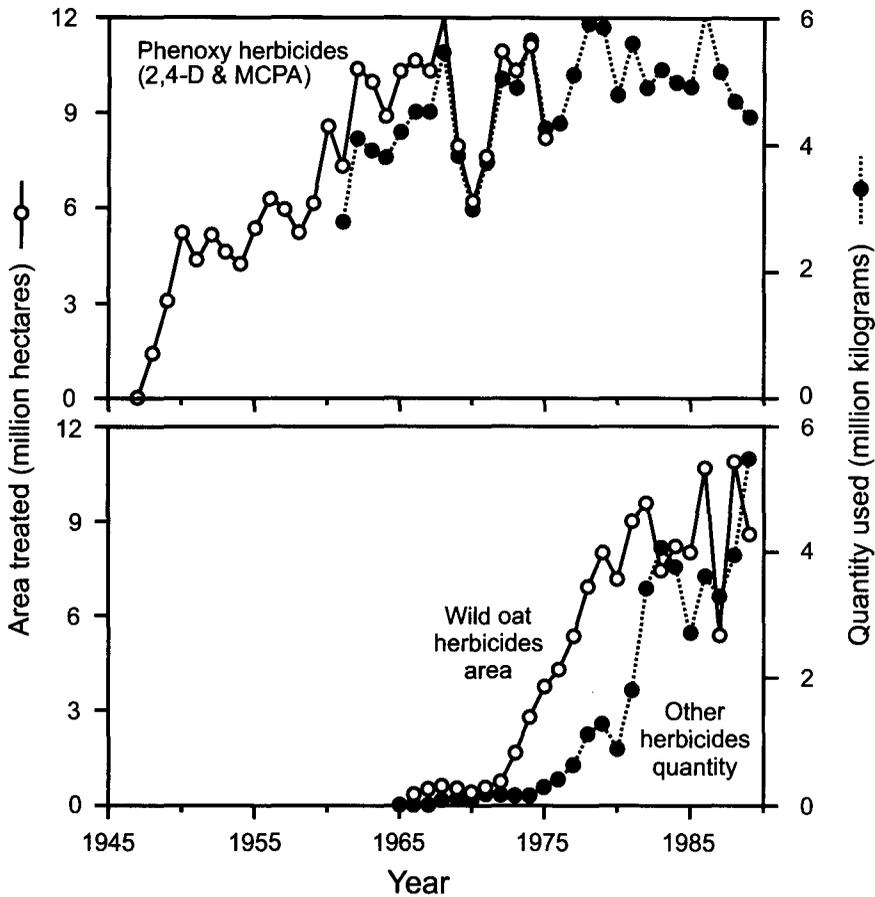


Figure 2. The use (quantity and area treated) of herbicides in Manitoba, Saskatchewan and Alberta between 1947 and 1989. Categories are those used by the Manitoba Department of Agriculture. Statistics for phenoxy herbicides include 2,4-D and MCPA, "other herbicides" (bromoxynil, dicamba, dichlorprop, linuron, glyphosate, picloram, propanil and unspecified others), and wild-oat herbicides (asulam, atrazine, barban, diclofop methyl, difenzoquat, EPTC, flamprop methyl, triallate and trifluralin). Data were obtained from Anonymous (1947-1989).

the mid-1960s when it stabilized at about 10 million hectares treated annually (almost half of improved arable land) or 4,000 tonnes applied annually. Since the early 1970s, new groups of "specialty" herbicides introduced to control wild oats (*Avena fatua*) and other specific weeds in field crops have increased the number of active ingredients in use to 250 as of 1994 (Environment Canada 1996). The net result over the past 50 years is that a larger

number of pesticides have become available in greater quantity for off-site transport.

Off-site Transport of Pesticide Residues

There is considerable evidence for off-site movement of pesticide residues on the Great Plains, in gaseous and droplet drift (particularly when applied aerially), drift of wind-blown particulates to which pesticides are adsorbed, or transport of dissolved pesticides in surface water runoff, snow-melt, or groundwater flow (e.g., Leonard 1988; Smith et al. 1988; Waite et al. 1992, 1995). Moreover, these processes need not be confined to local pesticide transport, particularly if a pesticide formulation is volatile. Atrazine, a herbicide used widely for corn production in the central Great Plains, has been detected in air at the Experimental Lakes Area of northwestern Ontario (Muir and Grift 1991), hundreds of kilometers away. The means and extent to which pesticides move off-site from cropland can vary with method of application (ground sprayer or aircraft), spray droplet size, atmospheric conditions (wind velocity, relative humidity, and temperature) at the time of application, and the physico-chemical properties of the pesticide and its formulation (volatility, water solubility, adsorption coefficients, and photolability). Following deposition on soil or foliage, precipitation can wash residues into receiving streams, resulting in correlation of pesticide spikes with high streamflow after a storm (Fig. 3). The difficulty in relating off-site transport to pesticide use in a watershed, however, is that chemicals vary in water solubility, volatility, tendency to adsorb to suspended particulates, and other parameters that ultimately determine residues in streamflow. The result is that chemicals and their concentrations may not reflect local use (Waite et al. 1992). For example, a study of agricultural herbicides in the Ochre River of western Manitoba, in which chemical use and the ensuing load transported in the river were quantified, showed that herbicides widely used in the watershed (e.g., diclofop-methyl) were comparatively minor constituents of the river load compared to less used herbicides (e.g., 2,4-D) (Table 2).

Pesticide Residues in Prairie Wetlands

Over 80% of ponds used by waterfowl on the Canadian prairies have had their margins affected by agricultural burning, haying, grazing or cultivation (Caswell and Bazin 1997). Pesticides can enter prairie wetlands when

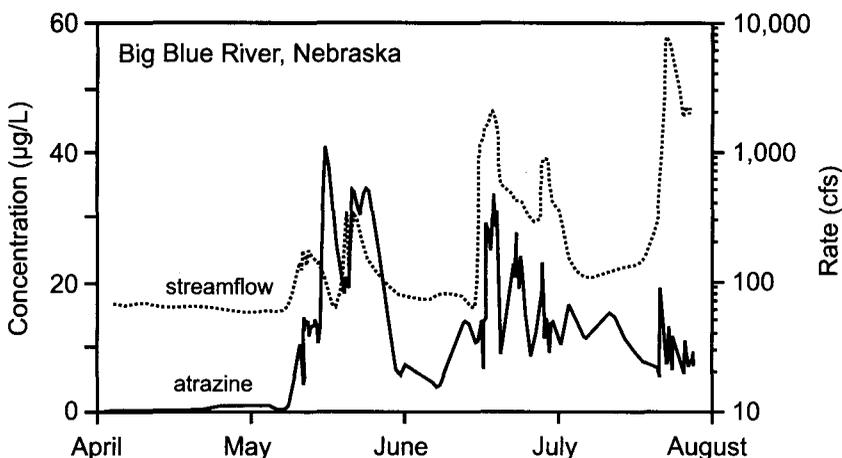


Figure 3. Transport of atrazine herbicide residues in water of the Big Blue River, Nebraska as a function of stream flow (1990). Modified from Thurman et al. (1991).

their basins are tilled in dry periods or as a result of direct overspray during aerial pesticide application, drift of airborne aerosols or particulates, runoff from adjacent treated fields, and discharge from contaminated groundwater (Grue et al. 1989). "Potholes" may be especially subject to contamination as they typically occupy topographic depressions that are natural destinations for surface runoff. Being small in size and closely interspersed with cropland, they are also easily over-sprayed during aerial pesticide applications. This may explain why, for example, the amount of ethyl parathion deposited on five North Dakota potholes (0.21-0.40 kg/ha) was higher than on the adjacent sunflower fields (0.06-0.12 kg/ha) over which the insecticide was sprayed (Tome et al. 1991).

Despite compelling evidence of off-site transport, data on pesticides in prairie rivers and lakes (e.g., Gummer 1980; Waite et al. 1992; Donald and Syrgiannis 1995), and considerable public and regulatory interest in wetlands, there have been surprisingly few studies of pesticide occurrence in prairie wetlands *per se* (Tables 3, 4). Available data indicate that residue levels typically occur in the range of parts per billion (e.g., Waite et al. 1992; Frankforter 1995). However, we report only the frequency of detection rather than absolute pesticide levels because, in the absence of corresponding toxicological information, concentrations in water have limited

TABLE 2
HERBICIDE LOAD IN THE OCHRE RIVER, MANITOBA (1984).
DATA ARE FROM MUIR AND GRIFT (1987)

Herbicide	Total use in watershed (kg/year)	River load (g/year)
diclofop-methyl	5,928	36
dicamba	3,285	698
trifluralin	984	119
bromoxynil	890	15
triallate	708	43
2,4-D	171	1,300

comparative value. Grover et al. (1997) monitored farm ponds in southern Saskatchewan between 1987 and 1989, finding that nearly all ponds contained detectable levels of 2,4-D (Table 4), presumably as a result of its widespread use. Pesticides were more frequently detected in ephemeral freshwater lakes in Saskatchewan which are favored by waterfowl for feeding and nesting habitat whereas residues were less frequently detected in permanent saline lakes (Table 5; Donald and Syrgiannis 1995).

The assumption that pesticides arise in prairie wetlands due to off-site transport from areas of use implies that the frequency of pesticide detection should, therefore, vary with the predominant land use in the wetland watershed. Supporting evidence comes from observations that 53% of wetlands in Nebraska rangeland (where pesticides are assumed to be used less frequently than in cultivated areas) contained detectable herbicides, as opposed to 80% of wetlands in areas of mixed agriculture, and 96% of wetlands in areas of active cropland (Frankforter 1995).

Pesticide Persistence and Dissipation Processes

Pesticide dissipation refers to residue loss as a result of degradation processes (photolysis, abiotic hydrolysis, and biodegradation) and transfer

TABLE 3
 FREQUENCY OF HERBICIDE DETECTION IN NEBRASKA
 WETLANDS (1994). DATA ARE FROM FRANKFORTER (1995).

Herbicide	Frequency of detection (n = 60)
alachlor	18%
atrazine	78%
deethylatrazine (atrazine metabolite)	55%
deisopropylatrazine (atrazine metabolite)	18%
cyanazine	33%
metolachlor	40%

into air (volatilization), adsorption to suspended particulates, sediments and biota, and outflow in surface and groundwater. The relative importance of these processes, which vary with properties of the chemical and the site, determines persistence. Pesticides such as atrazine, entering wetlands primarily as nonpoint source loads in runoff and groundwater, are probably among the most recalcitrant. By comparison, more labile pesticides such as bromoxynil may dissipate before entering wetlands or, when input directly to wetlands by aerial application, may degrade rapidly (e.g., Muir et al. 1991).

There is considerable information on the dissipation of agricultural pesticides under controlled laboratory conditions and in lakes but the degree to which these data apply to wetlands is unclear. There are several features of wetlands, most of which relate to their shallow character, that could increase or decrease the observed dissipation as compared to that in other water bodies. Wetlands generally support high levels of biological productivity (Mitsch and Gosselink 1993), one manifestation of which is profuse submersed and emergent plant growth that results in high surface area relative to the wetland's water volume. Area to volume ratios from Delta Marsh, Manitoba, for instance, range as high as 15 m² per m³ of bottom in areas <1 m deep (Goldsborough and Robinson 1996). This increases opportunities for surface adsorption, chemical sequestering in plant tissue, microbial biodegradation on surfaces, and exposure to solar irradiance for pesti-

TABLE 4
 FREQUENCY OF HERBICIDE DETECTION IN SASKATCHEWAN
 PONDS (1987-89). DATA ARE FROM GROVER ET AL. (1997).

Herbicide	Frequency of detection (n = 150)
2,4-D	93 - 100%
diclofop	46 - 95%
bromoxynil	50 - 85%
MCPA	33 - 70%
trallate	28 - 63%
dicamba	17 - 55%
trifluralin	0 - 18%

cide photolysis. Most wetland sediments are richly organic (>20% dry mass), providing surfaces for pesticide adsorption. As wetlands are characteristically <2 meters deep, sunlight may reach the bottom, further increasing the potential for photolytic decomposition. Enzymatic degradation reactions may be facilitated in the shallow warm water. Dissolved organic carbon (DOC), generally higher in wetlands than in lakes (e.g., Thurman 1985; Robarts and Waiser 1998), absorbs ultraviolet radiation that otherwise promotes photolysis. On the other hand, some constituents of DOC may act as sensitizing agents that facilitate degradation (Cessna and Muir 1988). The significance of DOC as a determinant of pesticide photolysis is especially intriguing in the context of changes in UV-B irradiance due to atmospheric ozone depletion (e.g., Vincent and Roy 1993). Finally, the shallow and, in many cases, ephemeral nature of prairie wetlands means that evaporative concentration of residues will occur to a greater extent than in deeper, more stable water bodies.

Pesticide fate in prairie wetlands is poorly understood, complicated by the large variety of pesticide compounds, limited information on pesticide transformation products, and the difficulties of studying pesticide fate in the complex wetland matrix. However, research indicates that common pesticide contaminants of surface and groundwaters disappear rapidly from wetland waters, primarily as a result of adsorption by the organic fraction in sediments and decomposing litter. For example, pesticide fate studies using

TABLE 5
 FREQUENCY OF PESTICIDE DETECTION (N, NUMBER OF
 SAMPLES) IN SASKATCHEWAN LAKE WATER
 AS A FUNCTION OF ITS SALINITY (1988 - 1991).
 DATA ARE FROM DONALD AND SYRGIANNIS (1995).

Pesticide	Group 1	Group 2	Group 3
	(oligosaline) 1,730-5,600 $\mu\text{S/cm}$	(mesosaline) 5,800-19,380 $\mu\text{S/cm}$	(eusaline - hypersaline) 28,000-83,000 $\mu\text{S/cm}$
α -HCH	78% (9)	88% (8)	33% (6)
lindane	78% (9)	63% (8)	17% (6)
2,4-D	100% (9)	75% (8)	50% (6)

wetland microcosms and mesocosms have shown that atrazine, fonofos, metolachlor, or trifluralin becomes rapidly associated with sediments, with the formation of persistent pesticide-humus complexes leaving little chance of subsequent desorption of the parent pesticide (Huckins et al. 1986; Matter 1993; Crumpton et al. 1994, 1997).

A summary of wetland dissipation data (Fig. 4) based on pesticide additions under controlled field conditions (Table 6) indicates half-lives (time for residues to decrease by 50%) ranging from less than a day for bromoxynil to several months for hexazinone. Some dissipate via zero-order kinetics (linear change with time) whereas first-order kinetics (exponential concentration change) are appropriate for others. Waite et al. (1992) found that no water sample collected from Saskatchewan ponds over a two-year period contained detectable levels of bromoxynil, an observation consistent with its rapid dissipation when applied experimentally to water (Fig. 4). Decreases in glyphosate concentration in ponds in eastern Manitoba was concurrent with increases in the concentration of its primary metabolite, aminomethylphosphonic acid (AMPA) (Goldsborough and Brown 1993).

Research indicates that the rate of pesticide dissipation in wetlands may vary with the quantity and composition of vegetation. Lee et al. (1995) reported that atrazine dissipated most quickly from the water column of mesocosms deployed in a Kansas wetland when emergent plants were present (half-life = 62-72 days), as opposed to rates in the presence of submersed plants or in open water (96-112 days and 94-99 days, respectively). The

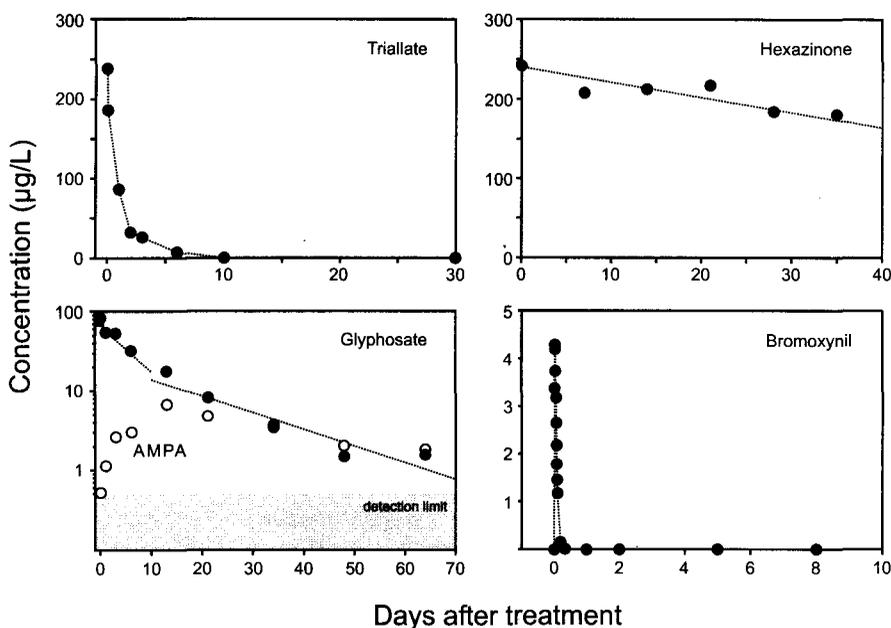


Figure 4. Dissipation of several common herbicides added experimentally to natural wetlands or wetland mesocosms in Manitoba and Saskatchewan. A. Triallate data from Désy (1996). B. Hexazinone data from Goldsbrough (unpublished). C. Glyphosate data from Goldsbrough and Brown (1993). D. Bromoxynil data from Muir et al. (1991). Note that the time and concentration ranges differ for each panel.

basis for this observation is unclear; enhanced dissipation due to high surface area of emergent macrophytes should also apply when submersed plants were present.

Rudimentary predictions of the environmental behavior of a pesticide in water can be made based on its chemical properties; water-soluble chemicals, for instance, are likely to persist in water longer than more insoluble chemicals. There are many mitigating factors, however, such as the quantity of DOC and plant surface area. An interesting laboratory study that may have implications for wetland pesticide dissipation found that photolysis of the insecticide methyl parathion was stimulated in proportion to the quantity of phytoplankton present (Table 7; Zepp and Schlotzhauer 1983). These algae can be seasonally abundant in wetlands (e.g., Robarts et al. 1995) so that pesticide degradation may vary with changes in biotic (e.g., grazer density) and abiotic (e.g., nutrients) conditions regulating algal abundance.

TABLE 6
LIST OF SOME PESTICIDES ADDED EXPERIMENTALLY
TO NATURAL WETLANDS OR WETLAND MICROCOSMS
IN CENTRAL NORTH AMERICA.

Pesticide	Type	Reference
2,4-D	herbicide	Forsyth et al. (1997)
alachlor	herbicide	Lee et al. (1995)
atrazine	herbicide	Klaassen and Kadoum (1979), Huckins et al. (1986), Johnson (1986), Lee et al. (1995), Detenbeck et al. (1996)
bromoxynil	herbicide	Muir et al. (1991)
carbofuran	insecticide	Johnson (1986), Klaassen and Kadoum (1979)
chlорpyrifos	insecticide	Giddings et al. (1997), Hann and Goldsborough (unpublished data)
clopyralid	herbicide	Forsyth et al. (1997)
cyanazine	herbicide	Fintschenko et al. (1995)
diazinon	insecticide	Giddings et al. (1996)
diclofop-methyl	herbicide	Arts et al. (1996)
difenzoquat	herbicide	Goldsborough (unpublished data)
fonofos	insecticide	Huckins et al. (1986), Johnson (1986)
glyphosate	herbicide	Goldsborough and Brown (1993)
hexazinone	herbicide	Goldsborough (unpublished data)
phorate	insecticide	Dieter et al. (1995), Johnson (1986)
pichloram	herbicide	Forsyth et al. (1997)
sethoxydim	herbicide	Goldsborough (unpublished data)
simazine	herbicide	Goldsborough and Robinson (1983, 1985)
terbutryn	herbicide	Goldsborough and Robinson (1983)
triallate	herbicide	Arts et al. (1996), Désy (1996), Johnson (1986), Waiser and Robarts (1997)
trifluralin	herbicide	Huckins et al. (1986), Johnson (1986)

Modeling Pesticide Persistence in Wetlands

It is often impractical, for logistic, financial or ecological reasons, to determine the environmental behavior of a pesticide in wetlands via experimental additions. An alternative initial approach is to mathematically model

TABLE 7
 EFFECT OF THE BIOMASS OF PHYTOPLANKTON ALGAE,
 MEASURED AS CHLOROPHYLL CONCENTRATION ($\mu\text{G/L}$),
 ON THE RATE OF PHOTOLYTIC DECOMPOSITION
 OF THE INSECTICIDE METHYL PARATHION.
 DATA ARE FROM ZEPP AND SCHLOTZHAUER (1983).

Chlorophyll ($\mu\text{g/L}$)	Photolysis constant	Ratio to control
0 (control - no algae)	0.06	-
0.0068	0.06	1.0
0.68	0.10	1.7
1.8	0.16	2.7
6.3	0.39	6.5
6.8	0.53	8.8

processes affecting pesticide degradation and partitioning between air, water, and soil. These models, when combined with features of a hypothetical receiving wetland, may allow the focusing of *in situ* research efforts on specific processes or environmental compartments that are critical to determining the net distribution of a pesticide.

While several computer models are available for predicting pesticide persistence and environmental fate (Mackay and Paterson 1993), only recently have they been applied to wetlands (e.g., Alvord and Kadlec 1996). Consequently, the accuracy of these models for wetlands remains to be determined. One model that is conceptually simple yet sufficiently robust to provide reasonable simulations across a wide range of conditions is the Quantitative Water, Air, Sediment, Film Interactions (QWASFI) model. QWASFI is a modification (Southwood et al. 1998) of the QWASI model of Mackay et al. (1983) that provides for pesticide partitioning into organic films at the air/water interface, a behavior common for hydrophobic pesticides (Muir et al. 1992). The scenario modeled by QWASFI is a simplified aquatic environment consisting of five compartments among which a chemical potentially moves: water, sediment, suspended solids and biota, surficial film, and air. All compartments are well mixed with uniform properties (an assumption unrealistic of natural conditions that may lead, for example, to artificially high exposure of residues to adsorptive surfaces) and changes in

TABLE 8
 INPUT PARAMETERS USED TO MODEL THE BEHAVIOR OF
 ATRAZINE IN A SIMULATED, 1 M DEEP WETLAND MESOCOSM
 IN DELTA MARSH, MANITOBA.

Parameter (units)	Input value	Reference / comment
Atrazine molecular mass (g/mol)	215.7	Solomon et al. (1996)
Atrazine vapor pressure (Pa)	3.84E-05	Solomon et al. (1996)
Atrazine solubility - water (mol/m ³)	0.153	Solomon et al. (1996)
Atrazine octanol/water partition coefficient	479	Solomon et al. (1996)
Ambient temperature (°C)	25	typical midsummer value
Sediment organic C content (%)	15	Goldsborough, unpubl. data
Volume - water (m ³)	25	5 m x 5 m x 1 m enclosure
Volume - sediment (1 cm thickness - m ³)	0.25	based on enclosure area
Volume - suspended sediment (m ³)	6.25E-04	Goldsborough, unpubl. data
Volume - biota (m ³)	0	Goldsborough, unpubl. data
Volume - film (100 µm thickness - m ³)	2.50E-03	Muir, pers. comm.
Area - air/film interface (m ²)	25	based on enclosure area
Area - sediment/water interface (m ²)	25	based on enclosure area
Area - film/water interface (m ²)	25	based on enclosure area
Mass transfer coefficient - air (m/h)	8.36	Smith et al. (1981)
Mass transfer coefficient - water (m/h)	7.17E-03	Smith et al. (1981)
Mass transfer coefficient - film (m/h)	7.17E-03	assumed equal to water
Degradation rate - sediment (h ⁻¹)	0.003	Muir (1988)
Degradation rate - water (h ⁻¹)	0.007	Burkhard and Guth (1976), Muir (1988), Crumpton, unpubl. data
Degradation - film (h ⁻¹)	0.007	assumed equal to water
Atrazine input - air (mol/m ³)	0	film input only
Atrazine input - water (mg/L)	0	film input only
Atrazine input - sediment (mg/g dry weight)	0	film input only
Atrazine input - inflow (mg/L)	0	film input only
Atrazine input - film (mg/L)	200	aerial spray input (see text)

the quantity of the modeled chemical in each compartment are assumed to occur with time. In other words, the dynamic nature of the environment is recognized.

Modeling of environmental movement of chemicals by QWASFI is done using the concept of fugacity (Mackay 1979), which is the "escaping tendency" of a molecule to migrate from one environmental compartment to another. Fugacity relates to mass diffusion as temperature relates to heat diffusion. Chemicals move from high to low fugacity, which is usually expressed in units of pressure (Pascals) although fugacity is linearly proportional to concentration. When the fugacities of two compartments are equal, they are in equilibrium.

The QWASFI model, based on a computer spreadsheet (Southwood et al. 1989), requires as input, various parameters describing the nature of the receiving system and the properties of the modeled chemical (Table 8). Some of the latter data are available in the literature; others must be estimated from empirical relationships with known parameters (e.g., Kenaga and Goring 1980). For the purposes of demonstration, we modeled the environmental behavior of atrazine in a simple wetland system, specifically a 5 meter x 5 meter mesocosm that we have used for toxicological studies in Delta Marsh, Manitoba. Our rationale was that atrazine is a widely used agricultural herbicide so it is a common constituent of surface water in much of the Great Plains (e.g., Thurman et al. 1991; Frankforter 1995; Alvord and Kadlec 1996; Detenbeck et al. 1996). Unlike many agricultural pesticides, for which basic chemical properties are unavailable, atrazine has been widely studied so most of the input parameters are available. Atrazine input to the film compartment was calculated from the recommended application rate for Manitoba of 200 grams per hectare (Manitoba Agriculture 1997). Being moderately water soluble (33 mg/L at 25°C), we hypothesized *a priori* that atrazine would be relatively persistent in the water column although its moderate octanol-water partition coefficient (479) indicates that it should also partition into sediments. Degradation due to photolysis, hydrolysis and biodegradation was estimated from rates determined in the laboratory, whose applicability to a wetland setting can be questioned.

In the model simulation, atrazine disappeared from the water column of the wetland with a first-order half-life of 2 days (Fig. 5) and it subsequently appeared in the sediments, an observation that is confirmed by microcosm and mesocosm experiments (Huckins et al. 1986; Detenbeck et al. 1996). Herbicide degradation affected dissipation, as shown by the difference in model results when this factor was set to zero (Fig. 5). Most

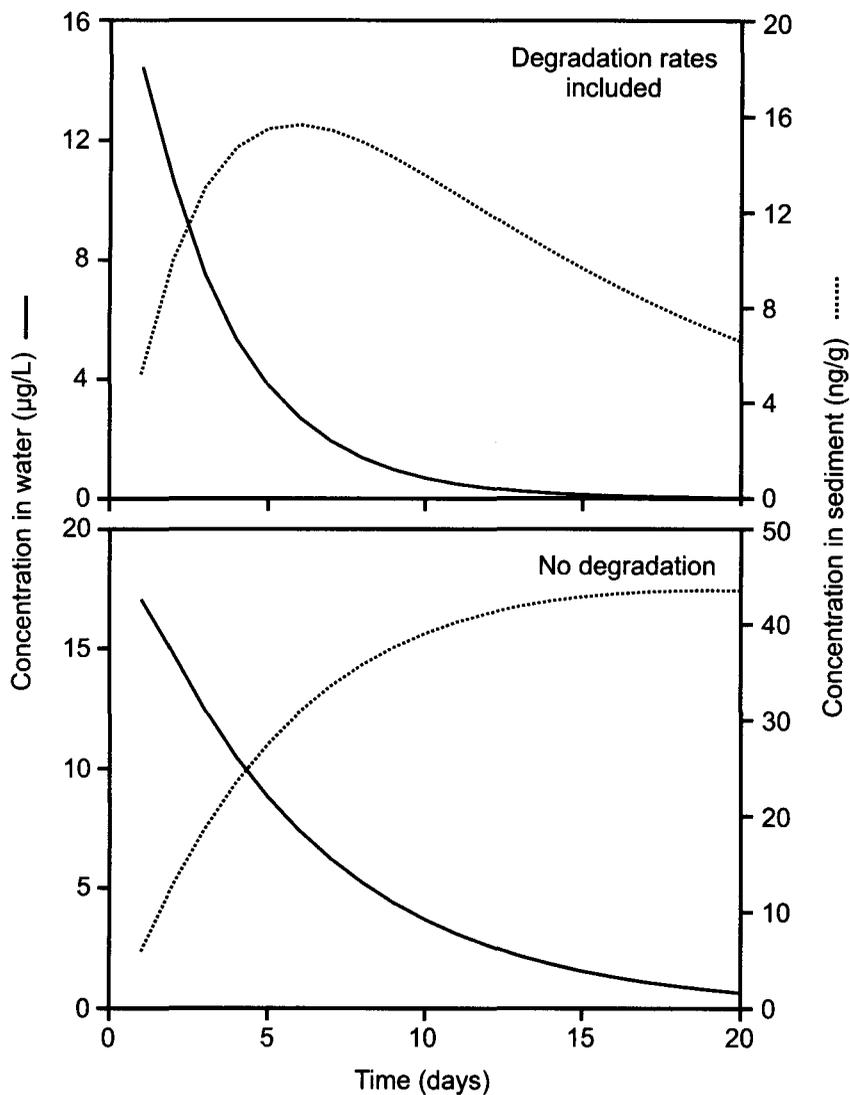


Figure 5. Sample output from two iterations of a QWASFI model for the environmental behavior of the herbicide atrazine in a simulated wetland mesocosm (25 m² surface area; 25,000 L volume). In the second iteration, atrazine degradation rates in sediment, water and film were set to zero.

published studies on atrazine dissipation in wetlands concur that the herbicide disappears "rapidly" from the water column although the reported half-life varies ten-fold (Crumpton unpublished data). Even controlled studies in wetland mesocosms report half-lives ranging from about 7 days (Crumpton et al. 1997; Detenbeck et al. 1996) to greater than 60 days (Klaassen and Kadoum 1979; deNoyelles et al. 1982, Lee et al. 1995). Thus, wetlands appear to vary widely in their efficiency as pesticide dissipaters. Most of the reported variability of atrazine half-lives can be explained, however, by an area-based, first-order loss model (Crumpton 1998). If pesticide loss is due primarily to adsorption in organic sediments, then half-lives (derived from a volume-based, first-order model) are inappropriate for comparing systems having different depths. The published results, however, are consistent with an area-based, first-order model in which surfaces such as sediment and litter provide most of the active sites for pesticide adsorption and in which loss rates are limited by transport to these sites. Moreover, if pesticide-humus complexes are the ultimate fate of adsorbed pesticides, models should accurately predict not only pesticide flux from wetland water to sediment, but also subsequent pesticide desorption from wetland sediments if contamination events are followed by a flush of pesticide-free water.

A concern is the extent to which the case of atrazine can be generalized to include other pesticides. For short-lived pesticides, degradation might be expected to compete effectively with adsorption in wetland systems. Because of their relatively labile nature, however, these pesticides may be less common contaminants of receiving waters in agricultural watersheds. If adsorption is the dominant fate of most pesticides of concern, then wetland assimilative capacity for pesticides in general will be simpler to understand and model.

Research Needs

Information on the quantity and distribution of pesticides in wetlands is needed before informed predictions of their toxicological impact to wetland flora and fauna can be made. Unfortunately, there are currently too few data on too few chemicals to enable more than superficial evaluations. We contend that focusing field research effort on the environmental fate of a wide suite of pesticides will not be productive, as the results are likely to be both chemical- and site-specific without general applicability to the entire Great Plains. Instead, we advocate the wider use of predictive models, with validation based on field data for a few selected pesticides monitored under

a well-defined range of environmental conditions. A caveat is that before such models can perform adequately, additional model development and testing under conditions typical of prairie wetlands are needed. Particular emphasis should be placed on the roles of chemical adsorption to surfaces in the high area to volume environment of prairie wetlands, and the magnitude and determinants of photolysis, particularly under a scenario of increased input of ultraviolet radiation. Therefore, we feel that future research should adopt process-oriented rather than case-study approaches to pesticide distribution in wetlands.

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References

- Alvord, H. H. and R. H. Kadlec. 1996. Atrazine fate and transport in the Des Plaines wetlands. *Ecological Modelling* 90:97-107.
- Anonymous. 1947-1989. Herbicides used for agricultural weed control in western Canada. Manitoba Department of Agriculture, Economics Branch, Statistics Section.
- Arts, M. T., J. V. Headley, and K. M. Peru. 1996. Persistence of herbicide residues in *Gammarus lacustris* (Crustacea: Amphipoda) in prairie wetlands. *Environmental Toxicology and Chemistry* 15:481-88.
- Batt, B. D. J., M. G. Anderson, C. D. Anderson, and F. D. Caswell. 1989. The use of prairie potholes by North American ducks. In *Northern Prairie Wetlands*, ed. A. van der Valk, 204-27. Ames: Iowa State University Press.
- Burkhard, N. and J. A. Guth. 1976. Photodegradation of atrazine, atraton and ametryne in aqueous solution with acetone as a photosensitizer. *Pesticide Science* 7:65-71.

- Caswell, F. D. and R. C. Bazin. 1997. Prairie waterfowl status report: a briefing document (July 1997). Winnipeg, MB: Canadian Wildlife Service.
- Cessna, A. J. and D. C. G. Muir. 1988. Photochemical transformations. In *Environmental Chemistry of Herbicides, Volume 2*, ed. R. Grover and A. J. Cessna, 199-263. Boca Raton, FL: CRC Press.
- Crumpton, W. G. Unpublished data.
- Crumpton, W. G., S. W. Fisher, T. M. Isenhardt, M. P. Matter, and A. G. van der Valk. 1994. Transformations and fate of nitrate and atrazine in freshwater wetlands. Ames, IA: Project completion report, Leopold Center for Sustainable Agriculture.
- Crumpton, W. G., G. Atchison, C. Rose, E. Seabloom, S. Beauvais, J. Stenback, and S. Brewer. 1997. Experimental determination of ecological fate and effects of agrichemicals in surface waters of the western cornbelt ecoregion of the United States. Washington, DC: US Environmental Protection Agency, Project completion report.
- deNoyelles, F., W. D. Kettle, and D. E. Sinn. 1982. The responses of plankton communities in experimental ponds to atrazine, the most heavily used pesticide in the United States. *Ecology* 63:1285-93.
- Dézy, J. 1996. Fate and effects of triallate in a prairie wetland. Master's thesis, University of Saskatchewan.
- Detenbeck, N. E., R. Hermanutz, K. Allen, and M. C. Swift. 1996. Fate and effects of the herbicide atrazine in flow-through wetland mesocosms. *Environmental Toxicology and Chemistry* 15:937-46.
- Dieter, C. D., W. G. Duffy, and L. D. Flake. 1995. Environmental fate of phorate and its metabolites in northern prairie wetlands. *Journal of Freshwater Ecology* 10:103-9.
- Donald, D. B. and J. Syrgiannis. 1995. Occurrence of pesticides in prairie lakes in Saskatchewan in relation to drought and salinity. *Journal of Environmental Quality* 24:266-70.
- Environment Canada. 1996. *The State of Canada's Environment - 1996*. Ottawa, ON: Government of Canada.
- Fintschenko, Y., E. M. Thurman, F. deNoyelles, and D. G. Huggins. 1995. The fate and degradation of cyanazine in wetlands. Preprint of paper presented at the 209th ACS National Meeting, 35:274-77. Anaheim, CA: American Chemical Society, Division of Environmental Chemistry.
- Forsyth, D. J., P. A. Martin, and G. G. Shaw. 1997. Effects of herbicides on two submersed aquatic macrophytes, *Potamogeton pectinatus* L. and

- Myriophyllum sibiricum* Komarov, in a prairie wetland. *Environmental Pollution* 95:259-68.
- Frankforter, J. D. 1995. Association between local land use and herbicide concentrations in wetlands of the Platte River Basin, Nebraska. In *Versatility of Wetlands in the Agricultural Landscape*, ed. K. L. Campbell, 539-48. Tampa, FL: American Society of Agricultural Engineers.
- Giddings, J. M., R. C. Biever, M. F. Annunziato, and A. J. Hosmer. 1996. Effects of diazinon on large outdoor pond microcosms. *Environmental Toxicology and Chemistry* 15:618-29.
- Giddings, J. M., R. C. Biever, and K. D. Racke. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environmental Toxicology and Chemistry* 16:2353-62.
- Goldsborough, L. G. and D. J. Brown. 1993. Dissipation of glyphosate and aminomethylphosphonic acid in water and sediments of boreal forest ponds. *Environmental Toxicology and Chemistry* 12:1139-47.
- Goldsborough, L. G. and G. G. C. Robinson. 1983. The effect of two triazine herbicides on the productivity of freshwater marsh periphyton. *Aquatic Toxicology* 4:95-112.
- Goldsborough, L. G. and G. G. C. Robinson. 1985. Effect of an aquatic herbicide on sediment nutrient flux in a freshwater marsh. *Hydrobiologia* 122:121-28.
- Goldsborough, L. G. and G. G. C. Robinson. 1996. Pattern in wetlands. In *Algal Ecology in Freshwater Benthic Ecosystems*, ed. R. J. Stevenson, M. L. Bothwell, and R. L. Lowe, 77-117. San Diego, CA: Academic Press.
- Grover, R., D. T. Waite, A. J. Cessna, W. Nicholaichuk, D. G. Irvin, L. A. Kerr, and K. Best. 1997. Magnitude and persistence of herbicide residues in farm dugouts and ponds in the Canadian prairies. *Environmental Toxicology and Chemistry* 16:638-43.
- Grue, C. E., M. W. Tome, T. A. Messmer, D. B. Henry, G. A. Swanson, and L. R. DeWeese. 1989. Agricultural chemicals and prairie pothole wetlands: Meeting the needs of the resource and the farmer—U.S. perspective. *Transactions of the North American Wildlife and Natural Resources Conference* 54:43-58.
- Gummer, W. D. 1980. Pesticide monitoring in the prairies of western Canada. In *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, ed. B. K. Afghan and D. Mackay, 345-72. New York: Plenum Press.

- Gurney, S. E. and G. Jones. 1997. Toxic algae occurrence and distribution in Manitoba surface waters. *Proceedings of the Rural Water Quality Symposium*, 99-111. Winnepeg, MB: Canadian Water Resources Association.
- Hartzler, R., W. Wintersteen and B. Pringnitz. 1997. Pesticides used in Iowa crop production in 1995. Ames: Iowa State University Extension Pamphlet PM-1718.
- Huckins, J. N., J. D. Petty, and D. C. England. 1986. Distribution and impact of trifluralin, atrazine, and fonofos residues in microcosms simulating a northern prairie wetland. *Chemosphere* 15:563-88.
- Johnson, B. T. 1986. Potential impact of selected agricultural chemical contaminants on a northern prairie wetland: A microcosm evaluation. *Environmental Toxicology and Chemistry* 5:473-85.
- Kenaga, E. E. and C. A. I. Goring. 1980. Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota. In *Aquatic Toxicology*, ed. J. G. Eaton, P. R. Parrish and A. C. Hendricks, 78-115. Philadelphia, PA: American Society for Testing and Materials, ASTM STP 707.
- Klaassen, H. E. and A. M. Kadoum. 1979. Distribution and retention of atrazine and carbofuran in farm pond ecosystems. *Archives of Environmental Contamination and Toxicology* 8:345-53.
- LaBaugh, J. W., T. C. Winter, V. A. Adomaitis, and G. A. Swanson. 1987. Hydrology and chemistry of selected prairie wetlands in the Cottonwood Lake area, Stutsman County, North Dakota, 1979-82. Denver, CO: U.S. Geological Survey Professional Paper 1431.
- Lee, K. E., D. G. Huggins, and E. M. Thurman. 1995. Effects of hydrophyte community structure on atrazine and alachlor degradation in wetlands. In *Versatility of Wetlands in the Agricultural Landscape*, ed. K. L. Campbell, 525-38. Tampa, FL: American Society of Agricultural Engineers.
- Leonard, R. A. 1988. Herbicides in surface waters. In *Environmental Chemistry of Herbicides, Volume 1*, ed. R. Grover, 45-87. Boca Raton, FL: CRC Press.
- Mackay, D. 1979. Finding fugacity feasible. *Environmental Science and Technology* 13:1218-23.
- Mackay, D., M. Joy, and S. Paterson. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. *Chemosphere* 12:981-97.
- Mackay, D. and S. Paterson. 1993. Mathematical models of transport and fate. In *Ecological Risk Assessment*, ed. G. W. Suter, 129-52. Boca Raton, FL: Lewis Publishers.

- Manitoba Agriculture 1997. *Guide to Crop Protection*. Winnipeg, MB: Manitoba Department of Agriculture.
- Matter, M. P. 1993. Sorption kinetics of atrazine and hydroxyatrazine in freshwater wetlands. Master's thesis, Iowa State University.
- Mitsch, W. J. and J. G. Gosselink. 1993. *Wetlands*, 2nd edition. New York: Van Nostrand Reinhold.
- Muir, D. C. G. 1988. Dissipation and transformations in water and sediment. In *Environmental Chemistry of Herbicides, Volume 2*, ed. R. Grover and A. J. Cessna, 1-88. Boca Raton, FL: CRC Press.
- Muir, D. C. G. and N. P. Grift. 1987. Herbicide levels in rivers draining two prairie agricultural watersheds (1984). *Journal of Environmental Science and Health B22*:259-84.
- Muir, D. C. G. and N. P. Grift. 1991. Personal communication to senior author. Winnipeg, MB: Freshwater Institute.
- Muir, D. C. G., D. F. Kenny, N. P. Grift, R. D. Robinson, R. D. Titman, and H. R. Murkin. 1991. Fate and acute toxicity of bromoxynil esters in an experimental prairie wetland. *Environmental Toxicology and Chemistry* 10:395-406.
- Muir, D. C. G., A. L. Yarechewski, and B. R. Neal. 1992. Influence of surface films on the fate of deltamethrin following aerial application to prairie ponds. *Environmental Toxicology and Chemistry* 11:581-91.
- Robarts, R. D. and M. J. Waiser. 1998. Effects of atmospheric change and agriculture on the biogeochemistry and microbial ecology of prairie wetlands. *Great Plains Research* 8:113-36.
- Robarts, R. D., D. B. Donald, and M. T. Arts. 1995. Phytoplankton primary production of three temporary northern prairie wetlands. *Canadian Journal of Fisheries and Aquatic Sciences* 52:897-902.
- Sheehan, P. K., A. Baril, P. Mineau, D. K. Smith, A. Harfenist, and W. K. Marshall. 1987. The impact of pesticides on the ecology of prairie-nesting ducks. Technical Report Series No. 19, Ottawa, ON: Canadian Wildlife Service.
- Smith, A. E., D. Waite, R. Grover, L. A. Kerr, L. J. Milward, and H. Sommerstad. 1988. Persistence and movement of picloram in a northern Saskatchewan watershed. *Journal of Environmental Quality* 17:262-68.
- Smith, J. H., D. C. Bomberger Jr., and D. L. Haynes. 1981. Volatilization rates of intermediate and low volatility chemicals from water. *Chemosphere* 10:281-89.

- Solomon, K. R., D. B. Baker, R. P. Richards, K. R. Dixon, S. J. Klaine, T. W. La Point, R. J. Kendall, C. P. Weisskopf, J. M. Giddings, J. P. Giesy, L. W. Hall, and W. M. Williams. 1996. Ecological risk assessment of atrazine in North American surface waters. *Environmental Toxicology and Chemistry* 15:31-76.
- Southwood, J. M., R. C. Harris, and D. Mackay. 1989. Modeling the fate of chemicals in an aquatic environment: the use of computer spreadsheet and graphics software. *Environmental Toxicology and Chemistry* 8:987-96.
- Southwood, J. M., D. C. G. Muir, and D. Mackay. 1998. Modeling agrochemical dissipation in surface microlayers following aerial deposition. *Chemosphere* 36. In press.
- Thurman, E. M., D. A. Goolsby, M. T. Meyer, and D. W. Kolpin. 1991. Herbicides in surface waters of the midwestern United States: the effect of spring flush. *Environmental Science and Technology* 25:1794-96.
- Tome, M. W., C. E. Grue, and L. R. DeWeese. 1991. Ethyl parathion in wetlands following aerial application to sunflowers in North Dakota. *Wildlife Society Bulletin* 19:450-57.
- van der Kamp, G. and M. Hayashi. 1998. The groundwater recharge function of small wetlands in the semi-arid northern prairies. *Great Plains Research* 8:39-56.
- Vincent, W. F. and S. Roy. 1993. Solar ultraviolet-B radiation and aquatic primary production: damage, protection, and recovery. *Environmental Review* 1:1-12.
- Waiser, M. J. and R. D. Robarts. 1997. Impacts of a herbicide and fertilizers on the microbial community of a saline prairie lake. *Canadian Journal of Fisheries and Aquatic Sciences* 54:320-29.
- Waite, D. T., R. Grover, N. D. Westcott, H. Sommerstad, and L. Kerr. 1992. Pesticides in groundwater, surface water and spring runoff in a small Saskatchewan watershed. *Environmental Toxicology and Chemistry* 11:741-48.
- Waite, D. T., R. Grover, N. D. Westcott, D. G. Irvine, L. A. Kerr, and H. Sommerstad. 1995. Atmospheric deposition of pesticides in a small southern Saskatchewan watershed. *Environmental Toxicology and Chemistry* 14:1171-75.
- Zepp, R. G. and P. F. Schlotzhauer. 1983. Influence of algae on photolysis rates of chemicals in water. *Environmental Science and Technology* 17:462-68.