## PHOSPHORUS RELEASE FROM HERBICIDE-KILLED MILLFOIL

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D.S. Painter and K.J. McCabe NWRI Contribution No. 88-34

Lakes Research Branch National Water Research Institute Canada Centre for Inland Waters Burlington, Ontario, Canada L7R 4A6

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Abstract

The fate of tissue phosphorus after herbicide induced macrophyte senescence depends on abiotically and biotically mediated processes of an aquatic ecosystem. Decomposition of plant tissue may deplete the oxygen content in the water and a large flux of nutrients to the ecosystem could potentially stimulate the growth of planktonic algae. This study investigated the effect of sediment type on the fate of phosphorus released from decomposing Eurasian water milfoil (Myriophyllum spicatum L.) upon treatment of 2,4-D (2,4-Dichlorophenoxyacetic acid). Radiolabelled plant tips were placed in aerated 1.6 litre experimental chambers containing either no sediment (control), sand, clay or organic sediment. The decaying plant tips in the control chambers released only 7.1 to 26% of their radiolabelled tissue phosphorus into the water within 17 days and lost no further phosphorus thereafter. The sandy sediment had limited adsorbtion capabilities since it removed only 15.3% of the radiolabelled phosphorus from the water column while the clay sediment adsorbed 45.8%. The organic sediment had the greatest capacity for adsorbing phosphorus by removing 81.3% of the available phosphorus. The organic matter and cation exchange capacities of the sediments increased with increasing phosphorus adsorbtion. These results suggest that sediment type plays an important role in the fate of phosphorus released from decomposing plants.

Résumé

L'évolution du phosphore contenu dans les tissus de macrophytes après un traitement aux herbicides dépend des processus abiotiques et biotiques de l'écosystème aquatique en présence. La décomposition des tissus des plantes peut réduire la concentration d'oxygène dans l'eau et ceux-ci peuvent dégager une importante quantité de matières nutritives qui pourrait stimuler la croissance d'algues planctoniques. L'étude visait à déterminer l'évolution du phosphore dégagé par le Myriophylle en épi (Myriophyllum spicatum L.) en décomposition selon le type de sédiments après un traitement au 2,4-D (acide 2,4-dichlorophénoxyacétique). Les extrémités radiomarquées de plantes ont été placées dans des compartiments aérés de 1,6 litre dont certains étaient des compartiments témoins (ne contenant pas de sédiments) et d'autres contenaient des sédiments sableux, argileux ou organiques. Les extrémités en décomposition des compartiments témoins n'ont dégagé que 7,1 à 26 % du phosphore radiomarqué contenu dans leurs tissus pendant les 17 premiers jours de l'expérience puis n'en ont plus dégagé par la suite. Le potentiel d'adsorption du phosphore des sédiments sableux était faible : ceux-ci n'ont supprimé que 15,3 % du phosphore radiomarqué de la colonne d'eau, tandis que les sédiments argileux en ont adsorbé 45,8 %. Ce sont les sédiments organiques qui ont montré le plus grand potentiel d'adsorption du phosphore de l'eau : ils en ont supprimé 81,3 %. La teneur en matières organiques et le potentiel d'échange de cations augmentent à mesure que le potentiel d'adsorption du phosphore augmente. Les résultats obtenus suggèrent que le type de sédiments en présence influe grandement sur l'évolution du phosphore dégagé par des plantes en décomposition.

The use of herbicides to control nuisance aquatic plants is often looked upon unfavorably because of the potential for decaying plants to deplete oxygen in the water column and to release nutrients which may stimulate algal blooms. The documented consequences of herbicide control vary from study to study depending on the experimental design although, in natural ecosystems where sediment is present, lake deoxygenation rarely occurs and increased nutrient concentrations in the water column following herbicide treatment are not substantial. Sediment appears to play an important role in an ecosystem's ability to adsorb nutrients released from decaying plants upon herbicide The purpose of our study was to illustrate the treatment. importance of sediment to predict the fate of phosphorus released from Eurasian water milfoil (Myriophyllum spicatum L.) following treatment of 2,4-D (2,4-Dichlorophenoxyacetic acid) and to compare different sediment types for their abilities to adsorb phosphorus under aerobic conditions.

Plant tips in the control chambers with no sediment released only 7.1 to 26% of the radiolabelled tissue phosphorus into the water within 17 days and lost no further phosphorus thereafter. The sandy sediment exhibited a limited ability to adsorb phosphorus (15.3%) while clay sediment adsorbed 45.8%. Organic sediment had by far the best adsorbtion capabilities by removing 81.3% of the radiolabelled phosphorus from the overlying water. A trend of increasing organic content and cation exchange capacity with increasing phosphorus adsorbtion capabilities was also found in this study.

These results suggest that sediment type plays an important role in the fate of phosphorus released from decomposing macrophytes. Only a small fraction of the plants' tissue phosphorus was released to the water following inducement of death by a herbicide. No matter how insignificant the phosphorus flux may be, one should consider all the factors which may influence nutrient enrichment to the water such as sediment type and the potential for deoxygenation when considering possible methods of control for macrophytes.

#### Perspective gestion

L'emploi d'herbicides pour la répression des plantes aquatiques nuisibles fait souvent l'objet de critiques négatives à cause du risque que les plantes en décomposition absorbent l'oxygène de l'eau et dégagent des matières nutritives qui peuvent stimuler la prolifération d'algues. Les données sur les incidences de l'utilisation d'herbicides varient d'une étude à l'autre selon les conditions dans lesquelles les expériences ont été effectuées. Toutefois, dans les écosystèmes naturels où il se trouve des sédiments, on observe rarement la désoxygénation des lacs et le traitement aux herbicides n'entraîne par un fort accroissement des quantités de matières nutritives dans l'eau. Les sédiments semblent exercer une grande influence sur le potentiel d'adsorption par les écosystèmes des matières nutritives dégagées par les plantes en décomposition par suite d'un traitement aux herbicides. Notre étude visait à souligner l'importance des sédiments dans la prévision de l'évolution du phosphore dégagé par le Myriophylle en épi (Myriophyllum spicatum L.) après traitement au 2,4-D (acide 2,4-dichlorophénoxyacétique). Elle visait également à comparer différents types de sédiments quant à leur potentiel d'adsorption du phosphore en milieu aérobie.

Les extrêmités de plantes placées dans des compartiments en l'absence de sédiments ont dégagé dans l'eau seulement 7,1 à 26 % du phosphore radiomarqué contenu dans leurs tissus dans les 17 premiers jours de l'expérience et n'en ont plus dégagé par la suite. Le potentiel d'adsorption du phosphore des sédiments sableux était limité (15,3 %), tandis que celui des sédiments argileux l'était davantage (45,8 %). Toutefois, ce sont les sédiments organiques qui offraient, de loin, le meilleur potentiel d'adsorption, car ils ont éliminé 81,3 % du phosphore radiomarqué contenu dans l'eau surjacente. L'étude révèle également que la teneur en matières organiques et le potentiel d'échange de cations tendent à augmenter à mesure que le potentiel d'adsorption du phosphore augmente.

Les résultats obtenus portent à croire que le type de sédiments en présence joue un rôle important dans l'évolution du phosphore dégagé par des macrophytes en décomposition. Le traitement aux herbicides a entraîné le dégagement d'une petite proportion seulement du phosphore contenu dans le tissu des plantes. Même si le flux de phosphore est négligeable, il faudrait tenir compte de tous les facteurs - notamment le type de sédiments en présence et le potentiel de désoxygénation des plantes traitées - qui peuvent influer sur le dégagement de matières nutritives dans l'eau au moment du choix de méthodes de répression des macrophytes.

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## Introduction

Eurasian water milföil (<u>Myriophyllum spicatum</u> L.) is a nuisance aquatic plant which infests many eutrophic waters throughout North America (Nichols, 1975; Reed, 1977). A large dense bed of milfoil has the potential to release large quantities of nutrients upon death and decomposition since it is known to absorb nutrients far in excess of its normal metabolic requirements (Gerloff and Krombholtz, 1966; Wilson, 1972). The fate of these nutrients is of interest because of their potential to stimulate the development of planktonic algae (Walsh et al., 1971; Way et al., 1971) or resistant macrophytes. Deoxygenation of the water as a result of rapid organic matter decay and subsequent death of aquatic fauna are other potential consequences of weed control using herbicides.

Literature reports of nutrient release following herbicide induced death and decomposition of macrophytes are inconsistant. Carpenter and Adams (1978) postulated that herbicide control of Eurasian water milfoil in Lake Wingra could theoretically result in the release of 165 kg of phosphorus into the water column which is equivalent to 10% of the lake's external annual net loading of phosphorus. Significant releases of phosphorus from decaying plants have been observed by Simsiman et al. (1972), Daniel (1972), Walker (1963), Kistritz (1978) and Pokorny et al. (1971), although these studies were performed in relatively small enclosed areas which became anoxic. Kistritz (1978) recognized the limitations of relating results using this type of experimental design to the natural environment. He found that enclosing aquatic communities could result in the development of anaerobic conditions by artificially limiting reaeration.

Carpenter and Greenlee (1981) developed a simulation model to predict whether lake deoxygenation would occur following herbicide application to a lake. Their model predicted that the risk of deoxygenation is minimized at low water temperatures, high littoral water circulation, deep littoral depths, low levels of macrophyte biomass, low concentrations of nitrogen in macrophyte tissues and with littoral-pelagic mixing present. In 88% of the 128 simulations used in the factoral analysis, the model predicted that the littoral water would remain aerobic. To emphasize the infrequency of deoxygenation and secondary problems associated with decomposition, Bates et al. (1985) reported a study which showed that after 20 years of 2,4-D use to reduce excessive milfoil populations, no rapid or excessive depletion of dissolved oxygen or fish kills were observed. During this time there were no documented problems related to toxicity of 2,4-D to non-target organisms, severe water quality deterioration or complaints from the public.

Where deoxygenation does not take place, studies have shown that no substantial increases in nutrient concentrations in the water occur following herbicide treatment (Strange, 1976; Scott et al., 1985; Brooker and Edwards, 1973; Simpson and Pimental, 1972; Walsh et al., 1971; Fish, 1966; and Michaud et al., 1979). In one study the water quality actually improved following herbicide treatment to ponds (Boyle, 1980). The improved mixing capabilities resulting from macrophyte suppression were probably responsible for the observed reduction of ammonia and total phosphorus in the water, reduced planktonic algae, lower gross primary productivity and increased oxidation-reduction potential of the sediment.

In the laboratory, Nicholls and Keeney (1973) assessed the nutrient status of the water in the presence and absence of lake sediment under two aeration conditions. They identified sediment as a sink for the phosphorus released from decaying macrophyes which resulted in no apparent phosphorus accumulation in their aerobic sediment-water systems. They also concluded that anoxic conditions were required to result in phosphorus accumulation in the water.

Kistritz (1978) investigated the process of nutrient release from decaying macrophytes insitu in an enclosed system to assess the role of sediment, phytoplankton and suspended bacteria in the recycling of nitrogen and phosphorus. He found that decaying macrophytes in an anaerobic aquatic system accounted for 40-44% of the regenerated phosphorus and the phytoplankton accounted for 36% of the net increase of phosphorus. By comparison, the sediment surface contributed a significant portion (17-20%) of the total amount of orthophosphate liberated in each cylinder. Changes in the redox potential at the sediment surface probably accounted for the observed nutrient release from the sediment under anoxic conditions (Mortimer, 1971). Simsiman et al. (1972) reported decreases of orthophosphate in the overlying water following plant decomposition which they largely attributed to sorption by sediment and to a lesser extent, assimilation by algae. They proved this by measuring appreciable increases of orthophosphate in the interstitial water up to the 124th day post-treatment.

These studies illustrate the importance of sediment and dissolved oxygen content in a system when trying to understand the system's response to herbicide-induced death and subsequent release of nutrients from aquatic plants. The purpose of this study was to investigate the release of nutrients from decaying Eurasian water milfoil upon treatment of 2,4-D (2,4-Dichlorophenoxyacetic acid) in laboratory microcosms to examine the effect of sediment type on the fate of phosphorus liberated by the decaying plants. Methods and Materials

Plant Preparation

Healthy shoots of Eurasian water milfoil were collected from Buckhorn Lake in June, 1983. Thirty-six plant tips were selected, freed of attached silt, snails, algae etc. and clipped three nodes behind the apical bud. This length has been shown to be sufficient for regeneration (Kangesniemi, personal communication, B.C. Ministry of the Environment) and also provided uniformity of plant material.

Thirty-six plant tips were placed in a ten litre Belco jar containing two litres of aerated, distilled water for the purpose of starving the plant tips of phosphorus. A nutrient solution was made containing 1/10th of the recommended phosphorus (Gerloff and Fitzgerald, 1976). An excess of radioactive phosphorus (P33: half life = 25.3 days) was added to the media to encourage phosphorus uptake by the plant tissue. Prior to the addition of plant tips, 1 ml samples of the media were taken using a 1 ml syringe to establish the initial concentration of P33 available to the plants. The samples were combined with 4 mls of distilled water and 10 mls of PCS in a scintillation vial and counted on a 1217 Rackbeta Liquid Scintillation Counter (LKB Wallac) on the C14 channel for ten minutes. The C14 channel was used because its energy level (.156 MeV) is similar to that of P33 (.249 MeV).

At this point, the thirty-six phosphorus starved plant tips were introduced to the P33 enriched media. Periodic 1 ml samples were taken and analysed using the same method as described above. This was continued until the concentration of P33 in solution had decreased and stabilized thereby indicating that maximum uptake of phosphorus by the plants had occurred. Two extra days were allowed to ensure that the process was complete.

Following the P33 uptake period, the labelled plant tips were transferred using tongs to a beaker of distilled water where they were rinsed several times to remove any phosphorus which was adsorbed to the surface of the plants.

## Experimental Chambers

Twelve experimental chambers were set up in a temperature and light controlled incubator allowing approximately sixteen hours exposure to light at 20 °C. The glass chambers used in the investigation held 1.6 litres. Each chamber consisted of two halves held together by an aluminum fastener. The joint was coated with stopcock grease to ensure a tight fit between the two halves. The lid was coated in the same fashion and secured by a wire clamp. Two tubes were positioned through holes in the lid. The first tube connected the air supply to an air stone which maintained an aerobic environment and the second tube enabled samples to be taken from a syringe without removing the lid.

The bottom half of the chamber was filled with approximately 800 mls of sediment except for the three control chambers which contained no sediment. Of the remaining nine chambers, three were filled with sand collected from the Burlington area of Lake Ontario, three with clay from the Fifty Point area of Lake Ontario and the other three were filled with organic sediment from Buckhorn Lake, Ontario. All sediment samples were collected in June, 1983 using an Eckman grab and thoroughly mixed before the chambers were filled. The three sediment types were characterized by various physical and chemical parameters including texture (Duncan and LaHaie, 1973), cation exchange capacity (Chapman, 1965) and percent organic matter. The organic matter content of the soils were estimated by percent loss on ignition (550 °C for five hours). To each chamber, 800 mls of distilled water was added and adequate time was allowed for the sediment to settle before the plant tips were added.

## Experimental Design

The rinsed radioactively labelled plant tips were divided into twelve groups of three which were approximately equal in biomass and transferred to the experimental chambers. 2,4-D was introduced to each chamber on day 2 to initiate the plants' death and subsequent decomposition. The addition of 2,4-D was calculated to produce a concentration of 2 ppm which is the recommended dosage for milfoil control. Samples of the chamber water were taken at 0, 3, 8, 11, 14 and 17 days to establish the amount of P33 in the water of each chamber.

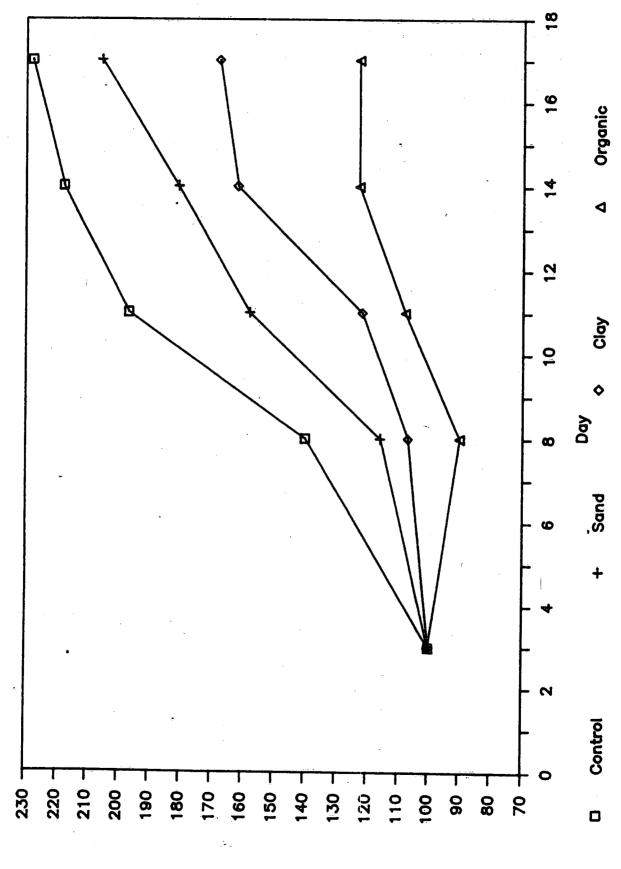
#### Results and Discussion

Sediments used in the investigation were characterized by texture, percent organic matter and cation exchange capacity (CEC). These sediments were texturally diverse, ranging from a sand to a clay loam to a predominantly organic sediment. The organic matter contents of the sediments ranged from 2% in the sand, to 5% in the clay, to 55% in the organic sediment. The CEC of the sediments revealed a trend similar to the organic matter content in that the sandy sediment had the lowest CEC (0.93 meq/100g), the clay sediment was intermediate (3.81 meq/100g) and the organic sediment had the highest CEC (41.33 meq/100g).

The amount of radiolabelled phosphorus that was actually released by the decaying plants over the 17 day period following hericide treatment ranged between 7.1% and 26.0%. Carpenter (1980) found that the percent of phosphorus leached from water milfoil varied with tissue phosphorus content and ranged between 10% and 50% at 12 days. He also found that the percent phosphorus released increased linearly with increasing tissue phosphorus content. A control with no sediment and no herbicide treatment was not used in this study since it is well documented that no leakage of phosphorus from the shoots to the surrounding water occurs (Peverly and Britton, 1978; Bristow and Whitcombe, 1971; Barko and Smart, 1981).

Upon herbicide treatment of water milfoil, rapid release of phosphorus can be expected. This phosphorus can either be utilized in further biomass production or be sorbed by the sediment (Nichols and Keeney, 1973). The release of radioactively labelled phosphorus was monitored for 17 days to assess not only the quantity but also the fate of the liberated P33. The rate of P33 released into the water of the control chambers, as calculated as a percentage of P33 present in each chamber at day 3, increased steadily during the first 14 days following herbicide treatment (Figure 1). At that time the concentration of P33 in the water began to stabilize indicating that the initial rapid release of phosphorus by the decomposing plants had occurred. Nichols and Keeney (1973) reported a similar increase in the phosphorus concentration over a 14 day period which then remained relatively constant for the duration of the experiment. This two week time period may therefore be considered the critical period for the release of phosphorus from decomposing Eurasian water milfoil upon treatment of herbicide.

Several workers have shown that sediment has a great capacity to adsorb phosphorus (MacPherson et al., 1958; Jitts, 1959; Harter, 1968; Williams et al., 1970; Latterell et al., 1971; Shukla et al., 1971). This study reveals that the type of sediment has a large effect on the amount of phosphorus it can adsorb. The same 14 day rise and subsequent levelling off as displayed in the control chambers was also observed in the chambers exposed to sediment (Figure 1). The sand exhibited a



Average P (% of day 3)

Figure

limited ability to adsorb phosphorus while the clay sediment had a greater capacity. The organic sediment displayed the highest capacity for adsorbing phosphorus. Table 1 shows the percent of the released phosphorus that was adsorbed by each sediment type after 17 days. After this period the sand was capable of adsorbing only 15.3% of the phosphorus released (expressed relative to control) while the clay sediment adsorbed 45.8%. The sediment that showed the greatest capacity to adsorb phosphorus was the organic sediment which removed 81.3% of the radioactively labelled phosphorus from the overlying water.

The actual amount of phosphorus which is available for further biomass production is therefore a function of both the initial tissue phosphorus content of the plant (Carpenter, 1980) and the sediment type. Six to 22% of the radiolabelled phosphorus was available in the water of the sand chambers 17 days after herbicide treatment. At the same time, 3.9% to 14.1% of the phosphorus was available in the overlying water of the clay chambers while only 1.3% to 4.9% was available in the water of the organic sediment chambers. Therefore, the organic sediment was by far the most capable of adsorbing phosphorus, leaving the least amount available for potential biological uptake.

In artificial pond ecosystems infested with milfoil, Scott et al. (1985) tested the water chemistry resulting from treatment of 2,4-D. They compared the treated ponds' water chemistry resulting from applications of both ester and amine forms of 2,4-D with the control ponds' water chemistry and

# TABLE 1. CHARACTERIZATION OF 3 SEDIMENT TYPES BY TEXTURE, PERCENT LOSS ON IGNITION (LOI), CATION EXCHANGE CAPACITY (CEC) AND PHOSPHORUS ADSORBTION CAPABILITY.

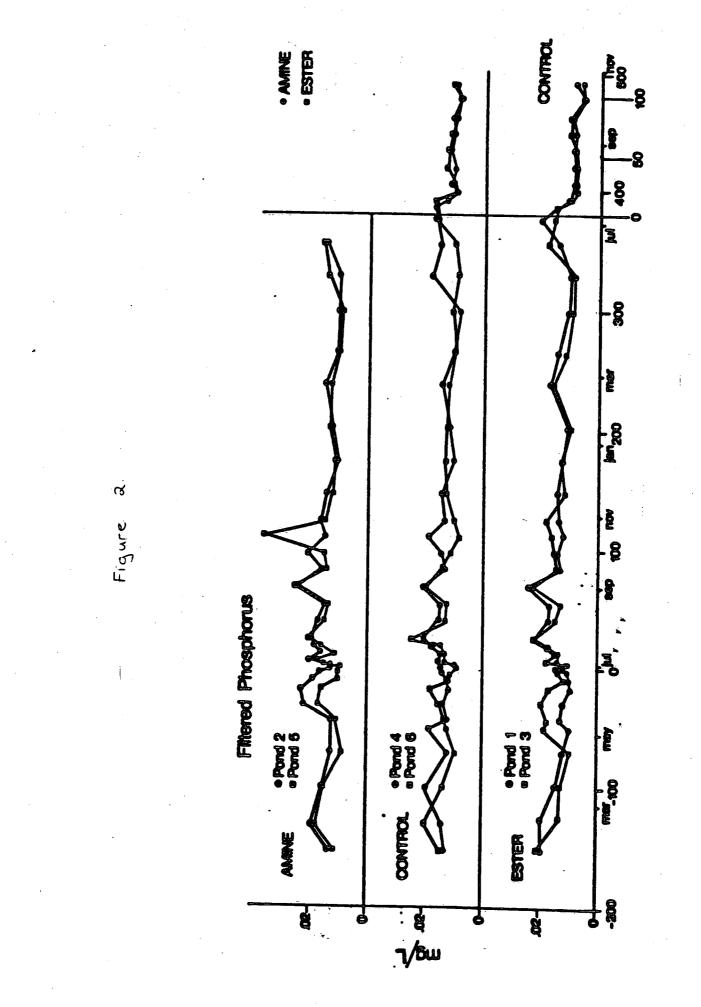
. <u></u>	TEXTURE	% LOI	CEC (meq/100g)	% OF RELEASED P <sup>33</sup> Adsorbed After 17 days
SAND	SAND	2	0.93	15.3
CLAY	CLAY LOAM	5	3.81	45.8
ORGANIC	ORGANIC	55	41.33	81.3

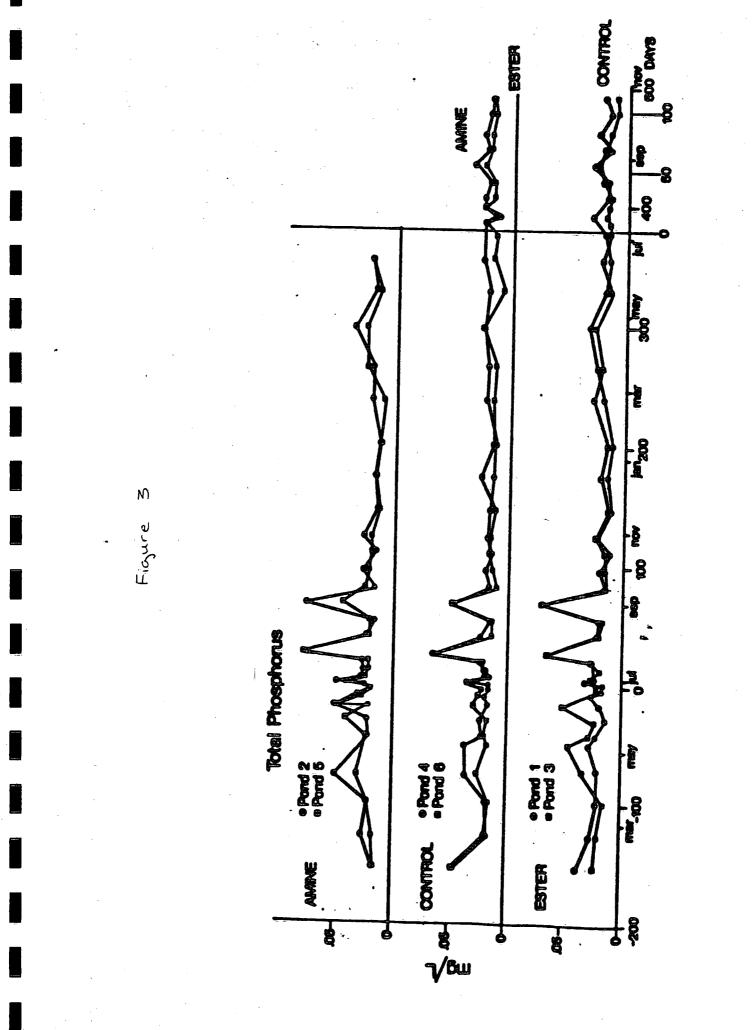
concluded that the collapse of the milfoil did not result in either dissolved oxygen depletion or nutrient enrichment in the water column. Data from Scott et al. (1985) for concentrations of filtered and unfiltered phosphorus in the water column are shown in Figures 2 and 3. The trends in water chemistry were similar in the treated and untreated ponds and the fluctuations observed in all ponds were a result of precipitation events. Clay sediment used in our study was collected from the same location as the site for the artificial ponds.

The sediment analyses from this study revealed a trend of increasing organic matter content with increasing phosphorus adsorption capabilities (Table 1). This was also reported by Williams et al. (1958). A possible explanation for this trend is that although the size of the individual particles of organic sediment are quite variable, they may be at least as small as the clay particles and much smaller than the sand particles (Brady, 1974). Since adsorption is a surface phenomenon, a fine textured sediment with a large surface area has greater adsorbing power than a coarse textured sediment.

A trend of increasing CEC with increasing phosphorus adsorption was also found in this study (Table 1). One of the main factors affecting CEC is again the surface area of the sediment (Brady, 1974). Therefore, sediment types which have large surface areas also have high CEC's and generally are capable of adsorbing more phosphorus.

From this study it is apparent that sediment type plays an important role in the fate of phosphorus released from





decomposing Eurasian water milfoil. It is also evident that a release of phosphorus to an aquatic system caused by herbicideinduced death of plants represents only a fraction of the plant's tissue phosphorus content. No matter how insignificant the phosphorus flux may be, any addition of biologically available phosphorus to a water body has the potential to generate algae blooms; possibly creating a worse situation than initially encountered. Therefore, when considering possible methods of control for macrophytes, one should consider all the factors which may influence phosphorus release to the water, such as sediment type and the potential for deoxygenation.

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