Descriptive and experimental studies on the biotic and abiotic determinants of selected pesticide concentrations in prairie wetland water columns

by

Bruce Friesen-Pankratz

A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
For the Degree of

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Abstract

The determinants of high use agricultural pesticide concentrations in the water columns of Prairie Pothole Region (PPR) wetlands were examined to evaluate if these ecosystems had characteristics of pesticide sinks. For an ecosystem to function as a pesticide sink it needs to receive, retain, and reduce pesticides.

A survey of sixty PPR wetlands (distance between two farthest sites 1,700 km) was conducted to determine the extent to which they received high use pesticides (atrazine and lindane). Sixty-two percent of the wetlands were contaminated with either atrazine or lindane. Pesticide presence was directly related to wetland proximity to pesticide use and precipitation prior to sampling. In June-July lindane presence was positively correlated with phytoplankton concentration; however, in August lindane presence was negatively correlated with phytoplankton concentration.

Laboratory and *in situ* (Delta Marsh, MB) experiments showed that phytoplankton can determine pesticide water column concentrations. For instance, phytoplankton can sorb lindane and remove it from the water column through sedimentation. The extent of pesticide sorption to phytoplankton (*Selenastrum capricornutum*) was directly related to the pesticides' octanol-water partition coefficient. Sorption to phytoplankton decreased volatilization of the pesticide trifluralin. The presence of wetland water column conditions (such as phytoplankton and other particulate matter) increased degradation of atrazine, lindane, and, glyphosate. *In situ* experiments did not detect any atrazine or lindane photolysis. The limited amount of ultraviolet penetration, due to attenuation by aquatic macrophytes, suspended particulates, and dissolved organic carbon, prevented photolysis from being a significant pesticide reduction mechanism in the studied wetlands.

PPR wetlands do posses characteristics of pesticide sinks in that they can receive, retain, and reduce pesticide concentrations. This understanding of wetlands as pesticide

sinks will be useful in managing natural and constructed wetlands. Wetland managers should be aware of the high percentage of wetlands that are at risk of receiving pesticides as these may alter ecosystem dynamics. Furthermore, knowledge of the role of algae in determining pesticide concentrations could be used to manage constructed wetlands so as to maximize pesticide retention and reduction.

Acknowledgements

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The research presented in this thesis truly represents a journey. Thanks to the above mentioned people and organizations I not only completed the journey but I enjoyed the ride.

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Chapter 1: Introduction

Agriculture of the North American Prairie Pothole Region (PPR) has always implemented measures to protect crops from pest damage. Early pest control strategies included primarily physical control measures such as burning and tilling fields (National Research Council 1996). Shortly after the conclusion of World War II, pesticide application became the primary means of pest control (Cunningham 1997). The term pesticide is a general term referring to chemicals which kill or control pest organisms such as insects, weeds, and fungi (Ware 1999). The majority of agricultural pesticides used in the PPR are xenobiotic meaning that they are of anthropogenic origin (Manitoba Agriculture and Food 2001).

Pesticides applied to agricultural fields have the potential to be transported into surrounding environments. Wetlands could potentially be the PPR environment most at risk of agricultural pesticide contamination. A reason for this is due to the abundant number of PPR wetlands (1.04 million hectares of wetlands in North and South Dakota alone, Kantrud *et al.* 1989a), these wetlands are often in close proximity to agricultural fields (Figure 1).

Once in a wetland the impact of a pesticide will be a function of its environmental fate. If a pesticide is rapidly degraded its effect on the environment would be expected to be minimal. Conversely, if a pesticide is persistent and readily bioavailable, it may have a great impact on the wetland ecosystem. Pesticide fate in aquatic ecosystems such as lakes, rivers, and groundwater has been extensively studied (e.g., Gould 1972, Meyer and Thurman 1996). However, relatively few studies have examined pesticide fate in wetland ecosystems (Goldsborough and Crumpton 1998, Davis and Froend 1999). Environmental conditions in prairie wetlands differ from other aquatic environments in which pesticide fate has been studied. Wetlands are typically shallower, warmer and more productive than other aquatic ecosystems (Mitsch and Gosselink 2000). Thus, extrapolation of pesticide

Figure 1. Photograph showing close spatial relationship between wetland and agriculture within the PPR.

persistence data from other aquatic environments to wetlands may be incorrect. An understanding of the determinants of pesticide concentrations in wetlands is needed in order to reduce the risk of wetland contamination and to evaluate the value of wetlands as pesticide sinks.

1.1. Prairie Pothole Region

The Prairie Pothole Region covers an area of 715,000 km^2 (Euliss *et al.* 1999) and extends across three Canadian provinces and five American states (Figure 2). The PPR corresponds to the extent of glacier movement during the Pleistocene Epoch (Mitsch and Gosselink 2000). The overall landscape of the PPR can be described as flat to gently rolling (Sheehan *et al.* 1987). The general geology of the PPR consists of a thin layer of glacial drift which covers stratified sedimentary Mesozoic and Cenozoic rock (Winter 1989). The main soil zones found in the PPR are the Black, Brown, and Dark Brown Soil Zones (Figure C2; Sheehan *et al.* 1987). The climate of the PPR is continental (Winter 1989), characterized by extreme temperatures ranging from 40°C in the summer to -40°C in the winter (Winter 1989). The PPR climate can also be described as being semi- arid and wetlands have a negative water balance with respect to the atmosphere (Winter 1989). Within the PPR there is a north to south gradient of decreasing precipitation as well as a west to east gradient of decreasing precipitation (Euliss *et al.* 1999). The PPR climate is also characterized by wet-dry cycles in which years of drought can be followed by years of abundant rainfall (Winter 1989). Tall grass, short grass, and mixed grass prairie can be found in the PPR (Ducks Unlimited 2001). In addition, the northern portion of the PPR contains aspen parkland, which is characterized by deciduous forests of poplar (*Populus balsamifera*) and quaking aspen (*P. tremuloides*) (Greenwood *et al.* 1995).

1.1.1 Wetlands

Wetland types

There are a number of ways to classify wetlands (Cowardin *et al.* 1979, Weller 1994, Environmental Protection Agency (EPA) 1995, Warner and Rubec 1997, Mitsch and

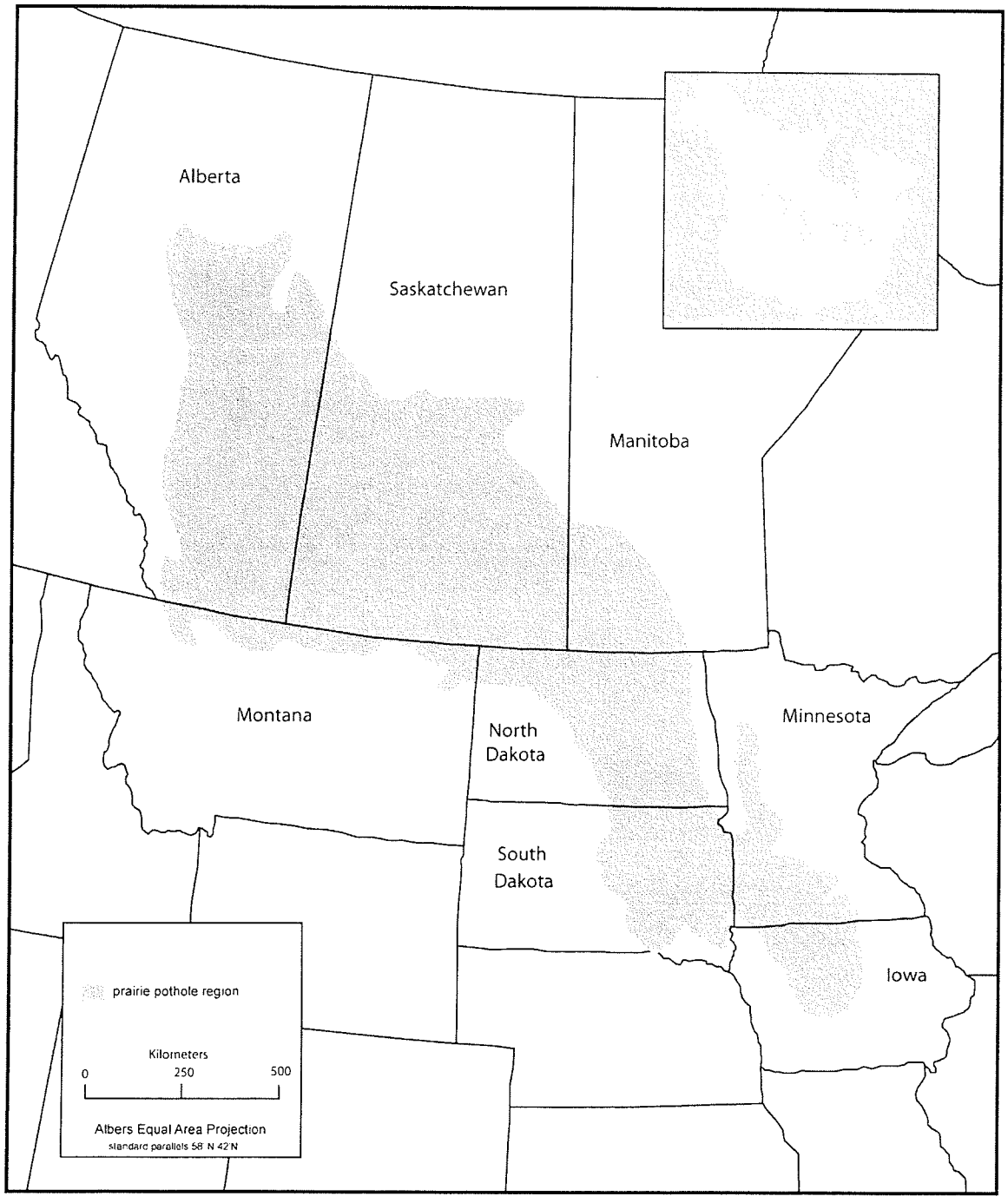


Figure 2. Map of the Prairie Pothole Region of North America.

Gosselink 2000). As the majority of the PPR lies within Canada (Figure 2) I will be using the Canadian Wetland Classification Scheme in my discussion. This classification scheme recognizes five wetland classes based on the "overall genetic origin of the wetland ecosystem and the nature of the wetland environment" (Warner and Rubec 1997) (Table 1). The most abundant wetland class found in the PPR is the marsh (Warner and Rubec 1997).

Most of wetlands in the PPR prairies are of glacial origin (Sheehan *et al.* 1987). During the Pleistocene Epoch when the glacier receded numerous topographical depressions were left behind (Winter 1989, Mitsch and Gosselink 2000). Later many of these depressions filled with water to form wetlands. They are often called potholes because they tend not to have permanent surface inflow or outflow channels (Winter and Woo 1990). Instead they receive water primarily from precipitation, surface runoff and groundwater inflow and lose water primarily through evaporation, transpiration and groundwater outflow (Winter 1989, Winter and Rosenberry 1995). Depending on the amount of precipitation, there can be great seasonal and annual variability in the number of pothole depressions that contain water (Kantrud *et al.* 1989a, Larson 1993, LaBaugh *et al.* 1996). Pothole wetlands are usually classified based on their water permanency (Stewart and Kantrud 1971, Sheehan *et al.* 1987, Warner and Rubec 1997) (Table 2).

Wetland societal values

PPR wetland functions can have corresponding societal values associated with them (Preston and Bedford 1988, Bond *et al.* 1992, Woodward and Wui 2001). For the purpose of the current discussion I will be addressing wetland functions and societal values by looking at the following general categories: wildlife habitat, hydrologic functions, and biogeochemical functions.

Wetlands are able to support a wide array of wildlife due to their unique position as environmental transition zones (Mitsch and Gosselink 2000). Waterfowl are one important group of wildlife that uses the wetland habitat and it has been estimated that the

Table 1 Description of the Canadian Wetland Classification system (Warner and Rubec 1997).

Wetland Class	Characteristics
Bog	Surface raised or level with surrounding terrain; water table at or slightly below the surface and raised above the surrounding terrain; surface waters acidic; moderately decomposed *Sphagnum* peat with woody remains of shrubs; most frequently dominated by *Sphagnum* mosses with tree, shrub or treeless vegetation cover; thickness of peat exceeds 40 cm
Fen	Surface is level with the water table, with water flow on the surface and through the subsurface; fluctuating water table which may be at, or a few centimeters above or below the surface; decomposed sedge or brown moss peat; graminoids and shrubs characterize the vegetation cover; thickness of peat exceeds 40 cm
Swamp	Peatland and mineral wetland; water table at or below the surface; highly decomposed weedy peat and organic material; coniferous or deciduous tress or tall shrub vegetation cover
Marsh	Mineral wetlands; shallow surface water which fluctuates dramatically; little accumulation of organic material and peat of aquatic plants; emergent aquatic macrophytes largely rushes, reeds, grasses, and sedges and some floating aquatic macrophytes
Shallow open water	Transitional between those wetlands that are saturated or seasonally wet (i.e., bog, fen, marsh, or swamp) and permanent, deep water bodies (i.e., lakes) that have a developed profundal zone

Table 2. Wetland classification based on water permanency (Stewart and Kantrud 1971, Sheehan *et al.* 1987).

Wetland Class	Wetland type	Water permanency	Predominant vegetation
I	Ephemeral	Water disappears in days to weeks	Wet meadow species
II	Temporary	Retain up to 50 cm of water for 4 to 12 weeks	Emergent
III	Seasonal	Generally have water throughout summer except during droughts	Emergent
IV	Semi-permanent	Contain water levels between 70 to 150 cm and do not dry out for several years	Emergent and submerged
V	Permanent	Permanently contain water levels up to 3 m in depth	Emergent and submerged

PPR of North America is responsible for 50 to 70% of the continent's waterfowl production (Batt *et al.* 1989, Millar 1989). Aside from waterfowl, wetlands also provide habitat for numerous other animals including migratory birds, mammals, amphibians, reptiles, fish, and invertebrates (Hubbard 1988, Fritzell 1989, Peterka 1989, Graff and Middleton 2003).

The wildlife wetlands support provides opportunities for people to enjoy nature through a variety of activities including bird watching, fishing, and hunting. Associated with the above recreational value of wetlands is an economic value. As people journey to wetlands for recreation they tend to spend money in the nearby communities on lodging, food, and supplies (Sorenson 1975, Gray *et al.* 1992, Wandschneider 1993, Wells 1999). The National Survey of Fishing, Hunting, and Wildlife Associated Recreation estimated that in 1991, $1.3 billion was spent on migratory waterfowl hunting in the US (Ducks Unlimited 2002). Landowners can also generate money by leasing their wetlands for recreational uses including hunting and fishing (Uhlig 1961).

The hydrological functions of wetlands can also directly impact nearby communities. Wetlands provide areas of water storage after precipitation events (Ludden *et al.* 1983, Hubbard and Linder 1986) and in so doing reduce downstream flood peaks and the severity of flood damage (Ogawa and Male 1986, Kittelson 1988, Preston and Bedford 1988, Miller and Nudds 1996, Juliano 1999). Another hydrological function of some prairie wetlands is in groundwater recharge (Meyboom 1966, Winter 1989, LaBaugh *et al.* 1998, van der Kamp and Hayashi 1998). Groundwater recharge is of great societal value as it provides groundwater for irrigation and drinking water (Poincelot 1986). For example, in Saskatchewan over 50% of the rural population uses groundwater for its domestic supply (Prairie Farm Rehabilitation Administration 2003).

Biogeochemical functions of wetlands can also have societal value. Wetlands are involved in the cycling of numerous elements including carbon (Mitsch and Gosselink 2000). The knowledge of the role of wetlands in sequestering carbon is still in its infancy

(Patrick 1994, Wetlands and Carbon Sequestration Workshop 1999). If wetlands function as net carbon sinks then they might affect the global climate by removing carbon from the atmosphere (Wetlands and Carbon Sequestration Workshop 1999, Wylynko 1999).

Another biogeochemical function of wetlands that can be of societal value is their ability to improve water quality, in part by reducing the suspended sediment load. Water flowing into wetlands experiences a decrease in velocity caused by the low gradient in wetlands and the high vegetation (Kadlec and Knight 1996). With a reduction in velocity, suspended sediments will tend to settle out of the water column (Boto and Patrick 1978, Gleason and Euliss 1998). The utilization and transformation of nutrients by wetland organism can also reduce the nutrient load of water flowing through a wetland (Kadlec and Knight 1996). There is also growing evidence that wetlands may have the capacity to reduce pesticide water column concentrations via pesticide mineralization or sorption (both adsorption and absorption) (McKinlay and Kasperek 1999, Kao *et al.* 2001, Larsen *et al.* 2001, Moore *et al.* 2001a,b, Runes *et al.* 2001a,b, Cheng *et al.* 2002, Moore *et al.* 2002). The ability of PPR wetlands to improve water quality is of value to society as both natural and constructed wetlands can be used as forms of wastewater treatment (P. McGarry, PFRA Manitoba, pers. comm., Pankratz 1995, CH2M Gore and Storrie Limited 1998).

Wetland conservation, restoration, and creation

In the past, farmers in North America tended to view wetlands as wastelands because they reduced the area of arable land (Aus 1969, Lynch-Stewart 1983). It is estimated that over half of the northern prairie wetlands in Canada and the US have been drained since European settlement (Lands Directorate 1986, Leitch 1989, Dahl 1990). Having gained an appreciation for the many values of wetlands, Canada and the US governments are now striving for no net-loss of their wetlands (Lynch-Stewart 1992, Lynch-Stewart *et al.* 1996). For instance, the objective of Canada's federal policy for wetland conservation is to "promote the conservation of Canada's wetlands to sustain their ecological and socio-

economic functions now, and in the future" (Government of Canada 1991). A way in which the policy is being implemented is through an attempt at no net loss of wetland functions on federal land (Government of Canada 1991).

Although some landowners will conserve or restore wetlands solely for their aesthetic value (Walter 1990, Pyrovetsi and Daoutopoulos 1999, Anonymous 2001), others need monetary incentives (van Kooten and Schmitz 1992, Josephson 1993). Programs that are currently active in compensating landowners for conserving or restoring their wetlands include the United States Fish and Wildlife Society's Waterfowl Production Area program and the North American Waterfowl Management Plan. The non-governmental organization Ducks Unlimited has also been successful in wetland conservation. Ducks Unlimited's Conservation Plan uses a number of approaches to conserve wetlands. For instance landowners can enter into a conservation easement with Ducks Unlimited (Marrone 2002). The easement allows for wetlands to be kept in an undeveloped state while benefits to the landowner include reduced estate, income, and property taxes. Due to governmental and non-governmental incentives the amount of farmland in conservation and wetland reserve programs in PPR states rose by over 20% between 1992 and 1997 (National Agriculture Statistics Service 2001).

1.1.2 Agriculture

Types of agriculture

The climate and soil characteristics of the PPR are well suited for both crop and livestock agriculture (Leitch and Fridgen 1998). The types of crops grown on the prairies differ annually and spatially. Forecasted market prices and the development of new seed varieties influence the crops planted from year to year (Auer 1989, Morin 1999). Spatial differences in the type of crop planted within the PPR are due in part to variations in soil and climate. The major field crops on the Canadian prairies, in terms of hectares, are spring wheat (*Triticum aestivum*), canola (*Brassica napus*), and barley (*Horduem vulgare*)

(Table 3). In contrast the major crops of the American portion of the PPR are corn (*Zea mays*), soybeans (*Glycine max*), and spring wheat (Table 3).

PPR agriculture also includes livestock production. The PPR environment is suitable for cattle production as the vegetation of much of the prairies is able to provide suitable pasture and rangeland (Uresk 1986, Smith and Hoppe 2000). Swine production is another important livestock commodity in the PPR. In Manitoba pork and pork products generated over $500 million in revenue in 2001 (Manitoba Agriculture, Food and Rural Initiatives 2003). Swine production in the PPR tends to involve intensive agricultural practices (Centre for Studies in Agriculture, Law and the Environment (CSALE 1996). Intensive swine operations concentrate animals into small sterile environments. As the animals' living environment is concentrated so is the waste generated by intensive livestock operations (CSALE 1996).

A recent shift in prairie agriculture has been from small family farms to large corporate ones (D'Souzza *et al.* 1998). The average farm size in Manitoba and Saskatchewan from 1971 to 1996 increased by 45% and 36%, respectively (Statistics Canada 2001). Although economic efficiency may increase with farm size, environmental quality and rural development tend to decrease (Wilson and Tyrchniewicz 1995, D'Souzza *et al.* 1998).

Value of agriculture

As the world's population increases, PPR agricultural food production continues to be of great societal value (Cohen 1995, Canadian Wheat Board 2002). The value of agriculture to the PPR is reflected in the economy of the region (Leitch and Fridgen 1998). Income generated directly by the sale of agricultural commodities grown in the PPR generates billions of dollars. For example, in Manitoba in the year 2000, over three billion dollars were generated by agriculture. Agriculture is also of value to the PPR as it was the foundation on which most rural communities have formed (Wilson and Tyrchniewicz 1995, D'Souza *et al.* 1998).

Table 3. Top three crops, based on area seeded, in the Prairie Pothole Region of Canada (Statistics Canada 2001) and the USA (National Agriculture Statistics Service 1997).

Crop ranking	Canada (thousand hectares)	USA (thousand hectares)
1	Spring Wheat (8173)	Corn (9308)
2	Barley (4316)	Soybeans (8418)
3	Canola (3740)	Spring wheat (5565)

Agrochemical use

To increase yields, farmers in the PPR frequently use agrochemicals. Extensive use of agrochemicals by prairie farmers started shortly after World War II (Forsyth 1989, Korol and Girard 1996, Goldsborough and Crumpton 1998). The use of agrochemicals may not be sustainable as it is linked to environmental and human health risks. For example, agrochemical application on the prairies has led to the contamination of aquatic environments such as rivers (Tornes and Brigham 1997) and groundwater (Barbash and Resek 2000). Prairie wetlands have also been contaminated by agrochemicals (Neely and Baker 1989, Donald *et al.* 1999, 2001). For instance, the total phosphorous (TP) concentration of all 20 North Dakota wetlands sampled by Dentenbeck *et al.* (1996) (TP 0.11 to 6.11 mg/L P) were in the hypereutrophic range (TP > 0.100 mg/L P, Wetzel 2001). In addition, Donald *et al.* (1999) detected agricultural pesticides in over 73% of the 51 Saskatchewan wetlands they sampled.

1.2 Introduction to my study

An improved understanding of the effects of wetland conditions on pesticide fate would allow for accurate risk assessments of the impact of pesticides on wetland ecosystems. In addition, understanding the determinants of pesticide fate in wetlands would allow for an evaluation of the pesticide sink value of these environments.

The overall objective of my study was to determine if PPR wetlands have the characteristics of pesticide sinks. To be of value as a pesticide sink, PPR wetlands need to receive pesticides, retain pesticides and reduce pesticide amounts. These three "Rs" (receive, retain, and reduce) of pesticide sinks were used as a framework to design my study (Figure 3).

Receive pesticide inputs

To be a sink, an environment needs to first receive the contaminant in question (Figure 3). A few studies have been done on pesticide contamination of PPR wetlands (Donald *et al.* 1999, Anderson *et al.* 2002) but none of these studies has examined

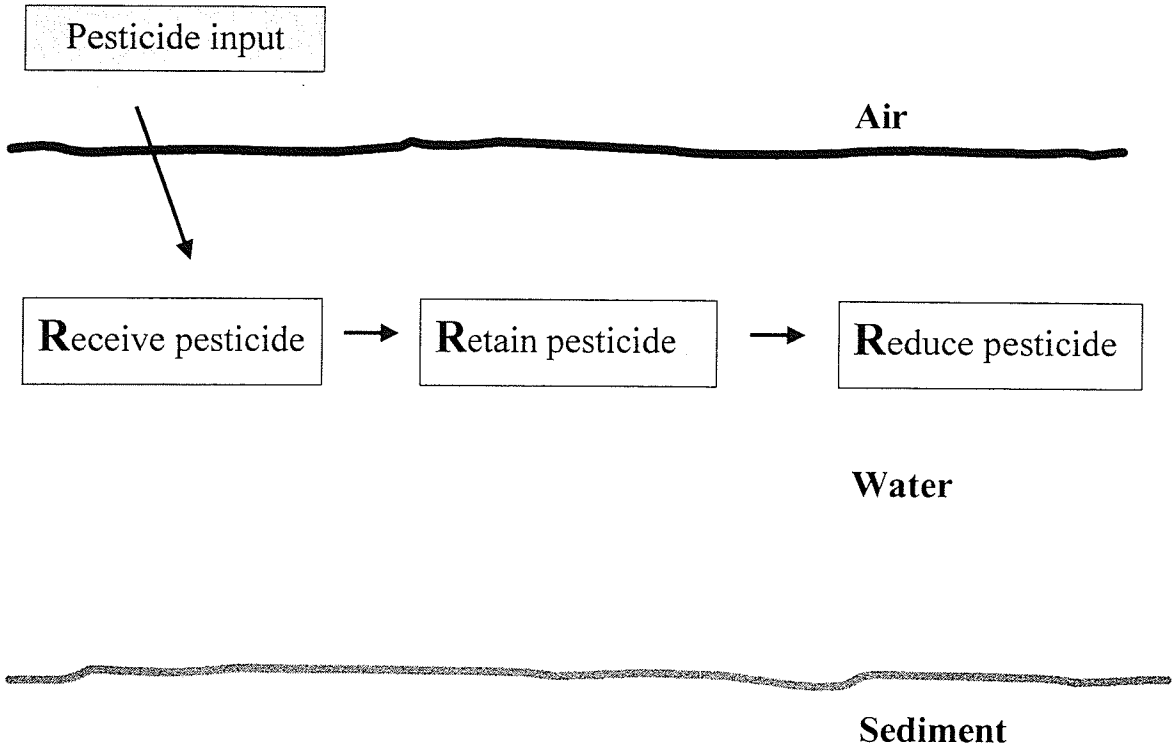


Figure 3. Conceptual diagram showing the three main processes (1. receive pesticides, 2. retain pesticide, 3. reduce pesticide concentration) that are involved in wetlands that are pesticide sinks.

pesticide concentrations over the large spatial scale represented by the PPR (715,000 km^2, Euliss *et al.* 1999). The susceptibility of wetlands to pesticide contamination across the PPR needs to be better understood in order to evaluate their value as pesticide sinks.

Retain pesticide inputs

If an ecosystem receives pesticides but cannot retain them, then the ecosystem will not have value as a pesticide sink. Pesticides that enter wetlands and remain in the water column are prone to export from the wetland via surface water flow (Krieger 2001). In contrast pesticides sorbed to wetland sediments or macrophytes will have a lower chance of being lost in surface water flow. Another potential transport mechanism of pesticides from wetlands is via volatilization (Figure 3). If significant amounts of pesticides are lost from wetlands via volatilization then this ecosystem may not function as a sink for pesticides.

Reduce pesticide

In order to function as a pesticide sink, an environment also needs to reduce the amount of the pesticide. For instance, if a wetland retains pesticides but does not reduce their concentrations they may still have negative effects on the biota which live in or visit the wetland. Pesticide amounts will be reduced if the pesticide undergoes abiotic or biotic degradation (Figure 3).

1.2.1 Pesticides studied

The study was designed to investigate aspects of the three Rs of pesticide sinks as they apply to high use pesticides in wetland environments. There are over 100 agricultural pesticide active ingredients in use in the PPR (Thelin 1998, Saskatchewan Agriculture and Food 2001). Of these, I chose to focus my study on lindane because it is recalcitrant and has been detected in a high percentage of PPR wetlands (Donald *et al.* 1999). Lindane was also chosen because at the time of the study agricultural lindane use was being phased out (A. Vaughn, Gustafson Canada, pers. comm. 2002). Thus, the effects of lowered agricultural lindane application on lindane detection in wetlands could be

examined. In addition I also studied the pesticides atrazine, glyphosate, trifluralin, and 2,4-D because these pesticides differ from lindane in their use patterns (atrazine) and chemical characteristics (Table 4).

Lindane

The insecticidal qualities of lindane (gamma-hexachlorocyclohexane) were discovered in 1941 (Smith 1991). Its use has since spanned across both the medical and agricultural sectors. For example, lindane has been used for treating ecto-parasites found on humans and animals and for controlling insect pests on a variety of crops (Saskatchewan Agriculture and Food 2001). On the Canadian prairies, this insecticide has been primarily used as a seed treatment for canola to prevent flea beetle (*Phyllotreta cruciferae*) attacks (Saskatchewan Agriculture and Food 2001). It has been estimated that over 90% of the canola planted in western Canada in the 1990s was treated with lindane (R. McLeod, Gustafson Canada, pers. comm. 1999). Due to its persistent nature, lindane use on canola in the US is prohibited (R. McLeod, Gustafson Canada, pers. comm. 1999).

Lindane kills insects by altering their neurological functions. Although the exact mechanisms involved in lindane's insecticidal ability remain uncertain, it is believed that lindane blocks ion pores and/or interferes with gamma-amino-butyric acid (GABA) receptors (Pest Management Regulatory Agency 1999). Major lindane metabolites such as alpha- and beta-hexachlorocyclohexane and beta-PCCH are also toxic to insects. Due to their lipophilic nature these chemicals (lindane and its metabolites) can bioaccumulate and reach toxic concentrations in higher trophic levels such as fish (Roche *et al.* 2000). Lindane is also a human health risk because it is a carcinogen and suspected endocrine disruptor (Table 5).

Lindane can degrade in the environment via photolysis and microbial degradation (Bintein and Devillers 1996, Fellenberg 2000, Manz *et al.* 2001). However, due to its high quantum yield (yield of photochemical products per total number of photons absorbed), photolysis is not a major environmental loss mechanism of lindane from

Table 4. Pesticide properties that determine their environmental fate. Values were selected by Hornsby *et al.* (1996) from a large data set to represent what they thought were the best estimates of the given properties.

Pesticide	Water solubility (mg/L)	Field half life (days)	Sorption coefficient (mL/g)	Vapour pressure (mm Hg)
Lindane	7	400	1100	3.30×10^{-5}
Atrazine	33	60	20	2.89×10^{-7}
2,4-D (acid)	890	10	20	8.00×10^{-6}
Glyphosate	12,000	47	24,000	0
Trifluralin	0.3	60	8000	1.10×10^{-4}

Table 5. Some human health related concerns of studied pesticides as ranked by the Pesticide Action Network (2003).

Pesticide	Endocrine disrupter	Carcinogen
Lindane	Suspected	Known
Atrazine	Suspected	Known
Glyphosate	Not likely	Not likely
Trifluralin	Suspected	Possible
2,4-D	Suspected	Possible

fields. In contrast, microbial degradation of lindane can be an important loss pathway of lindane from soil (Harner *et al.* 1999, Datta *et al.* 2000, Singh *et al.* 2000, Okeke *et al.* 2002). For instance, Okeke *et al.* (2002) reported lindane half-life of 2.5 weeks due to biodegradation by soil bacteria. To date, studies of lindane microbial degradation in wetlands have not been conducted.

Off-field transport of lindane has led to the contamination of many prairie wetlands (Donald *et al.* 1999, Anderson *et al.* 2002). Donald *et al.* (1999) detected lindane in 73% of the 51 Saskatchewan wetlands that they sampled. The most significant form of off-field transport of lindane is volatilization. As lindane on the prairies has primarily been applied as a seed treatment the risk of it volatilizing may, at first, appear to be low. However, 30% of the lindane applied as a canola seed treatment was lost from a field in Saskatchewan (Waite *et al.* 2001). As canola grows, the lindane-treated seed coats are "pushed" to or above the surface of the soil exposing lindane to the atmosphere (Waite *et al.* 2001). Lindane above the surface of the soil can have a greater volatilization potential than lindane found on the soil surface (Schneider and Schunert 1991). Transport of lindane by surface runoff can also occur but usually to a much lower extent than its loss via volatilization. Liess *et al.* (1999) reported that between 0.01% and 0.07% of applied lindane was transported off an agricultural field by surface runoff.

Atrazine

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine), a group 5 herbicide (Table 6) was introduced for agricultural use in 1958 (Cremlyn 1991, Shaffeek 1996). On the prairies, it is primarily used to control weeds in cornfields. Atrazine use within the PPR is considerably higher in the southeastern portion of the region (> 19 kg/ km^2/year), where more corn is grown, as compared to the northern portion of the region ($\leq$ 1 kg/km^2/year) (R. McLeod, Gustafson Canada, pers. comm., Thelin 1998).

The recommended time frame for atrazine application is during the two- to four-leaf stage of corn (Lyon *et al.* 1992). This pesticide is toxic to plants because it inhibits the

Table 6. Herbicide groups, mode of action, and examples of formulated products of herbicides studied in this thesis (Saskatchewan Agriculture and Food 2001).

Group	Mode of action	Example of a pesticide active ingredient	Example of formulated product used in the PPR
3	Mitotic inhibitors	Trifluralin	Rival
4	Growth regulators	2,4-D	Attain
5	Photosynthetic inhibitors	Atrazine	Laddok
9	EPSP inhibitors	Glyphosate	Roundup

Hill Reaction of photosynthesis (Esser *et al.* 1975, Ashton and Crafts 1981, Cremlyn 1991). Atrazine possesses an atom with a lone pair of electrons that can bind to the vital enzyme or the electron acceptor of the Hill Reaction (Ashton and Crafts 1981, Cremlyn 1991). By binding to this vital enzyme, atrazine prevents the transport of electrons between the primary electron acceptor of photosystem II (PSII) and plastoquinone (Ashton and Crafts 1981, Cremlyn 1991). With photosynthesis blocked, the plant will eventually die due to lack of energy. However, plants treated with atrazine usually die too quickly to attribute their death solely to a lack of nutrition. Instead, the rapid death is most likely due to membrane disruption (lipid peroxidation) by the free electrons generated when atrazine blocks PSII (Ware 1999). Metabolites such as dethylatrazine and deisoprpylatrazine are also phytotoxic (EPA 2002a). Atrazine can also have toxic affects on animals. For instance, Hayes *et al.* (2003) have linked the demasculation in leopard frogs to atrazine exposure.

Atrazine applied to agricultural fields has an average half-life of sixty days (Hornsby *et al.* 1996). Atrazine can be biodegraded by a number of naturally occurring soil microbes (Goux *et al.* 1998, Shapiro *et al.* 2000, Moorman *et al.* 2001, Rousseaux *et al.* 2001, Wackett *et al.* 2002). Goux *et al.* (1998) demonstrated that microbial communities isolated from subsurface sediments could rapidly mineralize atrazine (half-life 56 to 62 hours). If exposed to sufficient sunlight, atrazine can also be degraded by photolysis (Balmer *et al.* 2000, Gong *et al.* 2001). Gong *et al.* (2001) attributed the short half-life of atrazine (4-8 min) near the soil surface to photolysis. In addition, the triazine ring can be degraded via hydrolysis (Wolfe *et al.* 1990).

Applied atrazine that is not degraded may be available for off-field transport. The major loss of atrazine from fields is usually through surface runoff (White *et al.* 1967, Hall *et al.* 1972, Hall 1974, Hyer *et al.* 2001, Schilling and Wolter 2001, Shukla *et al.* 2001, Gaynor *et al.* 2002). Rector *et al.* (2003) reported 5% losses of applied atrazine from corn fields exposed to natural precipitation. Atrazine can also be lost from fields

through volatilization (Thurman and Cromwell 2000, Rice *et al.* 2002). Groundwater infiltration of atrazine can also occur (Verstraeten *et al.* 1999, Bayless 2001, Rowden *et al.* 2001). Accinelli *et al.* (2002) demonstrated that soil characteristics are important in determining the extent to which atrazine leached. Their results showed that atrazine concentrations in the leachate from silty loam soils (0.5% of applied) were less than from silty clay soils (2% of applied).

Glyphosate

Introduced in 1971 by Monsanto, glyphosate (*N*-phosphonomethylglycine), is a nonselective broad-spectrum post-emergent group 9 (Table 6) herbicide that is used in both agricultural and nonagricultural settings across the prairies (Duke 1988). Due to its nonselective character, glyphosate is not applied directly to actively growing crops, as it would kill both crop and weed alike. Therefore, glyphosate is used prior to planting or as a spot treatment to kill weeds (Shaffeek 1996). Glyphosate may be applied directly to glyphosate-resistant crops such as Roundup Ready canola and soybeans (Saskatchewan Agriculture and Food 2001). These crops have been genetically modified to contain resistance to glyphosate.

The application of glyphosate is usually accomplished by spraying with ground equipment (Duke 1988, Shaffeek 1996, Saskatchewan Agriculture 2001). Ground incorporation of glyphosate does not provide effective weed control because glypohosate strongly sorbs to the soil due to its high sorption coefficient (24,000 mL/g) (Ashton and Crafts 1981, Hall 1996).

In plants, glyphosate is believed to inhibit 5-enolopyruvylshikimate acid -3-phosphate (EPSP), the enzyme involved in aromatic amino acid synthesis (Jaworski 1972, Ashton and Crafts 1981, Cole 1985, Duke 1988, Hall 1996, Franz *et al.* 1997). Inhibition of EPSP by glyphosate leads to the production of the toxic intermediate shikimate-3-phosphate (Hall 1996). Glyphosate may also adversely affect plant growth hormones and photosynthesis (Cole 1985). Symptoms of plants treated with glyphosate

include necrosis (death of tissue) and chlorosis (yellowing of leaves) (Ashton and Crafts 1981, Cole 1985). Although the exact mechanism is unknown, glyphosate can also be toxic to invertebrates such as zooplankton at environmentally realistic levels (Chen *et al.* 2004). Both glyphosate and its major metabolite AMPA are practically non-toxic to fish (LC50 greater than 100 mg/L) (Monheit 2002). Based on current research pesticide regulatory agencies do not suspect any human health risks of applying glyphosate within the recommended rate (Table 5, Williams *et al.* 2000).

The sorption strength of glyphosate reduces its susceptibility to off-field transport (Edwards *et al.* 1980). Surface waters however, could receive glyphosate from agricultural fields if the chemical were sorbed to soil particles being carried by the surface water (Edwards *et al.* 1980). For instance Edwards *et al.* (1980) have reported losses of 0.5%-2% of applied glyphosate from agricultural fields.

Trifluralin

Trifluralin (2,6-dinitro-N,N-dipropyl-4(trifluoromethyl)benzenamine) a group 3 herbicide (Table 6) came into agricultural use in the 1960s (Ashton and Crafts 1981, Agriculture Canada 1989). Due to its volatility, trifluralin is not aerially applied but is incorporated into the soil (Agriculture Canada 1989, Saskatchewan Agriculture and Food 2001).

Once in a plant shoot or root trifluralin inhibits plant mitosis (Saskatchewan Agriculture and Food 2001) by preventing the polymerization of tubulin (Ashton and Crafts 1981). Without tubulin the microtubules needed for mitosis cannot be formed and mitosis ceases (Campbell *et al.* 1999). This eventually leads to the death of exposed plants. Trifluralin posses a risk to humans as it is a suspected endocrine disruptor and possible carcinogen (Table 5). Currently, trifluralin metabolites have not been investigated adequately enough to make generalizations regarding their toxicity (Pesticide Action Network 2003).

Photolysis (Balmer *et al.* 2000) and volatilization (Rice *et al.* 2002) are usually the most important processes determining the field persistence of trifluralin (Kidd and James 1991, Rice *et al.* 2002). Trifluralin strongly sorbs to soil and thus the risk of trifluralin leaching to the groundwater is low (Malterre *et al.* 1998, Russo *et al.* 2001). Malterre *et al.* (1998) reported only 1% of trifluralin had leached to a depth of five centimeters of silty clay soil over a one year period. Surface water runoff of trifluralin is also usually quite low (0.001 to 0.8% of applied, Sheets *et al.* 1972, Willis *et al.* 1975), as most of the herbicide will be sorbed to the soil. Loss of trifluralin in surface water can occur if the water velocity is high enough to move soil particles (Silburn *et al.* 2002).

2,4-dichlorophenoxyacetic acid

The group 4 herbicide (Table 6), 2,4-dichlorophenoxyacetic acid (2,4-D) was introduced shortly after World War II and is one of the oldest herbicides still in use (Templeman 1955, Cremlyn 1991, Hall 1996). Initially used primarily as a wartime defoliant (Tschirley 1969, Boffey 1971), 2,4-D has proven to provide effective agricultural control of broad leaf weeds (Shaffeek 1996). The agricultural application of 2,4-D involves either aircraft or ground equipment (Shaffeek 1996).

2,4-D behaves similar to the plant growth hormone auxin (indol acetic acid) (Loos 1975, Hall 1996). Death of 2,4-D treated plants is due to deregulated plant growth and associated complications such as unconstrained mobilization of reserves, breakdown of repair mechanisms, and loss of plant tissue function (Loos 1975, Hall 1996). Although designed as a herbicide, 2,4-D may also negatively effect animals including humans. For instance, human cases of non-Hodgkin's lymphoma have been linked to the extent of 2,4-D use within the sample area (Sandborn *et al.* 2004).

The persistence of 2,4-D in soil is extremely short with an average half-life of less than seven days (Hornsby *et al.* 1996). Degradation of 2,4-D in soil is due mostly to microbial activity (Musarrat *et al.* 2000, Crespin *et al.* 2001, Seifert *et al.* 2001).

Despite having a short soil half-life 2,4-D can be transported off fields and cause the contamination of aquatic environments (Lent *et al.* 1993, Rawn *et al.* 1999 a,b, Cessna *et al.* 2001, Donald *et al.* 2001). 2,4-D is most susceptible to off-field transport via surface runoff (Ryals *et al.* 1998, Ma *et al.* 1999). Estimates of 2,4-D loss in surface runoff vary depending on rain intensity and can be as high as 10% of applied chemical (Assmussen *et al.* 1977, Smith *et al.* 1978).

1.2.2 Study Approach

Survey and experimental studies are the two approaches used for investigating pesticide persistence in the environment. Surveys of pesticide persistence can involve periodic sampling of natural environments to determine their pesticide levels. Experimental pesticide persistence studies involve introducing a known concentration of a pesticide into an experimental unit and determining its dissipation rate. Both approaches have their related advantages and shortcomings. For instance, surveys can provide information on the extent of pesticide contamination in the environment. Surveys can also identify what factors are correlated with pesticide detection. But because surveys are descriptive (non-experimental), they are not able to accurately determine casual effects. For instance, survey data may show that an environmental variable is directly related to pesticide detection. However, it cannot be assumed that the variable increases pesticide detection, as the two may be covariates of each other or covariates with other unmeasured variables.

Controlled experiments can be designed to determine causal effects of specific variables on pesticide detection or persistence. When designing experiments the problem of scale needs to be addressed as few scientists have the luxury of conducting whole ecosystem manipulations. *In situ* mesocosms, which delineate a portion of the environment in question, are valuable study units as they are often large enough to contain the major components of an ecosystem (Graham *et al.* 1999, Rand *et al.* 2001). For example, mesocosms such as littoral enclosures would contain both the water column

and the sediment of a studied ecosystem like a wetland. If the impact of only a few wetland environmental variables on pesticide persistence is to be studied, microcosms can be used. Both microcosms and mesocosms, however, may have low accuracy due to the fact that they do not encapsulate all the components within an ecosystem (Boyle 1983). Furthermore the effects of the structural edges of experimental units can influence results (Sanford *et al.* 2001, Williams *et al.* 2002). For example, the walls of an *in situ* mesocosm would provide additional surface area for algal growth within the mesocosm as opposed to normal "un-walled" conditions in a wetland.

Given the advantages and shortcomings of each approach (Hall and Giddings 2000, Schulz *et al.* 2002), I chose a combination of approaches to investigate pesticide persistence in PPR wetlands. For instance, the survey approach would indicate the actual level and extent of atrazine and lindane contamination of PPR wetlands. Comparing atrazine and lindane levels in wetlands surveyed at different times of the year would provide a general understanding of the water column persistence of these pesticides. The experimental approach was used to determine the effect of environmental factors such as organic matter on the water column persistence of atrazine, lindane, glyphosate, trirfluralin and 2,4-D.

Study Objectives and hypotheses

In order to have value as a pesticide sink, PPR wetlands need to first receive pesticides. To gain an understanding of the extent to which PPR wetlands receive pesticides I conducted a survey of atrazine and lindane concentrations in sixty wetlands that had great spatial distribution across the PPR (Figure 4). The approach also investigated which environmental variables were related to atrazine and lindane detection in the wetlands. I hypothesized that wetland proximity to pesticide use, and precipitation prior to wetland sampling would be related to pesticide detection because both of these variables can influence the amount of pesticide transport to wetlands. I also hypothesized that wetland sediment organic matter would be related to pesticide detection in wetland

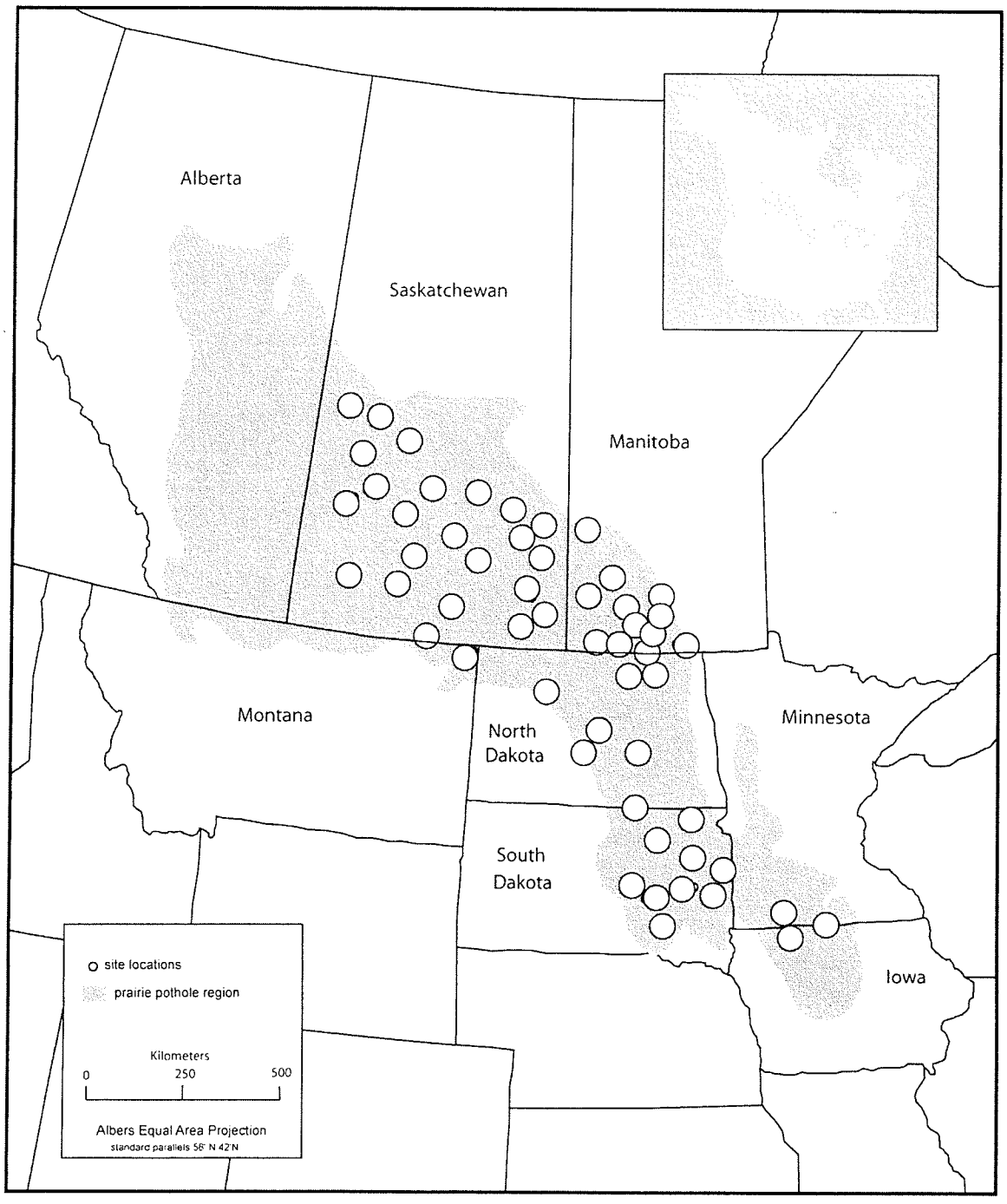


Figure 4. Map of the PPR showing the location of wetlands surveyed between 1999 and 2001 for environmental conditions and pesticide (atrazine and lindane) concentrations.

water columns because it is the component of the sediment that most readily sorbs pesticides from the water column (Karickhoff *et al.* 1979, Schellenberg *et al.* 1984, Rao 1990). If supported, this would provide further evidence for the value of Best Management Practices (BMPs) which aim to reduce pesticide transport to off-field environments (Seelig 1998). For instance, BMPs instruct that in order to limit pesticide loss in surface runoff pesticides should not be applied when rain has been forecasted. In addition if my hypothesis regarding the role of wetland sediment organic matter is supported then wetlands with pesticide sink value could be identified based on their sediment organic matter content.

Results from the survey portion of the study were used as a guide to design experiments that investigated the ability of wetlands to retain pesticides. The survey of wetlands showed that there was a relationship between lindane detection and phytoplankton chlorophyll. This relationship was investigated with microcosm and mesocosm experiments. I hypothesized that increases in phytoplankton concentrations would result in lowered pesticide water column persistence because the pesticide would be removed from the water column through sorption to phytoplankton and subsequent sedimentation.

I also investigated the relative effect of various pools of wetland organic matter (dissolved organic carbon (DOC), suspended particulate organic matter (POM), sediment organic matter, macrophytes) on pesticide water column persistence. In general, I hypothesized that as organic matter concentrations increased pesticide persistence in the water column would decrease because the pesticides would be sorbed to the organic matter. If wetland organic matter can sorb pesticides and remove them from the water column then the transport potential of the pesticides would be reduced and the wetland environment would function as a sink for the pesticide in question.

In order to retain pesticides wetlands also need to limit the extent of pesticide volatilization. I hypothesized that volatilization would be a significant loss mechanism of

the pesticide lindane from wetlands. Lindane has a relatively high vapour pressure (3.3 x 10^{-5} mm Hg, Hornsby *et al.* 1996) and is thus susceptible to volatilization. In addition the warm, thoroughly mixed water of wetlands could provide conditions that are favourable for pesticide volatilization. If this hypothesis is supported then the value of wetlands as sinks for lindane may not be high due to lindane loss via volatilization.

Photolysis of pesticides can reduce their persistence within environments. Because of the high potential for light to penetrate the entire water column in wetlands, some have speculated that pesticide photolysis may be a major pesticide dissipation route in wetland water columns (Lartiges and Garrigues 1995, Goldsborough and Crumpton 1998). The elevated levels of suspected photosensitizers such as phytoplankton and DOM may also enhance pesticide photolysis in wetlands (Goldsborough and Crumpton 1998). I hypothesized that under wetland conditions exposed to ambient ultraviolet light conditions atrazine and lindane persistence would be shorter due to greater pesticide photolysis than in reduced ultraviolet light conditions. If this hypothesis is supported it would provide further evidence for the ability of wetlands to act as sinks for the selected pesticides.

The experiments were performed in the Botany laboratory at the University of Manitoba as well as *in situ* in Delta Marsh, Manitoba (Figure 5). Delta Marsh was also the location for the mesocosm experiments. The rationale for using Delta Marsh as the location for the mesocosm experiments was as follows: 1) availability of enclosures amenable to experimental manipulation, 2) background biological and chemical literature, including work on pesticide persistence.

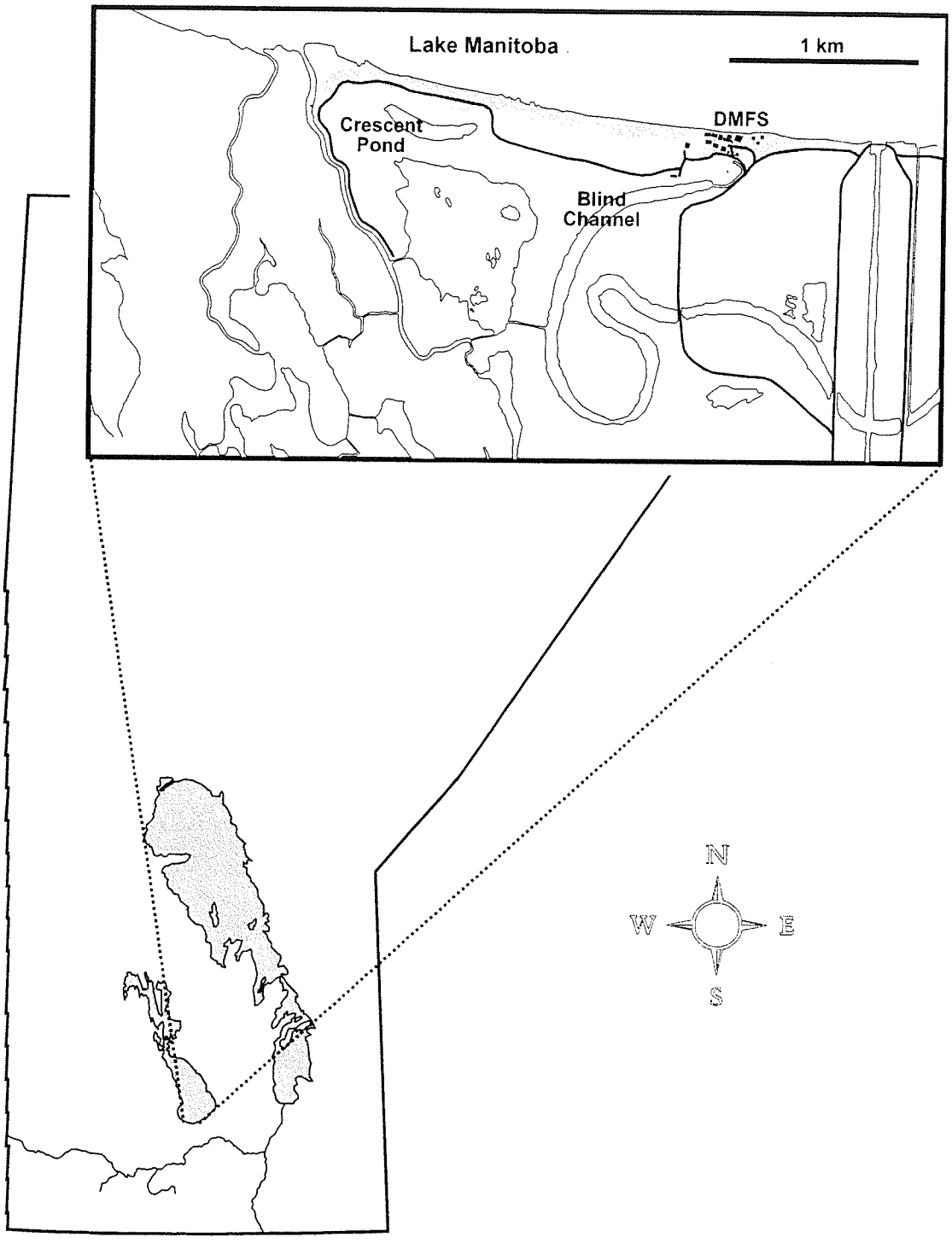


Figure 5. Map of the west side of Delta Marsh, MB showing the location of Blind Channel and Crescent Pond study sites (DMFS = Delta Marsh Field Station).

Chapter 2: Literature Review

PPR wetlands are susceptible to inputs of agrochemicals (fertilizers and pesticides) due to their close proximity to agricultural land, and their depressional orientation within the landscape (Neely and Baker 1989). Agrochemicals can enter wetlands through point and non-point contamination. Once in a wetland the fate of agrochemicals will determine the extent of impact they will have on the ecosystem.

2.1 Non-point source contamination

2.1 .1 Surface runoff

One important mechanism of agrochemical transport from fields is surface runoff (Davis *et al.* 1981, Patty *et al.* 1997, Pommel and Dorioz 1997, Nash and Halliwell 2002). Surface runoff occurs when snow melt, precipitation, or irrigation rate exceeds the infiltration rate of soil and the accumulating surface water becomes greater than the surface storage capacity (Seelig 1998, Wolfe 1999). Surface runoff flowing over agricultural fields can transport fertilizers and pesticides (North Dakota State University of Agriculture and Applied Science 1975, Neely and Baker 1989, Gallimore *et al.* 1999, Hanson and Trout 1999, Konda and Pasztor 2001) and deposit them in aquatic environments such as wetlands (Wentz 1988, Neely and Baker 1989, Page *et al.* 1995).

The characteristics of agrochemicals will determine the extent and manner to which they are lost in surface flow. Generally, chemicals that are not readily volatilized and which have long soil half-lives will be more available for transport in surface runoff (Neely and Baker 1989, Chen *et al.* 2002). The sorption ability of a chemical, usually quantified by the soil sorption coefficient K_d, is also important in determining the extent of surface water loss. Chemicals with low K_d values (<0.1) tend to travel with water as it percolates through the soil and are thus not readily available for surface water transport (Neely and Baker 1989). Chemicals that have high K_d values (>100) do not readily percolate into the soil but will instead sorb to soil particles. These chemicals will be lost

to surface flow only if the substrata they are sorbed to are eroded and transported (Frank *et al.* 1979, Ghardiri and Rose 1991). Chemicals with intermediate K_d values ($0.1 < K_d < 100$) do not infiltrate the soil readily and their adsorption to particles is weak, thus, these chemicals are frequently lost in solution to surface runoff (Neely and Baker 1989).

The amount of surface runoff and consequently the amount of chemical loss via runoff are determined by precipitation or irrigation events. The volume of precipitation or irrigation is directly related to the potential for chemical transport in surface runoff (Hall 1974, Cessna *et al.* 1994, Liess *et al.* 1996, Konda and Pasztor 2001, Mickelson *et al.* 2001). For instance Konda and Pasztor (2001) showed no detectable atrazine (applied at recommended rate of 1000 g a.i./ha) loss in surface runoff from a corn field (average slope of land 2% sandy loam) until a rainfall event of over 40 mm occurred.

The elapsed time since chemical application and surface runoff will be inversely related to the amount of chemical transport (Hall *et al.* 1972, White *et al.* 1976, Wauchope 1978, Glotfelty *et al.* 1984, Thurman *et al.* 1992, Goolsby and Battaglin 1993, Spalding *et al.* 1994, Donald *et al.* 1999, Konda and Pasztor 2001). Spalding *et al.* (1994) showed that maximum pesticide concentrations in surface water draining agricultural fields occurred one to two weeks after pesticide application and concentrations decreased as the season progressed. A survey by Thurman *et al.* 1992 also showed that the highest concentrations of triazine herbicides (30 to 40 μg/L) in surface runoff occurred from May-June shortly after pesticide application. As the season progressed pesticide concentration in the surface runoff decreased and in August less than 3 μg/L of triazine was detected. Hall *et al.* (1972) also showed how as elapsed time since atrazine application increased the amount of pesticide in surface runoff decreased (Figure 6).

The characteristics of the field will, in part, determine the extent of surface runoff and agrochemical loss. The slope of a field will be directly related to the potential for surface runoff as the greater the slope the greater the potential for surface runoff (Seelig 1998). In addition, if fields contain soils that have low water penetration there will be a

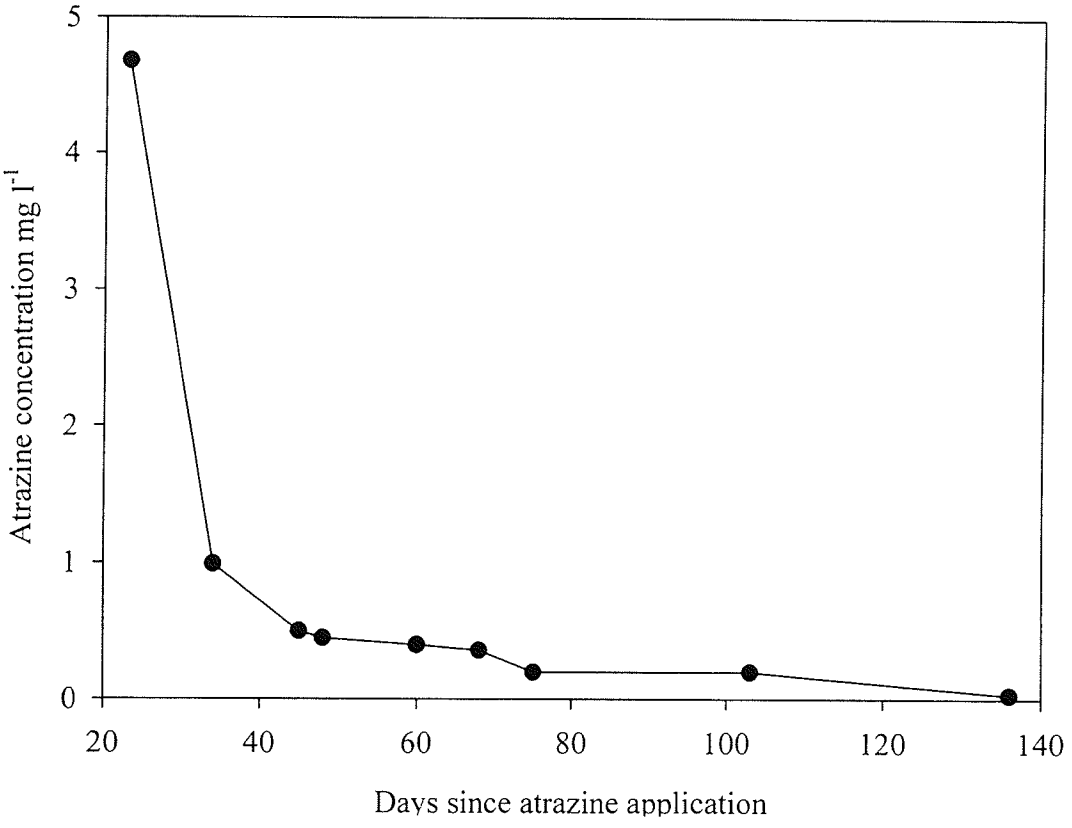


Figure 6. Relationship between atrazine concentration in surface runoff from a silty clay loam cornfield in Pennsylvania and the elapsed time since atrazine application (modified from Hall *et al.* 1972).

greater volume of runoff and a greater potential for chemical loss in the surface water (Neely and Baker 1989).

Farming practices can also determine the extent of agrochemical loss in surface runoff. The crop planted by the producer can influence runoff contamination as different crops have varying effects on the amount of soil erosion and chemical loss (Hargrave and Shaykewich 1997, Douglas *et al.* 1998). For instance Douglas *et al.* (1998) demonstrated that total nitrogen (TN) loss in the dissolved state was significantly greater (alpha = 0.05) from fields planted with winter wheat (2.5 kg/ha/year) as opposed to fields planted with spring peas (TN = 0). Hargrave and Shaykewich (1997) also demonstrated that the type of crop planted can influence the amount of nutrient loss in surface runoff. These authors showed that during the study period (1988 to 1990) TN loss from corn fields in surface runoff (478.5 kg/ha) was 99.5% greater than TN loss from alfalfa fields (2.4 kg/ha).

Agrochemical application practices and the chemical formulation used can also influence the amount of chemical transport in surface runoff. Chemicals incorporated into the soil will be less available for transport in surface runoff as opposed to those applied to the soil surface or to foliage (Timmons *et al.* 1973, Wauchope 1978, Baker and Laflen 1979, Neely and Baker 1989, Currie and Williamson 1995). Mickelson *et al.* (2001) applied atrazine (2.24 kg/ha) to agricultural fields which were either left untilled or were chisel plowed and then tilled after atrazine application. The atrazine concentration in surface water from the non-tilled fields (33 µg/L) was significantly higher (alpha = 0.1) than that from the tilled fields (10 µg/L). The formulation of a pesticide can alter its chemical characteristics (water solubility and sorption strength) and in turn its susceptibility to transport in surface runoff (Wauchope 1978, Christensen *et al.* 1993). For instance, the pesticide 2, 4-D, is more soluble in acid formulation (890 mg/L at 25°C) as compared to ester formulation (100 mg/L at 25°C) (Hornsby *et al.* 1996).

Tillage practices can affect the amount of surface water runoff and thus have the potential to affect agrochemical loss (Neely and Baker 1989, Hargrave and Shaykewich

1997, Schreiber and Cullum 1998, Green and Turner 2002). Zero and conservation tillage, can reduce the amount of surface runoff by 60% as compared to conventional tillage (Neely and Baker 1989). With a reduced amount of surface runoff the potential of agrochemical loss in surface runoff will also be reduced.

Atmospheric deposition

Agrochemicals are lost to the atmosphere most frequently through volatilization (Spencer and Cliath 1990, Majewski and Capel 1995, Seiber and Woodrow 1995, Oenema *et al.* 2001, Haith *et al.* 2002, Rice *et al.* 2002). A chemical's Henry's Law constant can be used to predict the volatilization potential of a chemical as a high Henry's Law constant represents high volatility potential and a low Henry's Law constant represents low volatility potential. The Henry's Law constant is calculated from a chemical's vapor pressure and water solubility (Equation 1) and is directly related to volatilization potential (Smith and Bomberger 1980, Choy and Reible 2000, Weiner 2000).

Equation 1: Henry's Law constant = vapor pressure/water solubility

Volatilization occurs at the interface between surfaces and air (Weiner 2000). Thus, chemicals incorporated into the soil will have a lower chance of volatilization as opposed to those that are aerially applied (Taylor *et al.* 1977, Fenn and Miyamoto 1981, Sommers *et al.* 1981, Mengel *et al.* 1982).

Loss of agrochemicals to the atmosphere occurs in two phases (Taylor *et al.* 1976, Taylor *et al.* 1977, Glotfelty *et al.* 1983, Spencer and Cliath 1990). The first phase is evaporation. The second phase is a function of the chemical's concentration in the air as well as air movement. Near the evaporative surface there is a microlayer of stagnant air where diffusion of the chemical is important in determining its loss. Once diffused away from the surface, air movement will cause the chemical to disperse. Thus, wind can increase volatilization rates by increasing chemical diffusion rates away from the

evaporative surface (Harris and Lichtenstein 1961, Hargrove 1988, Hoff *et al.* 1992, Haugen *et al.* 1998).

Agricultural practices can also influence agrochemical volatilization rates. Cultivation of fields shortly after pesticide application may increase pesticide loss to the atmosphere. Lichtenstein and Schultz (1961) applied Aldrin (4 pounds per 5 acres) to two fields of loam soil. One field they disked on a daily basis the other field they did not. At the end of three months the field that had been disked had lost 70% of the applied Aldrin whereas the un-disked field had only lost 53% of the Aldrin. The authors attributed the greater Aldrin loss in the disked field to greater volatilization as the disking would have caused a repeated exposure of incorporated pesticide to the air where it would have been available to volatilize.

Environmental conditions such as high temperatures and high soil moisture content can also increase the chance for agrochemical volatilization (Harris and Lichtenstein 1961, Turner *et al.*1977, Dorfler *et al.* 1991, Stork *et al.* 1998). For instance, Stork *et al.* (1998) showed that fenpropimorph volatilization from a field increased from 1.6% of applied pesticide at 20°C to 12% of applied pesticide at a temperature of 29°C.

Atmospheric storage of agrochemicals is usually temporary with the chemicals returning to the earth during wet (precipitation) or dry deposition events (Busser 1990, Cleeman *et al.* 1995, Waite *et al.* 1995, Bucheli *et al.*1998, Hillery *et al.* 1998, Dubus *et al.* 2000). If atmospheric deposition of agrochemicals occurs over a wetland, the wetland will become contaminated with the chemicals. Donald *et al.* (1999) documented a relationship between rainfall and pesticide concentrations in Saskatchewan wetlands. They found that 60% of wetlands that received higher rainfall (> 90 mm 15 days prior to wetland sampling) had pesticide concentrations that exceeded government guidelines for the protection of aquatic life. In contrast, 0% of wetlands that received lower rainfall (< 21 mm) had pesticide concentrations that exceeded government guidelines (0.01 mg/L).

In addition to its role in volatilization wind may also transport pesticides via soil erosion (Larney *et al.* 1999). In an experiment conducted in an agricultural field in South Dakota, Clay *et al.* (2001) demonstrated that atrazine concentrations in wind-erodible soil particles were 77% higher than the concentration found in non-wind-erodible particles. The estimated average annual wind erosion on the prairies is high. For example, on the Canadian prairies, the annual soil erosion attributed to wind is 160 million tones (Saskatchewan Interactive 2002). Due to this high amount of soil lost to wind erosion future studies should examine the input of agrochemicals to wetlands from wind-eroded soil.

2.2 Point source contamination

Like non-point source contamination, point source contamination of wetlands by agrochemicals is determined by farming practices. An agricultural practice that contributes to the point source contamination of wetlands is the aerial spraying of pesticides. Incidental, direct spraying of wetlands by spray planes can add high concentrations of pesticides to wetlands (Sheehan *et al.* 1987, Goldsborough and Crumpton 1998). For instance Tome *et al.* (1991) determined that the amount of ethyl parathion deposited on five wetlands in North Dakota (0.21 to 0.40 kg/ha) was higher than the amount deposited on the adjacent sunflower fields (0.06 to 0.12 kg/ha). Additionally, livestock allowed access to aquatic environments such as wetlands could defecate or excrete directly into the water contaminating the wetland with nutrients, bacteria and other constituents (Ritter 1999).

2.3 Ecological impacts of agrochemicals in wetlands

2.3.1 Nutrients

Many of the practices of intensive agriculture such as tillage, limited fallow rotation, and stubble burning may necessitate fertilizer additions to obtain sufficient nutrient status to generate profit-producing yields (McNabb 1999, Uri 1999). Consequently fertilizer use

in the PPR has increased over the years (Figure 7) (Harre and Bridges 1988, Goldsborough and Crumpton 1998).

Although plants require both macro- and micronutrients for their survival it is macronutrients that tend to be most limiting in agricultural soil (Ritter and Bergstrom 1999). Thus, the major ingredients of fertilizers used in the PPR are composed of macronutrients, primarily nitrogen and phosphorous formulations (Fageria *et al.* 1997, Sharpley and Rekolainen 1997) (Table 7). Nitrogen and phosphorus also tend to be the two nutrients most limiting in aquatic environments (Correll 1998). Plants require nitrogen and phosphorous for a number of processes including the synthesis of amino acids, nucleic acids and adensine triphosphate (Raven *et al.* 1986).

Direct effects of nutrients

The direct role of nutrients in determining the trophic status of aquatic environments has been explored extensively (Goldman and Horne 1983, Schindler 1988, Hecky and Kilham 1988, Elser *et al.* 1990, Wetzel 2001). In Canada, eloquent experiments by David Schindler (Schindler *et al.* 1971, Schindler and Fee 1974) revealed the importance of macronutrients in determining primary production in lakes of the Canadian Shield. Wetlands of the PPR differ chemically, physically, and biologically from the lakes of the above studies yet they tend to react to N and P additions in generally the same way: with an increase in primary production (Kiers North 2000, McDougal 2002).

There are various assemblages of wetland primary producers that may be affected by nutrient additions. These assemblages include phytoplankton, benthic algae, metaphyton, and macrophytes (Table 8). Of the four assemblages of primary producers, phytoplankton are usually the best adapted to utilize nutrient inputs to the water column (Sand-Jensen and Borum 1991). Phytoplankton are found entrained in the water column and are completely surrounded by water and any nutrients found therein. Another characteristic that enhances the ability of phytoplankton to acquire nutrients from the water column is their high surface area to volume ratio (Reynolds 1984). Experiments involving nutrient

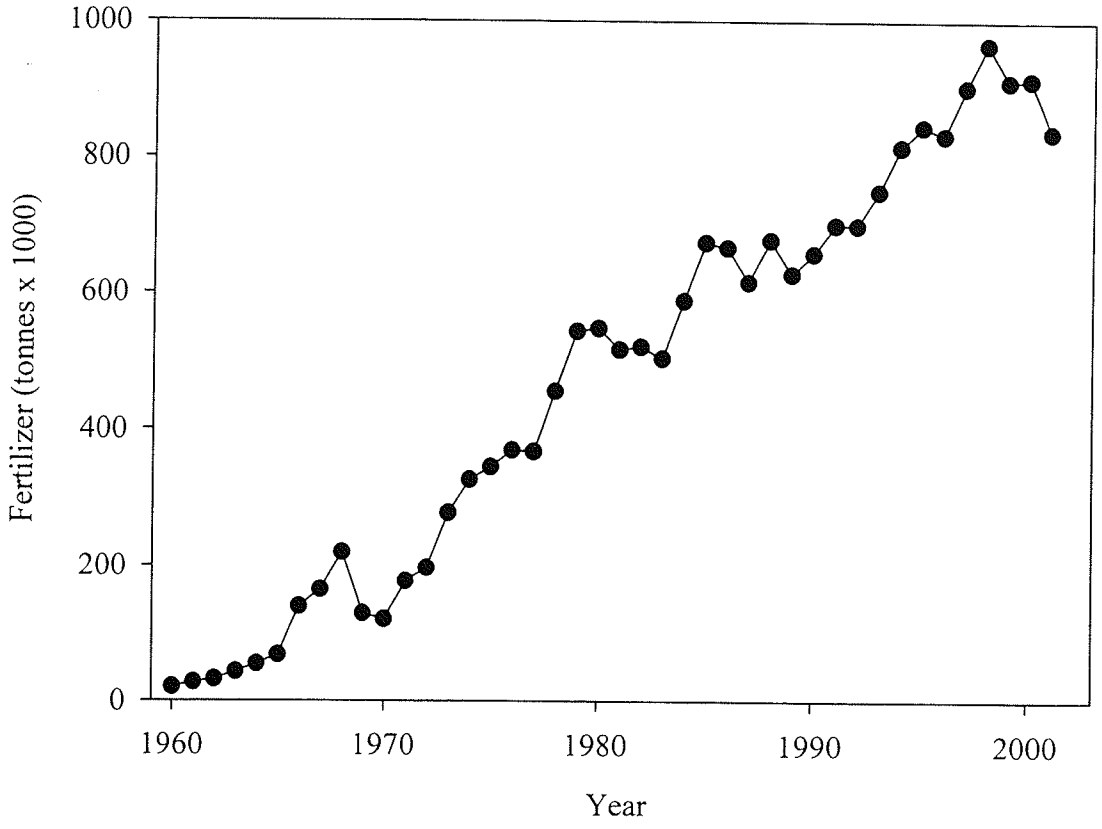


Figure 7. Annual fertilizer (nitrogen and phosphorous) sales in Manitoba. (Manitoba Agriculture, Food and Rural Initiatives 2003).

Table 7. Top three selling fertilizers (thousand tonnes) in Manitoba during the years 1999 to 2001 (Manitoba Agriculture, Food and Rural Initiatives 2003).

	Fertilizer formulation		
Year	Ammonium phosphate (N+P)	Urea (N)	Anhydrous ammonia (N)
1999	211	206	181
2000	234	207	184
2001	213	206	165

Table 8. Description of wetland primary producers (from Goldsborough and Robinson 1996, Scheffer 1998).

Macrophytes	Emergent	Plants rooted in the sediment that have at least part of their shoot rising up past the water surface
	Submerged	Plants, non-rooted or rooted in the sediment that have shoots which extend into but not out of the water column
	Floating	Plants, non-rooted or rooted in the sediment that have floating portions
Algae	Epipelon	Motile algae inhabiting soft sediments
	Epiphyton	Algae growing on the external surfaces of macrophytes
	Metaphyton	Algae originating from the epiphyton found in cohesive floating and subsurface mats
	Phytoplankton	Algae entrained in the water column

additions to aquatic environments including lakes and wetlands have reported a significant increase in phytoplankton concentrations (Schindler and Fee 1974, Murkin *et al.* 1994, Spencer and Ellis 1998, Kiers North 2000, Wetzel 2001, McDougal 2002).

Wetland benthic algae exposed to nutrient additions can also exhibit increased abundance. In the past benthic algae have often been ignored in nutrient addition experiments perhaps due to the traditional focus of aquatic plant ecology that has concentrated on phytoplankton (Sand-Jensen and Borum 1991). In deep lakes with limited photic zones and correspondingly limited benthic algae the above focus is warranted. Wetlands, however, are shallow and their photic zone can extend to the sediment. Wetland nutrient addition studies that have measured benthic algae have reported a response similar to, or greater than, the response seen in phytoplankton (Murkin *et al.* 1994, McDougal *et al.* 1997).

Rooted submersed and emergent macrophytes can utilize nutrients found in both the sediment and the water column (Denny 1972, Hutchinson 1975, Werblan 1979, Barko and Smart 1980, Bayley *et al.* 1985, Neely and Davis 1985, Spencer and Bowes 1990). Although the response is usually not as rapid as that seen with algae, additions of nutrients can also cause increases in macrophyte biomass production (Werblan 1979, Bayley *et al.* 1985, Neely and Davis 1985).

The literature pertaining to nutrient additions to aquatic environments, including wetlands, suggests that agricultural nutrient additions will cause an increase in wetland primary production (Sand-Jensen and Borum 1991). Which primary producer assemblage will be most impacted by nutrient inputs will depend upon wetland characteristics such as water column stability, depth, and the presence or absence of herbivores. Wetlands are dynamic and exist in alternative stable states dominated by either algae or macrophytes. Models by Goldsborough and Robinson (1996) and Scheffer (1998) incorporate nutrient inputs as an important destabilizing force in the switch from one stable state to the next.

Nutrient addition in the form of ammonia can be toxic to fish (Thurston *et al.* 1981, Broderius *et al.* 1985). Depending on the pH and water temperature of the system ammonia can exist in either the ionized or unionized condition (Table 9) (Emerson *et al.* 1975). It is the unionized form of ammonia that is most toxic (Thurston *et al.* 1981) and thus agricultural surface runoff flowing into warm alkaline wetlands could result in the death of sensitive organisms.

Indirect effects of nutrients

The direct effects of nutrient additions are not isolated but proceed to impact various aspects of the physical, chemical, and biological environment of wetlands. Elevated phytoplankton levels or blooms can significantly increase light attenuation by either absorbing or scattering light (Kirk 1983). The resulting low-light environment that is generated by phytoplankton blooms may be unsuitable for a variety of organisms. Low light environments generated by high phytoplankton levels are not suitable for pike (*Esox lucius*) and perch (*Perca fluviatilis*) as these fish rely on visual cues for hunting (Scheffer 1998). Descriptive and experimental studies have also documented the loss of submersed macrophyte biomass and diversity in wetlands and shallow lakes experiencing increased algal levels (Harman and Doane 1970, Moss 1976, 1979, 1983, 1998, Osborne and Moss 1977, Scheffer 1998).

The loss of submersed vegetation under eutrophic conditions is a complex process involving a number of factors (Balls *et al.* 1989, Irvine *et al.* 1989, Stansfield *et al.* 1989, Moss 1998). Phytoplankton and epiphyton can shade submersed macrophytes leading to their decline (Sand-Jensen 1977, Sand-Jensen and Sondergaard 1981, Twilley *et al.* 1983).

A reduction in submersed macrophytes caused by eutrophication can initiate an alteration of the wetland community. Waterfowl feed upon a variety of macrophytes and their associated invertebrates (Bartonek and Hickey 1969, Sugden 1973, Anderson and Low 1976, Hohman 1985). Aquatic invertebrates seek refuge from predation in

Table 9. Un-ionized NH_3 as a percent of total ammonia (by temperature and pH) (Alleman 1998).

Temperature	pH				
(°C)	6.5	7.0	7.5	8.0	8.5
20	0.13	0.40	1.24	4.82	11.2
25	0.18	0.57	1.77	5.38	15.3
28	0.22	0.70	2.17	6.56	18.2
30	0.26	0.80	2.48	7.46	20.3

macrophytes and can feed upon them or the epiphytes that they support (Pip 1978, Hunter 1980, Timms and Moss 1984, Engel 1988, Kornijow *et al.* 1995). Like invertebrates, fish young of the year also use vegetation to avoid predation (Grimm and Backx 1990, Wright and Shapiro 1990). Many fish species also use macrophytes for spawning habitat and/or as substratum for egg deposition (de Nie 1987, Giles 1992, Moss 1998, Scheffer 1998). Thus, by lowering submersed macrophyte levels the indirect effect of nutrient additions can determine the species richness of a wetland (Moore *et al.* 1989, Wisheu *et al.* 1991, Spiels and Mitsch 2000).

Elevated phytoplankton abundance can also reduce the species richness in wetlands by altering the chemical environment. As algal cells decompose during and after a bloom, oxygen levels may drop below that which are required to support sensitive organisms (Barica 1975, Ayles *et al.* 1976, Coulombe and Robinson 1981, Suthers and Gee 1986).

Depending on the predominate taxa, phytoplankton blooms can produce elevated levels of toxins that can negatively affect animals associated with the wetland. Toxins produced by certain species of phytoplankton include neuro- and hepatotoxins (Codd *et al.* 1989, Gurney and Jones 1997). Toxin producing algae are frequently detected in prairie aquatic environments. For instance, Gurney and Jones (1997) detected algal hepatotoxins in 84% of the livestock dugouts sites they sampled in Manitoba. Blooms of toxic phytoplankton can reach levels high enough that they produce concentrations of toxins that are lethal to fish as well as other animals that come in contact with the water (Olson 1960, Tencalla *et al.* 1994, Gurney and Jones 1997). It has also been speculated that some cases of avian botulism may be due to algal toxins (Murphy *et al.* 2000).

2.3.2 Pesticides

Pesticides are used in agriculture to increase yields by eliminating or reducing crop pests. Pesticides are effective because their mode of action interferes with life processes of their target organisms. Often the modes of action of pesticides affect general life processes that are not specific to their target (Carson 1962, Jepson 1989, Helfrich *et*

al. 1996). If such pesticides enter wetlands they can have direct effects such as reduced metabolic activity or death of sensitive organisms. Direct effects of pesticides on wetland organisms can initiate a cascade of indirect effects. Pesticides can indirectly affect organisms by altering their environment and or food availability. Indirect effects results are often difficult to predict because they require a thorough understanding of ecosystem connections. Despite the great potential for pesticide contamination of wetlands relatively few studies have looked at pesticide levels in this environment (Table 10).

Direct effects of pesticides

The direct toxicity of pesticides on organisms can be divided into acute and chronic toxicity, with chronic toxicity being further divided into subacute and chronic effects (Ware 1999). Acute toxic effects are defined as those that result in death of exposed organisms in a short period of time relative to the lifespan of the organism (Ware 1999). The acute toxicity of a chemical to a particular organism is usually determined using standard single species bioassays that calculate the lethal concentration 50 (LC50) (Hubert 1984). The LC50 is the concentration of the chemical that will kill 50% of the exposed organisms within a specified time frame (i.e., 24, 48, or 96 hours).

Pesticides are designed to kill pests by interfering with essential life processes. Most herbicides have their toxic effect by impeding photosynthesis while insecticides tend to affect normal neurological functions of insects. Thus, pesticides entering wetlands can kill wetland organisms by affecting normal photosynthesis and neurological processes. Pesticide additions to aquatic environments have caused the rapid death of sensitive organisms including primary producers, invertebrates, and vertebrates (Herman *et al.* 1986, Brock *et al.* 1992, Peterson *et al.* 1994, Forsyth *et al.* 1997, Giddings *et al.* 1997). The sensitivity of wetland organisms to pesticides differs taxonomically (Ma *et al.* 2002). For instance, Ma *et al.* (2002) showed that the green algae *Scenedesmus obliqnus* and *Chlorella pyrenoidosa* had different sensitivities to a number of pesticides. *S. obliqnus* was 24 times more sensitive to thiophanate methyl and 80 times more sensitive to

Table 10. Pesticide residues detected in natural PPR wetlands.

Location of wetland	Pesticides detected	Reference
Alberta, Canada	2,4-D, AMPA, Bromoxynil, Carbathin, Clopyralid, Dicamba, Dichorprop, Glyphosate, Imazamethabenz, Lindane, Picloram, MCPA, MCPP, Triallate	Anderson *et al.* 2002
North Dakota, USA	Methyl parathion	Tome *et al.* 1991
Saskatchewan, Canada	2,4-D, Bromoxynil, Dicamba, Diclofop-methyl, Lindane, MCPA, MCPB, Triallate, Trifluralin	Donald *et al.* 1999
Saskatchewan, Canada	2,4-D, Bromoxynil, Dicamba, Diclofop, MCPA, Triallate,Trifluralin	Grover *et al.* 1997

chlorothalonil than *C. pyrenoidosa*. In addition, some organisms are capable of developing resistance to pesticides (Hamilton *et al.* 1987, Landis *et al.* 1996). Thus, pesticide contamination could directly alter community composition by selecting for resistant or tolerant taxa (Hersh and Crumpton 1989, Molander and Blanck 1992, Matthews *et al.* 1996, Neumannn and Dudgeon 2002).

Despite precautionary measures pesticide concentrations in aquatic environments can, on occasion, reach levels that are acutely toxic to sensitive organisms (Sakai 2001, 2002). Donald *et al.* (1999) based on their survey of Saskatchewan wetlands estimated that between 9 to 24% of Saskatchewan wetlands had pesticide levels that exceeded Canadian governmental guidelines for the protection of aquatic life. In wetlands, the occurrence of acutely toxic pesticide levels may be limited to the springtime when the majority of agricultural pesticides are applied and off-field transport of pesticides is highest (Goolsby and Battaglin 1993) (Figure 6). In contrast, the occurrence of subacute levels of pesticides in aquatic environments could occur throughout the year (Robson and Barrett 1977, Dewy 1986). Exposure to pesticide concentrations slightly below acute levels can result in abnormal changes to an organism's morphology and life functions. Feeding and clearance rate inhibition as well as alterations of swimming patterns have also been reported in invertebrates exposed to subacute levels of pesticides (Kersting, and Honing 1981, Gliwicz 1986, Meador 1986, Lampert *et al.* 1989, Goodrich and Lech 1990, Ferrando *et al.* 1993, Dodson and Hanazato 1995, Hartgers *et al.* 1999, Hanazato 2001). For instance, *Daphnia pulex* exposed to subacute concentrations of lindane (0.25 mg/L) showed a 50% decrease in stroke frequency of their filtering limbs as compared to controls which did not contain lindane (Gliwicz 1986).

Some pesticides can also cause a reduction in the reproductive rate of aquatic animals (Canton *et al.* 1975, Schober and Lampert 1977, Blockwell *et al.* 1999, Sancho *et al.* 2001). Pesticides may affect reproduction by acting as estrogen imitators causing the feminization of exposed organisms (Colborn *et al.* 1993, Raloff 1994, Dodson and

Hanazato 1995, McLachlan and Arnold 1996). For instance, Hayes *et al.* (2003) have shown that hermaphroditism occurred in leopard frogs (*Rana pipiens*) exposed to atrazine at a concentration of 0.1 µg/L.

Aquatic primary producers are not exempt from subacute pesticide toxicity. A commonly reported response to subacute pesticide exposure in aquatic primary producers is a reduction in photosynthesis (Wong 2000, Babu *et al.* 2001, Dorigo and Leboulanger 2001, Pennington *et al.* 2001, Seguin *et al.* 2001, Gunanzon and Nakahara 2002). Wong (2000) demonstrated that subacute concentrations of the herbicides glyphosate (2 mg/L) and paraquat (0.02) significantly reduced the photosynthetic rate of the alga *Scenedesmus quadricauda* as compared to controls (photosynthetic rate: control 129 µL O_2/mL/h, glyphosate treatment 80 µL O_2/mL/h, paraquat treatment 108 µL O_2/mL/h). The herbicides also significantly reduced the chlorophyll-*a* concentration of the alga cells (control 2.4 x 10^{-9} mg/cell, glyphosate 1.6 x 10^{-9} mg/cell, paraquat 1.8 x 10^{-9} mg/cell).

Pesticide induced changes in growth rate and motility of aquatic primary producers have also been reported (Brown *et al.* 1976, Forney and Davis 1981, Johnson 1986, Abou-Waly *et al.* 1991, Abou-Waly and Shabana 1993, Chang 1997, Sabater *et al.* 2002). For instance Sabater *et al.* (2002) demonstrated that the growth rate of *Scenedesmus acutus, S. subspicatus, Chlorella vulgaris,* and *C. saccharophila* cultures were significantly reduced by herbicides at concentrations (bensulfuron-methyl 0.015 mg/L, cinosulfuron 8 mg/L) that have been reported in surface waters. A prairie wetland enclosure experiment demonstrated that low levels (0.1 mg/L) of the herbicide 2,4-D reduced vegetative growth of macrophytes (*Myriophyllum sibiricum* and *Potamogeton pectinatus*) by about 40% (Forsyth *et al.* 1997). An experiment by Chang (1997) showed that pesticides also have the potential to influence the motility of flagellated algae. In Chang's experiment the freshwater alga *Chlamydomonas sp.* exposed to lindane (5 mg/L) exhibited an acceleration of movement that lasted for five minutes. The effect of lindane

on algal movement could be due to an interference of the normal intracellular calcium flux which controls flagella activity.

Chronic toxic effects, as their name implies, take a longer time to develop. Determining the effect of chronic pesticide exposure is a difficult task as long-term studies are needed which eliminate the impact of other environmental variables as well as genetic predisposition to measured effects (Madhun and Freed 1990). However, a result of chronic exposure to pesticides that can be determined relatively easily is bioaccumulation. The term bioaccumulation refers to the combined effects of both bioconcentration and biomagnification (Ongley 1996, Egeler *et al.* 1997, Caldas *et al.* 1999). Bioconcentration describes the increase in pesticide levels from the environment to the biota via partitioning. Lipophilic pesticides such as organochlorines tend to partition out of the water column and into lipid material found in organisms (Hamelink *et al.* 1971, Grimes and Morrison 1975, Campbell *et al.* 2000, DeLorenzo *et al.* 2002). Long-term partitioning of pesticides out of the water and into organisms could eventually lead to toxic pesticide levels (Kawano *et al.* 1988). Biomagnification involves the increase of pesticide concentration from one trophic level to the next. Lipophylic pesticides are recalcitrant and are thus highly conserved in organisms. Thus, when organisms from one trophic level consume contaminated organisms from a lower trophic level much of the pesticide is passed on to the consumer (Muir *et al.* 1988, Evans *et al.* 1991, Albanis *et al.* 1996). Given the nutrient dynamics of food pyramids the result of biomagnification is an increase in pesticide concentration "up" the pyramid. The "higher" the food pyramid the greater the biomagnification potential (Kidd *et al.* 1998). This increase up the food pyramid could result in toxic pesticide concentrations at higher trophic levels (Carson 1962).

The direct effect of pesticides on wetland organism production can, on occasion, be positive. Studies have documented the direct stimulation of bacterial and algal growth due to pesticide exposure (Loeppky and Tweedy 1969, Birmingham and Colman 1976).

For instance, Birmingham and Colman (1976) showed that when cultured in nitrogen-free media containing Dursban (100 µg/L) the algae *Anabaena flos-aquae* and *Chlamydomonas reinhardii* showed a 58% and 18% increase in growth rate, respectively, over controls. The authors believed that the increase in growth rate was due to the algae utilizing the insecticide as a nutrient source. In a laboratory microcosm experiment, Waiser and Robarts (1997) demonstrated increased growth of bacteria in lake water in the presence of the herbicide Triallate. The increase in bacterial growth may have occurred because the bacteria were using the Triallate as a carbon source (Waiser and Robarts 1997).

Indirect effects of pesticides

The indirect or secondary effects of pesticides on ecosystems have frequently been overlooked because of a lack of knowledge of all the ecological interconnections involved. A classic example of the lack of understanding of the interconnections of ecosystems comes from Brunei where the insecticide Dieldrin was used to control mosquitoes (Miller 1994). Upon insecticide application in the 1950s a large number of insects died which resulted in a trophic cascade of unexpected secondary events including those summarized in Figure 8. The secondary effects of pesticides in wetlands can be just as dramatic as the Brunei example and may ultimately lead to a shift in alternative stable states.

Pesticide-induced shifts in alternative stable states may be caused by reductions to various wetland organisms. For instance, pesticides by limiting algal growth could help maintain a wetland in the Open Marsh stable state (Figure 9). Phytoplankton and benthic algae tend to be more sensitive to pesticides than macrophytes (Butler 1977). This may be due to the greater surface area: volume ratio seen in algae. In the springtime pesticide levels in aquatic environments tend to be the highest as this is the time when the risk of pesticide inputs from surface runoff, aeolian deposition and overspray are the greatest.

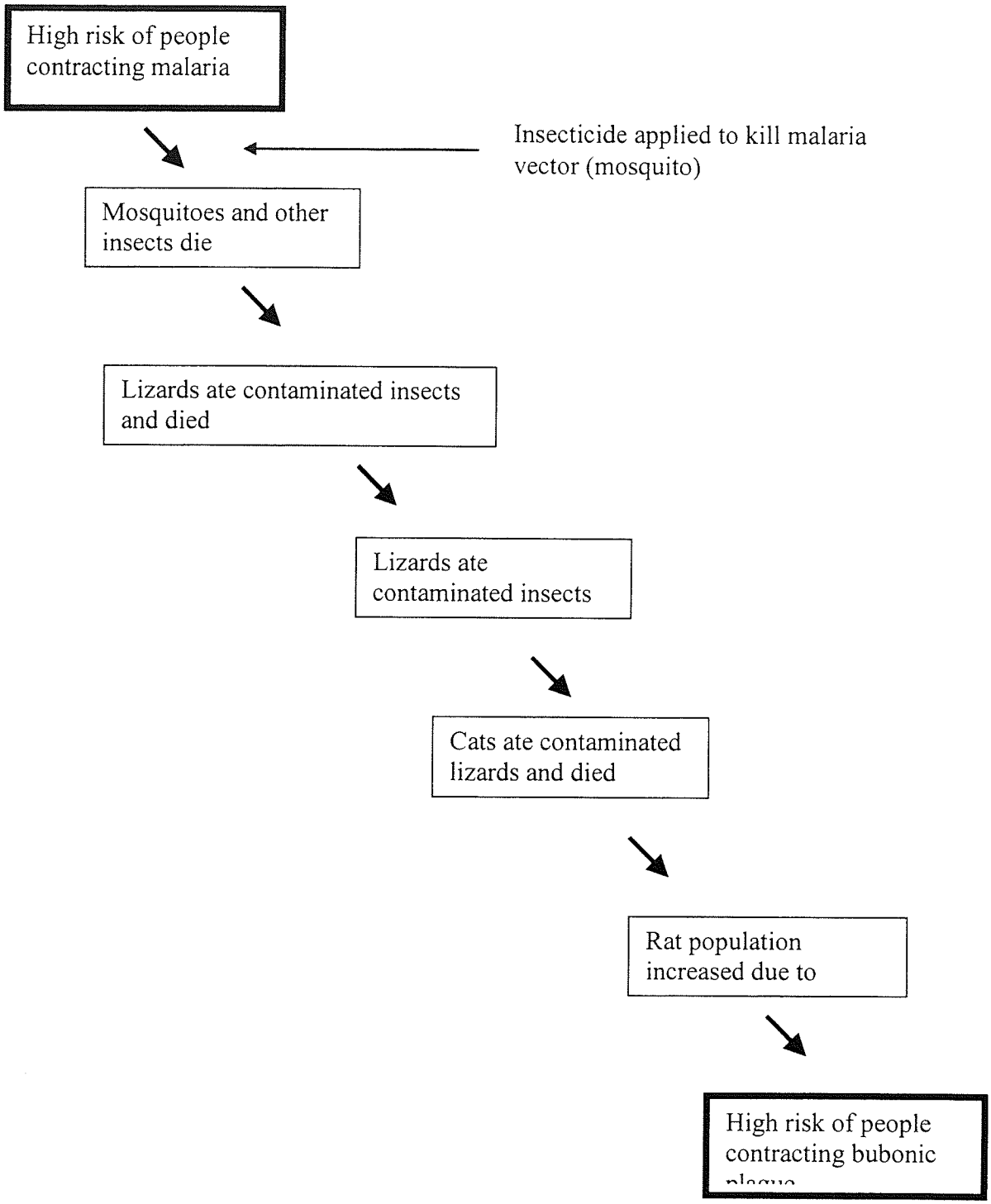


Figure 8. Insecticide induced switch from high risk of humans contracting malaria to high risk of humans contracting the bubonic plague (after Miller 1994).

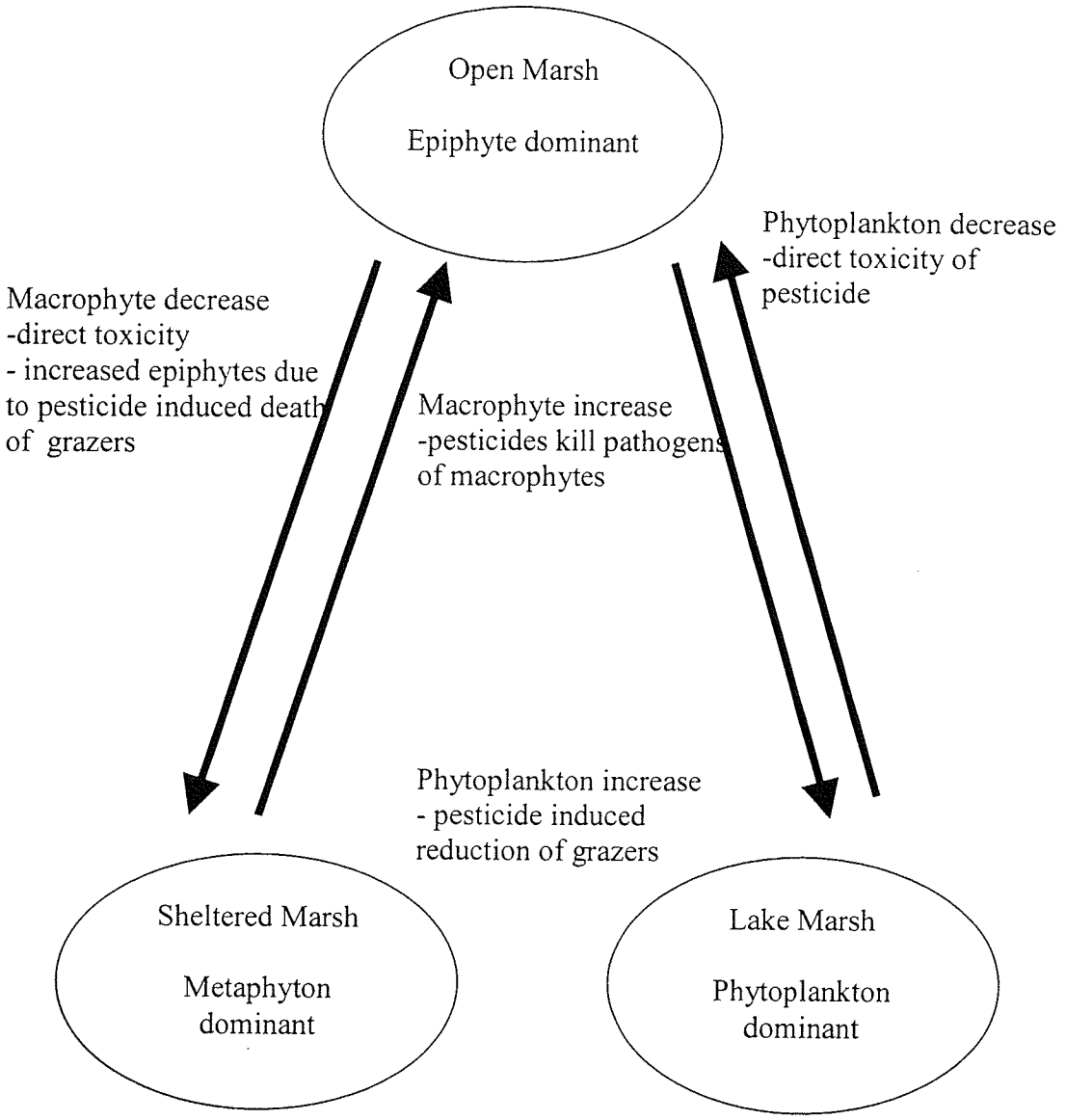


Figure 9. Potential pesticide-induced shifts in wetland alternative stable states (after Goldsborough and Robinson 1996).

The elevated pesticide levels during the spring could limit algal production and allow macrophytes to become established.

Fungicides could also potentially contribute to shifts in wetland stable states. Van den Brink *et al.* (2000) added the fungicide carbendazim at various concentrations (3.3, 33, 100, 330, 1000 µg/L) to freshwater microcosms which contained lake water and sediment along with the macrophyte *Elodea nuttallii* which were encaged in mesh (55 µm) to prevent grazing by macroinvertebrates. Macrophyte ash free dry weight was significantly ($p < 0.05$) higher at fungicide concentrations of 330 µg/L (71.1 g) and 1000 µg/L (67.7 g) as compared to the controls (49.6 g). The authors suggest that increased macrophytes in the presence of the fungicide may be due to a reduction in macrophyte pathogens. Further study is needed to determine the affect fungicides and other pesticides have on macrophyte pathogens. However, if certain fungicides prove to favour macrophytes then their presence could favour the macrophyte dominated stable state (Figure 8).

Pesticide-induced reductions to invertebrate concentrations can also cause shifts in wetland stable states. There is a long history of research which has documented pesticide-induced increases in algal concentrations due to a reduction of grazing pressure (Hurlbert *et al.* 1972, Fliedner and Klein 1996, Pearson and Crossland 1996, Barry and Logan 1998, Van den Brink *et al.* 2000, Rand *et al.* 2001). Insecticide-induced reduction in grazing pressure may be sufficient enough to cause a shift in wetland stable states. A switch from vegetated (macrophytes) to phytoplankton dominated systems upon insecticide application has been demonstrated (Shapiro 1979, Lampert *et al.* 1986). Additionally, Stansfield *et al.* (1989) using the paleolimnological record demonstrated that the change in some English Broads from vegetated to phytoplankton domination coincided with a reduction in grazers due to pesticide contamination. Like the reduction of phytoplankton grazers, insecticides can also reduce epiphytic grazers (Mitchell *et al.* 1993, Kersting and van den Brink 1997). This could lead to an abundance of epiphytes

that could in turn cause a decrease in macrophytes due to shading and a switch in stable states from the Open Marsh to the Sheltered Marsh state (Figure 9).

Insecticide-induced reduction of algal grazing can also influence the algal species present. Under intensive grazing pressure inedible algae may have a competitive advantage over edible ones (Porter 1977). However, with grazing pressure reduced/ removed by insecticide additions the competitive advantage of inedible algal forms is reduced and a shift in algal species can occur (Hurlbert *et al.* 1972, Hurlbert 1975). For example Hurlbert *et al.* (1972) after treating ponds with Dursban found that the crustacean *Moina sp.* and the spined alga *Schroederia* sp. were no longer present. The authors' interpretation of these results was that the Dursban had directly killed the crustacean. However they attributed the absence of the *Schroederia sp.* to the indirect effect caused by reduced grazing pressure. The spiked nature of *Schroederia sp.* makes it inedible to zooplankton such as *Monia* sp. The author's believed that with the death of the crustacean, the spined alga had lost its competitive advantage over smaller "non-spined" phytoplankton species.

Secondary effects of pesticide additions can also influence habitat availability. Herbicides that kill macrophytes in turn diminish the important habitat that they provide. Macrophytes provide habitat for macroinvertebrates. A study by Hargeby *et al.* (1994) showed that macroinvertebrate biomass was 96% higher in areas of a lake vegetated with *Chara tomentosa* (14.5 g dry mass/m^2) than in unvegetated areas (0.5 g dry mass/m^2). Macrophytes can also provide a refuge for zooplankton from fish predation. For example zooplankton such as *Daphnia* sp. exhibit diurnal vertical migration in which they migrate to vegetation during the day and then migrate to open water at night when the predation risk is lower (Timms and Moss 1984).

Associated with the death of macrophytes is a subsequent increase in detritus (Robson and Barrett 1977). Detritus provides surface area for benthic algal attachment, cover and food for invertebrates (Campeau *et al.* 1994). Thus, herbicide-induced

macrophyte death could lead to increases in detritivores and other organisms associated with litter (Harp and Campbell 1964). Aside from herbicide action, increases in litter accumulation can also be a result of insecticides that kill or reduce invertebrate dertritivores (Cuppen *et al.* 1995, 2000, and 2002).

Pesticide additions can also influence the water chemistry of wetlands. Dissolved oxygen (DO) can be lowered during the aerobic decaying process of organism killed by pesticides (Simsiman 1974, Robson and Barrett 1977, Cuppen *et al.* 1997). Similarly when pesticide induced algal blooms crash the ensuing decomposition of the algae can reduce DO levels (Crossland 1984). Anoxic conditions, which are generated by the decay of organisms killed by pesticides, can also enhance nutrient release from the sediment (Goldsborough and Robinson 1985, Mitsch and Gosselink 2000). Additionally, pesticide induced death of the epipelon can enhance sediment nutrient release. Epipelon play an important role in regulating the transport of nutrients from the sediment to the water column (Carlton and Wetzel 1988). If this algal group were removed or reduced, due to pesticide action, nutrients from the sediment would be more available to the water column. For example, in an *in situ* enclosure experiment Goldsborough and Robinson (1985) observed that wetland enclosures which received simazine treatments of 1 mg/L and 5 mg/L had higher net sediment nutrient fluxes as compared to controls (Table 11).

2.4 Water quality guidelines

The potential impact pesticides can have on aquatic ecosystems (Chapter 1) has led to the development of federal water quality guidelines. These guidelines typically are based on results from single species bioassays. However, the applicability of results from single species bioassays may not be relevant to the "real world". The reason for this is that the experimental units in which single species bioassays are conducted do not contain all the environmental variables that can influence the toxicity of pesticides (Kimball and Levin 1985, Brock *et al.* 1993, Dodson and Hanazato 1995, Hanazato and Dodson 1995, Sakai 2001, Schulz and Dabrowski 2001). For instance, bioassays conducted in

Table 11. Sediment water column nutrient flux ($mg/m^2/d$) in experimental wetland enclosures exposed to varying levels of the herbicide simazine (Goldsborough and Robinson 1985).

Simazine concentration	Ammonia	Total reactive phosphorous	Silicon
No simazine	4.63	0.49	5.25
0.1 mg/L	4.68	-0.90	-92.95
1.0 mg/L	35.79	5.34	207.59
5.0 mg/L	65.58	19.65	247.95

experimental units containing only water do not take into consideration the influence of sediment on pesticide fate and toxicity. The use of mesocosm experiments may generate a better approximation of the risk of pesticides to non-targets because they incorporate more components of the natural environment (Boyle 1983). However, mesocosm experiments are more complex than bioassays and are thus relatively rarely conducted as compared to bioassays (Caquet *et al.* 1996). Consequently, the results from bioassays are typically used by governments to set water quality guidelines. If such water quality guidelines are adhered to, pesticides may still impact wetland ecosystems in significant ways.

Another shortcoming of federal guidelines is that they have traditionally been set using single pesticide bioassays with single species. From the surveys that have been conducted, it is evident that contaminated wetlands will usually have more than one pesticide detected in them (Table 10). Pesticides and their degradation products can interact with one another and have different effects on organisms when applied separately or in combination with other pesticides (Stratton 1983, 1984, European Inland Fisheries Advisory Commission 1987, Kungolos *et al.* 1999, Belden and Lydy 2000, Deneer 2000, Strachan *et al.* 2001). For example, Belden and Lydy (2000) demonstrated that the addition of atrazine had a synergistic effect on the toxicity of chlorpyrifos to *Chironomus tentans* larvae (Figure 10). Conversely, Stratton (1984) showed that the major degradation products of atrazine (deisopropylated atrazine (DIA) and deethylated atrazine (DEA)) had antagonistic effects on the photosynthesis of *Anabaena inaequalis*. By using water quality guidelines established with single pesticide tests, the impact of pesticide interactions is ignored (Battaglin and Fairchild 2002). Like single pesticide bioassays, single species bioassays ignore potentially important pesticidal effects on the ecosystem. Guidelines based on single species bioassays disregard all the secondary trophic interactions of pesticide additions.

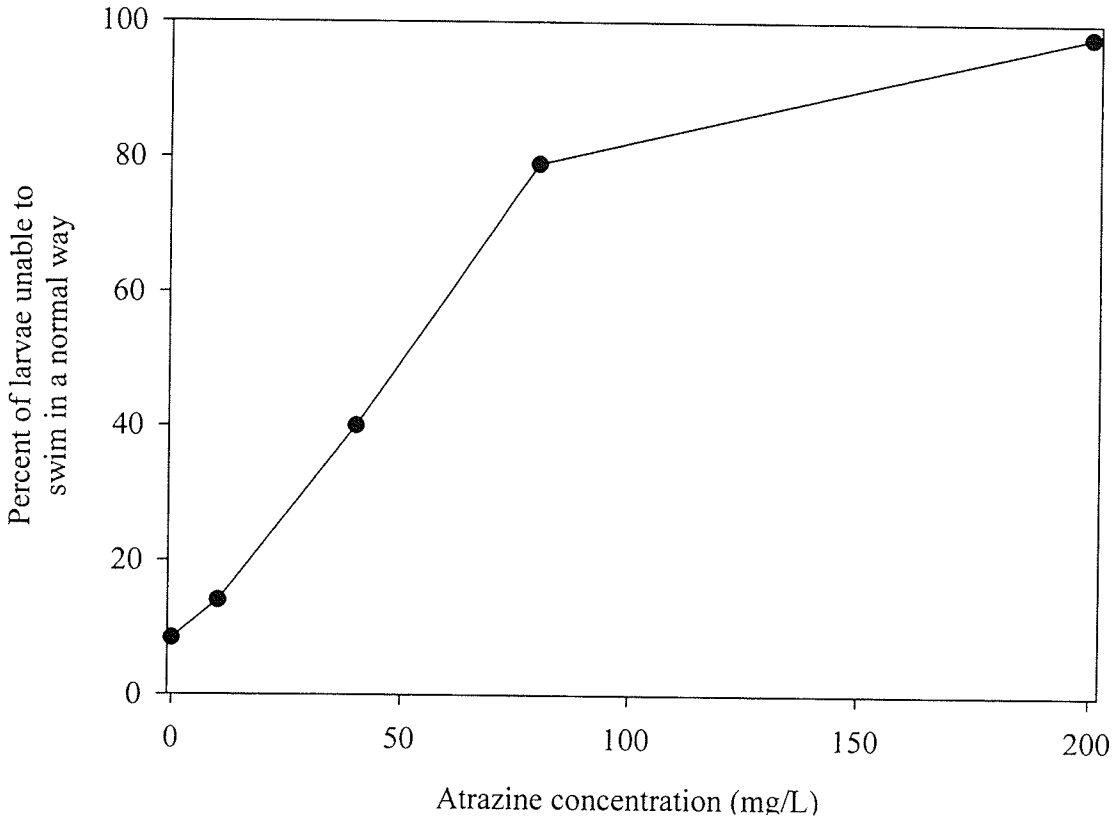


Figure 10. Synergistic effects of atrazine on the toxicity of chlorpyrifos (10 μg/L) exposure to *Chironomus tentans* larvae in a microcosm experiment (modified from Belden and Lydy 2000).

In some cases, guidelines based on bioassays could overestimate pesticide effects. Simple laboratory bioassays do not incorporate components of wetlands that may reduce pesticide toxicity. As will be described in detail in the following sections, wetlands potentially provide a large surface area for pesticide sorption. The toxicity and bioavailability of pesticides in the sorbed-phase is usually lower than in the aqueous phase (Karickhoff and Morris 1984, Staples *et al.* 1985, Karuppiah *et al.* 1997). For example using the bacterial assay Microtox, Karuppiah *et al.* (1997) showed that metolachlor was toxic to the *Vibrio fischeri* (effective concentration 50 (EC50) = 24.2 mg/L, the EC50 is the concentration of a chemical that causes a measured effect in 50% of the test organisms, in the Karruppiah *et al.* study the measured effect was a reduction in bioluminescence of the bacteria). However, in the presence of wetland sediments metolachlor was not toxic to the bacteria. The authors suggested that the sediments sorbed the metolachlor and made it unavailable to the bacteria. Sorption of pesticides to dissolved substances can also reduce their toxicity. Lee *et al.* (1993) showed that the presence of dissolved humic materials (DHM, at 50 mg/L) significantly ($p < 0.05$) reduced the toxicity of diazinon to *Daphnia magna* (48h-LC50 = 1.6 µg/L) as compared to controls which contained no DHM (48h-LC50 = 0.8 µg/L). Pesticide degradation and transport mechanisms found in wetlands can also reduce the toxic effect of pesticides by reducing the pesticide concentration. Because laboratory bioassays tend not to include all aspects of pesticide dissipation they may at times overestimate the effects of pesticide additions to wetlands. For instance, Fairchild *et al.* (1998) showed that metribuzin at a concentration of 19 µg/L was toxic to the macrophyte *Najas* sp. in single species laboratory bioassays. However, *Najas* sp. growing in pond mesocosms exposed to metribuzin at a concentration of 75 µg/L did not exhibit any decreased growth (Fairchild and Sappington 2002).

2.5 Pesticide fate in wetlands

The fate of pesticides in a variety of aquatic environments has been studied (Faust and Hunter 1971, Gould 1972, Muir *et al.* 1985, Meyer and Thurman 1996). However, there is paucity in the literature pertaining to pesticide fate in wetlands (Goldsborough and Crumpton 1998). A reason for the lack of wetland/pesticide studies could be attributed to the past assumption that the fate of pesticides would be the same in wetlands as it is in other aquatic environments. However, the higher organic matter content of wetlands, as compared to lakes, as well as the shallower nature of wetlands suggests that the fate of pesticides in lakes and wetlands may differ.

Retention and transformation of pesticides will determine their fate in wetland ecosystems. The physical, chemical, and biological characteristics of wetlands will all influence the extent of pesticide retention and transformation.

2.5.1 Retention

Pesticide retention in wetlands and other environments determines the amount of pesticide transport, transformation and bioavailability (Sharom *et al.* 1980 a,b, Sharom and Solomon 1981b, Crossland 1982, Kosinski and Merkle 1984, Nair and Schnoor 1994). Pesticides are retained in the solid environment via adsorption and absorption mechanisms. Pesticide adsorption refers to the accumulation of pesticide molecules at the solid-water or solid-air interface (Koskinen and Harper 1990). There are various mechanisms involved in pesticide adsorption (Table 12). Due to the heterogeneity of adsorption sites (Hance 1988) a pesticide molecule may be adsorbed simultaneously by a number of different mechanisms (Senesi 1992).

Unlike adsorption, pesticide absorption involves pesticides entering into the matrix of the sorbent. Sorbents can absorb pesticides directly from the water via hydrophobic partitioning. Many pesticides are hydrophobic and will partition out of water and into similar environments such as particulate organic matter and aquatic organisms (Matsumura 1977, Senesi 1992). Aquatic organisms can also absorb hydrophobic

Table 12. Pesticide adsorption types and mechanisms involved in pesticide sorption.

Adsorption type	Mechanism involved	Pesticide susceptible
Ionic bonds	Pesticide forms an ionic bond with molecules at the surface of the substrata	Paraquat (Hance 1988)
Covalent bonds	Pesticide forms a covalent bond with molecules at the surface of the substrata	Hydroxy-metabolites of triazine herbicides (Capriel and Haisch 1983, Kloskowski and Fuhr 1985)
Hydrogen bonds	Pesticide forms a hydrogen bond with molecules at the surface of the substrata	Atrazine (Li and Felbeck 1972)
Ligand exchange	Pesticide displaces an inorganic hydroxyl or water molecule of a metal ion at the surface of the substrata	Atrazine (Laird 2001)
Cation bridging	Formation of an inner sphere complex between an exchangeable cation of the substrata and a pesticide	Pyridine (Farmer and Mortland 1966)
Protonation	Pesticide forms a complex with a proton at the surface of the substrata	Methyl-thiotriazine (Hayes 1970)
London-van der Waals forces	Dipole-dipole interactions between pesticide and substrata surface molecules	Atrazine (Laird 2001)

pesticides from their food (Herbes 1977, Khan 1977). For instance, Albanis *et al.* 1996 showed that the lindane concentration in herons from Greek wetlands was higher than in their prey. The authors attributed the higher lindane concentration in the herons to biomagnification of lindane from their food.

The term sorption incorporates both adsorption and absorption mechanisms and can be used interchangeable with the term retention. The mathematical calculation of pesticide sorption in aquatic environments is similar to that originally calculated for the soil environment (Muir 1988) and is described with the Freundlich equation (Equation 2) (Bell and Tsezos 1987).

Equation 2. $C_s = k_d C_L$ *where* C_s *= sorbed-phase concentration,* k_d *= sorption coefficient,* C_L *= total solute concentration.*

As mentioned earlier, pesticide characteristics will determine their sorption mechanisms and sorption potential (Table 12). The most frequently used measure of pesticide sorption potential is the octanol-water partitioning coefficient (K_{ow}) (Weber *et al.* 1983). K_{ow} values have been calculated for most pesticides and can be found in pesticide handbooks and manuals (Hatzios 1998). Calculation of K_{ow} involves determining (at equilibrium and at a constant temperature) the concentration of pesticide in each compartment of a two-compartment system (water and octanol) (Equation 3).

Equation 3. K_{ow} *= pesticide concentration in octanol ÷ pesticide concentration in water determined at equilibrium and at a constant temperature*

Octanol is used because it has very similar characteristics to natural sorbents such as lipids (Clark 1999, Choy and Reible 2000). Pesticides with low water solubility and high lipophilicity will readily partition into the octanol compartment and thus will have high K_{ow} values. In natural environments, high K_{ow} pesticides will tend to partition out of the water column and into similar hydrophobic environments such as organic matter whereas low K_{ow} pesticides will be found to a greater extent in the aqueous phase.

Like the sorbate, the characteristics of the sorbent are also important in determining pesticide sorption (Piccolo *et al.* 1998). Organic matter content is often cited as the most important component of sorbents that determines pesticide sorption (Karickhoff *et al.* 1979, Schellenberg *et al.* 1984, Rao 1990, Senesi 1992). Generally, as the organic matter content of the sorbent increases so does its ability to sorb pesticides. For instance, sediments rich in organic material, such as those found in wetlands, have higher pesticide sorption capacities than those sediments or soils with relatively lower organic matter (Mersie and Seybold 1996, Karuppiah *et al.* 1997). Similarly, organisms with higher lipid content will be more capable of pesticide sorption than organisms with relatively lower lipid content (Canton *et al.* 1977, Kent and Currie 1995). Extracellular substances such as the mucilage found associated with some algae and the EPS in bacterial biofilms will also enhance pesticide sorption (Hansen 1979, Wolfaardt *et al.* 1994b *et al.* 1998, Headley *et al.* 1998).

The size of the sorbent can also influence its pesticide sorption capabilities. Studies have reported an inverse relationship between particle size and organic chemical sorption (Kay and Elrick 1967, Richardson and Epstein 1971, Voice and Weber 1983, Gupta *et al.* 2002). The above relationship may be due to smaller particles having higher organic carbon content (Voice and Weber 1983, Weber *et al.* 1983) and/or a greater surface area to volume ratio (Geller 1979, Sharom and Solomon 1981a).

Differences in pesticide sorption rate and extent may also be attributed to the sorbent's age. Older microbial cells may have lower sorption abilities than younger ones due to a lower amount of sorption sites (Young and Banks 1998). With age microbial cells tend to have less chitin in their cell wall and chitin is an important sorption site for pesticides (Young and Banks 1998). Younger aquatic macrophytes may also be more efficient at sorbing pesticides than their older counterparts. Weinberger and Greenhalgh (1985) demonstrated that young sprigs of *Ceratophyllum demersum* sorbed five times more pesticide per gram than older sprigs. Younger plants may be more efficient at

sorbing pesticides due to their higher surface area for sorption due to a greater abundance of finer leaves.

Differences in sorption abilities may also occur between living and dead organisms (Voerman and Tammes 1969, Gao *et al.* 2000a,b). In a laboratory experiment using activated sludge from the city of Hamilton (ON) wastewater treatment plant it was discovered that dead fungal cells (*Rhizopus arrhizus*) sorbed 27% more lindane than living fungal cells (Tsezos and Bell 1989). Uptake of pesticide may be greater for dead cells than living ones due to the loss of metabolic protection against pesticide transport and increased membrane permeability of the dead cell (Tsezos and Bell 1989). On the other hand, pesticide sorption may be higher in living organisms versus dead ones due to the effects of biomagnification. Sometimes there is no difference in the pesticide sorption rate between living and dead organisms. In a laboratory experiment Rice and Sikka (1973) showed there to be no difference in DDT uptake between living and dead cells of the algae *Skeletonema costatum* and *Cyclotella nana*. Canton *et al.* (1977) after exposing cultures of *Chlamydomonas* sp. to the insecticide gamma-HCH (1 mg/L) for five days found that there was no difference in insecticide concentrations between living and dead *Chlamydomonas sp.* (155 μg/kg). Mac Rae (1985) also demonstrated that there was no significant difference ($p > 0.05$) in lindane sorption (from water) between living (sorbed 19% of applied lindane) and heat killed (sorbed 25% of applied) bacteria (*Rhodospseudomonas sphaeroides*).

Environmental conditions will also play a role in pesticide sorption. Increases in temperature tend to influence pesticide sorption indirectly through temporal effects on water solubility and vapor pressure (Bailey and White 1970). Increases in temperature cause more of the pesticide to be in solution and/or may increase volatilization thus limiting the amount of chemical available for sorption (McGlamery and Slife 1966, Mills and Biggar 1969, Young and Banks 1998). However, in some environments the opposite

has been reported indicating that instances can occur in which pesticide sorption involves endothermic reactions (McGlamery and Slife 1966, Dao and Lavy 1978).

The pH of an environment can also influence the extent of pesticide sorption. Pesticide sorption tends to increase with decreasing pH (Clay and Kaskinen 1990, Wang *et al.* 1991, Ruggiero *et al.* 1992, Wang *et al.* 1992, Roy and Krapac 1994, Madsen 2000). There are a number of ways in which pH can affect sorption. The pH determines the extent of ionization of weakly acidic and basic pesticides. Once ionized, these pesticides can be adsorbed via ionic mechanisms (Koskinen and Harper 1990, Senesi 1992). The availability of hydrogen ions in low pH environments also enhances sorption via ligand bridge formation (Young and Banks 1998) whereas elevated pH levels weaken sorption associated with hydrogen bonds (Wang *et al.* 1990).

Abiotic and biotic pesticide sorption sites can be found in aquatic environments. The surface microlayer found on water surfaces of wetlands and other aquatic environments is capable of pesticide sorption (Crossland 1982) and can be efficient at sorbing pesticides that enter aquatic environments from the atmosphere (Muir *et al.* 1991, 1992). Pesticides associated with surface microlayers may be mixed into the water column or sorbed to suspended solids (Maki and Hermansson 1994, Samsoe-Petersen *et al.* 2001). Loss to the water column may account for why pesticides are not always detected in surface microlayers (Anderson *et al.* 2002).

In the water column, dissolved and particulate substances provide pesticide sorption sites. DOM can be efficient at sorbing hydrophobic pesticides (Hassett and Anderson 1979, Carter and Suffet 1982). Non-organic dissolved substances such as ions may also sorb pesticides (Wahid and Sethunathan 1979). Suspended solids capable of sorbing pesticides include clays and particulate organic matter (Clausen *et al.* 2001, Fushiwaki and Urano 2001, Sheng *et al.* 2002). Members of the plankton, the living component of suspended solids, can also sorb pesticides from the water column (Canton 1977,

Schauberger and Wildman 1977, Casserly *et al.* 1983, Itagaki *et al.* 2000, DeLorenzo *et al.* 2002).

Aside from the microorganisms already mentioned other wetland organisms can sorb pesticides. Benthic invertebrates as well as fish can sorb pesticides directly from the water or from their diet (Khan 1977, Arts *et al.* 1996). Many aquatic macrophytes also strongly sorb pesticides (Gao *et al.* 2000b, Hand *et al.* 2001). The three general classes of aquatic macrophytes, floating (Kanazawa *et al.* 1975, Rawn *et al.* 1982, Muir *et al.* 1985), emergent (Crossland 1982, Moore *et al.* 2002), and submergent (Weinberger and Greenhalgh 1985, Feurtet-Mazel *et al.* 1996, Gobas *et al.* 1991, Brock *et al.* 1992, Crum *et al.* 1998, Karen *et al.* 1998) all have portions within the water column which can sorb pesticides. Moore *et al.* (2002) determined that approximately 16% of the insecticide chlorpyrifos which flowed into a constructed wetland in South Africa was retained by macrophytes (*Juncus effusus, Leersia* sp., *Ludwiga* sp.). Additionally emergent and submergent macrophytes can sequester pesticides obtained from the sediment (Karren *et al.* 1998).

Pesticides can be found in wetland sediment due to sorption from the water column (Voice and Weber 1983, Samsoe-Petersen *et al.* 2001, Moore *et al.* 2002). As in other environments, the organic matter content of the sediment is the most influential factor in determining its sorption potential (Means *et al.* 1980, Weber *et al.* 1983). Sorbed pesticides may also occur in the sediment due to the sedimentation of suspended solids and detrital material that have pesticides sorbed to them (Pionke and Chesters 1973, Richardson and Epstein 1971, Schauberger and Wildman 1977, Sharom and Solomon 1981b, Muir *et al.* 1985, Mersie *et al.*1998, Itagaki *et al.* 2000). The sorption of pesticides to sediment as well as other surfaces can be enhanced by the presence of bacterial biofilms (Wolfaardt *et al.* 1994b, Headley *et al.* 1998). In addition, burrowing benthic organisms may increase the depth of pesticide sorption via burrow formation (Karickhoff and Morris 1985, Gerould and Gloss 1986).

At equilibrium, pesticide sorption is coupled with desorption from the sorbent. With pesticides, especially nonpolar ones, pesticide hysteris occurs in which sorption is greater than desorption (McGlamery and Slife 1966, Mersie and Seybold 1996). Thus, non-polar pesticides desorption from organic material may be insignificant (Sharom *et al.* 1980b, Sharom and Solomon 1981b, Noegrothati and Hammers 1992, Hand *et al.* 2001) and the ability of wetlands to eliminate pesticides from their outflow can be attributed in part to pesticide retention (Kao *et al.* 2001, Moore *et al.* 2002).

Reduce pesticide amounts

The amount of pesticide released into the environment can be decreased due to abiotic and biotic degradation. This degradation may be partial or complete. The complete transformation of pesticides is known as mineralization and its products include carbon dioxide, water, methane (in anaerobic conditions) and inorganic products that are free to enter natural geocehemical cycles (Neilson 2000). In contrast, partial pesticide transformation produces organic metabolites that may be as toxic as the parent pesticide (Chapter 1).

Some pesticides are more recalcitrant than others and one important chemical group that increases a pesticide's resistance to transformation is the halogens (Fellenberg 2000, Manz *et al.* 2001). The reason pesticides with halogens are recalcitrant is due to the stability of halogen-carbon bonds.

An environmental factor that determines both biotic and abiotic pesticide transformations is temperature. The effect of temperature on pesticide transformation rates can be described by the Arrhenius equation which states that the higher the temperature, the faster the chemical reaction will proceed (Larson *et al.* 1981, Wolfe *et al.* 1990, van Loon and Duffy 2000, Morrica *et al.* 2001). For instance, Morrica *et al.* (2001) in a laboratory experiment showed that every 10°C raise (over a range of 15 to 55°C) caused a 3- to 5-fold increase in the hydrolysis rate of the herbicide imazosulfuron. Other

environmental factors that have specific effects on either biotic or abiotic pesticide transformations are discussed below.

Hydrolysis

A number of pesticide functional groups are susceptible to hydrolysis (Table 13) (Armstrong and Konrad 1974, Muir 1988, Smith 1988). Pesticide hydrolysis may be biotic or abiotic (Smith 1988, van Loon and Duffy 2000) and can occur in the water column or sediment (Wolfe *et al.* 1990). The products of pesticide hydrolysis are typically less toxic than their parent compound (Coats 1991, Stumm and Morgan 1996). Pesticide hydrolysis involves reactions between water and pesticides and results in chemical bond cleavage and the addition of H^+ or OH^- to the pesticide (Smith 1988, Muir 1988, van Loon and Duffy 2000).

The pH of aquatic environments can influence pesticide hydrolysis (Wolfe *et al.* 1977, Muir 1988, Vega *et al.* 2000). Acid-mediated hydrolysis describes reactions in which protons catalyze bond breaking and thus the reaction rate increases as the pH decreases (Sarmah *et al.* 2000, Morrica *et al.* 2001, Hultgren *et al.* 2002). Conversely, the reaction rate of base-mediated hydrolysis will increase with increases in pH (Coats 1991, Huang and Mabury 1998). In base-mediated hydrolysis the OH anion acts as the nucleophile and is consumed in the reaction (Wolfe *et al.* 1990). Aside from acid- and base-mediated hydrolysis there are also hydrolysis reactions that are not influenced by the pH of the environment (Wolfe *et al.* 1990, Hong *et al.* 2001). These reactions are referred to as neutral or pH independent reactions. Under the pH range typically found in prairie wetlands (6.8 to 10.8), base-mediated and pH independent pesticide hydrolysis would tend to be favoured (Scifres *et al.* 1973, Muir 1988, LaBaugh 1989, Wolfe *et al.* 1990, Comber 1999, Stangroom *et al.* 2000).

The extent and nature of sorptive surface area in aquatic environments also influences pesticide hydrolysis rates. Sorption of pesticides may increase pesticide hydrolysis as sorbents, both organic and inorganic, can catalyze pesticide hydrolysis

Table 13. Pesticide functional groups susceptible to degradation via hydrolysis (from Wolfe et al. 1990).

Functional Group	Specific pesticide
Amides	Naproamide
Anilides	Propanil
Carbamates	Aldicarb
Carboxylic acid esters	2,4-D
Nitriles	Bromoxynil
Organohalides	Lindane
Organophosphate	Chlorpyrifos
Oximes	Thiodicarb
Triazine ring	Atrazine

(Fowkes *et al.* 1960, Rosenfield and van Valkenberg 1965, Armstrong *et al.* 1967, Li and Felbeck 1972, Mersie and Seybold 1996, Wei *et al.* 2001). However, sorption of pesticides by some sorbents can render the pesticide inaccessible for hydrolytic transformation (Perdue and Wolfe 1982, Wei *et al.* 2001). The role of wetland pesticide sorbents in determining pesticide hydrolysis has not been described in the literature.

Phototransformation

Pesticide phototransformation can represent a major dissipation route for pesticides released into the environment (Stumm and Morgan 1996, Vulliet *et al.* 2002). Pesticide photolysis on soil and plant surfaces has been studied extensively as it relates to pesticide efficacy (Balmer *et al.* 2000). The study of pesticide photolysis in the atmosphere has also been explored rather comprehensively due to its impact on long-range atmospheric transport (Graedel 1982, Unsworth *et al.* 1999, Atkinson *et al.* 1999). Pesticide photolysis can also occur in aquatic environments (Santos and Rezende 2002, Vulliet *et al.* 2002). There is considerable literature pertaining to pesticide photolysis under laboratory conditions with artificial light but there exists relatively little information on pesticide photolysis in natural aquatic environments such as wetlands (Konstantinou *et al.* 2001).

The ultimate energy source that will drive pesticide photolysis in natural environments such as wetlands is ultraviolet radiation (UV-R) from the sun (Cox and Kemp 1971, Hirahara *et al.* 2001). Hence, climatic, temporal, and geographic conditions that influence UV-R levels will also impact pesticide photolysis rates (Sundstrom and Ruzo 1977, Zepp and Cline 1977, Baughman and Lassiter 1978, Pirisi *et al.* 1996). Components of wetland water columns, such as suspended and dissolved substances can also attenuate UV-R and consequently, pesticide photolytic rates will be a function of water depth and clarity (Baughman and Lassiter 1978).

The first law of photochemistry (Grotthus-Draper Law) requires that light must be absorbed for a reaction to take place (Zepp and Cline 1977, Harris 1984). Substances that absorb light (chromophores) become unstable and undergo a variety of processes to return

to a stable state (Wayne 1970, Cox and Kemp 1971). The "stable state returning processes" that are important in driving pesticide photolysis involve chemical reactions (Zepp and Cline 1977, Miller and Zepp 1979). The two general types of pesticide photolysis that could occur in wetlands: (1) direct photolysis (2) indirect photolysis, can be differentiated based on the chromophore that absorbs the light (Harris 1984, Stumm and Morgan 1996).

Direct pesticide photolysis involves pesticides directly absorbing photons of light (van Loon and Duffy 2000). Pesticides absorbing light < 290 nm will not be affected by direct photolysis under natural conditions as theses wavelengths do not penetrate the atmosphere (absorbed by ozone) (Wolfe *et al.* 1990). Once light has been absorbed, the pesticide becomes energetically unstable having an electron state with excess energy (Cessna and Muir 1988). The excess energy can then be used in photolytic reactions to transform the pesticide (Equation 4) (Wayne 1970, Cox and Kemp 1971, Vialaton *et al.* 2001). However, the quantum yield for pesticides will be too high for direct photolysis to occur in aquatic environments such as wetlands under natural light conditions (Keum *et al.* 2002).

Equation 4. $$pesticide \xrightarrow{hv} pesticide\ excited \xrightarrow{lysis} products$$

Indirect photolysis involves the absorption of light not by the pesticide but by other chromophores (van Loon and Duffy 2000). Indirect photolysis can be further divided into photosensitized reactions and photo-mediated reactions. Photosensitized reactions involve the absorption of light energy by chromophores known as photosensitizers. Upon light absorption, photosensitizers become excited and can then pass their excess energy on to pesticides where it is used to degrade the pesticide (Equation 5) (Sundstrom and Ruzo 1977, Zepp and Baughman 1978, Racke 1993, Hapeman *et al.* 1998 a,b). The transfer of energy from photosensitizers to pesticides occurs via radiative and non-radiative mechanisms (Miller and Zepp 1979, Choudhry *et al.* 1979).

Equation 5. $sensitizer \xrightarrow{hv} sensitizer\ excited$

$$sensitizer\ excited + pesticide \xrightarrow{lysis} products$$

The other type of indirect photolysis involves photo-mediated pesticide reactions (Equation 6). Here the chromophore after absorbing light energy degrades to produce free radicals. The newly formed species then proceed to degrade pesticides through free radical induced reactions.

Equation 6. $Chromophore + light \rightarrow free\ radical$

$$Free\ radical + pesticides \rightarrow pesticide\ transformation\ products$$

The hydroxy radical ('OH) is a reactive, nonselective, free radical that can degrade pesticides (Mill *et al.* 1980, Haag and Hoigne 1985, Stumm and Morgan 1996, Hiskia *et al.* 1997, Pichat 1997, Hapeman and Torrents 1998, Benitez *et al.* 2002). Ambrust (2000) has suggested that 'OH mediated pesticide oxidation will be the most significant abiotic pesticide transformation process in shallow waters with low light attenuation. Other free radicals that can be formed by photolysis include carbonate radicals and singlet oxygen (Zepp *et al.* 1977, Haag and Hoigne 1986, Burrows *et al.* 2002). Singlet oxygen usually reacts quickly to form 'OH that can then proceed to react with pesticides (Benitez *et al.* 2002).

The extent of pesticide photolysis in wetlands will be a function of available light, as well as chromophores capable of facilitating indirect photolysis. Components of wetland water columns can affect photolysis in physical and photochemical ways (Zepp 1982). Shading by macrophytes, phytoplankton and suspended solids can attenuate light and reduce photolysis potential (Lund-Hoie and Friestad 1986, Auger *et al.* 2000). For example, Lund-Hoie and Friestad in a laboratory experiment determined that the shorter photolytic half-life of glyphosate in deionized water (8.4 days) as opposed to lake water (67.2 days) was due to the greater UV penetration in deionized water. Suspended solids such as clays and organic material can also sorb pesticides and make them unavailable for

photolysis (Zepp and Schlotzhauer 1981, Bobe *et al.* 1998, El-Nahhal *et al.* 1999, Petty *et al.* 2001). Bobe *et al.* (1998) showed that the photodegradation rate of the insecticide fipronil was inversely related to the organic matter content present. In their photolysis experiment, solutions with 0.1% organic matter had a lower fipronil half-life (147 h) than in solutions with 6.5% organic matter (217 h).

In contrast to the above, some components of wetland water columns may favour pesticide photolysis. The availability of photosensitizers in aquatic environments will determine the extent of photosensitized photolysis. Natural photosensitizers include riboflavin (Rejto *et al.* 1983, Harrison and Venkatesh 1999) and epicuticular components (Pirisi *et al.* 1998, Venkatesh and Harrison 1999). Algae may also act as photosensitizers. In a laboroatory experiment Zepp and Schlotzhauer (1983) showed that cultures of algae were capable of accelerating the photolysis of organic chemicals. For instance, the photolysis of aniline in the presence of *Chlamydomonas* sp. was 50 times faster than in distilled water. The authors also demonstrated that substances released by heat-killed *Chlamydomonas* sp. cells also accelerated aniline photolysis.

The concentration of chromophores in wetlands that are capable of photolytically producing free radicals will determine the extent of photo-mediated pesticide transformation. Hydrogen peroxide can form in natural waters (Draper and Crosby 1983) and when subjected to UV-R produces OH (Draper and Wolfe 1981). However, Hagg and Hoigne (1985) have suggested that the above process will be too slow in natural waters to be a significant source of OH. They argue that the most important chromophore involved in photo-mediated degradation in aquatic environments is usually nitrate (Equation 7) (Haag and Hoigne 1985).

Equation 7: $NO_3^- + light \rightarrow NO_3^- * \rightarrow NO_2 + O^-$

$O^- + H_2O \rightarrow OH^- + OH$

The role of dissolved organic matter (DOM) in pesticide photolysis in wetlands is complex and varies depending upon the characteristics of the pesticides and DOM

involved. DOM can facilitate indirect pesticide photolysis by either acting as photosensitizers or through the photolytic production of free radicals (Khan and Schnitzer 1978, Zepp *et al.* 1981, Choudhry 1984, Faust and Hoigne 1987, Minero *et al.* 1992, Lartiges and Garrigues 1995, Kamiya and Kameyama 1998, Schindelin and Frimmel 2000, Stangroom *et al.* 2000 Keum *et al.* 2002). DOM can also inhibit pesticide photolyis (Kochany and Maguire 1994a, Mountacer *et al.* 1998, Bachman and Patterson 1999, Konstantinou *et al.* 2001). DOM can inhibit photolysis in a variety of ways. Physically, DOM can reduce the energy available for photolysis by attenuating light (Durand *et al.* 1991, El Azzouzi *et al.* 1999a, Konstantinou *et al.* 2001). Chemically, DOM can limit the amount of photo-mediated pesticide degradation by scavenging free radicals and making them unavailable to react with pesticides (Haag and Yao 1992, Torrents *et al.* 1997, Brezonik and Brekken 1998, Stangroom *et al.* 1998, Schindelin and Frimmel 2000). Further study is needed that examines not only the quantitative effects but also the qualitative effects of DOM on pesticide photolysis in aquatic environments such as wetlands (Hapeman *et al.* 1998a,b).

Another aspect of wetlands that can either accelerate or inhibit pesticide photolysis is the pH of the water (Raschke *et al.* 1998, Harrison and Venkatesh 1999). Low pH levels may enhance (Bhattacherjee and Dureja 1999, El Azzouzi *et al.* 1999b, Bouhaouss *et al.* 2000) or inhibit (Comber 1999, Ambrust 2000) pesticide photolysis. One way pH levels may impact photolysis (photo-mediated degradation) is by influencing the OH concentration. Low pH levels can cause a reduction in the photolytic production of OH that in turn would lower the pesticide transformation rate (Beltran *et al.* 2000). In addition, the photolysis of some pesticides may not be influenced by the pH of the water they are found in (Wilson and Mabury 2000, Meunir *et al.* 2002).

Although pesticide photolysis can lead to complete mineralization (Moctezuma *et al.* 1999, Prevot *et al.* 1999, Barcelo 2001), transformation products are usually produced. The toxicity of photolytic products may be lower (Lin *et al.* 1999), equal to (Duke *et al.*

1991, Lee *et al.* 1999, Pehkonen and Zhang 2002) or greater than (Mansour *et al.* 1999, Scrano *et al.* 2002) the parent compound (Felsot and Pederson 1991, Day 1991). The photolytic products can also have a synergistic effect with the remaining parent compound causing higher toxicity than that seen prior to photolysis (Dzyadevych *et al.* 2002). There has been relatively little work done on identifying and testing the toxicity of pesticide photo-transformation products (Pehkonen and Zhang 2002).

Other abiotic reactions

Non-photolytic oxidation reactions involving naturally occurring oxidation agents can occur in water (Spencer *et al.* 1980, Smith 1988, Coats 1991, Hapeman and Torrents 1998 a,b, Beltran *et al.* 2000). Under reducing environments abiotic reduction of pesticides can also contribute to pesticide transformation (Macalady *et al.* 1986). As most studies do not differentiate between biotic and abiotic pesticide reduction, the significance of abiotic pesticide reduction is difficult to ascertain (Wolfe *et al.* 1990). Extracellular enzymes released by microorganisms for extracellular digestion or during plasmolysis can also transform pesticides (Miskus *et al.* 1965, Wolfe *et al.* 1990, Neilson 2000).

Biotic

Living organisms facilitate biotic pesticide transformations and thus factors that influence the biota will in turn determine the extent of pesticide transformed. The variables that determine biotic concentrations in wetlands are not static but vary annually, seasonally, and daily. As these variables vary temporally, so will the biotic transformation rates of pesticides (Watson 1977, Rubin *et al.* 1982, Jones and Alexander 1986).

Microorganisms are ubiquitous and are capable of rapid adaptation to changes in their environment (Wright 1971, Bollag and Liu 1990, Shelton and Karns 1998). Thus, it is not surprising that microorganisms are responsible for a significant amount of the biotic transformation of pesticides that occurs within the environment (Getzin 1981,

Munnecke *et al.* 1982, Lewis *et al.* 1984, Mac Rae 1985, Bekhi and Kahn 1986, Mandelbaum *et al.*1993, Racke 1993, Topp *et al.*1995).

Wetlands, due to their characteristically high organic matter and warm summer temperatures tend to provide ideal conditions for microbial growth (Mitsch and Gosselink 2000). For instance, Verma *et al.* (2003) reported fungal biomass concentrations as high as 5.8 mg of C per gram of ash free dry mass litter in Saskatchewan wetlands. High microbial growth would reduce pesticide persistence in wetlands if the microbial community consists of organisms that are capable of pesticide degradation. Few studies have specifically studied microbial pesticide degradation in wetlands (Anderson *et al.* 2002).

The first condition that must be met is that the wetland supports microbes capable of degrading the pesticide in question. Pesticide degrading microbes can occur in wetlands. For example, Larsen *et al.* (2001) isolated microbes from sediment from a Danish wetland that were capable of degrading isoproturon, mecoprop and metsulfuron-methyl. Larsen *et al.* (2001), in addition to Kao *et al.* (2001) and Anderson *et al.* (2002), have also shown that atrazine can be microbially degraded in wetland sediment. One factor that can determine whether or not a wetland contains pesticide degrading microbes is the wetlands exposure history to the pesticide in question. For instance, Anderson *et al.* (2002) showed that atrazine mineralizing bacteria were present in an Ohio wetland that received agricultural runoff but were not present in a wetland that was isolated from agricultural runoff. The authors attribute this difference in the microbial community to past exposure to atrazine. The microbes in the wetland that received agricultural runoff had prior exposure to atrazine and consequently may have adapted mechanisms to degrade this pesticide. In contrast, the isolated wetland had no prior exposure to atrazine which was reflected in the microbial community not being able to mineralize the pesticide.

Availability of suitable substrata for microbial colonization is another conditions that can influence the extent of microbial pesticide degradation in wetlands. Organic matter is

frequently a limiting factor in the growth of microorganisms (Atlas and Bartha 1992). Thus, increases in organic matter content can favour microbial growth and, in turn, pesticide degradation (Simsiman and Chesters 1976, Pritchard 1987). For instance in a simulated lake impoundment experiment Simsiman and Chesters (1976) showed that the persistence of the herbicide Diquat was related to the amount of organic matter present. In their experiment Diquat was added (1.5 μg/mL) to vegetated (*Myriophyllum spicatum* and *Elodea canadensis*) and non-vegetated lake impoundments. At the end of 180 days, only 25% of the total added Diquat remained in the vegetated impoundment (in water and plant tissue) whereas over 98% of the Diquat remained in the non-vegetated impoundment. The authors attributed the difference in Diquat loss to greater microbial concentrations in the vegetated impoundment. Lee *et al.* (1995) also showed that atrazine half-life in vegetated (*Typha latifolia, T. angustifolia*) wetland mesocosm was shorter (58 to 70 days) than in non-vegetated mesocosm (85 to 115 days). These authors suggested that the vegetated mesocosms could have supported a greater microbial population which could in turn lead to greater microbial degradation of atrazine.

Another way wetland vegetation may affect microbial degradation of pesticides is if the vegetation produces oxygen rich rhizospheres. Rhizospheres occur around the roots of plants (Anderson *et al.* 1993). Oxygen transferred to the root system can leak into the rhizosphere (Dunbabin *et al.* 1988, Reddy *et al.* 1989a,b, Schnoor *et al.* 1996, Grosse and Frick 1999). The higher oxygen content of rhizospheres can support microbial concentrations up to 100 times that of surrounding areas (Atlas and Bartha 1992). Given their higher microbial concentrations rhizospheres can represent areas of enhanced microbial pesticide transformation (Nesbitt and Watson 1980, Schmidt and Alexander 1985, Curl and Truelove 1986, Nichols *et al.* 1997, Gish *et al.* 1998, McKinlay and Kasperek 1999, Arthur *et al.* 2000, Girbal *et al.* 2000). For instance, in a wetland microcosm experiment conducted in England, McKinlay and Kasperek (1999) showed that microbial activity in the rhizosphere of *T. latifolia* caused a more rapid loss of

atrazine (atrazine dropped below detection limit (0.01μg/ml) in 10 days) than in sterilized controls (atrazine dropped below detection after 41 days). Other authors have demonstrated that pesticide degradation is greater under aerobic conditions. For example, Larsen *et al.* (2001) demonstrated that isoproturon and metsulfuron-methyl were microbially mineralized in wetland sediment only if aerobic conditions were present. Larsen *et al.* (2001) also showed that atrazine microbial mineralization in Danish wetland sediments was greater in aerobic conditions (4.5% of atrazine mineralized) than in anaerobic conditions (2% mineralized).

Nutrient availability in wetlands could also determine the extent of microbial pesticide transformation. If nutrients are not limiting, microbes may not utilize pesticides as a nutrition source but instead opt for more accessible nutrient forms. In laboratory experiments, Mandlebaum *et al.* (1993) and Gebendinger and Radosevich (1999) have shown that nitrogen additions can suppress soil microbial transformations of atrazine. In other cases, nutrients may stimulate microbial pesticide transformation by acting as a supplementary substrate (Schmidt and Alexander 1985, Schmidt *et al.* 1992). In addition, work by Kuritz *et al.* (1995, 1997) has shown that nitrate may be necessary for degradation of certain pesticides. Nitrate stimulates the bacterial *nir* operon to produce enzymes including those involved in pesticide transformations (Kuritz *et al.* 1995, 1997). Other studies have documented the coupling of denitrification reactions with xenobiotic biotransformations (Haggblom *et al.* 1993).

Suspended solids can also influence pesticide microbial transformation in wetlands. Microbial transformation rates for pesticides can, at times, be decreased in the presence of certain suspended solids such as clays. The association between pesticides and suspended clays may be such that the pesticide is no longer available to be microbially transformed (Weber and Coble 1968, Subba-Rao and Alexander 1982, Orgam *et al.* 1985). For instance, Weber and Coble (1968) showed that diquat mineralization occurred in liquid cultures of soil microorganisms. However, when montmorillonite clay was

added to the cultures (at a concentration so that all the diquat was sorbed), no mineralization of diquat was detected. Conversely, suspended solids could increase pesticide microbial transformation within the water column if they provide suitable substrate for bacterial colonization (Aly and Faust 1964, Alexander 1974).

Aquatic macroorganisms such as macrophytes, invertebrates, and vertebrates can also metabolically transform pesticides (Khan *et al.* 1977). Pesticide transformation rates in macroorganisms are dictated by pesticide entry into the organism and enzyme availability (Hatzios 1988, Wei and Vossbrinck 1992, Gao *et al.* 2000a,b).

Pesticide transformation by macroorganisms, as in the case of microorganisms, involves broad-spectrum enzymes (Hatzios 1988, Gao *et al.* 2000a,b). Arguably the most ubiquitous and effective group of enzymes capable of transforming pesticides is the P450 cytochrome complex (Blakeslee 1997, Hanioka *et al.* 1998, Walker 1998, Perkins *et al.* 1999, Jensen 2000, Stehr *et al.* 2000, Scott and Wen 2001). The enzymes of the P450 cytochrome complex add oxygen atoms to hydrophobic pesticides making them more water soluble and thus easily excreted (Blakeslee 1997).

Until recently, the extent of pesticide transformation by aquatic macroorganisms had not been investigated extensively. Pesticide transformation in aquatic plants is becoming of interest as plants could play an important role in phytoremediation of contaminated waters (Arthur and Coats 1998).

2.6 Pesticide Fate Models

Ecotoxicological studies commonly develop and utilize mathematical models to predict the environmental fate and effects of toxicants such as pesticides (Schnoor 1996). These models require the input of a number of variables pertaining to the characteristics of the pesticide and environment in question. Pesticide fate models usually incorporate aspects of pesticide degradation and the fugacity concept, which describes the tendency of molecules to "escape" from one compartment into the next (Schnoor 1996).

Given the paucity of pesticide-wetland studies it is not unexpected that no wetland pesticide models *per se* have been developed. However, a few investigators have applied general aquatic pesticide models to the wetland environment. Cromwell (1997) applied a general pesticide model (Chapra 1997) (Equation 8) to wetland ponds subjected to experimental atrazine additions.

Equation 8. $M_{day} = (M_{day-1})e^{-(k\,photo + k\,hydro + k\,vol + k\,sed + k\,bio)}$

where M = mass of atrazine added, k = the first order rate coefficient, photo = photolysis, hydro = hydrolysis, vol = volatilization, sed = sedimentation, bio = biodegradation

Cromwell used published values for the first order rate coefficients for the various pesticide fates. The Cromwell study revealed that the above model was only able to predict field results with the addition of a loss parameter that was an order of magnitude greater than any of the rate coefficients.

Goldsborough and Crumpton (1998) applied the Quantitative Water, Air, Sediment, Film Interactions (QWASFI) model (Southwood *et al.* 1989) to a wetland mesocosm environment to estimate the atrazine water column half-life. The atrazine half-life of two days, calculated by Goldsborough and Crumpton (1998) using the QWASFI was somewhat lower than published values (7 to 60 days) (deNoyelles *et al.* 1982, Detenbeck *et al.* 1996). The discrepancy between models and experimental data suggest that general pesticide aquatic models may not always be reliable in predicting the persistence of pesticides in wetlands. This may be due to differences in conditions between the model environment and those seen in PPR wetlands.

2.7 Summary

Agriculture has negatively impacted PPR wetlands through the addition of agrochemicals. As agrochemical use continues it is important to understand the fate and impact of these chemicals in wetland environments. Although more research in the area would be welcome, a working knowledge of the influence of fertilizer additions on

wetlands can be found in the literature. Fertilizer additions tend to increase primary production and can result in changes in wetland stable states.

Like fertilizers, pesticides may also impact wetlands and initiate fluctuations in wetland stable states. However, compared to fertilizers, the effects and fate of pesticides in wetland environments have not been as extensively studied. As pesticides can impact natural environments efforts should be made to reduce their effects. A solution to the environmental threat of pesticides would be to invoke a complete ban on pesticide use. Yet pesticide use is so closely intertwined with the global economy that a complete pesticide ban in the near future is unforeseeable. Hence, it is imperative to seek ways to minimize the environmental effects of pesticide use. Wetlands, both natural and constructed, may minimize the environmental effects of pesticides. To mitigate the effects of pesticides, wetlands would have to transform and or retain a significant amount of pesticide. PPR wetlands may have high pesticide retention capabilities due to their low water velocity and high biomass. Wetland productivity may also favour microbial and photolytic pesticide transformation processes. In addition, the temperature and light regime of wetlands, due to their shallow nature, could favour abiotic pesticide transformation (photolysis and hydrolysis).

From the literature pertaining to pesticide fate in aquatic environments, as well as the knowledge of pesticide chemistry and wetland characteristics, generalizations of pesticide fate in wetlands can be made. However, extrapolation of results from other aquatic environments to wetlands may be inaccurate due to the environmental differences encountered. Until additional research is conducted, specifically in the wetland environment, the fate of pesticides in wetlands remains in question.

The study of pesticide fate in wetlands is not trivial given the variety of pesticides used and the spatial and temporal variability of wetland conditions. A good starting point for future investigations would be an examination of the influence of predominant

wetland characteristics, such as their elevated productivity, on the fate of representative pesticides.

Chapter 3: Intrinsic and extrinsic determinants of atrazine and lindane presence in PPR wetlands

3.1 Introduction

The Prairie Pothole Region (PPR) of North America is an area of intensive agricultural production (Neave *et al.* 2000) and high wetland density (12 wetlands/km^2 Sheehan *et al.* 1987). Within the PPR it is common to find wetlands close to areas of agricultural pesticide use (Frankforter 1995). Surveys have detected pesticides in over 70% of sampled wetlands (Donald *et al.* 1999, Anderson *et al.* 2002).

It is necessary to understand the factors that are most influential in determining wetland pesticide presence in order to reduce pesticide contamination of wetlands. Aside from Donald *et al.* (1999), no other survey in the current literature relates pesticide presence in natural PPR wetlands to environmental factors. Although Donald *et al.* (1999) made a convincing argument for the importance of rainfall in determining pesticide presence, they did not report on the influence other variables such as temperature or organic matter might have on pesticide presence in wetlands.

Pesticide presence will be a function of variables extrinsic and intrinsic to the wetlands. Extrinsic variables are those which are not measured within the confines of a prescribed topographic basin. Extrinsic variables suspected of influencing pesticide presence in wetlands include climate and surrounding land use. Climatic variables can determine the extent of pesticide transport to wetlands (Wentz 1988, Neely and Baker 1989, Page *et al.* 1995). For example, air temperature influences the amount of pesticide volatilized from agricultural fields whereas precipitation can determine the extent to which pesticides in the atmosphere are deposited in wetlands (Hoff *et al.* 1992, Haugen *et al.* 1998). Precipitation can directly influence pesticide transport to wetlands by determining the intensity and amount of surface runoff (Konda and Pasztor 2001, Mickelson *et al.* 2001). Air temperature and precipitation can influence crop growth,

which may determine the timing and extent of agricultural pesticide application (United States Department of Agriculture (USDA) 2000). This will ultimately dictate the amount of pesticide available for off-field export to environments such as wetlands. Surrounding land use can also determine the amount of pesticide transported to wetlands. Wetlands in close proximity to areas of pesticide application may be at a greater risk of pesticide contamination than those wetlands further removed from areas of application.

Intrinsic wetland variables, those which are measured within the confines of the wetland basin, can also be important in determining pesticide presence. Wetland organic matter can provide surface area for pesticide sorption (Johensen *et al.* 1987, Stomp *et al.* 1994, Mersie and Seybold 1996, Sheng *et al.* 2002). Organic matter can also influence pesticide degradation by providing substrata for microorganisms capable of pesticide degradation (Pritchard 1987).

I chose to study atrazine and lindane due to their different use patterns within the PPR. Atrazine is applied predominately on corn (*Zea mays* L). Within the PPR the majority of corn is grown in the south (Table 14) and consequently this is where most atrazine use occurs (Thelin 1998, USDA 2000). For instance, in 1992, the average use of atrazine in North Dakota was < 1.1 pounds/mile^2 whereas in Iowa average atrazine use was > 66.5 pounds/mile^2 (Thelin 1998). Lindane use during the period of this survey occurred in the northern (Canadian) portion of the PPR. For example, in Manitoba, lindane was applied as a seed treatment on over 280,000 acres in 1999 (Manitoba Crop Insurance Corporation (MCIC) 2001). In the Canadian PPR, during the years of the survey approximately 90% of the lindane use was for canola (*Brassica napus* L) seed treatment (R. McLeod, Gustafson Canada, pers. comm. 2000, Science and the Environment Bulletin 2001). Volatilization is the main off-field transport mechanism for lindane (Donald *et al.* 1999, Waite *et al.* 2001). Emergence of the canola seed leaves makes the lindane readily available for volatilization (Schneider and Scheunert 1991, Waite *et al.* 2001). In the United States lindane seed treatment of canola is prohibited but

Table 14. Corn acreage seeded within PPR provinces (Manitoba Agriculture and Food, Agricultural Statistics 2003) and states (National Agricultural Statistics Service 1997) in 2000.

Province or state	Acres (000) seeded	Percent of total
Manitoba and Saskatchewan	145	< 1
Montana	60	< 1
North Dakota	1080	4
South Dakota	4300	17
Minnesota	7200	29
Iowa	12300	49
Total	25085	100

lindane can be used as a wheat and corn seed treatment. However, lindane use in PPR states was not reported during the years of the survey (United States Department of Agriculture (USDA) 1999a, USDA 2000).

The years of the survey (1999 to 2001) represent a transition period in lindane use on the Canadian prairies. Anticipating a ban on lindane sales, pesticide distributors began in the late 1990s to promote other canola seed treatments (i.e. thiamethoxam) and, after the 1999 season, distributors went so far as to voluntarily remove lindane products from the market (A. Vaughn, Gustafson Canada, pers. comm. 2002). Thus, an assessment of lindane persistence in wetlands could be made by examining lindane levels in wetlands during times of declining use (1999) versus times of lowered or no use (2000 and 2001).

The objective of my study was two-fold: 1) to determine the extent of detection of the pesticides atrazine and lindane in PPR wetlands; and 2) to determine if extrinsic and intrinsic wetland variables were related to frequency of atrazine and lindane detection. I hypothesized that lindane detection would be greater in Canadian wetlands than in American wetlands due to higher lindane use in Canada. Similarly, I hypothesized that atrazine detection would be greater in US wetlands due to higher regional atrazine use. If my hypotheses are supported, then the extent of wetland contamination could be reduced by reducing local pesticide use. I also hypothesized that sediment organic matter would be negatively correlated with pesticide water column detection because sediment organic matter has been shown to sorb pesticides and remove them from the water column (Kadlec and Alvord 1993, Detenbeck *et al.* 1996, Kao *et al.* 2001, Moore *et al.* 2002).

3.2 Materials and methods

Study area

Sixty wetlands were selected within the PPR of two Canadian provinces (Manitoba, Saskatchewan) and five American states (Iowa, Minnesota, Montana, North Dakota, South Dakota) (Figure 4). The distance between the two farthest sites was approximately 1,700 km. Survey sites were not selected at random but *a priori* to maximize their spatial

variability across the study region (Laing and Smol 2000, Skjelkvale *et al.* 2001). The site selection processes was difficult given the great number of wetlands within the PPR, the absence of a comprehensive wetland database, the region's large area (715,000 km^2, Euliss *et al.* 1999) and the limited timeframe for sampling. Sites selected were either semi-permanent or permanent wetlands (Class 4 and 5; Stewart and Kantrud 1971) that were within one kilometer of public roads for ease of sampling access. Semi-permanent and permanent wetlands were selected to increase the likelihood that they would contain water at the time of sampling.

In Canada the PPR was divided into blocks 2° latitude by 2° longitude. At least one wetland was selected within each block. The Canadian Wildlife Service's Spring Pond Count (CWSPC) was used for site selection. The CWSPC is conducted through aerial enumeration of wetlands (M. Shuster, Canadian Wildlife Service, pers. comm. 1998). Roads chosen were those that most closely paralleled the boundaries of the PPR as well as those that encompassed a wide spatial range within the PPR (Figure 11). Only wetlands accessible from public land (road allowance) were selected. This was done to avoid the often lengthy process of obtaining permission to access private land (Lesser 2001).

The Gleason database (Gleason and Euliss 1996) was used to select US wetlands with a wide spatial distribution. This database consists of wetlands on both public and private land. Again to avoid the process of obtaining permission to access private land I only selected wetlands that were managed by the United States Fish and Wildlife Service (USFWS).

Wetlands were sampled four times in the summer during the years 1999 to 2001. In 1999 the wetland sites were sampled between June 9 and July 22 (Round I) and again between August 9 and August 30 (Round II). All the sites were sampled again in 2000 (June-July) and the Canadian sites were sampled again in 2001 (June-July).

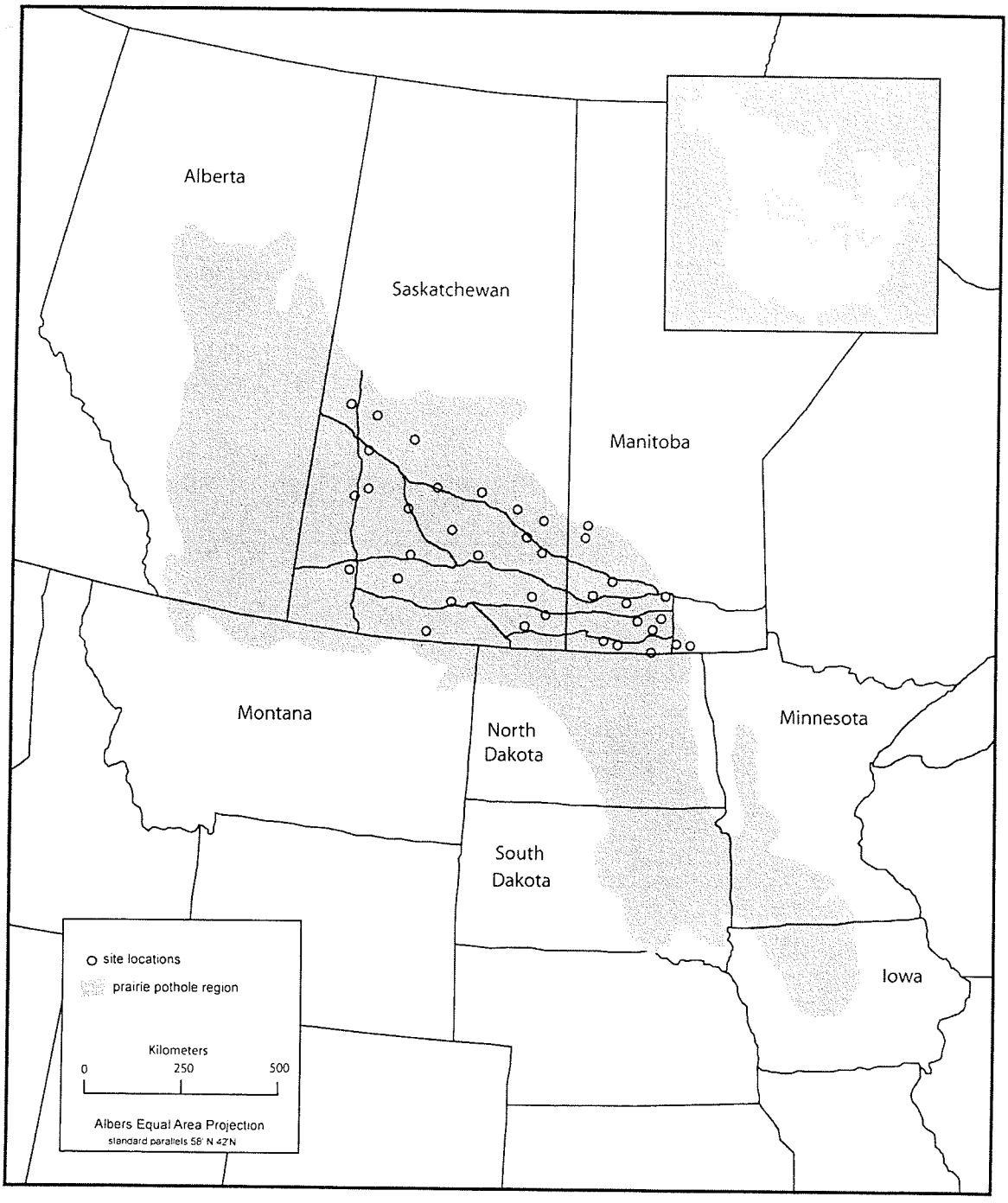


Figure 11. Location of roads used in selecting Canadian PPR wetlands to be surveyed for their environmental characteristics and pesticide (atrazine and lindane) concentrations.

Sampling protocol

Wetland extrinsic and intrinsic variables were selected based on their potential to influence pesticide contamination and detection (Table 15). The extrinsic variables recorded were of two general types: climatic and landscape. Average air temperatures, elapsed time between sampling date and last precipitation event, and the 15-day total precipitation prior to sampling date were collected from federal, state, and private weather stations located near the wetland sites (Appendix B). The average distance between wetland and weather station was approximately 16 km and the range was 1 to 40 kilometers. Landscape variables consisted of on-site observations. Buffers between wetlands and agricultural lands were defined as any non-cropland or summer fallow located between wetland sites and agricultural fields. Buffers were categorized as either fallow/grassland or treed. In addition to categorizing buffer type, buffer width was also estimated and wetlands were placed into one of two categories: 1) buffer width less than 15 meters; and 2) buffer width greater than 15 meters. Fifteen meters was chosen because it is the average buffer distance recommended for the prevention of pesticide contamination of wetlands (Manitoba Agriculture and Food 1999, Saskatchewan Agriculture and Food 1999). Buffer width and type can determine pesticide detection by influencing the extent of pesticide transport to wetlands (Crosbie and Chow-Fraser 1999, Benoit *et al.* 2000, Blanche *et al.* 2003). The approximate distance between wetlands and the nearest road was also measured. The distance between wetland and road may influence surface runoff to wetlands and, in turn, may determine pesticide presence in the wetlands.

The intrinsic variables sampled were selected based on their ability to influence pesticide persistence by their effect on pesticide sorption, degradation, or transport (Table 15). Surface water temperature, visible light transmittance, and pH were recorded as these can influence pesticide degradation rates (Zepp and Baughman 1978, Giddings *et al.* 1997). Water column and sediment organic matter were quantified as they can determine

Table 15. Extrinsic and intrinsic variables measured at wetland sites and rational for variable selection based on their potential effect on pesticide detection.

Variable	Potential effect on pesticide detection
Extrinsic	
Obvious inflow/outflow	Pesticide transport to and from wetland
Buffer type	Pesticide transport to wetland
Buffer width	Pesticide transport to wetland
Precipitation volume	Pesticide transport to wetland
Precipitation timing	Pesticide transport to wetland
Proximity to road	Pesticide transport to wetland
Intrinsic	
Temperature	Pesticide degradation
Light extinction	Pesticide degradation
pH	Pesticide degradation and sorption
Conductivity	Surface are for pesticide sorption
Dissolved organic matter	Surface area for pesticide sorption
Total suspended solids	Surface area for pesticide sorption
Phytoplankton chlorophyll *a*	Surface area for pesticide sorption
Submersed macrophyte biomass	Surface area for pesticide sorption
Percent sediment organic matter	Surface area for pesticide sorption

pesticide sorption (Mersise and Seybold 1996, Soderstrom *et al.* 2000). The presence or absence of any obvious permanent surface flow channels into or out of the wetlands was recorded as surface flow can influence pesticide presence through either pesticide import or export.

The depth of the wetlands was measured in the middle of the open water area using a graduated measuring line. Temperature near the water surface (10 cm depth) and just above the sediment (5 cm) was recorded at each site.

To quantify phytoplankton chlorophyll and dissolved organic carbon (DOC), two, one-litre depth-integrated water samples were collected from the center of each wetland using a stoppered acrylic tube (6.4 cm inner diameter, 1.5 m length) (McDougal 2002). This sampling method provided a well-mixed integration of the entire water column. The water samples were poured into pre-rinsed opaque polyethylene bottles and stored at 4°C prior to analysis. Samples were analyzed for phytoplankton chlorophyll content by filtering 250 mL through glass microfiber filters (grade GF/C, particle retention 1.2 microns, Whatman International Ltd. England). The filters were neutralized with three drops of saturated magnesium carbonate solution then frozen for a minimum of 24 hours to lyse algal cells. Filters were then placed in 90% methanol and kept in the dark for 24 hours to extract the pigments. Chlorophyll concentrations of the pigment extract were measured spectrophotometrically (Spectronic 601, Milton Roy Company, Rochester, NY) at 665 nm and 750 nm before and after acidification with 10^{-3} N HCl. Chlorophyll concentration (μg/L) was determined as of Marker *et al.* (1980). The DOC content of filtered (Whatman GF/C, particle retention 1.2 μm) water samples was determined using the persulfate-ultraviolet oxidation method (American Public Health Association 1992).

Sediment samples were collected in the middle of the open water area from each wetland site using a stoppered acrylic tube (6.4 cm inner diameter, 1.5 m length). The tube was pushed 10 cm into the sediment, stoppered and removed. The sediment (approximately 31 cm^3) in the tube was pushed out using a plunger into plastic bags. To

determine the organic matter content of the sediment, pre-weighed, oven-dried (100°C) sediment samples (2 cm^3) were combusted at 600°C for one hour then reweighed (Dean 1974).

A sample of submersed macrophytes was collected from the center of each wetland. An open-ended plastic barrel was used to delineate a 0.45 m^2 section of the sediments. Long-handled shears and a dipper sieve (1 mm mesh size) were used to cut and collect the above-ground portion of the macrophytes at the sediment surface. Collected macrophytes were placed into plastic bags for temporary storage and transfer to the laboratory. Samples were sorted to the genus level then dried at 104°C for 24 hours and weighed for calculation of biomass (g/m^2).

Whole water samples were also analyzed for total nitrogen (TN) and total phosphorus (TP) using the Hach digestion method (Ahn *et al.* 2003). The absorbance of digested samples at 890 nm and 410 nm were compared to standards to determine TP and TN, respectively (Ahn *et al.* 2003). In the center of the wetlands a Li-Cor LI-189 meter with an LI-192SA spherical submersible quantum sensor was used to record photosynthetically active radiation (400-700 nm) at 10 cm depth intervals. From these data, light extinction coefficients were calculated following Hudon *et al.* (2000).

Acrylic rods (Goldsborough *et al.* 1986) (90 cm length; 0.6 cm diameter) were used to sample periphytic algae at each site between June and July 1999. Four rods pre-scored at 10 cm intervals, were pushed 30 cm into the sediment in the center of the wetlands during the June-July portion of the survey. The rods were then collected during the second round of the survey (August) and the top 30 cm of each rod were placed into darkened screw top tubes. Rods were frozen for a minimum of 24 hours. Then 15 mL of methanol was added to the tubes that contained the rods. After being immersed in the methanol for 24 hours, spectrophotometric analysis of the methanol extract was the same as that used for phytoplankton.

Water samples were collected at the center of each site for pesticide analysis. One-litre amber glass bottles were acid washed and triple rinsed with deionized water. At each site the bottles were triple rinsed with water collected on site and then submersed 30 cm below the surface of the water for water collection (Donald *et al.* 1999). Samples were stored at 4°C prior to pesticide extraction.

The extraction of atrazine and lindane involved a liquid-liquid extraction using 500 ml of methylene chloride in a separatory funnel, according to Environmental Protection Agency (EPA) Method 8081A (EPA 1996). The extract was condensed using a rotary evaporate and then dried with Na_2SO_4. Extracts were analyzed for atrazine using high performance liquid chromatography (Waters HPLC Breeze System). Fifty microlitres of the sample were injected onto a Waters Symmetry C-18 column. A temperature of 30°C, flow rate of 1.0 mL/min, and UV detection of 214 nm were held constant throughout the analysis. The mobile phase consisted of acetonitrile and water and a gradient program of 38% acetonitrile (time 0 min), up to 75% (6 min), held at 75% (1 min), down to 38% (1 min), held at 38% (2 min). Extracts were analyzed for lindane using a Hewlett Packard 6890 gas chromatograph with an electron capture detector. One microlitre of the sample was injected onto a G & W DB5MS column at an initial temperature of 80°C. The temperature was ramped up at a rate of 20°C/min to a final temperature of 220°C, which was held for 4 min. The carrier gas was helium and the detection gases were nitrogen and air. The recovery efficiency for both atrazine and lindane was 81% from spiked solutions (2 µg/L). The detection limit was 0.001 µg/L for both pesticides.

Statistical methods

SAS Version 8.0 for Windows was used for statistical analysis. Data were log (x+1) transformed prior to analyses to stabilize the variance and approximate the normal distribution. Univariate analysis of variance (ANOVA) was conducted (proc glm) to determine which, if any, variables were significantly different between survey rounds. For comparisons of survey years, post hoc Tukey's tests were used to establish which years

differed significantly. Logistic regression analysis (proc genmod) was used to determine which, if any, of the continuous and categorical variables were significant in determining pesticide detection in the wetlands. This statistical tool was used because it allows for the simultaneous analysis of both continuous and discrete data (Kleinbaum 1994). One-way ANOVAs were also conducted separately on the continuous variables to see which ones were significantly different between wetlands with and without pesticide detection.

3.3 Results

Pesticide detection

Seventy-three percent of wetlands had detectable levels of atrazine or lindane in at least one year of the survey. Lindane residues (1.0 to 3.3 ng/L) never exceeded the Canadian guideline limit of 10 ng/L for the protection of aquatic life (Canadian Council of Resource and Environment Ministers 1987). The mean lindane concentration for sites with lindane detection was 1.9 ng/L and the median was 2.0 ng/L. Atrazine levels (1.0 to 4.8 µg/L) did, however, reach or exceed US governmental guidelines (1 µg/L) at sites in Iowa, Minnesota, North Dakota, and South Dakota. The mean atrazine concentration for sites with atrazine detection was 1.9 µg/L while the median was 1.3 µg/L. Detected concentrations of both pesticides were similar to published values for wetlands and aquatic environments elsewhere (Table 16).

Environmental conditions

The sites were shallow (range 20 to 110 cm) and did not display evidence of thermal stratification; the average difference between surface (10 cm depth) and sediment surface water temperature was 1.2°C (SE 0.1, n = 60). In addition, the water column pH was within the circumneutral to alkaline range for all the sites (range 7.14 to 10.06, median pH = 8.01). Furthermore, all sites had nutrient levels within the hypereutrophic range (TP > 0.1 mg/L, TN > 1.5 mg/L). The wetlands exhibited a wide range of values for the other measured variables (Table 17) which was not surprising given the various soil zones and climates that the PPR encompasses (Appendix C).

Table 16. Atrazine and lindane concentrations detected in aquatic environments of North America.

Pesticide	Environment	Reported levels	Reference
Atrazine	PPR wetlands	1.0 - 4.8 µg/L	Current study
	South Dakota wetlands	Maximum level detected 8 µg/L	EPA 1995
	Coastal wetlands	0.5 - 10 µg/L	Krieger 2001
	Agricultural streams entering Great Lakes	1 - 5 µg/L	Frank *et al.* 1979
	Midwest states surface water (lakes and streams)	Median 3.8 µg/L	Thurman *et al.* 1992
Lindane	PPR wetlands	1.0 - 3.3 ng/L	Current study
	Saskatchewan wetlands	Median 3.3 ng/L	Donald *et al.* 1999
	North Dakota Streams	Maximum 11 ng/L	Brigham 1994

Table 17. Mean (± SE, n = 150) and range of variables measured in PPR wetlands during the survey years 1999-2001.

Variable	Mean	Range
Depth (cm)	63.4 (1.9)	10.5 – 120
Temperature (°C)	20.9 (0.4)	11.9 – 31.0
Light extinction (n/cm)	-0.077 (0.01)	-0.0155 – 0.592
pH	8.39 (0.05)	7.10 – 10.02
Conductivity (mS/cm)	1309 (160)	124 – 6690
Total nitrogen (mg/L)	5.29 (0.30)	1.00 – 20.59
Total phosphorous (mg/L)	1.73 (0.10)	0.01 – 5.66
Dissolved organic carbon (µmol C/L)	1693 (112)	410 – 5750
Total suspended solids (mg/L)	35.74 (3.62)	0 – 193.33
Phytoplankton chlorophyll *a* (mg/L)	50.1 (6.3)	1.0 – 438.8
Submersed macrophyte biomass (g/m^2)	28.62 (3.20)	0 – 168.9
Percent sediment organic matter	10.23 (1.07)	3.60 – 53.70

Seasonal, annual, and spatial variability

Seasonal variation was investigated only in 1999, when sites were sampled twice (RI = June-July, RII = August). One-way ANOVA showed that wetlands exhibited significant ($p < 0.05$) seasonal differences in their water temperature (RI 21°C, RII 22°C), conductivity (RI 995 µS/cm, RII 1553 µS/cm), pH (RI 8.1, RII 8.5), TP (RI 2.0 mg/L, RII 3.1 mg/L) and DOC concentrations (RI 1693 µmol carbon/L, RII 2079 µmol carbon/L). The average elapsed time between wetland sampling and last precipitation event was significantly lower (one-way ANOVA $F_{1,111}=7.46$; $p = 0.007$) during RI (2.7 days) than RII (4.1 days).

The percent of wetlands with detectable levels of atrazine or lindane was higher in RI (61%) as compared to RII (23%) (Figure 12). Atrazine was detected in 10% of wetlands sampled during RI but was not detected during RII. Lindane was detected in 47% of the wetlands in RI but only in 24% of the wetlands sampled in RII (Figure 13). Of the 27 wetlands with lindane detection during RI, only eleven had detectable levels during RII. The average lindane concentration in RI (1.9 ng/L) was significantly higher than for RII (1.1 ng/L) ($F_{1,37} = 13.69$, $p < 0.001$).

Analysis of annual variability was done using data measured during the same time of the year to factor out seasonal variation noted above. No wetlands were dry during the 1999 survey (RI), but four wetlands were dry (no standing visible water) in 2000 and two were dry in 2001. One-way ANOVA identified which variables were significantly different between the survey years (Tables 18 and 19). The percent of sites with atrazine or lindane detection decreased over the years of the survey (Table 20, Figures 14 and 15). Neither detected atrazine nor detected lindane concentrations were significantly different ($p < 0.05$) between years (Table 21).

Pesticide detection differed depending on the location of the sites within the PPR. Canadian sites had higher detection of lindane (1999 - 68%, 2000 - 30%) than American

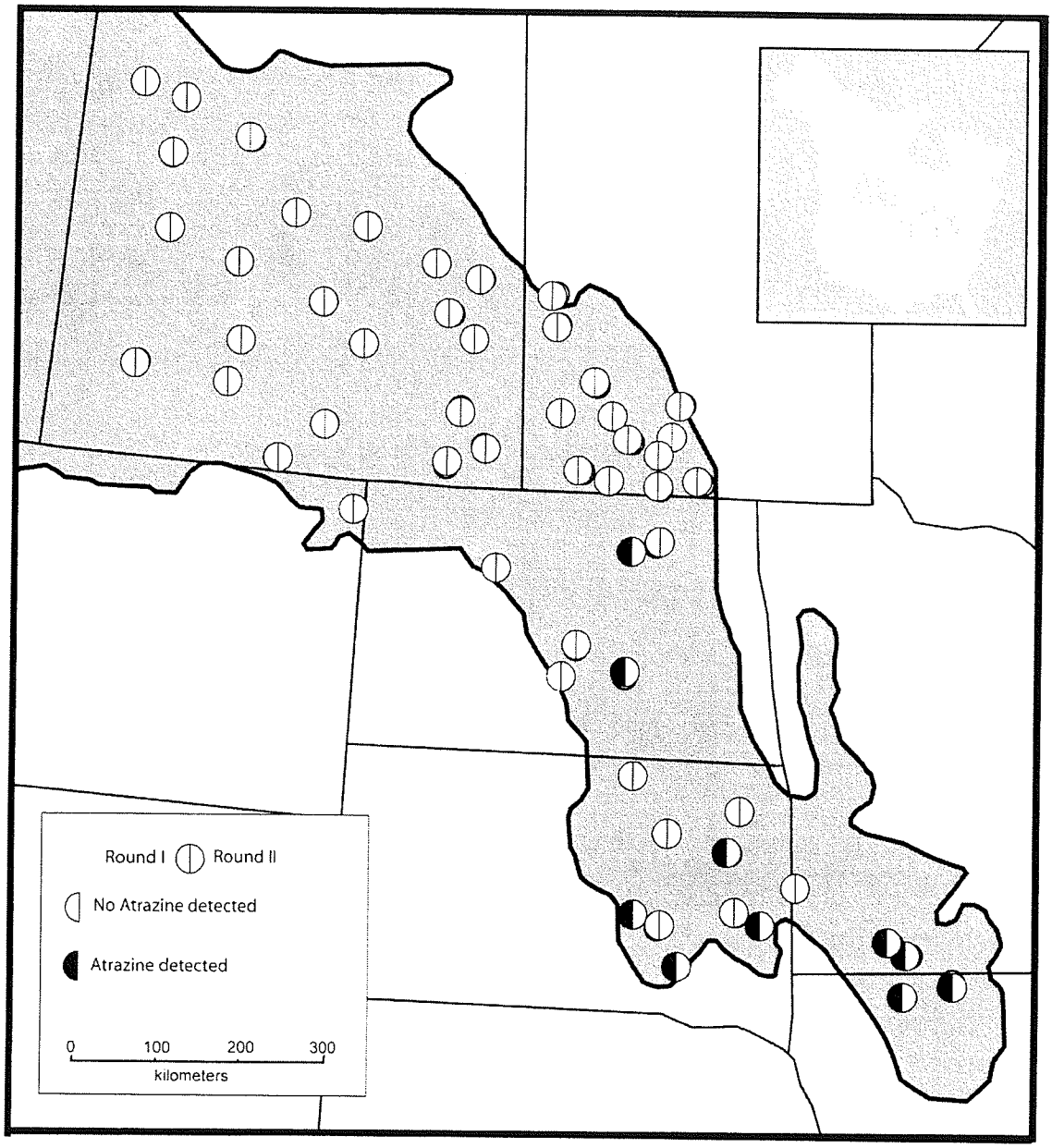


Figure 12. Wetland sites with atrazine detection (> 0.001 µg/L) during Round I (June/ July) and Round II (August) of 1999.

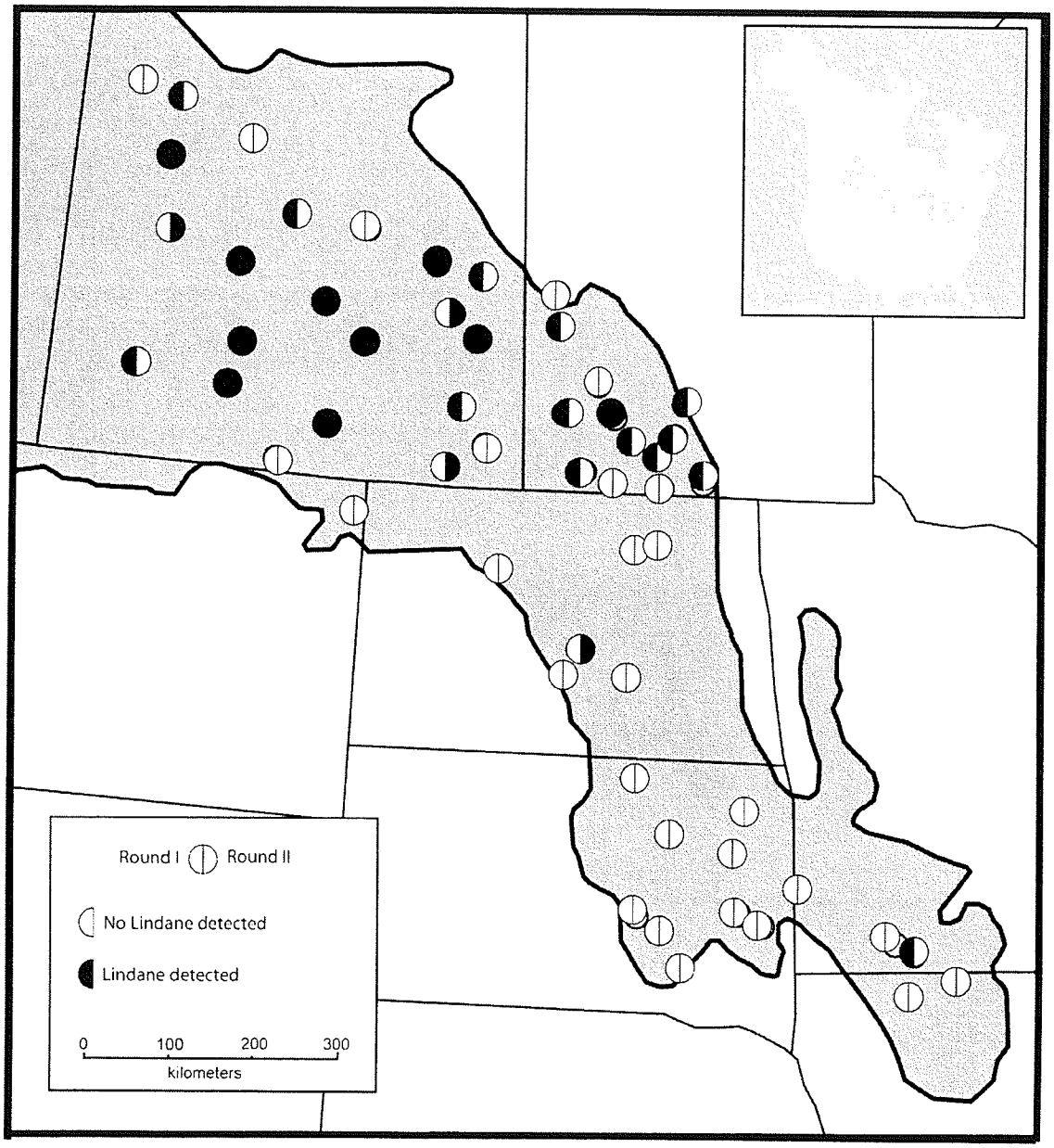


Figure 13. Sites with lindane detection (> 0.001 µg/L) during Round I (June/July) and Round II (August) of 1999.

Table 18. Variables (means; ± SE, 1999 n = 60, 2000 n = 56) measured during 1999 and 2000. Results of a one-way ANOVA significant at $p < 0.05$.

Variable	1999 (Round I)	2000	p-value
Total phosphorous (mg/L)	2.03 (0.12)	1.61 (0.19)	0.003
pH	8.14 (0.09)	8.62 (0.08)	< 0.001
Conductivity (µS/cm)	995 (112)	1814 (408)	0.003
Total suspended solids (mg/L)	43.95 (6.74)	25.92 (5.10)	0.003
Phytoplankton chlorophyll *a* (mg/L)	67.50 (11.49)	47.22 (11.27)	0.003
Light extinction coefficient (n/cm)	-0.08 (0.01)	-0.06 (0.01)	0.064

Table 19. Variables (means; ± SE 1999 n = 38, 2000 n = 37, 2001 n = 35) measured in Canadian wetlands during 1999, 2000, and 2001. Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Variable	1999	2000	2001	p-value
Depth (cm)	72.7^{A}(3.4)	65.3^{A}(3.6)	56.4^{B}(3.9)	0.007
Total nitrogen (mg/L)	5.97^{A}(0.78)	5.84^{A}(0.62)	7.10^{B}(0.69)	< 0.001
Light extinction coefficient (n/cm)	-0.08^{A}(0.01)	-0.05^{B}(0.01)	-0.05^{B}(0.01)	0.014

Table 20. Percent of sampled wetlands with pesticide concentrations above detection limits (atrazine = 0.001 mg/L, lindane = 0.001 µg/L). Number in parenthesis indicates sample size.

Year	Atrazine	Lindane	Either atrazine or lindane
1999	17 (60)	40 (60)	57 (60)
2000	4 (55)	20 (55)	40 (55)
2001	0 (35)	9 (35)	9 (35)

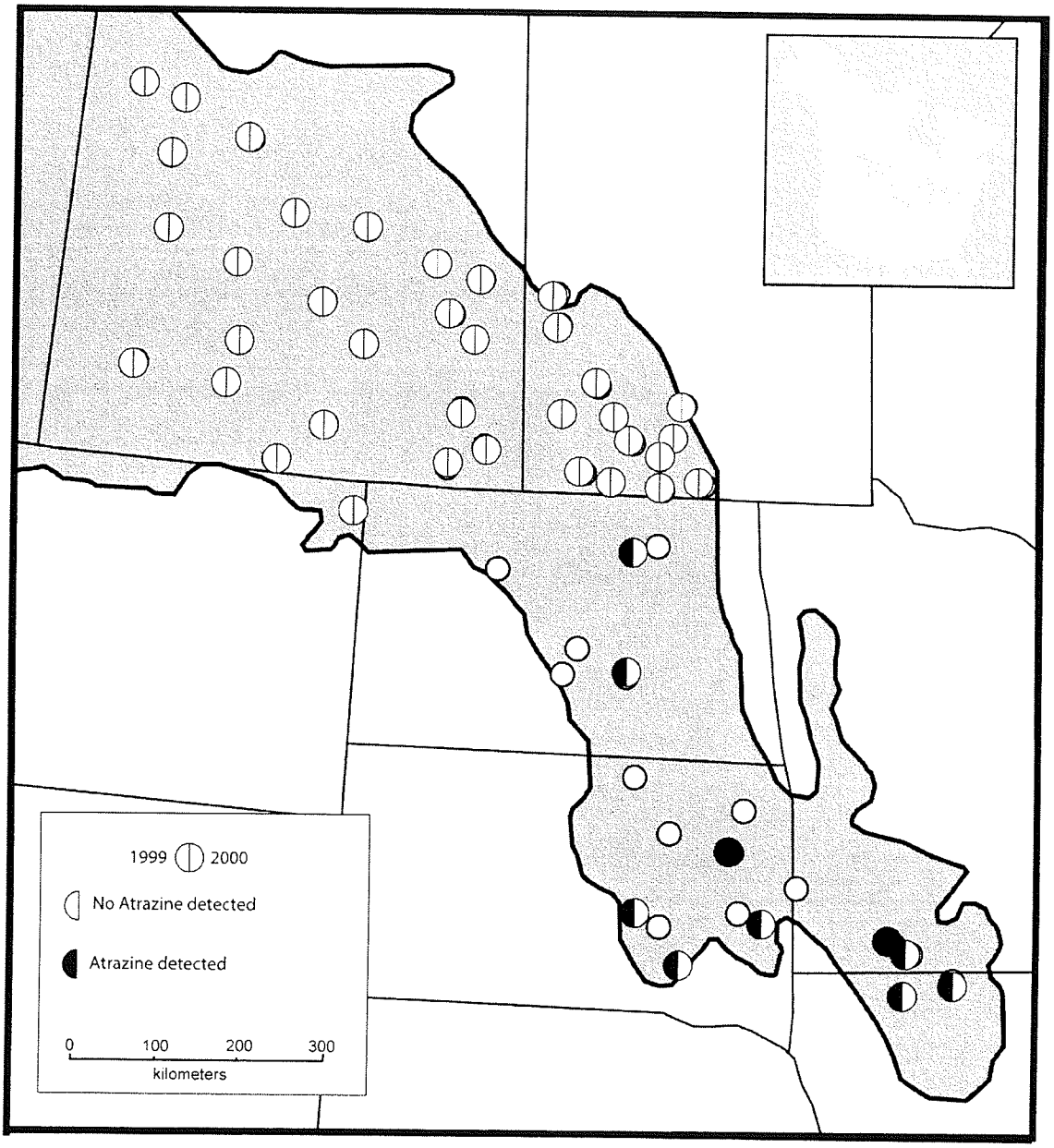


Figure 14. Sites with atrazine detection during the 1999 and 2000 surveys.

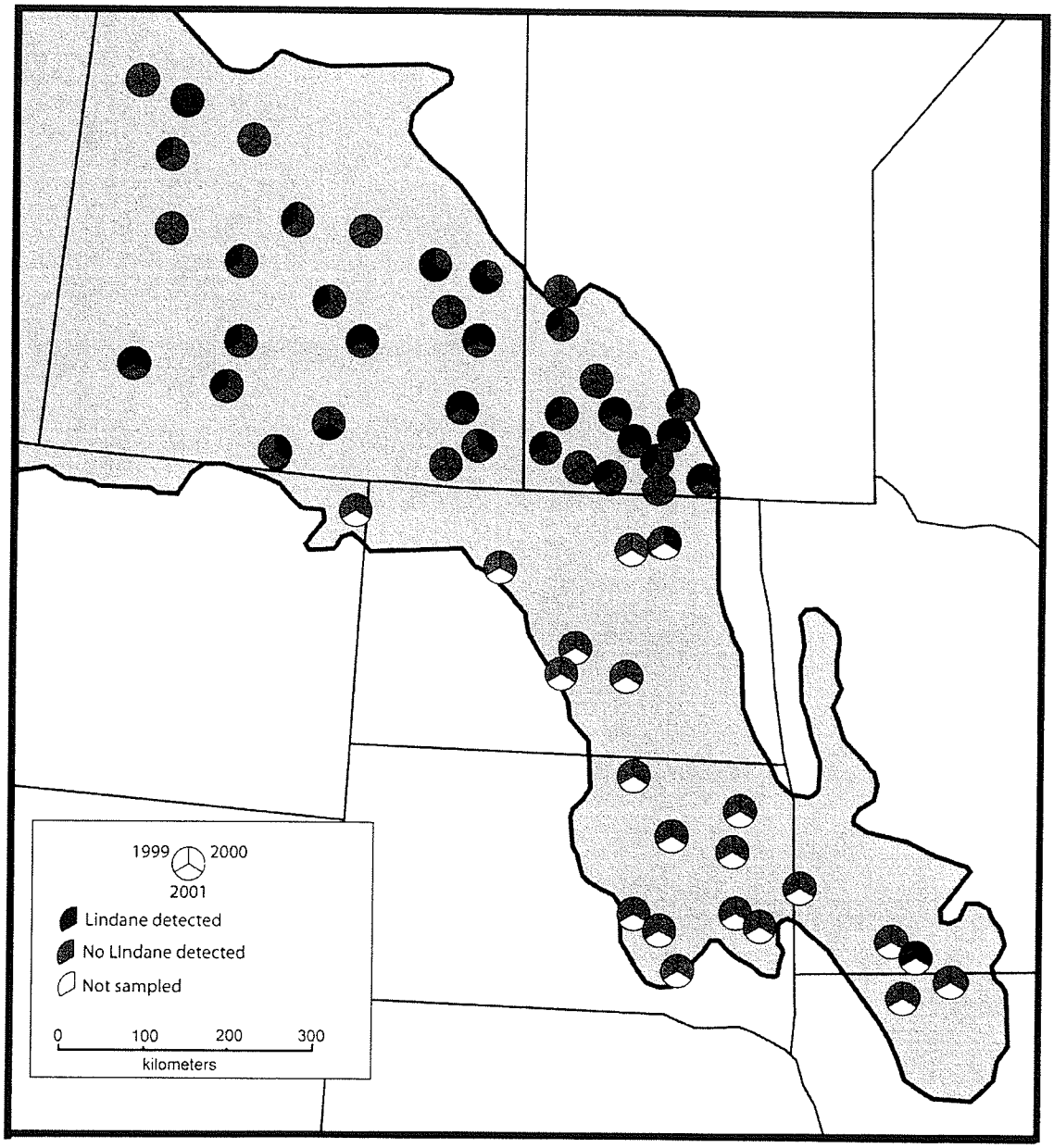


Figure 15. Sites with lindane detection during the 1999, 2000, and 2001 surveys.

Table 21. Mean (± SE) pesticide concentrations in wetlands that had pesticide concentrations above detection limits (atrazine = 0.001 mg/L, lindane = 0.001 µg/L).

Year	Atrazine	Lindane
1999	2.0 mg/L (0.4)	0.002 mg/L (0.001)
	n = 10	n = 24
2000	1.3 mg/L (0.2)	0.002 mg/L (0.002)
	n = 2	n = 11
2001	No detection	0.002 mg/L (0.002)
		n = 3

sites (1999 5%, 2000 11%) whereas atrazine was detected only in American sites (1999 45%, 2000 11%) (Figures 12-15).

Influence of measured variables on pesticide detection

Logistic regression analysis did not identify any variables (either continuous or discrete) as being significantly ($p < 0.05$) related to pesticide (either atrazine or lindane) detection in the wetlands.

Due to the annual, seasonal, and spatial differences in pesticide use, the data were divided into subsets (based on country and time of sampling) prior to further analysis of the data. For the US sites during RI (June-July 1999) ANOVAs identified "days since last precipitation" as the only variable that was significantly different ($p = 0.046$) between sites with atrazine detection (1.9 days) and those with no detection (3.5 days). Results from one-way ANOVAs for the 2000 survey of the US sites showed that none of the measured variables were significantly different ($p < 0.05$) between sites with and without atrazine detection. ANOVAs of the Canadian RI data (June-July 1999) showed that "15-day precipitation volume" was significantly higher ($p = 0.013$) in wetlands with lindane detection (47.83 mm) as opposed to wetlands with no detection (26.68 mm). Additionally, phytoplankton chlorophyll *a* in Canadian wetlands during RI was significantly ($p = 0.039$) higher in wetlands with lindane detection (37.66 µg/L) than in those with no detection (18.19 µg/L). Conversely, in Canadian wetlands during RII phytoplankton chlorophyll *a* was significantly ($p = 0.015$) lower in wetlands with lindane detection (19.69 µg/L) as compared to those with no lindane detection (39.00 µg/L). In the Canadian RII data, conductivity was the only other variable that was significantly different ($p = 0.035$) between wetlands with (1398 µS/cm) and without lindane detection (799 µS/cm). With the 2000 and 2001 Canadian wetland data sets none of the measured variables were significantly ($p < 0.05$) different between wetlands with and without lindane detection.

3.4 Discussion

The majority of wetlands within the PPR belong to the marsh wetland class, characterized by the occurrence of soft-stemmed emergent vegetation (i.e. *Typha* sp.) and shallow water (Mitsch and Gosselink 2000). Another characteristic shared by many PPR wetlands is their susceptibility to contamination by agrochemicals. Sixty-two percent of wetlands sampled had pesticide detection during at least one sampling period and nutrient concentrations were within the hypereutrophic range of all sampled wetlands (TP > 0.1 mg/L, TN > 1.5 mg/L). Although nitrogen and phosphorous do arise from natural sources, the close proximity of the wetlands to agricultural land suggests that the hypereutrophic nutrient levels were probably due to agricultural inputs (Neely and Baker 1989). Unlike nutrients, the source of xenobiotic pesticides (atrazine and lindane) in the wetlands is undoubtedly from an agricultural origin.

In order to reduce the risk of pesticide contamination of wetlands it is necessary to understand what determines pesticide presence in this ecosystem. Extrinsic variables, such as climate, land use, and agricultural practices can determine the extent of pesticide contamination whereas intrinsic variables can determine pesticide persistence. Thus, both extrinsic and intrinsic variables will contribute to pesticide presence in wetlands. As extrinsic and intrinsic factors vary seasonally, annually, and spatially so too will the extent of pesticide detection in wetlands.

Timing of pesticide application and wetland sampling

The timing of pesticide application to fields determined, in part, why wetlands sampled in June-July had greater percent pesticide detection and higher pesticide concentrations than did those sampled in August. Atrazine and lindane are primarily applied to agricultural fields in spring to early summer. As the elapsed time since pesticide application increases, the risk of pesticide off-field transport decreases as pesticides are sorbed or degraded within the field (Schreiber and Cullum 1998, Konda and Pasztor 2001). Thus, the chance of pesticide detection in off-field environments is

usually inversely related to the elapsed time since pesticide application (Konda and Pasztor 2001).

The timing of pesticide application in relation to wetland sampling could also explain annual differences in atrazine detection. As weather patterns differ annually the time of seeding corn can vary (NASS 2000). Atrazine is applied primarily to corn up until the fourth leaf stage. Due to climatic differences the seeding date for corn in the USA was earlier in 2000 as opposed to 1999 (NASS 2000). For example, in Iowa the majority of corn (95%) had been planted by May 7 as compared to only 51% planted by this date in 1999 (NASS 2000). With an earlier seeding date, the fourth leaf stage would have developed earlier in 2000 (NASS 2000) and atrazine application would have started and terminated earlier in 2000 than in 1999. Based on the above, the majority of agricultural atrazine application in 1999 would have been closer to the time of wetland sampling compared to 2000. This could have accounted for the greater atrazine detection in 1999 compared to 2000.

Proximity to pesticide use

The detection of atrazine in the south and lindane in the north parallels the use patterns of these two pesticides. The different climatic and soil conditions of the PPR support different agricultural crops (USDA 2000). The crops grown in an area will dictate the extent of pesticide use and in turn the extent of pesticide detection in the environment. Atrazine and lindane use during the survey years tended to be predominately on corn and canola, respectively. Because of different soil and climate conditions the majority of cornfields and atrazine use occur in the southeastern portion of the PPR (USDA 2000). In contrast the majority of canola fields and lindane use occur in the northern portion of the PPR (USDA 2000, Statistics Canada 2002).

Differences in pesticide legislation within the PPR also contributed to the higher detection of lindane in northern versus southern wetlands. Like the soil and weather environment, the political environment of the PPR also varies in time and space.

Pesticide use in the PPR countries (Canada and USA) is dictated by separate federal legislation. During the years of the survey lindane use on canola was prohibited in the US but was recommended in Canada. This difference in legislation may have contributed to the higher detection of lindane in Canadian versus US wetlands.

Pesticide use legislation could have also contributed to annual differences in lindane detection in Canadian wetlands. Anticipating an imminent federal ban, manufacturers voluntarily removed lindane, as a seed treatment for canola, at the end of 1999 (A. Vaughn, Gustafson Canada, pers. comm. 2002). For instance, the area in Manitoba seeded with lindane-treated canola decreased from 114,096 hectares in 1999 to 51,554 hectares in 2000 and 22,254 hectares in 2001 (MCIC). With less lindane being applied, the amount of lindane available for off-field transport decreased resulting in successively fewer wetlands with lindane detection in 2000 and 2001.

Although atrazine and lindane are capable of long-range transport (Barrie *et al.* 1997, Tornes *et al.* 1997, Harner *et al.* 1999) no evidence of this was seen in the surveyed wetlands. Long-range transport of atrazine can occur via surface water transport in rivers (Tornes *et al.* 1997) and atrazine has been detected in aquatic environments far removed from areas of atrazine use (United States Geological Survey 1997). The wetlands of the present survey, however, had limited if any connection to permanent surface water flow such as streams, and rivers. This may account for the lack of atrazine detection in wetlands located in areas of limited atrazine use.

Atrazine, and to a greater extent lindane, can also be transported in the atmosphere (Thurman and Cromwell 2000, Waite *et al.* 2001, Rice *et al.* 2002). Based on the principle of global distillation (Wania and Mackay 1993, Vallack *et al.* 1998) lindane and atrazine would be expected to move in a northerly pattern in the atmosphere of the PPR. Thus, lindane volatilized from Canadian fields would be transferred in the atmosphere further north and not south which may explain the lack of lindane detection in the southern portion of the PPR. Unlike lindane, the majority of atrazine use occurs in the

southern portion of the PPR. Once volatilized from southern PPR fields, atrazine is expected to move northward via global distillation and be deposited through precipitation in northerly environments. Through this mechanism atrazine may contaminate northern aquatic environments (Currie and Williamson 1995); however, my results did not show this. Annual differences in climate and atrazine use (i.e., precipitation, temperature, wind patterns, amount of atrazine applied) could account for its detection in northern environments during some years but not during other years.

Precipitation

Precipitation and surface flow can be important mechanisms in the transport of pesticides from agricultural fields to aquatic environments (Patty *et al.* 1997, Pommel and Dorioz 1997, Donald *et al.* 1999, Nash and Halliwell 2002). If we assume that pesticides arrive in wetlands as a result of precipitation then their concentration, and likelihood of detection, would be expected to be greatest immediately following precipitation events. In the PPR, precipitation and surface runoff tend be higher earlier in the summer (Sheehan *et al.*1987). This would help explain why there was higher pesticide detection in June/July than in August. In addition, the higher precipitation volume prior to sampling in wetlands with lindane detection suggests the importance of precipitation as a transport mechanism of pesticides to wetlands. The shorter elapsed time since precipitation and wetland sampling in wetlands with atrazine detection provides further evidence of the role of precipitation in determining pesticide presence in wetlands.

Intrinsic Wetland effects

Phytoplankton and conductivity were the only intrinsic wetland variables that were significantly related to pesticide detection. Phytoplankton and the dissolved ion content (measured as conductivity) have the potential to increase lindane detection by providing sorption sites within the water column. Conversely, phytoplankton can decrease pesticide detection in water columns through the settling of the phytoplankton-pesticide complex (Soderstrom *et al.* 2000). In addition some phytoplankton species are capable of

catalyzing pesticide photodegradation and their presence would decrease pesticide detection (Zepp and Schlotzhauer 1983, Kuritz 1999).

Lindane detection was positively correlated with phytoplankton chlorophyll *a* during June-July but inversely correlated with phytoplankton chlorophyll *a* in August 1999. Results from RI could be explained by arguing that lindane sorption to phytoplankton increased its detection in the water column. Conversely, RII results could be attributed to lindane removal from the water column via sorption to phytoplankton and the subsequent sedimentation of the phytoplankton-lindane complex. The reason(s) for the difference between rounds cannot be addressed from the current survey data. To understand the role, if any, phytoplankton play in determining lindane detection in PPR wetlands, a controlled experiment in which lindane persistence is monitored over a range of phytoplankton levels is needed.

Conductivity was the only other intrinsic wetland variable selected by the predictive model that was significantly different between wetlands with and without lindane detection. Wahid and Sethunathan (1979) found that lindane could sorb to dissolved ions. If lindane sorbed to dissolved ions in the wetlands it may have remained in the water column for extended periods of time and thus increased the chance of its detection. A direct correlation between lindane detection and conductivity was only seen during RII. Perhaps the lower dissolved ion content of the wetlands during RI (RI 995 µS/cm, RII 1553 µS/cm) did not provide a significant number of sorption sites to influence lindane detection.

Reasons why atrazine detection was not related to phytoplankton or conductivity could have been due to the chemical characteristics of atrazine. Atrazine has a much lower sorption coefficient (100 mL/g) than lindane (1100 mL/g) (Hornsby *et al.* 1996). If the effect of phytoplankton and conductivity on lindane detection was related to sorption then these effect may not be expected with atrazine due to its lower sorption coefficient.

The relatively few sites with atrazine detection may have also prevented the statistical identification of intrinsic factors important in atrazine detection.

The environmental variability encountered in the wetlands could have obscured the intrinsic effects on pesticide detection. For instance, sediment organic matter has been shown to reduce pesticide persistence in wetland water columns (Kadlec and Alvord 1993, Detenbeck *et al.* 1996). Thus, if exposed to similar pesticide inputs wetlands with higher sediment organic matter would tend to have lower pesticide water column persistence. However, wetlands in the present survey were presumably not subjected to the same levels of pesticide inputs. Thus, a situation could arise in which a wetland with high sediment organic matter had pesticide detection but a wetland with low sediment organic matter did not due to differences in pesticide input. Controlled experiments are needed to determine which, if any, intrinsic variables are related to atrazine and lindane persistence in wetlands.

Extrinsic determinants of pesticide detection and Best Management Practices

Ultimately, the amount and type of pesticide used by agriculture will determine the extent of contamination of environments such as wetlands. This was evident in the current study as the percentage of wetlands with lindane detection decreased with annual decreases in lindane use. Due to political and economic circumstances a global ban of all agricultural pesticide use is not foreseeable. However, pesticide applicators through the use of Best Management Practices (BMPs) can reduce the amount of pesticide used and still obtain their desired results. For instance, pesticide delivery efficiency can be increased with proper adjustments to pesticide spray equipment so as to produce pesticide droplets that are not prone to drift (Bode 1987, Himel *et al.* 1990). Integrated Pest Management (IPM) is another BMP that can reduce pesticide use (Maas *et al.* 1984). IPM involves pesticide use but also involves cultural, mechanical, and biological methods to control pests (Burn *et al.* 1987). Because it involves a variety of pest control methods,

IPM usually requires less pesticide use than pest control based solely on pesticides (Maas *et al.* 1984).

Precipitation can provide pesticide transport from field to wetland. Although pesticide applicators cannot control precipitation, they can control, to some extent, the timing of pesticide application through BMPs. BMPs recommend that pesticide application be avoided immediately prior to rainfall (Seelig 1998). This practice would reduce the amount of pesticide needed for pest control, as there would be less pesticide off-field transport. Less off-field transport would also reduce the risk of pesticide contamination of surface waters such as wetlands.

Timing of surveys

The timing of wetland sampling is important in determining pesticide detection and thus should be considered when designing future surveys. For instance, if a survey is conducted during the same time of year for a number of consecutive years, it may produce different pesticide detection rates depending on the year of the survey. Due to annual differences in the weather, the timing of pesticide delivery to the wetlands and the chance of pesticide detection can vary. Therefore, surveys designed to compare annual risk of pesticide detection should be designed to sample wetlands during times when the chance of pesticide detection is optimum. The optimum time for detection of pesticides in wetlands will vary depending upon the pesticide. For instance the optimum time to sample wetlands for surface applied pesticides such as atrazine would be immediately after the first major rainfall (> 40 mm) following pesticide application. With pesticides that are applied as seed treatments such as lindane, the pesticide will not be readily available for transport until after x-days after planting when the treated seed leaves emerge from the soil. Thus, the optimum time to sample wetlands for pesticides applied as seed treatments would be immediately after the emergence of the seed leaves. The timing of emergence will vary from region to region due to variability in the climate and soil conditions.

3. 5 Summary and conclusion

The seasonal, annual, and spatial variability of pesticide detection was related to corresponding seasonal, annual and spatial variability of extrinsic and intrinsic wetland variables. Extrinsic variables such as the climate and soil environment, along with federal legislation determine the extent of atrazine and lindane application in an area. The extent of atrazine and lindane application is, in turn, directly related to the risk of pesticide contamination of wetlands. By providing a mechanism for pesticide transport, precipitation is another extrinsic variable that is related to the risk of atrazine and lindane contamination.

Intrinsic wetland variables that appear to determine the extent of lindane detection include phytoplankton abundance and water conductivity. The phytoplankton and conductivity levels in a wetland may determine the available surface area for lindane sorption. As a consequence, wetlands with higher phytoplankton and conductivity levels may have a greater chance of lindane detection than wetlands with lower levels of these variables. Elevated phytoplankton levels may, however, decrease lindane persistence as suggested by the data collected in late summer. As seen in the current survey, phytoplankton can reach elevated levels in PPR wetlands and thus their role in determining the persistence of lindane and other pesticides should be investigated further.

Pesticide use is an integral part of prairie agriculture and will thus undoubtedly continue for some time (Avery 1995). Along with the continued use of pesticides comes the continued risk of pesticide contamination of the environment. By recognizing factors that are related to pesticide detection in environments such as wetlands, steps can be taken to limit the extent of pesticide contamination.

Chapter 4: The relative effects of sediment and water column organic matter on the water column persistence of atrazine in wetland microcosms

4.1 Introduction

In wetlands, pesticides in the water column may be more susceptible to export than those found in the sediment. Thus, the pesticide sink value of wetlands may be increased if the pesticide is retained in the sediments. Constituents of the sediment and water column have the potential to determine pesticide transport to the sediments. A number of studies (e.g. Kadlec and Alvord 1993, Detenbeck *et al.* 1996, Kao *et al.* 2001, Moore *et al.* 2002) have documented the inverse relationship between sediment organic matter and pesticide concentrations in wetland water columns. This relationship is due, in part, to pesticide sorption to wetland sediment organic matter. Organic matter in wetland water columns also has the potential to influence pesticide water column persistence. If pesticides are sorbed to dissolved organic matter (Wauchope and Myers 1985, Joy 2002) they might remain in the water column instead of partitioning into the sediment. Conversely, pesticide water column persistence might be reduced if pesticides are sorbed to particulate organic matter (POM). When the POM-pesticide complexes eventually sediment out of the water column it would transport the pesticide to the sediment (Soderstrom *et al.* 2000). Additionally, DOM or POM could reduce water column pesticide persistence by catalyzing pesticide photolysis and hydrolysis (Li and Felbeck 1972, Zepp and Schlotzhauer 1983, Minero *et al.* 1992, Bachman and Paterson 1999, Schindelin and Frimmel 2000).

Although the role of wetland sediment organic matter in determining pesticide persistence has been well studied (Kadlec and Alvord 1993, Detenbeck *et al.* 1996, Kao *et al.* 2001 and Moore *et al.* 2002) few studies have examined the role of DOM and POM

(Soderstrom *et al.* 2000). The objective of this study was to investigate the relative influence of DOM, POM, and sediment organic matter on the water column persistence of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] and its triazine-ring metabolites under controlled laboratory conditions in wetland microcosms. I hypothesized that sediment organic matter would be the form of organic matter most influential in reducing atrazine water column persistence in shallow wetlands ($d \leq 10$ cm) because of their low ratio of water to sediment surface area. Shallow wetlands conditions, such as those that occur in ephemeral and temporary wetlands, are encountered frequently within the PPR (Sheehan *et al.* 1987).

4.2 Materials and methods

Sample collection

Water and sediment samples were collected in July 1999 from 23 wetlands located within the Canadian provinces of Manitoba and Saskatchewan (Figure 16). The sample sites were located in semi-permanent wetlands (Warner and Rubec 1997) that were shallow, did not display evidence of thermal stratification, and had pH values greater than seven (Table 22). For the development of the microcosms depth-integrated water-column samples were collected using an acrylic tube (6.4 cm inner diameter, 1.5 m length) and stored in opaque glass bottles at 4°C (McDougal 2002). An acrylic tube (6.4 cm inner diameter, 2 m length) was also used to collect sediment samples for use in the microcosms. The tube was pushed 10 cm into the sediment and withdrawn. The sediment was extruded from the tube and placed into plastic bags. Water and sediment samples were kept on ice during transport to the analytical laboratory.

Sample analysis and microcosm setup

Sub-samples of the water were filtered (Whatman GF/C filters, 1.2 μm pore size) and the DOC content of the filtered water was determined using the persulfate-ultraviolet oxidation method (APHA 1992). The percent organic matter content of the sediment samples was determined upon combustion of dried samples at 600°C (Dean 1974). Total

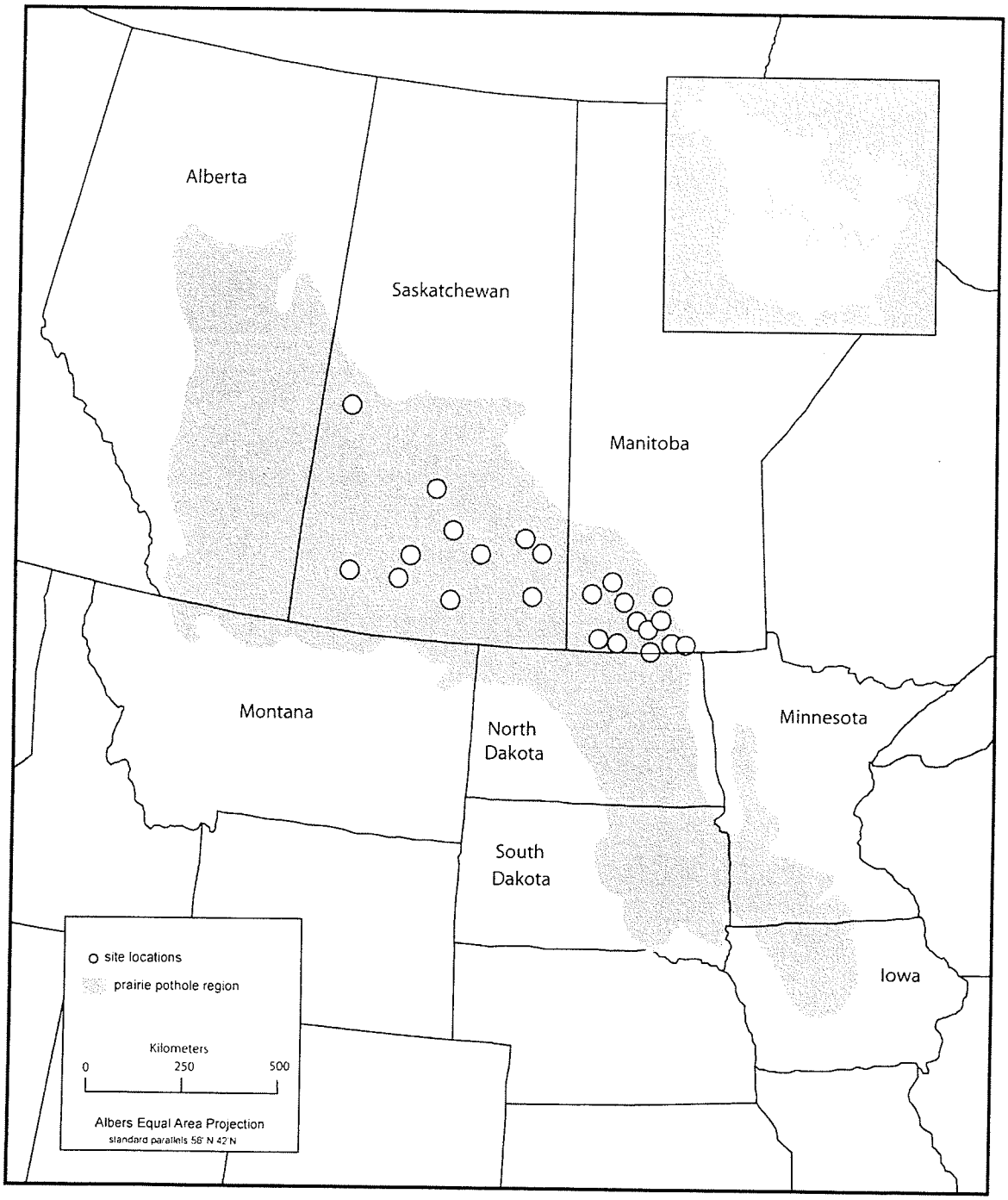


Figure 16. Map showing the location of wetland sites from which materials were collected for the microcosm study

Table 22. Characteristics of water and sediment sampled from Canadian prairie wetlands during July 1999.

Variable	Mean	Range
Water depth at sampling site (cm)	68	40 - 116
Difference (+) between water surface and sediment surface temperature (°C)	0.9	0 - 3
Water pH	8.5	7.8 - 10
Water Total Nitrogen (mg/L)	2.47	1.42 - 3.79
Water Total Phosphorous (mg/L)	2.00	0.45 - 2.75
DOC (μmolC/L)	1491	410 - 3000
POM (mg/L)	11	5 - 41
Percent sediment organic matter	15.1	5 - 53

nitrogen and total phosphorous concentrations of the water were determined as described in Chapter 3.

Sediment and water were added "fresh" (not frozen, sterilized, dried or otherwise preserved) to the microcosms, which consisted of 500 mL glass jars. Two hundred grams of whole sediment was added to the glass jars. Three hundred milliliters of wetland water, collected from the same site as the sediment, was then poured into the jars. The microcosm jars were placed inside larger glass jars (4 L) along with CO_2 traps and the large jars sealed with airtight caps (Figure 17). The CO_2 traps consisted of open glass scintillation vials (25 mL) containing 10 mL of 1 N NaOH (Anderson *et al.* 2002).

Four replicate microcosms were established for each of the wetland sites sampled. The microcosms were arranged using a randomized block design inside a constant environment chamber (250 μmol/m^2/sec constant fluorescent bulb irradiance, 28°C).

Microcosms were allowed to equilibrate for one week. Then the large glass jars were opened and 50 mL water samples were pipetted from the microcosms and filtered onto dried, pre-weighed filter paper (Whatman GF/C filters, 1.2 μm pore size). The filters were then dried at 100°C for 24 hours and weighed to determine total suspended solid (Stainton *et al.* 1977). Then the filters were combusted at 600°C for one hour and reweighed to calculate POM (mg/L) (Stainton *et al.* 1977).

Microcosms were then treated with 1 mg/L atrazine-ring-ul-^{14}C (21 μCi/μmol, Sigma Chemical Company, St. Louis, MO). One milligram of ring-labeled atrazine was dissolved in 10 liters of water to produce a 100 mg/L solution. Aliquots (2.5 mL) were pipetted from this solution evenly onto the surface water of each microcosm to give a final atrazine solution within each microcosm of approximately 1 mg/L. This concentration was within the range that has been detected in wetlands sampled within the PPR (1 - 4.8 mg/L) (Chapter 3).

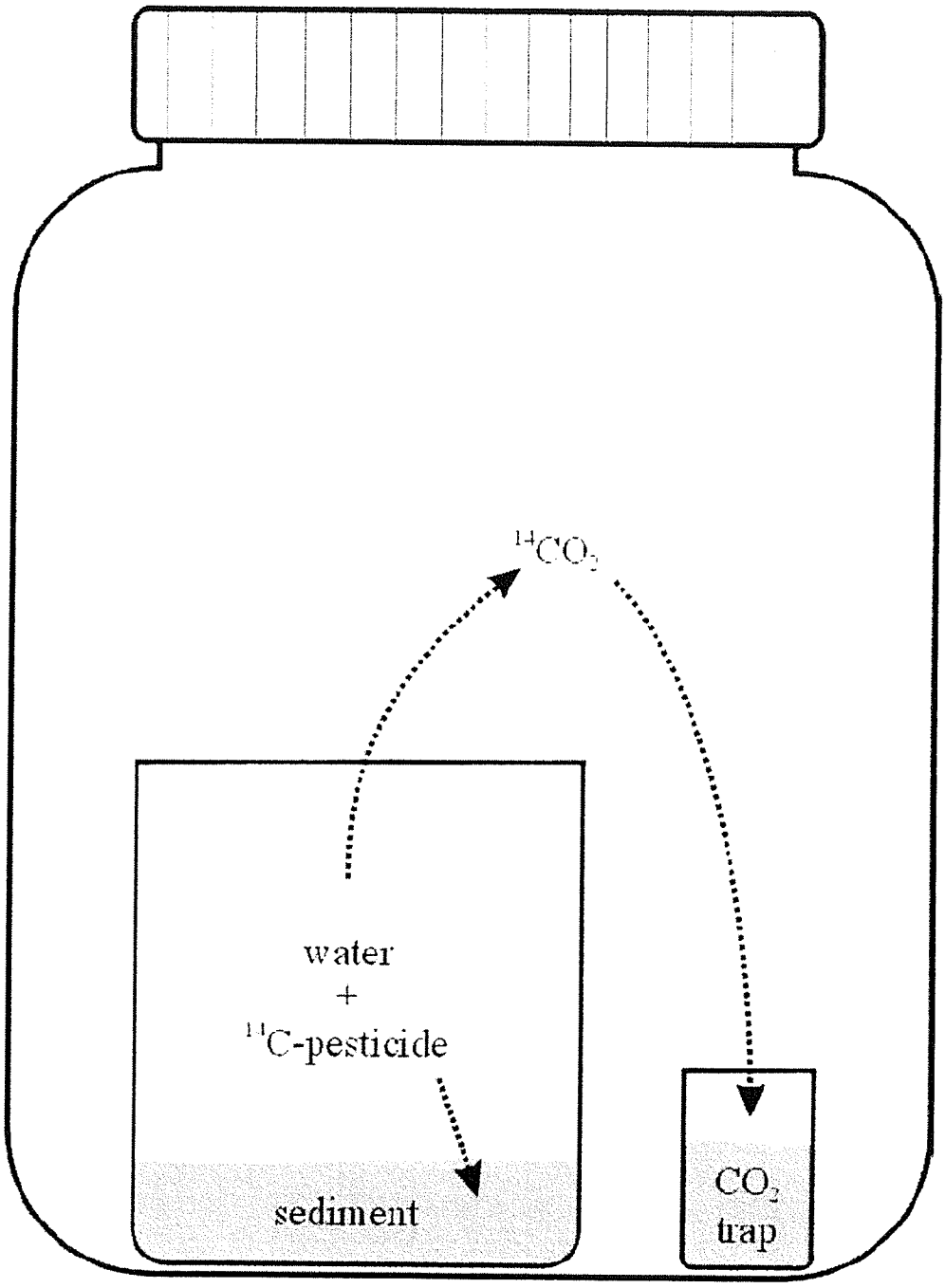


Figure 17. Microcosm design used to investigate atrazine dissipation from wetland water.

Sample Analysis

Water (1 mL) was removed from each microcosm and placed into glass scintillation vials on days 0, 1, 2, 4, 8, 16, and 32 after the addition of atrazine. Five milliliters of Scintisafe 30% liquid scintillation cocktail (Fisher Scientific, Fairlawn, NJ) was added to each vial. The sample was placed in the dark for 24 h to allow for self-quenching. The ^{14}C disintegrations per minute of the samples were then quantified with a Beckman Model LS 7500 liquid scintillation counter.

The NaOH from the CO_2 traps was collected with replacement on days 1, 2, 4, 8, 16, and 32, and its ^{14}C radioactivity was determined as above. If ^{14}C were to be detected in the traps it would be due to $^{14}CO_2$ produced during the mineralization of ^{14}C atrazine.

Statistical analyses

The first-order half-life of atrazine in the water column of each microcosm was determined using non-linear regression ($Mt = M_1e^{-kt}$) (SigmaPlot 2001 for Windows V.8). Relationships between DOC, POM, and sediment organic matter and atrazine water column persistence were investigated using univariate regression analysis (SigmaPlot 2001 for Windows V.8).

4.3 Results and Discussion

Dissipation of ^{14}C-atrazine/metabolites from the water-column of the microcosms followed first order kinetics ($r^2 > 0.90$) (Figure 18). The calculated water-column half-life of ^{14}C-atrazine/metabolites (mean 6.0 days; range 2.7 to 11.6 days) in the microcosms was within the range of published values for atrazine in wetlands (Goldsborough and Crumpton 1998, Detenbeck *et al.* 1996).

Atrazine mineralization was not detected in any of the microcosms, as the ^{14}C radioactivity of the CO_2 traps never exceeded background levels. Microorganisms can acquire nitrogen from atrazine and mineralize the pesticide in the process (Gebendinger and Radosevich 1999). However, if other more accessible forms of N are available microorganisms will tend not to mineralize atrazine (Gebendinger and Radosevich 1999).

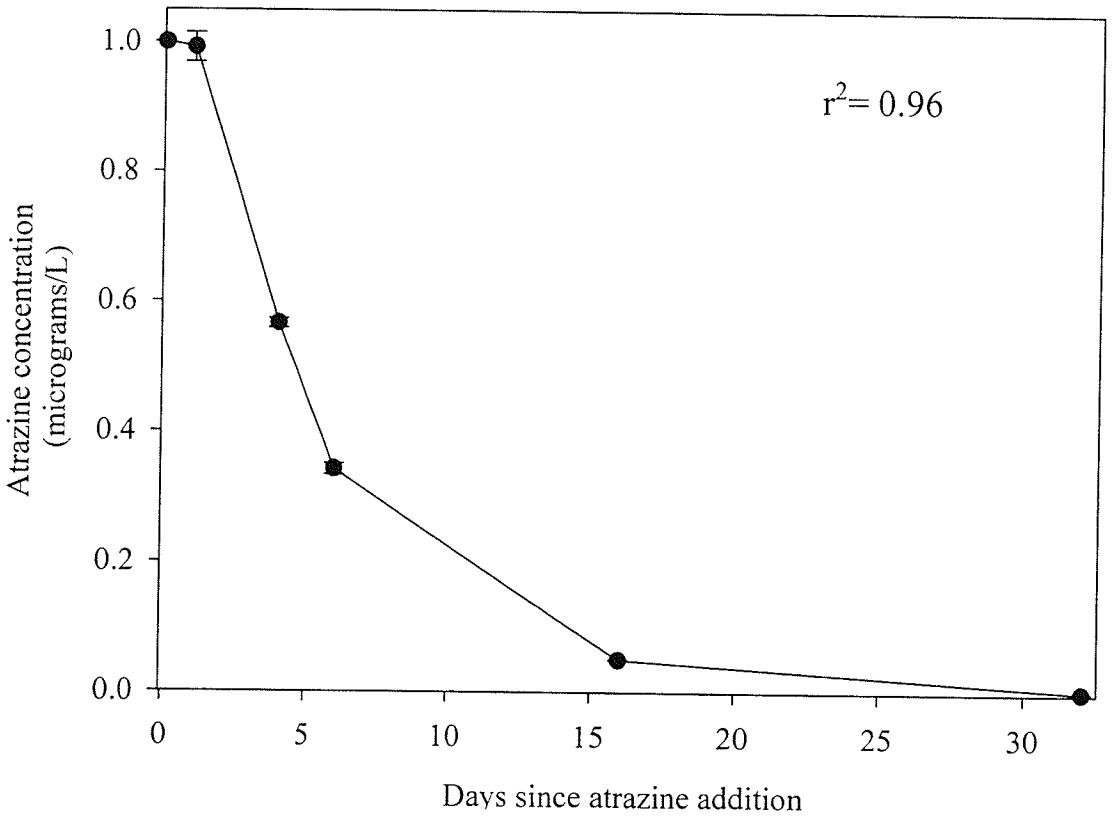


Figure 18. Mean (± SE, n = 4) atrazine dissipation from the water column of wetland microcosms. Sediment and water collected for microcosm from Site 1, Delta Marsh, Manitoba.

The conditions of the microcosms were presumably not N-limited as the water and sediment used were collected from hypereutrophic wetlands.

Sediment organic matter accounted for a significant ($p < 0.001$) amount (46%) of the variation in ^{14}C-atrazine/metabolite half-life (Figure 19). Sediment organic matter can function as a nutrient source for microbes and is usually directly related to microbial production (Pritchard 1987). Had atrazine mineralization been detected, the inverse relationship between sediment organic matter and atrazine/metabolite persistence (Figure 19) could have been attributed to higher atrazine mineralization in microcosm whose sediments had higher organic matter. However, the lack of detected atrazine mineralization suggested that the relationship between sediment organic matter and water-column half-life was a function of ^{14}C-atrazine/metabolite sorption to the sediment and not enhanced mineralization.

The regression equation calculated in Figure 19 was applied to studies from the literature to determine how well it could predict atrazine half-life. Application of the regression equation to the wetland experiments of Detenbeck *et al.* (1996) and Moore *et al.* (2000) resulted in half-life values that were close to but lower than actual measured values (Table 23).

Unlike sediment organic matter, neither DOC ($r^2 = 0.05$; $p = 0.30$) nor POM ($r^2 = 0.05$; $p = 0.32$) was significantly related to ^{14}C-atrazine/metabolite water column half-life. This suggested that sediment organic matter was more influential in determining atrazine persistence than the role of POM or DOC. However, organic matter quality can be important in determining its effect on pesticide fate (Gunnarsson and Granberg 1999, Flores-Cespedes *et al.* 2002). The quality of DOC and POM may not have been similar in all the microcosms. This could have obscured any relationships between water column organic matter and atrazine persistence.

The shallow depth of the microcosms might have also limited the effect of water column organic matter on ^{14}C-atrazine/metabolite persistence. The microcosms had a low

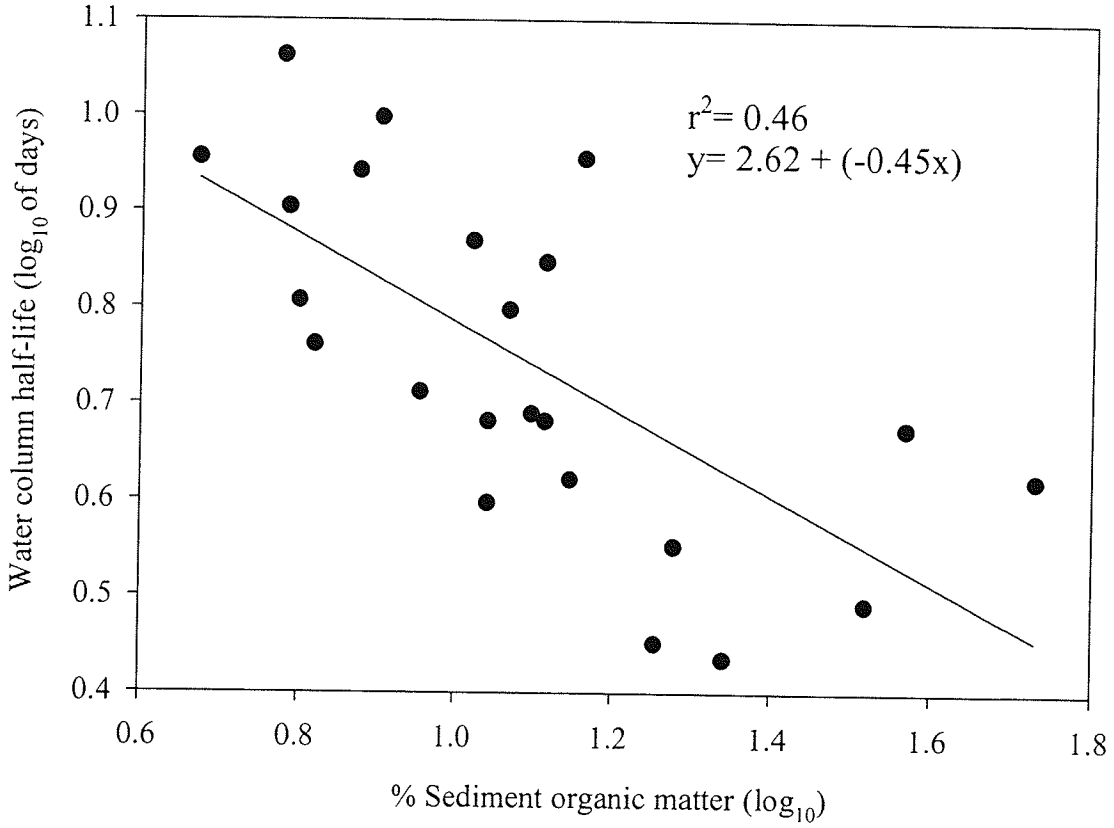


Figure 19. Regression of sediment organic matter against ^{14}C-atrazine/metabolites water-column half-life in wetland microcosms. Microcosms contained unsterilized sediment collected from Manitoba and Saskatchewan wetlands, July 1999.

Table 23. Comparison of actual atrazine half-life in prairie wetlands to that predicted by the regression line of Figure 19.

Reference	Percent sediment organic matter	Predicted water column half-life	Actual water column half-life
Detenbeck *et al.* 1996	8.6	6.6 days	8.4 days
Moore *et al.* 2000	1.6	14.1 days	16 - 48 days

ratio of water to sediment surface area (5.97 mL/cm^2 as compared to 100 mL/cm^2 for a hypothetical one meter deep wetland). This lower water to sediment surface area ratio would have increased the contact between atrazine/metabolites and the sediment. Due to their shallow depth the total amount of DOC and POM would also have been lower in the microcosms than in deeper environments. Thus, in shallow wetlands ($\leq$ 10cm) sediment organic matter would be expected to be more important than DOC and POM in determining atrazine sink potential. To determine the relative roles of DOM, POM, and sediment organic matter in deeper wetlands further experiments are needed.

4.4 Conclusion

Of the three pools of organic matter routinely quantified by aquatic surveys, only sediment organic matter influenced ^{14}C-atrazine/metabolite water column persistence in the microcosms. ^{14}C-atrazine/metabolite persistence was inversely related to sediment organic matter content. This suggested that the relative atrazine sink value of wetlands could be estimated from survey data, which report percent sediment organic matter. However, as the experiment was conducted in shallow microcosms these results might only be applicable to shallow wetlands ($\leq$ 10 cm).

Chapter 5: Effects of nutrient enrichment on atrazine and lindane persistence in wetlands

5.1 Introduction

Prairie Pothole wetlands located near agricultural fields are susceptible to contamination by agricultural pesticides and fertilizers (Neely and Baker 1989, Frankforter 1995). Fertilizers can influence pesticide fate in aquatic environments by affecting the extent of pesticide degradation and sorption. For instance nitrate, a major ingredient in agricultural fertilizers, can facilitate pesticide photolysis via nitrate-mediated reactions (Torrents *et al.* 1997). Addition of fertilizers to wetlands can cause shifts from clear macrophyte dominated states to turbid phytoplankton dominated ones (Goldsborough and Robinson 1996, Scheffer 1998). Macrophytes and phytoplankton can influence pesticide fate by providing surface area for pesticide sorption (Weinberger and Greenhalgh 1985, Soderstrom *et al.* 2000). Phytoplankton can also act as catalysts of pesticide photodegradation (Zepp and Schlotzhauer 1983).

The objective of this study was to determine the influence of fertilizer additions on the water column persistence of atrazine and lindane. These pesticides were chosen because they have been detected in prairie wetlands (Chapter 3, Donald *et al.* 1999, Anderson *et al.* 2002) and have been used widely in prairie agriculture (Saskatchewan Agriculture and Food 2001). The pesticides were also selected because they have different chemical characteristics which may influence the effect nutrient additions will have on their persistence. For instance lindane has a higher sorption coefficient (1100 mg/L) than atrazine (100 mg/L) (Hornsby *et al.* 1996). I hypothesised that fertilizer additions would reduce the aqueous water column persistence of the pesticides because the nutrients would increase primary production which in turn would increase the surface area for pesticide sorption.

5. 2 Materials and Methods

The enclosure experiment was conducted in Blind Channel a turbid (15 NTU) paleochannel of the Assiniboine River located in Delta Marsh (Figure 5). Blind Channel is connected to Lake Manitoba and its hydrology is influenced by the lake. The emergent vegetation of Blind Channel is characterized by *Typha* sp. and *Phragmites* sp. Due to its high turbidity Blind Channel has limited submergent macrophyte growth. The mean water depth of Blind Channel is approximately one meter.

In two separate studies twelve floating enclosures (5 m x 5 m) were anchored in the Blind Channel of Delta Marsh (Figure 20) on June 12, 2000 and May 20, 2001. The enclosures consisted of 40 cm wide plywood frames (supported by polyethylene foam blocks) and a translucent polyethylene curtain (6 mm) that extended from the plywood frames into the sediment to an approximate depth of 30 cm (Figure 21). The curtain was embedded into the sediment with metal bars and enclosed a sediment area of 25 m^2 per enclosure. At the time of installation each enclosure contained a volume of approximately 22,500 L in 2000 and 27,500 L in 2001. Gee-type minnow traps were placed in each enclosure shortly after the curtains were installed and fish caught in the traps were removed from the enclosures for a period of three weeks.

After a three week pre-treatment period to allow for recovery from the disturbance caused by enclosure installation, enclosures were assigned one of three treatments in such a way as to maximize interspersion of treatments and minimize structural edge effects (McDougal 2002) (Figure 22). Four enclosures received a single addition of lindane (henceforth referred to as Lin enclosures). Four enclosures received a single addition of lindane and weekly addition of inorganic N and P (LinNP). Four enclosures received neither lindane nor nutrient additions and were thus the procedural controls (Control). In 2000 the lindane addition (July 5) occurred the same week as the start of the weekly nutrient additions (July 2) whereas in 2001 the lindane was added on July 12, four weeks after the start of weekly nutrient additions.

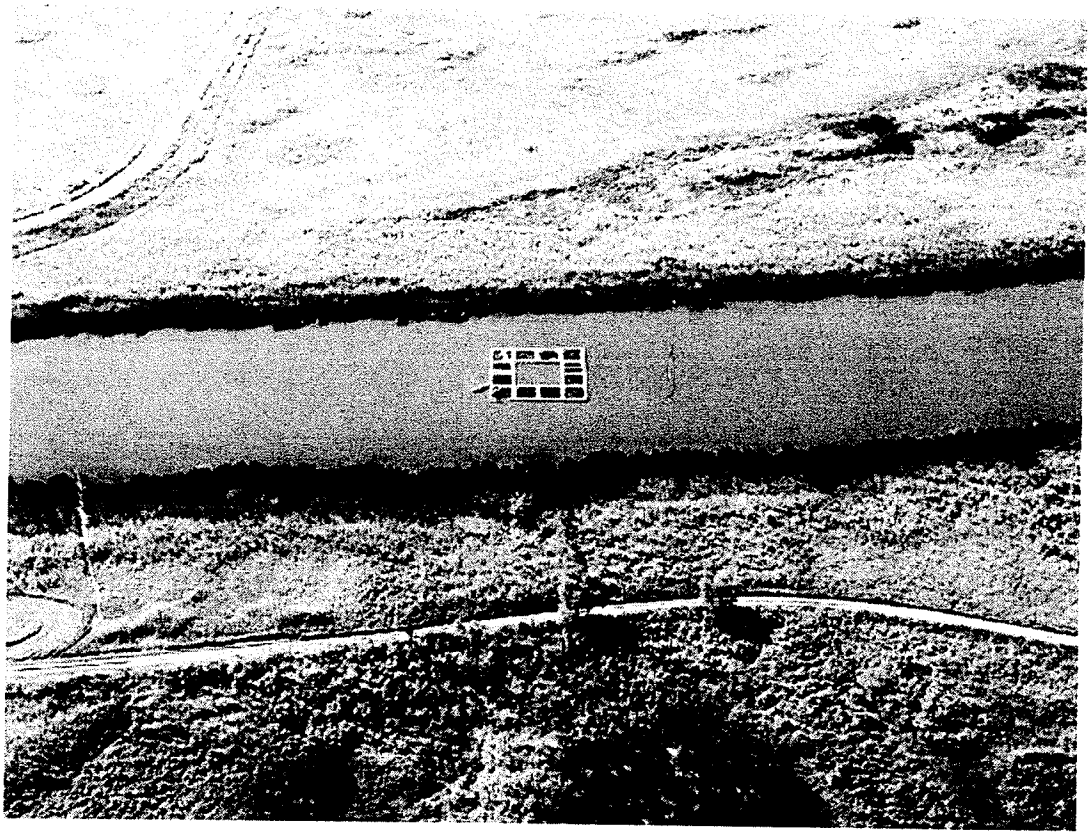


Figure 20. Aerial photo of enclosures located in Blind Channel (2000).

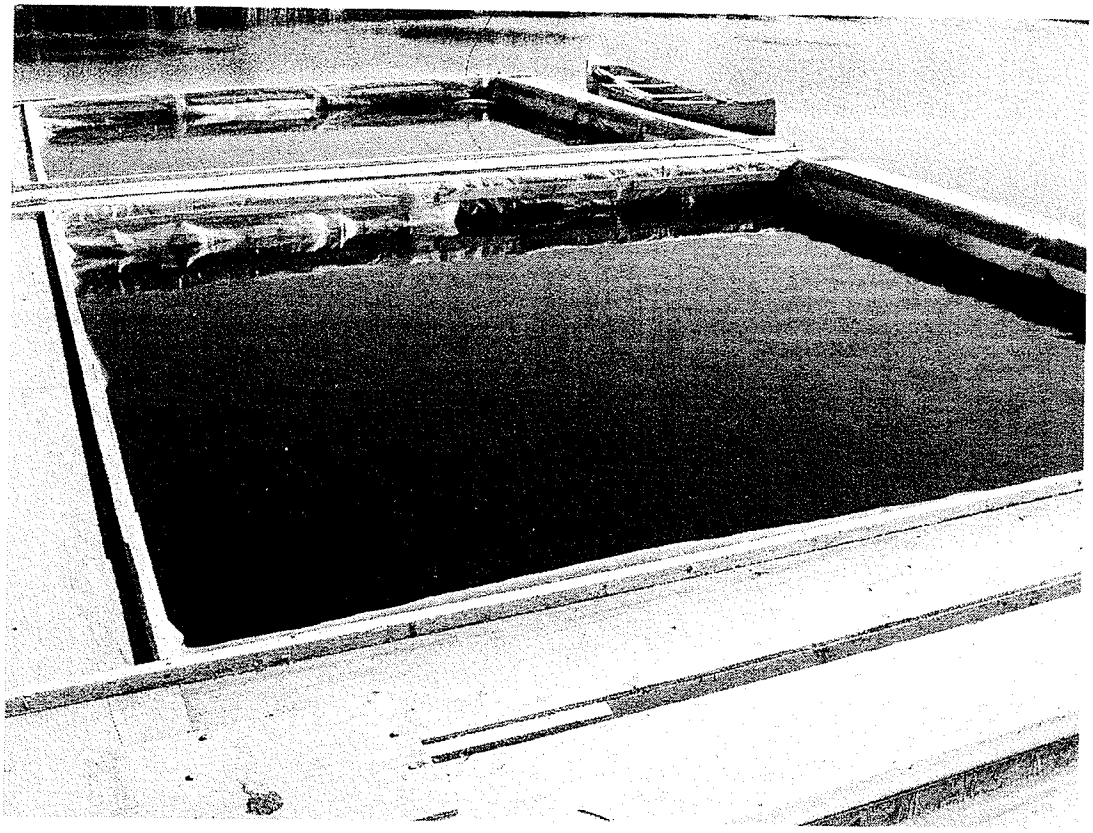


Figure 21. Two of the twelve enclosures (5 m x 5 m) located in Blind Channel (2000). The picture shows the plywood frame with the attached polyethylene curtain.

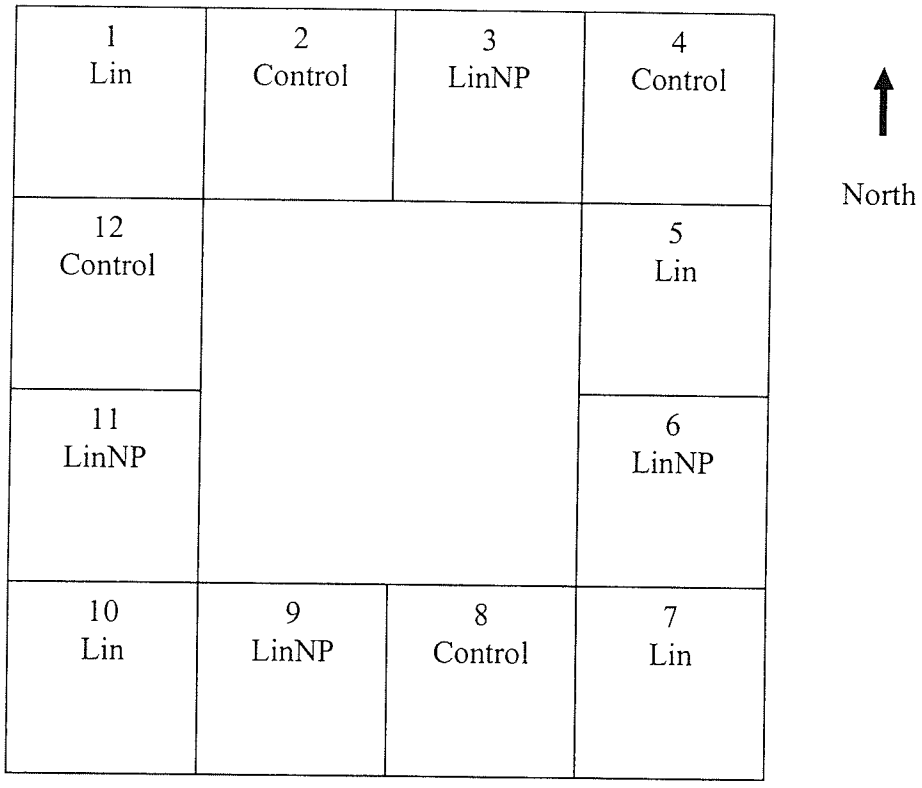


Figure 22. Schematic diagram of the mesocosm enclosures at Delta Marsh. Each enclosure is 5 m by 5 m. "Control" enclosures were not manipulated; "Lin" enclosures received a single application of lindane; "LinNP" enclosures received nitrogen and phosphorous additions once weekly.

Inorganic N ($NaNO_3$) and P ($NaH_2PO_4 \cdot 2H_2O$) were added every week from July 2 to August 28, 2000 and June 14 to August 27, 2001. The approximate mass ratio of N to P added was 15:1. The final cumulative nutrient loading was 24.7 gN/m^2, 3.6 gP/m^2 in 2000 and 32.9 gN/m^2, 4.8 gP/m^2 in 2001. The dry chemicals were dissolved in 1 L of carbon filtered water in the laboratory. Then the dissolved nutrients were mixed in 10 L of enclosure water and distributed evenly using a watering can over the surface water of the LinNP enclosures. To prevent aerial transfer of nutrients into Lin and Control enclosures the nutrient solution was sprinkled from a height of approximately five centimeters from the surface of the water.

In 2000, lindane was added on July 5 to the Lin and LinNP enclosures as the formulated product Vitavax RS Flowable (Gustafson Canada) at a nominal concentration of approximately 1 µg/L. This concentration was chosen based on lindane water column half-life (46 days) calculated from Crescent Pond (Chapter 7). Thus, at a starting concentration of 1 µg/L, lindane was expected to remain above the detection limit for the duration of the experiment. The formulated product was mixed with carbon-filtered water to produce a 6.8 g/L lindane solution. From this solution 1 mL was removed and made up to 1 L to produce a 6.8 mg/L solution. For each Lin and LinNP enclosures 3.5 mL from the 6.8 mg/L solution were mixed with a litre of carbon-filtered water and then mixed with approximately 20 L of enclosure water and sprinkled evenly using a watering can over the surface of each treated enclosure. The lindane additions occurred on the same day as the start of the weekly nutrient additions. The same precautions as described for the nutrient additions were taken to prevent lindane transfer to the Control enclosures and lindane was not detected in water samples collected from the Control enclosures.

In 2001 the addition of lindane occurred on July 12, four weeks after the start of weekly nutrient additions. Technical-grade lindane (99% purity, Sigma Chemical Co., St. Louis, MO) was added to the Lin and LinNP enclosures to reach an approximate concentration of 2 mg/L in these enclosures. This elevated concentration over the 2000

study was chosen so that lindane levels would be above detection limits in each of the sampled compartments (water, sediment, and macrophyte) at the end of the experiment. For the Lin and LinNP enclosures, 50 grams of lindane was added to 2 L of methanol. The methanol-lindane mixture was added 500 mL at a time to 10 L of enclosure water, mixed and then dispensed over the enclosure surface water using a watering can. Average water column lindane concentration 1 hour after lindane addition was 1.8 mg/L.

Sampling and analysis

Extinction profiles of photosynthetically active radiation (PAR; 400-700 nm) through the water column were measured on a weekly basis at the center of each enclosure using a Li-Cor LI-189 meter with an LI-192SA submersible quantum sensor. Weekly measurements of water depth (metre stick), surface water temperature and conductivity (YSI 30 temperature/conductivity instrument) were also made at the center of each enclosure. In addition, depth integrated water column samples were collected weekly from the middle of each enclosure using a stoppered acrylic tube (6.4 cm inner diameter, 1 m length). Water samples were transported to the laboratory in opaque 1 L plastic bottles that had been triple rinsed with Blind Channel water. Water samples were analyzed for pH ammonium-N (NH_4-N) (hypochlorite method), nitrate+nitrite-N (NO_3-N) (UV spectrophotometry), total reactive phosphorous (TRP) (acid molybdate method), suspended solids, and turbidity (Stainton *et al.* 1977, APHA 1995). Three 250 mL water samples were collected from depth integrated water samples and analyzed for phytoplankton chlorophyll as described in Chapter 3. For periphytic algal sampling, acrylic rods (0.64 cm diameter, 90cm length) (Goldsborough *et al.* 1986) were positioned vertically in the northwest corner of each enclosure on June 12, 2000 and May 20, 2001. The rods were placed in a grid of 6 x 6 rods. During sampling, three rods were randomly removed without replacement and analysed for chlorophyll ($\mu g/cm^2$) as described in Chapter 3.

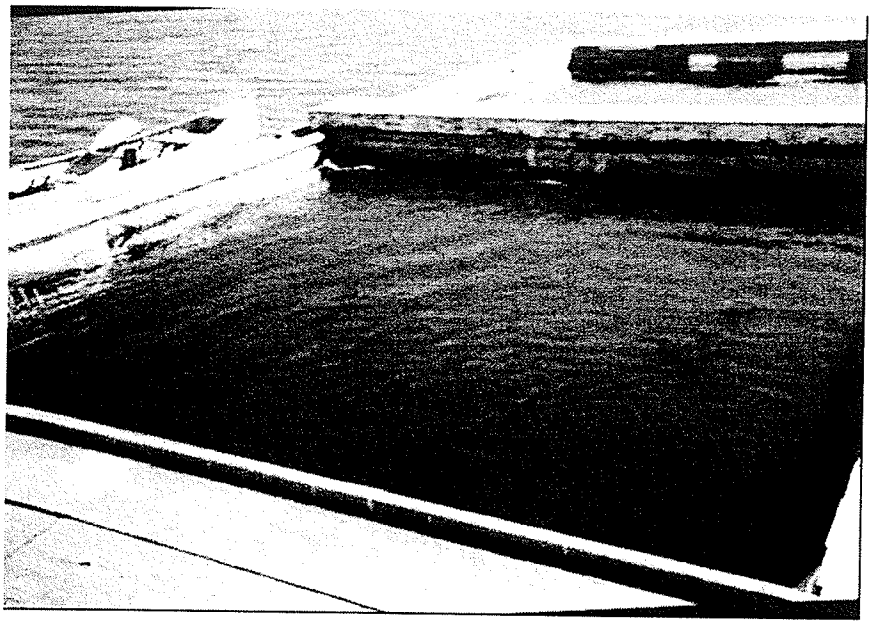
At the end of the experiment (September 4, 2000, September 22, 2001) submersed macrophyte above-ground biomass was sampled at the center of each enclosure. An open-ended plastic barrel was used to delineate 0.45m^2 area of sediment from which macrophytes were collected with long handled clippers and a dipper sieve. Three such samples were collected per enclosure. Macrophyte samples were dried at 104°C prior to weighing. In addition, biweekly estimates of the percent of enclosure area (observable from the surface) that was covered by submersed macrophytes were made in 2001 (Figure 23). At the end of the experiment (September 4, 2000, September 22, 2001) triplicate surficial sediment samples (10 cm deep) were collected from the center of each enclosure The samples were analyzed for sediment organic matter content as described in Chapter 3.

On August 14, 2001, sediment traps (Figure 24) were placed in the center of each enclosure. The traps were designed to collect material that sedimented out of the water column. The traps consisted of 500 ml plastic containers fastened to wooden stakes 2 m in length. The traps were collected two weeks later and their contents filtered and analysed for POM (mg/L) and chlorophyll *a* (µg/L) as described in Chapter 3.

Lindane analysis

Depth integrated water samples were collected from each enclosure prior to lindane addition and on days 1, 4, 8, 16, 32, and 56 following lindane addition in 2000 and days 1, 2, 4, 8, 16, 25, 36, and 72 following lindane addition in 2001. Whole water samples (2000 and 2001) and filtered (2001) water samples were analysed for lindane using the procedure described in Chapter 3. Unfiltered contents of the sediment traps (water and sediment) were mixed and also analysed for lindane as in Chapter 3. In 2001, sediment and submersed macrophyte samples collected from one randomly chosen Lin enclosure and one randomly chosen LinNP enclosure were shipped on ice to Norwest Laboratories, Winnipeg where they were analysed for total lindane using gas chromatography (EPA

A



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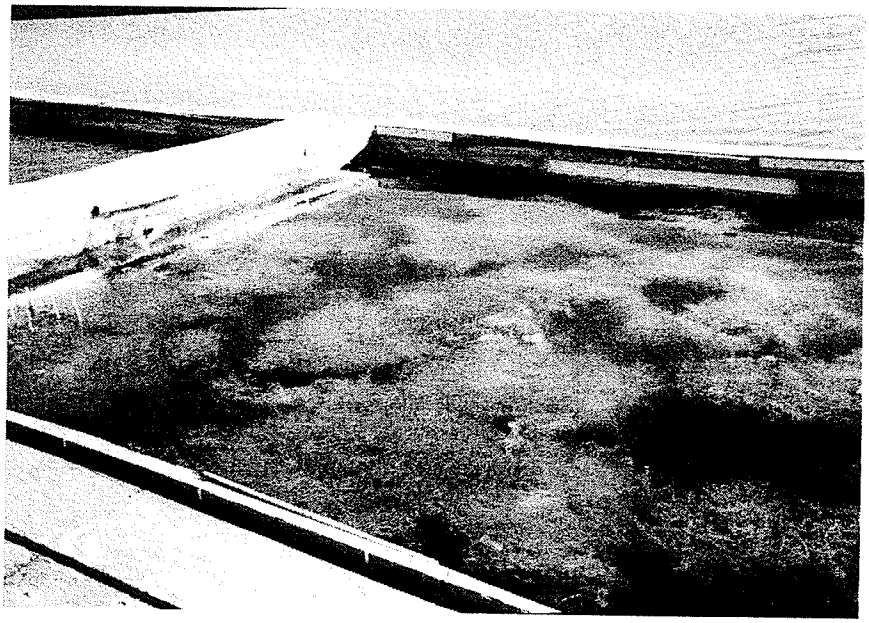


Figure 23. Estimates of macrophyte cover. Enclosure A < 10%, enclosure B > 90%.using a plastic acrylic tube (6.4 cm inner diameter, 1.5 m length).

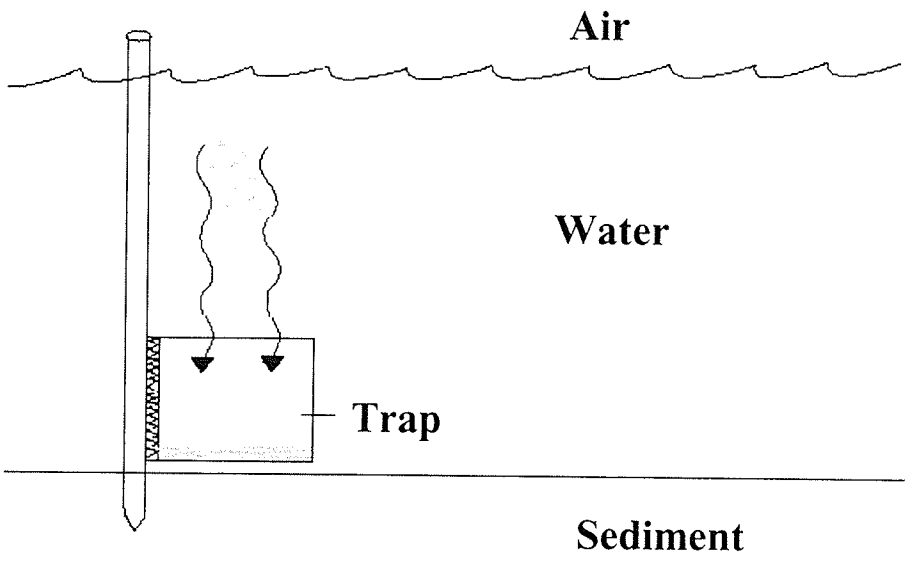


Figure 24. Schematic of sediment trap used in experimental enclosures in Blind Channel.

method 8081). Collection of the sediment and macrophyte samples for lindane analysis followed that described above.

Sediment resuspension

In 2001, sediment in the enclosures was disturbed experimentally to determine the role of resuspended sediment as a source of lindane to the water column. Resuspension of contaminated sediment may be a potential source of lindane to the water column. Using a canoe paddle (plastic head 25 cm x 30 cm, aluminium stock 1.3 m) the sediment 1 m from the enclosure walls and center walkway was disturbed by sticking the paddle into the sediment and turning it. At approximately 30 cm intervals along the enclosure walls and center walkway the paddle was pushed into the sediments to a depth of approximately 10 cm and then turned 180 degrees. Three water samples were collected immediately before and one hour after sediment disruption and analyzed for POM, chlorophyll and lindane as described above.

Pesticide loss from experimental vials

In 2001, an experiment was conducted in small Pyrex vials (44 mL) to determine the influence of nutrients on pesticide fate in wetland water. The small vials created a more controlled environment than the wetland enclosures which allowed for a more precise evaluation of the effects of nutrient additions on pesticide persistence. On 24 July 2001, water was collected from outside the Blind Channel enclosures and added unfiltered to 50 clear Pyrex vials (44 mL). Half the vials were enriched with inorganic N (18 mg/L $NaNO_3$) and P (1.2 mg/l $NaH_2PO_4 \cdot 2H_2O$) while the other half was not. The nutrient enriched and the non-enriched water was spiked with 2 mg/L atrazine (residue analysis grade, Supleco, USA) or 2 mg/L lindane (99% pure, Sigma-Aldrich Canada). In addition, deionised water (DW) treatments were prepared in a similar fashion as the BC water treatments to yield the following: 1) 2 mg/L atrazine, 2) 2 mg/L atrazine + nutrients, 3) 2 mg/L lindane, 4) 2 mg/L lindane + nutrients. The vials were positioned randomly on the frame of the enclosures approximately 30 cm above the water surface (Figure 25). The

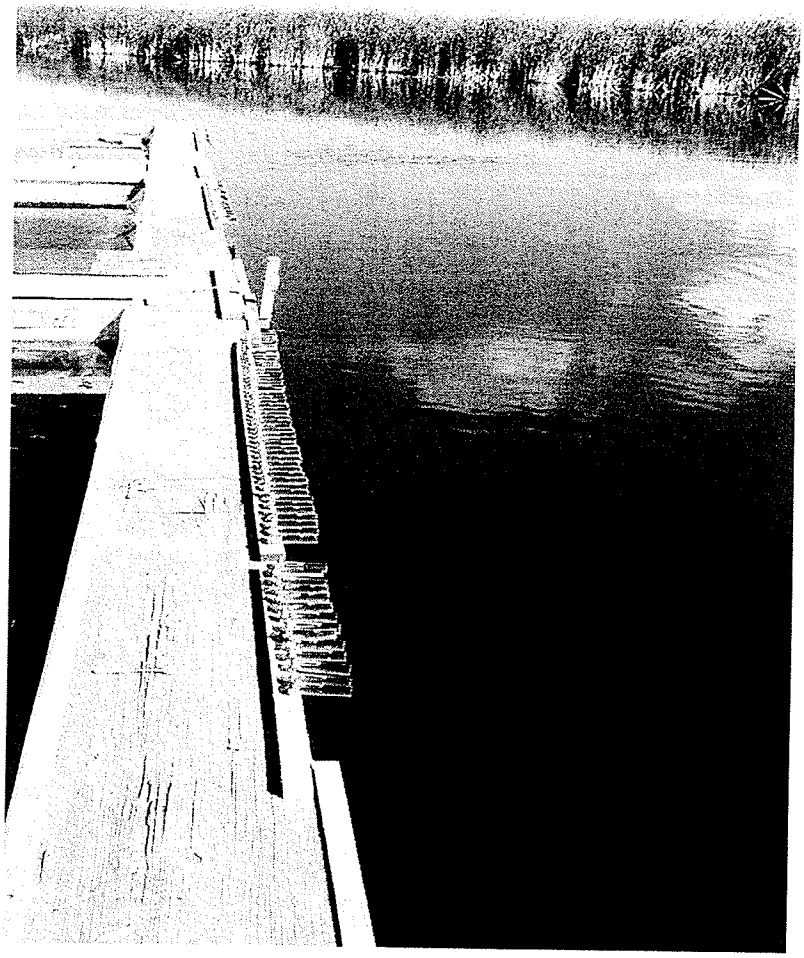


Figure 25. Position of experimental vials containing water and atrazine or lindane located 30 cm above the surface of Blind Channel.

lindane concentration used (2 mg/L) was the same as that used in the enclosure portion of the study so that comparisons could be made between the two experiments. The atrazine concentration was the same as the lindane concentration, so comparisons could be made between nutrient effects on lindane and atrazine persistence. The above treatments allowed for comparisons between pesticide persistence in low and high nutrient environments under different water conditions (wetland water vs. deionised water). Water from the vials was sampled on days 0, 2, 6, 10, 32, and 60 and quantified for atrazine and lindane concentrations as in Chapter 3.

Pesticide water column half-life calculation

The first-order half-life of the studied pesticides was determined using non-linear regression ($Mt=M_T e^{-kt}$). SigmaPlot V. 8.0 was used to find the slope of the lindane or atrazine concentration over time (k).

Statistical analyses

The SAS System for Windows (V. 8, SAS Institute Inc.) and SigmaPlot V. 8.0 were used to perform the statistical analyses. Data were log (x +1) transformed prior to analyses to stabilize the variance and approximate the normal distribution. Statistical tests were evaluated at alpha = 0.05 level of probability. Repeated measures analysis of variance (ANOVA) (proc mixed) and Tukey post hoc tests were used to determine if enclosure treatments were significantly different over the weeks of the experiment. For variables that were not measured on a weekly basis, one-way analysis of variance (ANOVA) (proc glm) followed by Tukey post hoc tests were used to determine if treatments were significantly different. An analysis of covariance (proc glm) was conducted for both years of the enclosure experiment to model lindane half-life as a function of treatment and time-averaged covariates.

5. 3 Results

Nutrient concentrations in enclosures

Post nutrient addition NO_3-N (2000 $F_{2,9}$= 7.71 p = 0.011; 2001 $F_{2,9}$= 191.99 p < 0.0001) (Figure 26) and TRP (2000 $F_{2,9}$= 21.54 p = 0.0004; 2001 $F_{2,9}$= 171.86 p < 0.0001) (Figure 27) concentrations in the LinNP enclosures where higher than the Lin and Control enclosures, which did not differ from each other. Post nutrient addition NH_4-N concentrations were not significantly different among treatments in 2000 ($F_{2,9}$= 0.13 p = 0.879) (Figure 28). In 2001 post nutrient addition NH_4-N concentrations in the LinNP enclosures diverged significantly ($F_{2,9}$= 15.39 p = 0.0012) from the Lin and Control enclosures, which did not differ from each other (Figure 28). Mass ratios of dissolved inorganic nitrogen (NH_4-N + NO_3-N) to dissolved inorganic phosphorous (approximated from TRP) in both years of the study were below the Redfield ratio of 15:1 (Figure 29).

Biota in enclosures

Post nutrient treatment phytoplankton chlorophyll *a* concentrations in the LinNP enclosures diverged significantly (2000 $F_{2,9}$= 7.15 p = 0.014; 2001 $F_{2,9}$= 16.37 p = 0.001) from the Lin and Control enclosures, which did not differ significantly from each other (Figure 30).

Periphyton chlorophyll *a* was not significantly different among treatments (2000 Lin = 0.39 μg/cm^2, LinNP = 0.55 μg/cm^2 Control = 0.60 μg/cm^2 $F_{2,9}$= 1.45 p = 0.2852; 2001 Lin = 3.03 LinNP = 3.87 Control = 3.04, $F_{2,9}$= 1.02 p = 0.399) (Figure 31). Periphyton chlorophyll *a* concentrations were not significantly (p > 0.05) correlated with phytoplankton chlorophyll *a* concentrations in any of the treatment enclosures during either year of the experiment.

Throughout the experiment in 2001 submersed macrophyte cover was observed to be greater in the Lin and Control enclosures than in the LinNP enclosures (Table 24). At the end of the experiment in 2000 and 2001, submersed macrophyte biomass was significantly lower in the LinNP enclosures (2000 $F_{2,9}$ = 10.10 p = 0.005; 2001 $F_{2,9}$ =

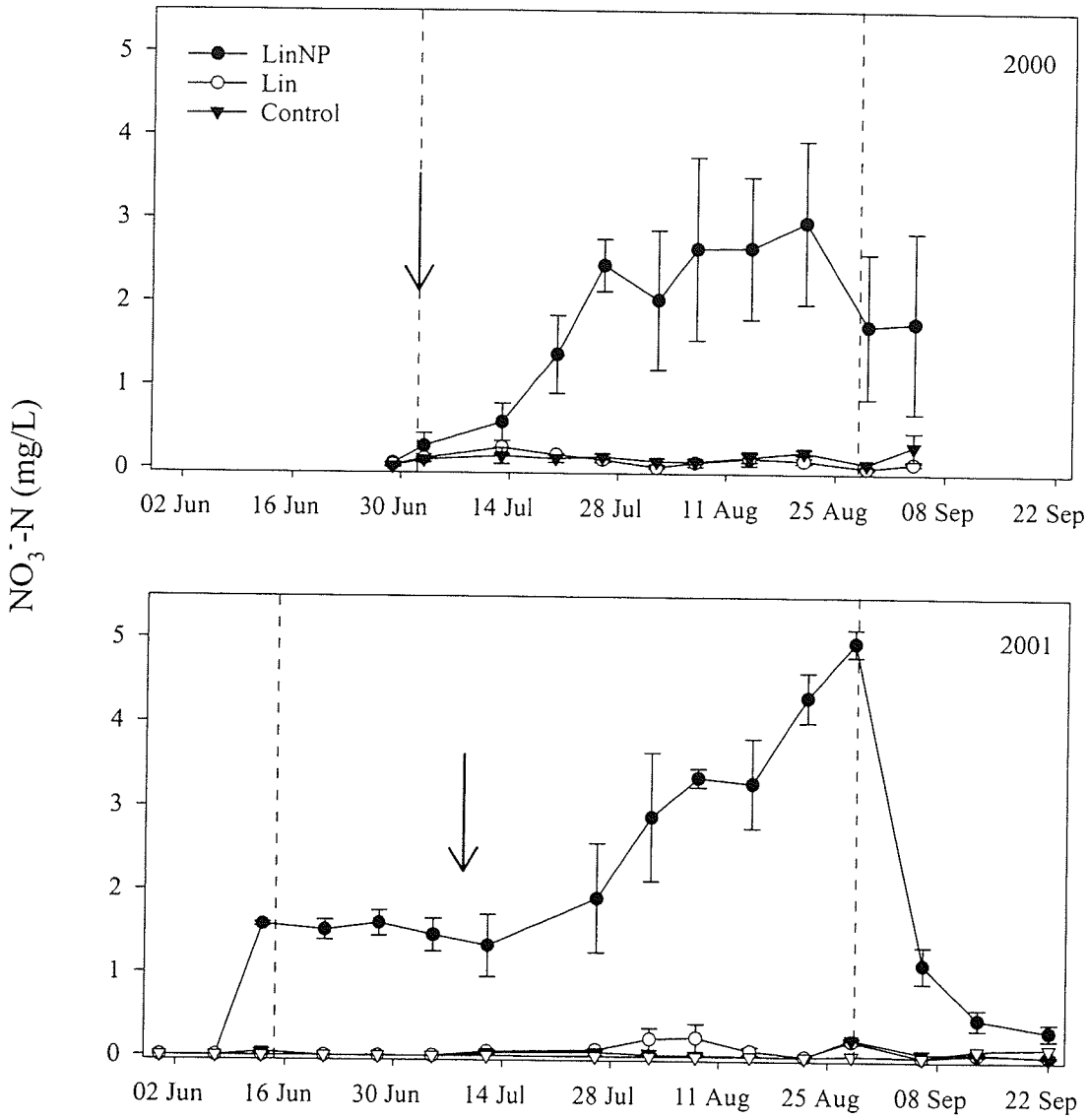


Figure 26. NO_3-N concentrations (mg/L; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

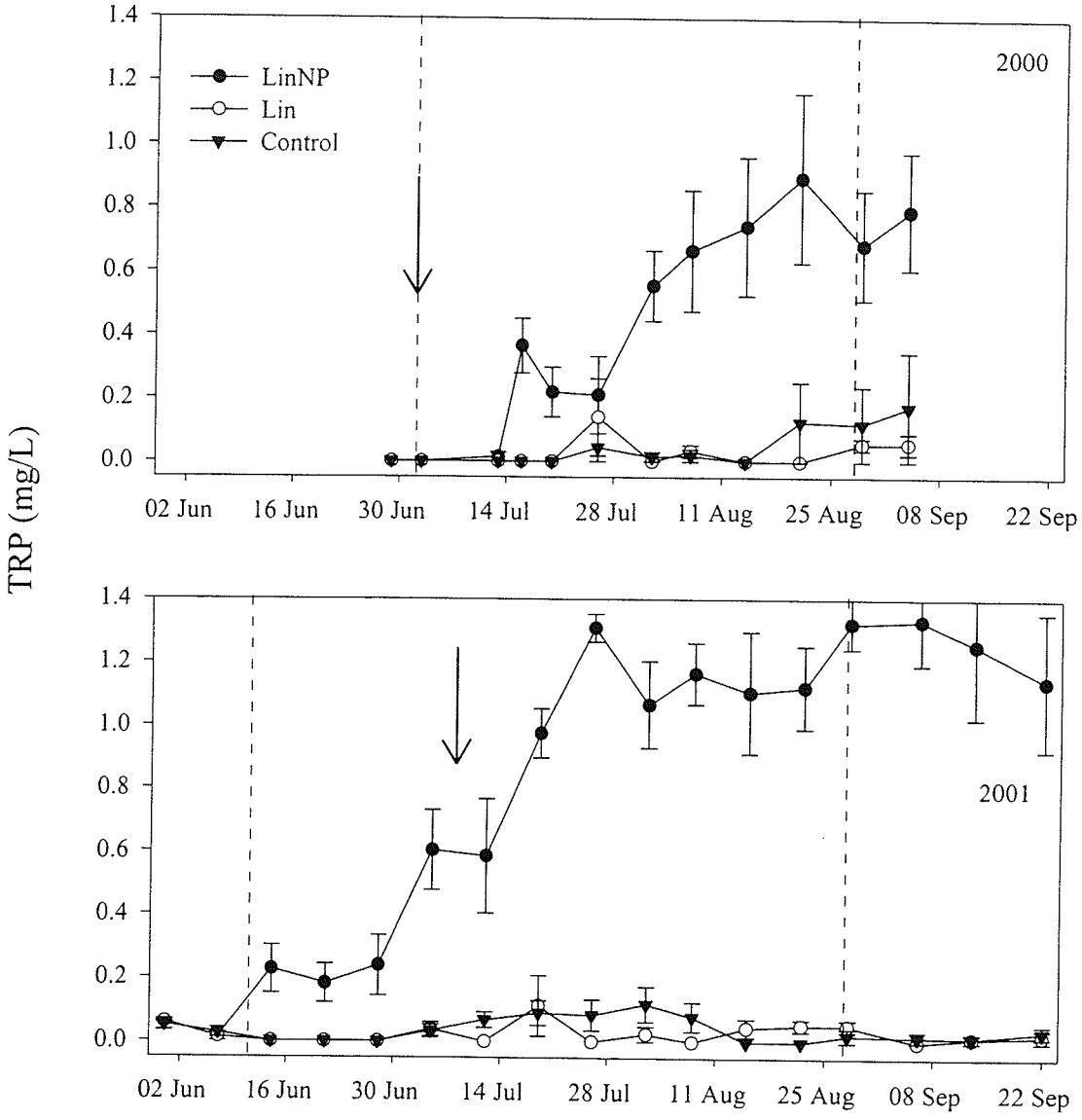


Figure 27. TRP concentrations (mg/L; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

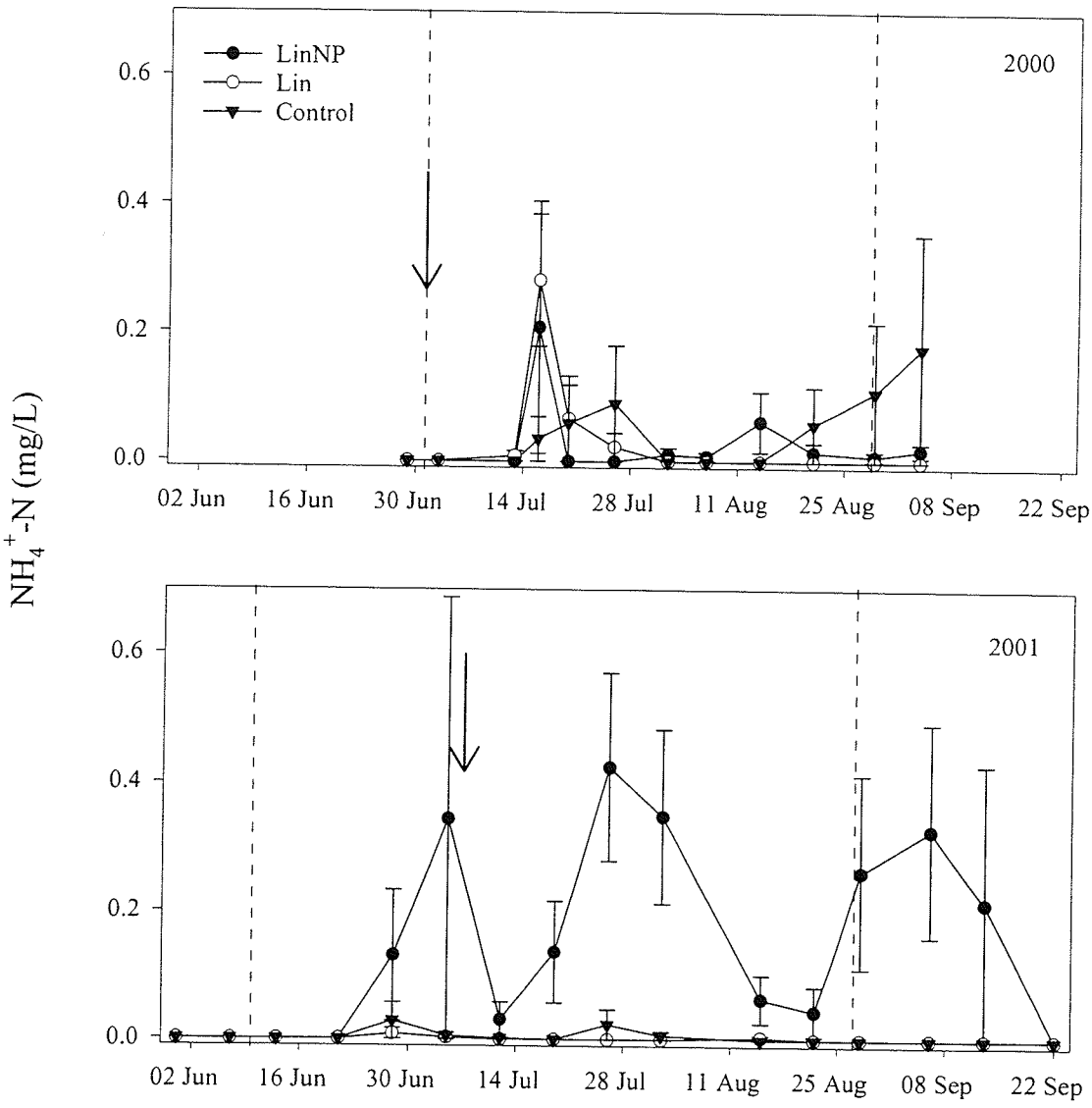


Figure 28. NH_4-N concentrations (mg/L; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

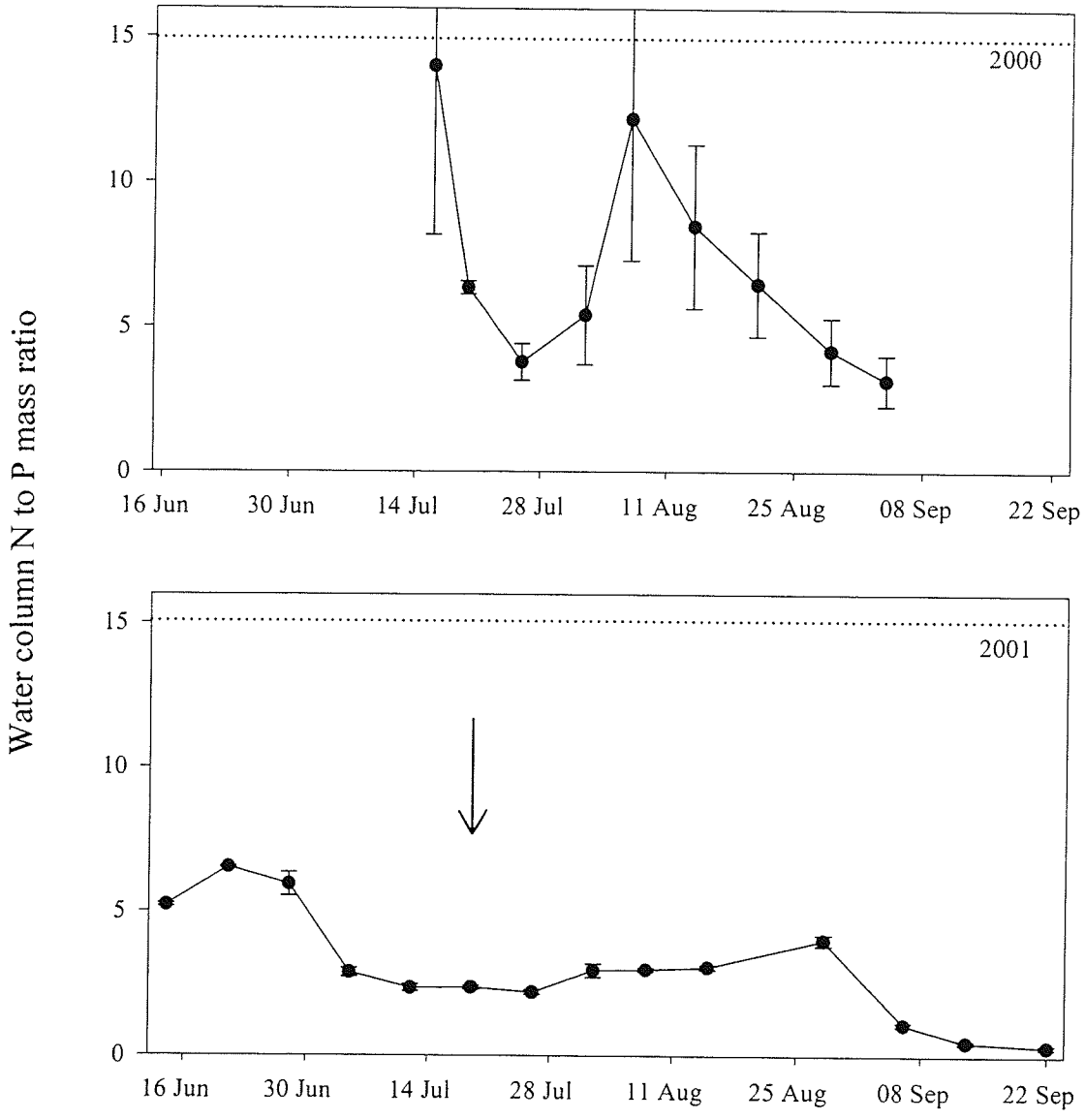


Figure 29. Total inorganic N to P mass ratios (± SE n = 4) in Blind Channel enclosures in 2000 and 2001. The horizontal line at 15 indicates the Redfield ratio.

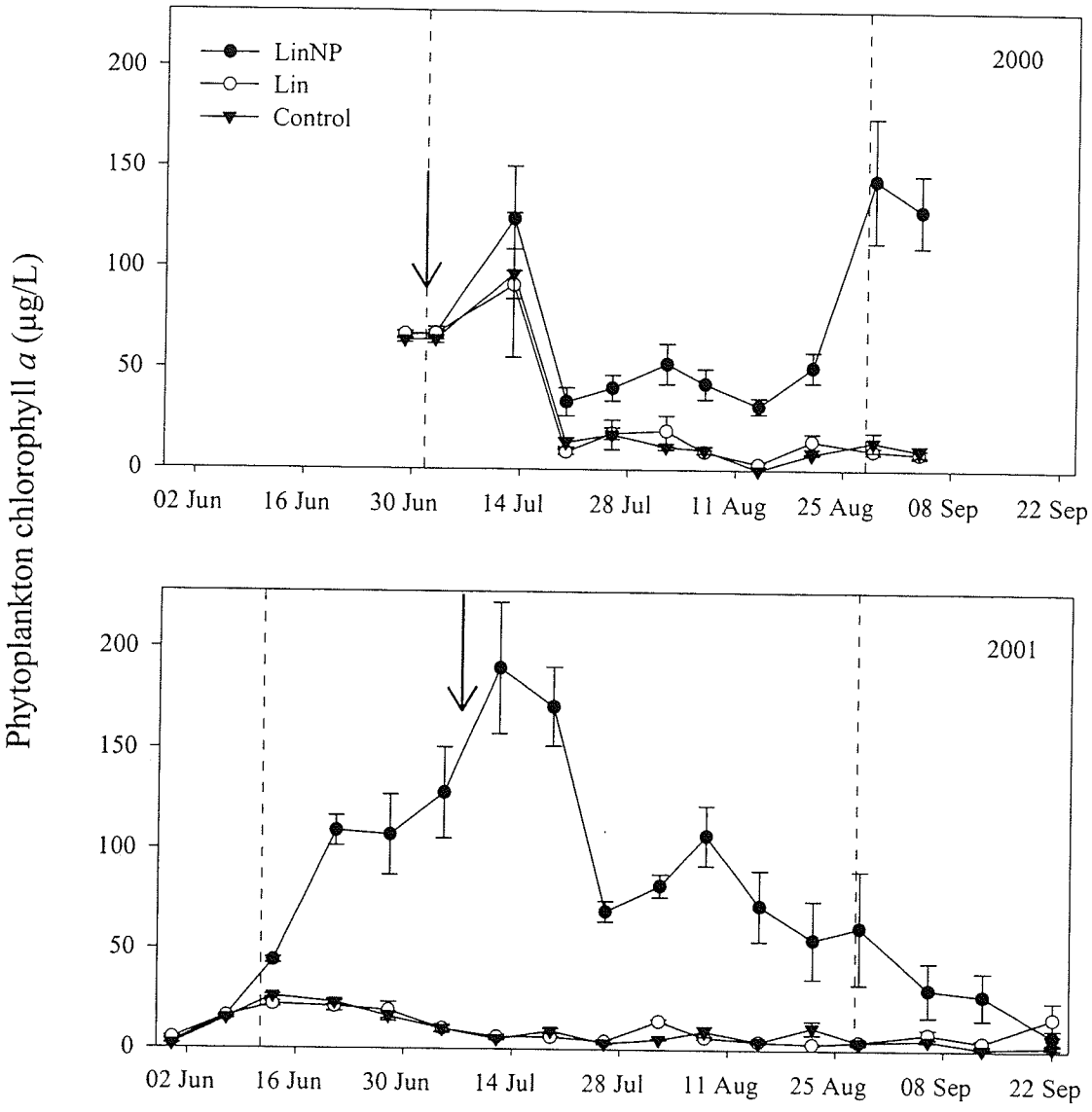


Figure 30. Phytoplankton chlorophyll *a* in (µg/L; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

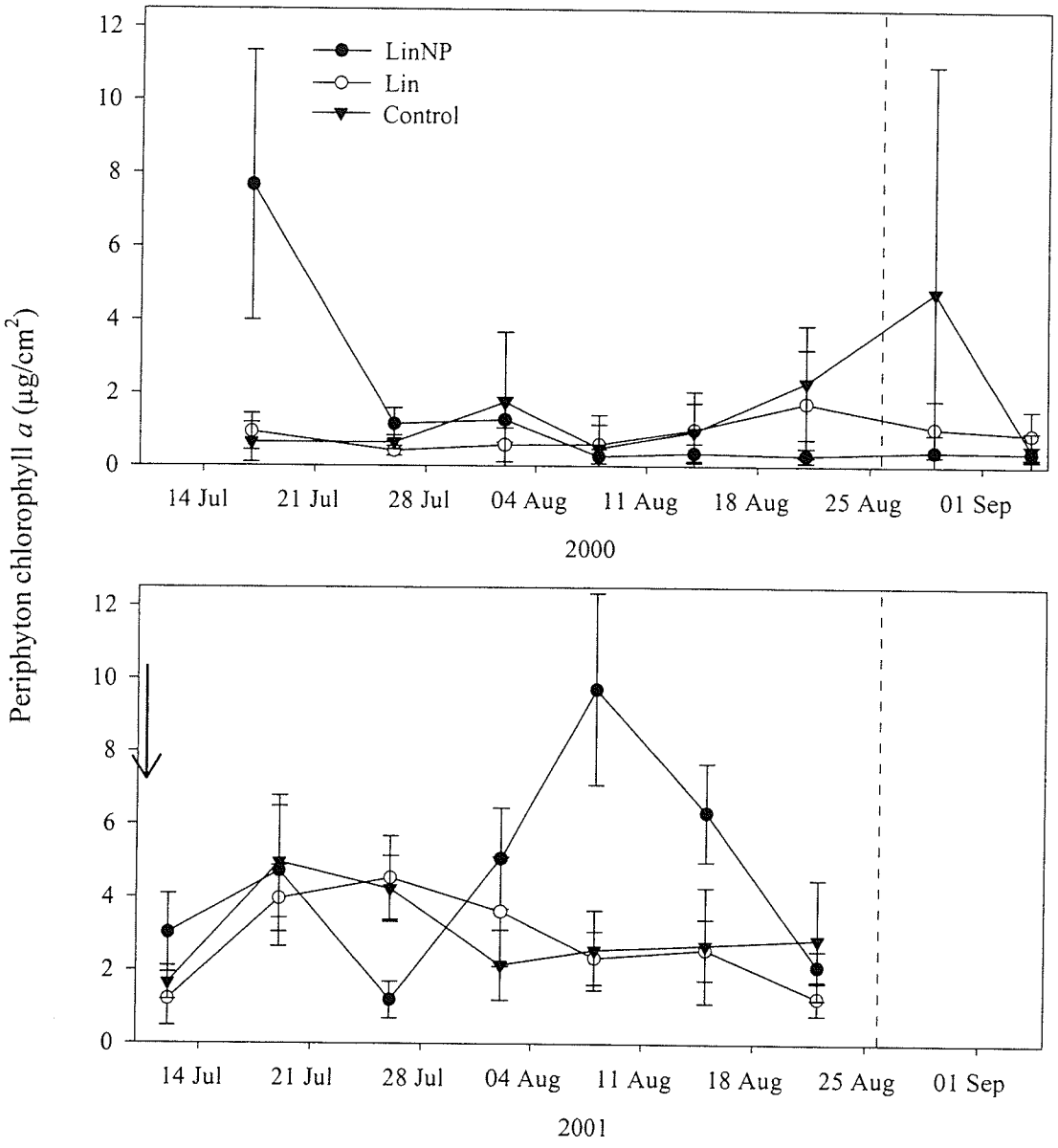


Figure 31. Periphyton chlorophyll *a* concentration (µg/cm^2) in Blind Channel enclosures (2000 and 2001). Arrow indicates dates of lindane addition to Lin and LinNP. Dotted lines indicate end of weekly nutrient additions to LinNP.

Table 24. Percent surface area (mean; ± SE n = 4) of enclosures covered by submersed macrophytes in experimental enclosures in Blind Channel, 2001. ANOVAs were performed separately for each date. Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Month	LinNP	Lin	Control	p-values
June	$0.5^{A}(0.1)$	$17.5^{A}(4.7)$	$23.8^{A}(5.1)$	0.164
July	$1.5^{A}(0.6)$	$33.8^{B}(4.9)$	$23.8^{B}(4.8)$	0.050
August	$1.3^{A}(0.6)$	$45.0^{B}(6.7)$	$36.3^{B}(5.7)$	0.032

13.96 p=0.0017) but was not significantly different between Lin and Control enclosures (Table 25).

Other variables

Sediment organic matter was not significantly different among treatments ($p > 0.05$) (Table 26). Water depth in the enclosures declined as the experiment progressed. Water depth was not significantly different among enclosure treatments (2000 Lin = 72 cm, LinNP = 71 cm, Control = 72 cm $F_{2,9} = 0.78$ $p = 0.488$; 2001 Lin = 100 LinNP = 101, Control = 100 cm, $F_{2,9} = 0.39$, $p = 0.691$). Surface water temperatures were not significantly different among treatments (2000 Lin = 22°C LinNP = 22°C Control = 22°C $F_{2,9} = 1.88$, $p = 2.08$; 2001 Lin = 20°C LinNP = 21°C Control = 20°C $F_{2,9} = 0.76$ $p = 0.497$). Sediment surface water temperatures were also not significantly different among treatments in either year (2000 Lin = 21°C, LinNP = 21°C, Control = 21°C, $F_{2,9} = 1.37$ $p = 0.303$; 2001Lin=19 °C, LinNP = 19°C, Control = 19°C, $F_{2,9} = 1.55$ $p = 0.264$). Post nutrient addition water column pH was significantly higher in the LinNP enclosures (2000 Lin = 9.32 LinNP = 9.88 Control = 9.26 $F_{2,9} = 25.17$ $p < 0.001$; 2001 Lin = 8.83 LinNP = 9.36 Control = 8.67, $F_{2,9} = 7.77$ $p = 0.011$) than in the Lin and Control enclosures, which did not differ significantly from each other. Conductivity showed a general increasing trend as the experiment progressed (Figure 32). Post nutrient addition conductivity was significantly higher in LinNP enclosures (2000 $F_{2,9} = 7.00$ $p = 0.015$; 2001 $F_{2,9} = 10.02$ $p = 0.005$) but did not differ significantly between Lin and Control enclosures (Figure 32). Turbidity also diverged significantly ($p < 0.05$) in the LinNP enclosures after nutrient additions (Figure 33). Turbidity was correlated with phytoplankton chlorophyll *a* concentrations (Figure 34). Particulate organic matter (2000 Lin = 10.3 mg/L LinNP = 27.2 mg/L Control = 10.8 mg/L $F_{2,9} = 10.77$ $p=0.004$; 2001 Lin = 4.9 mg/L LinNP = 19.1 mg/L Control = 5.6 mg/L $F_{2,9} = 15.56$ $p = 0.001$) diverged significantly in the LinNP following nutrient additions but did not differ significantly between Lin and Control enclosures. Particulate inorganic matter was significantly higher

Table 25. Submersed macrophyte dry weight (g/m^2; ± SE n = 4) in enclosures at the end of the experiment. ANOVAs were performed separately for each date. Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Year	LinNP	Lin	Control	p-value
Sept. 4, 2000	3.64^{A} (3.64)	68.77^{B} (13.16)	78.74^{B} (17.55)	0.005
Sept. 22, 2001	6.58^{A} (3.22)	88.84^{B} (10.47)	92.54^{B} (20.63)	0.002

Table 26. Sediment organic matter (percent dry weight; ± SE n = 4) in enclosures at the end of the experiment. ANOVAs were performed separately for each date.

Year	LinNP	Lin	Control	p-value
Sept. 4, 2000	20.23 (0.86)	19.46 (0.06)	19.62 (0.59)	0.802
Sept. 22, 2001	18.15 (0.22)	17.89 (0.20)	17.72 (0.04)	0.932

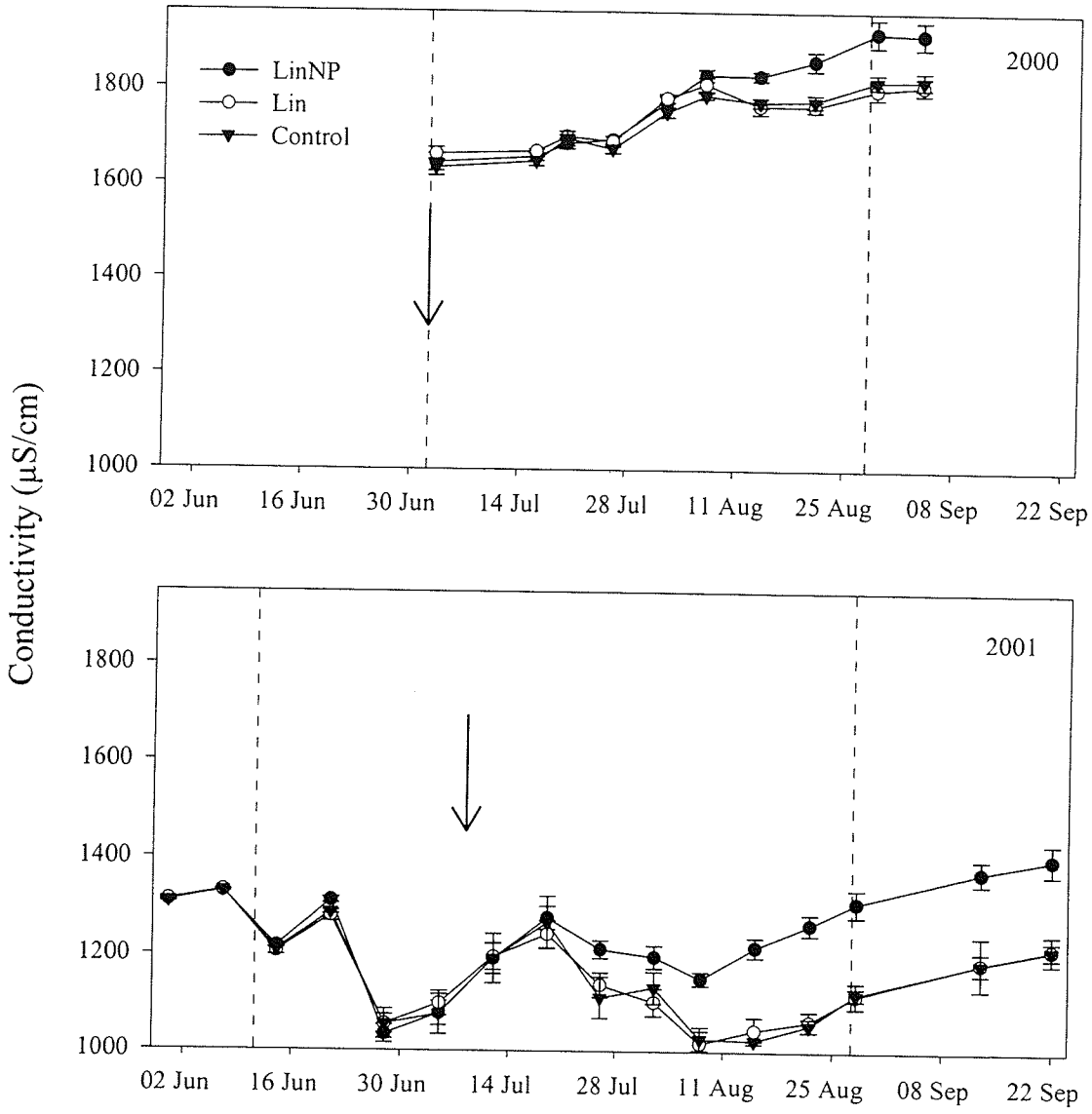


Figure 32. Conductivity in (µS/cm; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

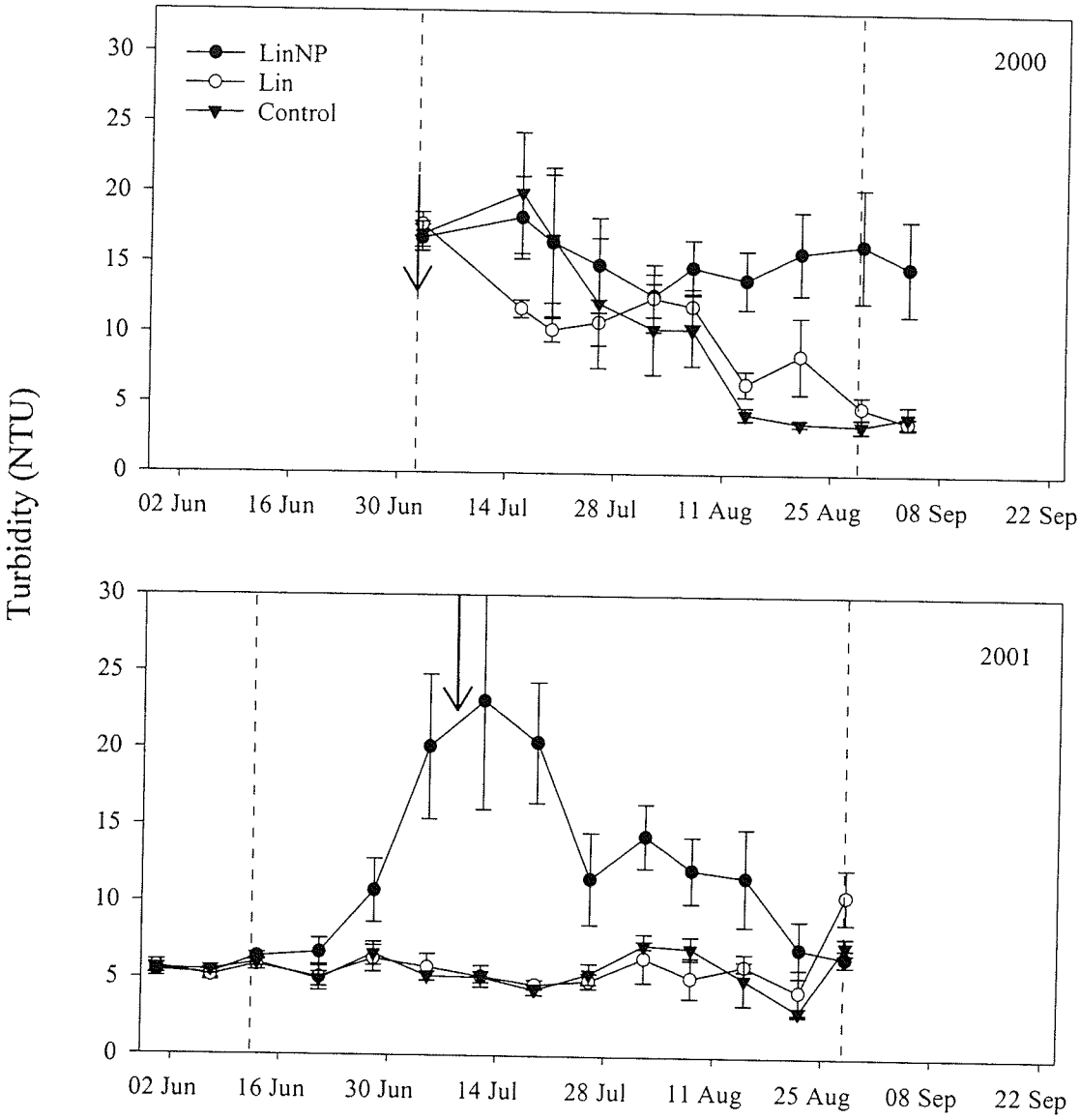


Figure 33. Turbidity (NTU; ± SE n = 4) in Blind Channel enclosures in 2000 and 2001. Arrow indicates date of lindane addition to Lin and LinNP. Dotted lines indicate start and end of weekly nutrient additions to LinNP.

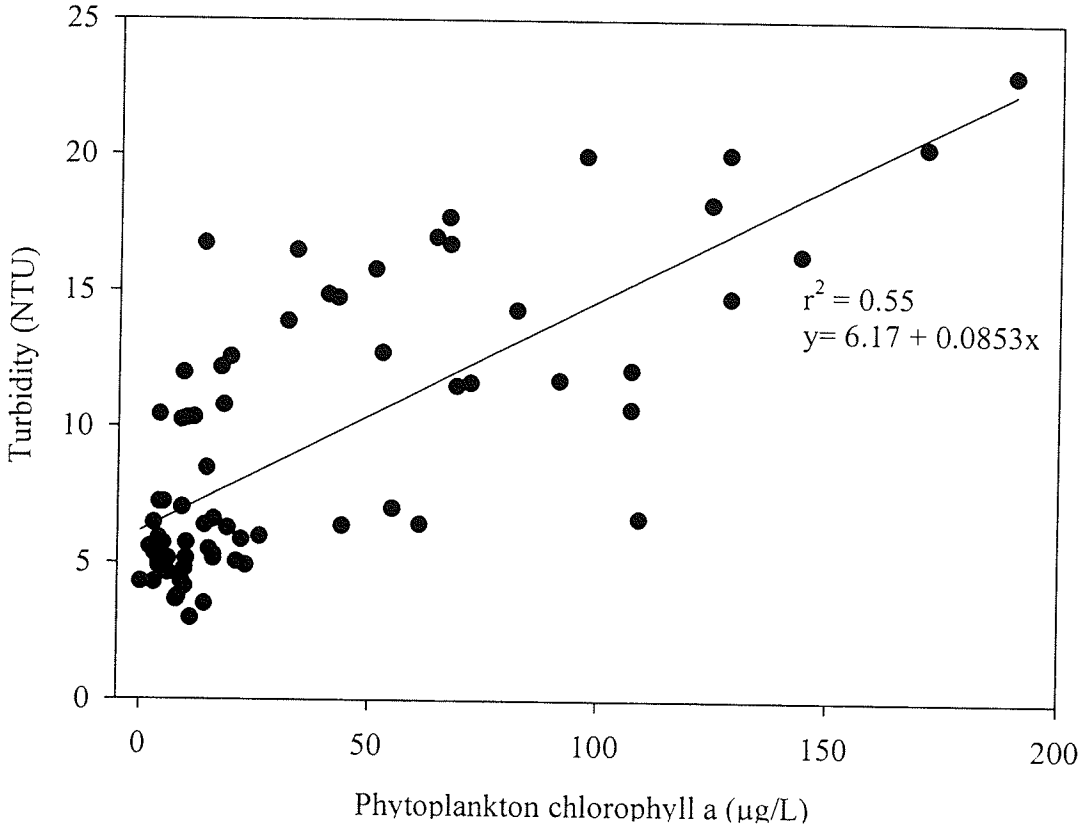


Figure 34. Regression of average phytoplankton chlorophyll *a* against turbidity (NTU) in Blind Channel enclosures.

in LinNP enclosures in 2001 (Lin = 0.1 mg/L, LinNP = 0.5 mg/L Control = 0.1 mg/L, $F_{2,9}$= 7.82 p = 0.011) but did not differ significantly among treatments in 2000 (Lin = 0.1 mg/L, LinNP = 0.2 mg/L, Control = 0.1 mg/L, $F_{2,9}$= 1.72 p = 0.233). Post nutrient addition light extinction coefficients were significantly higher (2000 Lin = -0.0136 LinNP = -0.0232 Control = -0.0162 $F_{2,9}$ = 4.88 p = 0.037; 2001 Lin = -0.0141 LinNP = -0.0209 Control = -0.0147 $F_{2,9}$= 12.23 p = 0.003) in the LinNP enclosures. Organic sedimentation rate was significantly higher in LinNP treatments than in the Control and Lin treatments, which did not differ from each other (Table 27). Inorganic sedimentation rate was not significantly different among treatments (Table 27). Mean chlorophyll *a* concentrations in the sediment traps were significantly higher ($F_{2,9}$= 12.18, p = 0.003) in LinNP (mean 2.3 mg/L, SE ± 0.3 n = 4) treatments than in the Control (0.1 mg/L SE ± 0.3 n = 4) and Lin (0.3 mg/L SE ± 0.9 n = 4) treatments, which did not differ from each other.

Annual differences

In all three treatments sediment organic matter was significantly higher in 2000 than in 2001 (Table 28). All three treatments also had significantly ($p < 0.05$) lower water depth in 2000 than in 2001, whereas water temperature, conductivity, pH and inorganic particulates were significantly higher in 2000 (Table 28). Submersed macrophyte biomass, and total reactive phosphorous and ammonium concentrations were not significantly ($p < 0.05$) different between years (Table 28). Turbidity, phytoplankton chlorophyll *a*, TSS, and organic particulates were significantly higher in Lin and Control treatments in 2000 than in 2001 but did not differ between years in the LinNP treatments (Table 28). In 2000, at the time of lindane addition, only NO_3-N was different ($p < 0.05$) between Lin and LinNP treatments (Table 29). However, at the time of lindane addition in 2001, nutrient concentrations as well as conductivity, pH, and phytoplankton chlorophyll *a* concentrations were significantly different ($p < 0.05$) between Lin and LinNP treatments (Table 30).

Table 27. Sedimentation rates ($g/m^2/d$, ± SE n = 4) in the enclosures measured on August 3, 2001. ANOVAs were performed separately for each sediment type. Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Sediment type	LinNP	Lin	Control	p-value
Inorganic	4.6^{A} (0.8)	1.8^{A} (0.6)	3.8^{A} (0.9)	0.424
Organic	4.7^{A} (0.2)	1.1^{B} (0.1)	1.5^{B} (0.1)	< 0.001
Total	9.3^{A} (0.9)	2.9^{A} (0.3)	5.3^{A} (1.0)	0.055

Table 28. Seasonal (June-August) mean values (± SE n = 4) for environmental variables measured in Blind Channel enclosures in 2000 and 2001. Means followed by same letters are not significantly different at $p < 0.001$ (One-way ANOVA followed by Tukey's test).

Variable	LinNP		Lin		Control	
	2000	2001	2000	2001	2000	2001
Depth(cm)	72.3^{A} (0.6)	100.4^{B} (0.4)	70.8^{A}(0.5)	100.1^{B} (0.5)	72.2^{A}(0.4)	101.2^{B}(0.7)
Temp.(°C)	22.27^{A} (0.04)	20.45^{B} (0.05)	22.26^{A}(0.02)	20.39^{B} (0.07)	22.42^{A} (0.08)	20.54^{B} (0.07)
Cond.(mS/cm)	1742^{A}(5)	1178^{B}(11.2)	1750^{A}(5)	1178^{B}(8)	1784^{A}(7)	1234^{B}(8)
pH	9.27^{A} (0.04)	8.63^{B}(0.05)	9.33^{A}(0.04)	8.70^{B} (0.04)	9.88^{A}(0.04)	9.09^{B}(0.04)
$N\text{-}NO_3$(µg/L)	133^{A}(8)	103^{A} (16)	172^{A}(28)	29^{B}(7)	1613^{A}(260)	1467^{A}(171)
$N\text{-}NH_4$(µg/L)	42^{A}(17)	32^{A} (14)	21^{A}(7)	1^{A}(0.5)	27^{A}(10)	62^{A}(23)
TRP(µg/L)	42^{A}(18)	49^{A} (18)	23^{A}(6)	23^{A}(1)	430^{A}(46)	440^{A}(50)
Turbidity (NTU)	10.25^{A} (0.85)	5.84^{B} (0.08)	9.75^{A}(0.38)	5.45^{B} (0.14)	16.25^{A} (1.39)	11.88^{A} (0.73)
POM(mg/L)	10.86^{A} (0.66)	5.83^{B} (0.04)	11.08^{A} (0.45)	5.85^{B} (0.20)	24.96^{A} (2.18)	16.94^{A} (1.34)
PIM(mg/L)	2.77^{A} (0.03)	0.48^{B} (0.04)	3.97^{A}(0.40)	0.53^{B} (0.07)	3.91^{A}(0.45)	1.04^{B}(0.07)
SedOM(% dry wt)	19.62^{A} (0.30)	17.73^{B} (0.04)	19.45^{A} (0.21)	17.75^{B} (0.23)	20.23^{A} (0.43)	17.83^{B} (0.22)
Submersed macrophytes (g/m^2)	78.74^{A} (8.77)	92.54^{A} (10.31)	68.77^{A} (6.58)	86.63^{A} (3.86)	3.63^{A}(1.82)	6.58^{A}(1.61)
Phytoplankton chlorophyll *a* (µg/L)	31.25^{A} (3.11)	14.46^{B} (0.96)	30.75^{A} (2.74)	12.97^{B} (1.17)	69.75^{A} (6.40)	78.95^{A} (7.13)
Periphyton chlorophyll *a* ($µg/cm^2$)	0.60^{A}(0.08)	3.04^{B} (0.48)	0.39^{A}(0.05)	3.03^{B} (0.36)	0.55^{A}(0.03)	3.87^{B} (0.42)

Table 29. Mean values (± SE, n = 4) for environmental variables measured in the enclosures in 2000 on the day of lindane addition (July 5) to Lin and LinNP enclosures. Means followed by same letters are not significantly different from each other ($p < 0.05$ One-way ANOVA followed by Tukey's test). ND = no detection.

Variable	Lin	LinNP	Control	p-value
Depth (cm)	734 ^{A} (0.3)	756 ^{A} (0.8)	758 ^{A} (0.5)	0.520
Temperature (°C)	20.1 ^{A} (0.02)	20.1 ^{A} (0.03)	20.1 ^{A} (0.01)	0.748
Conductivity (mS/cm)	1662 ^{A} (7)	1644 ^{A} (9)	1633 ^{A} (9)	0.488
pH	9.4 ^{A} (0.01)	9.3 ^{A} (0.01)	9.3 ^{A} (0.02)	0.254
NO_3-N (µg/L)	58.8 ^{A} (10.4)	673.3 ^{B} (71.3)	30.8 ^{A} (8.2)	0.021
NH_4-N (µg/L)	ND	ND	ND	
TRP (µg/L)	ND	ND	ND	
Turbidity (NTU)	17.7 ^{A} (0.4)	16.8 ^{A} (0.5)	17.3 ^{A} (0.4)	0.845
POM (mg/L)	20.3 ^{A} (1.5)	21.1 ^{A} (1.7)	20.7 ^{A} (1.1)	0.304
PIM (mg/L)	7.4 ^{A} (0.2)	5.8 ^{A} (0.9)	10.7 ^{A} (1.2)	0.545
Phytoplankton chlorophyll *a* (µg/L)	136.3 ^{A} (9.8)	132.2 ^{A} (4.2)	134.4 ^{A} (2.0)	0.378
Periphyton (µg/cm^2)	3.1 ^{A} (0.4)	5.0 ^{A} (1.0)	4.6 ^{A} (0.8)	0.345

Table 30. Mean values (± SE, n = 4) for environmental variables measured in the enclosures in 2001 on the day of lindane addition (July 12) to Lin and LinNP enclosures. Means followed by same letters are not significantly different from each other at $p < 0.05$ (One-way ANOVA followed by Tukey's test). ND = no detection.

Variable	Lin	LinNP	Control	p-value
Depth (cm)	99.3 ^{A} (0.6)	101.3 ^{A} (0.4)	99.4 ^{A} (0.5)	0.637
Temperature (°C)	22.7 ^{A} (0.03)	22.8 ^{A} (0.03)	22.6 ^{A} (0.04)	0.583
Conductivity (µS/cm)	1195 ^{A} (13)	1192 ^{A} (16)	1180 ^{A} (17)	0.857
pH	8.64 ^{A} (0.02)	9.42 ^{B} (0.2)	8.52 ^{B} (0.09)	0.026
$N\text{-}NO_3$ (µg/L)	52.8 ^{A} (9.4)	1326.8 ^{B} (188.1)	36.8 ^{A} (6.3)	0.003
$N\text{-}NH_4$ (µg/L)	ND	30 (13.7)	1.5 ^{A} (0.8)	0.362
TRP (µg/l)	ND	583.5 (90.8)	67.5 ^{B} (12.3)	0.007
Turbidity (NTU)	5.2 ^{A} (0.3)	23.1 ^{B} (3.5)	5.2 ^{A} (0.1)	0.006
POM (mg/L)	5.4 ^{A} (0.5)	34.8 ^{B} (0.5)	4.0 ^{A} 0.3	0.035
Particulate inorganic matter (mg/L)	0.1 ^{A} (0.1)	0.7 ^{A} (0.2)	0.1 ^{A} (0.1)	0.218
Phytoplankton chlorophyll (µg/L)	6 ^{A} (1)	190 ^{B} (32)	6 ^{A} (1)	0.010
Periphyton chlorophyll ($\mu g/cm^2$)	1.7 ^{A} (0.3)	3.0 ^{A} (0.5)	1.6 ^{A} (0.2)	0.293

Phytoplankton chlorophyll *a* concentrations, at the time of lindane addition, did not differ ($F_{1,6}$ = 1.58 p = 0.256) between the LinNP enclosures of 2000 (132 µg/L) and the LinNP enclosures of 2001 (190 µg/L). However at the time of lindane addition the Lin enclosures of 2000 had significantly higher ($F_{1,6}$ = 411 p < 0.001) phytoplankton chlorophyll *a* concentrations (136 µg/L) than the Lin enclosures of 2001 (6 µg/L).

Lindane

Total lindane dissipated from the water column of the enclosures following first-order kinetics (Figure 35). Lindane water column half-life in the enclosures ranged from 0.6 to 10.7 days. In 2000 lindane half-life was not significantly different ($F_{1,6}$= 0.02 p=0.894) between Lin (mean 2.6 days SE = 0.3 n = 4) and LinNP (mean 2.5 days SE = 0.3 n = 4) treatments. In 2001, lindane half-life was significantly longer ($F_{1,6}$= 9.95 p = 0.02) in the Lin treatments (10.1 days SE = 0.3 n = 4) than in the LinNP treatments (4.4 days SE = 0.9 n = 4). Lindane was not detected (detection limit = 0.001 µg/L) in the Control enclosures in either year.

The percent of lindane retained in filters was significantly higher ($F_{1,54}$=23.56 p < 0.001) for water samples collected from LinNP enclosures (19.2%) than for samples collected from Lin enclosures (3.3%). Lindane was below detection limit (0.05 ppm) in the sediments collected at the end of the experiment in 2001. In 2001, lindane concentration of single submersed macrophyte samples collected in Lin and LinNP enclosures was 0.19 ppm and 0.012 ppm, respectively.

Lindane half-lives in Lin enclosures were significantly different ($F_{1,6}$ = 95.54 p < 0.001) between 2000 (2.6 days) and 2001 (10.1 days). In contrast, lindane half-lives in the LinNP treatments were not significantly different ($F_{1,6}$ = 0.934 p = 0.37) between years (2000 half-life = 2.5 days; 2001 half-life = 4.4 days).

Lindane dissipation and environmental conditions

In 2000, none of the environmental variables were significantly (p > 0.05) related to lindane half-life. However, in 2001 analysis of covariance revealed that phytoplankton

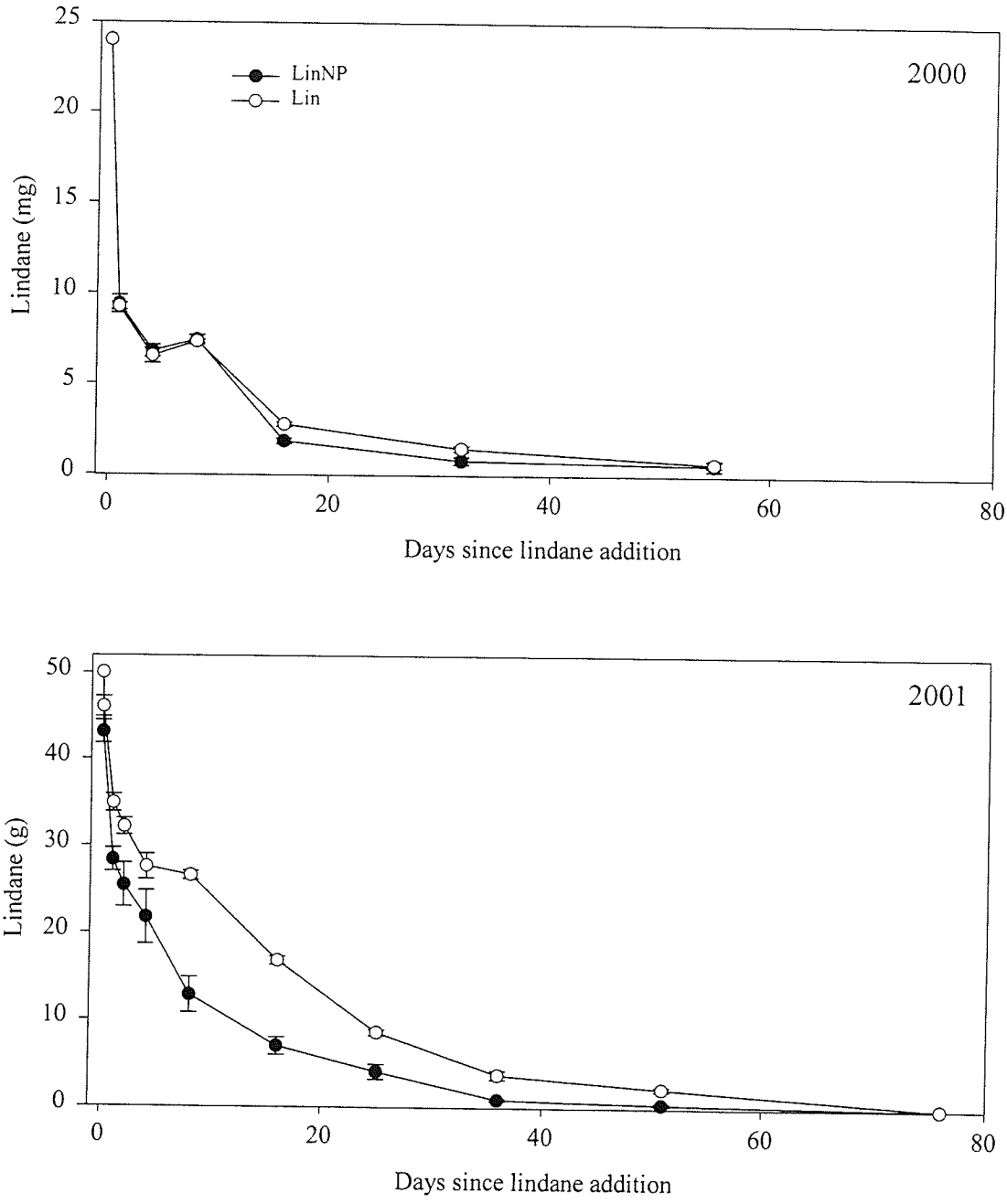


Figure 35. Lindane (mean, ± SE, n = 4) dissipation from the water column of Blind Channel enclosures in 2000 and 2001.

chlorophyll *a* ($t = -2.61$, $p = 0.048$) was negatively related to lindane half-life. Univariate linear regression showed that lindane half-life was negatively related to phytoplankton chlorophyll *a* (Figure 36).

Sediment resuspension experiment

One hour after sediment disruption in 2001 the particulate matter concentration of the enclosures was significantly higher ($p < 0.05$) than pre-disturbed levels accept for POM in the LinNP enclosures (Table 31). Water column chlorophyll concentrations tended to be higher in the enclosures after sediment disruption (Table 31). Water column nutrient levels were not significantly different ($p > 0.05$) after sediment disruption (Table 31). Lindane concentration of the water column was also not significantly ($p > 0.05$) different between samples collected before and one hour after sediment disruption (Table 32).

Vial experiment

The dissipation of pesticides from the water followed a first-order dissipation rate for all the treatments ($r^2 > 0.7$). Pesticides half-lives ranged from 33 to 71 days for atrazine and 74 to 128 days for lindane. Nutrient enrichment did not have a significant effect on the persistence of either pesticide (Table 33). However, the source of the water did influence the persistence of both pesticides as pesticides in distilled water persisted longer than those in BC water (Table 33).

5. 4 Discussion

Enclosure experiment

Nutrient enrichment can lower lindane water column persistence in wetlands. The addition of inorganic nitrogen and phosphorous to the enclosures reduced lindane water column persistence in 2001 but not in 2000. In both years lindane dissipated from the water column following first order kinetics, with the majority of lindane being lost shortly after addition. This meant that the environmental conditions present at the time of lindane addition would have been the most influential in determining lindane half-life. In 2000

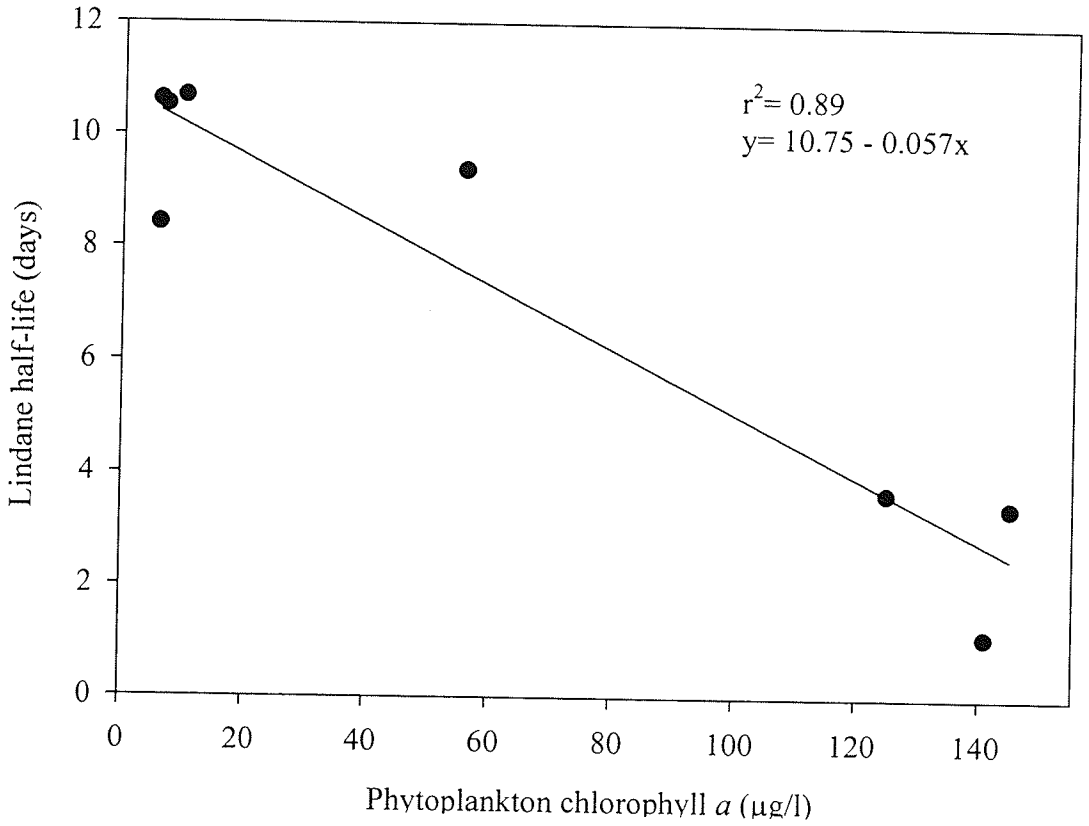


Figure 36. Regression of average phytoplankton chlorophyll *a* against lindane water column half-life in Blind Channel enclosures.

Table 31. Variables measured in the water column of the enclosures before and one hour after sediment disruption. ANOVAs were performed separately for each treatment.

Treatment	Variable	Before	One hour after	p-value
Control	Pheophytin	1 (0.5)	2 (1.0)	0.833
	Chlorophyll *a*	4 (1.0)	18 (2.0)	0.013
	Total chlorophyll	5 (0.5)	20 (1.7)	0.006
	PIM	0.08 (0.04)	26.08 (2.64)	0.003
	POM	4.58 (0.70)	21.13 (1.67)	0.004
	TRP	66.5 (4.0)	66.0 (13.3)	0.986
	NO_3-N	215.5 (8.38)	131.75 (26.58)	0.184
	NH_4-N	0	0	
Lin	Pheophytin	3 (0.3)	1 (0.2)	0.044
	Chlorophyll *a*	4 (2.0)	36 (10)	0.173
	Total chlorophyll	5 (0.5)	36 (9.9)	0.191
	PIM	0	37.85 (5.88)	0.018
	POM	2 (0.34)	23.92 (3.79)	0.028
	TRP	21.5 (10.8)	32.0 (9.2)	0.724
	NO_3-N	192.5 (16.3)	94 (18.8)	0.095
	NH_4-N	0	0	
LinNP	Pheophytin	0.3 (0.1)	8 (4.0)	0.351
	Chlorophyll *a*	62 (28.0)	66 (28.0)	0.954
	Total chlorophyll	62 (28.4)	73 (26.7)	0.892
	PIM	0.17 (0.05)	37.39 (7.33)	0.017
	POM	7.42 (1.62)	28.25 (5.13)	0.100
	TRP	1322 (39.6)	1312 (36.4)	0.516
	NO_3-N	4953.3 (82.6)	4768.3 (105.4)	0.929
	NH_4-N	231.3 (77.0)	261.5 (75.4)	0.893

Table 32. Lindane concentration (mg/L; ± SE, n = 4) in the water column of enclosures before and after sediment disruption, 2001. ANOVAs were performed separately for each treatment.

Treatment	Before sediment disruption	One hour after sediment disruption	p-value
Lin	0.10 (0.01)	0.10 (0.01)	0.955
LinNP	0.02 (0.01)	0.02 (0.01)	0.988

Table 33. Mean (± SE n = 3) percent of initial pesticide remaining in the experimental vials at the end of the experiment. Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Pesticide	BC	BC + nutrients	DW	DW + nutrients	p-value
Atrazine	32.3 ^{A} (± 4.1)	31.7 ^{A} (± 2.9)	48.3 ^{B} (± 0.9)	48.0 ^{B} (± 5.1)	0.010
Lindane	50.0 ^{A} (± 6.0)	56.5 ^{A} (± 2.5)	70.5 ^{B} (± 0.5)	67.3 ^{B} (± 5.1)	0.001

Lin and LinNP treatments, at the time of lindane addition, only differed in terms of their NO_3-N concentrations. Lindane half-life was not significantly different between treatments in 2000, which suggested that NO_3-N did not have a direct effect on lindane persistence in Blind Channel.

Lindane half-life was significantly shorter in the LinNP enclosures in 2001. In addition to higher nutrient concentrations, LinNP enclosures, at the time of lindane addition in 2001, also had significantly ($p < 0.05$) higher pH, and phytoplankton concentrations. The reason these water column variables were significantly different between Lin and LinNP enclosures in 2001 but not 2000 was due to differences in the timing of nutrient and lindane additions between the years. In the current experiments and those of Kiers North (2000) a time lag of between 8 to 10 days occurred between nutrient additions and significant phytoplankton responses in Blind Channel. In 2000, lindane was added to enclosures three days after nutrient additions began and consequently, phytoplankton was not significantly different between Lin and LinNP enclosures. However, in 2001 lindane was added four weeks after the start of nutrient additions at a time when the phytoplankton had already responded to nutrient additions. Of the variables measured in 2001 only phytoplankton chlorophyll *a* was identified by ANCOVA as being related to lindane half-life. Phytoplankton can influence pesticide half-life by providing surface area for sorption (Soderstrom *et al.* 2000). Phytoplankton in the enclosures was capable of sorbing lindane as demonstrated by the significantly higher amount of lindane in unfiltered versus filtered samples. When phytoplankton cells settled out of the water column they would have transported any sorbed lindane with them (Soderstrom *et al.* 2000). The higher sedimentation rate in the LinNP enclosures could then have accounted for their lower lindane water column persistence. Other studies have demonstrated that the addition of nutrients can increase sedimentation rates by increasing phytoplankton concentrations (Skei *et al.* 2000, P. Badiou, Botany Department, University of Manitoba, 2002).

If nutrients and lindane are added simultaneously to a wetland no effect of nutrient on lindane persistence is anticipated. This is because nutrients have an indirect effect on lindane persistence through the stimulation of phytoplankton growth and a time lag of over a week is needed in order for the nutrients to significantly increase phytoplankton concentrations. The timing of nutrient and lindane transport to PPR wetlands will not usually be simultaneous. Nutrients (in the form of fertilizers) are usually added to agricultural fields in the fall or in the spring. Once applied the fertilizers would have the potential to be transported to wetlands via surface runoff. Lindane is applied to agricultural fields (canola fields) as a seed treatment (Saskatchewan Agriculture and Food 2001). Off-field transport of lindane occurs via volatilization once the canola seed leaf has emerged from the soil (Waite *et al.* 2001). Given the timing of fertilizer and lindane additions to canola fields the fertilizer would be available for off-field transport to wetlands earlier than the lindane. Thus, the situation could arise where lindane reaches a wetland that is already experiencing high phytoplankton growth due to earlier fertilizer inputs. If this is the case then the nutrients could reduce lindane water column persistence indirectly by stimulating phytoplankton growth.

Aside from nutrient concentrations, climatic conditions can also influence phytoplankton concentrations. Variables that influence phytoplankton growth, such as water temperature and amount of PAR, can vary temporally due to differences in air temperature and cloud cover, respectively. Thus lindane water column persistence could vary annually within the same wetland if it is exposed to different climatic conditions.

The sediment resuspension experiment did not provide evidence that sediment mixing in wetlands contributes to lindane dissipation from the water column. Sediment resuspension in wetlands can be caused by biotrubation and wind (Lougheed *et al.* 1998, Schallenberg and Burns 2001). If contaminated sediments are resuspended they can be a source of pesticides to the water column (Hazardous Substance Research Centre 1997). Although sediment resuspension in this experiment increased chlorophyll *a* levels it did

not increase lindane concentrations. This may be due to lindane degradation within the sediments. Sediment samples collected two weeks after the resuspension experiment did not have lindane at detectable levels. This suggested that lindane degraded in the sediments. Had the resuspension experiment been conducted shortly after lindane addition an effect on lindane concentration may have been more likely as there would have been less time for lindane degradation within the sediment.

Although submersed macrophytes sorbed lindane they did not have as significant an effect as phytoplankton had on lindane persistence. The nutrient concentration of a wetland can indirectly determine the extent of submersed macrophyte growth (Goldsborough and Robinson 1996, Scheffer 1998). The high phytoplankton levels of nutrient enriched LinNP enclosures limited light transmittance and resulted in low submersed macrophyte levels. In contrast Lin enclosures had clear water and elevated submersed macrophyte levels. The shorter half-life of lindane in the LinNP enclosures suggested that phytoplankton played a greater role in lindane persistence than submersed macrophytes. Wetlands can occur in alternative stable states dominated by either phytoplankton or macrophytes (Scheffer 1998). Based on the current study lindane water column persistence would be expected to be shorter in wetlands that are phytoplankton-dominated as opposed to those that are dominated by macrophytes.

Vial experiment

Nutrient additions do not always play a direct role in influencing the persistence of pesticides in aquatic environments. Although nitrate additions have the potential to decrease pesticide persistence by facilitating mediated photolysis through the production of hydroxy radicals (Hiskia *et al.* 1997, Torrents *et al.* 1997), natural organic matter can readily scavenge hydroxy radicals (Brezonik and Fulkerson-Brekken 1998). Thus, in the vials containing Blind Channel water nitrate-mediated photolysis may not have occurred due to the high organic matter present. However, nitrate-mediated photolysis was also not observed in the distilled water which had no organic matter. This suggested that perhaps

the UV levels present during the experiment were not high enough to induce nitrate-mediated photolysis.

The organic matter content of Blind Channel water created a more favourable environment for pesticide loss as opposed to the organic matter deficient distilled water. The experimental vials were sealed so that pesticide loss could only be due to degradation. The organic matter content could have reduced pesticide concentrations by affecting both abiotic and biotic degradation. Organic matter can catalyze pesticide hydrolysis and photolysis (Miller and Zepp 1979, Zepp *et al.* 1981, Zepp and Schlotzhauer 1983). Organic matter by increasing microbial concentrations can also increase microbial degradation of pesticides (Moorman *et al.* 2001). Future experiments need to be specifically designed to examine how wetland organic matter influences atrazine and lindane degradation.

5.5 Conclusion

Enclosure and vial experiments showed that N and P did not have a direct effect on atrazine or lindane persistence. However, nutrients did indirectly affect lindane persistence in the enclosures, by stimulating phytoplankton growth. Phytoplankton could have affected lindane persistence by sorbing lindane and transporting it out of the water column via sedimentation. Sediment resuspension late in the study did not increase lindane water column levels. This, along with the relatively short water column half-life of lindane, suggested that wetlands are of value as lindane sinks.

Chapter 6: Atrazine and lindane photolysis potential in two prairie wetlands of different water clarities

6. 1 Introduction

The extensive use of agricultural pesticides on the Canadian prairies has led to the contamination of a high percentage of prairie wetlands (Chapter 3, Donald *et al.* 1999, Anderson *et al.* 2002). For instance, Donald *et al.* 1999 detected the insecticide lindane in 73% of the Saskatchewan wetlands that they surveyed. Despite wetland susceptibility to pesticide contamination relatively little information exists in the literature pertaining to the fate of pesticides in prairie wetlands (Goldsborough and Crumpton 1998). Pesticide photolysis can represent a major environmental dissipation route (Crosby 1972, Zepp and Cline 1977, Torrents *et al.* 1997). For pesticide photolysis to occur under ambient solar radiation the reaction usually needs to be catalyzed by photosensitizers (Chapter 2). Phytoplankton and DOM are naturally occurring substances that have the potential to act as pesticide photosensitizers (Zepp and Schlotzhauer 1983, Schindelin and Frimmel 2000, Stangroom *et al.* 2000 Keum *et al.* 2002). Due to the high potential for light to penetrate the entire water column, it has been speculated that pesticide photolysis may be a major pesticide dissipation route in shallow environments such as wetlands (Lartiges and Garrigues 1995, Goldsborough and Crumpton 1998, Mansour *et al.* 1999). In addition, pesticide photolysis potential may be expected to be high in wetlands that have elevated levels of suspected photosensitizers such as phytoplankton and DOM (Goldsborough and Crumpton 1998). Conversely, it could be argued that elevated suspended solids could reduce pesticide photolysis potential by attenuating UV (Konstantinou *et al.* 2001).

The objective of this study was to evaluate the pesticide photolysis potential of two wetlands that had different suspended solid concentrations. The pesticides studied, atrazine and lindane, have both been detected in prairie wetlands (Donald *et al.* 1999,

Anderson *et al.* 2002). I compared the persistence of these pesticides in wetlands of high and low suspended solid levels and exposed to different light treatments (ambient light, dark). Because both atrazine and lindane can be photodegraded I hypothesized that, within the same wetland, pesticide persistence in ambient light treatments would be shorter than in darkened treatments. Due to the ability of suspended solids to attenuate light I also hypothesized that pesticide persistence in ambient light treatments would be shorter in the wetland with lower suspended solids than higher suspended solids because there would be more light available for pesticide photolysis.

6. 2 Materials and methods

Study site

The study was conducted during the 2001 growing season at the Delta Marsh Field Station, University of Manitoba (Figure 5). Delta Marsh is a 18,500-hectare wetland on the south shore of Lake Manitoba, Canada. Two study sites, Blind Channel and Crescent Pond, were selected in the marsh based on differences in water clarity (Table 34). Blind Channel (BC) is connected to Lake Manitoba whereas Crescent Pond (CP) is not connected to the lake and is supplied only by groundwater. Differences in water clarity between the sites are related, in part, to the presence of carp (*Cyprinus carpio*) in BC but not in CP. Through their feeding and spawning activities carp can resuspend sediments and increase turbidity (Lougheed *et al.* 1998).

Experimental design

On June 11, surface water (10 L) samples were collected from both BC and CP. Triplicate sub-samples (400 mL) were analyzed for suspended organic and inorganic matter, as described in Chapter 3. Water samples were also analyzed for total reactive phosphorous (TRP), NH_4-N, NO_3-N, pH, and conductivity using standard methods (Stainton *et al.* 1977, APHA 1992).

For each site location, half the collected water was spiked with 2 µg/mL atrazine (residue analysis grade, Supleco USA) and the other half with 2 µg/mL lindane (99%

Table 34. Mean (± SE, n = 10) of weekly water clarity parameters measured in Blind Channel and Crescent Pond from June 19 to August 25, 2000.

Parameter	Blind Channel	Crescent Pond
Phytoplankton chlorophyll *a* (µg/L)	32.6 (1.0)	14.5 (1.5)
Total suspended solids (mg/L)	23.5 (0.8)	3.7 (0.8)
Turbidity (NTU)	14.3 (0.4)	3.8 (0.2)

pure, Sigma-Aldrich Canada). The pesticide concentrations were chosen so that they would be well above the detection limits of the instruments (0.001 μg/L) throughout the experiment. For each location and pesticide, half the spiked pesticide solutions were added to 44 dark vials (40 mL, Pyrex) and the other half was added to 44 clear vials. The dark vials had been painted black and then taped with black plastic tape so that no light penetrated. The clear vials were not altered and did allow for light transmission (Figure 37). Pyrex® containers have been commonly used to investigate pesticide photolysis, as they are optically translucent across a wide spectral range, including the UV-A wavelengths (310 - 400 nm) that are photolytic (Konstantinou *et al.* 2001, Parra *et al.* 2002, Vialaton and Richard 2002). BC pesticide solutions were positioned randomly at a depth of 10 cm on three floats within BC. The floats consisted of PVC tubing attached to a square wooden frame (50 cm x 50 cm). The vials were positioned horizontally on a brace connected to the wooden frame (Figure 38). Similarly, vials filled with CP pesticide solutions were positioned randomly on floats within CP.

Sampling and analytical methods

Surface water temperature, suspended solids, and turbidity were measured on a weekly basis at each of the two sites. Temperature was measured at the depth of the vials with a handheld thermometer. Suspended solids were quantified as described above. Water column turbidity was measured with a Hach 2100A turbidimeter. Qualitative field observations of macrophyte percent cover growth around the vials were made weekly.

The percent of surface UV to which the pesticide solutions were exposed over the course of the experiment was quantified using polysulfone film (PSF) as a UV dosimeter (Dunne 1999). PSF strips were positioned horizontally above the water surface, at a depth of 10 cm, and within experimental vials at a depth of 10 cm. Upon exposure to UV-A and UV-B (250-330 nm) the opacity of PSF increases linearly (Dunne 1999). This increase in opaqueness was quantified by measuring, using spectrophotometry, the PSF's absorbance at 330 nm before and after UV exposure of 8 h. The percent of surface UV that reached a

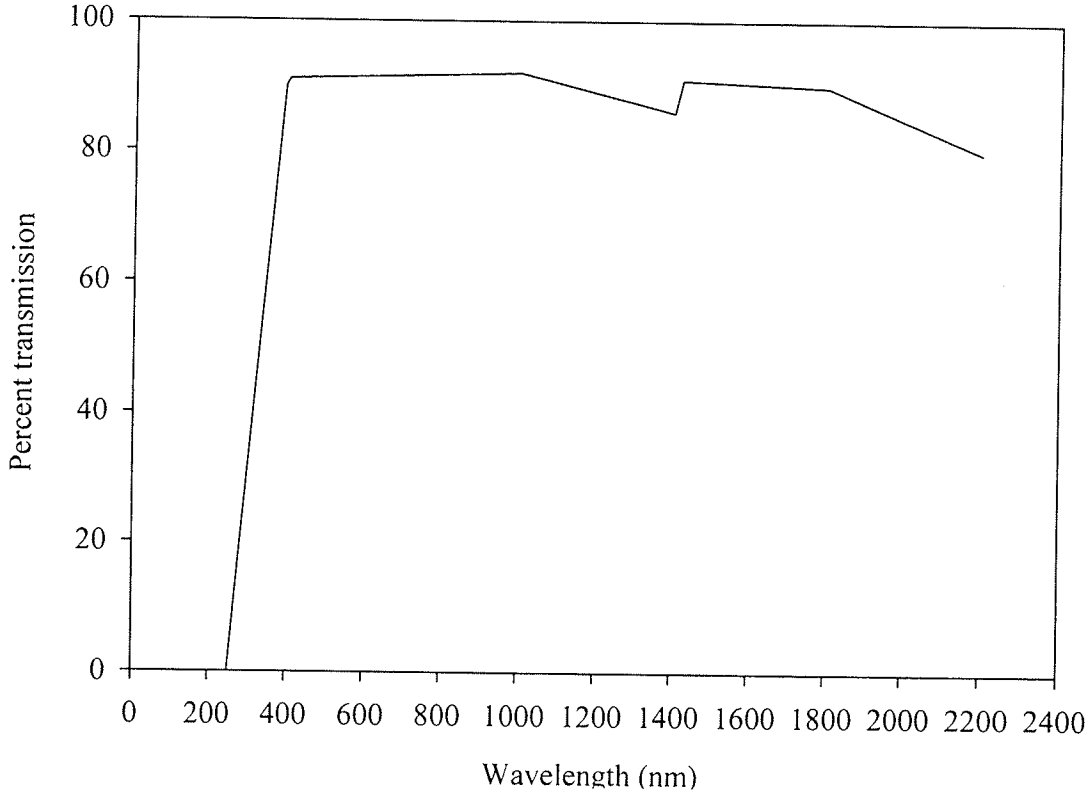
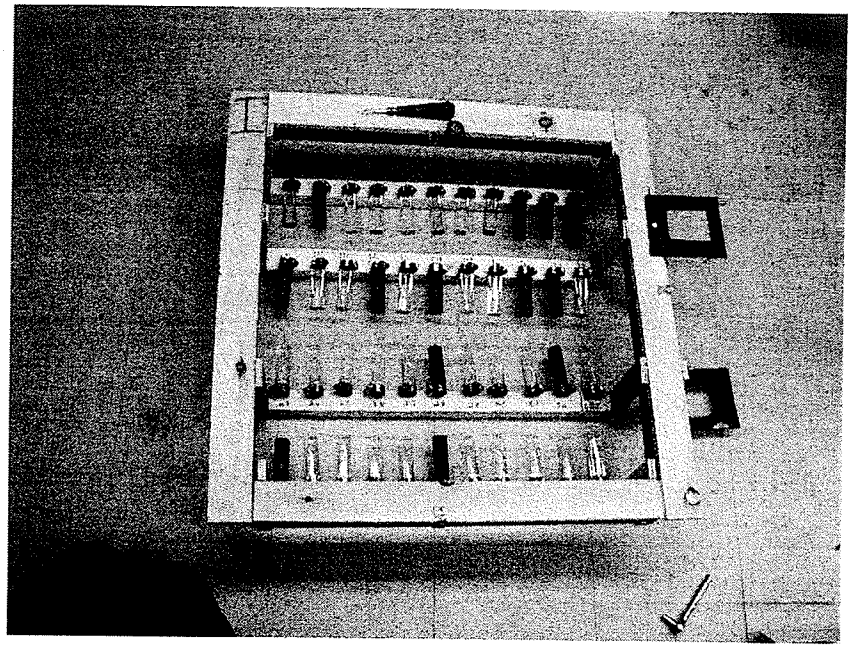


Figure 37. Transmission spectrum for Pyrex® (Melles Griot 2001).

A



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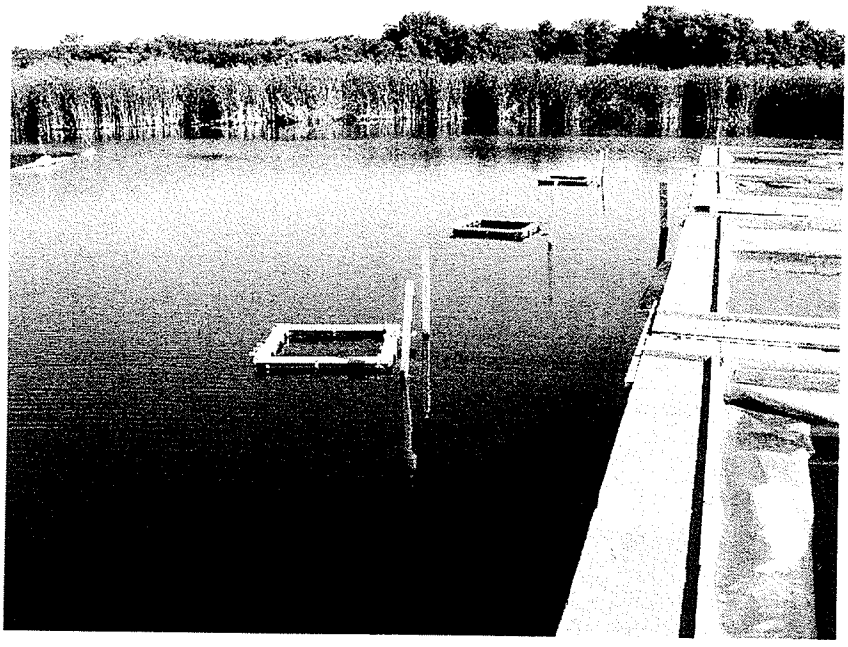

Figure 38. Floats used to hold vials at a depth of 10 cm (A). Floats containing experimental vials positioned in Blind Channel (B).

depth of 10 cm was determined by comparing the absorbance (300 nm) of PSF strips exposed to surface UV and PSF strips that had been positioned at a 10 cm depth. Similarly, the percent of surface UV in the experimental vials was determined by comparing the absorbance (300 nm) of surface PSF strips to PSF strips that had been positioned inside vials at a depth of 10 cm.

For each of the treatments, three vials were randomly removed without replacement on days 1, 2, 4, 8, 16, and 32 days following the start of the experiment and analyzed for either atrazine or lindane. Atrazine samples were analyzed by high performance liquid chromatography (Waters HPLC Breeze System) as in Chapter 3. The analysis of lindane samples involved a liquid-liquid extraction followed by GC analysis with an ECD (Chapter 3). The recovery efficiency for atrazine was 83% from spiked solutions of 2 μg/mL. For lindane the recovery efficiency was 81% from spiked solutions of 2 μg/mL.

Statistical analysis

The SAS System for Windows V.8 and SigmaPlot 2001 V.8 were used for the statistical analyses. The first-order half-life of atrazine and lindane was determined using non-linear regression ($Mt=M_T e^{-kt}$). For each treatment the mean pesticide concentration (atrazine or lindane) from the three vials analyzed on each sampling day was used in the non-linear regression equation to estimate its half-life. One-way ANOVA was conducted to determine if the environmental conditions between the two sites differed. One-way ANOVA followed by a Tukey's test was also conducted to determine if pesticide persistence was significantly differed among the experimental vials. Relationships between suspended solids and pesticide persistence were investigated using univariate regression analysis.

6. 3 Results and Discussion

The water added to the vials at the beginning of the experiment differed between sites. BC water had significantly higher ($p < 0.05$) suspended organic and particulate inorganic matter concentrations than CP water (organic matter BC 17.8 mg/L, CP 5.6

mg/L; inorganic matter BC 4.8 mg/L CP 1.3 mg/L). The pH and nutrient levels also differed between BC and CP water (Table 35).

Average ambient suspended solids were significantly higher ($F_{1,16}$= 19.0; $p < 0.001$, n = 7) in BC (21.8 mg/L) as opposed to CP (3.9 mg/L). Turbidity was also significantly higher ($F_{1,16}$= 89.3; $p < 0.001$, n = 7) in BC (13.8 NTU) than in CP (6.4 NTU).

Water temperature, however, was not significantly different ($F_{1,16}$= 0.002; p = 0.95, n = 7) between sites (BC = 21.6°C , CP = 21.7°C). At the beginning of the experiment the area where the vials were placed was free of macrophytes at both sites. However, approximately two weeks into the experiment floating macrophytes (*Lemna minor*) became established at the study site in CP. Macrophytes remained absent from the BC throughout the study.

The loss of pesticides in the vials followed first order decay kinetics for all treatments (Figure 39). Pesticides showed half-lives of 32 to 42 days for atrazine and 91 to 128 days for lindane (Table 36). The pesticide half-life values calculated in this study fell with in the range of reported values (atrazine 8 to 350 days, Diana *et al.* 2000; lindane 30 to 151 days, Sang *et al.* 1999). The longer half-life of lindane compared to atrazine could have been due to the recalcitrant nature of its six chlorine bonds.

The persistence of the pesticides was not influenced by vial type (clear or dark) (Table 36), which suggested that pesticide photolysis did not occur. The absence of detected pesticide photolysis in this experiment could be attributed to high UV attenuation. At the study sites, less than 10 % of surface UV reached a depth of 10 cm (BC 8.0%, CP 6.6%) and the percent of surface UV that penetrated the experimental vials was less than 2.0% (BC 1.7%, CP 1.9%). Although the Pyrex vials attenuated some of the available UV, the majority of UV attenuation was attributed to the environment at the study sites. In BC, the elevated suspended solid levels could have reduced UV penetration by scattering and absorbing light. In CP, suspended solid levels and turbidity were significantly lower, yet UV transmittance was less than that seen in BC. A reason for the

Table 35. Water pH and nutrient levels in experimental vials (means of three samples). Water collected from Blind Channel and Crescent Pond.

Variable	Blind Channel	Crescent Pond
pH	8.56	7.95
$N\text{-}NO_3$ (mg/L)	0.038	0.0174
$N\text{-}NH_4$ (mg/L)	< 0.05	< 0.05
TRP (mg/L)	0.116	0.0281

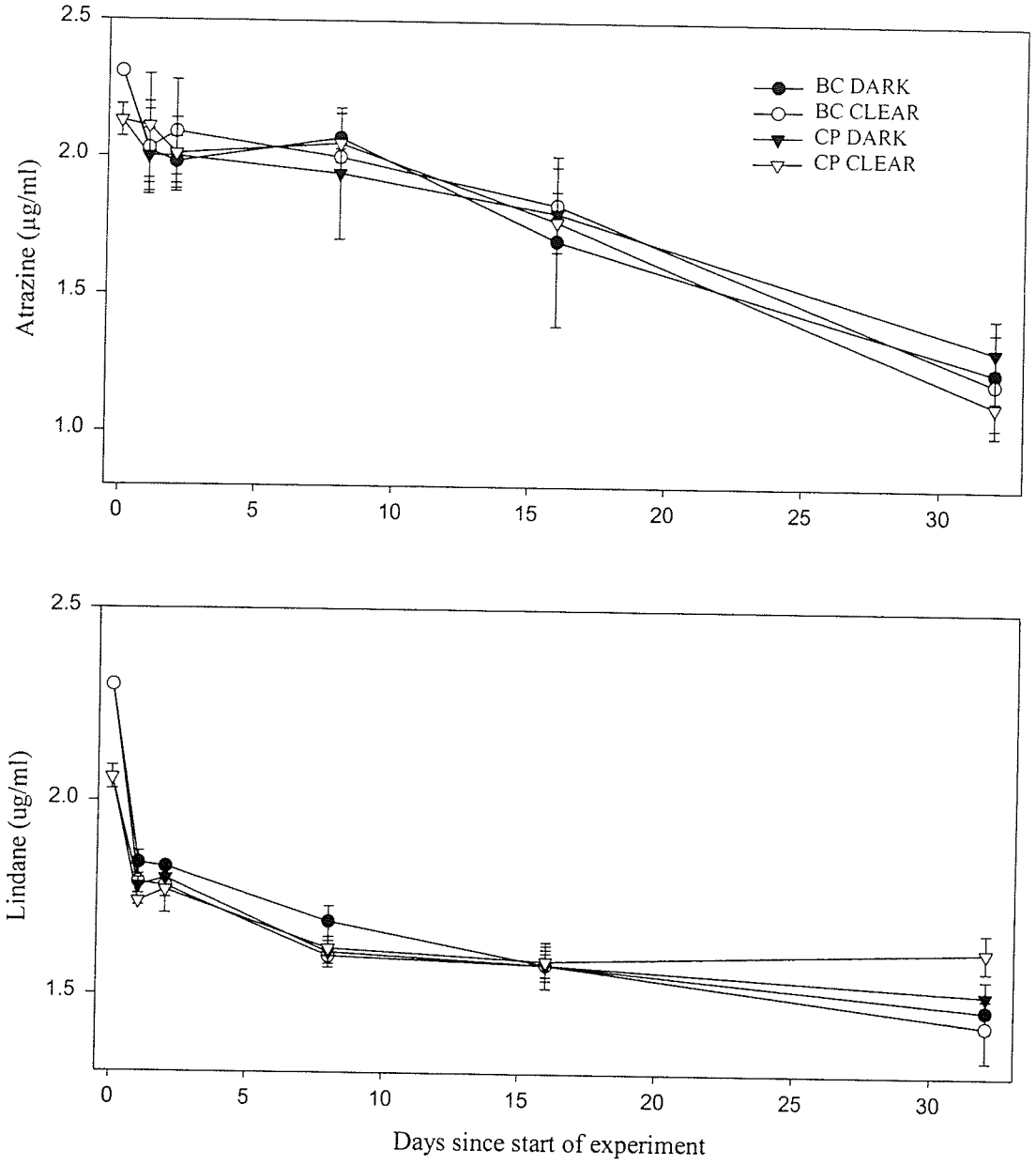

Figure 39. Atrazine and lindane dissipation from experimental vials. "BC" vials contained water from Blind Channel; "BC DARK" vials were painted black and contained water from Blind Channel. "CP" vials contained water from Crescent Pond; "CP DARK" vials were painted black and contained water from Crescent Pond. Vials with Blind Channel water were placed at a depth of 10 cm in Blind Channel. Vials with Crescent Pond Water were placed at a depth of 10 cm in Crescent Pond.

Table 36. Pesticide half-life (days) in experimental vials at different locations and exposed to different light conditions.

Pesticide	Location	Clear	Dark
Atrazine	Blind Channel	41.0	41.8
	Crescent Pond	39.6	31.9
Lindane	Blind Channel	96.3	91.2
	Crescent Pond	128.3	121.6

lower UV transmittance in the clear water of CP could have been due to a surface cover of duckweed (*L. minor*). The duckweed shaded the environment below it and consequently reduced pesticide photolysis potential. In addition, non-coloured dissolved organic matter (DOM) could have contributed to UV attenuation at both sites. Future studies of pesticide photolysis in wetlands should consider the affect of non-coloured DOM on UV attenuation.

Wetland abiotic and biotic characteristics did not influence atrazine half-lives as atrazine in BC showed similar dissipation rates as atrazine in CP. In contrast, lindane was significantly (Table 37) more persistent in CP water as compared to BC water. Differences in lindane persistence between the two study sites may be accounted for by differences in suspended solid content. CP water had lower suspended solids and a longer lindane half-life as compared to BC, which had higher suspended solids. The microbial concentration of water columns is usually directly related to suspended solid concentrations (Pritchard 1987). BC had higher suspended solid concentrations and presumably higher microbial concentrations than CP. Lindane can be microbially degraded in wetland settings (Raghu *et al.* 2002). Therefore, the difference in lindane persistence between the two sites could have been due to potentially higher microbial degradation of lindane in BC. If the above assumption is correct why did it not apply to atrazine persistence? The reason here may be related to the extent of prior exposure of the microbial consortia to each pesticide. Prior exposure can determine the ability of microbial consortia to degrade a pesticide (Gebendinger and Radosevich 1999). Lindane was widely used in the study region and had been detected in Delta Marsh while atrazine had not (Chapter 3). Consequently the microbial consortia at the study site may have been more capable of degrading lindane as opposed to atrazine. Future studies on pesticide fate in wetland water columns should be designed to examine the influence of suspended solids on the microbial degradation of pesticides.

Table 37. Mean (± SE n = 3) percent of initial pesticide remaining after 32 days in experimental vials exposed to different light levels at two different locations (BC = Blind Channel, CP = Crescent Pond). Means followed by same letters are not significantly different at $p < 0.05$ (One-way ANOVA followed by Tukey's test).

Pesticide	BC clear	BC dark	CP clear	CP dark
Atrazine	51.3 ^{A} (± 5.8)	53.0 ^{A} (± 9.3)	58.0 ^{A} (± 2.1)	61.3 ^{A} (± 3.9)
Lindane	62.3 ^{A} (± 3.9)	64.3 ^{A} (± 5.8)	77.4 ^{B} (± 2.8)	73.5 ^{B} (± 2.0)

6. 4 Conclusion

This study indicated that photolysis of atrazine and lindane will be insignificant in prairie wetlands that have rapid UV attenuation. Rapid UV attenuation can be due to elevated suspended solid levels as well as floating macrophytes. Therefore it may be inaccurate to assess the pesticide photolysis potential of a wetland based solely on water clarity data.

This study also indicated that lindane persistence was significantly different in wetlands of different suspended solid levels. Suspended solid levels in prairie wetlands can vary both temporally and spatially. Thus, lindane half-life calculated for one wetland may not apply to others or even to the same wetland under different conditions.

Chapter 7: Influence of photolysis and volatilization on lindane persistence in wetland enclosures

7. 1 Introduction

Over 50% of the original wetlands in the PPR have been lost or altered due to agricultural drainage (Turner *et al.* 1987, Bildstein *et al.* 1991, Cox 1993, Young 1994). This has lead private and public organizations to encourage wetland conservation and restoration. A strategy that these organizations use is public awareness campaigns promoting wetland values. One wetland value that has been promoted is their potential to act as pesticide sinks (e.g., Gabor *et al.* 2001). Environments that function as pesticide sinks are valuable to society because they reduce pesticide transport and bioavailability. For instance, a wetland acting as a pesticide sink could prevent pesticide transport to sources of human drinking water such as the groundwater.

The extent of pesticide degradation and export will determine whether or not an environment can function as a pesticide sink. Due to their shallow depth the potential for light transmittance to the sediment is greater in wetlands than in deeper aquatic environments thus it has been speculated that pesticide photolysis may be a major pesticide dissipation route in shallow environments such as wetlands (Lartiges and Garrigues 1995, Goldsborough and Crumpton 1998, Mansour *et al.* 1999). Furthermore, the elevated dissolved and particulate matter content, typical of prairie wetlands, may increase pesticide photolysis by acting as photocatalysts (Goldsborough and Crumpton 1998). Despite speculation that wetland environments favour pesticide photolysis there have been few studies conducted that have examined pesticide photolysis potential of wetlands (Miller and Chin 2002).

Unlike photolytic studies, there are a number of studies which have examined pesticide export from wetlands (Kao *et al.* 2001, Krieger 2001, Moore *et al.* 2001a,b, 2002). These studies have demonstrated that pesticide export from wetlands in

groundwater and surface water is minimal due to pesticide sorption to wetland sediments. However, there is paucity in the literature concerning pesticide loss from wetlands via volatilization. Volatilization from surface waters can represent an important loss mechanism for pesticides with relatively low water solubility and high Henry's Law constants (Maguire 1991, Rawn and Muir 1999). Pesticide volatilization rates from surface waters increase as the water temperature increases (McConnell *et al.* 1993, Ridal *et al.* 1996, James *et al.* 2001). Thus, the warm summer water temperatures of prairie wetlands could promote pesticide volatilization. If volatilization from wetlands represents a significant pesticide fate process, then the value of wetlands as pesticide sinks may be diminished.

The objective of this *in situ* enclosure study was to determine the role photolysis and volatilization play in determining the water column persistence of lindane. I chose to study lindane because it has been detected in a high (> 70%) percentage of prairie wetlands (Donald *et al.* 1999). Lindane was also chosen because it can be degraded by indirect photolysis (Saleh *et al.* 1982) and it is prone to volatilize due to its relatively low vapour pressure (3.3×10^{-5} mm Hg) (Hornsby *et al.* 1996). Because lindane can undergo indirect photolysis I hypothesized that lindane exposed to ambient UV levels would have a shorter half-life than lindane exposed to lower UV levels. I also hypothesised that lindane persistence in open wetland experimental units would be shorter than in covered experimental units. I hypothesized this because the volatilization potential would be greater in the open experimental units and I believed that due to lindane's high Henrys law constant that volatilization would be an important lindane loss route from wetlands.

7. 2 Materials and methods

The study site was located in Crescent Pond, an isolated, shallow (mean depth 90 cm) pond found within Delta Marsh, MB (Figure 5). Delta Marsh is a large (18,500 hectares) wetland complex located on the south shore of Lake Manitoba. Crescent Pond is characterized by clear water (4.0 NTU) and encroaching emergent macrophytes. Within

Crescent Pond clumps of *Typha* sp. frequently become dislodged from the sediment. Once dislodged from the sediment these clumps float and can be blown across the pond by the wind.

Twelve cylindrical littoral enclosures (circumference = 240 cm, height = 120 cm) were installed in the northeast portion of Crescent Pond on June 5, 2000. The enclosures were formed by encircling PVC sheets (240 cm x 120 cm x 1.5 mm thick) on their long axis and joining the ends together with adhesive (Goldsborough 1985). The enclosures were pushed into the sediment to a depth of approximately 20 cm. The water depth at the study site when the enclosures were positioned was approximately 90 cm. The volume of water in the enclosures at the beginning of the experiment was approximately 413 L.

The experiment was designed to examine if UV-R and/or volatilization affected lindane persistence in the wetland enclosures. A randomized block design was used to assign the following UV/volatilization treatments in quadruplicate to the enclosures: 1) enclosures uncovered 2) enclosures covered with UV transparent plastic 3) enclosures covered with UV-opaque plastic (Figure 40). The UV-transparent plastic that was used was Acrylite OP4® (70% cut off below 280 nm) and the UV opaque plastic that was used was Acrylite OP3® (100% cut off below 400 nm) (Tank *et al.* 2003). To allow for water sampling the plastic covers were fastened 5 cm above the enclosures (Figure 41). The plastic covers were also applied to reduce volatilization potential as they limited air movement over the enclosures (Harris and Lichtenstein 1961, Zhang and Moore 1997).

The experiment began on 15 June 2000 after a ten day pre-treatment period to allow for recovery from the disturbance caused by enclosure installation. Lindane, as the formulated product Vitavax RS Flowable (Gustafson, Canada) was added to each enclosure to reach an approximate concentration of 10 µg/L. This concentration was chosen so that lindane concentrations would be above detection limits for the duration of the experiment. To add lindane to the enclosures the formulated product was first diluted with distilled water to produce a 4 g/L solution. From this solution 1 mL aliquots were

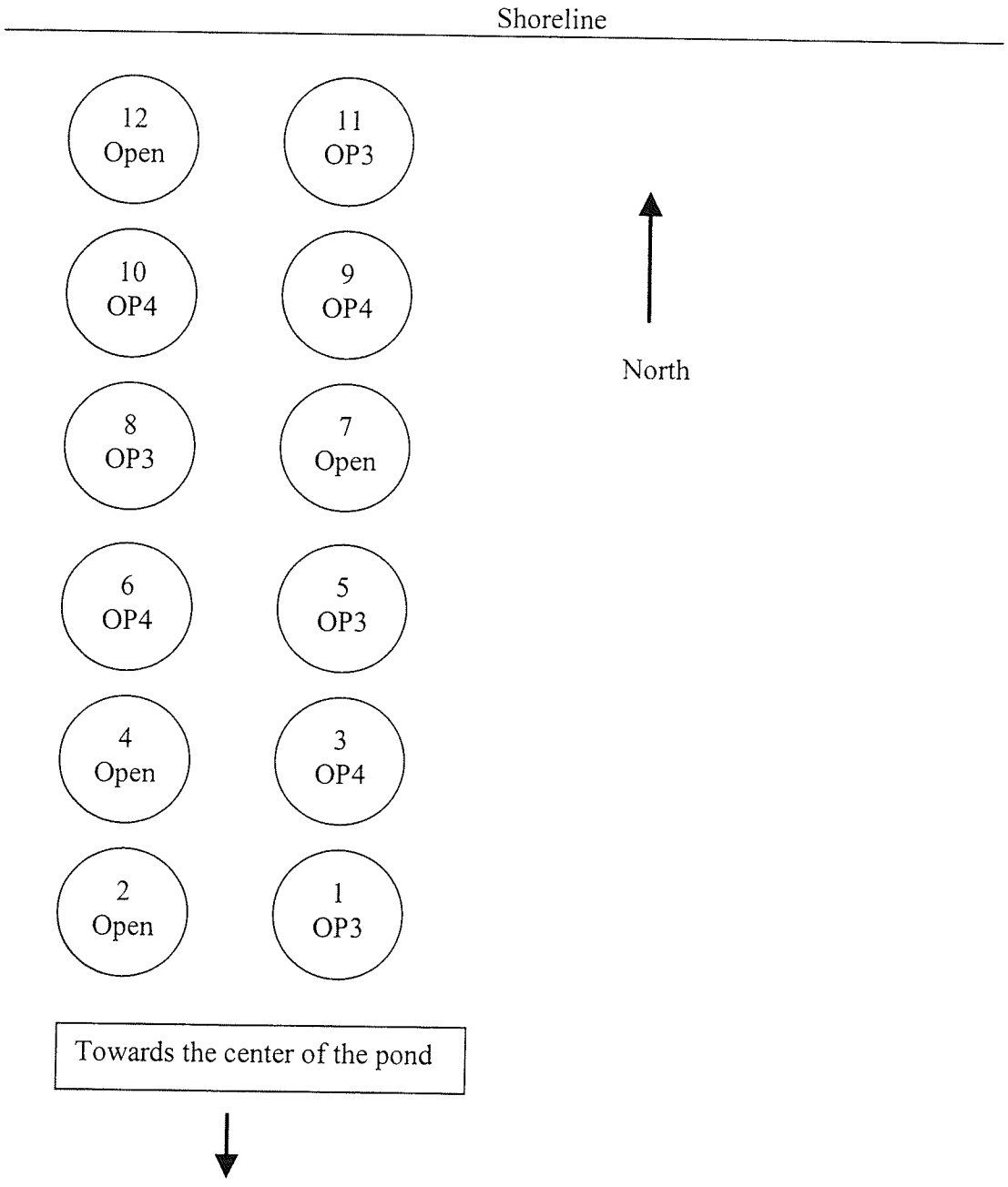

Figure 40. Arrangement of experimental enclosures within Crescent Pond.

Figure 41. Photo of experimental enclosure in Crescent Pond used to study lindane photolysis and volatilization. Floating *Typha* sp. clumps can be seen in the background.

pipetted into volumetric flasks and made up to one litre with water collected from each enclosure. Once the solutions were mixed, they were sprinkled evenly using a watering can onto the surface of the enclosures.

On a biweekly basis from 15 June to August 28 whole water column samples were collected using stoppered acrylic tubes (6.4 cm inner diameter, 1.5 m length) (McDougal 2002) from each enclosure and analyzed for pH, conductivity, NH_4-N, total reactive phosphorous (TRP), particulate organic matter (POM), and chlorophyll *a* (Stainton *et al.* 1977, APHA 1992). The water depth of the enclosures was measured with a metre stick on a biweekly basis. On days 1, 4, 16, 32, 55, and 73 after lindane addition, water column samples were collected for lindane analysis using the same type of integrated water column sampler as described in Chapter 3. Lindane extraction and analysis also followed that of Chapter 3.

Polysulfone film (PSF) was used as an UV dosimeter to monitor the transmittance of UV through the OP4 and OP3 plastic (Chapter 6, Dunne 1999). Upon exposure to UV (250-330 nm) the opacity of PSF increases linearly (Dunne 1999). On June 28, July 20, and August 2, and 19 the amount of UV transmittance to a depth of 10 cm was determined in each enclosure by placing 10 cm x 10 cm sections of PSF for seven hours (9:00 am to 4:00 pm) at the surface of the water and at a depth of 10 centimeters. The PSF sections were collected after the assay and kept in the dark prior to analysis. Four 2.5 x 5 cm sub-sample strips were removed from the center of each PSF section and their absorbance at 330 nm was measured with a Spectronic 601 (Milton Roy Company, Rochester, NY) spectrophotometer. Percent of ambient UV in the enclosures was calculated by dividing the mean absorbance at 330 nm measured in the OP3 and OP4 treatments by that measured in the open treatments.

One enclosure from each treatment was randomly selected at the end of the experiment. Surficial sediment cores (10 cm) were collected from the center of each enclosure using an acrylic tube (see Chapter 3). The samples were sent on ice to Norwest

Laboratories (Winnipeg) where the lindane was extracted using sonication and analyzed for total lindane using gas chromatography (EPA method 8081, detection limit 0.02 mg/kg, 98% recovery efficiency).

Statistical analysis

The first-order half-life of lindane in the water column of each enclosure was determined using non-linear regression ($Mt = M_T e^{-kt}$) in SigmaPlot Version 8. Analysis of variance (ANOVA) and multi variable analysis of variance (MANOVA) were conducted with the SAS System for Windows Version 8. MANOVA and ANOVA were done to determine if environmental conditions were significantly different based on enclosure treatment. Post-hoc statistical contrasts that compared best linear unbiased predictors (BLUPs) were conducted using SAS (proc mixed) to determine if enclosure position influenced lindane half-life. The BLUPs calculated were essentially estimates of the treatment (Open, OP3, OP4) means, adjusted for an enclosure-specific effect (position) (L. Armstrong, Ducks Unlimited Canada, pers. comm. 2002).

7. 3 Results

The OP4 plastic covers allowed over 95% ambient UV transmittance whereas the OP3 covers allowed less than 55% UV transmittance (Figure 42). Repeated measures ANOVA revealed that the percent ambient UV in the enclosures was significantly ($F_{2,9}$ = 3105, $p < 0.0001$) lower in OP3 than in OP4 or uncovered enclosures.

Enclosure treatments did not have significantly different water temperature ($F_{2,9}$ = 1.22 p = 0.34), ammonia ($F_{2,9}$= 3.60, p = 0.08), TRP ($F_{2,9}$= 3.99 p = 0.06), N-NO_3 ($F_{2,9}$= 2.64, p = 0.13), sediment organic matter ($F_{2,9}$= 0.069 p = 0.93), POM ($F_{2,9}$ = 2.84 p = 0.11), phytoplankton chlorophyll *a* ($F_{2,9}$ = 0.73 p = 0.51) or pH ($F_{2,9}$ = 2.87 p = 0.11). However, water conductivity ($F_{2,9}$ = 64.55 $p < 0.001$) was significantly different between treatments. A post hoc Tukey's Test revealed that Open enclosures (1414 µs/cm) had significantly lower conductivity than OP4 (1587 µs/cm) enclosures.

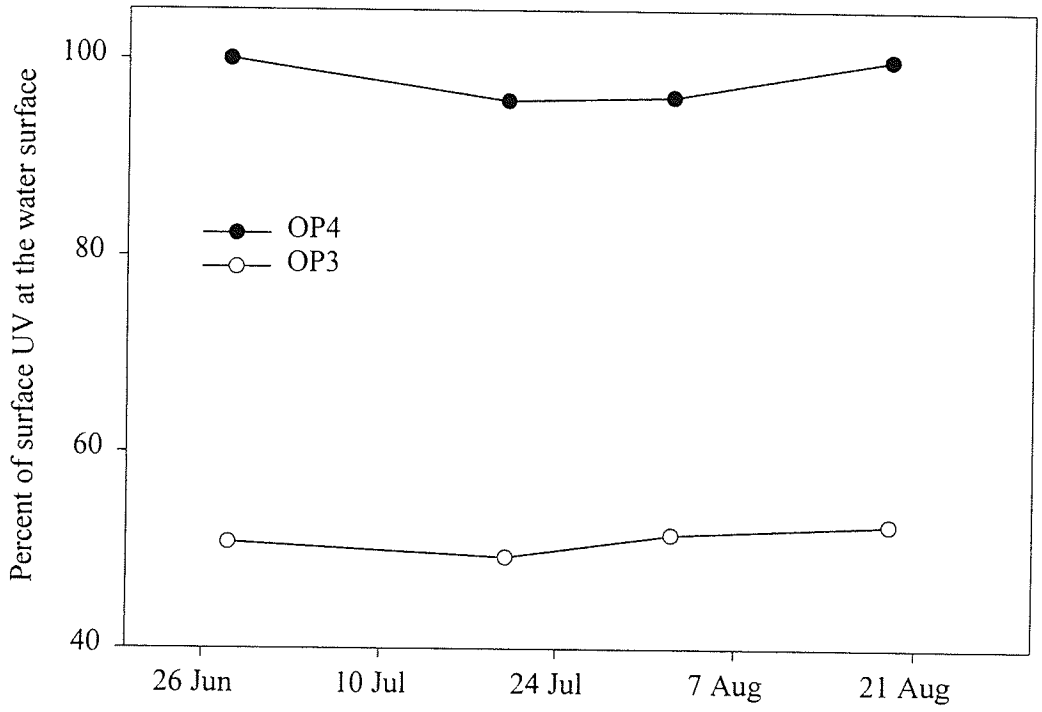

Figure 42. Percent of ambient UV (in uncovered mesocosms) at the water surface of Crescent Pond mesocosms covered with either OP3 or OP4 plastic (June 28 to August 19, 2000). UV levels were measured using PSF.

At the end of the experiment, lindane was below detection limits (0.05 mg/kg) in the sediment of the sampled Open and OP3 enclosures but was detected in the sampled OP4 enclosure (0.13 mg/kg).

Lindane dissipated from the water column of the enclosures following the first order decay equation (Figure 43). The water column half-life of lindane ranged from 19.0 to 57.5 days (Table 38). Lindane half-life was not significantly different among the treatments ($F_{2,9} = 0.124$ $p = 0.885$).

Enclosure position within the pond was related to lindane water column half-life. The four enclosures closest to the center of the pond (enclosure numbers 1-4, Figure 41), hereafter referred to as the central enclosures, had shorter lindane half-lives than the other enclosures, referred to as the non-central enclosures. Contrasts that compared the BLUPs corresponding to the central enclosures vs. the non-central enclosures revealed that the difference in half-life between the two groups was statistically significant (t-statistic with nine degrees of freedom = -34.83, $p < 0.0001$). BLUP analysis also showed that the central enclosures had significantly lower POM, NH_4-N, and TRP than the noncentral enclosures (Table 39).

The position of the enclosures also affected the observed frequency in which *Typha* sp. clumps were observed to collide and congregate with the enclosures. During the experiment floating *Typha* sp. clumps would move across the pond during high winds. From observations made during enclosure sampling these clumps would tend to collide first with the enclosures closest to the north shore (non-central enclosures, numbers 5-12).

7. 4 Discussion

This study suggested that photolysis was not a significant dissipation route for lindane from the wetland enclosures. Studies have shown that lindane can undergo indirect photolysis in natural waters under ambient light (Saleh *et al.* 1982). The indirect

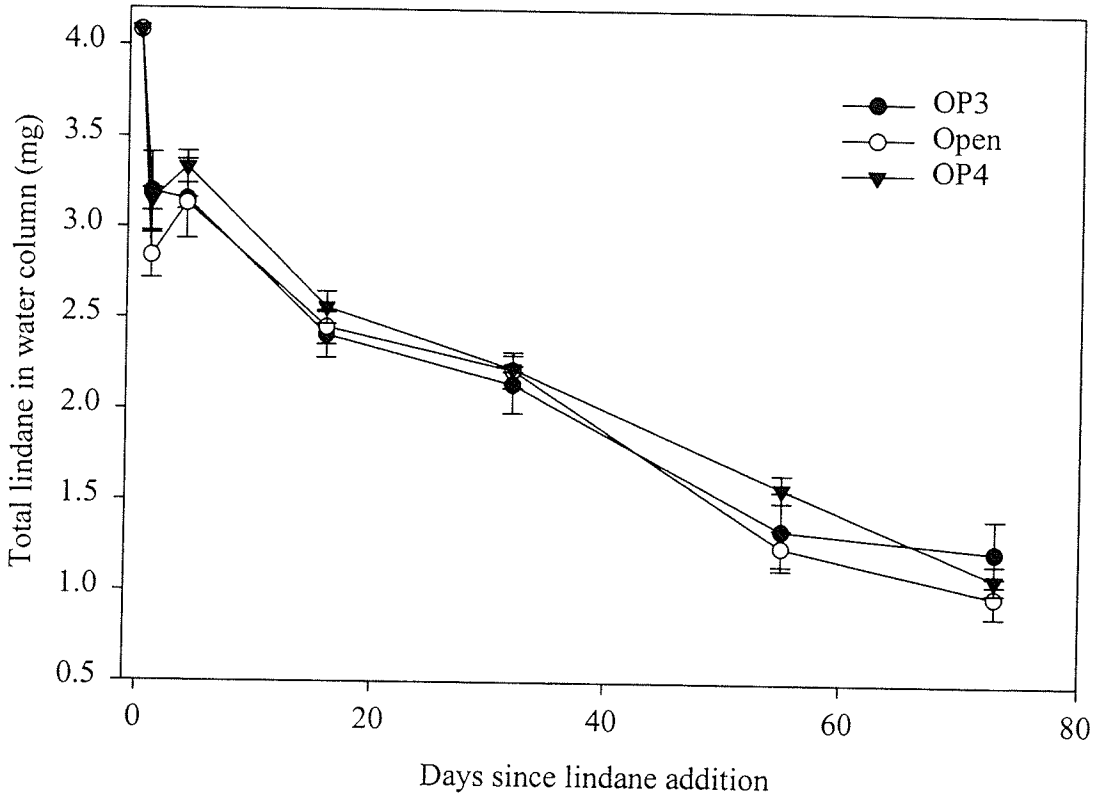

Figure 43. Lindane concentrations (mean, ± SE, n = 4) over time in the water column of mesocosms located in Crescent Pond. "Open" enclosures were not covered; "OP4" enclosures were covered with UV transparent plastic; "OP3" mesocosms were covered with UV opaque plastic.

Table 38. Lindane water column half-life in experimental enclosures in Crescent Pond.

Treatment	Enclosure No.	Half-life (days)
OP3	1	19.0
	5	50.2
	8	57.5
	11	52.1
OP4	3	35
	6	47.7
	9	46.2
	10	46.2
OPEN	2	31.5
	4	29.6
	7	52.1
	12	48.8

Table 39. Mean (± SE, central enclosures n = 4, non-central enclosures n = 8) of environmental variables in central and non-central enclosures, with results of one-way ANOVA.

Variable	Central enclosures	Non-central enclosures	p-value
Temperature (°C)	21.1 (0.02)	21.2 (0.02)	0.946
Depth (cm)	77 (0.8)	75 (0.1)	0.784
pH	8.6 (0.03)	8.5 (0.02)	0.528
POM (mg/L)	9.3 (0.28)	19.0 (0.70)	0.024
Phyto chlorophyll (µg/L)	32.98 (1.96)	32.63 (2.09)	0.934
Sediment OM (% dry weight)	17.87 (0.10)	17.84 (0.05)	0.119
TRP (µg/L)	107.8 (10.3)	261.8 (21.7)	0.007
NO_3-N (µg/L)	73.9 (9.0)	54.7 (3.8)	0.624
NH_4-N (µg/L)	647 (27)	1188 (41)	0.012

photolysis of lindane involves hydroxy radicals (Hiskia *et al.* 1997). Hydroxy radicals are most frequently formed in natural water through the photolysis of nitrate (Haag and Hoigne 1985). The reason lindane photolysis was not detected in the present experiment could have been due to the amount of hydroxy radicals. Hydroxy radicals once produced could have been scavenged by particulate and dissolved organic matter and thus made unavailable for the degradation of lindane (Brezonik and Fulkerson-Brekken 1998). In order to get a better understanding of lindane photolysis potential in wetlands future experiments should quantify hydroxy radical concentrations.

Lindane concentrations may not have been influenced by volatilization. The presence of a plastic cover was assumed to reduce volatilization potential, by limiting air flow over the enclosures. However, lindane persistence was not significantly different between covered and OP4 enclosures. For lindane to volatilize from aquatic environments it needs to be present at the water air interface (Maguire 1991). Lindane has a high sorption coefficient (K_{oc} = 1100, Hornsby *et al.* 1996). The enclosures had elevated water column and sediment organic matter. Lindane sorbed to organic matter in the enclosures would not have been available for volatilization (Guenzi and Beard 1974, Mackay 1977).

Lindane persistence was not related to the conductivity of the enclosure water. Conductivity was significantly higher in covered (OP3 and OP4) enclosures; however, lindane persistence was not significantly different. Increased dissolved ion content (measured by conductivity) can increase the water column persistence of lindane by providing sorption sites for lindane within the water column (Wahid and Sethunathan 1979). The difference in conductivity between the covered (1414 µS/cm) and uncovered (1587 µS/cm) Crescent Pond enclosures may not have been great enough to elicit a detectable effect on lindane persistence.

Lindane persistence can vary spatially within the same wetland. In Crescent Pond central enclosures had significantly lower lindane water column persistence than non-central enclosures. Central enclosures also differed from non-central enclosures by having

lower NH_4-N, TRP and POM. When sediments are disturbed they can release NH_4-N, TRP, and POM to the water column (Schallenberg and Burns 2001, Bradshaw 2002). The enclosures were isolated from the rest of the pond so the only source of nutrients to the enclosures would have been from the atmosphere or the sediments. However, as covered and uncovered enclosures of the same "position" group (central and non-central) did not have different nutrient levels, the major source of nutrients to the water column was presumably the sediments. Consequently, NH_4-N, TRP and POM increases could be used as a proxy of sediment disruption.

The non-central enclosures had higher NH_4-N, TRP and POM concentrations and presumably greater sediment disruption than the central enclosures. The detection of lindane in the sediment of one of the sampled enclosures at the end of the experiment suggested that the sediments could have been a source of lindane to the water column. Thus, the non-central enclosures may have had longer lindane persistence due to greater sediment resuspension. Sediment resuspension may have been greater in the non-central enclosures as these enclosures, due to their position, were at greater risk of being hit by floating *Typha* sp. clumps.

The difference in POM and nutrient concentrations in the central and non-central enclosures could have been due to spatial heterogeneity of the sediment. Phytoplankton chlorophyll *a* was not significantly different between central and non-central enclosures. This suggested that the difference in POM was due to sediment input and not increased phytoplankton levels. The difference in NH_4-N and TRP could also be attributed to input from the sediment, as no nutrients were added to the enclosures. The extent of sediment resuspension is a function of the characteristics of the sediment (Wolowich 1985). Sediment characteristics can vary spatially within aquatic environments (EPA 1998, Lorah 2003). Although sediment organic matter was not significantly different between central and non-central enclosures, other sediment characteristics that were not measured, such as pH and water content could have differed between the two enclosure groups.

The enclosures did not contain any fish so the primary sediment resuspension force would have been external to the enclosures. As the enclosures were in close proximity to each other they would have been subjected to the same climactic conditions. However, the frequency of *Typha* sp. clumps collisions with the enclosures was greater for the non-central enclosures. Thus, the differences in lindane persistence were probably a result of greater sediment resuspension in the non-central enclosures caused by collisions of floating *Typha* sp. clumps. These collisions could have disturbed the sediment causing the resuspension of lindane and prolonging its water column persistence. In natural settings floating *Typha* sp. clumps could also be significant in determining lindane water column concentrations. For instance, if a *Typha* sp. clump collides with rooted emergent macrophytes some of the sediment around the macrophytes could be disturbed and resuspended. If the sediment contained pesticides then the pesticide too would be resuspended.

7. 5 Conclusion

Despite their warm and shallow water, pesticide volatilization and photolysis might not be favoured in prairie wetlands. The persistence of lindane was not different between covered and uncovered enclosures. This suggested that the volatilization potential of lindane from wetlands is low. These results would support the claim that for lindane wetlands can act as a sink by limiting lindane export. No UV effects on lindane persistence were observed in the enclosures. This suggested that photolysis was not an important degradation process of lindane. Thus, for lindane, arguments for the value of wetlands as pesticide sinks due to their enhanced photolysis potential would not be supported.

The position of the enclosures within the wetland was related to lindane water column persistence. This relationship could have been due to spatial differences in sediment disruption. In order to better understand the value of wetlands as lindane sinks the role of sediment as a lindane source to the water column needs to be investigated.

Chapter 8: Influence of phytoplankton *(Selenastrum capricornutum)* on the persistence of four commonly used herbicides

8. 1 Introduction

Sorption to organic substrata can determine the bioavailability, persistence, and transport potential of pesticides within aquatic environments (Soderstrom *et al.* 2000, Joy 2002, Windenfalk 2002). Studies have shown that wetland sediment organic matter is capable of pesticide sorption (Kadlec and Alvord 1993, Detenbeck *et al.* 1996, Kao *et al.* 2001 and Moore *et al.* 2002). Dissolved and particulate organic matter found in wetland water columns may also have the potential to sorb pesticides (Wauchope and Myers 1985, Soderstrom *et al.* 2000). One component of the organic matter content of wetlands is the phytoplankton. Numerous studies have examined the impact pesticides have on phytoplankton (Hurlbert 1975, Wong 2000, Babu *et al.* 2001, Dorigo and Leboulanger 2001, Pennington *et al.* 2001, Seguin *et al.* 2001, Gunanzon and Nakahara 2002). However, few studies have examined the effect of phytoplankton on pesticide fate (Zepp and Schlotzhauer 1983, Soderstrom *et al.* 2000).

The objective of this study was to determine the extent to which the planktonic alga *Selenastrum capricornutum* could sorb the following four pesticides: 1) 2,4-D, 2) atrazine, 3) glyphosate, and 4) trifluralin. I hypothesized that the extent of pesticide sorption to the alga would be directly related to the soil sorption coefficient of the pesticide. I also hypothesized that pesticide persistence would be shorter in the presence of the alga. This was hypothesized because I assumed that as in soil environments (Skipper *et al.* 1978, Moorman *et al.* 2001) pesticide degradation rate would increase in aquatic environments when organic matter (alga) content is increased.

8. 2 Materials and methods

Algae and culture conditions

Selenastrum capricornutum was chosen for the study because it is easy to grow and there is an abundance of pesticide toxicological data related to it (EPA 2002b) (Table 40). A pure culture of *S. capricornutum* (Carolina Biological Supply Co., Burlington, NC) was cultured using standard algal culturing methods (James 1978) in Guillard's Fresh Water Enrichment Basal Salt Mixture (Sigma Chemical Col., St Louis, MO) for seven days so that the culture was in the exponential growth phase (light 250 μmol/m^2/s, temperature 25°C). After the 7-day culturing period, 250 mL aliquots of the algal culture were placed into 300 mL glass jars. Fifty mL subsamples were then removed from each of the jars and analyzed for chlorophyll *a* as in Chapter 3.

Algal cultures were subjected to the following treatments in quadruplicate: 1) 5 ppb ring labelled 2,4-D (specific activity 10 μCi/μmol; American Radiolabeled Chemicals Inc. St. Louis, MO); 2) 5 ppb ring labelled atrazine (analytical-grade, Supleco Chemical Co., Bellefonte, PA); 3) 5 ppb glyphosate (specific activity 2.4 μCi/μmol; Sigma Chemical Co. St. Louis, MO); 4) 5 ppb ring labelled trifluralin (specific activity 16.8 μCi/μmol; Sigma-Aldrich Canada Ltd. Oakville, ON); and 5) no pesticide additions. The pesticide concentrations used were chosen because they represented environmentally realistic concentrations that can occur in surface waters following surface runoff from agricultural fields (Goolsby and Battaglin 1993, Coote and Gregorich 2000). Concentrations of pesticides added were below the EC50 values for *S. capricornutum* (Table 40).

Two hundred fifty millilitre aliquots of growth media (without algal inoculum) were also placed into glass jars (300 mL). The jars containing only growth media were also subjected to the following treatments in quadruplicate: 1) 5 ppb 2,4-D; 2) atrazine; 3) 5 ppb glyphosate; and 4) 5 ppb trifluralin.

Table 40. Effective concentrations of pesticide that caused a 50% inhibition of growth rate (EC50) in *Selenastrum capricornutum.*

Pesticide	Exposure length	EC50	Reference
2,4-D	96 h	24 mg/L	European Commission 2001
	96 h	> 30 mg/L	Taya and Ashtamkar 1997
	96 h	42 mg/L	Fairchild *et al.* 1997
Atrazine	72 h	0.054 mg/L	Hartgers *et al.* 1998
	96 h	0.235 mg/L	Fairchild *et al.* 1997
	120 h	0.053 mg/L	Brassard *et al.* 2003
Glyphosate	72 h	8 mg/L	Gro Tec, Inc. 2002
	72 h	15 mg/L	Value Garden Supply 1993
	96 h	2.6 mg/L	Monsanto Company 2003
Trifluralin	96 h	0.140 mg/L	Taya and Ashtamkar 1997
	96 h	0.673 mg/L	Fairchild *et al.* 1997
	120 h	0.007 mg/L	Monsanto Company 2002

Each 300 mL jar along with a CO_2 trap (see Chapter 4) was then placed into separate 1.5 L glass Mason jars and the Mason jars were sealed with air tight lids. The purpose of the CO_2 traps was to collect any radiolabeled carbon given off through pesticide mineralization. The Mason jars were then arranged on a laboratory countertop using a randomized block design. The experiment was kept short (32 d) purposely so deterioration in the physiological condition of *S. capricornutum* was minimized. Once a day, the Mason jars were opened and Pasteur pipettes were used to bubble 25cm^3 of air into the bottom of each 300 mL jar to resuspend any material that had settled out of the water. On days 0, 1, 2, 4, 8, 16, and 32, after the addition of the pesticides 1 mL samples were pipetted out of the glass jars and into glass scintillation vials. Five millilitres of Scintisafe 30% liquid scintillation cocktail (Fisher Scientific, Fairlawn, NJ) was added to each vial. The sample was kept in the dark for 24 h to allow for self-quenching. The disintegrations per minute of the samples were then quantified with a Beckman Model LS 7500 liquid scintillation counter. The CO_2 traps were collected with replacement on days 1, 2, 4, 8, 16, and 32. The ^{14}C radioactivity of the traps was determined as described above. On day 32, water samples were also collected from each of the experimental jars, filtered (grade GF/C, particle retention 1.2 μm, Whatman International Ltd. England) and analyzed for ^{14}C radioactivity using liquid scintillation as described above. The difference in radioactivity between the filtered and unfiltered samples was used to determine the extent of herbicide sorption to particulate organic matter. To get an estimate for the amount of pesticide volatilized from the jars the sum of the ^{14}C in the traps and in the cultures was subtracted from the total amount of ^{14}C added.

Pesticide half-life calculation and statistical analyses

The first-order half-life of the pesticides was determined using non-linear regression ($Mt=M_T e^{-kt}$). SigmaPlot Version 8 was used to calculate the slope of the pesticide concentration over time (k).

The SAS System for Windows (v. 8, SAS Institute Inc.) was used to perform one-way ANOVA on the chlorophyll *a* and pesticide half-life data. Data were log (x +1) transformed prior to analyses to stabilize the variance and approximate the normal distribution. Statistical tests were evaluated at alpha = 0.05 level of probability. The relationship between pesticide sorption coefficients and percent pesticide sorbed was investigated using the univariate regression analysis option in SigmaPlot.

8. 3 Results

Average chlorophyll *a* concentration of the algal cultures at the start of the experiment (659.2 µg/L) was significantly higher ($F_{1,38} = 324$; $p < 0.001$) than at the end of the experiment (478.5 µg/L). On day 32 chlorophyll *a* concentrations in algal cultures were not significantly different among treatments ($F_{4,15} = 0.25$; $p = 0.90$).

There was no ^{14}C-pesticide/metabolites retention by the filter alone as ^{14}C-pesticide/ metabolite concentrations in filtered and unfiltered samples of non-algal cultures were not significantly different ($p > 0.05$). Differences in ^{14}C-2,4-D/metabolites concentrations between filtered and unfiltered algal culture samples were also not significant ($F_{1,6} = 0.376$; $p = 0.562$) (Table 41). However, ^{14}C-atrazine/metabolites, ^{14}C-glyphosate/ metabolites, and ^{14}C-trifluralin/metabolites concentrations were significantly lower in filtered algal samples versus unfiltered algal samples (Table 41). The percent of total ^{14}C-pesticide/metabolites in the cultures that was sorbed to particulates was significantly correlated with the pesticide's sorption coefficient (Figure 44).

^{14}C-pesticide/metabolites dissipated from treatments following first-order decay kinetics (Figure 45). Half-lives of ^{14}C-2,4-D/metabolites and ^{14}C-atrazine/metabolites were not significantly different between algal and non-algal cultures (Table 42). ^{14}C-glyphosate/metabolites in algal cultures had significantly lower half-lives ($F_{1,6} = 12.89$ $p = 0.012$) than in non-algal cultures (Table 42). Conversely, ^{14}C-trifluralin/metabolites half-life in algal cultures was significantly higher than in non-algal cultures ($F_{1,6} = 426$ $p < 0.001$).

Table 41. Herbicide concentrations (mean, ppb; ± SE n = 4) in unfiltered and filtered algal culture samples measured on day 32 of the experiment; p-values from one-way ANOVA.

Herbicide	Unfiltered	Filtered	p-value
2,4-D	4.28 (0.03)	4.23 (0.03)	0.562
Atrazine	4.38 (0.01)	4.22 (0.02)	0.011
Glyphosate	3.55 (0.04)	2.97 (0.09)	0.021
Trifluralin	3.32 (0.03)	3.00 (0.04)	0.017

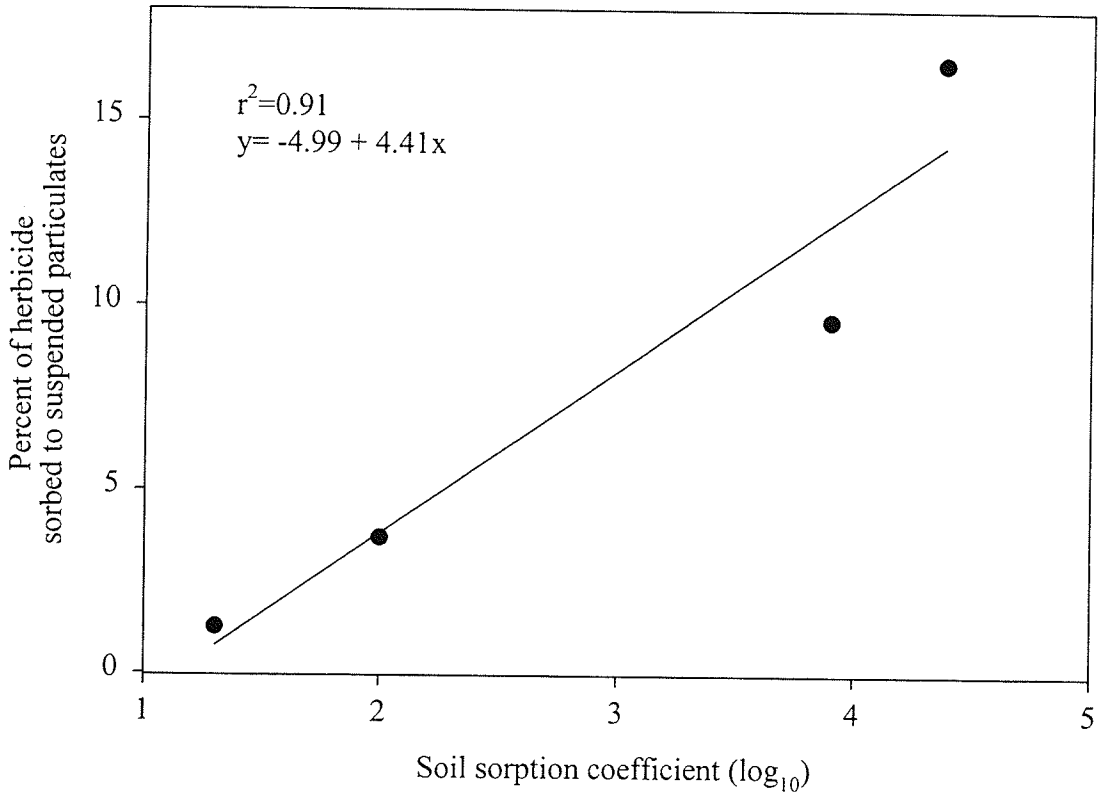

Figure 44. Regression of soil sorption coefficients (Hornsby *et al.* 1996) and percent of herbicide sorbed after 32 days to particulates in experimental vials containing *Selenastrum capricornutum*.

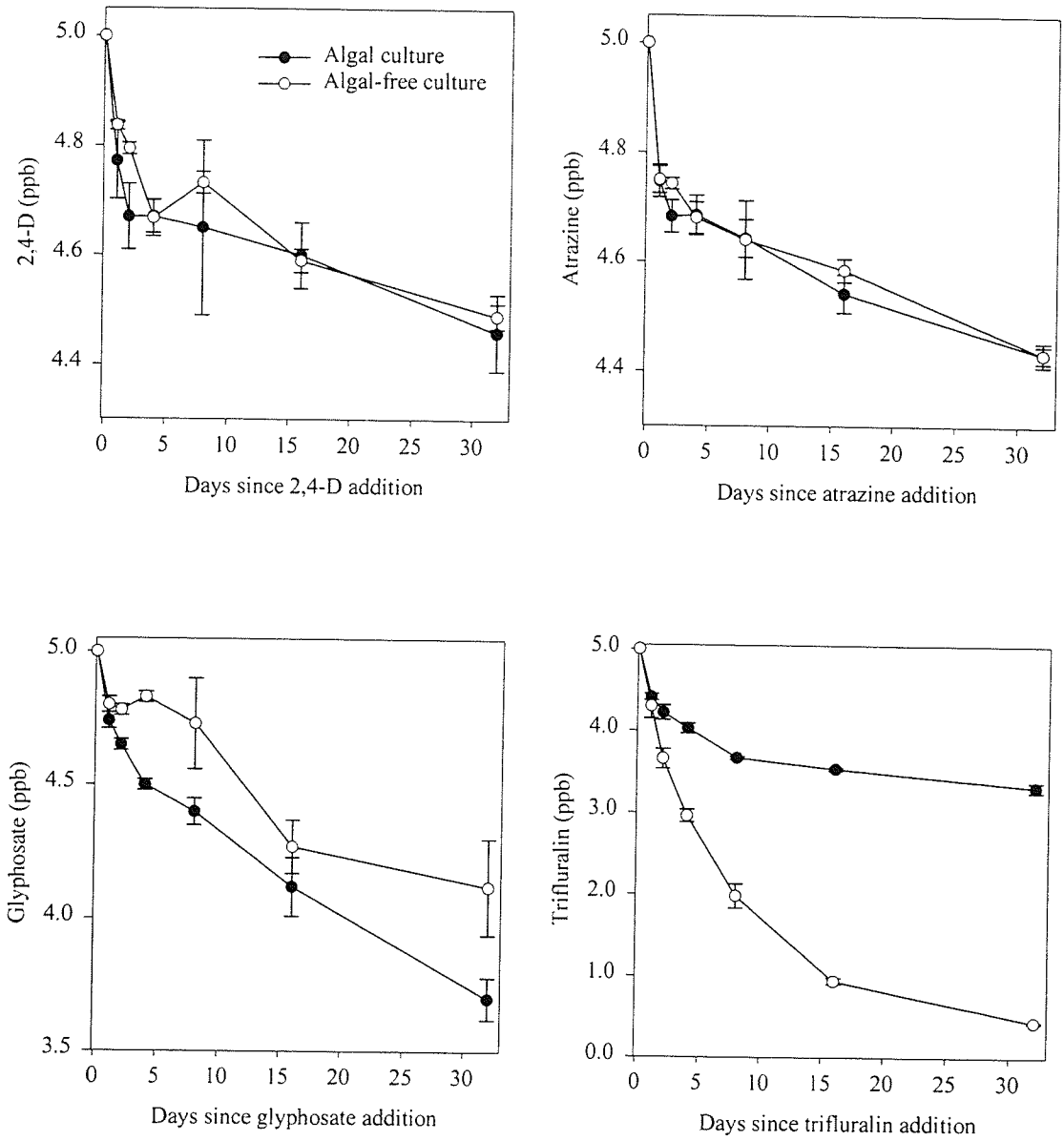

Figure 45. Pesticide concentrations (± SE, n = 4) in non-algal cultures (growth media) and algal cultures (growth media + *S. capricornutum*) over time. Initial concentration of each herbicide was 5.0 ppb.

Table 42. Mean half-life (days ± SE; n = 4) of four ^{14}C-labeled pesticides over a 32-day period in cultures of *Selenastrum capricornutum* as compared to algal-free media; p-values from one-way ANOVA. These data are for all ^{14}C-products and would include metabolites with ^{14}C. This may account for the longer half-life than reported in studies that have looked at just the parent compound.

Herbicide	Non-algal culture	Algal culture	p-value
2,4-D	258 (21)	263 (54)	0.066
Atrazine	262 (36)	242 (3)	0.336
Glyphosate	115 (8)	76 (2)	0.026
Trifluralin	6 (1)	61 (3)	< 0.001

Table 43. Percent of added ^{14}C (mean; ± SE n = 4) of four ^{14}C-labeled pesticides over a 32-day period in cultures of *Selenastrum capricornutum*, as compared to alga-free media; p-values from one-way ANOVA.

Herbicide	Non-algal culture	Algal-culture	p-value
2,4-D	0.54 (0.05)	0.58 (0.14)	0.756
Atrazine	0.30 (0.06)	0.44 (0.10)	0.085
Glyphosate	1.97 (0.13)	5.39 (0.31)	0.004
Trifluralin	3.04 (0.21)	1.06 (0.17)	< 0.001

Table 44. Percent of added ^{14}C volatilized (mean ± SE; n = 4) of four ^{14}C-labeled pesticides over a 32-day period in cultures of *Selenastrum capricornutum*, as compared to alga-free media; p-values from one-way ANOVA.

Herbicide	Non-algal culture	Algal-culture	p-value
2,4-D	6.9 (0.5)	10.2 (0.7)	0.102
Atrazine	5.6 (0.7)	8.3 (0.2)	0.112
Glyphosate	15.6 (1.8)	20.7 (0.8)	0.239
Trifluralin	88.5 (0.1)	32.6 (0.6)	< 0.001

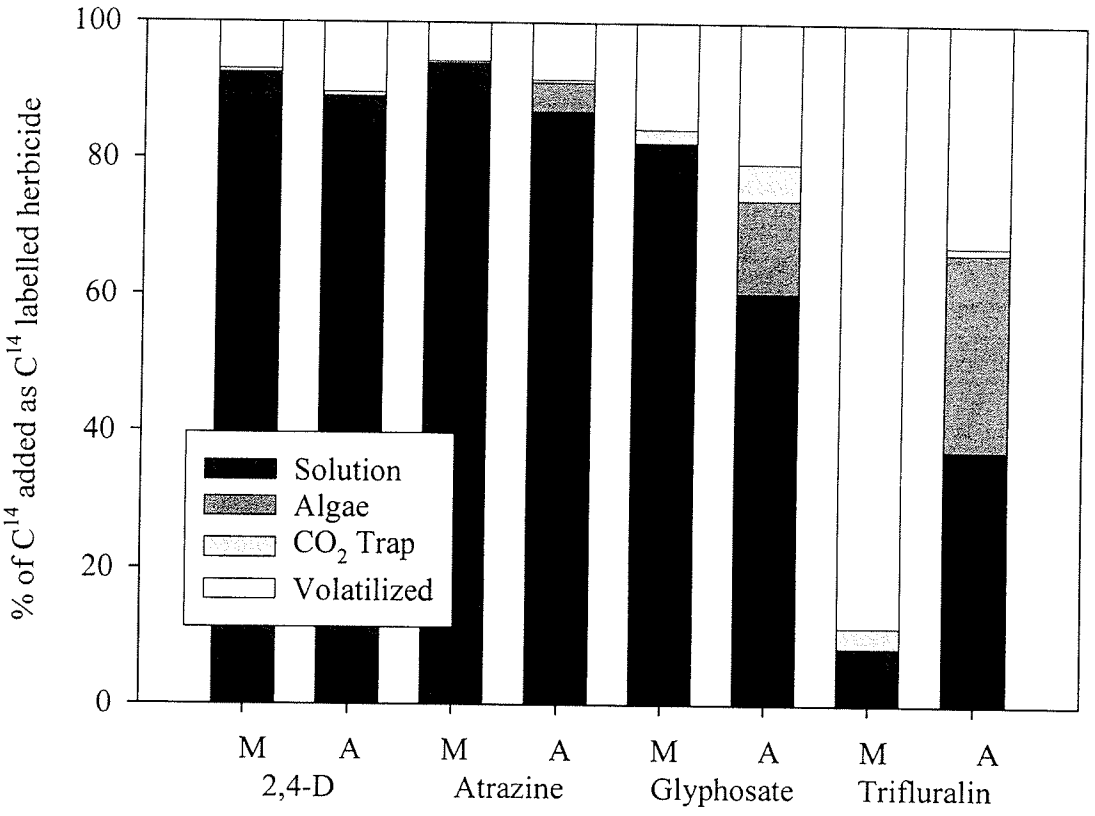

Figure 46. Mass balance of ^{14}C in the form of ^{14}C-labeled herbicides added to microcosms containing media with (A) and without algae (M) (*Selenastrum capricornutum*).

The amount of ^{14}C in the CO_2 traps from the 2,4-D and atrazine treatments was not significantly different ($p > 0.05$) between algal and non-algal cultures (Table 43). The amount of ^{14}C in traps from the glyphosate treatments was significantly higher in the algal cultures ($F_{1,6} = 58.17$ $p < 0.001$) as compared to non-algal cultures (Table 43). In contrast, the amount of ^{14}C in traps from the trifluralin treatments was significantly lower in algal cultures versus non-algal cultures ($F_{1,6} = 55.90$ $p < 0.001$).

The amount of ^{14}C volatilized from the 2,4-D, atrazine, and glyphosate treatments was not significantly ($p > 0.05$) different between algal and non-algal cultures (Table 44). However, ^{14}C volatilization from trifluralin treatments was significantly lower ($F_{1,6} = 2252$, $p < 0.001$) in algal cultures as compared to non-algal cultures (Table 44).

Mass balances at the end of the experiment (day 32) summarize the distribution of the ^{14}C-pesticide/metabolites (Figure 46). On day 32 the majority of the ^{14}C in the 2,4-D (algal 89%, non-algal 93%) , atrazine (algal 87%, non-algal 94%) and glyphosate (algal 60%, non-algal 82%) treatments remained in solution. However, in the trifluralin treatments less than 50% of the ^{14}C remained in solution on day 32 (algal 37%, non-algal 9%). In all the treatments volatilization was the process that accounted for the greatest amount of ^{14}C loss from the cultures (6 to 88% of added pesticide). Mineralization of the pesticides was low (< 6% of added pesticide) in all the cultures.

8. 4 Discussion

This study demonstrates that published pesticide soil sorption coefficients are good predictors of the extent to which these chemicals sorb to algal cells in culture. The extent of pesticide association with the algae was correlated with the pesticide's sorption coefficient. This meant that *S. capricornutum* was capable of sorbing pesticides in similar manner as soil organic matter from which the pesticide sorption coefficients were calculated (Hornsby *et al.* 1996). The ability of *S. capricornutum* to sorb pesticides suggested that phytoplankton and other seston could be important in determining pesticide fate in aquatic environments which have high phytoplankton concentrations. For

example, phytoplankton concentrations in eutrophic prairie wetlands frequently exceed 100 µg/L and have the potential to reach the phytoplankton levels used in the current experiment (Chapter 3). Pesticides in the water column of eutrophic wetlands could be removed from solution by sorbing to phytoplankton. Pesticides sorbed to phytoplankton could eventually be removed from the water column when the phytoplankton dies and sinks to the sediment.

Glyphosate persistence was reduced in the presence of algae. In the soil environment studies have shown that increases in organic matter content can decrease glyphosate persistence (Moorman *et al.* 2001). Similarly, this experiment showed that increases in water column organic matter content (algae) can also decrease glyphosate persistence. Glyphosate is susceptible to biotic mineralization (Schuette 1998). Addition of organic matter to environments such as agricultural fields can increase microbial degradation of glyphosate by increasing the microbial content (Moorman *et al.* 2001). Thus, the higher mineralization of glyphosate in the algal cultures could have been due to a higher microbial content. Future experiments should be designed to determine if phytoplankton can increase glyphosate degradation by increasing the density of glyphosate degrading microbes.

In contrast to their effect on glyphosate, algae increased the persistence of trifluralin. Trifluralin is prone to volatilize from soil and water surfaces due to its relatively high Henry's Law constant (4 $Pa.m^3/mol^3$) (Sanders and Seiber 1983, Sunito *et al.* 1988). However, trifluralin sorbed to organic matter and other sorbents would not be available for volatilization (Guenzi and Beard 1974, Mackay 1977). In this experiment the amount of trifluralin in solution was significantly lower in the algal cultures. In addition, the percent of trifluralin volatilized from the algal cultures was significantly lower than from non-algal cultures. Thus, the greater persistence of trifluralin in the algal cultures could have been a result of lowered volatilization rates due to trifluralin sorption to the algae.

8. 5 Conclusion

The extent to which the planktonic alga *S. capricornutum* sorbed the studied herbicides could be predicated upon the herbicides' soil sorption coefficient. This suggested that phytoplankton could have a similar ability as soil or sediments to sorb herbicides. Sorption is important in determining the environmental fate of pesticides. Phytoplankton concentrations in eutrophic wetlands can reach levels similar to those used in this study. Thus wetland phytoplankton, by sorbing pesticides, could have the potential to play a role in determining pesticide persistence. For instance, sorption of volatile pesticides, such as trifluralin, to phytoplankton could increase their water column persistence by decreasing the extent of volatilization.

Chapter 9: Discussion

Atrazine and lindane detection were related to wetland proximity to pesticide use and to precipitation prior to wetland sampling. The percent of wetlands with lindane or atrazine detection was directly related to the extent of chemical use within the area. For instance, lindane use was higher in the Canadian PPR than in the US and consequently Canadian wetlands had higher detection rates for lindane. Similarly, atrazine detection occurred only in wetlands located in the southeast portion of the PPR, which is an area of high atrazine use.

Total precipitation prior to sampling was also related to pesticide detection in 1999. Wetlands that received higher precipitation 15 days prior to sampling had a greater chance of lindane detection. Wetlands with a shorter elapsed time between wetland sampling and last precipitation event had a greater chance of atrazine detection. Precipitation can directly and indirectly transport pesticides to wetlands. Rain can wash volatilized pesticides out of the atmosphere and into wetlands. In addition, after a precipitation event the resulting surface water flow can transport pesticides from fields to wetlands. One reason why precipitation was not related to pesticide detection in other years of the survey may have been the low number of wetlands with pesticide detection.

Conductivity and phytoplankton chlorophyll *a* were related to lindane detection in 1999. Dissolved ions (measured by conductivity) could have influenced lindane detection by providing surface area for lindane sorption within the water column (Wahid and Sethunathan 1979). Lindane sorbed to dissolved ions would remain in the water column. Conductivity was only related to lindane detection later in the year when the concentration of dissolved ions was higher. The higher conductivity later in the year was due to the evaporation of water from the wetlands. Phytoplankton can also provide sorption sites for lindane within the water column. Phytoplankton (measured as chlorophyll *a*) had a different relationship with lindane detection in wetlands in June/July

than in August. In June/July, phytoplankton chlorophyll *a* was positively correlated with lindane detection. This may have been due to the lindane remaining in the water column longer in wetlands with higher phytoplankton concentrations. However, in August phytoplankton chlorophyll *a* was negatively correlated with lindane detection. These results could be attributed to lindane removal from the water column via sorption to phytoplankton and the subsequent sedimentation of the phytoplankton-lindane complex. The seasonal difference in the relationship between phytoplankton and lindane detection may have been due to seasonal and spatial environmental variability encountered in the wetlands.

Sediment organic matter was not related to atrazine or lindane detection in the surveyed wetlands. This was unexpected as experiments have shown that sediment organic matter can sorb pesticides from the water column (Detenbeck *et al.* 1996, Kao *et al.* 2001, Moore *et al.* 2002). Differences in pesticide use and inputs to wetlands throughout the study region may have obscured the role sediment organic matter plays in water column pesticide detection.

Results from microcosm and mesocosm experiments showed that increases in wetland organic matter concentrations decreased water column persistence of atrazine, lindane, and glyphosate. Due to increased sorption to the sediment, atrazine persistence decreased as sediment organic matter increased. In *in situ* mesocosm experiments, lindane persistence was shorter when phytoplankton levels were high at the time of lindane addition. Atrazine, lindane, and glyphosate had lower persistence in microcosm experiments when in the presence of POM. However, POM did not influence 2,4-D persistence. In addition, POM increased the persistence of trifluralin. This increase could have been due to lowered volatilization potential of trifluralin sorbed to POM.

Photolysis of atrazine and lindane was not detected in wetland water columns. This was likely due to low (less than 10 % of surface UV at a depth of 10 cm) UV transmittance within the water columns of the studied wetlands. UV attenuation in the

wetlands could have been due to shading by suspended particulates and DOC (Morris *et al.* 1995). The amount of UV reaching the Earth's surface is increasing as stratospheric ozone depletion continues (Zepp *et al.* 2003). UV can damage DOC and limit the ability of DOC to attenuate UV (Whitehead *et al.* 2000). Acid deposition can also damage DOC and reduce its ability to attenuate UV (Donahue *et al.* 1998). Thus, the role of UV in determining pesticide fate in wetlands may become more important as UV levels and acid deposition continue to increase.

9.1 Overall objective revisited

My objective has been to study the determinants of water column persistence of selected pesticides to determine if PPR wetlands have the potential to act as sinks for these pesticides. The descriptive and experimental approaches (Table 45) used in my study complemented each other and helped me achieve this objective.

Receive pesticide inputs

As stated earlier an ecosystem must receive a contaminant if it is to function as a sink for that particular contaminant. Results from Chapter 3 indicated that 62% of PPR were contaminated with pesticides (either atrazine or lindane). Mechanisms which are involved in the off-field transport of atrazine and lindane can also transport other pesticides. Thus, the probability is high that wetlands with atrazine or lindane detection also contained other pesticides. The high percentage of PPR wetlands contaminated with atrazine or lindane would suggest that wetlands within the PPR meet the first criterion of a pesticide sink; that is, they receive pesticide inputs.

Retain pesticide inputs

Wetlands must be able to retain pesticides inputs if they are to have value as pesticide sinks. If a pesticide is removed from the water column its potential for loss in surface flow is reduced. The experiment in Chapter 4 demonstrated that sediment organic matter can determine atrazine water column persistence by sorbing the pesticide. In addition, the experiments in Chapters 5 and 8 demonstrated that phytoplankton can sorb

Table 45. Pesticide sink properties of wetlands examined in each chapter of the thesis.

Property	Chap.	Hypothesis	Implications concerning pesticide sink value
Receive pesticide	3	Higher percent of lindane detection in Canadian wetlands: *Supported* Higher percent of atrazine detection in US wetlands: *Supported*	Wetlands across the PPR are susceptible to pesticide inputs and thus meet this criterion of pesticide sinks
Retain pesticide	3	Sediment organic matter is negatively correlated with pesticide water column detection: *Not supported*	Lindane detection was positively correlated with phytoplankton concentration. This provided new insight into the determinants of pesticide fate in wetland water columns.
	4	Sediment organic matter in the form of organic matter most influential in reducing atrazine water column persistence: *Supported*	Wetlands with higher sediment organic matter may have greater value to act as pesticide sinks.
	5	Nutrient additions reduce water column conditions by increasing surface area (POM) for sorption: *Supported*	Wetlands with higher POM concentrations may have greater value as pesticide sinks.
	7	Lindane volatilization is a major loss mechanism from wetland mesocosms: *Not supported*	Limited volatilization of lindane supports claim that wetlands may act as sinks.

Table 45 continued.

Reduce pesticide	6	Photolysis of atrazine and lindane occurs in wetland water columns: *Not supported*	Enhanced photolysis is not a contributing factor to the value of wetlands as atrazine and lindane sinks.
	7	Lindane photolysis occurs in wetland mesocosms: *Not supported*	Enhanced photolysis is not a contributing factor to the value of wetlands as lindane sinks.
	8	Phytoplankton increase herbicide mineralization: *Supported* for glyphosate; *not supported* for 2,4-D, atrazine or trifluralin	The high phytoplankton level seen in some wetlands may increase their value as sinks for glyphosate.

the pesticides; atrazine, glyphosate, lindane, and trifluralin. Once sorbed, the pesticide can be removed from the water column when the phytoplankton to which it is sorbed undergoes sedimentation.

Pesticides can also be transported out of aquatic environments via volatilization (Strachan and Eisenreich 1988, Severinsen *et al.* 1996, Barrie *et al.* 1997, Ridal *et al.* 1997, Harner *et al.* 1999). However, volatilization of lindane from wetland mesocosms was not detected (Chapter 7). This may have been due to the lindane being sorbed to water column substrata, making it unavailable for volatilization. Pesticides are only available to volatilize from aquatic environments if they are free in solution. Results from the experiment in Chapter 8 indicated that in the presence of organic matter such as phytoplankton the volatilization potential of pesticides such as trifluralin will be reduced. As the above results are for only two pesticides in two specific environments (Crescent Pond and experimental microcosms) they do not preclude the possibility that volatilization may transport pesticides from wetlands. What the results do imply is that pesticide volatilization may be lower in environments with high water column organic matter.

Based on their characteristically high organic matter content PPR wetlands are anticipated to have value as sinks for atrazine, lindane, and trifluralin. This is because once these pesticides enter wetlands they will tend to sorb to the organic matter and consequently their potential to be transported via surface flow or volatilization will be reduced.

Reduce pesticide amounts

In order to function as a pesticide sink, wetlands need to not only retain pesticides but they need to reduce their environmental concentrations. Results from the experiments in Chapters 5 and 8 indicated that wetland water characteristics such as high POM can favour the degradation of atrazine, lindane, and glyphosate. Particulate organic matter could have enhanced pesticide degradation by providing substrata for microorganisms

capable of pesticide degradation. Although wetland conditions may have reduced the amount of added pesticide it is important to keep in mind that they may not have reduced its ecological impact. The reason for this is due to the potential toxicity of pesticide metabolites.

PPR wetlands do have value as sinks for the selected pesticides

PPR wetlands have the potential to act as sinks for the pesticides considered by this thesis because they receive pesticides, have the ability to retain pesticides, and reduce their concentrations (Figure 47). PPR wetlands are at risk of receiving pesticide (atrazine and lindane) inputs due to their close spatial relationship to agricultural land. The selected pesticides can be retained in PPR wetlands through sorption to sediment organic matter and macrophytes. The selected pesticides by sorbing to water column organic matter may also be retained in wetlands if the organic matter-pesticide complex undergoes sedimentation. Removal of pesticides from the water through sorption to organic material will also limit pesticide bioavailability. In addition, wetland conditions such as elevated POM levels can decrease pesticide concentrations by enhancing pesticide degradation.

The value of PPR wetlands to act as pesticide sinks will vary depending upon the pesticide in question and the wetland conditions present. Based on experimental evidence the ability of a PPR wetland to act as a pesticide sink will be directly related to the sorption coefficient of the pesticide in question. For instance, wetlands may have a greater potential to act as sinks for glyphosate (soil sorption coefficient 24,000 mL/g), lindane (1100 mL/g), and trifluralin (8000 mL/g) than they would for atrazine (20 mL/g) or 2,4-D (20 mL/g. The wetland's organic matter content will also determine the extent to which it can act as a pesticide sink. Results from my thesis indicate that wetlands with higher water column and sediment organic matter content will have greater sink value for the studied pesticides. On this basis I conclude that pesticide soil sorption coefficient and wetland organic matter content are two key drivers that would be useful in a future, more wide-ranging study of prairie wetland sink potential.

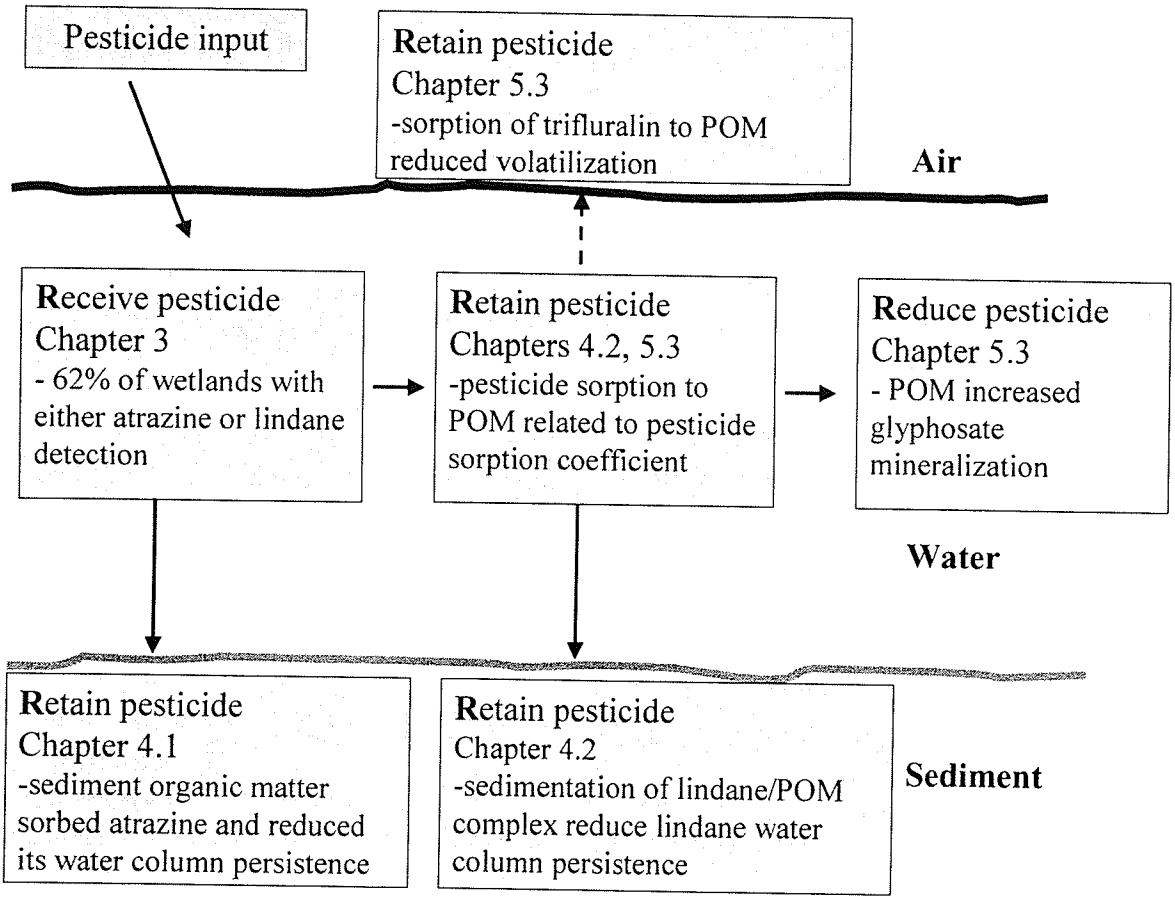

Figure 47. Conceptual diagram of wetlands as pesticide sinks revisited.

9. 2 Recognition of the role of POM

Results from the experiments in Chapters 5 and 8 demonstrate that POM concentration can be an important determinant of relative pesticide persistence in prairie wetlands. From a review of the literature it is apparent that past researchers have rarely considered the effects of POM such as phytoplankton when studying pesticide fate in wetlands. Researchers that have recognized POM have tended to focus on its effects on pesticide photolysis (Miller and Chin 2002). My study shows that sorption to POM could have a significant effect on pesticide fate.

The importance of pesticide sorption to wetland POM may have been over looked in the past due to the way that pesticide sorption studies were conducted in the past. Studies of pesticide sorption began with research in agricultural fields. These studies showed that soil organic matter could sorb pesticides and tended to be the most important factor in determining the efficacy and off-field transport of pesticides (Cheng 1990). When scientists began to investigate pesticide sorption in aquatic environments the primary focus was on the sediment, as this environment was most similar to the soil environment. Studies have shown that POM in aquatic environments can also sorb pesticides and influence their fate (Allan 1986). However, the majority of pesticide fate studies in wetlands have not examined the role of POM. Elevated POM levels can occur in PPR wetlands. For instance, PPR wetlands are prone to nutrient inputs from agricultural fields. These nutrient inputs can cause phytoplankton blooms. In addition, the feeding and spawning activity of wetland fish can cause sediment resuspension and elevated POM levels. Thus, in eutrophic wetlands and wetlands with benthivorous fish I believe that at times POM could play an equally important role in determining pesticide fate as sediment organic matter.

Results from Chapter 5 demonstrate that the relative roles of POM and sediment organic matter in determining pesticide water column persistence will be a function of the depth of the wetland. The percent of the water column in contact with the sediment

depends on the depth of the wetland. Thus, in shallow wetlands sediment organic matter may play a more important role in determining pesticide persistence than POM. I would also expect that in deep ($\geq$ 1 m) phytoplankton-dominated wetlands POM would play as equal a role in pesticide water column persistence as sediment organic matter.

9. 3 Pesticide wetland persistence and toxicity tests

My finding that pesticide half-lives were shorter in natural wetland water than in distilled water calls into question the widespread protocols for measuring pesticide dissipation in laboratory studies, because most natural water sources (and certainly most wetland waters) rarely approximate distilled water. Experiments used to set guidelines for the protection of aquatic life are conducted in distilled or otherwise purified water so that toxic effects can be attributed solely to the chemical in question (EPA 1996). Therefore pesticide toxicity tests conducted in "pure water" could overestimate pesticide toxicity in wetland water. Tests used to set guidelines usually measure acute toxicity but ignore chronic toxicity. Standard toxicity tests also ignore secondary effects of pesticides. Thus, using guidelines that overestimate acute toxicity may help to offset the unaccounted for chronic and secondary effects of the pesticide.

9. 4 Pesticide persistence and environmental/experimental conditions

This study highlighted the potential for pesticides to have significantly different persistence depending on wetland environmental and experimental conditions. For instance, lindane water column half-life was found here to range from 2.5 to 128 days (Table 46). Factors that accounted for the variation in lindane half-life included experimental design as lindane half-life was longer in experimental units that only consisted of the water column component. In addition, environmental differences also accounted for the differences in lindane half-life. For example, lindane persistence was longer in water that had lower suspended solids (Crescent Pond water) than in water with higher suspended solids (Blind Channel water). Thus, extrapolation of pesticide

Table 46. Half life of lindane in the water column, under various experimental conditions. BC = Blind Channel, CP = Crescent Pond, * = above water surface, Meso = mesocosm, Sed = sediments, Phyto = phytoplankton, Mac= macrophytes, DW = distilled water.

Ch.	Location	Year	Study Unit	Water source	Initial conc. (mg/L)	N+P added	Sed	Phyto	Mac	Half life (d)
4.2	BC	2000	Meso	BC	0.001	No	Yes	Yes	Yes	2.6
	BC	2000	Meso	BC	0.001	Yes	Yes	Yes	Yes	2.5
	BC	2001	Meso	BC	2	No	Yes	Yes	Yes	10.1
	BC	2001	Meso	BC	2	Yes	Yes	Yes	Yes	4.4
	BC*	2001	Vial	BC	2	No	No	No	No	50.0
	BC*	2001	Vial	BC	2	Yes	No	No	No	56.5
	BC*	2001	Vial	DW	2	No	No	No	No	70.5
	BC*	2001	Vial	DW	2	Yes	No	No	No	67.3
5.1	BC	2001	Vial	BC	2	No	No	Yes	No	96.3
	CP	2001	Vial	CP	2	No	No	Yes	No	128.3
5.2	CP	2000	Meso	CP	0.01	No	Yes	Yes	No	40.5

persistence from one wetland to another may only be accurate if the two wetlands share similar environmental characteristics.

The amount of pesticide added is another factor that could account for the differences in pesticide persistence between studies. If all environmental variables are kept constant throughout an experiment then the half-life (assuming it follows first-order kinetics) will be independent of initial concentration. However, the pesticide concentration added can influence the environmental conditions of the experimental unit and thus may affect pesticide half-life. Pesticide levels added to an experiment which are above "real world" concentrations in wetlands may result in different environmental conditions than those seen in natural wetlands. For instance, elevated pesticide levels in an experiment could result in increased phytoplankton due to a pesticide-induced reduction of grazers. Consequently, when extrapolating from experiments to the field similarities in environmental conditions (which may be due to differences in pesticide concentrations) between the two should be considered.

9. 5 Wetland conservation and management implications

Wetland managers attempt to conserve the functional values of wetlands in their charge (Davis 1993, Public Lands Workgroup 1994). An important wetland value is the habitat they provide for a diverse amount of organisms. However, the species diversity of wetlands in phytoplankton-dominated states is often compromised due to limited light transmission and low oxygen levels. There has been a conscious effort in Europe to manage aquatic ecosystems so that they are maintained in the macrophyte-dominated stable state (M. Scheffer, Wageningen Agricultural University, The Netherlands pers. comm. 2001). This effort has been undertaken in part to increase the species richness of these ecosystems. If wetlands within the PPR were managed so as to maintain the macrophyte-dominated state, these wetlands may have less value as pesticide sinks than if they were dominated by phytoplankton. This is because water column pesticide

persistence can be shorter in the phytoplankton dominated state (Chapter 5, Soderstrom *et al.* 2000).

PPR wetlands tend to be found embedded in a matrix of agricultural land and consequently wetland managers frequently interact with the farming community (Public Lands Workgroup 1994). It is thus important for wetland managers to be cognitive of the impact agriculture can have on wetland ecosystems. This study has demonstrated that; wetlands are at risk of pesticide contamination due to local agricultural use, and that there is a positive correlation between precipitation and pesticide detection. Knowing this, wetland managers should emphasize, to farmers, the importance of buffer zones around wetlands in order to reduce pesticide inputs. In addition, wetland managers concerned about pesticide concentrations in their wetlands should conduct their sampling shortly after the first precipitation event following pesticide application.

Wetland managers should also be aware that there is an incomplete understanding of the value of wetlands as pesticide sinks. With this awareness mangers would be prepared to address groups who may condone continued pesticide use based on the assumption that wetlands are effective pesticide sinks. To such arguments wetland mangers should be prepared to offer the following three reminders. Firstly, research has tended to look only at pesticide persistence in the water column. Pesticides could persist and have effects in other areas of the wetland such as the sediment. Secondly, pesticide chemistries are diverse and wetlands might not be sinks for pesticides with low sorption potentials. Thirdly, low levels of pesticides as well as pesticide metabolites in wetlands could have chronic effects on wetland biota and could lead to a trophic cascade of ecological effects, which might result in wetlands losing many of their functional values.

The further understanding of the determinants of pesticide fate in wetlands developed by my study also has implication for the design and management of constructed wetlands to mitigate environmental pesticide concentrations. For example, constructed wetlands exist that are designed to receive nutrient rich runoff from livestock

operations like cattle feedlots (CH2M Gore and Storrie Limited 1998). If these wetlands are in the vicinity of agricultural fields then a series of channels (Moore *et al.* 2001a,b) could be constructed so that runoff from agricultural fields would also enter the constructed wetlands. Increased algal concentrations, due to elevated nutrients from the livestock, could then sorb pesticides and potentially remove them from the water column. Of course to be of value as a pesticide sink the algae-pesticide complex would have to be retained in the wetland. In this regard increasing periphytic algal colonization (by adding artificial substrata) may be an effective strategy to limit the outflow of pesticides associated with algae.

9. 6 Recommendations for future work

There are over 100 pesticide active ingredients used on the prairies (Thelin 1998, Saskatchewan Agriculture and Food 2001). However, the fate of only a handful of these pesticides has been studied in the wetland environment (Goldsborough and Crumpton 1998). In order to understand the full value of wetlands as pesticide sinks the wetland fate of all "in use" pesticide active ingredients needs to be known. This would take a considerable amount of time due to the large number of "in use" pesticides within the PPR. I would recommend then that the best approach would be to start by studying the fate of pesticides that are most heavily used in the PPR. For instance, studies on the fate of trifluralin in wetlands are needed as this pesticide was applied to approximately 15,000 acres in Manitoba during the 2001 growing season (Manitoba Crop Insurance Corporation 2001). Results from mesocosm studies of individual pesticides may be specific to the pesticide studied. However, by studying pesticides, like trifluralin, which are widely used, the results although specific to the pesticide in question would have "general" implications across the PPR given the pesticides high use. Keeping in mind this focus on the most widely used pesticides I would offer the following three recommendations for future research:

i. Investigate microbial degradation of pesticides in wetlands

ii. Investigate the potential of wetland sediments to act as a pesticide source to the water column

iii. Investigate the effect of wetland DOM on pesticide fate.

Investigate microbial degradation of pesticides in wetlands

Microbial communities of wetlands may support microorganisms capable of degrading pesticides. Results from my study indicated that atrazine and lindane degradation was faster in wetland water as opposed to distilled water. These results may have been due to the presence of pesticide degrading microorganisms in the wetland water. Future experiments designed specifically to investigate the extent of pesticide microbial degradation in wetlands are needed. These experiments should start by comparing pesticide persistence in sterilized and unsterilized wetland water and sediments. If pesticide half-life is shorter in unsterilized water/sediment then work could be done to identify the microorganism(s) capable of pesticide degradation. Once identified and cultured these microorganisms could be used to bioaugment contaminated wetlands and increase their pesticide sink value.

Potential of wetland sediments to act as a pesticide source to the water column

Pesticides tend to be most available to the biota and for transport out of the wetland when they are found in the water column. Sorption of pesticides to the sediment would remove pesticides from the water column. However, resuspension of pesticide contaminated sediment could transport pesticides back to the water column (Chapter 7). In wetlands sediment resuspension can occur due to the effects of bioturbation and wind. Experiments designed to examine the flux of pesticides between the sediment and water column should be conducted to determine if wetland sediments are truly sinks for agricultural pesticides.

Effect of wetland DOM on pesticide fate

Little research has been done on the effect of DOM on pesticide fate in wetlands. Given the high DOM concentrations in many PPR this form of organic matter may play an important role in determining pesticide fate. Experiments should be conducted that compare pesticide persistence in wetlands of varying DOM levels. There are various sources and forms of DOM in wetlands. These varying forms may have different effects on pesticide persistence. Thus, experiments should also be conducted that compare the persistence of pesticides exposed to different forms of DOM. A better understanding of the effects of DOM on pesticide fate may help explain differences in pesticide concentrations from one wetland to the next.

9.7 A final comment

The Canadian and US governments of the early twentieth century regarded wetlands as agricultural land that was covered with water. Surprisingly, this simplistic view of wetlands can still be seen in the scientific literature as many of the studies on pesticide fate in wetlands have focused on the role of sediment organic matter without much consideration of components of the water column (Detenbeck *et al.* 1996, Merise and Seybold 1996). This focus may have been influenced by the fact that in agricultural fields soil characteristics tend to be the most significant determinants of pesticide persistence (Cheng 1990). Wetlands are more than fields covered with water and characteristics of the water column overlying the sediments may be important in determining pesticide fate. In order to understand pesticide fate in wetlands, researchers need to be aware of not only pesticide chemistries but also of the unique characteristics of wetland ecosystems.

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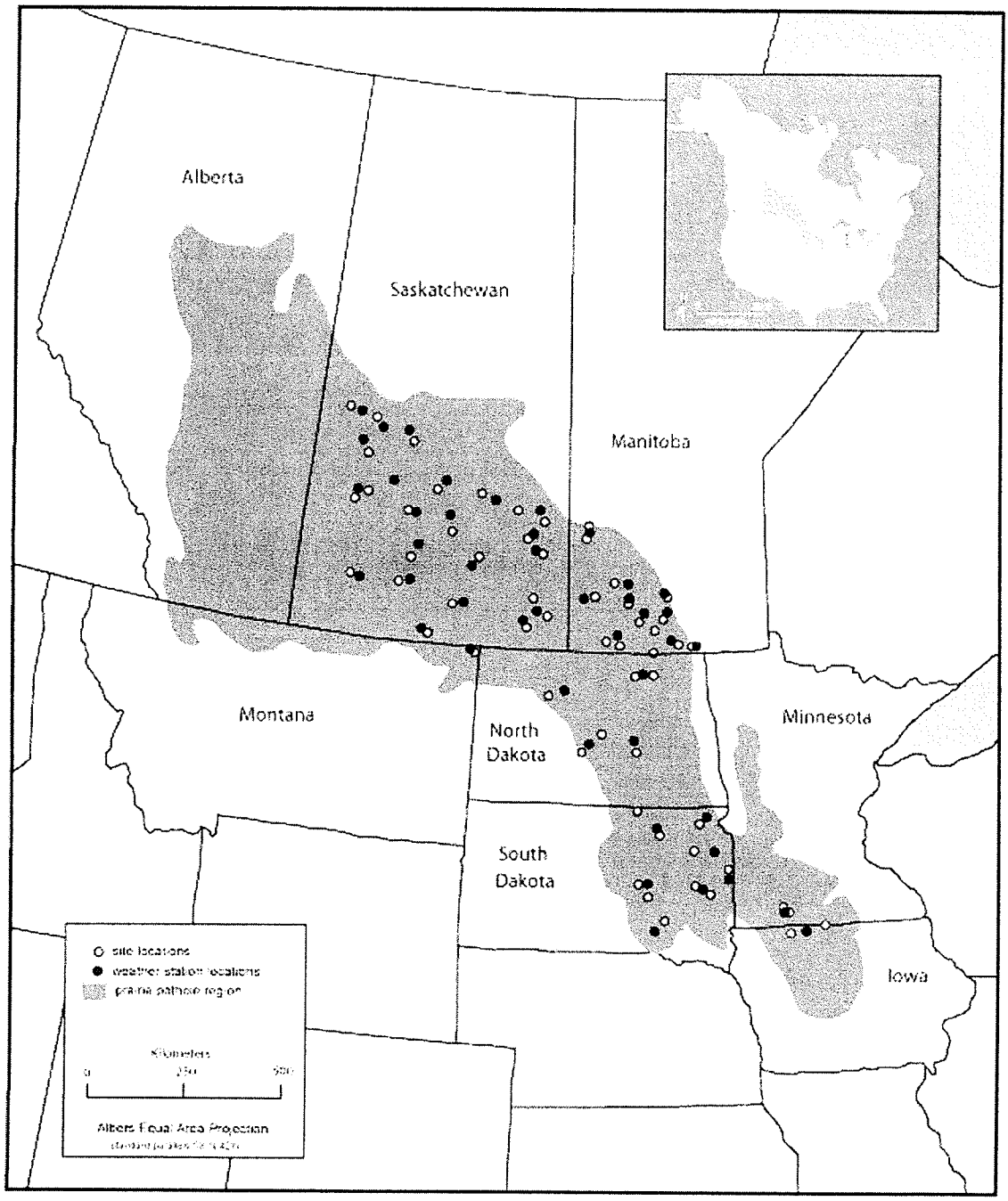
Appendix A. Geographical location (degrees latitude and longitude) of survey wetlands.

Site No.	Latitude (°)	Longitude (°)	Site No.	Latitude (°)	Longitude (°)
1	50.10	98.23	31	49.10	105.43
2	49.40	99.16	32	49.27	102.42
3	50.02	99.37	33	49.40	101.59
4	50.08	100.36	34	50.05	102.27
5	49.42	101.00	35	51.12	102.40
6	49.04	100.30	36	50.54	102.13
7	49.15	100.03	37	48.52	104.10
8	49.10	99.48	38	48.08	101.48
9	49.39	98.28	39	47.27	100.04
10	49.30	98.39	40	47.24	100.48
11	49.04	98.44	41	45.52	99.06
12	50.25	99.54	42	45.50	99.10
13	51.09	100.41	43	45.22	98.33
14	51.31	100.46	44	44.23	99.08
15	51.35	102.10	45	44.10	98.52
16	51.46	103.03	46	43.42	98.27
17	52.05	104.21	47	43.11	94.55
18	52.11	105.45	48	43.19	94.03
19	53.00	106.45	49	43.40	95.05
20	53.21	108.08	50	43.31	95.05
21	53.29	109.03	51	44.12	97.07
22	52.39	108.15	52	44.23	97.32
23	51.52	108.00	53	44.39	96.33
24	50.16	108.24	54	45.05	97.35
25	50.09	106.48	55	45.35	97.25
26	50.11	106.30	56	47.02	99.18
27	51.37	106.34	57	48.35	99.12
28	51.14	105.03	58	48.35	98.50
29	50.48	104.14	59	49.07	97.34
30	49.50	104.53	60	50.13	97.08



Appendix B. Location of weather stations from which climatic data (15-day precipitation volume and elapsed time between wetland sampling and last precipitation event) were collected.

Appendix C. Landscape variability and pesticide sink potential of PPR wetlands

C. 1 Introduction

The majority of wetlands in the Prairie Pothole Region (PPR) of North America have a common glacial genesis and are members of the freshwater marsh class (Mitsch and Gosselink 2000). These wetlands also share similar functions and values. For instance, PPR wetlands provide habitat for waterfowl and together they account for 50 to 70% of North America's total waterfowl production (Batt *et al.* 1989, Millar 1989). Additionally, the hydrodynamic functions of prairie wetlands are of value to society in terms of flood abatement (Preston and Bedford 1988, Miller and Nudds 1996, Juliano 1999). By retaining water after rain events and snowmelts, wetlands can slow the rate of downstream discharge and reduce the risk of floods (Ludden *et al.* 1983, Hubbard and Linder 1986).

Agencies promoting wetland conservation have suggested that PPR wetlands may function as pesticide sinks capable of reducing the adverse environmental effects of pesticide use (Manitoba Environment 1997, Gabor *et al.* 2001). To be of value as a pesticide sink, the amount of pesticide entering a wetland needs to be significantly more than the amount leaving it. Pesticide export can be lower than import if pesticides are retained or degraded within an environment. Environmental conditions that favour pesticide degradation or sorption include warm temperatures and high organic matter content, respectively (Mersie and Seybold 1996, Karuppiah *et al.* 1997, Morrica *et al.* 2001). Temperature has a direct effect on the rate of degradation of most pesticides (Morrica *et al.* 2001). Furthermore, a direct relationship between an environment's organic matter content and the extent of pesticide sorption has been reported in aquatic environments including North American wetlands (Mersie and Seybold 1996, Karuppiah *et al.* 1997). Organic matter in an environment can also determine the extent of microbial pesticide degradation, as microbial concentrations tend to be higher in environments rich in organic matter (Simsiman and Chesters 1976, Pritchard 1987).

The objective of this study was to characterise the level of environmental variability in PPR wetlands in order to determine if the pesticide sink potential of PPR wetlands could be predicted based upon their geographical location and the surrounding soil type. The climate (as dictated by wetland location) and soil type could determine the pesticide sink potential of wetlands through their effect on water temperature and organic matter content.

C. 2 Materials and Methods

Description of study area

Sixty wetlands were selected within the PPR of two Canadian provinces (Manitoba, Saskatchewan) and five American states (Iowa, Minnesota, Montana, North Dakota, South Dakota) (Figure 4). The distance between the two farthest sites was approximately 1,700 km. There are three major soil types within the study area: brown, dark brown, and black (Sheehan *et al.* 1987). Moraines and shallow depressions, formed during the Pleistocene epoch, characterize the morphology of the study area (Sheehan *et al.* 1987).

Site Selection

Survey sites were not selected at random but *a priori* to maximize their spatial variability across the study region (Laing and Smol 2000, Skjelkvale *et al.* 2001). The site selection processes was difficult given the great number of wetlands within the PPR, the absence of a comprehensive wetland database, the region's large area (715,000 km^2, Euliss *et al.* 1999) and the limited timeframe for sampling. Sites selected were either semi-permanent or permanent wetlands (Class 4 and 5; Stewart and Kantrud 1971) that were within one kilometer of public roads for ease of sampling access. Semi-permanent and permanent wetlands were selected to increase the likelihood that they would contain water at the time of sampling.

In Canada the PPR was divided into blocks 2° latitude by 2° longitude. At least one wetland was selected within each block. The Canadian Wildlife Service's Spring Pond Count (CWSPC) was used for site selection. The CWSPC is conducted through aerial

enumeration of wetlands (M. Shuster, Canadian Wildlife Service, pers. comm. 1998). Roads chosen were those that most closely paralleled the boundaries of the PPR as well those that encompassed a wide spatial range within the PPR (Figure 11). Only wetlands accessible from public land (road allowance) were selected. This was done to avoid the often lengthy process of obtaining permission to access private land (Lesser 2001).

The Gleason database (Gleason and Euliss 1996) was used to select US wetlands with a wide spatial distribution. This database consists of wetlands on both public and private land. Again to avoid the process of obtaining permission to access private land I only selected wetlands that were managed by the United States Fish and Wildlife Service (USFWS).

Field sampling and analysis

Field variables were selected based on their influence on pesticide sorption and degradation (Table C1). Wetlands were sampled between June and July 1999. The depth of the wetlands was measured in the middle of the open water area using a graduated measuring line. Temperature near the water surface (10 cm depth) and just above the sediment (5 cm) was recorded at each site.

To quantify phytoplankton chlorophyll and dissolved organic carbon (DOC), two, one-litre depth-integrated water samples were collected from the center of each wetland using a stoppered acrylic tube (6.4 cm inner diameter, 1.5 m length) (McDougal 2002). This sampling method provided a well-mixed integration of the entire water column. The water samples were poured into pre-rinsed opaque polyethylene bottles and stored at 4°C prior to analysis. Samples were analyzed for phytoplankton chlorophyll content by filtering 250 mL through glass microfiber filters (grade GF/C, particle retention 1.2 microns, Whatman International Ltd., England). The filters were neutralized with three drops of saturated magnesium carbonate solution then frozen for a minimum of 24 hours to lyse algal cells. Filters were then placed in 90% methanol and kept in the dark for 24 hours to extract the pigments. Chlorophyll concentrations of the pigment extract were

Table C1. Environmental variables measured in PPR wetlands and their influence on pesticide fate as reported in the literature.

Variable	Effect	Reference
Water temperature	Temperature has direct effect on abiotic degradation of pesticides	Morrica *et al.* 2002
Phytoplankton	Surface area for pesticide sorption	Sheng *et al.* 2002
	May provide substrata for pesticide transforming microbes	Pritchard 1987
DOC	Surface area for pesticide sorption	Chiou *et al.* 1986
Submersed macrophyte	Surface area for pesticide sorption	Karen *et al.* 1998
	May provide substrata and habitat for pesticide-transforming microbes	Girbal *et al.* 2000
Percent sediment organic matter	Surface area for pesticide sorption	Moore *et al.* 2002
	May provide substrata for pesticide-transforming microbes	Pritchard 1987

measured spectrophotometrically (Spectronic 601, Milton Roy Company, Rochester, NY) at 665 nm and 750 nm before and after acidification with 10^{-3} N HCl. Chlorophyll concentration (μg/L) was determined as of Marker *et al.* (1980). The DOC content of filtered (Whatman GF/C, particle retention 1.2 μm) water samples was determined using the persulfate-ultraviolet oxidation method (American Public Health Association 1992).

Sediment samples were collected in the middle of the open water area from each wetland site using a stoppered acrylic tube (6.4 cm inner diameter, 1.5 m length). The tube was pushed 10 cm into the sediment, stoppered and removed. The sediment (approximately 31 cm^3) in the tube was pushed out using a plunger into plastic bags. To determine the organic matter content of the sediment, pre-weighed, oven-dried (100°C) sediment samples (2 cm^3) were combusted at 600°C for one hour then reweighed (Dean 1974).

A sample of submersed macrophytes was collected from the center of each wetland. An open-ended plastic barrel was used to delineate a 0.45 m^2 section of the sediments. Long-handled shears and a dipper sieve (1 mm mesh size) were used to cut and collect the above-ground portion of the macrophytes at the sediment surface. Collected macrophytes were placed into plastic bags for temporary storage and transfer to the laboratory. Samples were sorted to the genus level then dried at 104°C for 24 hours and weighed for calculation of biomass (g/m^2).

Statistical Analysis

To determine if wetland location influenced pesticide sink potential, wetlands were divided into zones based on their geography and surrounding soil environment (Figures C1 and C2). The three geographic zones used were based upon latitude and consisted of the Northern group (54° - 50° N) (25 sites), the Central group (50° - 46° N) (20 sites), and the Southern group (46° - 42° N) (15 sites) (Figure 49). Wetlands were also divided into the following groups based upon the surrounding general soil type: Black Soil (39 sites), Brown Soil (4 sites), and Dark Brown Soil (17 sites) (Figure C2).

Data were log (x + 1) transformed prior to analyses to stabilize the variance and approximate the normal distribution. Multivariate analysis of variance (MANOVA) was done using the SAS System for Windows Version 8.0 (proc discrim) to determine if geographical location and soil type groups were bases for variation in physical, chemical, and biological variables. F-values were calculated from the Wilks Lambda test statistic.

One-way ANOVAs (proc glm) followed by Tukey post hoc tests were done to determine which variable(s) were significantly different among the assigned wetland zones.

C. 3 Results

The 60 study wetlands had water depths in the center averaging 69 cm (20 to 110 cm) at the time of the survey. There was no evidence of thermal stratification in the wetlands, as the average difference between temperature at a depth of 10 cm and at the sediment water interface was only 1.0°C (± 0.2, n = 60). Wetlands exhibited a wide range of phytoplankton total chlorophyll (mean 58.8 mg/L ± 8.2, n = 60, range 1.8 to 287.4 mg/L), DOC (1693 μmolC/L ± 112, n = 60, range 350 to 5750 μmolC/L), sediment organic matter (mean 10.2% of dry weight ± 1.1, n = 60, range 3.6 to 53.7%) and macrophyte biomass (mean 30.5 g/m^2 ± 6.0, range 0 to 176 g/m^2).

MANOVA revealed that wetland geographical groups were significantly different from each other ($F_{12,104} = 3.17$; $p < 0.001$). These results indicate that wetlands in at least one geographical group had significantly different environmental conditions from wetlands in other geographical groups. MANOVA of the wetland soil groups ($F_{12,104} = 3.39$; $p < 0.001$) also showed significant difference among groups.

An ANOVA followed by a Tukey's test revealed that water temperature was significantly ($p < 0.05$) lower in wetlands of the northern geographic group (mean ± SE, North 18.6 °C ± 0.9 n = 22, Central 21.9°C ± 0.4 n = 22, South 24.4°C ± 0.8 n = 16).

ANOVA followed by post hoc Tukey's tests revealed that wetlands in the black soil zone had significantly ($p < 0.05$) higher sediment organic matter (mean ± SE, 13.0% of

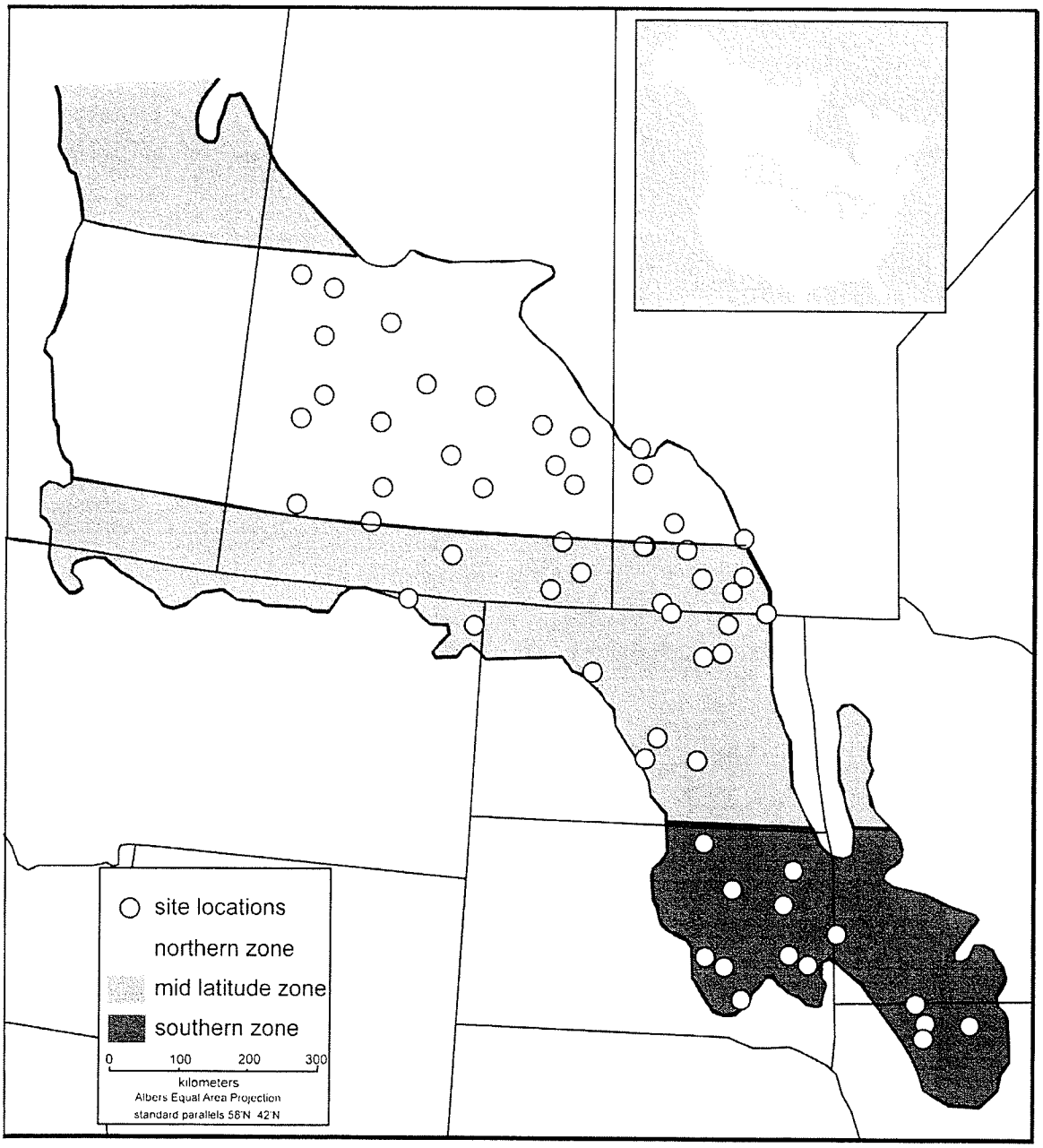


Figure C1. Map of the geographic zones used to determine if pesticide sink potential varied in a predictable manner based on wetland geography.

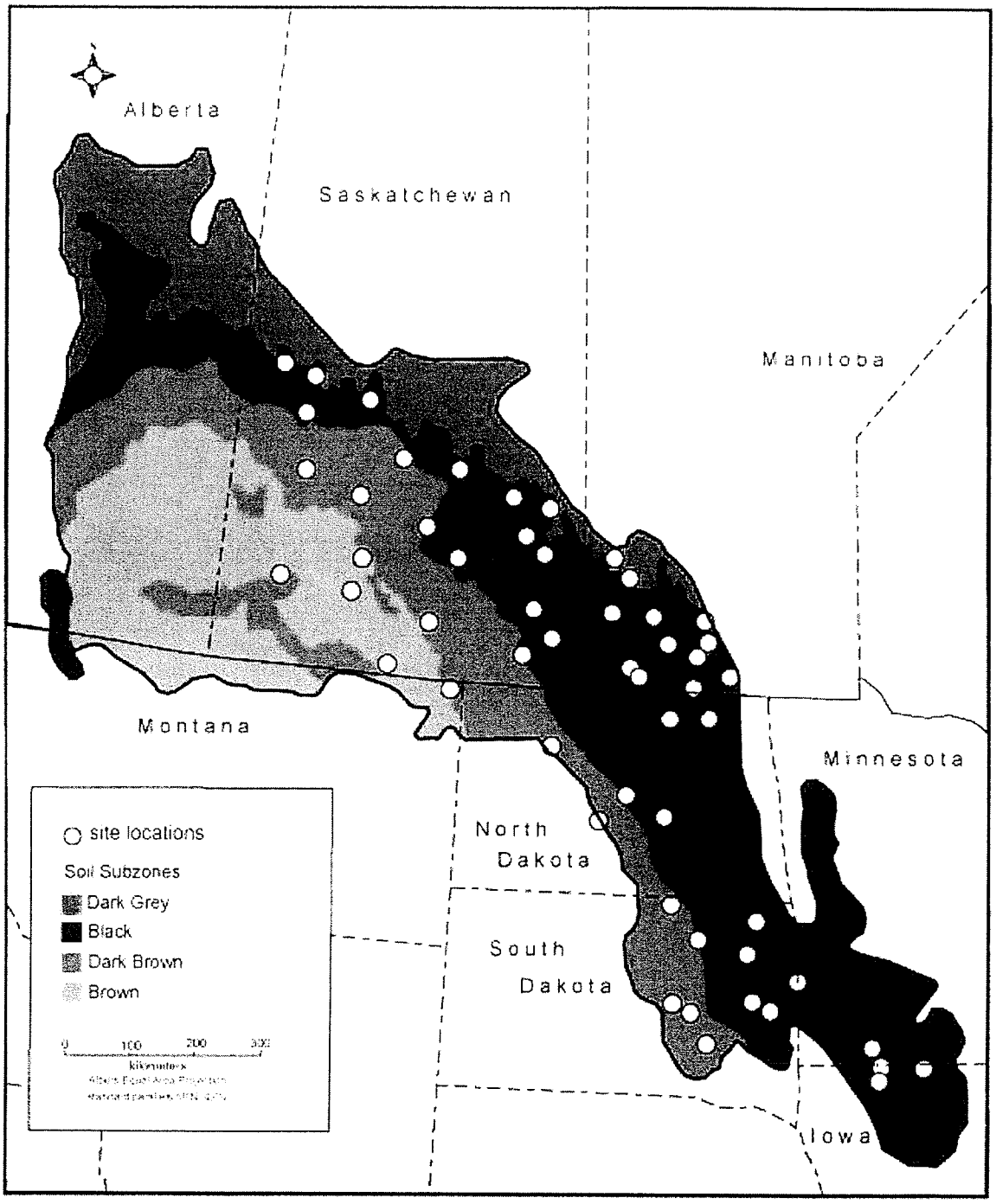


Figure C2. Map of the soil zones used to determine if pesticide sink potential varied in a predictable manner based on the soil type surrounding the wetlands.

dry weight ± 0.1 n = 39) than those wetlands in the Dark Brown (7.3% of dry weight ± 0.1 n = 14) and Brown (9.5% of dry weight ± 0.1 n = 7) soil zones.

C. 4 Discussion

Wetlands within the PPR have varying environmental conditions and consequently may have varying pesticide sink potentials. This variability will be due, in part. to the geographical location of the wetlands. Wetland water temperature tends to increase in a north-south gradient because of differences in climate within the region (Winter 1989). Temperature can directly increase pesticide degradation through its effects on biotic and abiotic chemical reactions (Larson *et al.* 1981, Wolfe *et al.* 1990, van Loon and Duffy 2000, Morrica *et al.* 2001). Thus, an argument could be made that the warmer water of southern PPR will have greater pesticide sink potential than northern PPR wetlands due to enhanced pesticide degradation. However, increased temperature could also decrease an environments pesticide sink potential if it led to increased pesticide volatilization (Stork *et al.* (1998). In this regard the cooler water temperatures of northern PPR wetlands may increase their pesticide sink potential by limiting volatilization. *In situ* experiments are needed to evaluate the exact consequence of increased temperature on the pesticide sink potential of wetlands. However, it does seem likely that, due to their differences in water temperature, wetland sink potential of northern wetlands will differ from their more southerly counterparts.

Aside from temperature, the only variable that could be predicted based upon wetland location was sediment organic matter. Wetlands within the Black Soil Zone had higher sediment organic matter concentrations than wetlands in the Dark Brown and Brown soil zones. Soil is frequently deposited in prairie wetlands through wind and water erosion (Martin and Hartman 1987, Gleason and Euliss 1998). The higher organic matter content of wetlands within the Black Soil Zone could then be attributed to the higher organic matter content of the surrounding soils. The higher sediment organic matter

content of Black Soil Zone may increase their pesticide sink potential by enhancing pesticide sorption and degradation (by increasing the microbial content).

The variability of water column and macrophyte organic matter content could not be predicted by the location of the wetland. This may be due to differences in hydrology and landuse within the geographic and soil zones. For instance, wetlands within the same geographic or soil zone may receive different amounts of surface inflow. Surface inflow can transport DOC, and nutrients (which may in turn influence phytoplankton and macrophyte concentrations) into wetlands. Wetlands in the same geographic and soil zone may have different fish and mammal biota which could influence water column and macrophyte organic content.

C. 5 Conclusion

The variability of wetland conditions within the PPR suggests that the pesticide sink potential of these wetlands will also vary. Northern wetlands may have different pesticide sink potential than southern wetlands due to their cooler temperatures. Additionally, wetlands in the Black Soil Zone, due to their higher sediment organic matter, may have greater pesticide sink potential than wetlands of other soil zones. The geographic and soil groups used could not account for a significant amount of the variability in water column organic matter or submersed vegetation. These parameters can be important in determining pesticide dissipation in aquatic environments. Thus, results from pesticide dissipation experiments conducted in one wetland may not always be accurately extrapolated to another even if the wetlands are in close proximity to each other or found in similar soil zones.