

**AN EVALUATION OF THE POLLUTANTS  
ENTERING ONTARIOS WETLANDS:  
HOW LANDUSE IMPACTS WETLAND HEALTH**

**AN EVALUATION OF THE POLLUTANTS  
ENTERING ONTARIOS WETLANDS:  
HOW LANDUSE IMPACTS WETLAND HEALTH**

**By**

**BARB CROSBIE, B.Sc.**

**A Thesis**

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**TITLE:** An Evaluation of the Pollutants Entering  
Ontarios Wetlands: How Landuse Impacts  
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## ABSTRACT

**CROSBIE, BARB, M.Sc. McMaster University, Hamilton, Ontario, Canada. May 1997. AN EVALUATION OF THE POLLUTANTS ENTERING ONTARIOS WETLANDS: HOW LANDUSE IMPACTS WETLAND HEALTH**

To assess the impacts of non-point source pollution on Ontarios wetlands I examined the landuse in the watershed, the water and sediment quality, and the aquatic vegetation in 22 wetlands. I characterized the primary contaminants that enter marshes in Ontario and relate their concentrations to the relative amounts and types of landuse in their watershed. I measured levels of nutrients, suspended particulates and trace organics in water and sediment. Species richness and structural diversity of the vegetative community was used as an indicator of wetland health. I included a comparison of two techniques, immunoassays and gas-chromatography (GC) to measure trace organics (PAHs and metolachlor; Chapter 1). Comparison of results from both techniques indicated that immunoassays overestimated analyte concentration by approximately a third. I utilized the immunoassay results, along with selected water quality variables, to characterize contaminants entering these wetlands (Chapter 2). Watersheds containing greater than 95% agriculture contributed the highest suspended particulate, compared with those dominated by urban or forested land. Using multivariate statistics I identified important water and sediment variables that structured these wetlands to be: total phosphorus (TP), ammonia nitrogen (TAN), suspended solids (TSS), specific conductance (COND), sediment phosphorus ( $TP_{sed}$ ) and inorganic material ( $Inorg_{sed}$ ) in the sediment. Of these TP, COND and  $Inorg_{sed}$  were negatively related to the submergent plant community, while  $TP_{sed}$  was positively related. There was no relationship between water quality and the



floating or emergent plants but the structural diversity of the plant community was negatively affected by poor water quality. The negative impact of developed land in the watershed on the health of the aquatic plant communities underscores the need to maintain natural areas to trap nutrients and sediments in runoff.

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## GENERAL INTRODUCTION

Wetlands are integral components of our ecosphere that are essential for the survival of terrestrial and aquatic organisms. Wetlands are areas that are seasonally or permanently flooded by shallow water as well as lands where the water table is close to the surface; in either case the presence of abundant water has caused the formation of hydric soils and has favoured the dominance of water tolerant plants (OMNR, 1993). This study focuses on marshes, which are concentric zones of plants of various life forms (submergent, emergent and floating) surrounding a deeper, open water area. This zonation results in structural plant diversity important for maintaining the biodiversity of the whole wetland community (Lillie and Evrard, 1991). Wetland dwelling species are dependent on these plants for habitat and/or food. For example, submergent vegetation is a vital component of the plant community because it provides food and/or habitat for waterfowl, benthic and pelagic invertebrates and warmwater fish. Aquatic plants also create or maintain suitable habitat by controlling floods, improving water and sediment quality, and preventing erosion of shorelines (Russell, 1987). They assimilate nutrients by uptake from the sediment or water column, and allow suspended solids to drop out of suspension by reducing flow velocities. These characteristics highlight some of the many ecological and economic benefits of wetlands and in particular the plant community.

Previous studies have shown that submersed aquatic plants are unable to survive in low light conditions, resulting from either high sediment loading or eutrophication (Chambers and Kalff, 1985; Hough et al., 1989). The dependence of wetland plants on good water quality increases their susceptibility to degradation in heavily disturbed areas.

Poor water quality can result in loss of species diversity and promotion of monocultures of opportunistic species. With the loss of macrophytes, phytoplankton and epiphytes dominate and further inhibit plant development (Phillips et al., 1978; Hough et al., 1989; Mitchell, 1989).

In Ontario an estimated 68% of wetland areas have been infilled or dredged to accommodate other land uses (ie. urban development, agriculture; Snell, 1987). Currently, measures to protect remaining wetlands are being implemented at three levels of government in Canada (i.e. Federal Policy on Wetland Conservation, Wetland Policy Statement), as well as internationally. Despite these measures, wetland losses in Southern Ontario are estimated at 0.2% annually (Snell, 1987). Therefore the impacts of external inputs on these systems needs to be better understood before we can effectively manage our remaining wetlands.

Examples of non-point source pollutants include suspended sediment, nutrients, pesticides and trace organics which are generally associated with landuse in the watershed. Previous studies have shown that increased suspended solids and nutrients are associated with agricultural and urban landuse (Peterjohn and Correll, 1984; Lowrance et al., 1996; Roth et al., 1996). Erosion from exposed soils and runoff from impervious surfaces are two sources of increased particulate loading. Eutrophication of urban and agricultural wetlands has resulted from increased fertilizer use and inputs from animal waste (Humenik et al., 1987). Combined sewer overflows, stormwater sewers and sewage treatment plants are major culprits discharging nutrient-rich waters (Marsalek, 1990). Trace organic pollutants are associated with both urban and agricultural practices. In urban areas the levels of PAHs are increased due to auto and industrial emissions (Maltby et al., 1995) while levels of herbicides increase due to farming in the watershed (Gaynor et al., 1995).

Unlike nutrients and suspended solids, the impact of trace organics on the wetlands has received little attention. Herbicides are non-selective and may have severe impacts on the wetland plant community (DeNoyelles et al., 1982). PAHs are lipophilic and tend to bind to sediments and therefore accumulate in this layer (Marvin et al., 1994). The effects of their uptake by plants or organisms poses risk to both ecosystem and human health since they accumulate in the food web. Because wetland health may be affected by more than one of these parameters it is important that the source and degree of impact of each be studied concurrently.

The link among water quality, landuse and plant community needs to be investigated to improve our understanding of the impacts of anthropogenic activity on wetland health. Programs involving the management of wetland areas are being developed despite our poor understanding of this relationship (SOLEC, 1995). Although we know that water quality can affect the plant community, the key variables have not yet been identified and in many instances, wetland restoration/preservation programs operate in the absence of a scientific basis.

My contribution to this is to establish the link between landuse and water quality, and that between water quality and wetland health. I will characterize the primary contaminants that enter marshes in Ontario and relate their concentrations to the relative amounts and types of landuse in their watershed. Twenty-two wetlands, located mainly in the Great Lakes basin, are included in this study. These wetlands have been evaluated under the Wetland Evaluation program of the Ontario Ministry of Natural Resources and are therefore no longer affected by point-source pollution. Additionally, for many of these wetlands, which are currently being restored, I had access to previously collected information, which complemented this database.

Trace organics may be an important pollutant in these wetlands. However traditional methods used in measuring these compounds are expensive, time consuming, require trained technicians and generate high volumes of waste. To alleviate the problems of expense and time of traditional methods (gas chromatography) for measuring their levels, I determined the reliability of immunoassays as an alternative method for measuring two organics, polycyclic aromatic hydrocarbons (PAHs) and metolachlor. This newer method is inexpensive, quick and easy to use; however, its reliability in measuring contaminants in field samples has not been established. To compensate for this I measured a random sample of 4% of the total number of samples using gas chromatography techniques. In Chapter 1, I compare immunoassay and gas chromatography (GC) results. Fourteen surface water samples were measured for metolachlor and 10 sediment samples were analyzed for PAHs using immunoassays. Of these four metolachlor and 5 PAH samples were also analyzed using Environment Canada GC methods. I found a significant relationship between these two methods, with immunoassays providing consistently higher results. A correction factor could be applied to the immunoassay results to provide measurements that would be expected if measured by traditional methods

The immunoassay results were used in Chapter 2, an investigation of the common contaminants entering wetland systems. The types of contaminants that I investigate fall into four categories: organic (PAHs, metolachlor), nutrient (total phosphorus, nitrate nitrogen), sediment (total and inorganic suspended solids, turbidity) and thermal/salt pollution (water temperature, specific conductance). I relate their levels to the distribution of agricultural, urban and forested land in the watershed. Agriculture contributes the highest levels of all contaminants, except for specific conductance and PAHs, which are higher in urban areas.

In Chapter 3, I use Principal Components Analysis (PCA) to target the key water and sediment variables that explain most of the variation in the dataset. Following this, the impact of these variables on the plant community is evaluated using Canonical Correspondence Analysis (CCA). The structural diversity of the aquatic vegetation is used as a measure of wetland health, which is also related to these key water quality parameters. Additionally, I relate the log sum of total phosphorus, inorganic nitrogen and suspended solids ("cumulative degradation index") to the amount of altered land in the watershed (agriculture plus urban), and explore the relationships of forest, agriculture and urban land to the characterized principal component scores. From these results I evaluate the impact of each type of landuse on wetland health, and suggest important monitoring variables. Additionally I discuss the importance of maintaining buffer strips and/or forested land in the watershed to prevent wetland degradation for non-point source pollution.

This study contributes much needed information to the restoration/preservation of wetlands in populated areas. It provides a good scientific basis for choosing variables to monitor wetland health which would assist in the development of more effective and efficient sampling programs. In light of current budget cuts, fewer long-term exhaustive studies are feasible and this study offers a solution to this problem. Additionally, it emphasizes the importance of maintaining forested land around the wetland and its tributaries, to lessen the impacts of non-point source pollution associated with altered land. I recommend that landuse developers and wetland managers work together to effectively protect remaining wetlands, to prevent problems associated restoration efforts in areas devoid of forest.



## **ORGANIZATION OF THIS THESIS**

Each of the main chapters are self-contained papers that will be submitted for publication. Hence, authorship varies and reflects the contributions from myself, Patricia Chow-Fraser (supervisor), Devon Cancilla and Donna Zaruk. In all cases the samples were collected and analyzed by myself. Additionally, each of these papers were written by myself. In the first chapter, authorship involves all four parties. Partial funding and lab space was provided by Environment Canada through Devon Cancilla. Donna Zaruk was responsible for my training in these analyses and operation of the gas chromatograph. The second and third chapters were authored by myself and Patricia Chow-Fraser.

**Chapter 1:**

**A Comparison of Immunoassay and Gas Chromatography  
Techniques for Measuring Two Organic Contaminants in Water  
and Sediment**

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## ABSTRACT

Traditional methods for measuring environmental contaminants such as trace organics and herbicides involve gas chromatography (GC) methods, these are expensive, time-consuming and require trained technicians. In light of current budget cuts, an inexpensive, quick and efficient method is required if long-term monitoring is to be maintained. Immunoassays are a suitable alternative because they provide semi-quantitative results at approximately one-tenth the cost, and produce measurements for about 40 samples in less than 2 hours. We collected water and sediment samples from 20 wetland systems in Ontario and analyzed 7 wetlands using GC methods and all 20 by immunoassays. From 14 of these wetlands surface waters were analyzed for metolachlor and from 10, the polycyclic aromatic hydrocarbons (PAHs) in the sediments were measured. A significant relationship was found between the two techniques ( $r^2=0.972$ ,  $p=0.0001$ ) with immunoassays providing consistently elevated levels over those provided by GC ( $y=1.007x + 0.713$ ). By applying a correction factor to immunoassay results, a closer approximation to gas chromatography measurements could be obtained for these samples. These results indicate that immunoassays are useful for targeting sites containing contaminant levels above guideline concentrations.

## INTRODUCTION

Contamination of aquatic systems is a subject of great concern as it poses risk to both environmental and human health. With an increase in the production, use and release of these potential contaminants, it is vital that their effects on the environment be monitored. The problem in tracking the fate of these compounds lies with the expense and time-consuming nature of the methods used to quantify them. Compounding this problem is the fact that new environmental contaminants are being produced annually (Baker et al., 1991), while governments are losing ground in regulating their use and release, and in monitoring their distribution in nature because of dwindling budgets.

Many organic compounds have proven to be carcinogenic and/or mutagenic to test organisms, especially a group of compounds known as polycyclic aromatic hydrocarbons (PAHs) (Marvin et al., 1994). Since PAHs are by-products of the incomplete combustion of fossil fuels, their distribution is ubiquitous and pose potential health risk to humans living in industrial and urbanized areas, throughout the world. They enter the natural environment via a variety of means such as atmospheric deposition, roadway runoff, and industrial effluents. Once they enter a watercourse, they readily adsorb to suspended particles, settle out of the water column, and accumulate in the sediment. Owing to their lipophilic nature, PAHs accumulate in the fats of benthic organisms that feed on detritus, and eventually become incorporated into higher trophic levels for example, benthivorous fish, invertebrate predators and waterfowl (Baker et al., 1991; Kukkonen and Landrum, 1995). Studies on fish indicate that PAHs can be accumulated and concentrated

in their tissues, while molluscs tend to concentrate them in their feces (Marvin et. al., 1994). In light of the well-established health risk of PAHs to both humans and non-humans, it is essential that these organic compounds be monitored vigilantly, to keep track of their distribution in the natural environment.

Herbicides constitute another group of organic compounds that are of concern to ecosystem health. They are widely used in agricultural and urban settings to control weedy species. Herbicides, when applied in excess, concentrate in creeks and streams that receive agricultural runoff. Even though regulatory agencies have placed limits on the amount of herbicide allowed to be applied aerially in one season, high levels of herbicide contamination still occur, especially when a large percentage of land in the watershed is receiving herbicide treatment. In turn, elevated herbicide levels in receiving waters destroy aquatic vegetation which are important functional components of wetlands since they provide habitat for fish, waterfowl and wildlife, and help assimilate incoming nutrients and filter out particulates. Herbicides selectively inhibit the growth of beneficial macrophytes, and permit proliferation of resistant and less desirable species, which ultimately leads to a plant community with lower diversity and an altered food web structure (DeNoyelles et al., 1982). An example of such a herbicide is metolachlor, a pre- and post-emergent herbicide used across N. America to control weedy plant species in agricultural lands. In a recent study, Gaynor et al. (1995a) indicated that agricultural runoff is the largest source of metolachlor in aquatic systems, and despite this, few monitoring programs include this contaminant because of the expense involved in sample processing and measurement.

Traditional methods used to analyze water and sediment samples for PAHs and metolachlor require the use of gas chromatographic (GC) methods which involves extensive sample preparation, extraction methods and clean-up processes (Hall et al., 1990;

Gruessner et al., 1995; Zaurk et al., 1995). With grants and budgets being cut, these extremely labour-intensive, cumbersome and expensive methods are no longer feasible for long-term monitoring programs. An alternative technique, based on enzyme-linked immunoassay (ELISA) has been developed, which yields semi-quantitative results, but is considerably cheaper to use and can be performed in a fraction of the time (Zaruk et al., 1995). In this study, we compare the performance of the immunoassay technique against a conventional GC method to measure concentrations of total PAHs in sediments and metalochlor in water samples collected from 15 creeks and wetlands in southern Ontario. We have included wetlands that range from moderately to severely degraded, which are associated with a variety of land use in the catchment area. Therefore, our results should indicate the feasibility of using immunoassays in routine monitoring programs where contamination from agricultural and highway run-off is suspected.

## METHODS

### *Field Sampling*

Sediment samples were collected from 3 sites (at an open-water site, a vegetated site, and in an incoming tributary) within 10 different wetlands (n=33) in 1995 (Table 1.1). The top 5 cm of sediment were collected using an Eckman Grab sampler, where possible, or a plexiglass tube 5 cm in diameter, equipped with a plunger. These samples were kept at 5°C until analysis and then placed in a dehydrator for a 24-hr period at 35°C to remove the water from the sediment. Subsamples were stored in a desiccator until analysis by either immunoassay or gas-chromatography mass-spectrometry (GC-MS).

Surface water samples were collected from 14 different marshes in 1996 during June and July. They were stored in the dark in amber bottles at 5°C until analysis. 1-L samples were collected from four marshes during June for GC-NPD (nitrogen-phosphorus detection) and immunoassay analysis, these homogenous samples were analyzed by the two techniques. All water samples were collected in washed and solvent rinsed glassware with teflon or foil-lined lids.

Lab, field and travel blanks and spikes were integrated in the sampling protocol for immunoassays, to account for any methodological source of error. Since only a 4% confirmation using GC methods was employed, along with the associated cost of processing these samples, the same sampling protocol as immunoassays was not followed. Only lab blanks and spikes were employed in GC analysis.

### ***Immunoassay Analysis***

The enzyme-linked immunoassay technique utilizes polyclonal antibodies coated to the walls of the microwells in the test kit, and an enzyme conjugate which competes for binding sites with the contaminant of interest present in the collected sample. The amount of the target compound(s) in the sample is thus inversely proportional to the amount of colour produced by the reaction. The coloured products were measured spectrophotometrically on a microplate reader fitted with the appropriate wavelength filter. Sample concentrations were measured using the optical density (OD) reading of each well, the machine providing a blank corrected OD. Duplicates, spikes and blanks were run on the kit to measure variation, recovery and contamination in both the lab and field.

### ***Metolachlor***

Quantix<sup>TM</sup> Metolachlor 1.0 Immunoassay Kits (Idetek, Inc., Sunnyvale, CA, U.S.A.) were used to measure the metolachlor concentrations in water samples. The quantification range for this kit was 0.1 to 4.0 µg/L for metolachlor. 200 µL of each of the standards, the negative control and the water samples were added to two consecutive wells on the immunoassay plate, except for the two blanks. 50 µL of the Enzyme Conjugate Solution was immediately added to the wells containing the various solutions. Samples were thoroughly shaken for 10-min to allow all metolachlor present in the samples to react with the conjugate in the wells. After shaking the plate was rinsed five times with the Wash Solution and then tapped on absorbent tissue to eliminate excess water. 200 µL of the Substrate Solution was added to all the wells and shaken for 10-min to allow colour development. A 50 µL aliquot of Stop Solution was added to terminate colour development, following which all the wells were read spectrophotometrically at 650 nm.



From the calibration standards, a six-point linear curve was generated to relate percent absorbance (%Bo, transformed by  $\log_{10} \text{Bo}/1-\text{Bo}$ ) to sample concentration (Fig 1.1).

### *PAHs*

The MILLIPORE EnviroGard™ Polynuclear Aromatic Hydrocarbons (PAH) in Soil Plate Kit (Millipore Intertech, U.S.A.) was used to extract and analyze total PAHs. The range was between 1.0 and 10 ng/g in soils and the kit was the most sensitive for pyrene. Five grams of dried sediment was extracted in 5 or 10 mL of methanol to release the sediment-bound PAHs (depending on particle size). 10  $\mu\text{L}$  of the sediment extracts and calibrators were diluted with 2 mL of a 10% methanol solution, to prevent evaporation of the extracts during analysis. 100  $\mu\text{L}$  of the two calibration standards, the negative control and each of the sample extract solutions were added to two of the wells on the plate, except for the two blank wells. In the same manner, 100  $\mu\text{L}$  of PAH-Enzyme Conjugate was added to all wells (except for the blanks) mixed for 1-min, covered with Parafilm to prevent evaporation and incubated for a 1-h period. After the incubation period the plate was vigorously shaken, rinsed five times with distilled water and tapped on absorbant tissue to remove excess water. 100  $\mu\text{L}$  of Substrate was added to each of the wells, mixed and incubated for an additional 30 min, again covered with Parafilm. To stop the reaction, 100  $\mu\text{L}$  of Stop Solution was added, mixed, and the samples were measured spectrophotometrically at 450 nm. A standard curve was generated from the calibration standards to relate the percent absorbance (%Bo, transformed by  $\log_{10} \text{Bo}/1-\text{Bo}$ ) to the concentration of the sample.

### *Gas Chromatography (GC) Analysis*

All solvents used were pesticide grade (Fisher Scientific) and analytical standards were greater than 98% purity. Spikes were made by diluting the analytical standards to a known concentration in methanol. Method blanks (ASTM Type I grade water), spikes, sample spikes and duplicates were run to measure contamination, recovery and variation within the lab and field. Instrument performance checks were used to test detector and chromatographic response, prior to sample runs. The instrument was calibrated by running calibration standards to quantify the target analytes and to ensure the response factors were within 20% of the initial calibration standard. Quantification was based on the height of the peak<sub>sample</sub> relative to the height of the peak<sub>standard</sub>.

### *Metolachlor*

Environment Canada Method 03-3151 was used for the analysis of metolachlor in water samples using liquid-liquid extraction and GC-NPD. Raw water samples were extracted for metolachlor with 100 mL plus 2x50 mL aliquots of dichloromethane. This extract was filtered through an Allihn funnel packed with anhydrous sodium sulphate to remove water and impurities, and 25 mL of dichloromethane was added to ensure complete extract recovery. 5 mL of iso-octane was added to the extract and concentrated to 3 mL on a S-EVAP Analytical Evaporator. Following this the flask was rinsed twice with 2 mL of iso-octane and concentrated to a final volume of 3 mL, using a Turbo Vap LV Evaporator. 10% deactivated florisil with 1 cm of anhydrous sodium sulfate was packed in a 500x20 mm ID column to separate the fractions A (triflan, diallate and triallate) and B (hoegrass, endaven, atrazine and metolachlor). 150 mL of 2% methanol in dichloromethane was added to the florisil column to elute the B fraction. 10 mL of iso-octane was added to the B fraction and brought down to 3 mL using a RotaVap Evaporator to eliminate the dichloromethane. This extract plus 2x2 mL rinsings of iso-octane was concentrated to a final volume of 3-4 mL using the Turbo Vap LV Evaporator. The final

concentrate was made up to 10 mL using iso-octane, and 100  $\mu$ L of this was placed in a microvial and crimp-capped.

A HP 5890 gas liquid chromatograph equipped with a split/splitless dual capillary injection port and electron capture detectors was used to detect the presence of metolachlor. The capillary column utilized was a 30 m x 0.25 mm with DB-1 (confirmation) and DB-5 (primary) columns with 25 micron film thickness and fused silica. 3  $\mu$ L of the Fraction B extract was injected on the column at 250°C with a 30 sec purge time. GC temperature programming was 90°C for 2 min, with a 6°C/min increase to a final temperature of 275°C which was held for 8 min. The temperature of the electron capture detector was at 350°C. The chromatogram reports from both of the columns were checked for properly integrated, defined peaks with symmetry. We checked for variation in the internal standard and made positive identification of compounds if their retention time was comparable to the calibration standard and if they were detected on both columns.

Fraction B was further concentrated to 1  $\mu$ L using the Turbo Vap LV Evaporator and 100  $\mu$ L of this fraction was placed and crimp-capped in a micro-vial. The HP 5890 gas liquid chromatograph equipped with a split/splitless dual capillary injection port and nitrogen phosphorous detector was used after confirmation on the GC-ECD to further concentrate and analyze the metolachlor. The capillary column was the same for the GC-ECD except that only the DB-5 primary column was used. Only 2  $\mu$ L of extract was injected at 250°C on the column with a similar purge time of 30 sec. The three programming rates for the GC column were: initial column temperature at 80°C for 2 min, then increased 10°C/min up to 140°C followed by 6°C/min up to 240°C, then 20°C/min to 280°C and held for 10 min. The nitrogen-phosphorous detector was at 290°C. The

chromatogram and reports were checked in a similar manner to the GC-ECD results except only one column was used.

### *PAHs*

Environment Canada Method 03-3751 was used for the analysis of 16 PAHs in sediments. Samples were collected from the top 5 cm of sediment and stored in glass jars at 5°C until analysis. Duplicates were taken from a homogenous mixture to measure batch run variation; no field duplicates were taken. Cleaned-up sediment (blank and spiked) was used to determine if matrix interactions occurred due to the nature of sediment.

20 g of dried sediment were used for analyses and 30-40% of Type I water was added to each sample. At this point spikes were added to appropriate samples and allowed to stand covered for 20 min, to permit thorough mixing with the sediment. Ultrasonification was carried out in 100 mL of 1:1 acetone in hexane for 3 x 3 min cycles. The supernatant was poured into an Allihn funnel packed with celite to remove particulate matter, filtered through, and an additional 25 mL of 1:1 acetone in hexane was added to maximize extract recovery. This extract was then placed on the RotaVap and concentrated to 200 mL. This was placed in a separatory funnel to which 100 mL of Type I water was added first, followed by 3x100 mL additions of dichloromethane, the bottom layer being retained with each extraction. These combined extracts were filtered through an Allihn funnel packed with anhydrous sodium sulphate, to remove excess water, followed by addition of 25 mL of dichloromethane to maximize extract recovery. 10 mL of iso-octane was added and samples were concentrated to 3 ml using the RotaVap. The clean-up process involved the use of 2.5 cm of anhydrous sodium sulfate and 8 cm of 3% deactivated silica gel packed in 12x350 mm glass chromatography columns. The B fraction

which contained most of the PAHs was obtained from the addition of 60 mL of 1:1 hexane in dichloromethane. 10 mL of iso-octane was added to this fraction and concentrated to 3 mL using the RotaVap. This concentrated extract plus 2x3 mL rinsings of iso-octane was placed on a vortex mixer and concentrated to 5 mL, to eliminate the dichloromethane in the extract. 5 mL of iso-octane was added and the 10 mL aliquot was concentrated to 3 mL on the Turbo Vap LV Evaporator. Iso-octane was added to make the final concentration up to 10 mL. To remove elemental sulphur from the extracts Protocol 04-004 was utilized. 1 mL of the fraction A extract three drops of triple distilled mercury (elemental, BDH Analar grade) was added, capped and put on a vortex for several minutes, the extract being transferred to a clean vial. These steps were repeated until black precipitate ceased to form. Following this procedure 100 µL subsamples of the extract were placed in micro-vials and crimp-capped.

The micro-vials were placed in their prescribed tray pattern on the HP 7673A autosampler of the HP 5890 Series 2 Gas liquid chromatograph equipped with a split/splitless dual capillary column injection port and a mass selective detector (MSD)-5971. The GC contained a 30 m x 0.25 mm ID with 25 micron film thickness, fused silica-RTX-5. The 2 µL subsamples were injected onto the column at 250°C after 30 sec. The temperature program for the GC was initially 80°C for 3 min followed by 60°C/min increase to 180°C, then 30°C/min to 280°C; the transfer line to the mass selective detector was 285°C with the ion source having a temperature of 150°C and the mass analyzer set at 180°C. The duration of the program was 22 min. The performance of the GC/MSD was checked by running a standard SPECTRA autotune which set the operating conditions for the MSD. Following this a conditioning PAH standard was run to check the selected ion chromatogram and spectra for well-resolved peaks and baseline for proper integration of

peaks. Ions were quantified when the retention time was within 0.3 min of the calibration standard.

## RESULTS

### *Quality Control*

The immunoassay results were combined for all kits to allow for statistical testing. The variation within the two replicate wells was 4.44% (n=72; for all kits), the average recovery was 82% (n=9) and the lab and field duplicates did not differ significantly (n=17; paired t-test, p=0.450). The mean  $r^2$  value for the regression lines of the 6-pt standard curves was 0.987 for metolachlor (Fig 1).

As with the immunoassays, the gas chromatography results were combined to test for significance. The average recovery for spiked samples was 70% (n=4) and no significant difference was found between lab and field duplicates (n=5; paired t-test, p=0.114). All runs on the gas chromatograph had well-defined peaks and did not deviate more than 20% from the calibration standard.

This comparison indicates that the performance of both techniques was within quality control limits found acceptable in a previous study by Gruessner et al. (1995). Therefore measurement variation could be attributed to real differences in the samples analyzed.

### *Comparison of Methods*

We grouped results by methodology (regardless of analyte) to permit rigorous statistical comparison of the immunoassay versus chromatographic techniques. A strong relationship was found between the two methods ( $r^2=0.972$ , Fig. 1.2). The intercept of

the line (0.713) indicated that samples measured by immunoassays overestimated contaminant concentrations provided by traditional GC methods, although this relationship was consistent throughout the range of concentrations (slope=1.007).

We found no significant differences between results measured with GC and with the immunoassay technique for either PAHs (Paired t-test; n=7; P=0.06) or metolachlor (Paired t-test; n=4; P=0.11). On average, immunoassays yielded concentrations that were 1380.91 ( $\pm$ 812.5) pbb and 0.44 ( $\pm$ 0.19) ppb higher for PAHs and metolachlor, respectively (Table 1.2). A study by Gascon et al. (1995) illustrated the influence of cross-reacting compounds in generating false positive results. After evaluating our complete set of immunoassay results, we found that 20% of the samples (n=85) measured by immunoassays may have been false positives. False positives have been a common problem in previous studies, for example Gruessner et al. (1995) found that 5.5% of their samples produced false positive results. However in this study only surface water samples from streams were used, avoiding the high cross-reactivity associated with soil samples containing humic substances (Gascon et al., 1995). In a study by Baker et al. (1993) almost half of their soil samples provided false positive results foralachlor in sediment samples. More concern is generated over the presence of false negative results, of which none were detected in this study.



## DISCUSSION

The use of immunoassays to quantify PAHs and metolachlor in sediment and water samples appears to be a viable alternative to GC analysis for moderately to severely polluted wetlands in southern Ontario. Although immunoassays yielded overestimates compared with GC techniques, the errors appeared consistent throughout the range of concentrations. Further sampling would be useful to determine whether this is the case in other wetlands. The tendency for immunoassays to yield higher estimates has also been noted in previous studies (Hall et al., 1993; Brady et al., 1995; Gaynor et al., 1995b), and is most likely because in field samples, many organic compounds, other than the target analyte, compete for binding sites in immunoassay kits. This was likely the case in this unique study since many of the field samples were collected from organic-rich wetland sediments. Despite organic matrix interactions involved in the sediment extraction and immunoassay analysis, comparable results were obtained. Additionally the non-selective nature of immunoassays allow other closely related compounds to compete for binding sites (Gascon et al., 1995). GC methods, however, are more selective since they detect compounds based on retention times of the contaminants. The peaks produced at the retention time(s) of interest provide quantifiable peaks for the associated compound. This selective and sensitive nature of the GC technique allows for specific detection of individual substances, while immunoassays quantify all structurally related compounds (Law and Biscaya, 1994).

Cross-reactivity has a direct influence on immunoassay pesticide quantification (Gascon et al., 1995) and may limit the usefulness of the technique for certain types of

environmental samples. Despite their non-selective nature, immunoassays are useful in monitoring programs to screen for overall pesticide concentration, which can then be followed by GC analysis, if concentrations warrant. In this study, GC analysis for metolachlor detected the presence of other herbicides which probably led to cross-reactivity in the immunoassay kits. The nature of the antigen in herbicide immunoassay kits allows for many triazines present in the water samples to cross-react. Even though the cross-reactivity values for other herbicides is less than 1%, the number of binding sites they could potentially occupy would result in elevated immunoassay levels. These cross-reactive products would also be responsible for the presence of false positives (Baker et al., 1993).

Another problem associated with quantifying field samples is the formation of secondary compounds resulting from exposure of the parent compound to an aqueous environment or sunlight, or through binding of the parent compound to particulate (Gaynor et al., 1995a). These new compounds formed can react with antibodies in the immunoassay kits if they are chemically similar to the parent compound, and thus lead to overestimates with the immunoassay technique (Baker et al., 1991, Huang et al., Gaynor et al., 1995). Only 16 PAHs were quantified by the GC methods, however immunoassays would react to all structurally similar compounds, including PAHs not quantified by the traditional method. This would lead to higher total PAH levels in those subsamples analyzed by immunoassays. The non-selectivity associated with immunoassays results in all PAHs competing for binding sites, whereas the GC methods only quantify PAHs of interest.

The principle for testing environmental samples is to target areas of concern. The results presented here suggest that this technique is accurate for monitoring purposes where

contaminants have predetermined target levels, set by government regulations.

Immunoassay results provide a good estimate of the actual level, accepted as that generated by GC methods. Additionally the immunoassays produced solely false positives, reducing the concern associated with overlooking an area which may have contaminant levels exceeding those set by regulations. In cases where target levels have been exceeded, GC methods should then be employed to measure the sample to provide a more accurate quantification and to identify concentrations of specific PAHs. Regardless of the levels detected by immunoassays a random 4% confirmation of the total sample number should be analyzed by GC methods. This rule of thumb would ensure that the immunoassay kits are producing reliable results, and tending to provide false positive results without false negatives.

As in all large-scale monitoring programs, there is pressure to balance the need for technique selectivity and increasing sample size. Savings in time and money stemming from the use of immunoassays could then be directed towards expanding the monitoring program to include a larger geographic area and increased sampling effort.

Table 1.1 Summary of the data collected from the 22 wetlands (AGRI=agriculture). Immunoassay data provided for metolachlor (METOL) and PAHs. x indicates that no information was collected for the parameter.

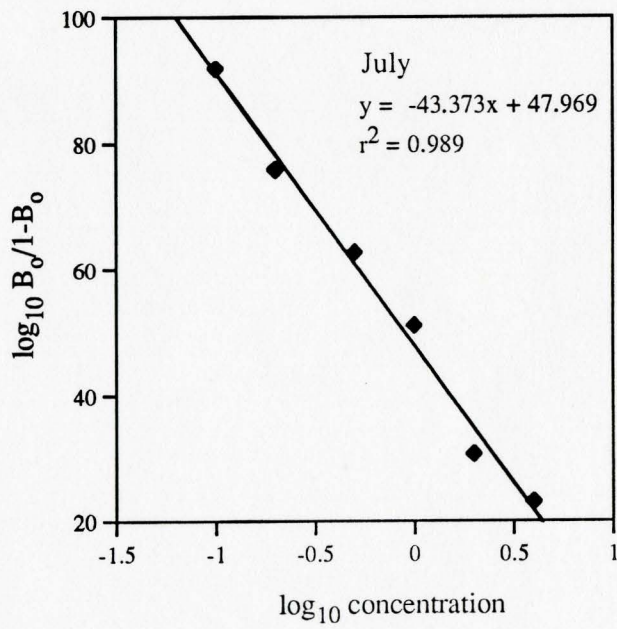
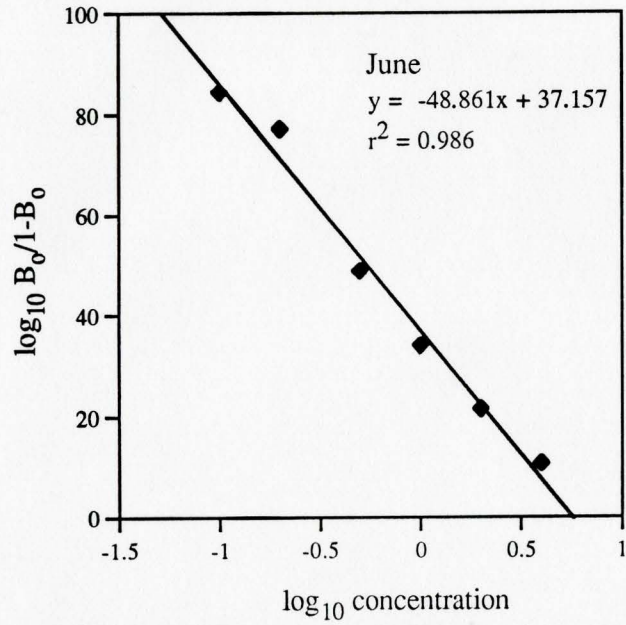
WETLAND	SITE	LATITUDE LONGITUDE	REGION	PAHs (ng/g)	METOL (µg/L)	SOIL TYPE	LAND USE
15 Mile Creek (15 MILE)	creek marsh	43° 10' 00" 79° 19' 00"	Niagara	10.84 12.34	x x	clay/silt clay/silt	AGRI
Big Creek Marsh (BIG CREEK)	creek marsh open	42° 57' 20" 80° 26' 50"	Simcoe	0.08 0.54 0.25	1.11 0.16 1.38	sand organic organic/sand	AGRI
Centreville Creek (CENTRE)	creek marsh	43° 54' 04" 79° 50' 00"	Maple	x x	0.03 x	sand organic	AGRI/FOREST
Christie Lake (CHRISTIE)	creek marsh	44° 47' 00" 76° 28' 00"	Carleton Place	x x	0.03 x	silt organic	FOREST
Cootes Paradise (COOTES)	creek marsh open	43° 16' 00" 79° 55' 00"	Cambridge	27.1 11.66 1.41	x x x	clay/silt clay/silt clay/silt	AGRI/FOREST /URBAN
Harris Lake (HARRIS)	creek marsh	45° 42' 00" 80° 22' 00"	Parry Sound	x x	0.03 x	clay/silt organic	FOREST
Hay Bay Marsh (HAY)	creek marsh open	44° 10' 30" 76° 55' 30"	Napanee	x x x	0.04 x x	sand organic organic	AGRI
Holiday Marsh (HOLIDAY)	creek marsh open	42° 02' 05" 83° 03' 00"	Chatham	x 5.76 0.11	2.35 1.47 2.44	clay/silt clay/silt clay/silt	AGRI
Humber River (HUMBER)	creek marsh	43° 38' 00" 79° 29' 00"	Maple	x x	0.35 x	clay/silt clay/silt	AGRI/URBAN
Joe's Lake (JOE)	creek marsh	45° 08' 00" 76° 41' 00"	Carleton Place	x x	0.05 x	organic organic	FOREST
Jordan Harbour (JORDAN)	creek marsh open	43° 11' 00" 79° 23' 00"	Niagara	x 12.34 10.84	1.05 1.88 1.59	sand/clay clay/silt clay/silt	AGRI
Martindale Pond (MARTIN)	creek marsh open	43° 10' 07" 79° 16' 00"	Niagara	1.48 1.23 12.64	x x x	clay/silt clay/silt clay/silt	AGRI/URBAN
Presqu'île Marsh (PRÉSQ)	marsh open	44° 00' 00" 77° 43' 00"	Napanee	x x	x x	organic x	FOREST/REC
Sawguin Marsh (SAWGUIN)	creek marsh open	44° 06' 00" 77° 23' 00"	Napanee	x x x	x x x	clay/silt organic organic	AGRI/FOREST
Second Marsh (SECOND)	creek marsh	43° 52' 00" 79° 51' 00"	Durham	2.28 14.92	x x	sand organic	AGRI/URBAN
Shebeshekong River (SHEBESH)	creek marsh	45° 24' 30" 80° 19' 00"	Parry Sound	x x	0.05 x	clay/silt organic	FOREST
Stump Lake (STUMP)	creek marsh open	44° 56' 48" 76° 38' 12"	Carleton Place	x x x	0.015 x x	x organic x	FOREST
Sutton Pond (SUTTON)	creek marsh open	42° 50' 00" 80° 18' 00"	Simcoe	1.28 1.54 3.06	x x x	sand/clay clay/silt clay/silt	AGRI/URBAN
Tay River Marsh (TAY)	creek marsh open	44° 52' 45" 76° 10' 30"	Carleton Place	x x x	0.058 x x	silt organic silt	AGRI/FOREST /URBAN
Tobies Bay (TOBIES)	marsh open	44° 51' 00" 79° 47' 00"	Parry Sound	x x	x 0.05	organic x	FOREST
Turkey Creek Marsh (TURKEY)	creek marsh	42° 14' 08" 83° 05' 07"	Chatham	28.84 5.09	1.27 0.19	clay/silt organic	URBAN
Waterford Ponds (WATER)	creek marsh open	42° 56' 10" 80° 18' 45"	Simcoe	2.06 0.07 0.41	x x x	sand/silt organic silt	AGRI

**Table 1.2** Immunoassay and gas chromatography results for PAH and metolachlor paired analyses. Each (site location) within the wetland is provided.

<b>WETLAND</b>	<b>GC (ppb)</b>	<b>IMMUNOASSAY (ppb)</b>	<b>ANALYTE</b>
JORDAN (marsh)	0.2	1.01	metolachlor
HOLIDAY (marsh)	0.04	0.78	metolachlor
TURKEY (marsh)	0.05	0.18	metolachlor
BIG CREEK (marsh)	0.09	0.18	metolachlor
FAREWELL (creek)	399.76	2280	PAHs
BIG CREEK (open water)	146.87	250	PAHs
15 MILE (creek)	427.91	5640	PAHs
WATER (marsh)	105.26	705	PAHs
BIG CREEK (creek)	0.00	80	PAHs

**Figure 1.1** Standard curves for June and July samples analyzed for metolachlor using immunoassay kits. The average  $r^2$  for the two curves was reported as 0.9875.

**Figure 1.1**

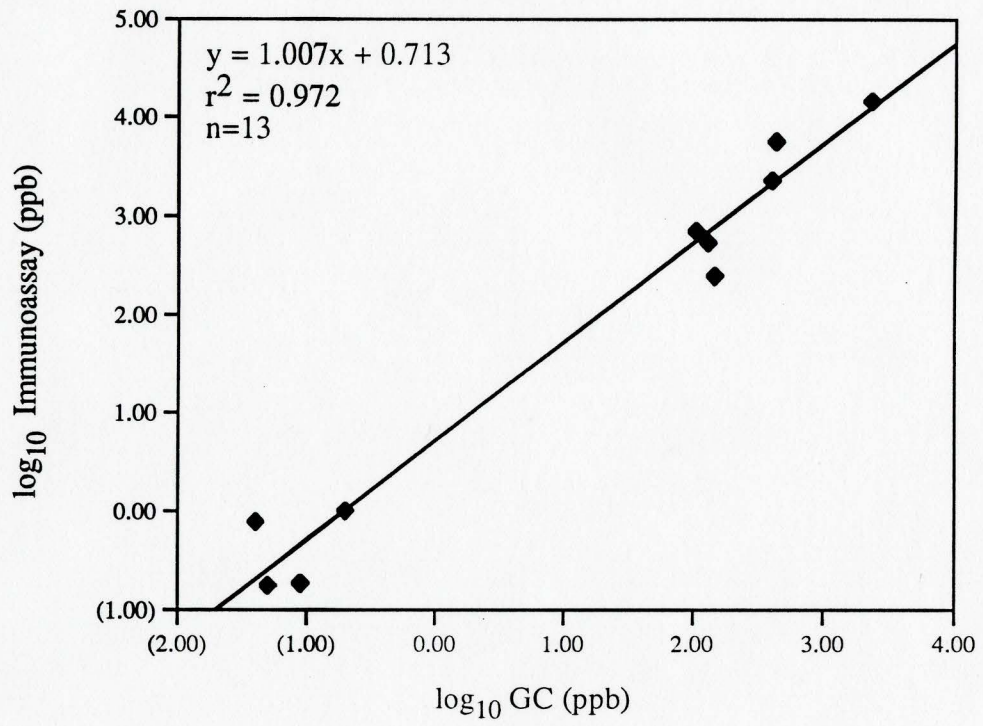




**Figure 1.2** Relationship between the two techniques, immunoassay and gas chromatography, for the PAH and metolachlor field samples.



**Figure 1.2**



**Chapter 2:**

**CHARACTERIZATION OF COMMON CONTAMINANTS  
ENTERING ONTARIOS WETLANDS**

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## ABSTRACT

In this study, twenty-two wetlands located across Ontario, with the majority lying in the watersheds of Lakes Ontario and Erie, were evaluated with respect to the types and levels of contaminants entering the wetlands. Levels of suspended particulates, nutrients, and metolachlor, as well as temperature and conductivity were determined for surface water samples, while levels of polycyclic aromatic hydrocarbons (PAHs) were determined for sediment samples. Wetlands were ranked according to the type of landuse in the drainage basins as follows: 1) 95% forested 2) mainly forested with <25% agricultural and/or urban 3) a mix of agricultural/forested with a buffer zone 4) mostly agricultural and urban, with <10% forested and 5) > 95% agricultural and <1% forested. Concentrations of phosphorus and suspended solids were significantly correlated with the type of landuse in the watershed, with watersheds dominated by agricultural use (category 5) having the highest concentrations of these constituents. Nitrogen levels were increased in wetlands with a large component of agricultural land in their watershed (category 3, 4 and 5). Temperature did not vary according to landuse categories, probably because of large geographical heterogeneity in the study set. Water conductivity was highest for wetlands with a large urban component (category 4), while the level of PAHs was significantly related to distance from roadways, type of roadway, and the size distribution of particles in the sediment. Since the majority of the contaminants (i.e. phosphorus and PAHs) entering wetlands are adsorbed to suspended particles, the level of suspended solids or turbidity in the water may be a simple and cost-effective indicator of pollutant loads to wetlands.

## INTRODUCTION

Wetlands serve many important ecological, social, educational and economic functions: they are essential for flood control; they attenuate sediments and nutrients that enter via creeks and runoff; and they provide excellent educational opportunities for the study of diverse terrestrial and aquatic organisms (Russell, 1987). The dynamic nature of these areas provides habitat for many waterfowl, marsh birds, and wildlife that rely on wetlands' unique transitional zone between water and land. They are also important nursery and spawning habitat for economically important sport fish species such as pike and bass. Wild rice is an example of an economically important harvestable product from wetlands. Given these qualities, it is not surprising that the Canadian government has estimated the value of wetlands in the billions (Environment Canada, 1991).

Unfortunately, there has been extensive loss of wetlands over the past century, especially in Southern Ontario. Infilling, dredging and draining have claimed up to 70% of wetlands that were present prior to human settlement (Smith et al., 1991). Many wetlands were drained or infilled for the development of urban and industrial areas. They were also dredged for navigation purposes to create ports for shipping. Since wetland soils are nutrient rich, many were also drained for cash crop farming. To meet the needs of the people settling in the Great Lakes basin, wetlands in southern Ontario have been reduced to only 10% of their original area (Snell, 1987). Fortunately, wetlands are now recognized as vital components of the ecosystem and this has resulted in implementation of a 'no net-loss' policy which attempts to protect remaining wetlands from further point source degradation.

Despite being protected from point source degradation, the health of wetlands is still being threatened by entry of non-point source contaminants. These contaminants lead to deteriorated water quality which severely limits the growth of aquatic plants, particularly submergent forms which spend all of their life stages within the water column (Mitchell, 1989). Non-point-source pollutants that contribute to water-quality degradation fall into four broad categories as follows: organic, nutrient, sediment and thermal/salt pollution.

The first category, organic pollutants, include trace organics and herbicides. A family of trace organic pollutants known as polycyclic aromatic hydrocarbons (PAHs), have recently received a great deal of attention because they are both mutagenic and carcinogenic (Marvin et al., 1994). Since they are by-products of the incomplete combustion of fossil fuels, they are found in automobile and industrial emissions, which then enter waterways during storm events via roadway runoff (Landrum, 1989). Consequently, they are very widely distributed, especially in urban centres, and may pose health risk to the aquatic biota in wetlands (Maltby et al., 1995). An example of a problem herbicide in southern Ontario is metolachlor. Levels in runoff have been linked to the amount of agricultural land in the watershed (Gaynor et al., 1995) and because of its non-selective nature, it can cause severe degradation of wetland vegetation in downstream sites (Langan & Hoagland, 1996).

The second category includes nutrients such as phosphorus, nitrate and ammonia. These contaminants are linked to both urban and agricultural activities in the watershed; they enter wetlands via runoff from combined sewer overflows, discharge from domestic sewage treatment plants and industrial treatment plants (Marsalek 1990), as well as from agricultural runoff (excessive fertilizer applications and contamination from animal wastes;

Humernik et al., 1987). When present in high concentrations, they can lead to eutrophication with attending nuisance algal blooms and poor water clarity.

The third category includes sediment that stem from soil erosion of exposed areas. Sediment loading from agricultural lands can be very high, and may depend on factors such as the size of the watershed that is farmed, the type of crop grown, and agricultural practices used (tilling, crop rotation versus leaving fields to fallow; Sidle and Sharpley, 1991). As amounts of impervious surfaces in urban areas increase, so too does the sediment load to receiving waters (Klein, 1979). Sediments that enter wetlands decrease water transparency, bury seeds and can lead to decline in submergent plants (Chambers and Kalff, 1985; Chambers and Prepas, 1988).

The last category includes thermal and salt pollution, these contaminants are mainly associated with urban development, in particular, road operation and construction (Lord, 1987). Both of these forms of pollution may have negative impacts on wetland biota. Water temperatures may increase as a result of stream channelization associated with road construction and urban development, and increased levels of suspended solids in runoff also tend to trap heat and result in warmer water (Klein, 1979). Steep temperature gradients in macrophyte stands result in increased plant biomass; changes in water circulation, leaf vertical density and leaf area affect the temperature dynamics in wetland plant communities. Increased loading of sodium and chloride ions via roadway/highway runoff from use of de-icing salts may affect plant species that are not salt tolerant (Fritzsche, 1992). Uptake of chloride ions by root systems and accumulation in the stems and leaves results in plant degradation.

In this study, we collected samples from the water and sediment of twenty-two marshes and their tributaries in Ontario, with the view of characterizing the main pollutants that enter these wetlands during the summer. We also relate the type and quantity of contaminants found in these marshes to landuse in their respective watersheds, and provide a means of predicting the relative impacts of different landuse on pollutant loads. This study will provide a basis for identifying wetlands that should be preserved and protected from future degradation, and allow planners to recommend changes to landuse designation to help restore degraded marshes.

## METHODS

Twenty-two marshes located mainly in the Great Lakes basin were studied (Fig. 2.1). These wetlands ranged from pristine to severely degraded, and occurred in basins that included several different combinations of landuse (see Table 2.1). This range of conditions permitted us to examine the relationship between landuse and the type and level of contaminants in creeks and wetlands. The geographic locations of all wetlands are presented in Table 2.2, along with information on the regional population size, distance from major urban centers, proximity to significant roadways, and intensity of herbicide application.

### *Landuse Delineation*

Maps from the 1:50 000 National Topographic Series were used to delineate the wetland watersheds. The latitude and longitude were used to locate the wetland on each map, and quickly approximate the watershed size. A piece of vellum tracing paper of appropriate size was laid on top of the topographic map (occasionally more than one map was involved). The wetland and its tributaries were traced first; next, the watershed was delineated from contour lines of the highest elevation and/or equidistant points between two tributaries of adjacent watersheds. Special features in the watershed such as railways, sewage treatment plants, quarries and dams were noted. The vellum was then placed on the Agricultural Landuse Series map(s) and lined up according to the wetland and its special features. The occurrence of forested (including forest and abandoned agricultural land), agricultural (all crops were grouped) and urban (rural and city were combined) land were recorded accordingly on the map. Planimetry was used to quantify the size of the



wetland, watershed and each of the three landuse types. Upstream lakes and detention areas were subtracted from the total watershed. Three replicates of each measurement were taken to ensure a reliable approximation.

Landuse information was unavailable for wetlands located in Parry Sound and Carleton Place districts. In its place, aerial and/or ground observation was used; most of these sites are located in remote areas with little development (5-10%; excluding Tay River Marsh). Another exception was for wetlands in the Niagara region, for which 1:25 000 landuse maps could be used to delineate the watershed because they included spot elevations.

#### *Field collection*

It was not possible for us to sample all twenty-two marshes during the same year. Therefore, approximately half of the study sites were visited twice in either 1995 or 1996. To determine year-to-year variation of the water quality parameters, a subset of five wetlands (Jordan Harbour, Big Creek Marsh, Turkey Creek Marsh, Cootes Paradise Marsh and Holiday Marsh) were visited in both years. These sites were also sampled four times in 1996 to determine temporal differences during the growing season.

On each visit, we used a 2-L van Dorn bottle to collect water from the middle of the column at three locations within each wetland system: 1) creek 2) near vegetation and 3) open water site. These samples were kept cool and in the dark until they were processed for nutrients and suspended solids. *In situ* measurements of water temperature and specific conductance were recorded using a H<sub>2</sub>O HYDROLAB<sup>TM</sup> equipped with a Scout 2 monitor. Water depths were also recorded at each site. Turbidity levels were measured in the field with a Hach turbidimeter (model 2100P) in triplicate.

Surface water samples from creek sites were collected with opaque 40-mL vials (previously rinsed with a mixture of acetone/petroleum ether) for metolachlor analysis. For only one of these wetlands (Tobies Bay) the open water site was substituted for the creek site because there was no obvious tributary. To determine spatial differences, four of the sites (Jordan, Big Creek Marsh, Turkey Marsh and Holiday Marsh) were sampled at the three different locations in each wetland, in June of 1996. We also sampled the creeks of these four wetlands in June and July to determine seasonal variation in metolachlor.

In 1995, we collected sediment samples from three sites, where possible, within ten different wetlands (n=29) to determine the concentration of PAHs. Samples were collected with an Eckman grab sampler or with a plexiglas tube equipped with a plunger when sediments were unconsolidated or contained a large amount of coarse debris.

#### *Nutrient and suspended solids analysis*

Water samples were analyzed for total phosphorus using a modified molybdenum blue method of Murphy and Riley (1962). Total nitrate nitrogen were determined with a cadmium reduction method using Hach reagents. Samples for total suspended solids and inorganic suspended solids (TSS and ISS, respectively) were first filtered through pre-weighed GF/C filters and then frozen. They were dried at 100°C for 1-h, placed in a desiccator for another hour and then weighed (TSS). Subsequently, filters were combusted at 550°C for 20-min and desiccated for 1-h for determination of ash-free weights. Inorganic suspended solids (ISS) was calculated as the difference between TSS and ash-free weight. We weighed all filters to the nearest 0.0001g using a OHAUS® AS120 balance.

### *Immunoassay Analysis*

For a detailed analysis of metolachlor and PAH analysis see the methods section of Chapter 1.

A comparison of these immunoassay results with replicate samples analyzed by conventional gas chromatography indicated that these immunoassay techniques yield reliable estimates of metolachlor and PAHs, although they consistently produce overestimates (by  $\ll 1 \mu\text{g/L}$ ); see Chapter 1). Nevertheless, the variations are reflective of true differences among sources and can be validly compared within studies.

### *Statistical Analysis*

All statistical analyses were performed with SAS.JMP for the Macintosh. Where appropriate, means and standard errors are presented in tables and figures.

## RESULTS

### *Spatial and Temporal Variation*

A two-way ANOVA including each wetland and sites (creek, vegetated and open water) was performed for the following variables: total suspended solids, turbidity, total phosphorus, nitrate nitrogen, temperature, conductivity and metolachlor. However, no significant differences were found between the creek, vegetated and open water sites ( $F > 0.05$ ). In addition, no differences were found between the July and August samples; however, temperature was found to differ in the five sites sampled on four occasions (1-way ANOVA;  $p = 0.0001$ ). For a discussion of the changing temperatures see Chapter 3. Therefore we averaged the values of the two dates for all 22 wetlands, in the remaining analyses.

### *Water Quality*

The concentrations of six different contaminants are plotted according to their landuse ranking (Table 2.3; Fig. 2.2 a-f). ISS was excluded since it is highly correlated with TSS ( $r = 0.96$ ), and provided redundant results. Landuse category 5 (95% agriculture) was associated with significantly higher levels of TSS, TP and TURB compared with any other category. Overall, sites with large amounts of disturbed land in their watershed (category 3, 4, 5) had significantly higher levels of nutrient and suspended contaminants compared with those in undisturbed land (category 1; Tukey-Kramer, Table 2.4). Trends in specific conductance (COND) of the water did not follow those of suspended sediments and phosphorus; wetlands with a strong urban component in their watershed (category 4) were associated with the highest mean, followed by sites with

extensive agricultural land (category 5). TNN increased in wetlands which contained a large agricultural component in their watershed (category 3, 4, 5) compared with those dominated by forested land. Although there were no differences in temperature for any landuse category, there was a general increase with percent developed land in the watershed. For all parameters except temperature, major differences were found between wetlands whose watersheds were primarily forested (category 1, 2) and those where greater than 75% of the watershed had been altered to urban and/or agricultural land (category 3, 4, 5).

### *Metolachlor*

Metolachlor concentrations were plotted against their respective wetland site and grouped according to the dominant landuse (Fig. 2.3). Not surprisingly, the highest metolachlor concentrations were found in wetlands where the majority of the land was used for agriculture. Urban lands had the second highest concentrations, although the levels were much lower.

To avoid biasing our results, we accounted for differences in herbicide application rates along with the type of landuse and came up with different landuse categories (Table 2.5). In this comparison, progression from category 1 to 5 reflects increasing rates of herbicide application along with high percentage of agricultural land in the basin (Fig. 2.4a). Viewed in this manner, it is clear that metolachlor concentrations in the creeks of wetlands in category 5 were almost four-fold higher than those in other categories (Tukey-Kramer;  $n=14$ ,  $p<0.0001$ ). In these heavily agricultural watersheds, metolachlor was not the only herbicide analyzed in samples. Conventional gas chromatography techniques (see Chapter 1) revealed that water samples taken from four of these wetlands contained traces of 6 other herbicides (Table 2.6).

### *PAHs*

Since highway runoff is a major contributor of PAHs to aquatic systems (Chow-Fraser et al., 1996; Maltby et al., 1996) the concentrations found in this study were categorized according to their distance away from nearest road and plotted against PAH concentration (Fig. 2.4b). This comparison illustrates that wetlands which had sampling sites less than 50m from the nearest roadway contained the highest levels of PAHs in their sediments (Tukey-Kramer;  $n=29$ ,  $p<0.0001$ ). These concentrations were significantly higher than those obtained from sampling sites greater than 200 m from the nearest roadway.

The relative levels of three PAHs for five of the wetlands in this study are compared to determine the influence of auto emissions from nearest roadways (Table 2.7). Two wetlands, Second Marsh and Turkey Creek Marsh are located less than 50m from an urban roadway, and had levels of phenanthrene, fluoranthene and pyrene that were significantly higher (ANOVA; Tukey-Kramer;  $P<0.05$ ) than those of the other three, which are located in less accessible areas which have no major roadways.

Since PAHs enter wetlands by adsorbing to particulates, we examined the size distribution of sediment in the various wetlands because small particles can adsorb disproportionately more PAHs, given their high surface-area-to-volume ratio. Near-vegetation sites were excluded from this analysis since sediments with high organic and humic levels often produce overestimates from immunoassays (Baker et al., 1993). Therefore, we used sediment corresponding to creek sites which contained less than 5% organic matter. Sediments dominated by small particles such as clay and silt were grouped

together and compared with those dominated by sand (Fig. 2.5). Clay and silt-dominated sediments had significantly higher levels of PAHs compared with those of more coarse grain (T-test,  $P < 0.02$ ). These fine-grained sediments tended to remain in suspension longer, and may therefore bring in a higher load of PAHs from the watershed.

## DISCUSSION

Contaminants entering wetlands were strongly related to landuse in the watershed. The primary contaminants found in these wetlands were those associated with agriculture, namely sediment and pollutants that are either dissolved in runoff or are adsorbed to the particulates. Other studies have shown similar results for streams where agricultural activity was associated with high loads of suspended sediment and phosphorus in its runoff (Byron and Goldman, 1989; Sorrano et al., 1996). In our study, it is clear that pollutants that enter these creeks also enter the wetlands.

The impact of altered landuse in the watershed of streams has been studied extensively (Klein, 1979; Byron and Goldman, 1989; Zampella, 1994; Roth et al., 1996). The most common contaminant associated with construction processes and clearing of land is suspended sediment. Not only is the structural nature of this contaminant detrimental to the wetland, but it also tends to carry with it bound nutrients, herbicides and organic contaminants (Hahn and Pfeifer, 1994). Our study confirms that in highly developed watersheds, especially where there is a high percentage of agricultural land, large loads of suspended sediment enter marshes via tributaries, and remain suspended in the water column (e.g. Holiday Marsh, Jordan Harbour, Cootes Paradise Marsh). In such instances, wetlands have clearly lost their ability to attenuate flows and filter out sediments. This is because a large proportion of the original vegetation has been lost so that only a fringe of vegetation remains along the shoreline. In certain of these wetlands, the problem is exacerbated by exposure to wind and wave which maintain the sediments in suspension (Hamilton and Mitchell, 1996; Chow-Fraser, pers. comm.). In contrast, wetlands which



were located in forested landscapes had clear water with vegetation that was abundant, diverse and interspersed.

The chief determinant of these two state of wetland health appears to be the type of landuse in the watershed. Two of the wetlands in this study appeared to be exceptions: Hay Bay and Big Creek Marsh. Good agricultural practices were maintained in their watersheds in addition to a forested buffer strip along their tributaries. In Hay Bay Marsh, agriculture is confined to orchards and livestock grazing, neither of which result in large amounts of exposed land. Additionally the intensity of farming is lower than in southwestern Ontario, where the land is used to its maximum potential. The watershed of Big Creek Marsh is on a sand plain, and erosion from this is not associated with high turbidity and phosphorus levels. Consequently, relatively good water clarity is maintained in the marsh despite the amount of agricultural land. These results suggest that in the presence of an extremely developed watershed, good management practices and favourable geology can alleviate the problem of high contaminant loads.

Water quality degradation is generally associated with the process of eutrophication. Phosphorus is usually the limiting nutrient for algae in freshwater wetland systems (Schindler, 1977). When concentrations of this nutrient is present in excess, phytoplankton growth is accelerated and algal blooms moves the system to one that is light limited for aquatic plants. These changes result in either decreased plant abundance or a wetland with lower diversity at all levels (Hough et al., 1989; Phillips et al, 1994). Our results indicate that this is more likely to occur in wetlands dominated by agricultural land. To a lesser degree, increased phosphorus concentration was also associated with urban areas, especially where agricultural land co-occurred. Since phosphorus tends to bind to sediments, it can be regenerated at the sediment-water interface under low redox conditions

(Golterman, 1995). Alternately, phosphorus can be released from the sediment layer when the gradient between the porewater and overlying water concentrations is high. This could inhibit improvements in water quality even once external inputs are decreased. Wetlands that have received previous nutrient inputs are therefore difficult to restore due to re-release from the sediments (Phillips et al., 1994).

Nitrogen levels were elevated in wetlands with large proportions of agricultural or urban land. This nutrient is contained in fertilizers, which are applied to increase crop yield. Fertilizers are also used in urban areas to produce green lawns and manicured golf courses. Although nitrogen is generally the limiting nutrient for aquatic plants in wetlands (Barko et al. 1991), nitrates that enter wetlands may become denitrified under anaerobic conditions. Additionally, nitrates are a key factor in the relationship between trophic state and the leaf biomass of the macrophyte community (Sinden-Hempstead and Killingbeck, 1996). In the literature, high nitrate levels caused *Phragmites*, an emergent macrophyte to allocate more energy to shoots rather than to roots, and thus compromised their ability to overwinter (Cizkova-Koncalova, 1992). The effects of high TNN levels is not conclusive and more research should be devoted to understand the relationship between TNN and growth of both emergent and submergent forms.

Many studies have examined the merits of using vegetation buffer strips to control nutrient and sediment inputs into streams (McColl, 1978; Peterjohn and Correll, 1984; Osborne and Kovacic, 1993; Lowrance et al., 1994). This study supports these previous findings; wetlands with watersheds dominated by forested land received lower concentrations of phosphorus. Retaining forested land near the wetland and tributaries to trap and attenuate excess nutrients is essential to prevent eutrophication of downstream waters. These findings emphasize the importance of good land management practices in

the presence of human disturbance to prevent increased loading of contaminants and avoid the difficult task of restoring a system that continues to reflect the previous inputs of contaminants.

Specific conductance is an additional measure of water fertility that is indirectly related to phosphorus levels in the water. Not surprisingly conductivity also increased in watersheds containing urban and agricultural landuse. A study by Zampella (1994) in differentially disturbed wetlands in the New Jersey pine barrens found that specific conductance also increased along a gradient of increasing disturbance. The use of road salts and inputs of other ions increased conductance levels, in addition to the presence of phosphorus ions. Higher levels were associated with wetlands whose watersheds were dominated by urban and/or agricultural lands. Although there are only a few urban-dominated watersheds in this study, without exception, high levels of specific conductance could be attributed to major roadways.

Variation in temperature was not significantly related to landuse change and this was possible confounded by difference in geography of these wetlands. Temperature changes tend to occur with loss of plant canopy associated with land clearing and when stream channelization decreases water depth and allows temperatures to increase (Klein, 1979). Thermal pollution has been shown to be an important factor contributing to changes in the community dynamics of fish species in streams (Roth et al., 1996), but has seldom been investigated in wetlands.

Gaynor et al. (1995) indicated that the concentration of herbicides in runoff is a function of the amount of agricultural land in the watershed. We could not confirm this because we did not sample during peak periods. In all likelihood our June and July

samples only measured residue metolachlor concentrations which occurred 4-6 weeks after herbicide application. Nevertheless, July samples were generally lower than those collected in June, and suggests that degradation of metolachlor had occurred. Since herbicides are light sensitive and break down quickly by photolysis, concern should be focussed on the initial exposure concentration (Gaynor et al., 1995). Although we cannot estimate the initial initial level of exposure, in two of these wetlands (Jordan Harbour and Holiday Marsh), levels of metolachlor were 1 ppb, and this is the minimum level capable of inhibiting the growth of aquatic macrophytes (DeNoyelles et al., 1982). Since TP and TSS levels were also high in these wetlands, it is difficult to ascribe the loss of plant diversity and abundance to any one factor.

The presence of PAHs in sediments appeared to be unrelated to the other contaminants of interest. No relationship was found between the different landuse ranks and the total concentration of PAHs, probably because of the homogeneous nature of the sample. Only 10 wetlands were sampled in 1995 (PAHs only analyzed in this year) of which all were located in the Toronto-Windsor corridor; for the most part, these sites lie in agriculture or urban landscapes that contain major roadways.

One factor important in determining total PAHs is the proximity of the sampling site to roadways, which is indirectly related to landuse. PAHs from auto emissions generally accumulate in roadway runoff, which is transported to aquatic ecosystems. A previous study by Hautala et al. (1995) found that PAHs in snow were significantly higher when sampled 10-30 m away from the highway compared with samples 150 m away. Maltby et al. (1995) also found that at distances less than 100 m from the roadway the water and sediment quality was altered. For a number of wetlands in Ontario that are located close to roadways, there were elevated levels of phenanthrene, fluoranthene and

pyrene in sediment, PAHs that are known constituents of auto exhaust (Table 2.7). These components of crankcase oil have been identified as the some of the major contributors of contaminants in urban runoff (Latimer et al., 1990). Maltby et al. (1995) identified these PAHs at sites where macroinvertebrate diversity was decreased, as a result of the loss of pollution-sensitive species.

Distribution of particle size appears to be another important factor determining total PAHs in sediment. Several studies have reported (Landrum, 1989; Baker et al. 1991; Kukkonen and Landrum, 1995) that the high volume-to-surface area of silt and clay provide more binding sites for PAHs, and our results support this finding. We speculate that these sediments are carried into the marsh and may potentially enter the food web through the benthos. Small sediments such as silt and clay offer the best growing medium for aquatic macrophytes and the primary habitat for benthic invertebrates (Barko et al., 1991). Submergent plants may be the most threatened since they are the group which utilizes these small sediments (Barko and Smart, 1983). This implies that PAHs have the potential to accumulate in both plants and benthic invertebrates, especially because plants contribute the organic material upon which benthic organisms feed (Baker et al. 1991 Kukkonen and Landrum 1995).

Bioturbation is associated with benthic activity and can result in the re-release of low molecular weight PAHs, which would then have the potential to accumulate in pelagic organisms such as zooplankton (Baker et al., 1991). This potential exposure of PAHs potentiates their entry into the food web at a number of different levels. Since wetlands generally support a broad range of organisms, the potential for PAHs to accumulate in the food web is immense, and this should be of concern for both ecosystem and human health

Disturbances in the landscape are causing increased levels of contaminants to enter many of Ontario wetlands, especially in the southwestern portion where major population centres lie. As long as cities continue to spread, and people converge on urban centres, contaminant inputs will continue to increase, and this will probably be detrimental to our remaining wetlands. However, as this study shows, good landuse management, such as the retention or creation of buffer strips, can alleviate some of the stress on wetland systems. By preventing an increase in the suspended solids load, and thereby other contaminants as well, some of the cumulative impacts may be reduced. Only when this is taken into consideration in planning exercises can the remaining wetlands be preserved in the populated and developed Great Lakes basin.

Table 2.1 Landuse categories based on the amounts of agriculture, urban and forested land in the watershed.

AMOUNT OF LAND TYPE	LANDUSE CATEGORY	WETLAND
> 95% forest	1	Christie Lake, Joe's Lake, Harris Lake, Stump Lake, Shebeshekong River, Tobies Bay
mainly forest with less than 40% agriculture and/or urban land	2	Presqu'ile Marsh, Tay River Marsh
agriculture/forest mix with a strong buffer zone present along the wetland and tributaries	3	Centreville Creek, Waterford Ponds, Hay Bay Marsh, Sawguin Marsh
agriculture and urban mix with less than 25% forest	4	Big Creek Marsh, Martindale Pond, Second Marsh, Turkey Creek Marsh, Cootes Paradise Marsh, Sutton Pond, Humber River, Jordan Harbour, Fifteen Mile Creek
> 95% agriculture with less than 1% forest	5	Holiday Marsh

Table 2.2 Location of sampling sites, types of land use in the watershed (AGRI=agriculture; FOREST= forest and abandoned agricultural lands; URBAN=urban/residential, mining; REC=conservation areas, provincial parks), distance to nearest city, region population size (Statistics Canada, 1995), type of roadway (Bill Merrit, MTO, pers. comm.), proximity of the sampling site to the roadway, relative use of the roadway and herbicide application in the area (Environment Canada, 1988).

WETLAND	LATITUDE LONGITUDE	LAND USE IN THE WATERSHED	DISTANCE TO CITY (km)	POPULATION SIZE OF THE REGION	ROADWAY TYPE	PROXIMITY OF SITE TO ROADWAY (m)	PESTICIDE APPLICATION (kg/ha)
15 Mile Creek	43° 10' 00" 79° 19' 00"	AGRI	5.6	416 740	rural	< 50	0-0.15
Big Creek Marsh	42° 57' 20" 80° 26' 50"	AGRI	16.8	107 347	rural	200-1000	0.15-0.3
Centreville Creek	43° 54' 04" 79° 50' 00"	AGRI/FOREST	3.5	875 678	rural	< 50	0-0.15
Christie Lake	44° 47' 00" 76° 28' 00"	FOREST	21.7	61 493	rural	>1000	0-0.15
Cootes Paradise	43° 16' 00" 79° 55' 00"	AGRI/FOREST/URBAN	7.0	479 561	urban	< 50	0-0.15
Harris Lake	45° 42' 00" 80° 82' 00"	FOREST	49.0	42 305	rural	>1000	0
Hay Bay Marsh	44° 10' 30" 76° 55' 30"	AGRI	7.0	40 906	rural	>1000	0-0.15
Holiday Marsh	42° 02' 05" 83° 03' 00"	AGRI	6.3	358 797	urban	< 50	0.15-0.3
Humber River	43° 38' 00" 79° 29' 00"	AGRI/URBAN	0.0	2 414 506	urban	< 50	0-0.15
Joe's Lake	45° 08' 00" 76° 41' 00:	FOREST	42.0	61 493	rural	50-200	0
Jordan Harbour	43° 11' 00" 79° 23' 00"	AGRI	10.5	416 740	urban	200-1000	0-0.15
Martindale Pond	43° 10' 07" 79° 16' 00"	AGRI/URBAN	2.1	416 740	urban	< 50	0-0.15
Presqu'ile Marsh	44° 00' 00" 77° 43' 00"	FOREST/REC	3.5	83 837	rural	50-200	0-0.15
Sawguin Marsh	44° 06' 00" 77° 23' 00"	AGRI/FOREST	6.3	40 906	rural	50-200	0-0.15
Second Marsh	43° 52' 00" 79° 51' 00"	AGRI/URBAN	4.9	470 895	urban	50-200	0-0.15
Shebeshekong River	45° 24' 30" 80° 19' 00"	FOREST	24.5	42 305	rural	200-1000	0
Stump Lake	44° 56' 48" 76° 38' 12"	FOREST	32.2	61 493	rural	< 50	0
Sutton Pond	42° 50' 00" 80° 18' 00"	AGRI/URBAN	2.1	107 347	urban	50-200	0-0.15
Tay River Marsh	44° 52' 45" 76° 10' 30"	AGRI/FOREST/URBAN	6.3	61 493	rural	>1000	0-0.15
Tobies Bay	44° 51' 00" 79° 47' 00"	FOREST	32.9	42 305	rural	< 50	0-0.15
Turkey Creek Marsh	42° 14' 08" 83° 05' 07"	URBAN	10.5	358 797	urban	< 50	0.15-0.3
Waterford Pond	42° 56' 10" 80° 18' 45"	AGRI	10.5	107 347	rural	>1000	0.15-0.3



Table 2.3 Summary of water-quality data for wetlands. All numbers represent the average of two dates except those designated by a superscript (a). "x" indicates no information was collected. (TEMP=temperature, COND=specific conductance, TURB=turbidity, TSS=total suspended solids, ISS=total inorganic suspended solids, TP=total phosphorous, PAHs=polycyclic aromatic hydrocarbons and METOL=metolachlor).

WETLAND	SITE	DEPTH (cm)	TEMP (°C)	COND (µS/cm)	TURB (FTU)	TSS (µg/L)	ISS (µg/L)	TP (µg/L)	TNN (µg/L)	PAHs (ng/g)	METOL (µg/L)
15 Mile Creek (15 MILE)	creek	92	22.5	743	58.8	43.80	34.80	230	480	10.84	x
	marsh	35	25.3	741	80.7	124.30	111.63	345	450	12.34	x
Big Creek Marsh (BIG CREEK)	creek	55	18.2	611	3.9	9.78	1.91	54	1770	0.08	1.11
	marsh	97	17.2	616	4.4	10.23	4.79	50	2890	0.54	0.16
	open	140	20.9	620	8.3	10.10	5.20	62	1994	0.25	1.38
Centreville Creek (CENTRE)	creek	21	16.1	624	2.9	4.90	1.95	45	220	x	0.03
	marsh	20	19.5	599	3.8	4.62	1.50	66	50	x	x
Christie Lake (CHRISTIE)	creek	120	21.6	150	2.3	11.14	1.54	33	0	x	0.03
	marsh	30	20.5	153	2.1	9.44	4.19	31	80	x	x
Cootes Paradise (COOTES)	creek	127	20.0	700	44.0	49.14	x	113	600	27.10	x
	marsh	20	25.0	689	48.5	48.57	32.61	145	320	11.66	x
	open	40	20.0	740	75.0	51.94	38.08	160	580	1.41	x
Harris Lake (HARRIS)	creek	140	20.3	39	44.0	3.74	1.14	81	50	x	0.03
	marsh	77	19.4	39	53.7	3.84	1.04	51	50	x	x
Hay Bay Marsh (HAY)	creek	130	21.0	533	8.6	14.58	9.98	75	60	x	0.04
	marsh	86	20.1	550	3.0	3.69	1.29	62	50	x	x
	open	40	21.0	575	1.7	4.30	0.50	30	0	x	x
Holiday Marsh (HOLIDAY)	creek	90	23.6	566	312	310.00	179.30	767	1580	x	2.35
	marsh	28	27.0	550	256	217.80	131.50	767	2200	5.76	1.47
	open <sup>a</sup>	55	22.8	576	357	183.80	116.80	570	600	0.11	2.44
Humber River (HUMBER)	creek	265	20.8	762	41.8	38.78	26.04	102	190	x	0.35
	marsh	25	22.5	735	67.8	57.34	37.29	214	140	x	x
Joe's Lake (JOE)	creek	275	21.4	211	2.1	3.89	2.39	2	30	x	0.05
	marsh	80	21.4	212.5	1.4	5.44	2.99	3	10	x	x
Jordan Harbour (JORDAN)	creek	75	22.4	553	17.3	18.53	14.03	130	30	x	1.05
	marsh	80	24.8	561	37.9	34.68	25.98	275	80	12.34	1.88
	open	247	24.3	550	36.4	38.86	28.16	216	100	10.84	1.59
Martindale Pond (MARTIN)	creek <sup>a</sup>	70	23.0	1047	45.2	35.30	29.47	183	500	1.48	x
	marsh	52	23.8	452	44.1	74.69	49.97	340	470	1.23	x
	open <sup>a</sup>	220	23.1	365	34.3	40.20	21.20	217	200	12.64	x
Presqu'ile Marsh (PRESQ)	marsh	75	23.2	337	1.5	4.84	0.74	55	40	x	x
	open	149	22.0	325	2.4	4.84	1.15	18	30	x	x
Sawguin Marsh (SAWGUIN)	creek	165	21.9	418	16.6	1.04	0	120	270	x	x
	marsh	80	21.5	390	2.9	6.44	1.79	77	170	x	x
	open	152	21.4	392	14.8	4.74	2.54	62	220	x	x
Second Marsh (SECOND <sup>a</sup> )	creek	20	21.2	824	16.6	18.97	12.10	85	770	2.28	x
	marsh	10	25.6	865	14.8	23.80	10.00	407	430	14.92	x
Shebeshkong River (SHEBESH)	creek	90	19.4	49	6.0	4.43	1.01	82	400	x	0.05
	marsh	80	19.7	49	6.1	9.53	4.23	69	330	x	x
Stump Lake (STUMP)	creek	385	21.90	130	1.6	2.04	0.99	74	0	x	0.02
	marsh	52	21.0	190	1.9	4.69	3.09	42	0	x	x
	open	100	21.60	142	1.9	4.04	1.35	31	10	x	x
Sutton Pond (SUTTON)	creek <sup>a</sup>	55	17.8	563	6.7	4.39	0	65	1970	1.28	x
	marsh	22	19.9	529	13.4	x	x	80	1730	1.54	x
	open <sup>a</sup>	3	19.2	642	7.9	x	x	130	1470	3.06	x
Tay River Marsh (TAY)	creek	210	21.7	191	3.5	4.39	0.94	45	0	x	0.06
	marsh	50	20.9	193	1.5	8.44	2.14	50	40	x	x
	open	167	21.8	200	3.0	4.84	1.59	36	0	x	x
Tobies Bay (TOBIES)	marsh	122	20.0	101	2.8	7.43	0.99	139	230	x	x
	open	187	17.0	120	4.6	11.88	5.66	98	300	x	0.05
Turkey Creek Marsh (TURKEY)	creek	145	23.7	749	59.1	51.49	36.39	166	0	28.84	1.27
	marsh	41	22.1	338	12.4	13.22	7.44	40	0	5.09	0.19
Waterford Pond (WATER)	creek	45	19.2	585	7.3	12.30	6.80	54	2920	2.06	x
	marsh	44	24.7	465	23.0	51.68	28.92	129	450	0.07	x
	open <sup>a</sup>	40	22.3	479	15.6	x	x	127	230	0.41	x

**Table 2.4** Results of Tukey-Kramer comparisons of the different landuse ranks with total suspended solids (TSS), total phosphorus (TP), turbidity (TURB), specific conductance (COND) and total nitrate nitrogen (TNN). Significant differences are indicated by different superscripts ( $p < 0.01$ ).

VARIABLE	CATEGORY	MEAN
TSS	5	258.10 <sup>a</sup>
	4	43.60 <sup>b</sup>
	3	28.60 <sup>bc</sup>
	2	4.50 <sup>c</sup>
	1	7.03 <sup>c</sup>
TP	5	699.51 <sup>a</sup>
	4	163.54 <sup>b</sup>
	3	131.37 <sup>bc</sup>
	2	62.48 <sup>c</sup>
	1	56.90 <sup>c</sup>
TURB	5	306.30 <sup>a</sup>
	4	38.24 <sup>b</sup>
	3	21.92 <sup>bc</sup>
	2	3.02 <sup>c</sup>
	1	2.70 <sup>c</sup>
COND	5	604 <sup>a</sup>
	4	665 <sup>ab</sup>
	3	586 <sup>ab</sup>
	2	376 <sup>ac</sup>
	1	150 <sup>d</sup>
TNN	5	1157 <sup>a</sup>
	4	627 <sup>a</sup>
	3	830 <sup>a</sup>
	2	126 <sup>b</sup>
	1	96 <sup>b</sup>

**Table 2.5** Landuse categories based on the amounts of agriculture, urban and forested land in the watershed plus the herbicide application rates in the region ( from Table 2.2).

<b>AMOUNT OF LAND TYPE</b>	<b>LANDUSE CATEGORY</b>	<b>WETLAND</b>
> 95% forest with no herbicide application	1	Christie Lake, Joe's Lake, Harris Lake, Stump Lake, Shebeshekong River, Tobies Bay
mainly forest with less than 40% agriculture and/or urban land and no herbicide application	2	Tay River Marsh
agriculture/urban/forest mix with herbicide application	3	Centreville Creek, Hay Bay Marsh,
mainly agriculture and urban with herbicide application	4	Turkey Creek Marsh, Humber River
> 75% agriculture with less than 1% forest plus herbicide application	5	Holiday Marsh, Jordan Harbour, Big Creek Marsh

Table 2.6 Metolachlor and other herbicides detected in the four samples collected in June and analyzed by GC-NPD (x=detected in sample).

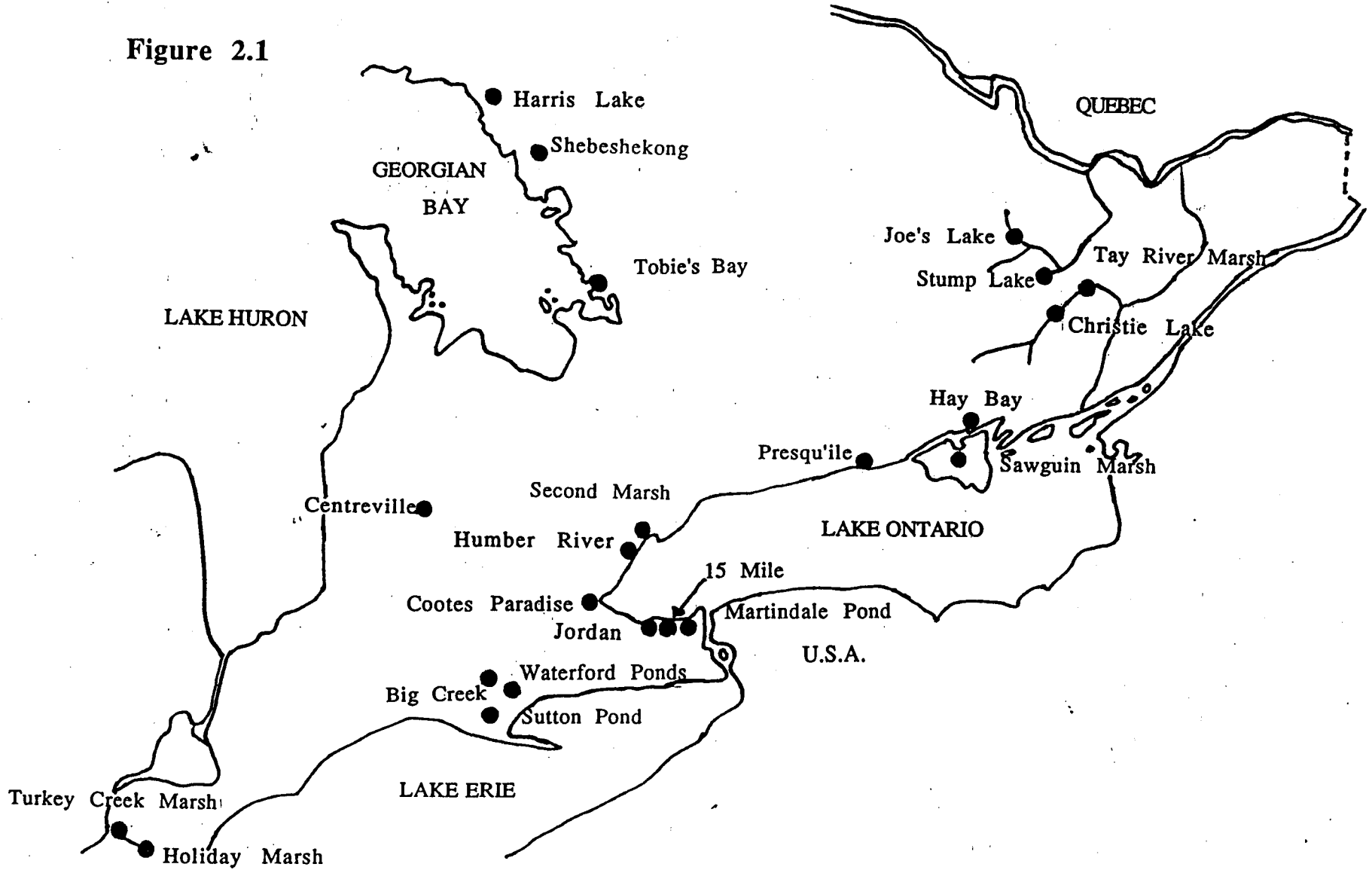
Wetland	Metolachlor	Butylate	D-Simazine	D-Atrazine	Metribuzine	Atrazine	Simazine
BIG CREEK	X		X	X		X	
JORDAN	X	X	X	X	X	X	X
TURKEY	X		X	X		X	
HOLIDAY	X		X	X		X	

Table 2.7 Concentrations of phenanthrene, fluoranthene and pyrene in five wetlands whose sediments were analyzed using GC-MS. Concentrations are presented, along with the type of roadway and landuse in the watershed.

WETLAND	PHENANTHRENE	FLUORANTHENE	PYRENE	LANDUSE AND (ROADWAY TYPE)
BIG CREEK	43.37	57.49	37.47	Agriculture (rural)
TURKEY	245.47	633.34	503.95	Urban (urban)
15 MILE	77.53	141.43	94.08	Agriculture (rural)
WATER	23.06	48.39	33.81	Agriculture (rural)
SECOND	337.9	709.04	467.64	Urban and Agriculture (urban)

**Figure 2.1** Map illustrating the wetlands sampled.

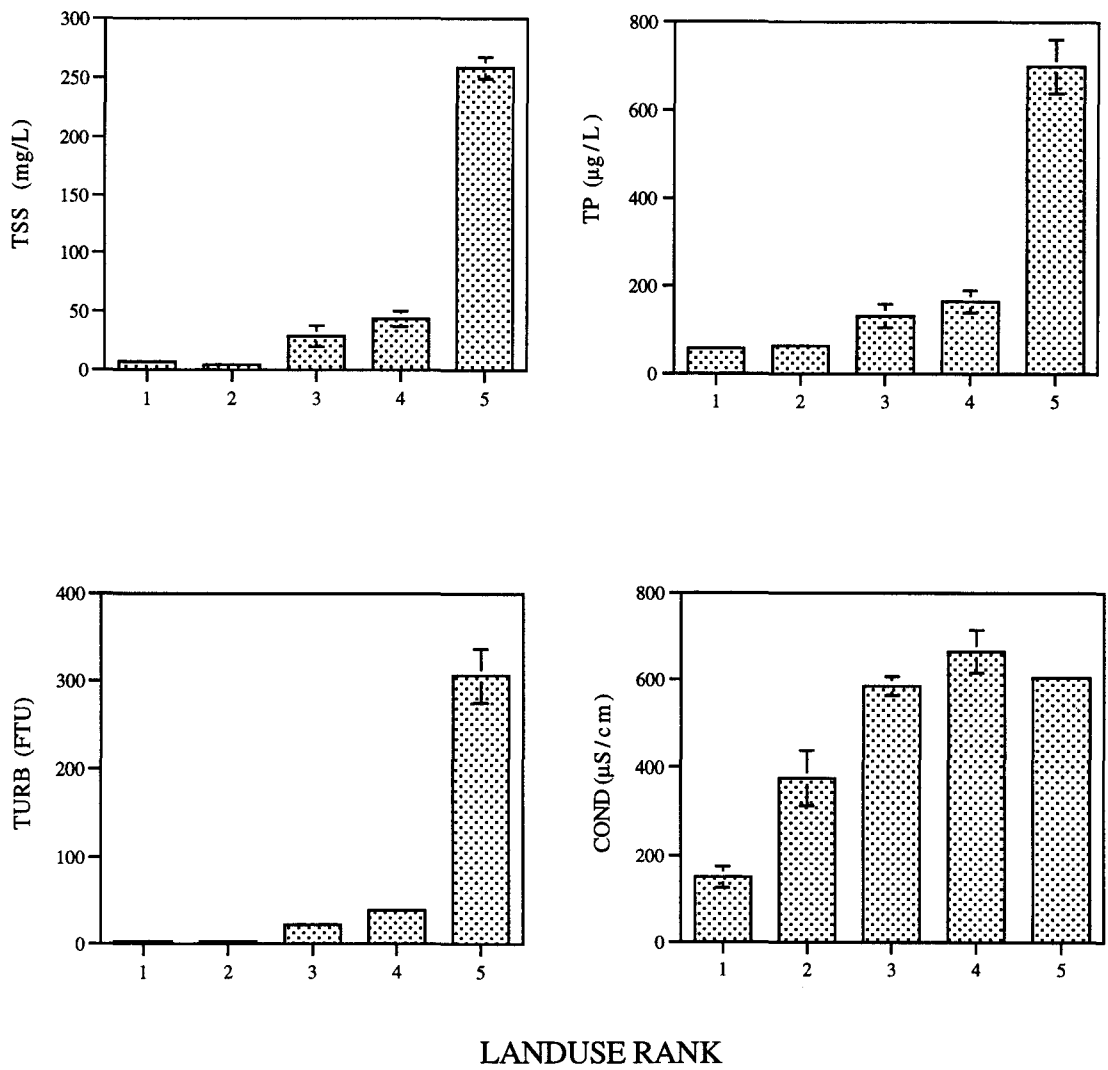
Figure 2.1



**Figure 2.2** Wetland sites grouped according to the landuse in their watersheds and plotted against the water quality parameters (TSS, TP, TURB, COND, TNN and TEMP). Means are presented with standard errors.



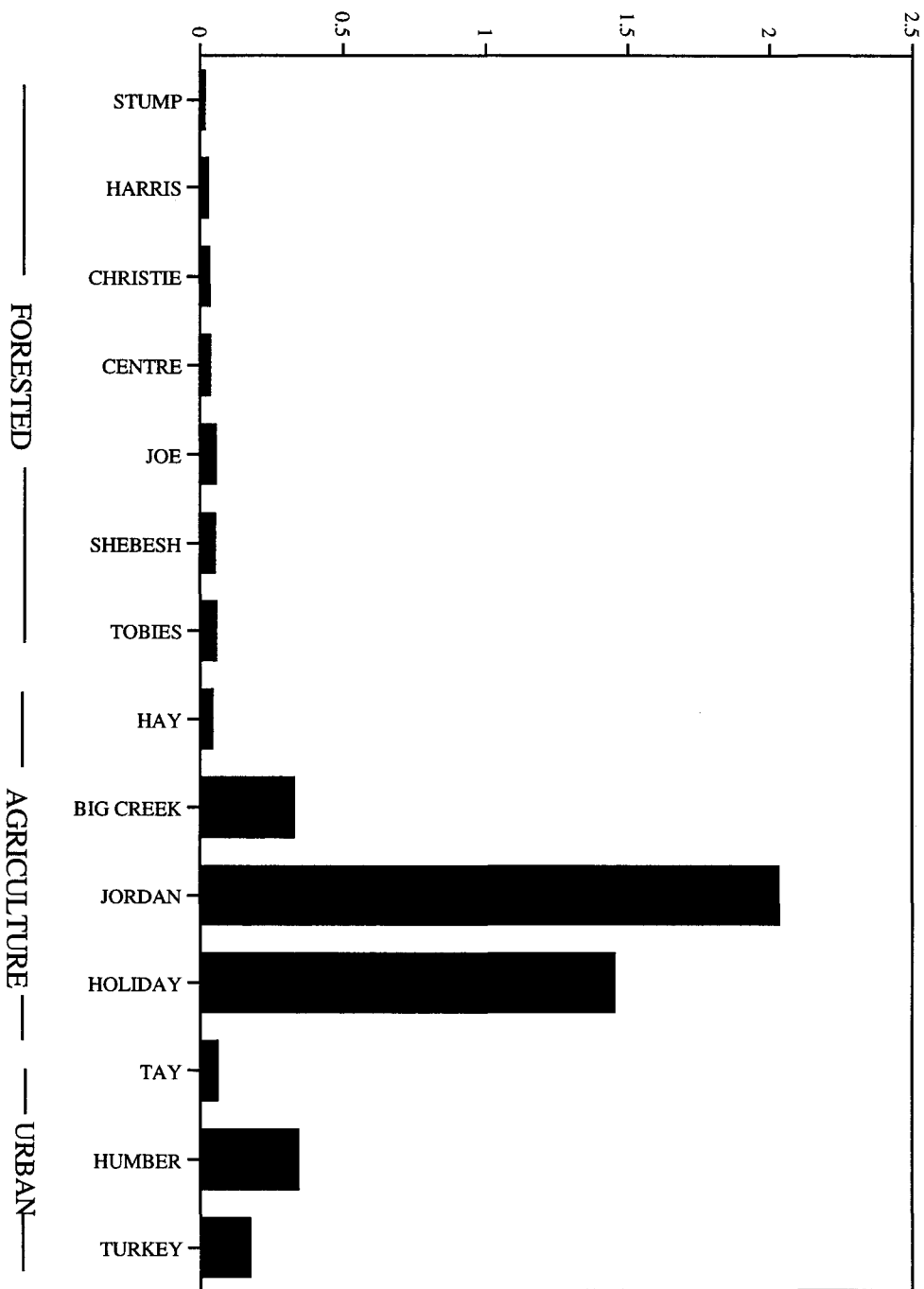
Figure 2.2



**Figure 2.3** Metolachlor concentrations in the 14 wetlands sampled. Sites are grouped according to the dominant landuse in their watershed.

METOLACHLOR (PPB)

Figure 2.3

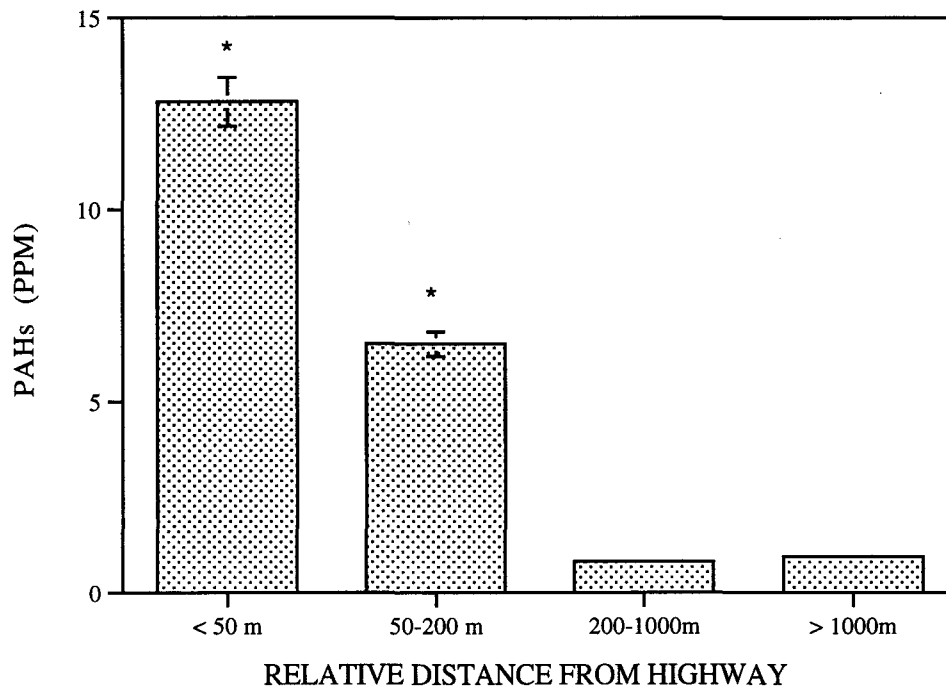
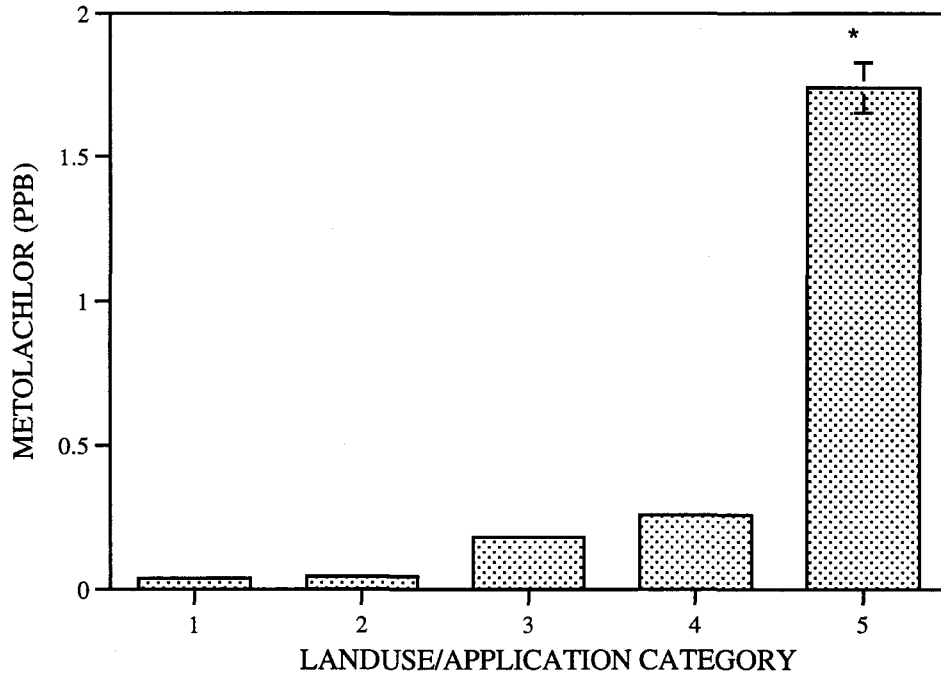


**Figure 2.4**

a) Wetland sites grouped according to their respective landuses and plotted against their respective metolachlor concentrations. Means are presented with standard errors. \* indicates a significant difference between categories (Tukey-Kramer,  $p < 0.05$ ).

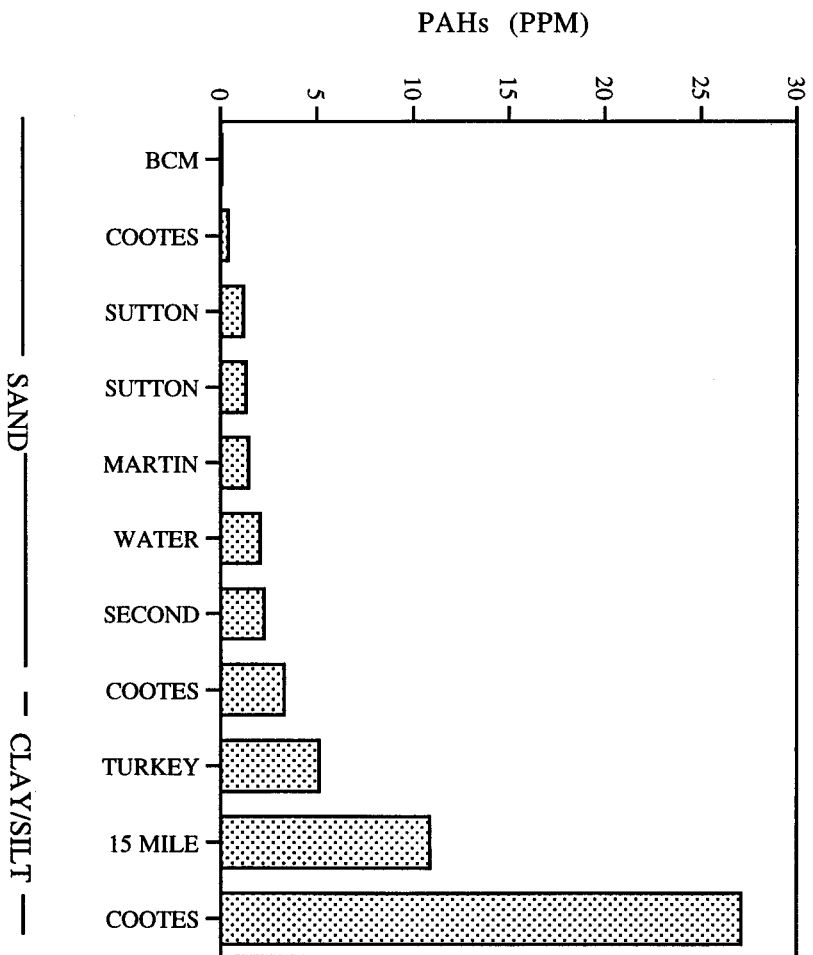
b) Wetlands grouped according to the distance of the sampling site from the nearest roadway and plotted against PAH concentration. Means and standard errors are presented. \* indicates a significant difference between distances (Tukey-Kramer,  $p < 0.05$ ).

**Figure 2.4**



**Figure 2.5** Creek sites plotted against their respective total PAH concentration and grouped according to their substrate size.

Figure 2.5



**Chapter 3:**

**Moving Past the Wetland Boundary: How Landuse Changes in  
the Watershed Affects the Water Quality and Vegetation in  
Wetlands**

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## ABSTRACT

This study assesses the impact of altered landuse on the aquatic plant community of twenty-two natural marshes in south and central Ontario. Water and sediment quality of wetlands were related to landuse (agricultural, urban or forested) in respective watersheds, and linked to the species richness and community structure of the aquatic plants. During July and August of 1995 and 1996, we monitored the water quality (nutrient, chlorophyll and suspended solids concentrations; water turbidity) and sediment quality (nutrient and organic content), and identified the type of aquatic vegetation in each wetland. Each marsh was sampled in three different habitat types: >10 m away from a plant stand (open), 3 m away from a plant stand (vegetated), and at a main tributary >100 m away from the inlet (creek). We found no temporal variation for any of the variables tested, either on a seasonal (for five of the wetlands sampled monthly in 1996) or year-to-year basis (same wetlands sampled in both years). However, there were significant differences with respect to the relationship between nutrient-chlorophyll, and that between phosphorus content and inorganic content in sediment for the three habitat types.

A Principal Components Analysis (PCA) was used to identify the primary water and sediment variables that structured the dataset. Variables associated with water clarity (turbidity, suspended solids, chlorophyll, Secchi depth) and primary nutrients (phosphorus and nitrogen) loaded heavily on the first principal component, which explained 45% of the overall variation in the dataset. Factors indicative of water and sediment fertility loaded heavily on the second component, which explained a further 16% of the remaining variation. Separate analyses corresponding to the three habitat types yielded similar

results. Parameters identified in the PCA were used in a Canonical Correlation Analysis (CCA) to determine their relationship to the aquatic plant community. Axes 1 and 2 of the CCA accounted for 97% of the variation in the dataset. The occurrence of submergent taxa was significantly correlated with sediment phosphorus content, and inversely related to the concentration of suspended solids and nutrients in the water column. By comparison, the distribution of emergent vegetation in the wetlands did not follow any consistent pattern with respect to either water sediment quality, whereas floating forms were inversely correlated with the inorganic content of the sediment. We calculated a "cumulative degradation index" that accounted for inputs of total phosphorus, suspended solids and inorganic nitrogen in each of these marshes. We found a significant log-linear relationship between this index and the percent of altered landuse (agriculture plus urban) in respective wetlands ( $r^2=0.31$ ;  $P=0.0001$ ). To separate the impacts of the different landuses we regressed the principal component scores for the first three axes against the amount of agricultural, urban and forested land. Agriculture was positively correlated to the first principal component ( $r^2=0.33$ ;  $P=0.0001$ ), which is explained by the nutrients and suspended material in the water column. Forest showed a negative correlation to this component ( $r^2=0.36$ ;  $P=0.0001$ ), indicating its value in attenuating nutrients and suspended sediments. The third component was positively correlated to urban development ( $r^2=0.116$ ;  $P=0.011$ ); this component is explained by exposure to wind, nitrate nitrogen and soluble phosphorus concentrations. Our results confirm that the overall health of wetlands (based on species richness and structural diversity of the aquatic plant community) is primarily dependent on the water and sediment quality, and that these are in turn influenced by the type of landuse in the watershed.



## INTRODUCTION

The presence of a healthy wetland is vital to the maintenance and functioning of the Great Lakes ecosystem. Wetlands are ecologically important ecosystems because they provide much needed habitat to a variety of water and terrestrial organisms (Russell, 1987). The unique transitional nature of wetlands, from terrestrial to aquatic, provides essential habitat for many rare and sensitive species. The diverse and unique community of the wetland environment provides excellent observation and study areas, which are popular to nature enthusiasts and researchers alike. The structural nature of this habitat confers economical benefits by filtering sediments and nutrients out of overlying water and acting as a natural water treatment plant. In addition, wetlands are able to control flooding in downstream catchments, prevent shoreline erosion and act as areas of groundwater recharge. These functions are representative of the ecological, social and economical benefits wetlands offer, which are vital to the global economy of the Great Lakes basin (Environment Canada, 1991).

The functional capacity of wetlands is heavily dependent on the structure, abundance and type of vegetation within. Structural diversity and interspersion are two factors important in determining the nature of the wetland community. For instance, submergent vegetation is important for waterfowl feeding, fish spawning and providing habitat for macroinvertebrates (Lillie and Evrard, 1994). By comparison, an emergent plant community provides important nesting grounds for marsh birds and waterfowl, and is an important food source for many mammalian species. Presence of both types are therefore required to support a diverse biotic community. A third type, floating

macrophytes are equally important for wave attenuation and nutrient assimilation. Good interspersions of these three vegetative types is characteristic of a healthy wetland association.

Wetland vegetation is extremely dependent on good water quality (Hough et al., 1989), which subsequently affects the sediment quality (Carpenter and Lodge, 1986). Water quality improvements occur in wetlands by plant filtration of suspended sediments and uptake of nutrients (Catallo, 1993). Suspended sediments often carry bound nutrients, which are essential for plant growth (Wall et al., 1996). The vegetation within the wetland utilizes nutrients by uptake from the water column followed by translocation into an organic material, which is stored in the plant tissues (Dorge, 1991). The uptake of these sediment-bound nutrients prevents their re-release into the water column, which could otherwise lead to eutrophication (Golterman, 1995). Subsequently reduced nutrient and sediment loads result in high light attenuation and create an environment conducive to plant growth; thus creating a positive feedback cycle that is a very important component of a healthy, functioning marsh.

The ability of wetlands to improve water quality may be hindered when the sediment or nutrient loads exceed the tolerance level of the plant community. Previous studies have demonstrated that altered land use degrades water quality in wetlands, creeks and lakes (Zampella, 1994; Lowrance et al., 1994; Roth et al., 1996). The general impacts are increases in suspended solids, nutrient and conductivity levels. However these studies only consider the inputs of a single watershed, and the impacts on the biotic community are often ignored. In addition, the impacts of agricultural versus urban land use are not treated individually and the relative contributions of each type is not known.



In the current fiscal environment, it is difficult to preserve or restore all the wetlands in the Great Lakes basin. By understanding the relative impact of each type of disturbance, managers can focus their efforts on those that are most likely to respond to interventions. Many of the wetlands located in the Great Lakes basin are likely degraded as a result of chronic pollutant loading rather than point-source pollution (see Chapter 2). The increased interest in restoring these areas requires better understanding the relationship among landuse in the watershed, water quality and health of wetland vegetation.

This study focusses on the factors affecting wetlands located primarily in the Great Lake's basin, to contribute a better understanding of the relative impact of non-point source pollution on the structural diversity of these marshes. The water quality, plant community and watershed landuse of twenty-two natural marshes were investigated and the interactions between each were examined. We chose wetlands based on a gradient of landuse disturbance to encompass a range of conditions from mainly forested watershed to agricultural or urban dominated. We measured the nutrient and suspended solids loads in the water and sediment for each wetland and recorded the structural diversity of wetland plants to determine the impact of landuse on wetland health.

This study will be useful for individuals responsible for preserving existing wetlands or those attempting to restore degraded ones. By linking wetland health to landuse, we will provide a basis for targetting healthy wetlands that should be preserved through restrictions on watershed development. Alternately, our results will also indicate the likelihood that wetlands in heavily disturbed watersheds will respond positively to interventions and remediation. The ability of wetland plants to recover from previous or current stresses must be evaluated to ensure that expensive remedial actions are not undertaken in vain or the support of public is diminished because of failures.

## STUDY SITES

Twenty-two wetlands, covering a broad spectrum from highly disturbed to pristine conditions, were sampled for a suite of water quality variables and vegetation in 1995 and 1996 (Fig. 2.1). Wetland sites were chosen based on the amount of urban, agricultural and forested land in their watershed, to ensure a sufficient gradient of disturbance. The majority of these wetlands are located within the Great Lakes basin, many being coastal wetlands (Table 3.1). Seven of the twenty-two wetlands are located on the Canadian Shield where the underlying bedrock consists of granite. The remaining are on limestone-dominated bedrock, characteristic of southern Ontario. One site sampled within each wetland was near the vegetation (vegetated) dominated by emergent, submergent or floating macrophytes; other sites included were an open water area (open) and an upstream creek (creek), where appropriate. These three sites were chosen to monitor the quality of water entering the wetland (creek), the water being exported (open), and the possible influence of the plant community (vegetated). Creek samples were collected at least 100m upstream of their outlet into the wetland and open water sites were a minimum of 10m away from the vegetation, downstream of the near-vegetation site (towards the outlet). The near-vegetation site was located 3m from emergent, submergent or floating vegetation. A summary of each wetland's location, size, soil type, exotic species and watershed size as well as its unique features are presented in Table 3.1.

## MATERIALS AND METHODS

### *Data Collection*

Large scale studies which consider a number of variables over a variety of locations can offer insight into the general principles and mechanisms controlling the overall state of an area (Day et al., 1988). In this study we collected water and sediment samples from 22 marshes, twice annually, in either 1995 or 1996. In addition Jordan, Cootes Paradise, Big Creek, Turkey Creek and Holiday Marsh were sampled monthly from June to September in 1996, as well as on two occasions in 1995, to discern seasonal and year-to-year variation. These analyses allowed us to determine whether it would be valid for us to combine the data from the two dates and years, and indicate whether two sampling dates were adequate for such large-scale comparisons. Delineation of landuse was explained in Chapter 2 and the percentage was presented in Figure 3.1.

*In situ* measurements of pH, dissolved oxygen (DO), specific conductance ( $\mu\text{S}/\text{cm}$ ) and temperature ( $^{\circ}\text{C}$ ) were recorded with a H2O Hydrolab<sup>TM</sup> equipped with a Scout2 monitor. Turbidity values were collected with a Hach turbidimeter (model 2100P) and Secchi depth transparencies were recorded in triplicate with a 20 cm disc. To allow for comparison between dates, the weather conditions (recent storms) were recorded.

On each sampling occasion, we collected water samples from the middle of the water column with a 1-L Van Dorn sampler. Water was placed in acid-washed nalgene bottles for nutrient analysis and were either frozen or acidified, and stored at 5  $^{\circ}\text{C}$  until analysis. Total phosphorus (TP) and soluble reactive phosphorus (SRP) were analyzed in

triplicate according to Murphy and Riley (1962); total ammonia nitrogen (TAN) and total nitrate nitrogen (TNN) were analyzed in duplicate with Hach reagents (APHA, 1992). Planktonic Chlorophyll<sub>a</sub> (CHL) was measured by filtering aliquots of whole water (50 mL to 1 L, depending on productivity) through GF/C filters. They were kept frozen until extraction in 10 mL of 90% reagent grade acetone, for a minimum 1-h in the freezer, after the lawns had been disrupted using a glass rod. Duplicate CHL concentrations were read at 665 and 750 nm and corrected for phaeophytin, using 3 M HCl. All the above techniques required the use of a Spec 301 spectrophotometer to measure the absorbance of the target analyte and conversion to a concentration from a standard curve, using Hach standards. Total suspended solids (TSS) were determined, in duplicate, by filtering an aliquot of water on pre-weighed Whatman GF/C filters. Frozen filters were placed into porcelain crucibles of known weights to be dried at 100 °C for a 1-h period, followed by a 1-h desiccation. The filters were weighed to the nearest 0.0001 mg and ignited at 550°C in a muffle furnace for 20-min, transferred to a desiccator for 1-h, and reweighed to determine total inorganic suspended solids (TSS).

Sediment samples were collected from the top 5 cm of sediment with either an Eckman grab sampler or a 5 cm diameter Plexiglas tube equipped with a plunger. They were frozen in clean, glass baby food jars (120 mL) until analysis. We dried the sediment samples at 100 °C determine their moisture content and then fired them at 550 °C in a muffle furnace to calculate the amount of inorganic material contained within the sediment (Inorg<sub>sed</sub>). Approximately 0.15-0.2 g of the Inorg<sub>sed</sub> material was boiled in 25 mL of 1 M HCl for 15-min, and then diluted to 100 mL. After neutralization using 10 M NaOH, a 20 mL aliquot was analyzed for the TP content of the sediment (TP<sub>sed</sub>) according to Murphy and Riley (1962). TP<sub>sed</sub> was expressed as mgTP/ g dry weight for the triplicate sediment subsamples.



The number of species present at each marsh was determined from field surveys in late August, when vegetative growth was at its maximum. Intensive vegetation analysis was performed *in situ* in both years. We recorded every new species encountered within a 3 m radius at the near-vegetation site. Since permission to sample these wetland areas was granted on the condition that the testing be non-destructive, we photographed any of the species we were unable to identify in the field. If differences between species were recognized but the species could not be identified, the number of different species in the taxa were recorded. At the creek and open water sites any new species present were noted. We consulted the vegetation lists created during the Wetland Evaluation by the Ontario Ministry of Natural Resources (OMNR) to help identify unknowns and confirm our identifications. The number of species in each taxon found during our survey is reported in Table 3.2. We also classified the plants according to structure as emergent, submergent or floating since each of these types functions differently in terms of habitat (Table 3.3). For example, emergents provide habitat for marsh birds such as redwing blackbirds, while submergents are good habitat for warmwater fish and waterfowl. Accordingly, every wetland was assessed in terms of structural diversity as follows: 1) wetlands with a fringe of emergent vegetation, 2) wetlands lacking one structural group, 3) wetlands with either good structure but lacking diversity or vice versa and 4) wetlands with good structural diversity and interspersion (Table 3.4). Pictures of each site were taken to visually aid in assigning wetlands to one of the four categories.

### *Statistical Analysis*

All statistical analyses were performed using SAS Jmp (SAS Institute Inc. 1982) software package. Only near-vegetation water quality data were included in the canonical analysis. Averaged data from the two sampling dates were used in the remaining analyses.

The initial matrix consisted of 14 environmental variables (water and sediment) and 22 marshes (Table 3.5). Species were grouped according to genus to reduce the number of variables and those taxa present in fewer than 5 of the wetlands were excluded, for a total of 18.

To reduce the complexity and highly correlative nature of the environmental variables, a Principal Components Analysis (PCA) was performed to extract those variables which explained the majority of the variation in the data set. These environmental variables were correlated with the PCA scores for interpretation purposes. The length of the line and its angle to the principal component axes indicates its importance (increases with length; acute=positive, obtuse=negative). The elimination of highly correlated variables permitted the use of Canonical Correspondence Analysis (CCA), to elucidate the relationship between the plant and environmental variables. Interpretations of the CCA biplot involved using the approximate covariances between the taxa and environmental parameters. The length and direction of the vector indicates the strength and nature of the correlation to the canonical axis, with stronger correlations associated with increased length (Jongman et al., 1995). The angle between the species and environmental lines indicates the correlation between these variables. Generally acute angles indicate positive relationships, obtuse are negative and no relationship is present if the lines are perpendicular. Results presented are based on data normalized to a mean of zero and a standard deviation of one. The response of species to environment conditions is generally unimodal in wetland communities, as was the case for these data.

Developed land in the watershed (agriculture and urban) has been found to contribute elevated nutrient and particulate loadings over forested or undisturbed lands (Ehrenfeld, 1983). Based on this, we constructed a "cumulative degradation index", as

an indication of the impact of changing landuse on wetland water quality. As a crude index of water quality degradation, we summed the  $\log_{10}$  of the concentrations of TSS (mg/L), TP, TAN, TNN (all  $\mu\text{g/L}$ ). We also calculated the amount of altered land as the sum of agriculture and urban, and expressed it as a percentage. The degradation index was regressed against the amount of altered land to determine if developed lands were related to poor water quality.

## RESULTS

### *Characterization of Water and Sediment Quality*

#### Spatial and Temporal Differences

We first determined if significant differences existed among the creek, vegetation and open water sites. One difference was found in the relationship between TP and CHL where the slope for the near-vegetation site was significantly lower than that for the other two sites (Fig. 3.2a). This suggests that macrophytes interfere with the phosphorus/algal relationship because the same amount of phosphorus at this site resulted in lower CHL values. Another difference was that the inverse relationship between the amount of inorganic material ( $Inorg_{sed}$ ) and phosphorus ( $TP_{sed}$ ) was absent for the vegetated site (Fig. 3.2b) where no relationship existed between these two parameters.

We compared data for water and sediment, where possible, to determine differences between samples collected in early July and late August. No significant differences were found for any of the parameters. Since these results indicated no significant temporal variation, data from both sampling trips were combined for further analyses. Five wetlands had been sampled on four dates in 1996 and a comparison of data for these revealed that only DO and TEMP changed significantly among the dates (Table 3.6; Tukey-Kramer,  $p < 0.05$ ). Higher levels of DO were found in early August when water temperature reached its maximum while temperature was colder in June and September at all five wetlands. These results suggest that two sampling dates adequately characterize the wetlands. Year-to-year variation was also investigated for these five wetlands and no differences were found for any of the parameters. The 1995 and 1996 data were combined

in the subsequent analyses, based on these results. These results indicate that except for temperature and dissolved oxygen, seasonal and year-to-year variation for all other environmental variables could be ignored.

### Important Water and Sediment Variables

PCA was utilized to determine the important variables structuring the dataset. Since we found significant differences in water quality among the creek, vegetation and open water sites, a separate PCA was run for each; however, they were similar so only the PCA for the entire dataset was presented (Fig. 3.3). Covariance plots were used to display the relationships between the environmental parameters and the component axes (PC 1-3). The combined PCA provided very similar information as those corresponding to the creek, vegetated and open water sites; consequently only the details of the combined PCA will be presented here. Only the first three principal components were retained in subsequent analyses. These principal components constituted 70% of the variation in the data, with each axis explaining a minimum of 9%. Approximately 45% of the variation was explained by the first principal component, with the second component explaining 16% and the third a further 9%.

The first principal component (PC1), an indicator of nutrient and sediment variables in the water column, was positively correlated with TURB, TP, CHL, TSS, ISS and TAN, and negatively correlated with SECCHI (Table 3.7). Variation in these parameters largely reflects the degree of degradation of water quality in the wetlands; sites that were more turbid were also more polluted with nutrients, suspended solids and have low SECCHI depths. The second principal component (PC2) was related to sediment fertility (TP<sub>sed</sub>) and composition (Inorg<sub>sed</sub>) and specific conductance (COND), a surrogate of water fertility, in the water column. Wetlands with low PC2 values are characterized by fertile

waters and infertile, inorganic soils. The third principal component (PC3) was positively related with wind speed (WIND) and water column TNN, with an opposite relationship to pelagic SRP (Fig. 3.3b). Wetlands with high PC3 scores were more exposed to wind, had higher turbidities (high TSS and ISS), and low phosphorus availability, possibly because the presence of suspended particles provide ample sites for phosphorus adsorption whereas in unexposed sites, much of the soluble phosphorus remains in the water column. TNN was elevated in wetlands that were more exposed, possibly representing sites which had lost ample plant cover to shelter the water from wind effects.

#### *Relationship Between Water Quality and Vegetation*

The PCA identified 13 water and sediment quality variables that were important in explaining variation in our wetlands. To relate these environmental parameters to the vegetation present in each wetland, we used another multivariate analysis, Canonical Correlation Analysis (CCA). This technique maximizes the taxon-environment correlation; however, CCA only produces reliable results when the number of variables is less than the number of study sites (Jongman et al., 1995). Since we had 13 environmental variables and 13 taxa (26) with only 22 wetlands we needed to reduce the number of variables. In addition, CCA requires that variables with high inter-correlations be removed, to eliminate misleading results.

To run a CCA we first eliminated redundant variables identified with PCA: SECCHI, TURB, TSS, ISS and CHL were highly correlated with TP ( $r > 0.85$ ) and therefore removed; SRP, TNN and WIND were excluded because collectively they explained less than 10% of the variation. This reduced the number of environmental parameters to 5; TP, COND, TAN, TP<sub>sed</sub> and Inorg<sub>sed</sub>. The plant taxa used in the analysis was reduced to 15 after exotic and non-representative species were excluded. 99% of the

variation was explained by the first canonical axis (CAN 1) with less than 1% being explained by the second canonical axis (CAN 2).

The canonical variates were correlated with the taxa and environmental variables to determine the canonical loadings. We plotted our canonical loadings for the first and second axis, with taxa and environmental variables presented on the biplot (Fig. 3.4). Significant correlations were found between axis 1 (CAN1) and TP, COND, TP<sub>sed</sub> and Inorg<sub>sed</sub>. A weaker correlation was found between CAN 1 and TAN. This axis was interpreted as a nutrient gradient in both the sediment and water.

Submergent vegetation types (9-15) were generally negatively associated Inorg<sub>sed</sub> and COND. In particular, *Utricularia*, *Najas*, *Vallisneria*, *Potamogeton* and *Ceratophyllum* were the submergent taxa that showed an inverse relationship with these two parameters. Weaker relationships were shown between these taxa and TP and TAN. Wetlands that include these taxa are low in nutrients and contain organic-rich sediments. A positive correlation between TP<sub>sed</sub> and these submergents also suggest that nutrient-rich sediment is essential for their growth.

The close association of *Pontederia*, an emergent taxa, with TP<sub>sed</sub> indicates that this plant may have similar requirements as submergents. By contrast, *Sagittaria*, another emergent taxa, was found in completely different environmental conditions, favoured in nutrient-poor sediments but nutrient-rich water that characterized degraded wetlands in our dataset. The distribution of other genera such as *Typha*, *Sparganium* and floating species such as *Nymphaea* and *Nuphar* were not related to water or sediment quality by this analysis. That emergent taxa were indiscriminately associated in this way suggests that we

may have overlooked an important factor that accounts for the distribution of emergent taxa in these wetlands.

The second canonical axis (CAN2) was positively associated with TAN and, to a lesser degree, with TP. Only *Decodon* showed a negative correlation to CAN2, and this suggests that it is inhibited by high nutrient levels in the water. All other taxa showed positive correlations, of varying strength, to this axis. No particular structural grouping of taxa was strongly related to this axis; *Cabomba*, *Scirpus* and *Elodea* showed the strongest positive correlations to this axis and to TAN. This suggests that these species are able to tolerate high nutrient levels in the water column.

We further investigated the relationship between species richness and various water quality parameters and found that the number of submergents in wetlands were inversely related to the concentration of CHL, nutrient and suspended solids in the water column (Table 3.8). Wetlands with good water clarity and low nutrient concentrations were associated with high species richness (up to 15 different species of submergents), whereas turbid wetlands with phosphorus-rich water had fewer than 2 species and often had no submergent taxa present. Again, no striking relationships were found for emergent and floating types.

### *Impact of Landuse on Water Quality*

High nutrient and sediment levels in the water column and high percentages of inorganic material in the sediment are the result of external impacts. The log values of the nutrient and sediment related environmental variables (TP, TAN, TNN, TSS) were summed (our "cumulative degradation index") and this was plotted against the percentage



of altered land in the watershed. A significant positive correlation was found between the cumulative degradation index and the percent altered land in the watershed (Fig. 3.5). Wetlands in forested landscapes had better water quality (lower index value) than those in developed areas, in particular those wetlands whose watersheds contained greater than 95% agricultural land. Wetlands receiving both urban and agricultural impacts (Cootes Paradise Marsh, Sutton Pond, Humber River, Waterford Ponds, 15 Mile Creek, Martindale Pond) tended to have higher index values than wetlands containing only agriculture (Hay Bay Marsh, Tay River Marsh, Sawguin Marsh, Centreville Creek), where both types of altered land were approximately equal. In addition, the index value for Holiday Marsh was much higher than that for Big Creek Marsh, even though both correspond to watersheds that are almost completely altered. Similar deviations were noted in pristine areas where Tobies Bay and Shebeshekong Rvier were higher than that for Joe's Lake and Stump Lake, despite similar amounts of altered land.

To determine the contributions of each type of landuse (agriculture, forest, urban) we plotted the amount of each type against the scores for the first three principal components (Fig. 3.6). Since we characterized each axis in the PCA analysis, these regressions enabled us to evaluate how each type of landuse affects the water quality. Agricultural land was positively correlated with the PC1 and negatively correlated with PC2. Wetlands in agricultural landscapes generally had high suspended particulate and nutrient loadings with productive water, while the fertility of the sediment is poor. Forested land showed the reverse relationship, with a negative correlation to PC1 and a positive correlation to PC2. Wetlands associated with this type of landuse have low nutrient and suspended particulate loads and low water fertility, but fertile sediments. PC3 was solely related to urban landuse and the correlation was negative. These wetlands are relatively sheltered, have low inorganic nitrogen levels, and high amounts of available

phosphorus. Similar trends between agriculture and urban landuses were found for PC1 (positive) and PC2 (negative); however, the relationship was not significant for urban land. This suggests that both these land types may contribute in similar ways to water and sediment quality.

The four environmental variables used to calculate the cumulative degradation index (TAN, TNN, TSS, TP) were plotted against the structural diversity category (Fig. 3.7). Each wetland was grouped into its appropriate category (Table 3.4) and the calculated means were plotted for each of the four categories. We found an inverse trend between the structural diversity of the plant community and nutrient and suspended solids in the water column. In all cases the highest nutrient and particulate levels were in wetlands containing only fringe vegetation. These levels generally decreased in wetlands with increasing structural diversity. In categories 3 and 4 (good to excellent structural diversity) the TAN, TNN and TP levels were very similar, suggesting that the wetlands in these two categories were able to filter and assimilate nutrients equally well.

## DISCUSSION

All of the water-column variables included in this study (Table 3.5) are routinely measured in environmental monitoring programs (Chapman, 1992). Our results indicate that many of these are redundant for predicting the health of wetlands in terms of water quality and structural diversity of the aquatic plant community. An effective program should include primarily, water-quality variables related to the light quality (TSS or turbidity) and nutrient concentration (TP, TNN, TAN), and secondly, the organic content and fertility of the sediment ( $TP_{sed}$  and  $Inorg_{sed}$ ; Table 8). A scaled down monitoring program such as this is sufficient for predicting the structural character of the marsh plants over the broad range of conditions encountered in our study (Fig. 3.7). Characterization of landuse in watersheds as either natural (forested) or altered (urban or agricultural) was sufficient for identifying the negative impacts on the water quality of creeks and wetlands that receive their runoff.

We found no significant temporal variation in our nutrient and suspended solids concentrations on either a seasonal (from June to September) or year-to-year basis. This suggests that grab samples taken at any point in the summer and in any year would provide representative water and sediment data for such large-scale synoptic surveys. The more important consideration when conducting these cross-wetland studies is to ensure that samples are collected under similar weather conditions. For example, during the 1996 August sampling trip, we sampled Christie Lake, Joe's Lake, Stump Lake and Tay River Marsh in the midst of a severe rainstorm, which caused corresponding TP values to increase ten-fold over those measured in June. From a detailed study of another marsh in

this study set (Cootes Paradise Marsh), we know that inflow from creeks and surface runoff tend to greatly inflate turbidity and TP values above ambient levels during storms, and that levels measured during the antecedent dry periods are significantly lower (Chow-Fraser, unpub. data). Since marsh ecosystems are vulnerable to such episodic events, it is essential that data be collected during “calm” weather conditions to permit meaningful comparisons.

Not surprisingly, temperature and dissolved oxygen concentrations varied significantly over the season (Table 3.6). These two variables closely track changes in air temperature, which follow normal climatological conditions for this part of the country. In 1995, air temperature changed from 19°C in June to a high of 30°C in August and the water temperature and dissolved oxygen increased accordingly. Increases in dissolved oxygen likely reflected the high level of photosynthesis occurring at the time of collection.

Specific conductance is a reflection of the ion content in the water column. As such it is a relative measure of fertility (phosphate and nitrate ions), and an indicator of pollution from roads and highways adjacent the wetlands. Sodium and chloride ions, the main constituents of de-icing salts used in winter road maintenance, enter receiving waters in high concentrations during snowmelt (Gjessing et al., 1984; Stotz and Krauth, 1984). A study by Zampella (1994) found that levels of conductivity in receiving waters varied according to the type of landuse in the watershed. Our results were similar, with lowest conductivity present in wetlands dominated by forested land, and highest in wetlands that are bordered by urban development (and by implication, highways and roadways).

We found significant intra-site variation with respect to the TP-CHL relationship. Slopes of the regression corresponding to creeks and open sites were significantly higher

than that for the vegetated site (Fig 3.2a), indicating that there is lower CHL per unit TP near macrophyte beds. This is consistent with previous studies in which algal biomass within macrophyte beds were depressed compared with that in non-vegetated sites (Hough et al., 1989; Mitchell, 1989; Ozimek et al., 1991; Schriver et al. 1995; Chow-Fraser, pers. comm.), the cause of which may be due to higher grazing pressure exerted by large zooplankton (e.g. *Daphnia*) that are associated with macrophytes, or inhibition by aquatic plants through shading and/or competition for nutrients. The TP-CHL relationship found here was compared to previous studies on lakes, marshes and creeks (Table 3.9). The comparison showed that the wetlands examined in this study were very similar to the TP-CHL relationship found in many lakes. Despite the similarity, water from the vegetated sites, in marshes containing abundant wetland vegetation, had less CHL per unit of TP than their open or creek sites; this suggests that the aquatic vegetation was competing with phytoplankton for TP. However wetlands with high TP and CHL values contained only fringe vegetation, and they would not be able to assimilate the high phosphorus loads. It is likely these wetlands acted more like lakes where phosphorus was utilized by the phytoplankton community, in the absence of abundant macrophyte growth.

Although there was a significant linear relationship between the inorganic and phosphorus content of sediment for creek and open site, we found no corresponding relationship for the vegetated site (Fig. 3.2b). This is probably because macrophytes mainly withdraws from the sediment phosphorus pool (Carignan and Kalff, 1980; Carpenter and Lodge, 1986; Barko et al., 1991), and may therefore have depleted the TP content in the sediment in our vegetated sites. Studies by Barko and Smart (1983) indicated that plants prefer small, inorganic particles because they provide more bound phosphorus which the plants can utilize. Consequently, senescence of this vegetation contributes to the organic content of the sediment. These intra-site differences confirm that

nutrient dynamics within these freshwater marshes are greatly influenced by the presence and amount of vegetation (Johengen & LaRock 1993).

Phosphorus is required for vascular plant growth but when present in excess, the increased productivity tends to be associated with decreased species diversity (Day et al., 1988). Phosphorus is also required for phytoplankton growth, and in most freshwater ecosystems, is the most limiting nutrient. The relative impact of eutrophication on the aquatic plant and algal communities have been investigated experimentally in the Norfolk Broads where advanced cultural eutrophication coincided with loss of submergents and proliferation of algal blooms (Phillips et al. 1978; Schriver et al. 1995). Our data support these observations; marshes that had high loadings of phosphorus in the water column tended to have a very reduced submergent plant community, and is probably because of shading by algae and suspended particles (Phillips et al., 1978; Hough et al., 1989; Mitchell, 1989; Ozimek et al., 1991; Strand and Weisner, 1996).

Submergent vegetation are used extensively by zooplankton, macroinvertebrates, waterfowl and fish for food and for habitat (Lillie and Evrard 1994; Shriver et al. 1995; Randall et al., 1996). They can attenuate wave action and trap incoming sediments. Catallo (1993) have also discussed how the loss of wetland vegetation results in a decline in the ability of the wetland to function as a sink for nutrients. When they disappear, the marsh is more vulnerable to wind and wave action, and is more likely to remain turbid, a condition that mitigates against the re-establishment of submergents. This negative feedback is complicated by the fact that without wetland plants assimilating nutrients from the sediment, phosphorus is loaded internally when the sediment becomes anoxic (Golterman, 1995) or when disturbed by bottom-feeding fish (Lougheed et al., submitted to "Canadian Journal of Fisheries and Aquatic Sciences") or bioturbation associated with

benthic activity (Phillips et al., 1994). In either case, the increased phosphorus loading usually leads to higher algal biomass, which contributes further to light limitation for the macrophytes.

In this study, the most taxonomically and structurally diverse macrophyte beds were found in soils that had both a high organic content, and a high phosphorus content. This is consistent with laboratory studies where plant growth was compared against a variety of soil types and were found to be best in organically rich and fertile substrate (Anderson and Kalff, 1988; Barko and Smart, 1986 and 1983). Decomposition of plant material builds up the organic layer and then trap phosphorus from the previous year's growth. Marsh areas with high inorganic content in their sediments tended to occur in the southwestern portion of the province where erosion from agriculture and urban/roadway development have greatly increased loading of inorganic sediment in these wetlands. This is particularly problematic because the soil type is dominated by silt and clay, small particles that tend to remain in suspension. Unlike organic soils, these sediment types are capable of releasing bound phosphorus if oxygen, pH or redox potentials are favourable (Golterman, 1995). Thus, even though the phosphorus content is low compared with the more organically-rich sediments, there is a greater chance for internal loading.

Emergent and floating vegetation did not appear to be affected by the type of sediment or water quality in the water column in this study. They were both tolerant of poor water quality and were found in majority of the wetlands studied (all 22 for emergents; 20 for floating). This is not surprising since Keddy and Reznicek (1986) have shown that the distribution of emergent taxa in Great Lakes wetlands are primarily controlled by water levels. They tend to proliferate in shallow water, regardless of the nutrient content of the sediment (Day et al. 1988), and are excellent at assimilating nutrients

from the sediment, especially phosphorus (Gersberg et al. 1986; Rogers et al. 1991; Johengen and LaRock, 1993). On the other hand, germination of floating plants may depend on water clarity and it is possible the range of conditions encountered in our study is not appropriate for determining the factors controlling the distribution of floating-leafed aquatics. Globally, the number of floating species is small and only a few studies have investigated the factors limiting their growth (Sinden-Hempstead and Killingbeck, 1996).

Weisner (1987) hypothesizes that as a wetland becomes more exposed to wind and wave action, the remaining plant species are forced landward. This may explain why we frequently encountered remnant fringe vegetation in degraded wetlands such as Cootes Paradise and Humber Marsh, where water clarity is very poor. This fringe consists almost exclusively of one or two species of emergent plants, whose site-to-site and year-to-year distribution tend to be regulated by water depths (LaBaugh, 1986; Chow-Fraser, 1996). Future studies should therefore incorporate this as a factor to determine the relative importance of fluctuating water levels in regulating the distribution of emergent plants across wetlands.

Another important factor that we have omitted in this study is altered hydrology on wetland health. Hydrological loadings are known to depend on the percent of impervious land in the watershed and the associated landuse along with the number or recharge areas upstream (Klein, 1979). Besides being the vehicle for transporting pollutants, the volume and rate of water input can undoubtedly cause changes and contribute to wetland degradation. Our study only considered the effects during baseflow, and purposely ignored changes during peak flows to make it tractable. Future studies should consider the relative impacts of altered hydrology and include it in the cumulative degradation index.



Landuse in the watershed was a key variable that determined the types and amount of pollutants entering a wetland ecosystem (See Chapter 2). In general, watersheds dominated by agricultural land tended to be associated with degraded marshes. For example, Holiday Marsh, which had the highest cumulative degradation index, had only a fringe plant community. This marsh is situated in an area with very low relief that is farmed intensively for cash crops such as corn, wheat and soybean. The bedrock material is clay loam and Brookston clay which are very fine particles that tend to stay in suspension. Tilling is practiced in about 50% of the farms, and this contributes a great deal of phosphorus-laden fine sediment to downstream sites. Besides agricultural runoff, urban and highway/roadway runoff also contributed to high degradation indices. For instance, Fifteen-Mile Creek, Centreville Creek, Cootes Paradise Marsh, Jordan Harbour, Second Marsh, Sutton Pond and Waterford Ponds are all located in southwestern Ontario, where they are affected by a combination of agricultural and urban/highway runoff. Sutton Pond had a high degradation index, despite a relatively small percent of altered landuse in the watershed. This may be because of urban development along its shores (apartment buildings) which would contribute additional point source runoff.

We also encountered instances where agriculturally-dominated watersheds were associated with structurally diverse and relatively healthy plant communities. A notable example is Big Creek Marsh, which lies in watershed that is extensively farmed. One reason for the lack of response from agricultural runoff is that Big Creek Marsh is situated in a sand plain. These larger and heavier sand particles settle out more rapidly and hence do not interfere with the light quality of the marsh, in spite of large inputs. In addition, buffer zones along the main tributary, whether forest or grassland, help filter out nutrients and suspended sediments upstream. Consequently, phosphorus levels were relatively low compared with other agriculture-based wetlands; however, nitrate levels were still

extremely high because of the prevalence of sod farms in the watershed that use fertilizers with high nitrogen ratios. Since nitrogen is generally the limiting factor for macrophyte growth (Barko et al., 1991), the combination of excess nitrate and good water clarity may explain why the plant community in Big Creek Marsh is relatively healthy, despite the dominance of agricultural lands in the watershed.

Hay Bay Marsh, located in the Bay of Quinte, also had a degradation index value that was much lower than would be anticipated based on the amount of altered land in its watershed. The tributaries entering Hay Bay Marsh are surrounded by forested buffer zones which help to attenuate suspended solids and nutrients. Additionally, the agriculture in this area is mainly used for livestock grazing and orchards, which involve much less exposed land and consequently less erosion. These livestock farms were large and provided extensive areas for grazing. In contrast, the surrounding landscape associated with farms in southwestern Ontario is virtually devoid of forested land, except where there are recently abandoned farmlands.

Wetlands with a large urban component included Humber Marsh, Martindale Pond, and Turkey Marsh. These wetlands were also degraded, but the cause of their degradation may have more to do with dissolved or soluble nutrient forms. The ambient levels of SRP are high in these marshes with low concentrations of TP and TSS. The protection of these wetlands from wind effects may allow phosphorus to remain in the water column instead of being bound to particulate matter (Lougheed et al., submitted to "Canadian Journal of Aquatic Fisheries and Aquatic Sciences"). Degradation index values associated with these urban wetlands were high except in the case of Turkey Marsh, which had low inputs of suspended solids and nutrients. This wetland was unique in that a rich aquatic flora existed, even though 89% of its watershed was urban. Nevertheless, as we have

documented elsewhere (see Chapter 2), there were very high levels of polycyclic aromatic hydrocarbons at this site. Therefore, even if urban wetlands are not subjected to high sediment and nutrient loads, they may receive high loads of organic contaminants that have potentially more harmful impacts on higher trophic levels in the foodweb (Maltby et al., 1996).

Wetlands whose watersheds are dominated by forested land had significantly lower concentrations of nutrient and suspended sediment (Fig. 3.5). Since naturally vegetated lands attenuate nutrients and sediments and only release nutrients during senescence, their presence in the watershed ensures that habitats downstream are enhanced during the growing season (Roth et al., 1996). We should point out, however, that development on the shores of the marshes can still exert a negative impact on the water quality of the wetland, as indicated by the higher than expected cumulative degradation indices for Shebeshekong River and Tobies Bay, both of which have cottage development on their shores. This type of development still results in increased sediment and nutrient loadings to the wetland, although not to the same degree as would occur from agricultural and urban runoff.

Our prediction based on landuse was not able to correctly identify the state of Tay River Marsh (Fig. 3.5) It is located in a watershed that has a mixture of agricultural, forested, and urban land. In addition to receiving sewage from the Town of Perth, it has also been dredged for navigation and recreational boating. Despite this mixture of negative impacts from agriculture, urban and recreational development, the marsh is in a very healthy state. Part of the reason for this is that agricultural land is used primarily for livestock grazing, which as we have pointed out, has lower impact compared with intensive cash crop farming. Although the Town of Perth exerts an impact, it has a very small

population, and the sewage treatment plant has effectively reduced the pollutant loads. And even though motor boating is permitted, speed limits are strictly enforced to afford some protection to the wetland vegetation. This example demonstrates that wetlands can remain healthy in spite of multiple impacts as long as they are moderate and mitigative measures are implemented.

From the foregoing analysis, it is clear that agricultural runoff results in the highest degradation indices and also exerts the most negative impact on the marsh vegetation. Reduced agricultural land mixed with urban development is associated with lower impacts, while forested land has the lowest impact. Byron and Goldman (1989) found similar results with respect to landuse impact on the water quality of streams in the Lake Tahoe watershed, California. Forested land, whether it is the dominant component or is only present as a buffer zone around streams and wetlands, appear to have a profound effect on the attenuation of suspended sediment and nutrients from point-source loadings (Peterjohn and Correll, 1984; Roth et al., 1996). Our study shows that they also have similar beneficial effects on naturally occurring wetlands that receive non-point source pollution.

Ammonia and nitrate nitrogen, suspended solids or turbidity, inorganic content of the sediment, and water-column and sediment phosphorus were the major determinants of wetland health because these are the ones that increase with amounts of exposed land, increased fertilizer application and pollution from animal waste that are associated with agricultural practices. A study on non-point source pollution by Humenik et al. (1987) also identified these as major water pollutants. They pointed out that “Best Management Practices” (BMPs), which are implemented to reduce loadings of nutrients and sediments should be applied at the watershed scale to have maximum benefit. This means that the decision to establish buffer strips to reduce pollutant loadings to aquatic systems (Osborne

and Kovacic 1993) should be made in terms of cost-effectiveness. For instance, some wetlands that are already severely degraded would not improve even if BMP's were implemented, especially those where the wetland vegetation has been reduced to a fringe, and which have other in-marsh impacts such as damage by the common carp (Whillans, 1996; Loughheed and Chow-Fraser, accepted for publication in "Canadian Journal of Fisheries and Aquatic Sciences"). Managers must also keep in mind that past nutrient loadings may have burdened the sediment layer to such an extent that internal loading of phosphorus may keep the wetland eutrophic for many years after nutrient abatement as in the case for the Norfolk Broads and Cootes Paradise Marsh (Philip et al., 1994; Chow-Fraser, pers. comm., respectively). High sediment loads may also have buried seed banks and inhibit recolonization of the plant community. In such instances, a joint program of in-marsh restoration (replanting, water-level regulation, carp control) together with an extensive basin-wide pollution-reduction program from non-point sources must be applied (Maynard and Wilcox, 1996).

Relatively healthy wetlands in this study contained greater than sixteen plant species of which eight were submergent (Table 3.7). By comparison, degraded wetlands generally had five or fewer species, with no submergent represented. There appears to be a threshold of about 10 units of TSS, and 50 units to TP, above which submergent plants cannot persist (Fig. 3.8). Given this, it is probably futile to re-introduce submergent taxa into degraded wetlands where water transparency cannot be improved substantially below this threshold. This has serious implications for restoration, preservation and protection efforts. Additionally it is imperative that phosphorus content of sediment from open-water sites be considered in view of internal loading problems discussed earlier.

The results of this study indicate that water turbidity, specific conductance, phosphorus content in the water and sediment, inorganic content of the sediment, the amount of ammonia nitrogen in the water column, and the amount of forested land within the watershed may be good predictors of the structural diversity of aquatic plants in Ontario wetlands. However, this model needs to be validated with an independent dataset before it can be generally applied. The dependence of diverse submergent vegetation on good water quality is particularly evident in this study. Additionally the type of particles and phosphorus in the sediment are important. Since a diverse aquatic plant community is essential for maintaining wetland function, loss of these species should be of general concern to everyone.

This study offers an important contribution to wetland management. More effective monitoring and restoration plans can be devised since this study extracted the important water quality variables for determining wetland health. This allows for the development of more efficient and effective sampling programs. Additionally, information regarding the individual impacts that different types of landuse (in particular altered vs forest) have on water quality offers new insight into where efforts to control inputs should be focussed. The results presented here suggest that emphasis should be placed on the conservation of forested land in the watershed. We recommend that wetland managers and developers should work together to mitigate potential impacts on wetland health. Only by the use of holistic management practices will wetlands effectively be protected from anthropogenic activities.

**Table 3.1** Summary of the geographic and physical parameters of each of the wetlands studied. Special features distinguishes elements in the wetland/watershed which affect the water and sediment quality (irrig'n=water used for irrigating crops; STP=sewage treatment plant; sand plain=bedrock overlain by sand; dam/resev=part of the water course either dammed or contained in a constructed reservoir; railway=railroad through wetland; restor'n=restoration project initiated for wetland; escarp't=influenced by the Niagara Escarpment; rec'n=recreation surrounding part of the wetland; prov. park=contained in a provincial park; channel=part of watercourse channelized; mining=quarry in the watershed; dredging=part of watercourse regularly dredged). \* indicates those wetlands on the Canadian Shield.

Wetland	MNR District	Latitude Longitude	Year Sampled	Wetland Type	Watershed Size (km <sup>2</sup> )	Wetland Size (ha)	Exotic Species	% organic (soils)	Special Features
Big Creek Marsh (BIG CREEK)	Simcoe	42° 57' 20" 80° 26' 50"	1995/1996	41% palustrine 59% riverine	200	61	purple loosestrife carp milfoil	18	sand plain dam irrig'n
Centreville Creek (CENTRE)	Maple	43° 54' 04" 79° 50' 00"	1996	riverine	35	13		>50	STP irrig'n
Christie Lake* (CHRISTIE)	Carleton Place	44° 47' 00" 76° 28' 00"	1996	riverine	66	113	milfoil	54	railway
Cootes Paradise (COOTES)	Cambridge	43° 16' 00" 79° 55' 00"	1995/1996	riverine	268	250	purple loosestrife carp	0	STP restor'n rec'n escarp't dam/resev irrig'n
Fifteen Mile Creek (15 MILE)	Niagara	43° 10' 00" 79° 19' 00"	1995	riverine	63	31	purple loosestrife carp milfoil	0	
Harris Lake* (HARRIS)	Parry Sound	45° 42' 00" 80° 82' 00"	1996	lacustrine	n/a	n/a	none	>50	very remote
Hay Bay Marsh (HAY)	Tweed	44° 10' 30" 76° 55' 30"	1996	92% lacustrine 8% riverine	225	1333	purple loosestrife carp	40	STP
Holiday Marsh (HOLIDAY)	Chatham	42° 02' 05" 83° 03' 00"	1995/1996	90% lacustrine 10% riverine	64	1177	purple loosestrife carp	5	low relief rec'n mining
Humber River (HUMBER)	Maple	43° 38' 00" 79° 29' 00"	1996	lacustrine	667	26.26	purple loosestrife carp milfoil	35	STP restor'n rec'n dam
Joe's Lake* (JOE)	Carleton Place	45° 08' 00" 76° 41' 00"	1996	riverine	268	204	milfoil	95	
Jordan Harbour (JORDAN)	Niagara	43° 11' 00" 79° 23' 00"	1995/1996	lacustrine	311	172	purple loosestrife carp milfoil	0	rec'n railway escarp't
Martindale Pond (MARTIN)	Niagara	43° 10' 07" 79° 16' 00"	1995	74% lacustrine 26% riverine	29	55	purple loosestrife carp milfoil	0	STP rec'n dam restor'n
Presqu'ile Marsh (PRESQ)	Napanee	44° 00' 00" 77° 43' 00"	1996	86% lacustrine 14% palustrine	22.2	992	purple loosestrife milfoil	70	prov. park
Sawguin Marsh (SAWGUIN)	Napanee	44° 06' 00" 77° 23' 00"	1996	55% riverine 45% lacustrine	91	2093	purple loosestrife milfoil	95	
Second Marsh (SECOND)	Lindsay	43° 52' 00" 79° 51' 00"	1995	lacustrine	85	106	purple loosestrife carp	10	rec'n restor'n STP dam
Shebeshekong River* (SHEBESH)	Parry Sound	45° 24' 30" 80° 19' 00"	1996	44% riverine 37% lacustrine 19% palustrine	107	108		25	
Stump Lake* (STUMP)	Carleton Place	44° 56' 48" 76° 38' 12"	1996	lacustrine	1060	93	milfoil	88	
Sutton Pond (SUTTON)	Simcoe	42° 50' 00" 80° 18' 00"	1995	palustrine	85	10	carp purple loosestrife	0	sand plain rec'n dam
Tay River Marsh* (TAY)	Carleton Place	44° 52' 45" 76° 10' 30"	1996	63% palustrine 37% riverine	669	553	purple loosestrife milfoil	85	channel dam STP dredging dam
Tobie's Bay* (TOBIES)	Parry Sound	44° 51' 00" 79° 47' 00"	1996	53% palustrine 47% lacustrine	9	194	milfoil	5	
Turkey Creek (TURKEY)	Chatham	42° 14' 08" 83° 05' 07"	1995/1996	riverine	5	32	carp purple loosestrife	50	STP channel rec'n
Waterford Ponds (WATER)	Simcoe	42° 56' 10" 80° 18' 45"	1995	71% riverine 16% lacustrine 11% palustrine	71	239	carp purple loosestrife	15	mining rec'n sand plain

Table 3.2 Summary of the number of species in each plant taxon found in the 22 wetlands; excluded from this list are those taxa that were found at fewer than five wetlands or exotic species (*Sparg*=*Sparganium*; *Potam*=*Potamogeton*; *Vallis*=*Vallisneria*; *Utricul*=*Utricularia*; *Cerato*=*Ceratophyllum*; *Pont*=*Pontederia*; *Sagitt*=*Sagittaria*; *Nymph*=*Nymphaea*).

Wetland	<i>Typha</i>	<i>Scirpus</i>	<i>Pont</i>	<i>Sparg</i>	<i>Decadon</i>	<i>Sagitt</i>	<i>Nuphar</i>	<i>Nymph</i>	<i>Vallis</i>	<i>Najas</i>	<i>Utricul</i>	<i>Potam</i>	<i>Elodea</i>	<i>Cabomba</i>	<i>Cerato</i>
15 MILE	1	0	0	0	1	1	1	1	0	0	0	1	1	0	0
BCM	1	1	0	0	0	1	1	1	1	1	0	3	1	1	1
CENTRE	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0
CHRISTIE	1	1	1	1	1	2	0	1	1	1	1	2	1	1	1
COOTES	3	0	0	0	0	0	0	1	0	0	0	1	0	0	0
HARRIS	1	0	1	0	0	0	1	0	1	0	1	2	0	0	2
HAY	1	1	0	1	0	2	1	1	1	2	1	4	1	3	1
HOLIDAY	1	0	0	0	1	1	1	0	0	0	0	1	0	0	0
HUMBER	1	1	0	0	0	0	1	0	0	0	0	1	0	0	0
JOE	1	1	1	0	1	0	1	1	0	1	1	5	1	0	0
JORDAN	1	0	0	0	0	1	1	1	0	0	0	1	0	0	0
MARTIN	1	1	0	1	0	1	0	1	0	0	0	0	0	0	1
PRESQ	1	0	0	0	0	0	1	1	1	2	1	4	1	0	1
SAWGUIN	1	0	0	1	1	0	0	1	1	2	1	3	1	0	1
SECOND	1	1	0	0	0	2	1	1	0	0	0	2	1	0	0
SHEBESH	1	2	1	0	0	1	1	0	1	1	1	4	0	0	1
STUMP	1	0	1	0	0	0	1	1	1	1	0	5	1	1	1
SUTTON	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0
TAY	1	1	1	1	1	0	1	1	1	2	1	5	1	1	0
TOBIES	1	2	1	1	0	0	1	1	1	0	2	2	1	1	1
TURKEY	1	1	0	0	0	0	1	1	1	1	0	3	1	1	1
WATER	1	0	0	1	0	0	1	1	0	0	1	0	1	1	1



Table 3.3 Various plant taxa identified in the wetlands are grouped according to their structural nature (numbers relate to Fig. 5). All taxa not assigned a number were excluded from CCA analysis since they were not well represented in these wetlands. Exotics, also excluded, are identified.

EMERGENT	FLOATING	SUBMERGENT
1 - <i>Typha sp.</i>	7 - <i>Nymphaea sp.</i>	9 - <i>Potamogeton sp.</i>
2 - <i>Sparganium sp.</i>	8 - <i>Nuphar sp.</i>	10 - <i>Utricularia sp.</i>
3 - <i>Pontederia sp.</i>	<i>Spirodela sp.</i>	11 - <i>Cabomba sp.</i>
4 - <i>Scirpus sp.</i>		12 - <i>Najas sp.</i>
5 - <i>Sagittaria sp.</i>		13 - <i>Elodea sp.</i>
6 - <i>Decodon sp.</i>		14 - <i>Vallisneria sp.</i>
<i>Rumex sp.</i>		15 - <i>Ceratophyllum sp.</i>
<i>Zizania sp.</i>		<i>Myriophyllum sp.</i> - exotic
<i>Lythrum salicaria</i> - exotic		

Table 3.4 Structural structural diversity grouping for each wetland. The criteria for each type of vegetation was required for the category to be assigned.

# SUBMERGENTS	# EMERGENTS	# FLOATING	CATEGORY	WETLAND
≥ 8	≥ 6	≥ 3	4	TAY, HAY, TOBIES, BIG CREEK
≥ 5	≥ 4	≥ 2	3	CHRISTIE, JOE, SAWGUIN, SHEBESH, TURKEY
≥ 2	≥ 2	≥ 2	2	HARRIS, MARTIN, PRESQ, SECOND, STUMP, WATER
< 2	< 2	< 2	1	15 MILE, CENTRE, COOTES, HOLIDAY, HUMBER, JORDAN, SUTTON

Table 3.5 Summary of the physical and chemical water/sediment parameters measured.

Wetland	SITE	DEPTH cm	SECCHI cm	pH	DO mg/L	COND mS/cm	TURB FTU	TSS mg/L	TP mg/L	CHL mg/L	SRP mg/L	TNN mg/L	TAN mg/L	INORG %	TP SED mg/g
15 MILE	MARSH	35	13	7.53	6.2	741	80.7	124	345	23.86	20	450	190	94	0.72
	CREEK	92	21	7.48	5.3	743	58.8	44	230	31.60	20	500	130	94	0.56
BCM	MARSH	97	97	7.14	9.9	610	4.4	10	50	3.41	13	3000	50	77	0.6
	OPEN	140	119	7.65	10.2	610	8.3	10	62	3.69	10	2000	50	82	0.76
	CREEK	55	55	7.10	7.5	620	3.9	5	54	1.57	19	2000	20	99	0.23
CENTRE	MARSH	20	12	7.62	6.5	599	3.8	5	66	2.56	13	50	80	64	1.41
	CREEK	21	10	7.70	8.4	624	2.9	5	45	1.98	26	220	10	98	0.52
CHRISTIE	MARSH	30	30	6.55	6.4	153	2.1	9	31	4.83	3	80	20	59	1.47
	CREEK	120	120	7.33	8.1	150	2.3	11	33	1.28	6	0	40	80	0.91
COOTES	MARSH	20	12	7.00	2.3	700	48.4	44	145	11.65	23	320	270	85	0.89
	OPEN	40	11	7.00	10.9	689	75.0	74	160	76.92	11	580	130	89	0.48
	CREEK	127	24	8.62	7.9	740	44.0	65	113	6.15	12	600	70	94	0.71
HARRIS	MARSH	77	77	5.96	6.5	39	1.8	4	81	1.99	4	50	30	44	1.92
	CREEK	140	140	6.22	8.2	39	1.5	4	50	2.42	3	50	0	85	0.60
HAY	MARSH	86	86	6.69	4.0	552	3.0	4	62	7.67	22	50	60	68	0.57
	OPEN	40	40	7.00	6.4	550	1.7	4	29	1.42	12	0	40	41	0.47
	CREEK	130	85	7.21	6.9	575	8.6	15	75	2.54	12	60	70	95	0.62
HOLIDAY	MARSH	15	3	8.00	7.5	550	286.0	222	618	142.00	18	2200	240	87	0.53
	OPEN	55	5	7.86	8.2	581	357.0	276	577	318.1	23	600	300	80	0.84
	CREEK	90	4	7.75	7.5	603	312.0	255	754	341.9	20	1600	240	97	0.71
HUMBER	MARSH	25	13	7.48	6.7	735	67.8	57	214	29.26	11	140	220	96	0.55
	CREEK	265	37	7.88	8.1	762	41.8	39	102	54.82	9	200	100	96	0.55
JOE	MARSH	80	80	6.51	6.8	212	1.4	5	23	7.08	2	0	50	x	x
	CREEK	275	160	7.05	6.7	211	2.1	4	27	3.56	2	30	20	41	2.00
JORDAN	MARSH	80	29	8.13	7.6	561	37.9	35	275	40.61	81	80	80	95	0.83
	OPEN	247	31	7.93	6.3	550	36.4	39	216	33.80	72	100	40	83	0.77
	CREEK	75	40	8.07	8.0	553	17.3	18	130	5.83	65	30	50	x	x
MARTIN	MARSH	127	20	7.07	4.5	453	44.1	75	339	45.44	116	500	160	92	0.75
	OPEN	70	18	7.35	6.6	365	34.3	40	217	9.94	100	200	200	92	0.74
	CREEK	70	24	7.54	7.1	1047	45.2	35	182	54.67	39	500	220	94	0.54
PRESQ	MARSH	75	75	7.10	7.7	337	1.5	5	54	2.42	2	30	20	79	0.99
	OPEN	149	100	7.72	8.2	325	2.3	5	18	3.27	5	40	50	84	0.76
SAWGUIN	MARSH	80	80	6.91	4.7	390	4.1	6	76	14.92	15	170	120	29	2.00
	OPEN	152	102	7.04	5.3	392	4.2	5	62	27.27	19	220	50	x	x
	CREEK	165	145	6.98	4.7	418	2.9	1	120	19.03	49	270	90	x	x
SECOND	MARSH	10	10	7.77	10.6	865	14.8	24	407	66.77	107	400	30	71	1.01
	CREEK	20	20	7.58	8.0	824	16.6	19	85	1.42	1	800	110	99	0.35
SHEBESH	MARSH	80	35	6.06	6.9	49	6.1	9	92	6.11	1	330	60	82	0.40
	CREEK	90	80	6.06	6.8	49	5.9	4	82	3.84	5	400	30	96	0.19
STUMP	MARSH	52	80	7.80	6.1	190	1.9	5	42	6.39	3	0	40	24	2.17
	OPEN	100	52	7.43	7.4	142	1.9	4	30	3.13	6	0	20	x	x
	CREEK	385	100	6.08	7.6	130	1.6	2	74	2.56	6	0	10	x	x
SUTTON	MARSH	22	22	8.24	15.0	529	13.4	42	80	18.46	3	1700	70	94	0.38
	OPEN	25	25	8.10	15.2	642	8.4	40	130	3.98	6	1500	50	92	0.54
	CREEK	55	55	7.72	8.4	581	6.7	4	64	1.46	6	2000	40	95	0.43
TAY	MARSH	50	50	7.16	8.1	193	1.5	8	50	3.41	4	40	30	26	2.03
	OPEN	167	160	7.77	7.4	200	3.0	5	36	1.99	5	0	50	93	0.39
	CREEK	210	180	7.66	7.2	191	3.5	4	45	2.99	7	0	40	x	x
TOBIES	MARSH	122	50	6.28	6.0	101	2.8	7	139	22.29	3	300	40	36	1.03
	OPEN	187	48	6.12	5.5	120	4.7	12	98	18.75	3	230	10	x	x
TURKEY	MARSH	41	41	7.92	9.4	338	12.4	13	40	45.28	12	0	20	80	0.82
	CREEK	145	24	7.48	5.8	749	59.1	51	166	22.16	29	0	150	93	1.19
WATER	MARSH	44	32	7.78	8.9	465	23.0	52	129	25.21	7	450	260	75	0.85
	OPEN	40	40	8.17	10.1	479	15.6	12	127	39.76	8	230	10	77	0.71
	CREEK	45	45	7.86	8.9	585	7.3	12	54	5.97	9	3000	10	82	0.77

**Table 3.6** Seasonal differences for DO, TEMP in the five wetlands sampled four times over the summer of 1996. Lines indicate dates whose means are significantly different (Tukey-Kramer,  $p < 0.05$ ).

PARAMETER	JULIAN DAY			
	156	184	221	248
DO	8.89	8.90	<u>10.06</u>	<u>7.19</u>
TEMP	<u>18.65</u>	<u>22.41*</u>	<u>24.70</u>	20.86

\* 156 is significantly different from 184 and 221 (no difference between 184 and 221)

**Table 3.7** Significant correlation coefficients ( $p < 0.05$ ) between principal component scores and their related environmental variables.

	<b>Variance Explained</b>	<b>Environmental Variables</b>	<b>PC1</b>	<b>PC2</b>	<b>PC3</b>
<b>PC1</b>	<b>45%</b>	<b>SECCHI</b>	-0.63		0.34
		<b>TURB</b>	0.91	0.35	
		<b>TP</b>	0.90		
		<b>CHL</b>	0.84	0.41	
		<b>TSS</b>	0.94	0.30	
		<b>ISS</b>	0.92		
		<b>TAN</b>	0.79		
<b>PC2</b>	<b>16%</b>	<b>COND</b>	0.56	-0.56	
		<b>INORG</b>	0.51	-0.67	
		<b>TP SED</b>	-0.41	0.68	-0.31
<b>PC3</b>	<b>9%</b>	<b>WIND</b>	-0.63		0.40
		<b>SRP</b>			-0.76
		<b>TNN</b>	0.37	-0.33	0.51

**Table 3.8 Relationships between the species richness and the water quality parameters for each structural group.**

<b>PLANT GROUP</b>	<b>PARAMETER</b>	<b>R-SQUARE</b>	<b>SLOPE</b>	<b>INTERCEPT</b>	<b>P-VALUE</b>
<b>SUBMERGENTS</b> n=21	CHL	0.194	-0.04	7.99	0.0401
	TAN	0.370	-0.03	10.25	0.0026
	TP	0.380	-0.02	9.61	0.0022
	TSS	0.314	-0.05	8.06	0.0067
	TURB	0.260	-0.04	8.06	0.0150
	COND	0.427	-0.01	12.62	0.0010
	INORG	0.369	-12.79	15.39	0.0027
<b>EMERGENTS</b> n=22	NONE SIGNIFICANT				
<b>FLOATING</b> n=20	INORG	0.219	-0.07	0.836	0.0278

**Table 3.9** The log TP/CHL relationship between the three sites within this study, along with results from previous studies in lakes, marshes and creeks. \* indicates those values generated in this study.

<b>Ecosystem</b>	<b>n</b>	<b>log TP</b>	<b>y-intercept</b>	<b>r-square</b>
<b>Lakes</b>				
Mazumder 1994	367	0.94	-0.35	0.71
Vyhnalek et al. 1994	111	0.98	-0.51	0.35
Chow-Fraser 1991	129	0.94	-0.51	0.72
Chow-Fraser et al. 1994	34	1.16	-0.67	0.70
<b>Wetlands</b>				
marsh*	22	0.97	-0.85	0.55
open*	13	1.34	-1.52	0.66
<b>Creeks</b>				
creek*	20	1.70	-2.49	0.71

**Figure 3.1**    **Distribution of landuses for each of the twenty-two wetlands**



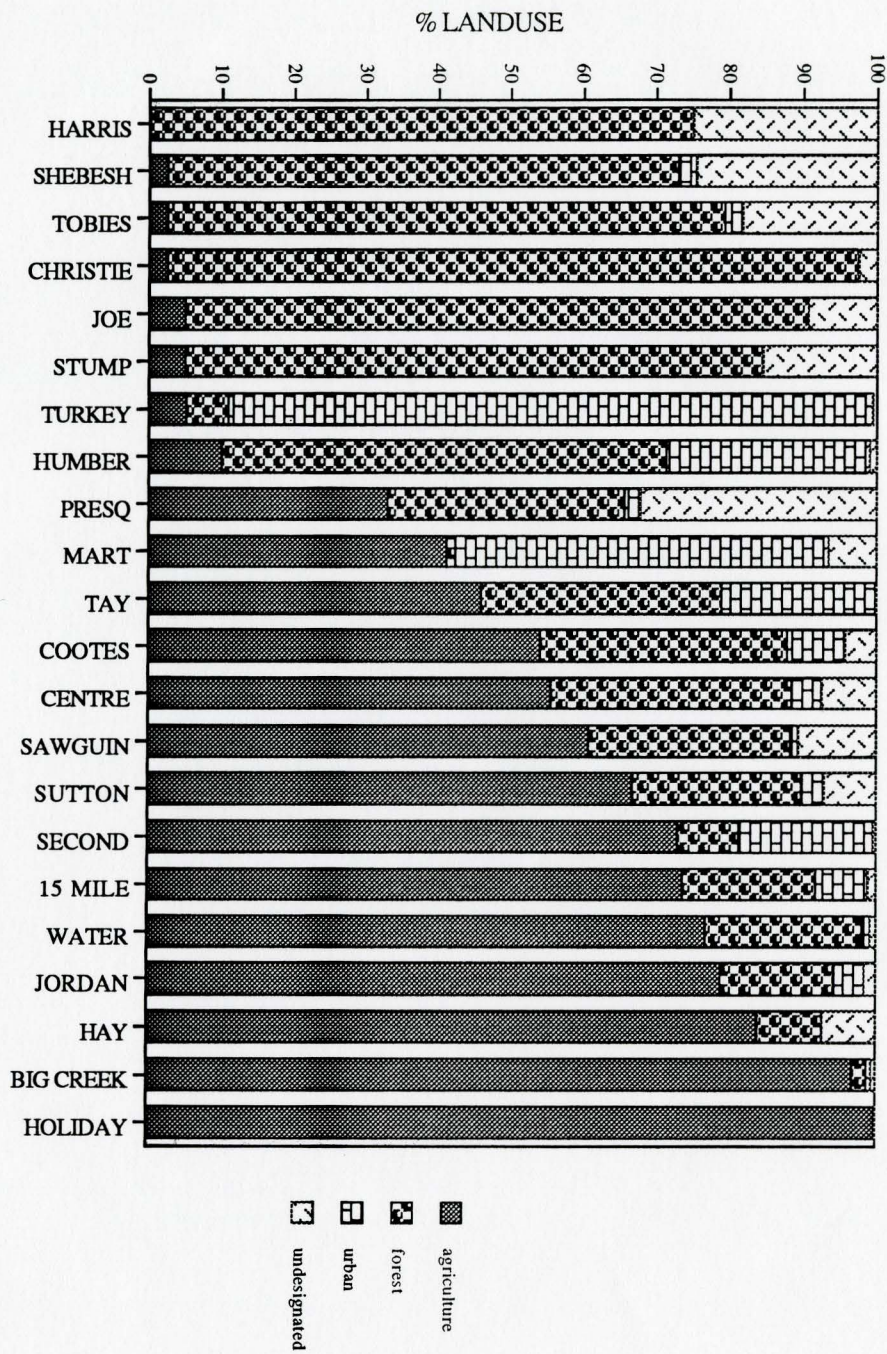
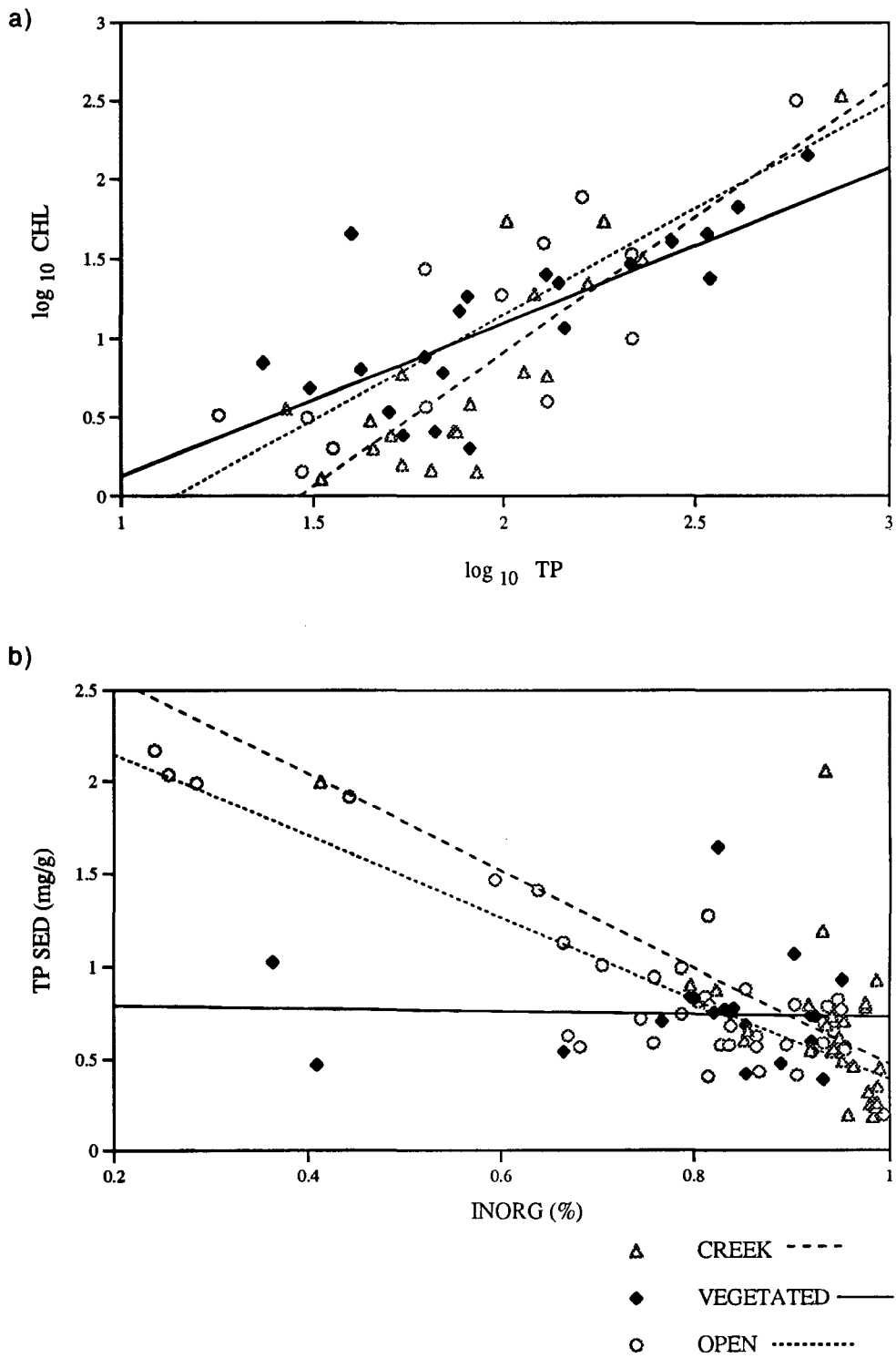


Figure 3.1

**Figure 3.2** a) Log TP-CHL relationship for the creek, open water and vegetated sites.

b) Relationship between total phosphorus and inorganic content of the sediment for creek and open water sites.

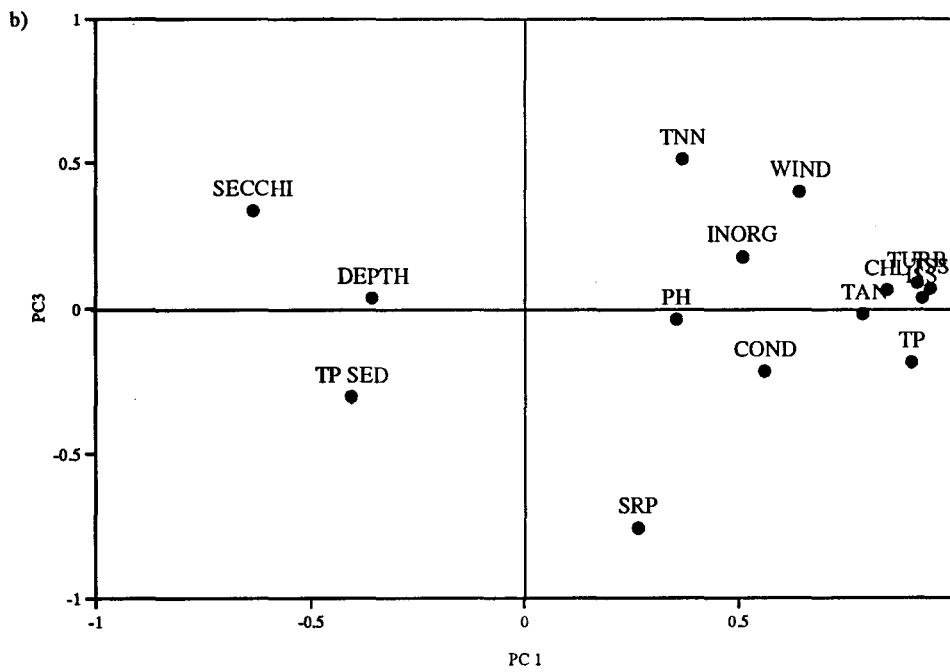
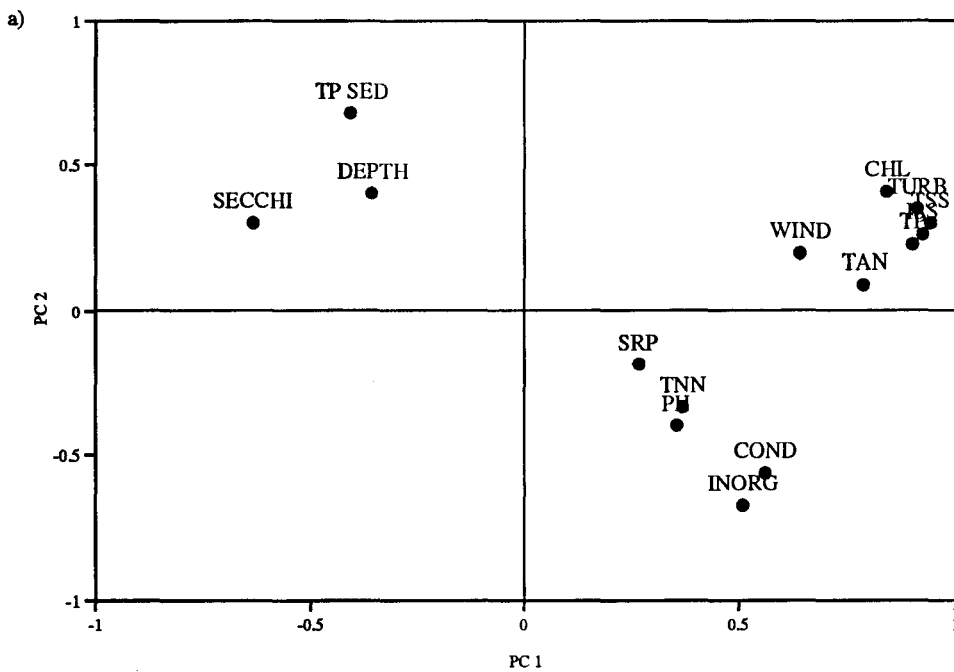
Figure 3.2



**Figure 3.3** a) Importance of the environmental variables in explaining the first and second principal components.

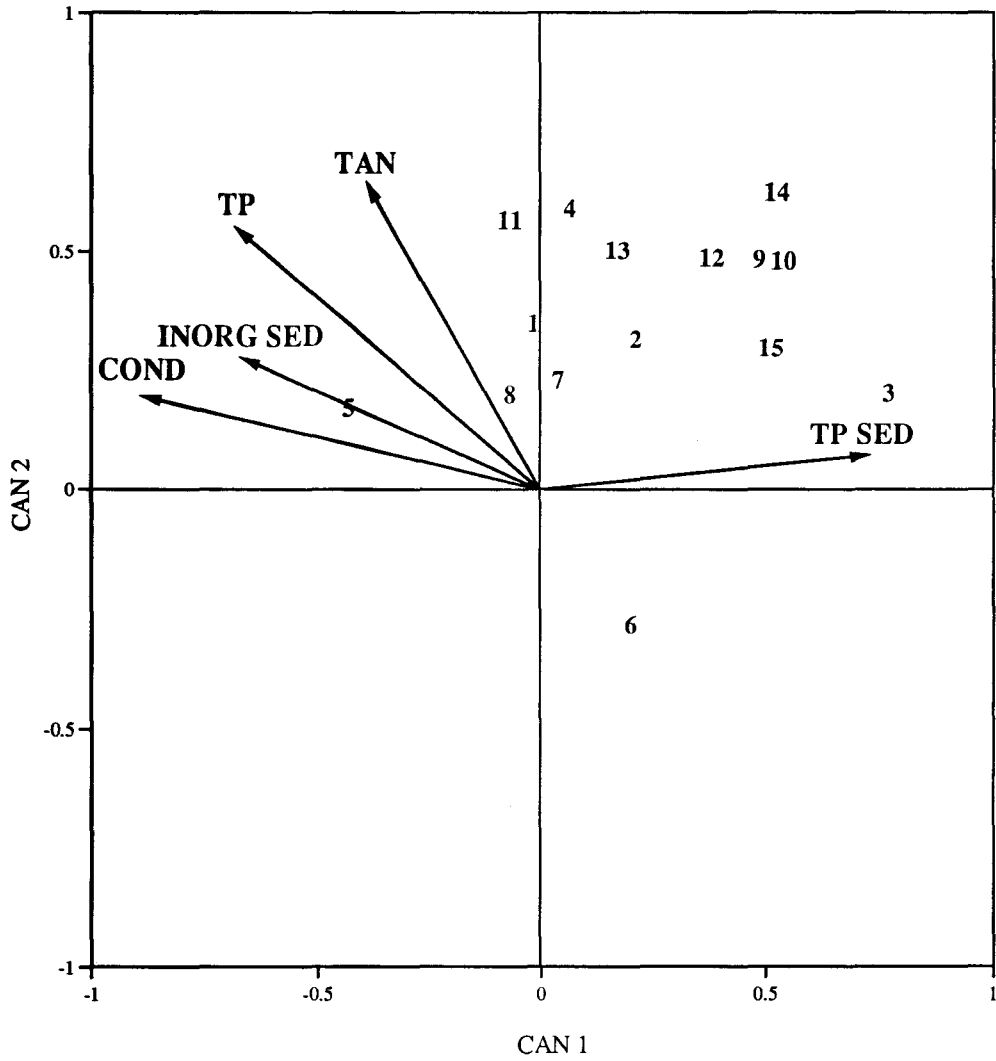
b) Importance of the environmental variables in explaining the first and third principal components.

Figure 3.3



**Figure 3.4** Canonical biplot of plant species and environmental variables. 1-6 correspond to emergents, 7-8 to floating and 9-15 to submergent vegetation.

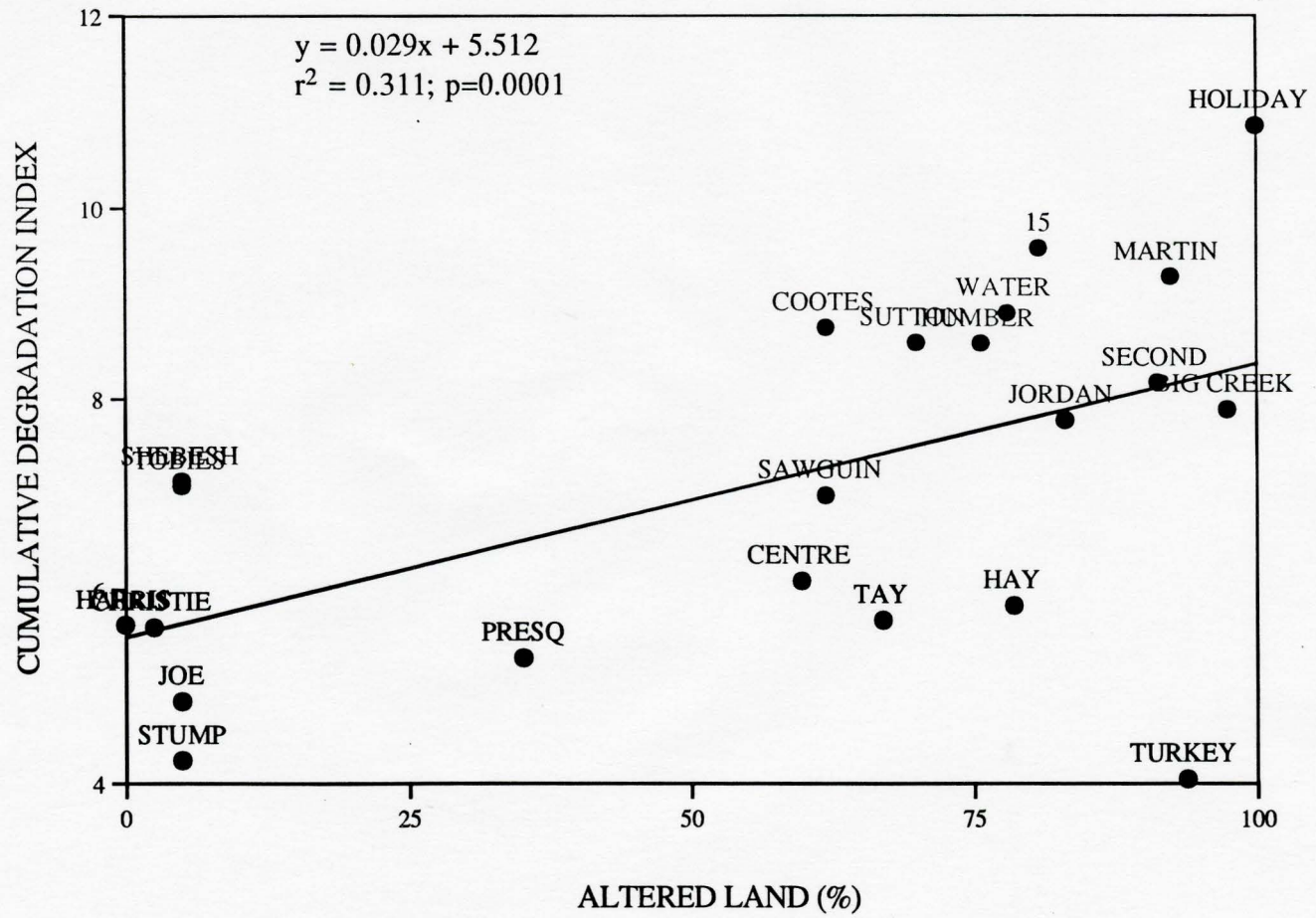
Figure 3.4



**Figure 3.5** Relationship between the cumulative degradation index and the amount of altered land in the watershed of each wetland

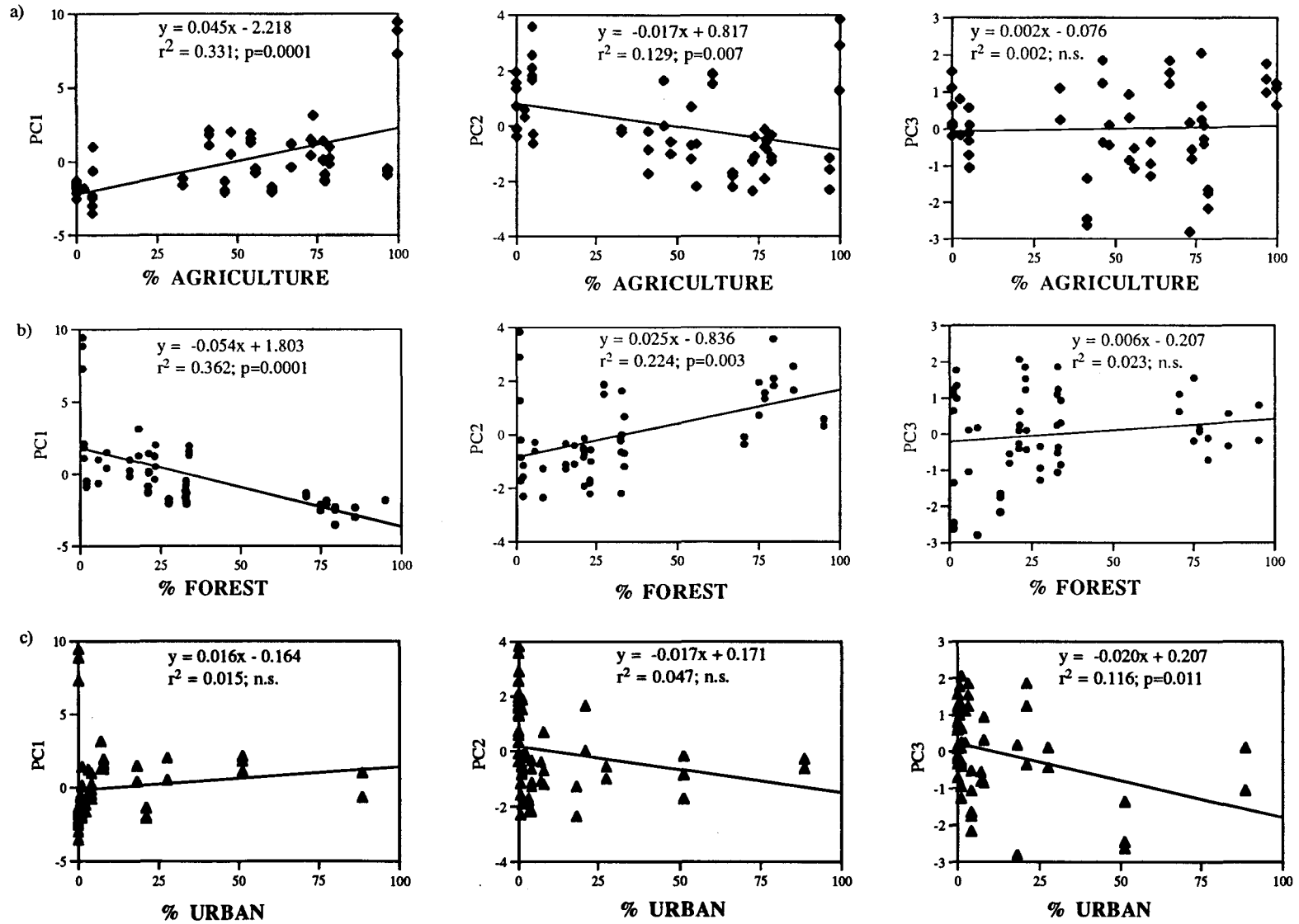


Figure 3.5



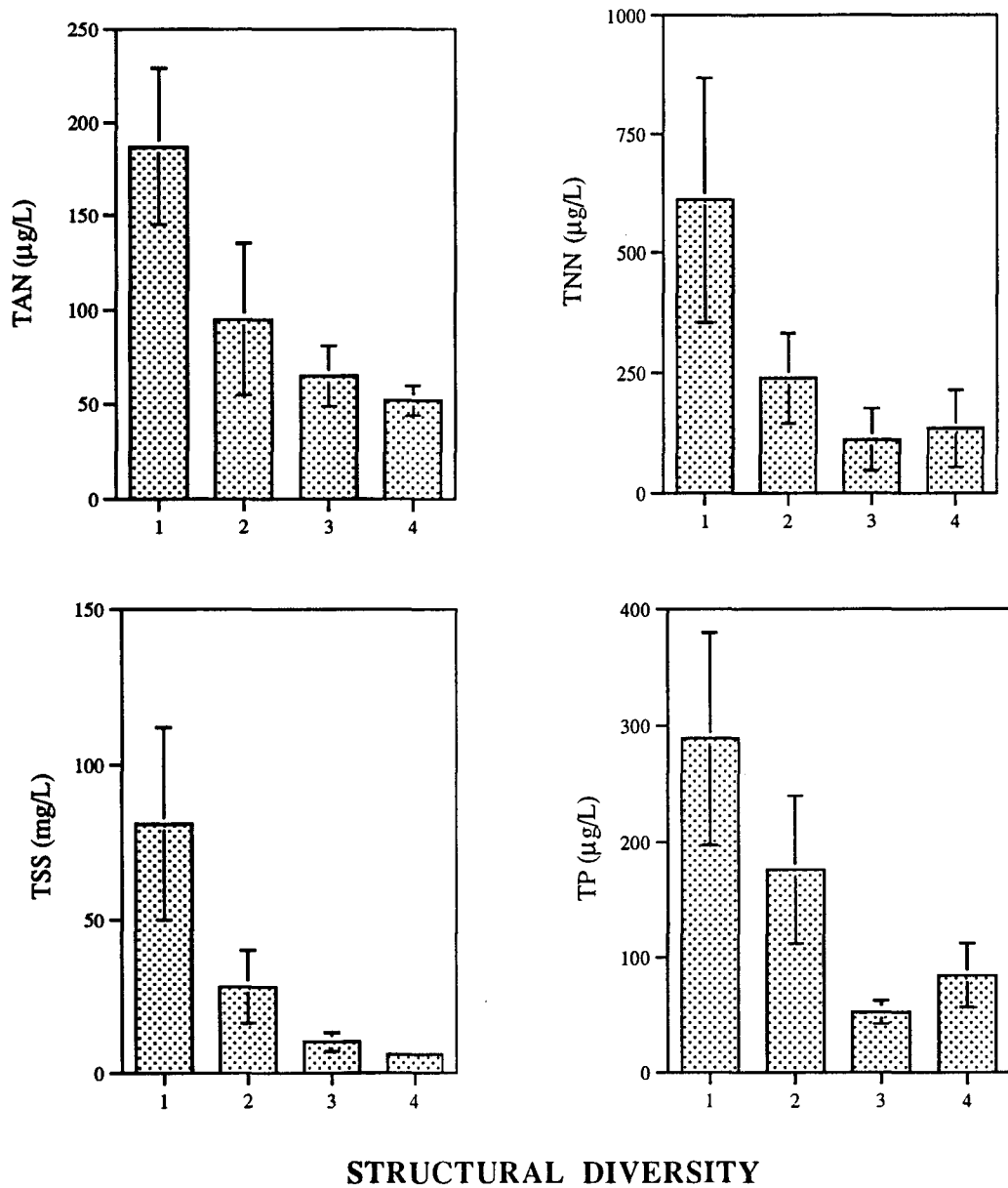
**Figure 3.6** Relationship between the distribution of landuse in the watershed for each wetland and the first three principal component site scores ( agricultural (a), forest (b), and urban (c)).

Figure 3.6



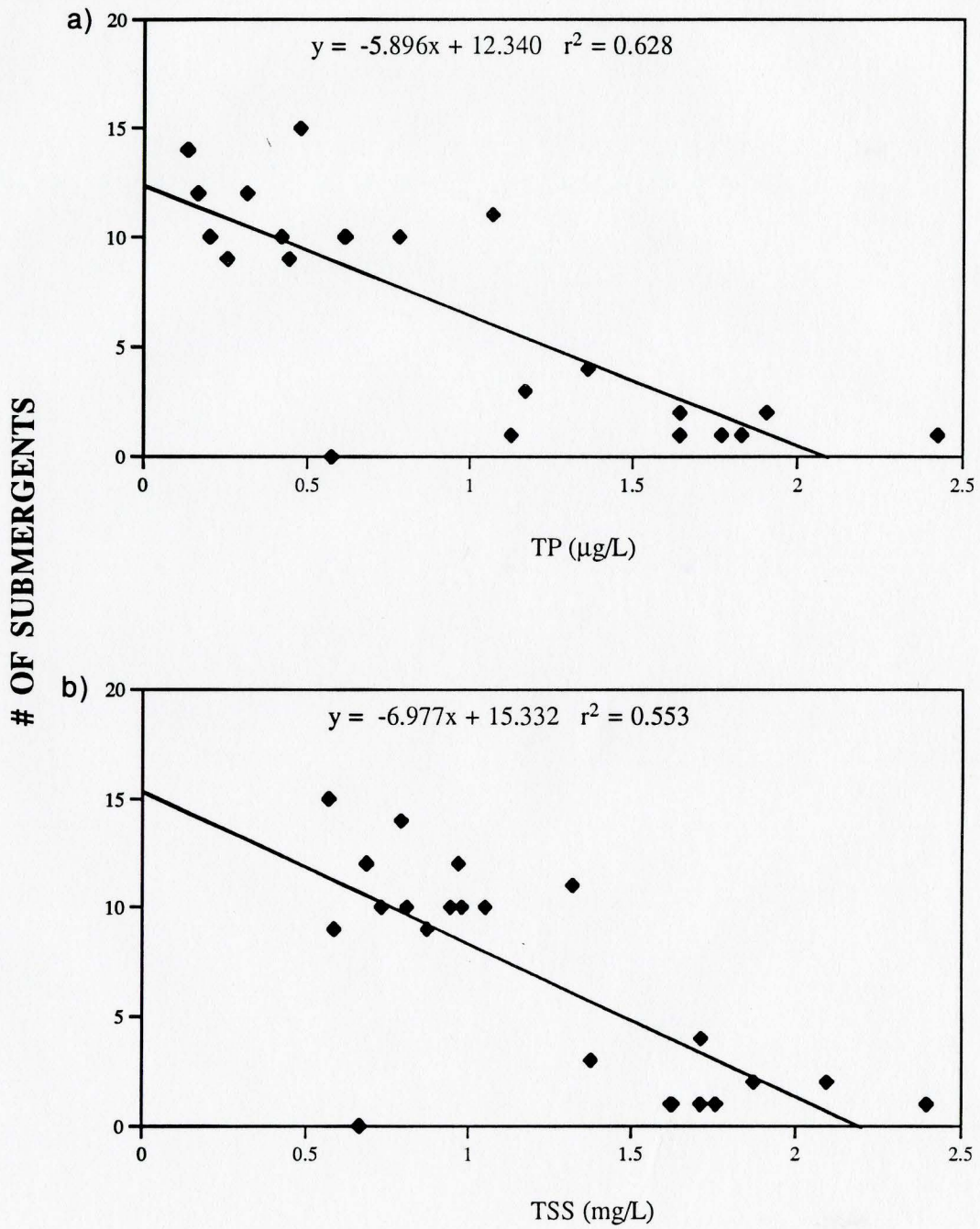
**Figure 3.7** Mean and standard errors for the TAN, TNN, TSS and TP levels of each structural diversity category.

**Figure 3.7**



**Figure 3.8** Relationship between the number of submergents and TP and TSS concentrations ( $\log_{10}$ ).

Figure 3.8





## SUMMARY

The results of this study indicate that the turbidity and suspended solids, specific conductance, the phosphorus in the water and sediment, the inorganic content of the sediment and the amount of inorganic nitrogen are important water quality variables that affect the structural diversity and health of aquatic plant communities. Additionally, landuse is one of the key factors in determining water quality in wetlands, with agriculture having the highest impact. Forested land is a vital component in the watershed, is appears to alleviate the problems of high nutrients and suspended sediments.

Specific conductance, total phosphorus in the water and sediment, ammonia nitrogen and the inorganic (or alternately organic) content of the sediment were associated with the plant community. Ammonia nitrogen and total phosphorus in the sediment showed a positive relationship to the submergent plant community. Wetlands with organic rich sediments and abundant ammonia nitrogen had both submergent and emergent plants. However, wetlands with high specific conductance, total phosphorus and inorganic soils were associated with poor plant communities. Floating plants were not related to any of these parameters. Further analysis indicated that submergent plants were negatively correlated to many water quality parameters. This supports previous research indicating that the submergent community is heavily dependent on good water quality.



The link between practices in the watershed and the nature of the plant community, although indirect, was found to be closely linked through the water quality. Forested lands were found to be closely associated with wetlands containing good water quality and clarity. An abundant, structurally diverse plant community was found in these wetlands. The opposite case was found in agricultural and/or urban landscapes (or mixed) where poor water quality was associated with wetlands whose plant community had been reduced to a fringe of emergent vegetation. The landuse management practices were important in determining the impacts in the plant community. Wetlands containing buffered areas around their tributaries had reduced nutrient and suspended solid loads; consequently their plant community was diverse and abundant. However the number of sites illustrating this were limited to two. In other cases agricultural development was associated with high suspended solid, nutrient and metolachlor levels in the water column. In addition, urban lands were associated with high soluble phosphorus, conductivity and PAH levels. The impacts of both types of disturbance generally result in a wetland with poor structural diversity, as a result of poor water and hence sediment quality.

Metolachlor and PAHs appear to be related to landuse and should be monitored in wetlands impacted by either agriculture or urban lands. Immunoassays were shown to be an effective method for monitoring the concentrations of these pollutants, alleviating the problems of high cost associated with gas chromatography techniques. However, a random sample of 4% of the total samples measured should be analyzed by gas chromatography, to ensure that accurate results are being produced by immunoassays.

## FUTURE RESEARCH

Many of the wetlands studied were previously impacted. However their prior state was likely similar to many of the remote, pristine sites. The key factors responsible for their degraded state are outlined in this study, however the parameters most important parameters causing their demise could not be isolated. Since the impacts of increased suspended sediment and nutrient loading has been discussed by others, the effects of trace organic contaminants should be investigated. In particular the impacts of PAHs and herbicides on wetland plants would provide valuable information, that would separate the impact of organic pollutants. However this type of study would only be effective on wetlands with disturbed landscapes. The use of immunoassays would offer a cheaper and more efficient tool to target sites with high levels of organic contaminants. The plant community at these sites could then be examined or experimentally manipulated to determine the effects of PAHs or herbicides.

Agricultural land appears to have the most detrimental affect on water quality and therefore wetland health. However, the type, intensity and amount of agriculture determining how severe the effects may be. Areas which are tilled, and receive herbicide and fertilizer application have a greater affect on wetland health. These practices result in high levels of suspended sediment, nutrients and herbicides entering wetlands; the effects of these pollutants on the plant community are detrimental. Efforts should focus on improving the runoff coming from these lands by altering these practices to lower the inputs of these pollutants.

The definite impact of high suspended solids, turbidity and nutrients on submergent plant growth has serious implications for remaining wetlands. This is extremely important to wetlands that are currently being restored. The landuse in the watershed must be evaluated and methods to reduce contaminant loadings need to be implemented. Current programs such as "Watershed Stewardship" initiated by conservation authorities help control the problem of inputs from landuse activities. However this study indicates the importance of forested land in the watershed as a means to further control inputs. Wetland restoration programs need to realistically consider this option. If the current inputs to the wetland can not be reduced to a level conducive to submergent plant growth then perhaps this should not be a goal of the project. In highly urbanized wetlands such as Martindale Pond, the feasibility of increasing forest cover around the tributaries should be considered. Often the tributaries have been channelized and this would not be possible. Alternatively, in agricultural wetlands the land around could be revegetated and this would help to attenuate nutrients and sediments, creating a natural filtering area capable of improving the quality of runoff.

However, if the inputs are not at problematic levels then perhaps the poor water quality is a result of internal loading from historic inputs. In this case, wetland restoration may not be feasible until the sediments are no longer contaminated. Two examples where this may be occurring are Cootes Paradise Marsh and Second Marsh. Current inputs from the tributaries are quite low in nutrients and suspended sediments but the levels in the marsh remain high. However, the vegetation is not responding, even with the efforts to control populations of the common carp. This suggests that quality of the sediment is poor, and this is hindering re-colonization of aquatic vegetation. In these cases, the vegetation may not respond unless the sediment is treated first.



The areas which are targeted for restoration are often based on community and political interest and not on potential for wetland rejuvenation. A wetland where past and present water quality is poor, with little hope for watershed improvement, will not likely respond to restoration efforts on the short term. This should be taken into account and perhaps resources should be spent on preserving another wetland with greater potential. This would generate more public support in environmental projects as their success would be seen as feasible. Related to this is that short term improvements are required to maintain political success, which is based on a four year term. Perhaps future projects should focus on wetlands which are of social importance but also have mitigative potential.

This study places the emphasis on the importance of watershed dynamics in shaping the wetland community. These results show that wetland restoration and preservation projects need to work at the ecosystem level, in particular the landuse in the watershed needs to be considered. Planners, developers and wetland managers need to work together to provide a landscape that will allow wetlands to be sustainable. This will result in preventive management and reduce the need for restoration programs.

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