

HERBICIDE CONCENTRATIONS IN WETLANDS
IN WEST CENTRAL MINNESOTA, 1992

by

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ABSTRACT

Thirty emergent, seasonally to semipermanently flooded wetlands in an intensively farmed area of west central Minnesota were sampled before and during the 1992 crop growing season to determine surface water concentrations of three widely used herbicide groups. Specifically, water obtained from ten isolated wetlands ("reference") on Federal Waterfowl Production Areas (WPAs), four WPA "treatment" wetlands, and 16 privately owned "treatment" wetlands was analyzed to determine whether, and to what extent, wetland basins both adjacent to, and isolated from, private agricultural lands contained measurable concentrations of alachlor, triazine and phenoxy acid herbicides. Surface water samples were screened for the three class herbicide types using enzyme-linked immunosorbent (ELISA) assays.

Low concentrations of all three herbicide classes were detected in surface waters from WPA "reference" wetlands. The range of triazine concentrations detected within the ten "reference" WPAs was 0.019-0.546 parts per billion (ppb), whereas alachlor and phenoxy acid concentration ranges were 0.048-0.432 ppb and 0.004-0.764 ppb, respectively. Presently, herbicide occurrence at these concentrations has not been shown to adversely impact aquatic macrophytes or invertebrates.

Triazine and alachlor concentrations in some "treatment" WPA ditches and private wetlands (4.17 and 5.27 ppb triazine, 2.41 and 6.56 ppb alachlor, respectively) were similar and exceeded maximum concentrations in "reference" WPA wetlands. Phenoxy acid herbicide concentrations in privately owned wetlands (0.000-1.100 ppb) and "treatment" (0.003-0.193 ppb) and "reference" WPA wetlands were found to have similar low concentrations.

Alachlor and triazine herbicide concentrations in the "treatment" wetlands suggest at minimum, the potential for aquatic toxicity, as indicated under laboratory conditions, and help define additional directions for assessment of pesticide exposure and related toxic effects to prairie pothole aquatic life.

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INTRODUCTION

Wetlands throughout the Prairie Pothole Region of North America serve as vital breeding grounds for migratory waterfowl, shorebirds, and wading birds. While agricultural drainage, drought, and various other land use changes over a period of many years have substantially reduced the number of such wetlands, the effects of more subtle ecological changes which may have altered the structure of wetland plant and animal communities are less obvious and not well documented. Sedimentation and chemical contamination are examples of degrading influences on wetland water quality which can reduce the availability of foods for breeding waterfowl. The rolling topography of Minnesota's Prairie Pothole Region combined with its high rainfall and the intensive use of both suitable and marginal land for agricultural production has raised the concern that agricultural pesticides in runoff from private croplands may be entering wetlands and adversely affecting their invertebrate and plant communities. Aquatic plant and animal communities of seasonal and semipermanent wetlands may have great potential for exposure to such runoff.

Agricultural herbicides entering prairie pothole wetlands may impact waterfowl through toxic sublethal effects or, indirectly, through toxic effects on aquatic plants and invertebrates, resulting in a reduction or alteration of waterfowl cover and/or food abundance (Grue et al. 1986). While herbicides generally degrade relatively rapidly in the environment, many persist for longer periods of time than organophosphate, carbamate and synthetic pyrethroid insecticides. In addition, most herbicides are applied to cropland in spring and early summer--seasons that coincide with periods of maximum precipitation runoff and migratory bird reproductive activity.

U.S. Fish and Wildlife Service (Service) Wetland Management Districts (WMDs) currently manage thousands of acres of Federal lands in Minnesota specifically for waterfowl production. In 1990, 15,825 pounds of active ingredients representing 20 herbicides were applied to 15,533 acres of Service-managed lands in Minnesota (USFWS 1990). The most heavily and most frequently used chemical was 2,4-D. In 1987, approximately \$100,000 was spent on noxious weed control on WMD lands affecting approximately 16,000 acres (USFWS, Briefing Document, MN Waterfowl and Wetland Management Complex, 1992). This amount

does not include the cost of chemicals for nesting cover establishment. In light of an increased emphasis on implementation of Integrated Pest Management (IPM) and reduction of chemical use on Service lands, two concerns come to light: implications of the use of agricultural chemicals on lands in close proximity to wetlands have not been determined; nor has it been determined how such use compares with adjacent private agricultural chemical uses in terms of resulting wetland water quality.

To address these concerns, the Twin Cities Field Office (TCFO) conducted a water quality survey to determine the frequency that wetland basins, both adjacent to and isolated from private croplands, contained measurable concentrations of three widely used herbicide groups (triazines, alachlors, phenoxy acid herbicides). This FY 92 Final Report is part of a larger ongoing, multi-year study of pesticide use in the prairie pothole region.

Importance of Prairie Potholes to Waterfowl

During the breeding period (including brood rearing), many waterfowl species exploit the protein-, lipid-, and calcium-rich food provided by aquatic invertebrates (Murkin and Batt 1987, Swanson and Duebbert 1989) and vegetation and fruits (Swanson et al. 1979) found in pothole wetlands. Invertebrates (e.g., snails, crustaceans, insects) appear to be critical for breeding females as a source of nutrients for egg production and body maintenance (Bartonek and Hickey 1969, Swanson et al. 1979, Swanson and Duebbert 1989), and are highly important in the growth and development of young waterfowl (Sugden 1973). Invertebrates are important components of wetland food webs because of their role in the conversion of plant energy to animal protein (Sather and Smith 1984). Invertebrate communities are dependent upon, and part of, healthy wetland ecosystems (Voigts 1976, Murkin 1983) and could thus be adversely impacted by herbicide runoff from adjacent agricultural fields. At low concentrations, herbicides can directly impact algae, protozoans, plankton, seeds, foliage, roots and tubers that invertebrates and hen waterfowl (e.g., gadwalls, mallards, pintails) depend upon for food and survival. Plant fruits may provide up to 27 and 23% of the diets of breeding mallard and pintail hens, respectively, while barnyard grass has been shown to comprise up to 71% of the diet of pintail hens that fed on tilled wetlands (Krapu 1974). In addition, although ducklings of all species are known to depend upon invertebrates during their early development, 15+ day-old gadwall and American widgeon ducklings shifted to diets dominated by plants (see Swanson and Duebbert 1989 for review).

Waterfowl wetland utilization studies have demonstrated the importance of providing optimal habitat in ephemeral, temporary, seasonal, and semipermanent wetlands for maximum prairie duck productivity. For example,

"Mallards and pintails begin their first nests in early spring, when most of the foods associated with semipermanent lakes are isolated at depths unavailable to dabbling ducks and ice still covers many permanent lakes. Ephemeral and temporary wetlands receive high use at this time. As the season progresses, seasonal wetlands become the major source of food used by renesting mallards and pintails, and shovelers and blue-winged teals are starting

their first nests. By late spring, water levels begin to recede on semipermanent wetlands, aquatic insects start to emerge, and submerged aquatic plants extend to the water surface and provide a substrate for invertebrates. Certain semipermanent wetlands provide an abundant and highly available food supply by late spring and early summer. At this time gadwalls are starting their first nests, and renesting dabbling ducks of other species are obtaining food from semipermanent lakes. Semipermanent wetlands also provide food for ducklings." (Swanson et al. 1979)

By midsummer, the only ducks left in most potholes are incubating and brood-rearing females and young-of-the-year. After fledging, these birds abandon small potholes for large water, usually long before freeze-up makes small wetlands unavailable.

Factors Relating to Increased Potential for Herbicide Runoff into Wetlands

In the United States, data for the Northern Plains indicate that the use of herbicides (pounds of active ingredient applied) increased 356% between 1966 and 1982 (USDA 1992). Herbicide and other chemical use on the predominant crops grown in Minnesota in 1990 (percentage of acreage treated) is given in Table 1. Ninety-five to 97 percent of the acreage planted to corn, soybeans and spring wheat was treated with herbicides that year. In addition, the adoption of conservation tillage practices by some farmers has resulted not only in a reduction in runoff and sediment transport from wetlands, but in an increased use of herbicides, and possibly an increased use of insecticides to control insects within crop residues (Martin and Hartman 1987, Allmaras and Dowrey 1985).

Impact of agricultural chemicals to wetlands occur directly by overspray (direct application of chemicals to wetlands), aerial drift, cultivation and treatment of dry wetland basins, or indirectly through volatilization and post-application runoff. Because herbicides are most frequently applied by farm operators using ground equipment (estimated number of acres to which herbicides were aerially applied in Minnesota declined from 1,101,753 in 1977 to 428,248 acres in 1990 (Minnesota Agriculture Statistics 1991)), runoff is likely the most significant route of entry into wetlands. Since most herbicides are applied during the period of high runoff potential, indigenous wetland biota may be periodically exposed to chronic or acutely lethal herbicide concentrations during storm events (Buhl and Faerber 1989).

Although the number of farms in Minnesota declined from 104,000 to 88,000 from 1980 to 1991, the average farm size increased (from 295 acres in 1982 to 341 acres by 1991) (Minnesota Agriculture Statistics 1991). Along with larger farm size has come increased mechanization and greater reliance on crop monocultures. Mechanization leads to greater physical disturbance of the habitat and greater monoculture occurrence increases the use of pesticides. In addition, the tendency for erosion of smaller-sized clay and silt particles in cultivated watersheds enhances the transportation of contaminants.

Study Area Description

Emergent, seasonally to semipermanently flooded wetlands were selected within the west-central agricultural area of Minnesota for surface water sampling. The study sites consisted of private landowner ("treatment") and Waterfowl Production Area (WPA) ("reference") wetlands within the Fergus Falls, Litchfield, and Morris WMDs. "Treatment" wetlands were defined as wetlands bordering agricultural croplands which had high potential for exposure to chemical influences. "Reference" wetlands were isolated from agricultural influence and were situated in interior portions of WPAs. The criteria utilized in selecting the counties for wetland sampling were (a) presence of crops which maximize use of the three selected herbicide classes; (b) maximum acreages planted in those crops; and (c) availability of WPA "reference" wetlands within each of the three WMDs.

Target wetland basin selection criteria included:

- (1) emergent, seasonally to semipermanently flooded basins;
- (2) privately owned wetlands bordered by target crops on at least 50% of their perimeters;
- (3) WPA wetlands isolated from cropland to the greatest extent possible;
- (4) size, depth, vegetative community, where present, be as similar as possible.

In addition, two WPA "treatment" wetlands and two WPA "treatment" ditches were sampled. The two WPA wetlands were situated adjacent to privately owned croplands. The two ditches (county-owned) traversed a single WPA.

Materials and Methods

Selection of Counties for Sampling

Review of available farm chemical use data for Minnesota indicated that field corn and small grains would be the best target crops for this study because of the relatively high rate of herbicide treatment each received. The percentage of estimated acreage planted to corn and small grains in the counties within each of the three WMDs was then determined (Minnesota Agriculture Statistics 1992). Pope County had the highest percentage of cropland planted to corn and small grains (68%) of all counties in the Morris WMD, followed by Swift, Stevens, and Big Stone Counties with 63, 65 and 59%, respectively. In the Litchfield WMD, Todd and Stearns Counties exceeded Meeker and Kandiyohi Counties with 72 and 73%, versus 62 and 63%, respectively. Lastly, in the Fergus Falls WMD, Douglas County had a higher percentage of acreage planted to corn and small grains (70%) than either Grant (64%) or Ottertail Counties (66%).

Additional criteria for county selections included maximizing the percentage of total corn and small grains acres to which the three target herbicide classes were applied. The data utilized for those determinations were

obtained from a 1990 Agricultural Pesticide Use Survey (Minnesota Department of Agriculture, unpublished data). The estimated percentage of corn acres to which the target herbicides were applied varied from 18 to 87% among all counties considered. The estimated percentage of small grain acres to which the targeted herbicide classes were applied varied from 49% to 88%. In the Morris WMD, Stevens and Pope Counties had the highest reported percentage of corn and small grain acres combined to which the target herbicides were applied 65 and 60%, respectively. Todd and Stearns Counties in the Litchfield WMD reported treatment of 85 and 72% of the corn and small grains with target herbicides versus Meeker and Kandiyohi counties with 55 and 53%, respectively. Lastly, Douglas County reported similar treatment of 64% of its corn and small grains compared to Grant and Ottertail Counties (both 63%).

Final selection of counties for wetland sampling was based on survey logistics. Recent drought history, distance from other candidate counties and sampling sites, and availability of suitable WPAs was considered. Due to the extensive ongoing drought in the extreme western counties, Big Stone and Stevens Counties were excluded. Based on the above criteria, the selected survey counties included: Pope (Morris WMD), Todd and Stearns (Litchfield WMD) and Douglas (Fergus Falls WMD), comprising an adjacent four county area within the three WMDs (Figure 1).

Selection of Wetlands for Sampling

Interior WPA wetlands served as reference wetland sites based on their isolation from agricultural runoff and, thus, their likely reduced chemical exposure. Each WMD initially identified specific WPAs for consideration based on the initial wetland criteria. TCFO staff then met with WMD staff in order to discuss and/or visit each WPA. The final ten WPA selections included four in the Morris WMD, three in the Fergus Falls WMD, and three in the Litchfield WMD.

Landowner contacts within the four counties occurred in March and April 1992. Privately owned wetlands ("treatment" wetlands) were selected based on the criteria discussed above and the landowner's agreement to allow his/her wetland to be sampled. During the initial visits, if prospective cooperating landowners were not home, a flyer was left which described the study and requested their cooperation. Attempts were made to contact targeted landowners up to four times. Attempts were made during the initial discussions with landowners to determine potential crop types to be planted adjacent to their wetlands. However, TCFO staff found this question to impede final cooperation of some landowners. Therefore, a high percentage of the private landowner's wetlands had unknown adjacent crop types at the initiation of sampling. Although corn and small grains were the targeted crop types, several private wetlands sampled were subsequently found to be bordered by soybean (n=2) or alfalfa (n=1) monoculture crops. A description of the private wetlands sampled is provided in Table 2.

Collection and Analyses of Surface Water

Surface water samples were collected from April through July 1992 at 30 wetland sites (10 "reference" WPA wetlands, 16 privately owned "treatment"

wetlands and four "treatment" WPA wetlands). After the initial sampling (pre-herbicide treatment) in April, dates of sampling followed heavy rainfall events to the extent possible in order to determine maximum runoff concentrations. Collection dates were: April 27-29, May 18-19, June 17-19, and July 27-29. Two weeks after the June sampling, the study areas received one to four inches of rainfall. Because of the limited number of enzyme-linked immunosorbent (ELISA) herbicide assay kits (described below) remaining and the fact that sampling had occurred only two weeks prior, we decided to wait for a possible later July rainfall event. That later event never occurred. Therefore, final samples were obtained the last week of July before the majority of the wetlands had completely dried up. An additional sampling (2 references, 4 treatments) occurred October 7-8 as a result of a request by the WMDs.

For each sampling episode at each wetland site, three surface water samples from equal distances around the perimeter of the wetland were obtained and combined. Samples were stored in chemically clean amber jars, which were placed on ice in coolers and refrigerated immediately upon return to the office. In addition to surface water collections, buffer zones around the perimeter of the wetlands were measured and recorded. Also, dominant aquatic plant species within each wetland during June and July were collected and identified.

Within 7 days following the first day of sampling, surface water samples were brought to room temperature and screened for triazine, alachlor, and 2,4-dichlorophenoxyacetic acid (2,4-D) concentrations using ELISA kits (EnviroGuard® plate kits). The ELISA immunoassay method serves as a screening tool which is rapid, reliable and inexpensive. Immunoassays use antibodies that recognize a specific contaminant and a contaminant-specific conjugate. The contaminant in the sample competes with the contaminant-conjugate for a finite number of sites in a test well. Samples containing low concentrations of a contaminant allow many contaminant-conjugate molecules to be bound by the antibody, resulting in a darker blue color. Conversely, samples containing high concentrations of a contaminant allow few contaminant-conjugate molecules to be bound by the antibody resulting in a lower intensity or lighter blue color. A Bio-Tek Model EL307 photometer using a 450 nanometer wavelength filter was used to measure the optical density (absorbance) of each well (wells included blanks, negative controls, calibrators and samples). Blanks, controls, calibrators and samples were run in triplicate and results were averaged for each sample. The range of R^2 values (correlation coefficients for fit of the calibration curves to the actual data) for alachlor, triazine, and 2,4-D assays were 0.98-0.99, 0.95-0.99, and 0.83-0.99 respectively. A spreadsheet in Lotus 123, based on the calibrator solution curve for each type of herbicide kit, was devised to automatically derive the herbicide concentration (ppb) from optical density data. Statistical tests of relationships between wetland herbicide concentrations and buffer zone characteristics were considered but not pursued due to the limited sample size and difficulties in quantifying those field characteristics which may have influenced runoff.

RESULTS

Concentrations of alachlor and triazine herbicides in privately owned wetlands were, in general, higher than in "reference" WPA wetlands. Mean monthly concentrations of both herbicide groups in private wetlands in each WMD were higher than mean monthly concentrations in the "reference" WPA wetlands (Figures 2 and 3). 2,4-D herbicides in privately owned wetlands and "treatment" and "reference" WPA wetlands were found to be of similarly low concentrations (Figure 4).

Waterfowl Production Area (WPA) Wetlands

Although alachlor and triazine herbicides are no longer used on Service lands, both were found at low concentrations in the WPA "reference" wetlands. Triazine and alachlor concentrations within those wetlands ranged from 0.019 to 0.546 ppb (Table 3) and 0.048 to 0.432 ppb (Table 4), respectively. Phenoxy acid herbicides (such as 2,4-D) concentrations, which are presently used on Service lands, ranged from 0.004 to 0.764 ppb (Table 5). Maximum triazine concentrations appeared in the "reference" wetlands in June, alachlor concentrations peaked in May, June, and July, and high phenoxy acid concentrations were found throughout the sampling period. While concentrations of all three herbicide groups in "reference" wetland samples were found to be low, the timing of increases in their respective concentrations tended to follow the trends observed in private wetlands. This strongly suggests the existence of aerial drift and/or precipitation deposition of herbicides into "isolated" wetlands. Presently, herbicide occurrence in wetlands with the observed concentrations is not known to significantly impact aquatic vegetation or invertebrates.

Mean monthly concentrations of triazines were similar among WMD "references" (Figure 5). However, Litchfield WMD "references" tended to have slightly higher concentrations than the others. This followed the observed pattern of higher privately owned wetland triazine concentrations in the Litchfield WMD than in the Morris or Fergus Falls WMDs (discussed below). Individual WPA monthly triazine concentrations are provided for Morris, Fergus Falls, and Litchfield WMDs in Figures 6, 7, and 8 respectively. Slightly higher mean monthly alachlor concentrations were found in Litchfield and Morris WMD "reference" wetlands than in those in the Fergus Falls WMD (Figure 9). Individual monthly alachlor concentrations for "reference" wetlands in the three WMDs are provided in Figures 10, 11, and 12. Slightly higher mean monthly 2,4-D concentrations were found in Fergus Falls and Morris WMD "reference" wetlands than those in Litchfield WMD (Figure 13). Individual monthly 2,4-D concentrations for "reference" wetlands in these three WMDs are provided in Figures 14, 15 and 16. Again, these subtle, yet noticeable differences in concentrations closely follow the trend observed in the private wetlands within each WMD.

Four "treatment" sites located within the 10 originally selected WPAs consisted of (a) wetlands in the Grandokken and Oden WPAs bordered by private cropland (Fergus Falls WMD) and (b) two county ditches flowing through the Krantz Lake WPA (Morris WMD). Both Grandokken and Oden WPA "treatment"

wetland mean and maximum alachlor concentrations exceeded those of the highest WPA "reference" wetlands (Table 6; Figures 17 and 18). However, in general, the "treatment" WPA wetlands had triazine concentrations similar to those in the "reference" wetlands (Table 7). In contrast, 2,4-D concentrations were higher in both Grandokken and Oden WPA "reference" wetlands than "treatment" wetlands. This could have reflected the usage of the chemical on the WPA sites. Triazine and alachlor mean and maximum concentrations in both Krantz Lake WPA ditches exceeded those of all WPA "reference" wetlands (Tables 6 and 7; Figures 19 and 20). Phenoxy acid herbicide concentrations detected in WPA "treatment" ditches were similar to the concentrations found in WPA "references" (Table 8; Figure 21), although the overall mean of the "reference" wetland concentration was slightly higher. This possibly reflected similar usage on upstream cropland as well as the WPA sites. In addition, phenoxy acid herbicides have minimal environmental persistence following application. Concentrations of 2,4-D at these low levels are not considered to be biologically significant.

Alachlor and triazine herbicide concentrations in the "treatment" WPA ditches and wetlands suggest some cause for concern that biologically significant herbicide concentrations may be introduced into interior WPA wetlands via ditches draining private croplands, or by way of direct runoff from adjacent croplands into "co-owned" WPA wetlands (under joint private/Federal ownership at the boundaries of WPAs).

Privately Owned Wetlands

Concentrations of the three herbicide groups in surface water samples from privately owned "treatment" wetlands varied among WMDs and within individual wetlands over time. The range of triazine concentrations measured within the 16 private wetlands was 0.31-5.27 ppb (Table 9), whereas alachlor and phenoxy acid herbicide concentration ranges were 0.009-6.56 ppb (Table 10) and 0.000-1.10 ppb (Table 11), respectively.

Mean monthly concentrations of triazines from privately owned "treatment" wetlands within Litchfield WMD were greater than Fergus Falls or Morris WMD throughout the sampling season (Figure 22). This followed the observed pattern of the higher "reference" WPA wetland triazine concentrations in the Litchfield WMD than in the Fergus Falls or Morris WMDs (discussed above). Individual privately owned "treatment" wetland monthly triazine concentrations are provided for Morris, Fergus Falls, and Litchfield WMDs in Figures 23, 24, and 25, respectively. While triazine concentrations in both Morris and Fergus Falls WMD private wetlands were low (rarely exceeding 0.4 ppb), some Litchfield WMD private wetlands had concentrations (5.27 ppb) up to six times the maximum concentration (0.85 ppb) found in either of the other two WMDs.

Higher mean monthly alachlor concentrations from Morris WMD privately owned "treatment" wetlands were higher throughout the sampling season than Litchfield WMD, which were higher than Fergus Falls WMD (Figure 26). Individual privately owned "treatment" wetland monthly alachlor concentrations are provided for Morris, Fergus Falls, and Litchfield WMDs in Figures 27, 28 and 29, respectively. The maximum alachlor concentration in a Morris WMD private wetland (6.56 ppb) was over twice the Litchfield (2.83 ppb) maximum

private wetland concentration, which was twice the maximum private wetland concentration in Fergus Falls WMD (1.180). A private wetland in Morris WMD (which had the second highest alachlor concentration (3.59 ppb) and mean concentration (2.83 ppb) in the study) was strongly influenced by upstream croplands. This was deduced from the fact that the particular wetland was surrounded by alfalfa and CRP lands where alachlor is not applied.

Similar low mean monthly 2,4-D concentrations occurred among privately owned wetlands in the three WMDs (Figure 30). Individual privately owned "treatment" wetland monthly 2,4-D concentrations are provided for Morris, Fergus Falls, and Litchfield WMDs in Figures 31, 32 and 33, respectively. The maximum 2,4-D concentration (1.10 ppb) occurred in the Fergus Falls WMD, which closely follows the trend observed in the "reference" wetlands (discussed above).

Based on the measured concentrations of the three herbicide classes in the privately owned wetlands, there were apparent differences in rates and timing of herbicide applications across the study area. Although the highest triazine concentrations in private wetlands in general tended to occur in June, timing of maximum concentrations varied somewhat among the WMDs. Triazine concentrations in Morris WMD private wetlands had a maximum concentration of 0.850 ppb occurring in June (Figure 23). Triazine concentrations in Fergus Falls WMD private wetlands had maximum concentrations occurring in April (0.651 ppb) and May (0.683 ppb) (Figure 24). Some Litchfield WMD private wetlands had maximum individual wetland concentrations of 1.55, 2.17, and 5.27 ppb occurring in April, May, and June, respectively (Figure 25).

Some Morris WMD private wetlands had relatively high alachlor concentrations (April, 3.59 ppb; May, 3.31 ppb; and July, 5.82 ppb) with a maximum (6.56 ppb) occurring in June (Figure 21). Litchfield WMD private wetlands exhibited trends similar to the Morris WMD, with elevated alachlor concentrations occurring within each sampling period although maximum concentrations were always lower than those for the Morris WMD (April, 1.92 ppb; May, 2.60 ppb; June, 2.83 ppb; and July, 1.30 ppb) (Figure 22). Alachlor concentrations in private wetlands sampled in the Fergus Falls WMD did not exceed 0.2 ppb, with the exception of one wetland where concentrations were 1.17 ppb (May), 1.03 ppb (June) and 1.18 ppb (July) (Figure 23).

Concentrations of detected 2,4-D in all private wetlands were low; never exceeding 1.10 ppb (Table 11). Cropland applications appeared to have occurred mainly in May, with elevated individual wetland concentrations occurring in April (0.58 ppb), May (0.55 ppb) and June (1.10 ppb). These low concentrations may reflect the limited use of 2,4-D on private croplands affecting the survey wetlands and/or the limited persistence of this herbicide class in the environment.

These findings suggest that there may be some cause for concern over what may be typically and realistically occurring herbicide introductions into "treatment" privately owned wetlands. Some of the alachlor and triazine concentrations that were introduced into the private wetlands may potentially impact sensitive plants or animal species.

Discussion

One of the least understood aspects of agricultural activity in the Prairie Pothole Region of Minnesota is the role that agricultural chemical runoff plays in the ecology of wetlands and their use by waterfowl. Wetland quality, which is strongly influenced by surrounding land use and associated vegetation, has been recognized as an important factor influencing waterfowl recruitment in the Prairie Pothole Region (Swanson and Duebbert 1989). Agricultural herbicides entering wetland ecosystems may have direct toxic effects on aquatic plants and invertebrates and, therefore, may indirectly affect the reproduction and survival of aquatic birds by altering food and cover (Grue et al. 1986). Therefore, investigations to identify potential impacts (i.e., herbicide runoff) that may alter waterfowl feeding ecology contribute to the understanding of identifying those specific physical, chemical, and biological conditions in wetlands which favor enhanced waterfowl productivity.

Results from a limited sampling of both isolated (WPA) and private wetlands indicate that widespread, low-level herbicide deposition in wetlands is occurring in the Prairie Pothole Region of Minnesota. While the relative importance of the various potential routes of entry of herbicides to wetlands (e.g., upland runoff, aerial drift or precipitation) is not clear, evidence from this study strongly suggests that runoff from adjacent and/or upper watershed croplands appears to be a major source.

Triazine and alachlor concentrations in the isolated WPA wetlands increased during the sampling period, although the use of both was halted on nearly all Service lands in 1988 due to environmental concerns (USFWS, 1990). In addition, observed concentration in the isolated wetlands followed the general temporal trends observed in private wetlands adjacent to fields which received herbicide treatments. Recent studies in Iowa have found small concentrations of herbicides (usually under 1 ppb, but up to 40 ppb) in rainfall samples. The compounds most often detected (atrazine, alachlor, metolachlor and cyanazine) were found in almost every rainfall event in Iowa from mid-April through July (Nations 1992). Presently, herbicide contributions to wetlands in Minnesota due to precipitation events have not been quantified.

Based on a limited number of samples, it is apparent that some county ditches (passing through WPAs as well as WPA wetlands bordered by or receiving runoff from private croplands) can acquire herbicide concentrations which exceed concentrations typically detected in adjacent isolated WPA wetlands. Concentrations of both triazines and alachlors were up to several orders of magnitude higher in "treatment" WPA ditches than concentrations found in adjacent isolated WPA wetlands. There is concern that WPA wetlands on ditch systems could potentially be receiving both higher concentrations and a greater variety of herbicides. Herbicide concentrations in some WPA wetlands adjacent to private croplands exceeded concentrations found in isolated WPA wetlands on the same WPA. Not surprisingly, monthly mean concentrations of alachlor and triazine were also higher in private wetlands than the

"reference" WPA wetlands. The above suggests that certain agricultural herbicides applied by farmers in west central Minnesota are entering, and may be adversely impacting, wetlands situated adjacent to or surrounded by croplands.

Findings from this study and others indicate that the presence (or persistence) of 2,4-D in surface water (present study) or sediments (Ruelle 1981) of wetlands in Minnesota are negligible. After analyzing 32 sediment samples collected from west central Minnesota WPAs, Ruelle (1981) concluded that FWS-managed wetlands in Minnesota farm areas were not phenoxy herbicide sinks. Phenoxy herbicide concentrations are generally lower in water than in terrestrial soils or lake bottom sediments. Although the second highest 2,4-D concentration found in this study was found on a WPA (Odens Unit; 0.764 ppb), levels on both WPAs and private wetlands generally did not exceed 0.3 ppb. These results correspond well with a study of agricultural watersheds in Ontario which found a mean 2,4-D water residue concentration of 0.2 ppb (range: <0.1-16 ppb) (Frank et al. 1978 as cited in Canadian Water Quality Guidelines 1987). Those mean 2,4-D concentrations are well below those known to cause even subtle adverse impacts on algal or phytoplankton communities. Therefore, it is recommended that attempts to detect 2,4-D concentrations in future studies be deemphasized.

Some alachlor concentrations measured in the present study are of concern. Concentrations as high as 6.56 ppb were found in surface water from private wetlands. The peak concentrations of alachlor and triazines occurring in most of the study wetlands were probably higher than the respective measured concentrations because sampling was delayed for one to three days after a rainfall event. The extent of herbicide runoff from treated fields is determined to a large extent by rainfall intensity and the time elapsed between herbicide application and rainfall events (Weber et al. 1980), which undoubtedly varied among farmers in this study. Once alachlor was introduced into wetlands, residue concentrations in the water column appeared to decrease slowly. Although specific herbicides within the alachlor class could not be identified, metolachlor and alachlor appear to be widely used in the state. Metolachlor is known to degrade slowly in soils, persisting to the next growing season (Frank et al. 1991), although reported persistence rates vary greatly for both compounds.

It is difficult to ascribe an adverse vegetative effect to even the higher alachlor concentrations found, since aquatic plant toxicity data in the literature are sparse for that class of compounds and generally address acute exposure only. Hartman and Martin (1985) found that alachlor concentrations as low as 10 ppb impaired the growth of *Lemna minor* by 50% in 48-hour tests. Buhl and Faerber (1989) determined that Lasso (alachlor) was one of four herbicides that posed the greatest risk to midges and other wetland biota with similar or greater sensitivities during a critical stream runoff event. Although chronic toxicity values derived from aquatic animal testing are extremely limited for alachlor, those values are not always sensitive enough to protect aquatic plants in receiving waters (Teraldsen and Norberg-King 1990).

Although most private wetlands had low triazine concentrations, some within

the Litchfield WMD contained concentrations up to 5.27 ppb. Such concentrations in wetland surface waters may potentially impact sensitive plant or animal species. Atrazine (the most heavily used triazine herbicide in Minnesota) concentrations as low as 1 ppb inhibited photosynthesis (deNoyelles et al. 1982) and 10 ppb inhibited growth in 37 algal isolates (Butler et al. 1975). Algae are important primary producers in freshwater systems. Hamilton et al. (1987) reported a reduction in attached algal productivity of 21-82% in lake concentrations of 0.8-1.56 ppb atrazine. *Vallisneria americana*, an important food source for canvasback ducks (*Athya vallisneria*), showed reduced growth at atrazine concentrations of 3.2-12 ppb (seven-week exposure). Atrazine decreased algal growth more than 40% at concentrations greater than 10 ug/L (Johnson 1986), although both producers and consumers in microcosms monitored over 30 days were affected by atrazine at concentrations of 10 ug/L or less. The probability of finding ppb or greater atrazine concentrations in wetlands in intensively cropped areas is high, because annual runoff losses of atrazine can be as high as 10% of the amount applied. As with alachlor, atrazine concentrations decreased slowly within the wetland water columns following runoff events. Results of other studies suggest that atrazine can persist from year to year in soil and water (Thurman et al. 1991).

Conclusions

Results from this study indicate that temporary, seasonal and semipermanent wetlands within agricultural settings in west central Minnesota may be receiving herbicides via runoff at concentrations which can adversely impact their flora and fauna. Private wetlands adjacent to croplands exhibited higher concentrations of both triazines and alachlors than wetlands on WPAs isolated by distance and topography from herbicide use. The higher measured concentrations of each herbicide group have been shown by others to impact primary producers, such as planktonic and filamentous algae, floating plants (e.g., *Lemna*), and some shallow-rooted broadleaved submergents (e.g., *Vallisneria*). Grass-like perennials such as cattails, rushes, sedges, and reeds were likely unaffected by herbicide concentrations measured in this study. Concentrations of 2,4-D were consistently low and similar among both private and "reference" wetlands. The 2,4-D concentrations measured in this study are not known to have adverse impacts to aquatic life.

At least some drainage ditches flowing through WPAs and WPA wetlands adjacent to private croplands contain herbicide concentrations which exceed concentrations found in isolated WPA wetlands. WPA wetlands on such ditch systems could potentially be receiving high concentrations of many herbicides. Concentrations of some herbicides measured in WPA "co-owned" wetlands adjacent to private croplands exceeded concentrations of the same herbicides found in isolated wetlands on the same WPAs.

Apparent differences in herbicide concentrations occurring within the three WMDs may reflect geographic, climatic, or cropping pattern differences, and local biases toward specific herbicides for given crop types or application rates across the districts. Subtle, but noticeable increases of triazine and alachlor herbicide concentrations in isolated WPA wetlands tended to parallel

the timing and direction of herbicide concentrations in private wetlands within the same districts. In addition to frequent, localized herbicide inputs to wetlands from agricultural runoff, results of this study suggest that widespread, low-level herbicide deposition is occurring across the prairie pothole region of western Minnesota even prior to the onset of spring planting. Probable herbicide transport mechanisms include long-range aerosol drift and/or precipitation events originating to the south.

The present study was essentially a reconnaissance, examining both anticipated worst- and best-case scenarios from an exposure standpoint. Several limitations inherent in the survey (and recognized beforehand) included: (a) a relatively small sample size; (b) the inability to determine in advance which crop types and associated herbicide usage would emerge adjacent to previously selected "treatment" wetlands; and (c) the inability of the ELISA immunoassay to identify major corn, small grain and soybean herbicides other than those in the triazine, alachlor and phenoxy acid herbicide classes.

Recommendations

Watershed slopes and cover types, crop types and tillage practices, amounts and types of wetland buffer vegetation, and watershed size can all influence the amount and composition of agricultural chemical runoff into wetlands and other surface waters. Measurement and correlation of those factors with observed wetland herbicide concentrations was beyond the scope of this study. Because herbicides are, by definition, phytotoxic, their potential impacts on wetland macrophyte and algal communities are of interest to the Service. The amount and types of herbicides entering wetlands partially or wholly within WPAs has generated interest among Minnesota WMD personnel. Because "co-owned" wetlands (wetlands only partially within the boundaries of WPAs) are numerous within the WMDs, it was suggested that a logical next step might be to determine whether, and to what extent, co-owned WPA wetlands were receiving herbicides via runoff from adjacent private agricultural lands. These questions arising from the present study were addressed in a FY 93 followup herbicide/wetland investigation. A comparison of herbicide concentrations in co-owned wetland basins with those in isolated WPA wetlands will provide WMD personnel information concerning the relative water quality of wetlands under their management. It could also provide Service management with information necessary to decide whether herbicide runoff into federal WPAs is sufficiently well defined and severe to warrant a request to pesticide regulatory agencies for corrective action.

Further attempts in the FY 93 study to characterize the herbicide "soups" existing in co-owned wetlands would be greatly advanced through examination of an expanded list of herbicides commonly used on corn and small grain crops. The addition of GC/MS analytical chemistry capability would allow the identification of approximately 25 individual herbicides and their metabolites, and expand the list of target crops to include soybeans, the second most widely grown crop in the Minnesota. This approach would improve our understanding of herbicide influxes to wetlands by: (a) affirming the present study's ELISA method results; (b) identifying specific chemicals applied (rather than herbicide groups); (c) identifying many herbicides not

detected by the ELISA method; and (d) allowing analysis of a more comprehensive list of target crop types. This would provide a better understanding of the chemical soup to which wetland biota in west central Minnesota are being exposed. More intensive research to assess herbicide impacts on wetland biota should be pursued only after the identification of specific chemicals and their concentrations typically found in wetlands is addressed.

Concurrent contamination of wetlands by more than one agricultural pesticide may alter the persistence of compounds, and thus, their potential toxicity to wetland wildlife. A potential scenario in prairie pothole wetlands might involve interactions of multiple herbicides (and potentially insecticides) comprising chemical "soups" unique to individual wetlands. The various ingredients comprising a particular "soup" could be individually, additively, or even synergistically toxic in certain combinations. For example, the presence of parathion (an insecticide) may increase the persistence of herbicides in soils (Sethunathan et al. 1977). Alternatively, herbicides (particularly atrazine) can increase the toxicity of parathion to insects (ibid.). The individual and interactive effects of herbicides in concentrations likely to be encountered in natural wetlands have received little study to-date. Such effects could be determined through field or microcosm research. However, we believe a survey of a broader array of herbicide combinations found in Service co-owned wetlands (FY 93 study) is necessary prior to such research in order to better define a "real world" wetland herbicide scenario.

In order to accurately determine runoff impacts of wetlands, several considerations should be addressed in future studies. First, accurate estimates of watershed runoff and pollutant loadings need to be determined. Actual storm runoff flow should be measured during high flow periods (i.e., automated samplers and recorders). Secondly, watershed size may be expected to strongly affect wetland runoff monitoring design and thus must be considered carefully. Baker (1988) made some conclusions regarding the effects of agriculturally dominated watershed areas which may be applicable such as:

- (a) peak pollution concentrations tend to be greatest in the runoff from small watersheds rather than large;
- (b) the duration of runoff events and associated pollutant loadings increases with the size of the watershed;
- (c) the annual variability in pollutant yield is greater in small watersheds than large watersheds.

In addition, while this study looked at only strong palustrine permanent and semipermanent emergent (Type III/IV) wetlands and drainage ditches, less permanent wetlands could potentially contain higher herbicide concentrations and thus be more severely affected.

TABLES

Table 1. Crop acreage percentages treated with pesticides in Minnesota, 1991*.

	Area Planted (1,000 acres)	Herbicide	Insecticide	Fungicide	Other
Corn	6600	96	13	**	**
Soybeans	5500	95	**	**	**
Spring Wheat	2100	97	6	7	**

* acres receiving 1 or more applications of specific pesticide classes.

** applied on less than one percent of acres.

Source: Agricultural Chemical Usage: 1991 Field Crops Summary. National Agricultural Statistics Service, USDA, March 1992.

Table 2. Descriptions of private landowner wetlands sampled in west-central Minnesota for herbicide concentrations, 1992.

Wetland Management District	Wetland I.D. Number	Location by County and Township	Crop Type(s)	Buffer Distance (feet)
Morris	1	<u>Pope County</u> Chippewa Falls	corn, small grain	0
	2	Chippewa Falls	soybean, hay, corn	6-18
	3	Gilchrist	alfalfa	7-11
	4	Gilchrist	soybean	18-20
Fergus Falls	1	<u>Douglas County</u> Brandon	alfalfa, corn	0-75-90
	2	Brandon	corn	99-125-200
	3	Brandon	corn	96-111
	4	Millerville	corn, small grain	20-31
	5	Millerville	soybean	30-35
	6	Millerville	corn, alfalfa	57-92
	7	Millerville	small grain, pasture	60-66
	8	Evansville	small grain	42-45
Litchfield	1	<u>Stearns County</u> Ashley	corn, soybeans alfalfa	0-36-45
	2	Ashley	corn, alfalfa	23-31-48
	3	Raymond	corn, small grains	31-72-140
	4	Sauke Centre	corn	30-39

Table 3. Surface water triazine concentrations (ppb) from reference Waterfowl Production Area (WPA) wetlands in west-central Minnesota, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake	0.028	0.158	0.281	0.080	0.137	0.028	0.281
Overby	0.035	0.074	0.170	0.058	0.084	0.035	0.170
Larson	0.035	0.121	0.233	0.102	0.123	0.035	0.233
Heidebrink	0.019	0.092	0.139	0.053	0.076	0.019	0.139
Mean	0.029	0.111	0.206	0.073	0.105		
Fergus Falls WMD:							
Grandokken	0.038	0.126	0.118	0.065	0.087	0.038	0.126
Reger	0.034	0.077	0.159	0.080	0.088	0.034	0.159
Odens	0.056	0.122	0.283	---- ^a	0.154	0.056	0.283
Mean	0.043	0.108	0.187	0.073	0.110		
Litchfield WMD:							
West Union	0.067	0.200	0.546	0.326	0.285	0.067	0.546
Sogge	0.056	0.244	0.278	0.096	0.169	0.056	0.278
Faber	0.052	0.164	0.210	0.127	0.138	0.052	0.210
Mean	0.058	0.203	0.345	0.183	0.197		

^a wetland dried up

Table 4. Surface water alachlor concentrations (ppb) from reference Waterfowl Production Area (WPA) wetlands in west-central Minnesota, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake	0.066	0.205	0.432	0.211	0.229	0.066	0.432
Overby	0.065	0.201	0.125	0.109	0.125	0.065	0.201
Larson	0.082	0.178	0.161	0.122	0.136	0.082	0.178
Heidebrink	0.057	0.240	0.132	0.125	0.139	0.057	0.240
Mean	0.068	0.206	0.213	0.142	0.157		
Fergus Falls WMD:							
Grandokken	0.074	0.173	0.185	0.214	0.162	0.074	0.214
Reger	0.053	0.068	0.080	0.062	0.066	0.053	0.080
Odens	0.048	0.154	0.139	--- ^a	0.123	0.048	0.154
Mean	0.058	0.132	0.135	0.138	0.117		
Litchfield WMD:							
West Union	0.085	0.256	0.283	0.150	0.194	0.085	0.283
Sogge	0.076	0.261	0.406	0.191	0.234	0.076	0.406
Faber	0.063	0.192	0.179	0.273	0.177	0.063	0.273
Mean	0.075	0.236	0.289	0.205	0.201		

^a wetland dried up

Table 5. Surface water 2,4-D concentrations (ppb) from reference Waterfowl Production Area (WPA) wetlands in west-central Minnesota, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake	0.087	0.157	0.116	0.188	0.137	0.087	0.188
Overby	0.059	0.547	0.107	0.036	0.187	0.036	0.547
Larson	0.217	0.067	0.040	0.057	0.095	0.040	0.217
Heidebrink	0.240	0.004	0.035	0.041	0.080	0.004	0.240
Mean	0.151	0.194	0.075	0.081	0.125		
Fergus Falls WMD:							
Grandokken	0.124	0.160	0.431	0.068	0.196	0.068	0.431
Reger	0.109	0.044	0.210	0.018	0.095	0.018	0.210
Odens	0.434	0.764	0.122	---a	0.440	0.122	0.764
Mean	0.222	0.323	0.254	0.043	0.211		
Litchfield WMD:							
West Union	0.363	0.062	0.031	0.063	0.130	0.031	0.363
Sogge	0.117	0.079	0.116	0.047	0.090	0.047	0.117
Faber	0.096	0.035	0.136	0.039	0.077	0.035	0.136
Mean	0.192	0.057	0.094	0.050	0.098		

^a wetland dried up

Table 6. Surface water alachlor concentrations (ppb) from treatment Waterfowl Production Area (WPA) county ditches and wetlands adjacent to private landowner croplands, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake County Ditch #1	0.396	0.406	0.809	0.451	0.516	0.396	0.809
Krantz Lake County Ditch #2	0.931	1.490	2.410	0.975	1.452	0.931	2.410
Fergus Falls WMD:							
Grankokken	0.015	0.368	0.521	0.339	0.331	0.015	0.521
Oden	0.256	0.250	0.183	0.156	0.211	0.156	0.256

Table 7. Surface water triazine concentrations (ppb) from treatment Waterfowl Production Area (WPA) county ditches and wetlands adjacent to private landowner croplands, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake County Ditch #1	0.079	0.114	1.900	0.115	0.552	0.079	1.900
Krantz Lake County Ditch #2	0.233	0.214	4.170	1.640	1.570	0.214	4.170
Fergus Falls WMD:							
Grankokken	0.070	0.077	0.186	0.092	0.106	0.070	0.186
Oden	0.139	0.170	0.258	0.106	0.168	0.106	0.258

Table 8. Surface water 2,4-D concentrations (ppb) from treatment Waterfowl Production Area (WPA) county ditches and wetlands adjacent to private landowner croplands, April-July, 1992.

Waterfowl Production Management Area Units	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
Krantz Lake County Ditch #1	0.165	0.124	0.049	0.030	0.092	0.030	0.165
Krantz Lake County Ditch #2	0.115	0.040	0.193	0.169	0.129	0.040	0.193
Fergus Falls WMD:							
Grankokken	0.003	0.048	0.033	0.019	0.026	0.003	0.048
Oden	0.038	0.009	0.057	0.080	0.046	0.009	0.080

Table 9. Surface water triazine concentrations (ppb) from privately owned wetlands in west-central Minnesota, April-July, 1992.

Private Treatment Wetlands	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
1	0.040	0.162	0.311	0.087	0.150	0.040	0.311
2	0.135	0.145	0.850	0.568	0.425	0.135	0.850
3	0.050	---- ^a	0.257	0.143	0.150	0.050	0.257
4	0.045	0.227	0.390	0.132	0.199	0.045	0.390
Mean	0.068	0.178	0.452	0.233	0.231		
Fergus Falls WMD:							
1	0.039	0.196	0.247	0.072	0.139	0.039	0.247
2	0.651	0.557	0.642	0.436	0.572	0.436	0.651
3	0.059	0.116	0.276	0.101	0.138	0.059	0.276
4	0.031	0.683	0.223	0.094	0.258	0.031	0.683
5	0.093	0.155	0.231	0.132	0.153	0.093	0.231
6	0.069	0.125	0.317	0.077	0.147	0.069	0.317
7	0.086	0.243	0.148	0.078	0.139	0.078	0.243
8	0.065	0.125	0.397	0.096	0.171	0.065	0.397
Mean	0.137	0.275	0.310	0.136	0.215		
Litchfield WMD:							
1	0.170	0.113	0.449	0.217	0.237	0.113	0.449
2	1.550	2.170	5.270	---- ^b	3.000	1.550	5.270
3	0.176	0.153	3.360	0.287	0.994	0.153	3.360
4	0.105	0.340	0.272	0.837	0.389	0.105	0.837
Mean	0.736	0.694	2.338	0.447	1.155		

^a wetland not sampled

^b wetland drained

Table 10. Surface water alachlor concentrations (ppb) from privately owned wetlands in west-central Minnesota, April-July, 1992.

Private Landowner Treatment Wetlands	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
1	2.770	3.310	6.560	5.820	4.610	2.770	6.560
2	1.760	2.550	1.290	2.200	1.950	1.290	2.550
3	3.590	--- ^a	2.740	2.170	2.830	2.170	3.590
4	0.056	0.493	1.190	0.771	0.628	0.056	1.190
Mean	2.044	2.118	2.945	2.740	2.505		
Fergus Falls WMD:							
1	0.012	0.268	0.236	0.183	0.175	0.012	0.268
2	0.012	1.170	1.030	1.180	0.848	0.012	1.180
3	0.009	0.116	0.112	0.106	0.086	0.009	0.116
4	0.449	0.629	0.128	0.108	0.329	0.108	0.449
5	0.100	0.237	0.183	0.272	0.198	0.100	0.272
6	0.036	0.164	0.174	0.104	0.120	0.036	0.174
7	0.168	0.141	0.221	0.175	0.176	0.141	0.221
8	0.145	0.100	0.216	0.113	0.144	0.100	0.216
Mean	0.116	0.353	0.288	0.280	0.260		
Litchfield WMD:							
1	0.711	0.779	1.400	1.300	1.050	0.711	1.400
2	1.920	2.600	2.830	---- ^b	2.450	1.920	2.830
3	0.140	0.546	0.149	0.105	0.235	0.105	0.546
4	0.248	0.269	0.465	0.282	0.316	0.248	0.465
Mean	0.755	1.049	1.211	0.562	1.013		

^a wetland not sampled

^b wetland drained

Table 11. Surface water 2,4-D concentrations (ppb) from privately owned wetlands in west-central Minnesota, April-July, 1992.

Private Treatment Wetlands	April	May	June	July	Mean	Min.	Max.
Morris WMD:							
1	0.005	0.033	0.111	0.079	0.057	0.005	0.111
2	0.101	0.553	0.057	0.035	0.187	0.035	0.553
3	0.000	----a	0.099	0.081	0.057	0.000	0.099
4	0.577	0.338	0.038	0.064	0.254	0.038	0.577
Mean	0.171	0.308	0.076	0.065	0.155		
Fergus Falls WMD:							
1	0.023	0.139	0.135	0.044	0.085	0.023	0.139
2	0.044	0.160	0.117	0.047	0.092	0.044	0.160
3	0.067	0.144	0.070	0.048	0.082	0.048	0.144
4	0.002	0.003	0.049	0.032	0.022	0.002	0.049
5	0.022	0.060	0.050	0.043	0.044	0.022	0.060
6	0.058	0.217	1.100	0.096	0.368	0.058	1.100
7	0.017	0.299	0.015	0.051	0.096	0.015	0.299
8	0.036	0.033	0.307	0.169	0.136	0.033	0.307
Mean	0.029	0.132	0.230	0.066	0.114		
Litchfield WMD:							
1	0.064	0.108	0.147	0.045	0.091	0.045	0.147
2	0.072	0.225	0.080	---b	0.126	0.072	0.225
3	0.024	0.113	0.064	0.034	0.059	0.024	0.113
4	0.021	0.056	0.043	0.128	0.062	0.021	0.128
Mean	0.045	0.126	0.084	0.069	0.115		

^a wetland not sampled

^b wetland drained

FIGURES

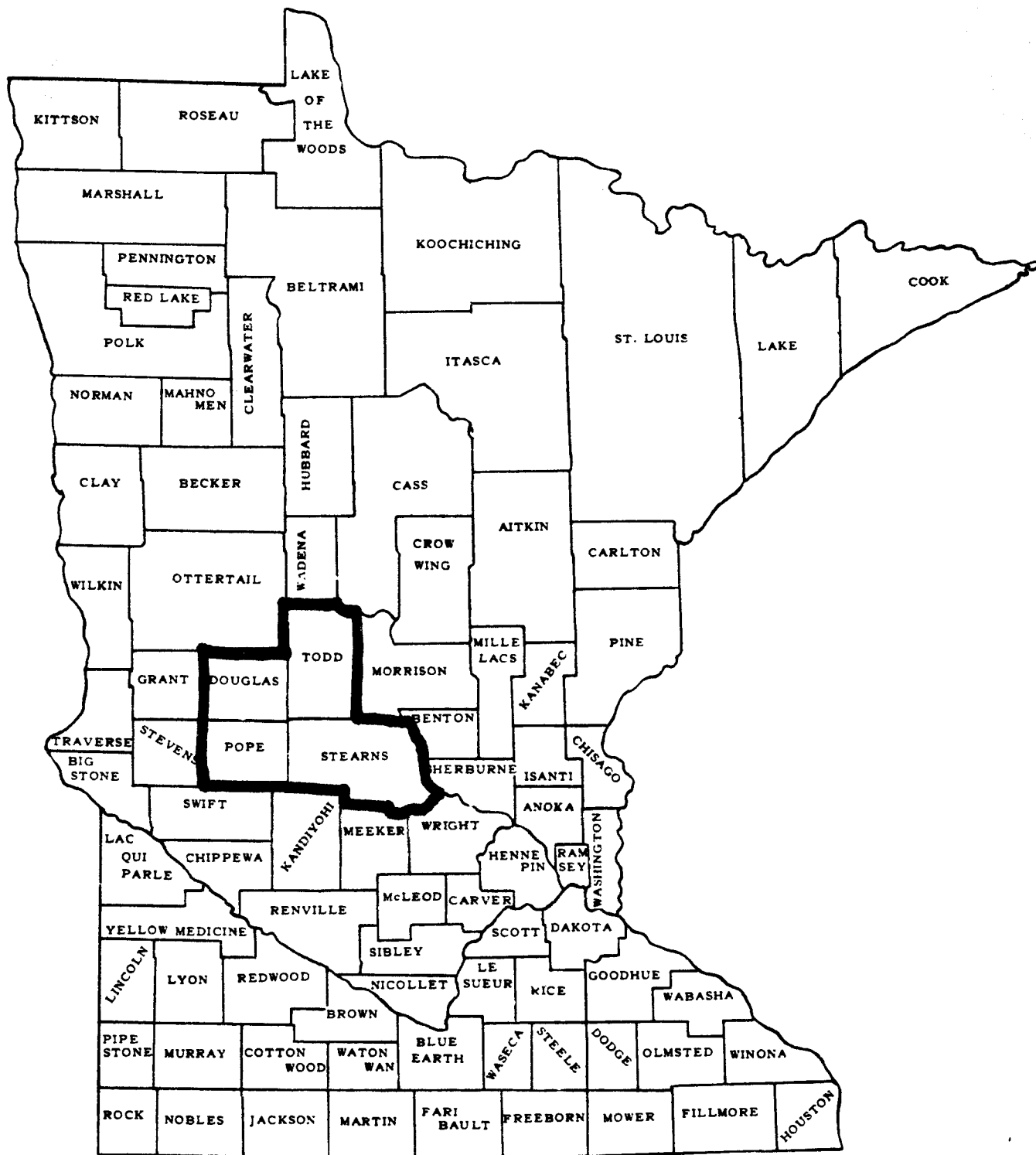


Figure 1. West-central counties of Minnesota selected for wetland sampling, April - July, 1992.

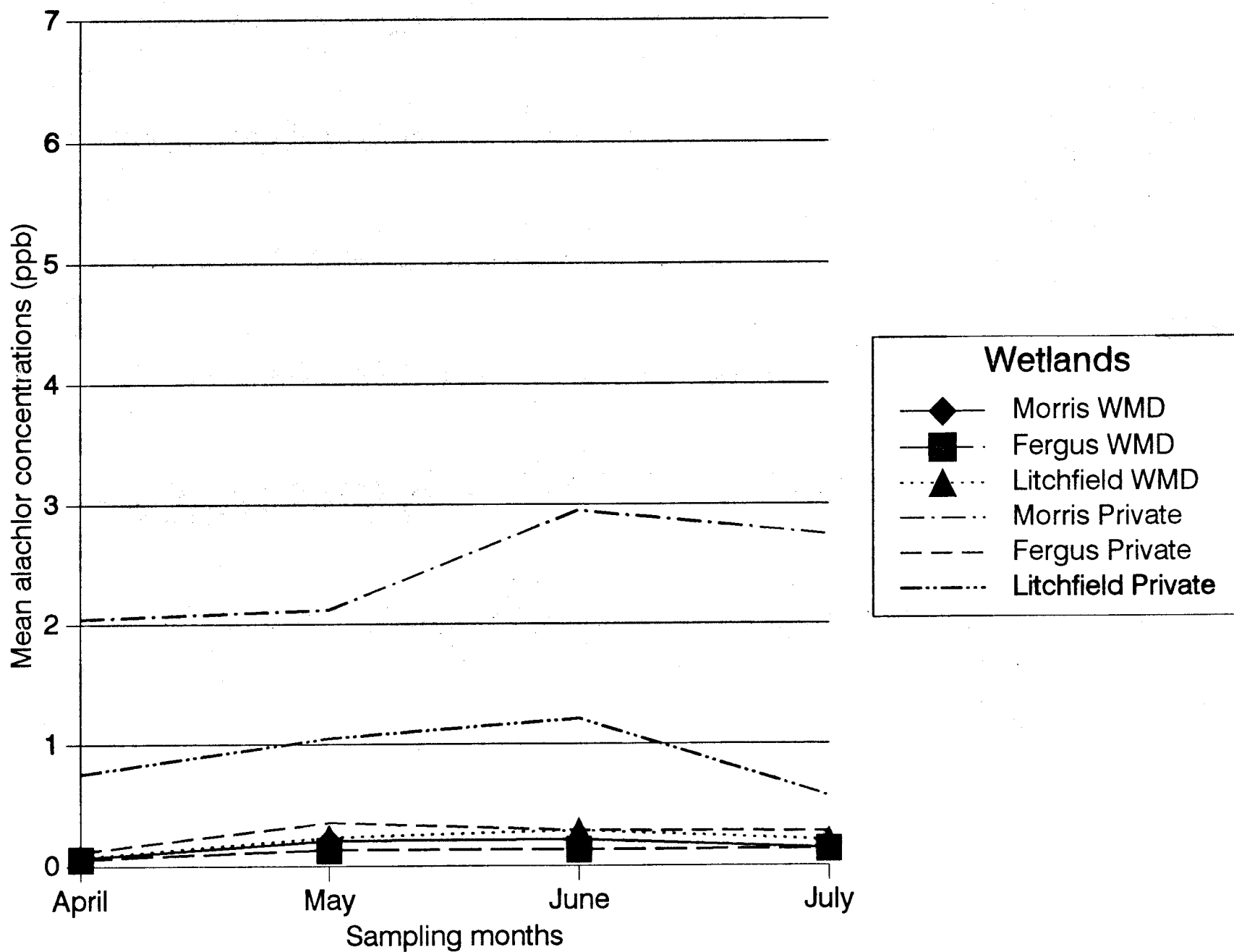


Figure 2. Mean monthly surface water alachlor concentrations (ppb) in privately owned and Federal WPA wetlands, April - July, 1992.

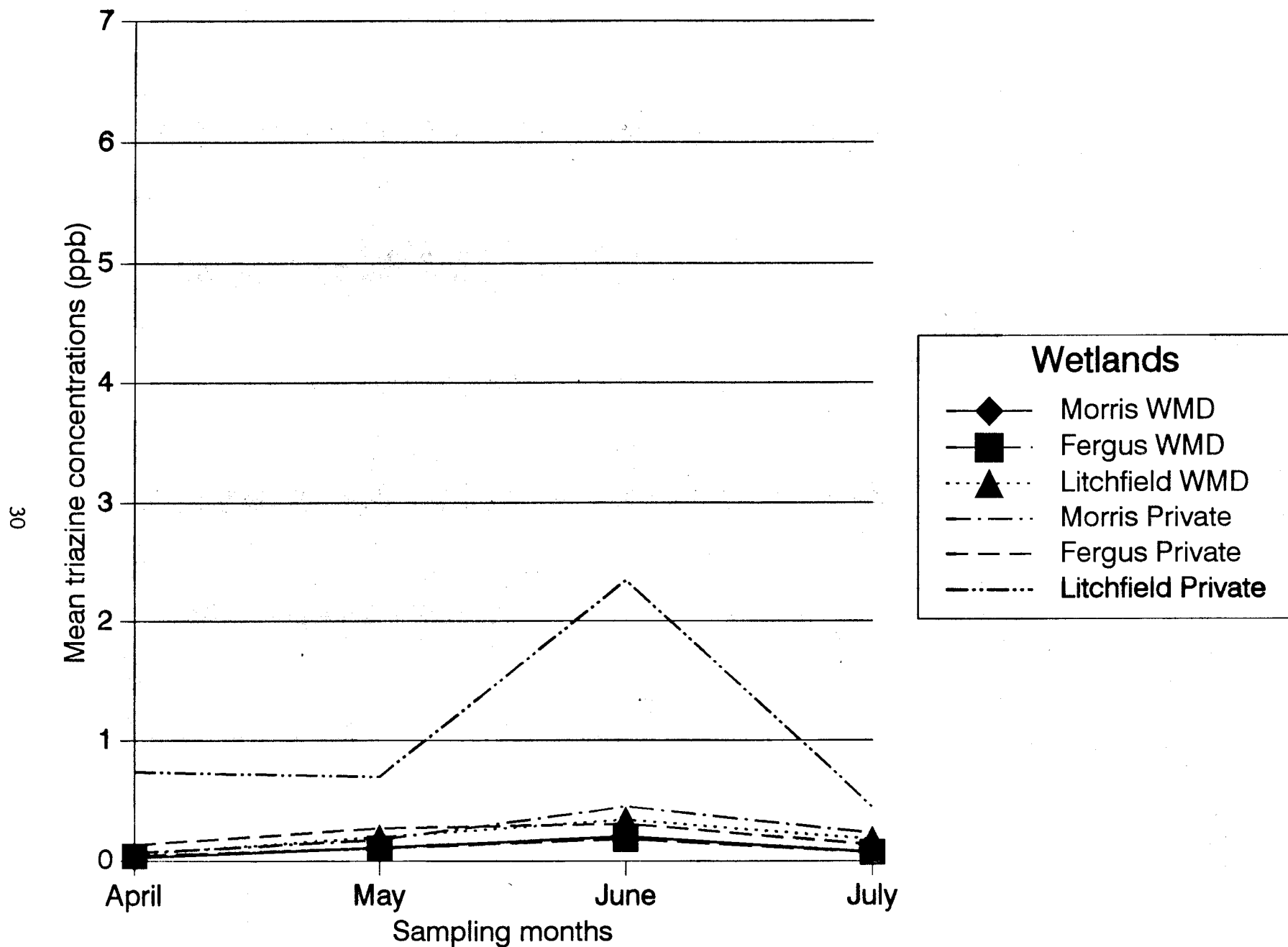


Figure 3. Mean monthly surface water triazine concentrations (ppb) in privately owned and Federal WPA wetlands, April - July, 1992.

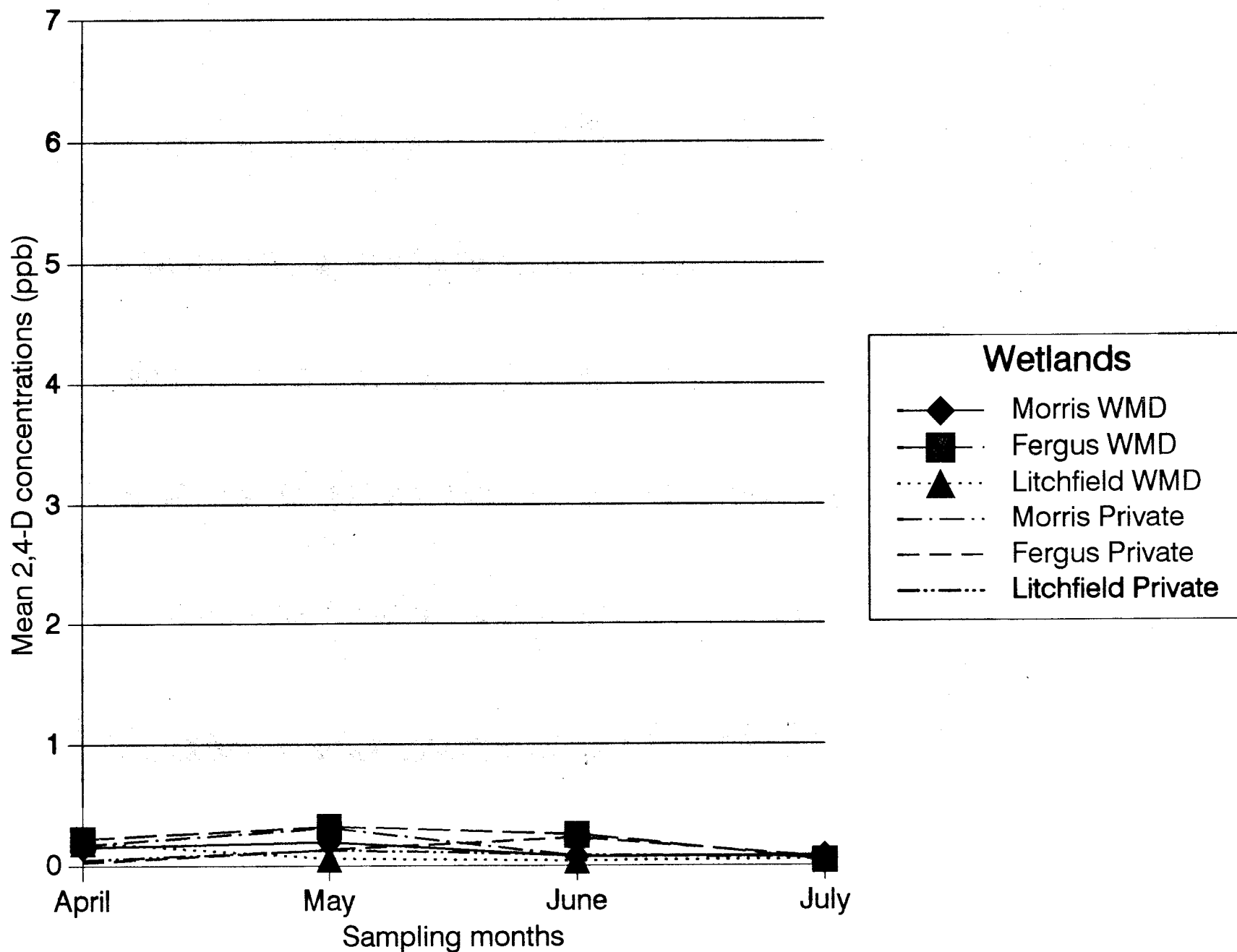


Figure 4. Mean monthly surface water 2,4-D concentrations (ppb) in privately owned and Federal WPA wetlands, April - July, 1992.

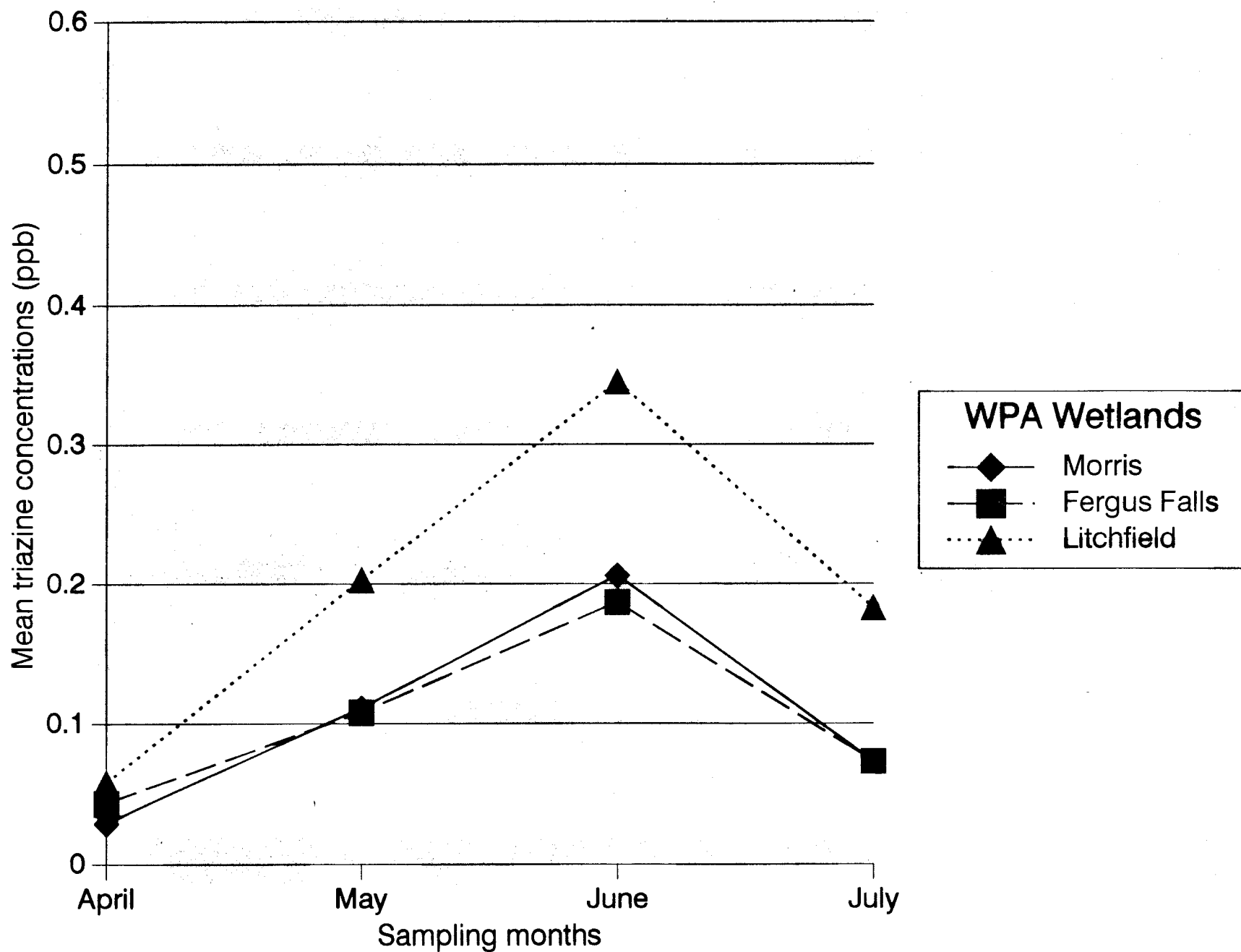


Figure 5. Mean monthly surface water triazine concentrations (ppb) in Morris, Fergus Falls, and Litchfield WPA wetlands, April - July, 1992.

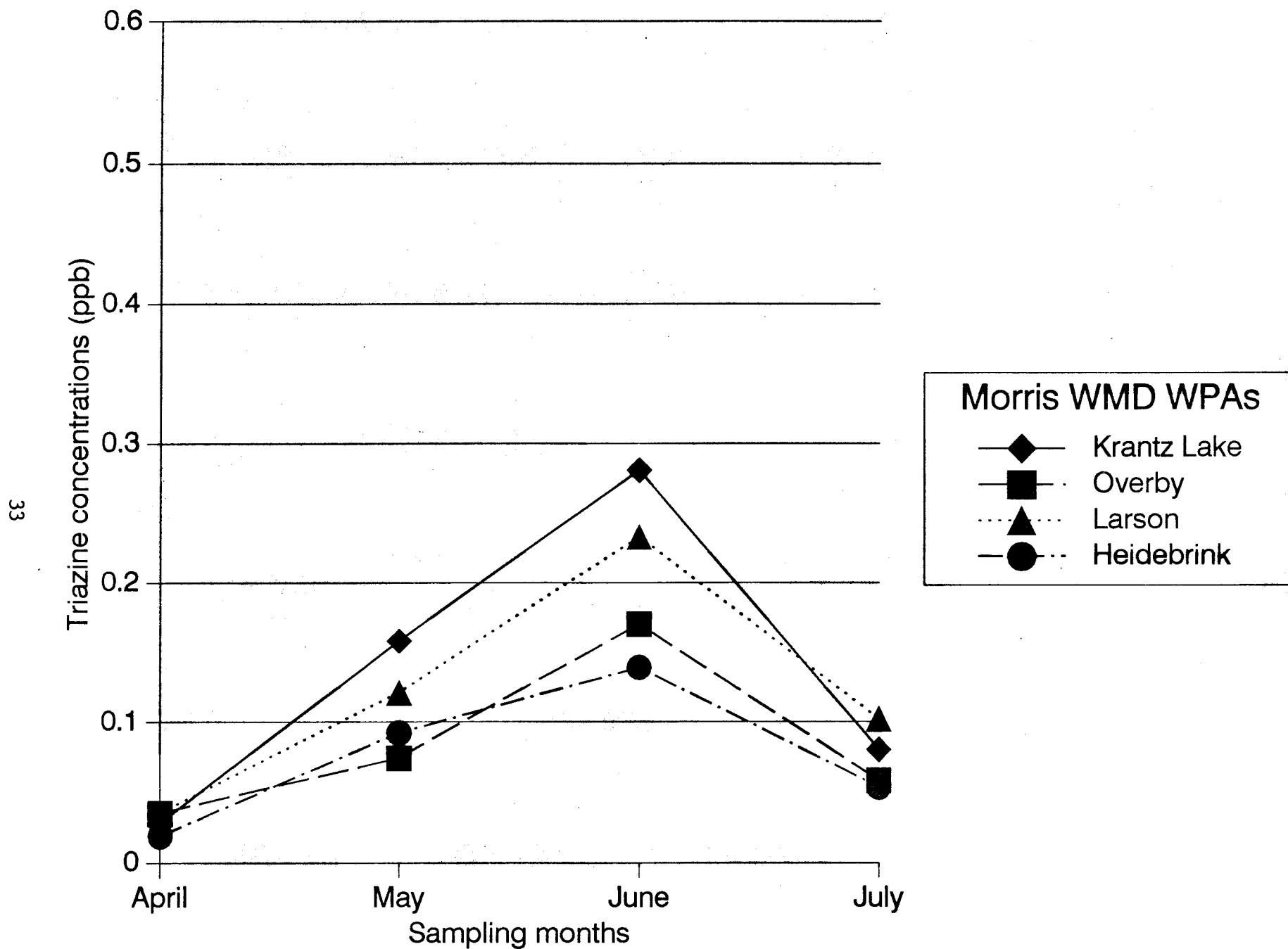


Figure 6. Surface water triazine concentrations (ppb) in Morris WPA wetlands in west-central Minnesota, April - July, 1992.

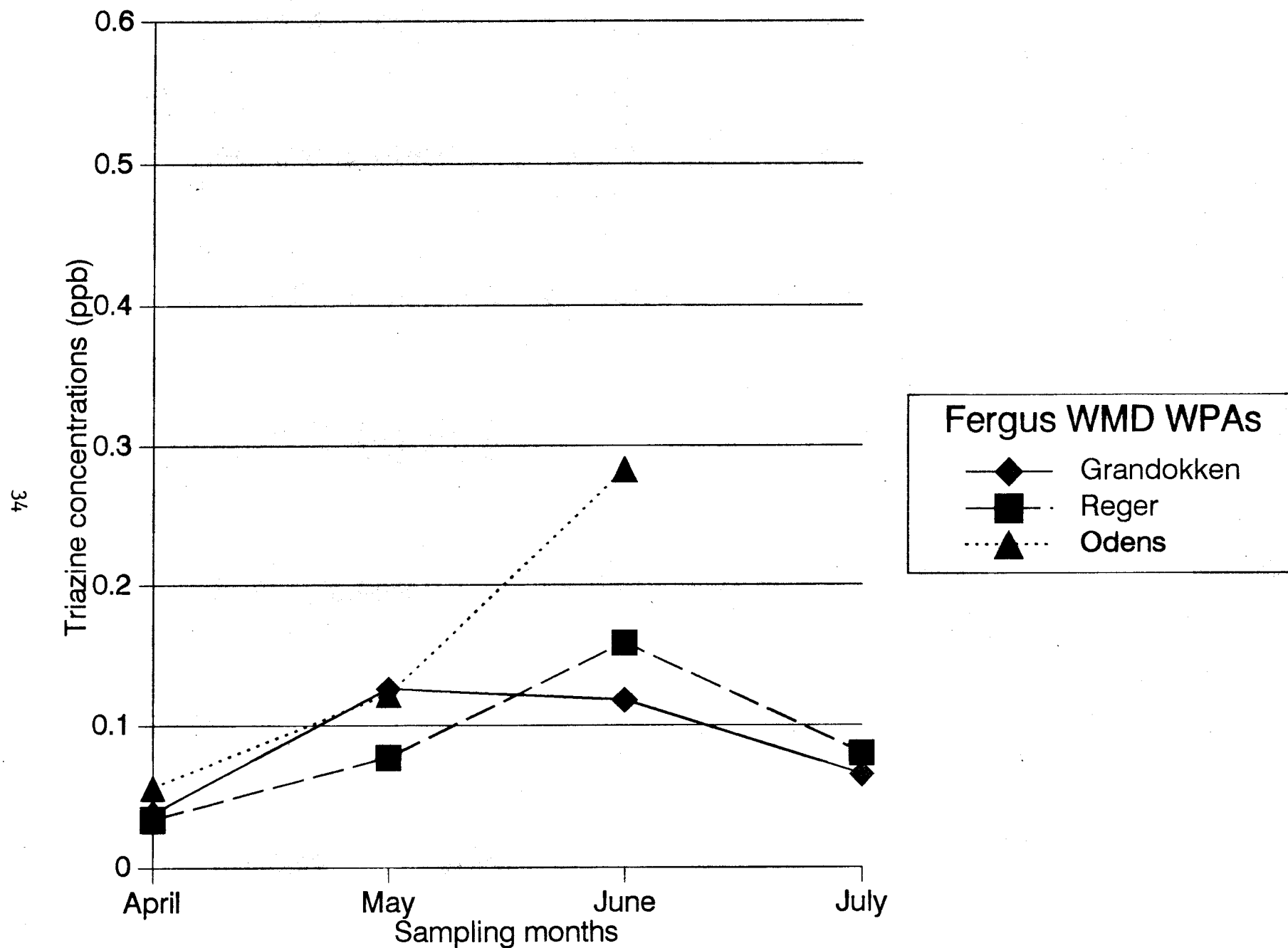


Figure 7. Surface water triazine concentrations (ppb) in Fergus Falls WPA wetlands in west-central Minnesota, April - July, 1992.

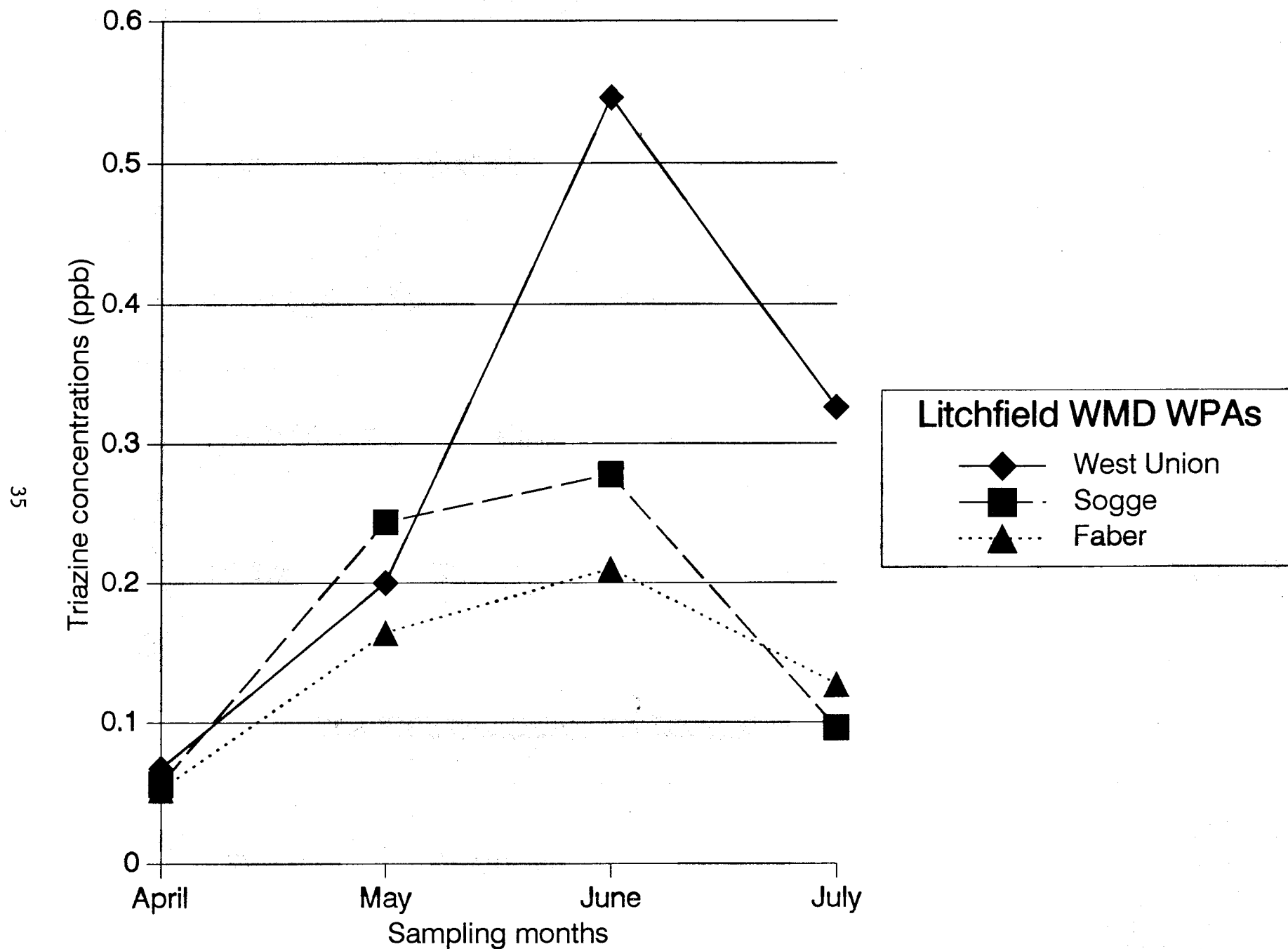


Figure 8. Surface water triazine concentrations (ppb) in Litchfield WPA wetlands in west-central Minnesota, April - July, 1992.

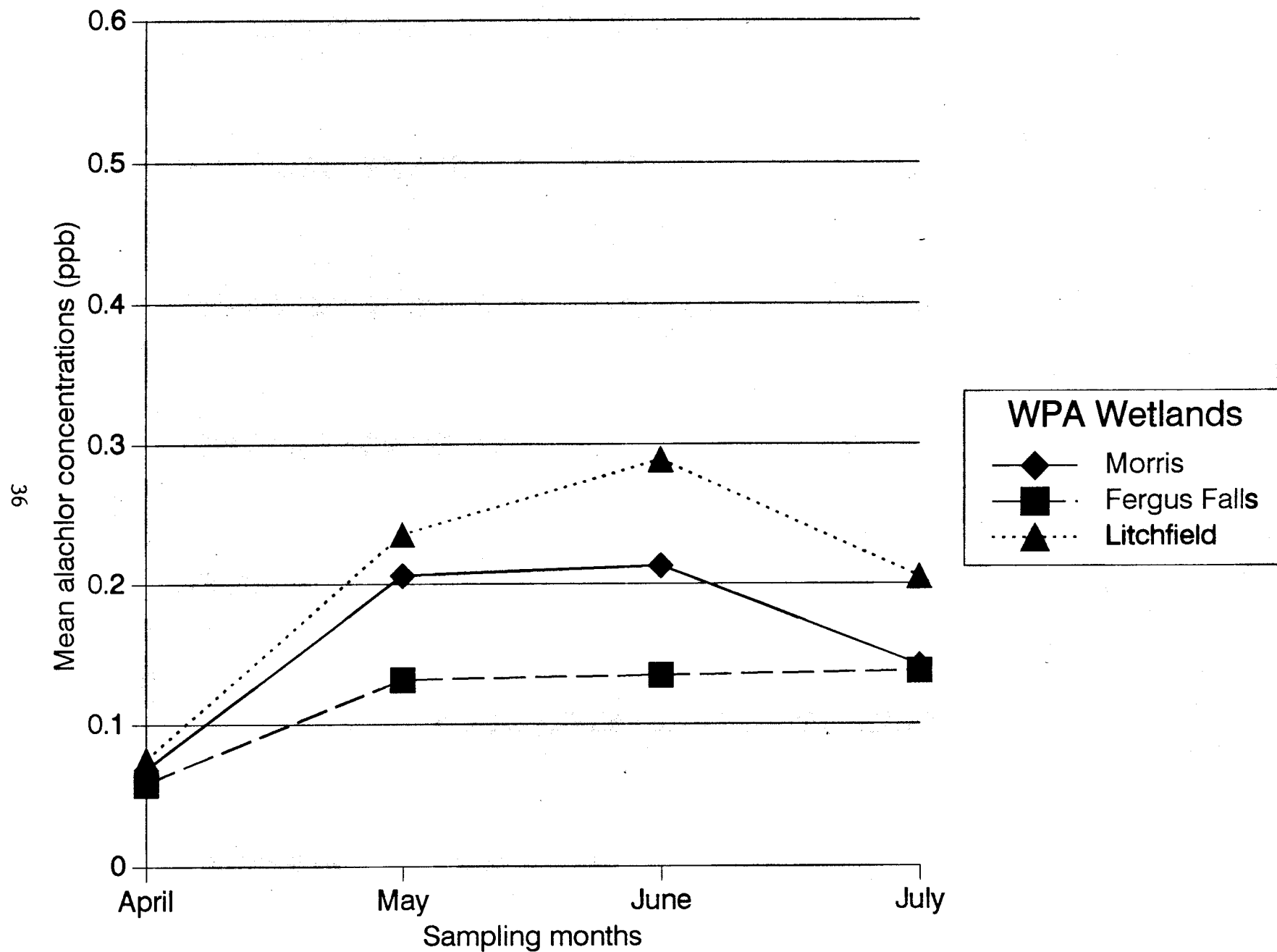


Figure 9. Mean monthly surface water alachlor concentrations (ppb) in Morris, Fergus Falls, and Litchfield WPA wetlands, April - July, 1992.

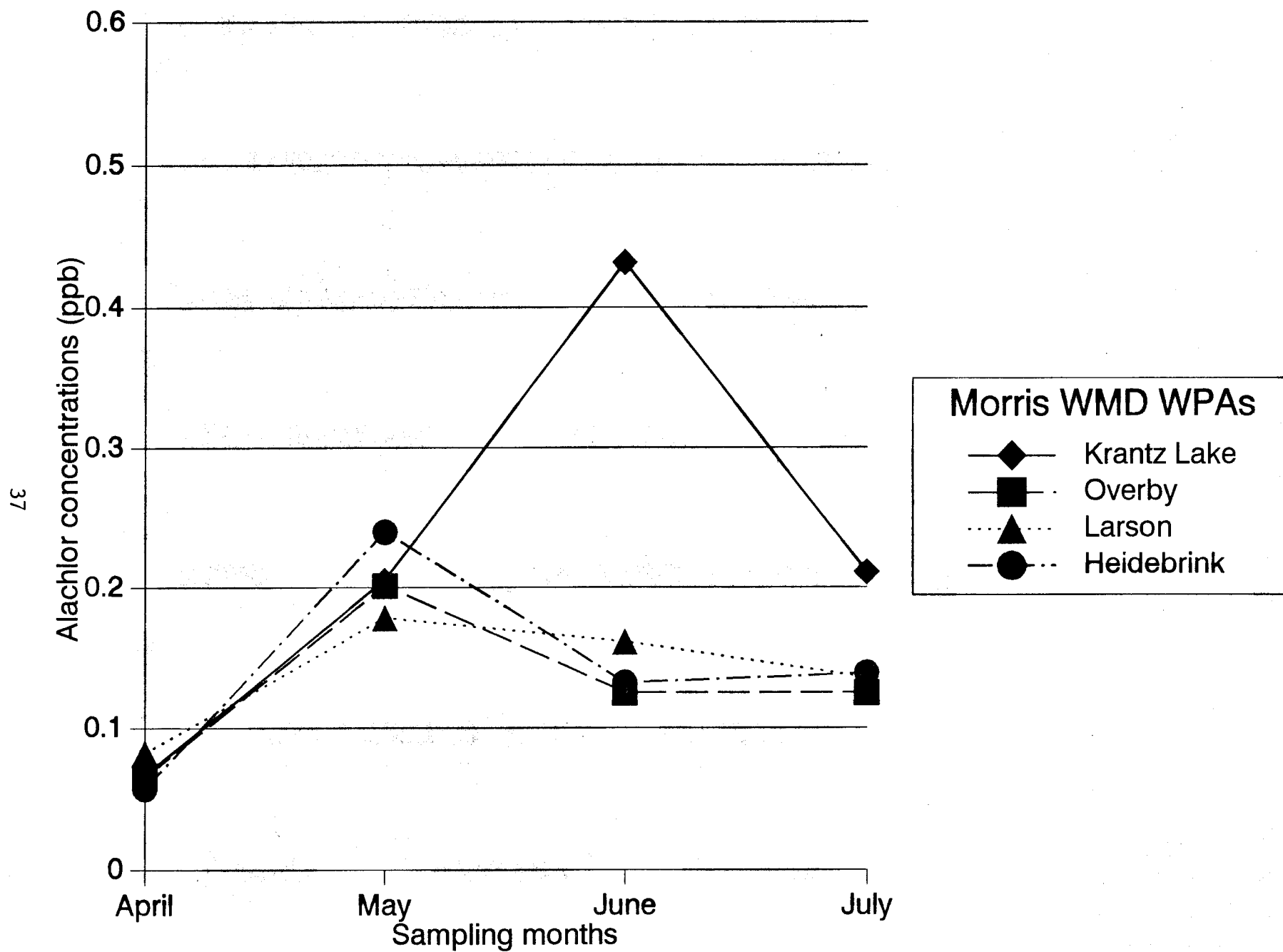


Figure 10. Surface water alachlor concentrations (ppb) in Morris WPA wetlands in west-central Minnesota, April - July, 1992.

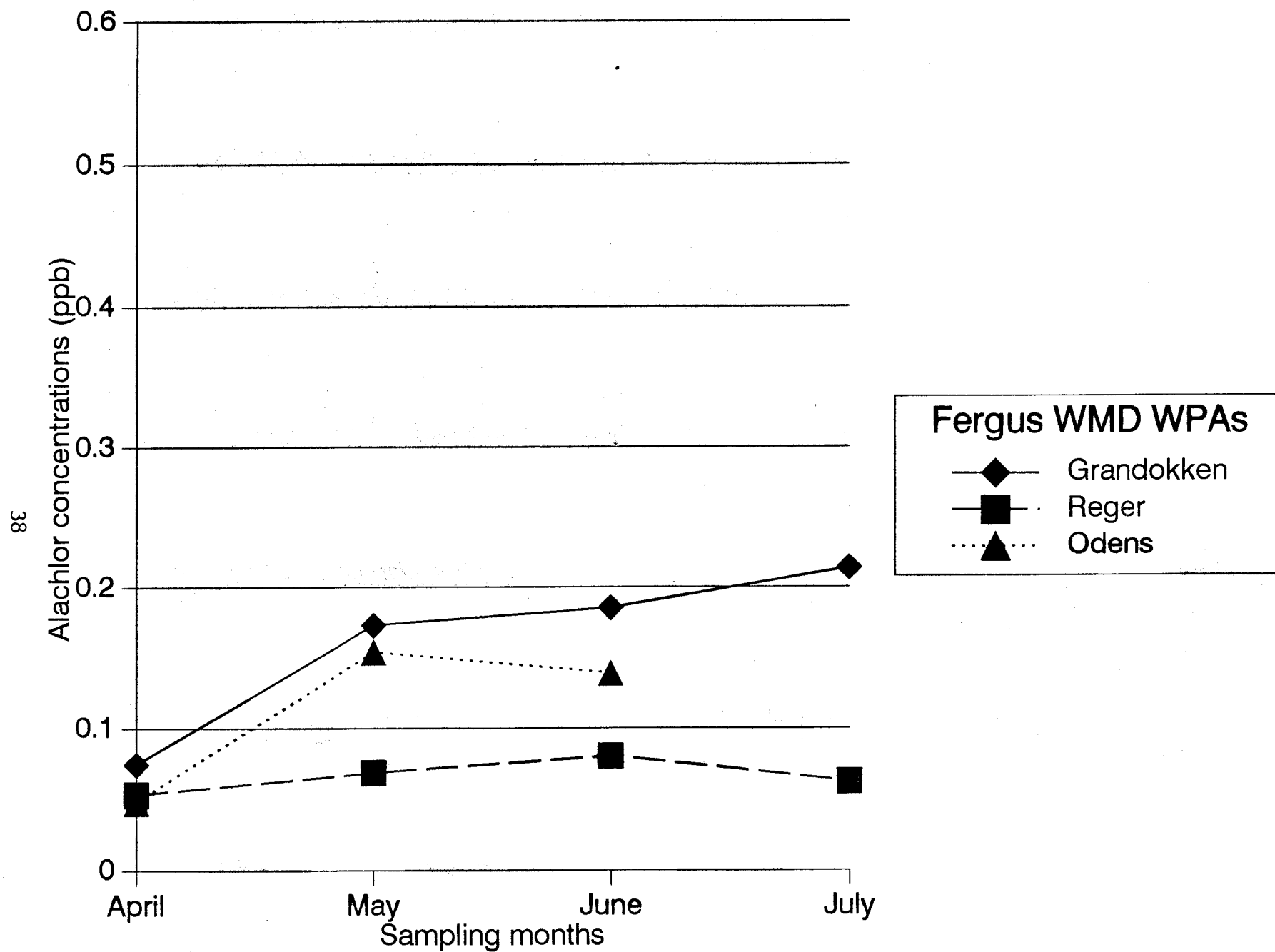


Figure 11. Surface water alachlor concentrations (ppb) in Fergus Falls WPA wetlands in west-central Minnesota, April - July, 1992.

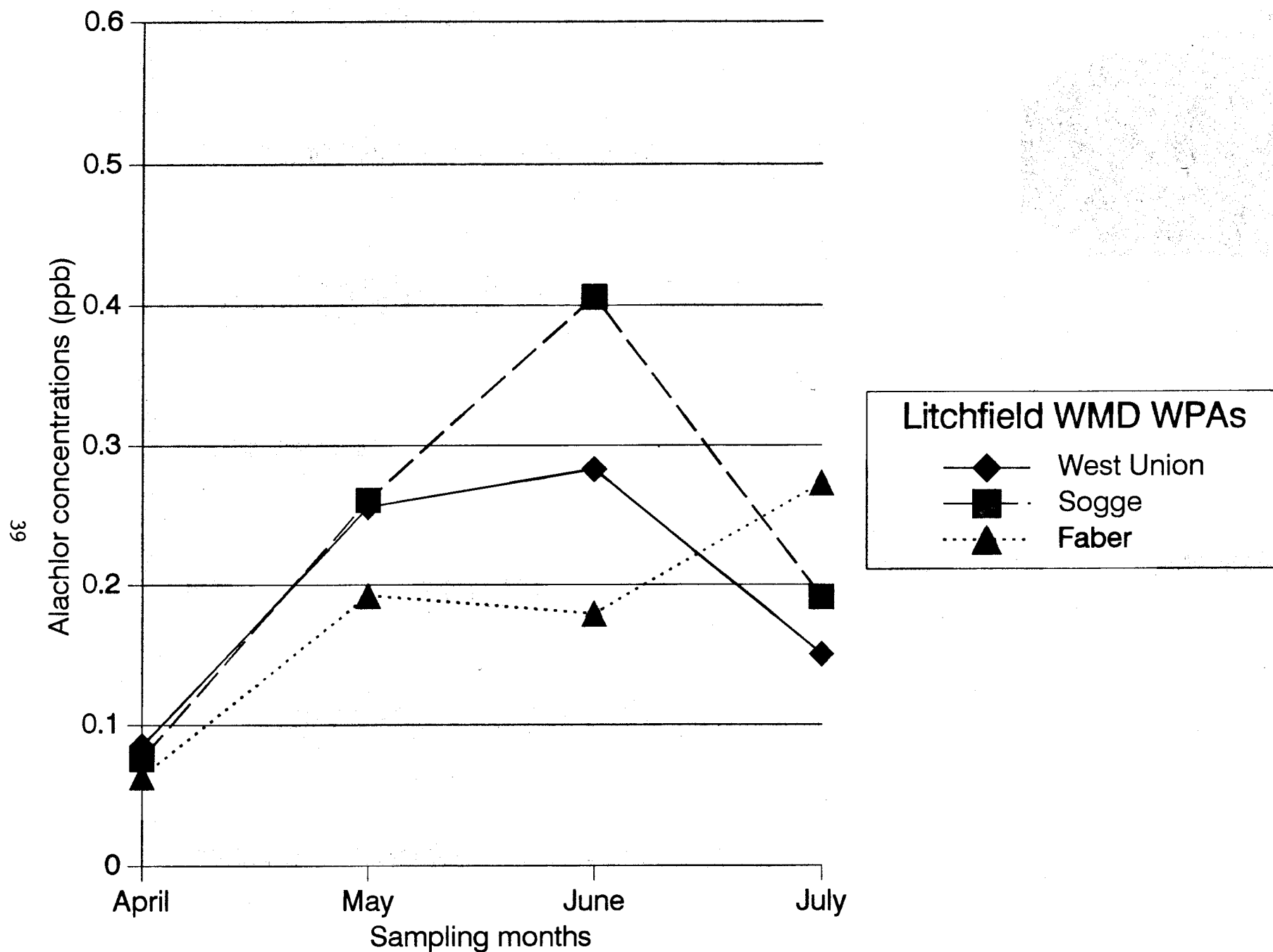


Figure 12. Surface water alachlor concentrations (ppb) in Litchfield WPA wetlands in west-central Minnesota, April - July, 1992.

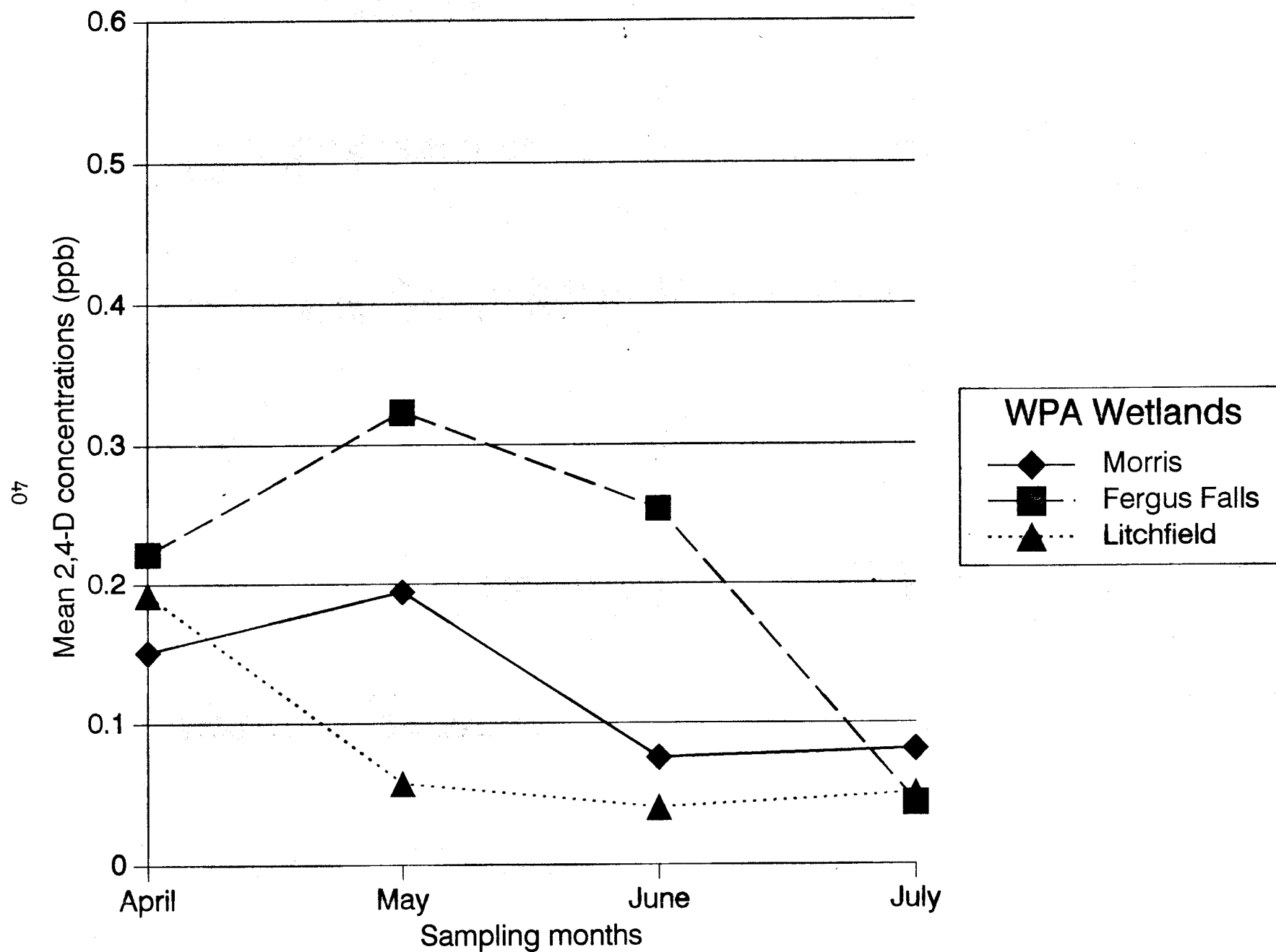


Figure 13. Mean monthly surface water 2,4-D concentrations (ppb) in Morris, Fergus Falls, and Litchfield WPA wetlands, April - July, 1992.

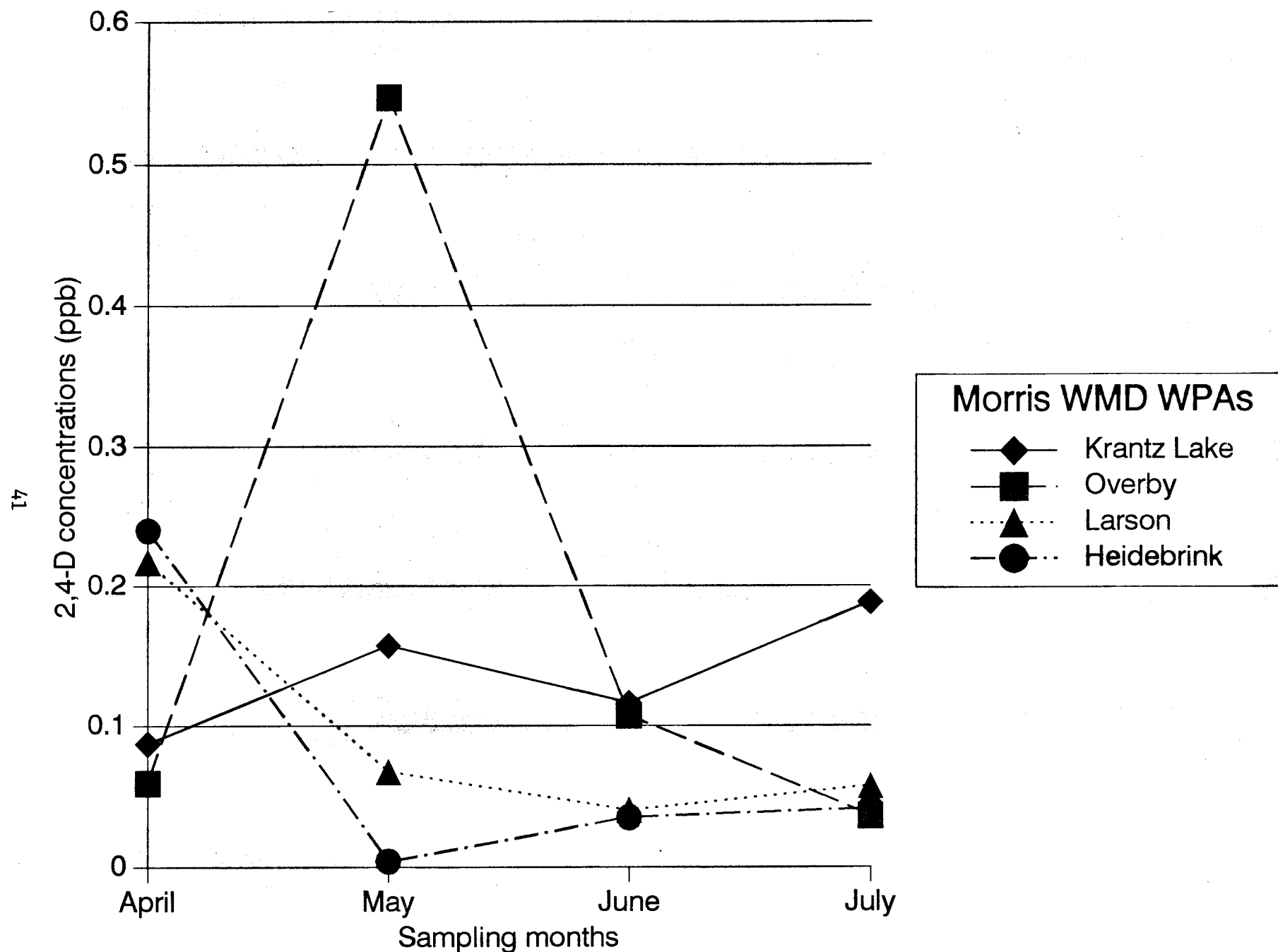


Figure 14. Surface water 2,4-D concentrations (ppb) in Morris WPA wetlands in west-central Minnesota, April - July, 1992.

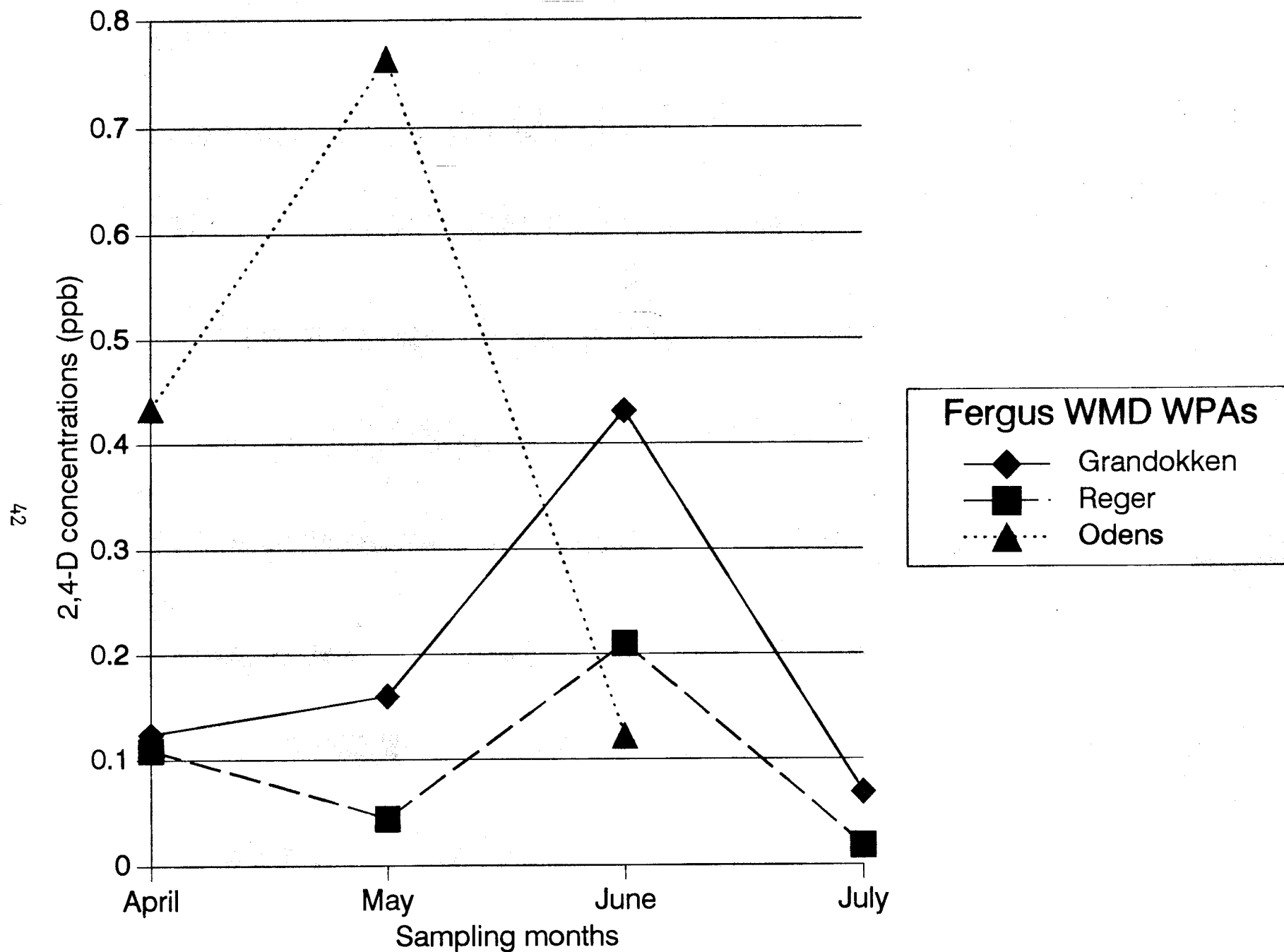


Figure 15. Surface water 2,4-D concentrations (ppb) in Fergus Falls WPA wetlands in west-central Minnesota, April - July, 1992.

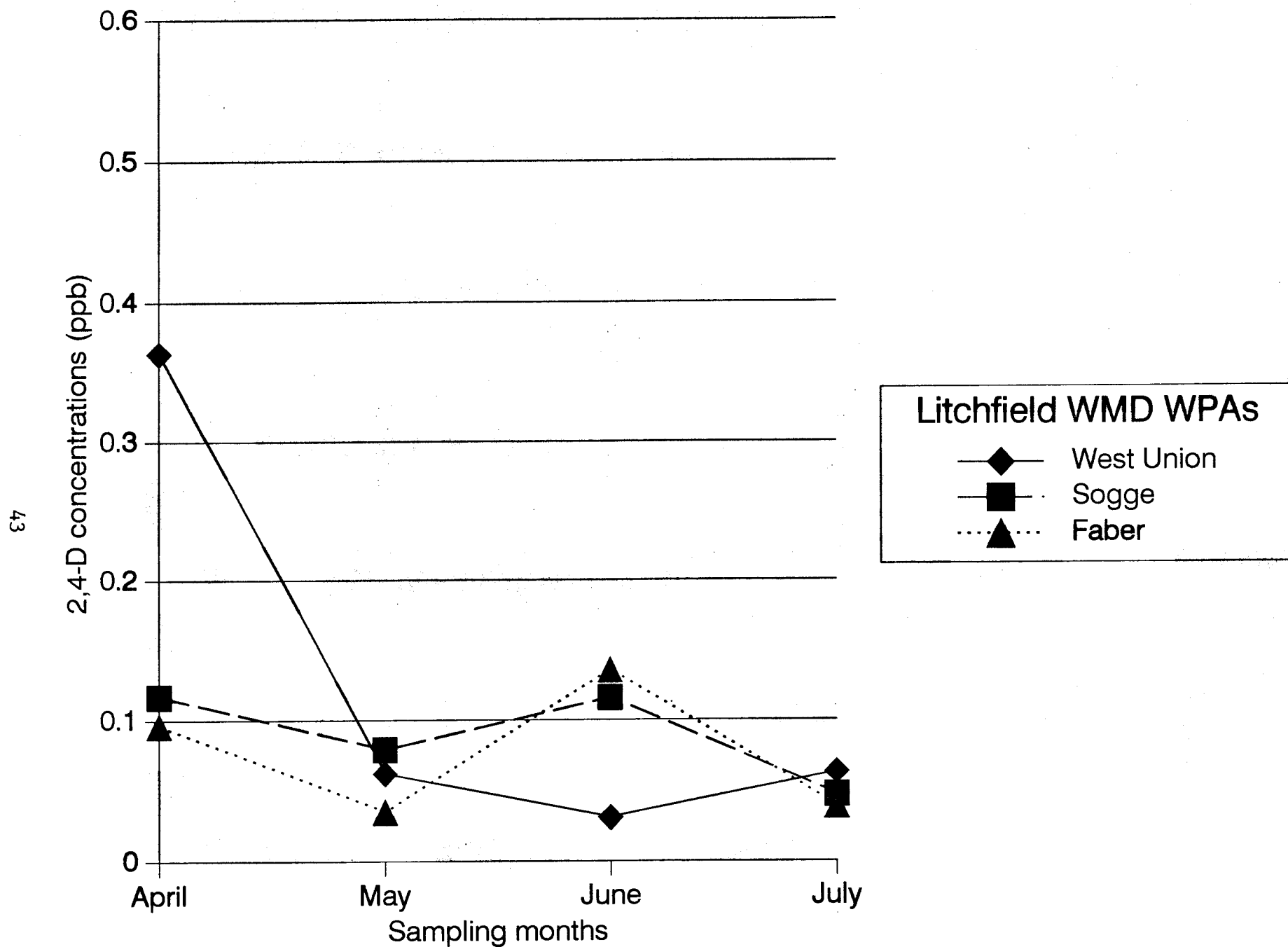


Figure 16. Surface water 2,4-D concentrations (ppb) in Litchfield WPA wetlands in west-central Minnesota, April - July, 1992.

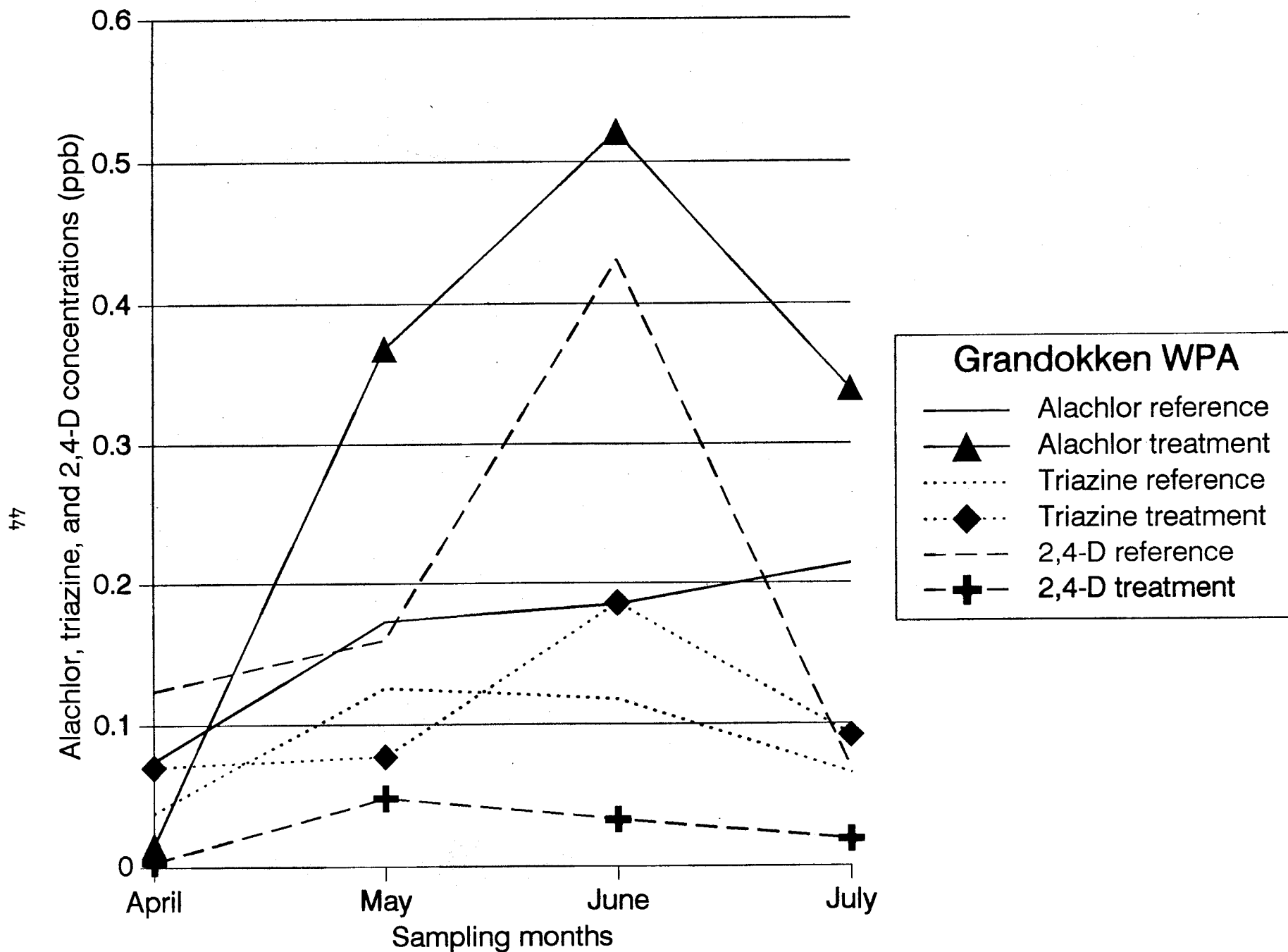


Figure 17. Surface water alachlor, triazine and 2,4-D concentrations (ppb) in a "reference" and "treatment" wetland on Grandokken WPA, Minnesota, April - July, 1992.

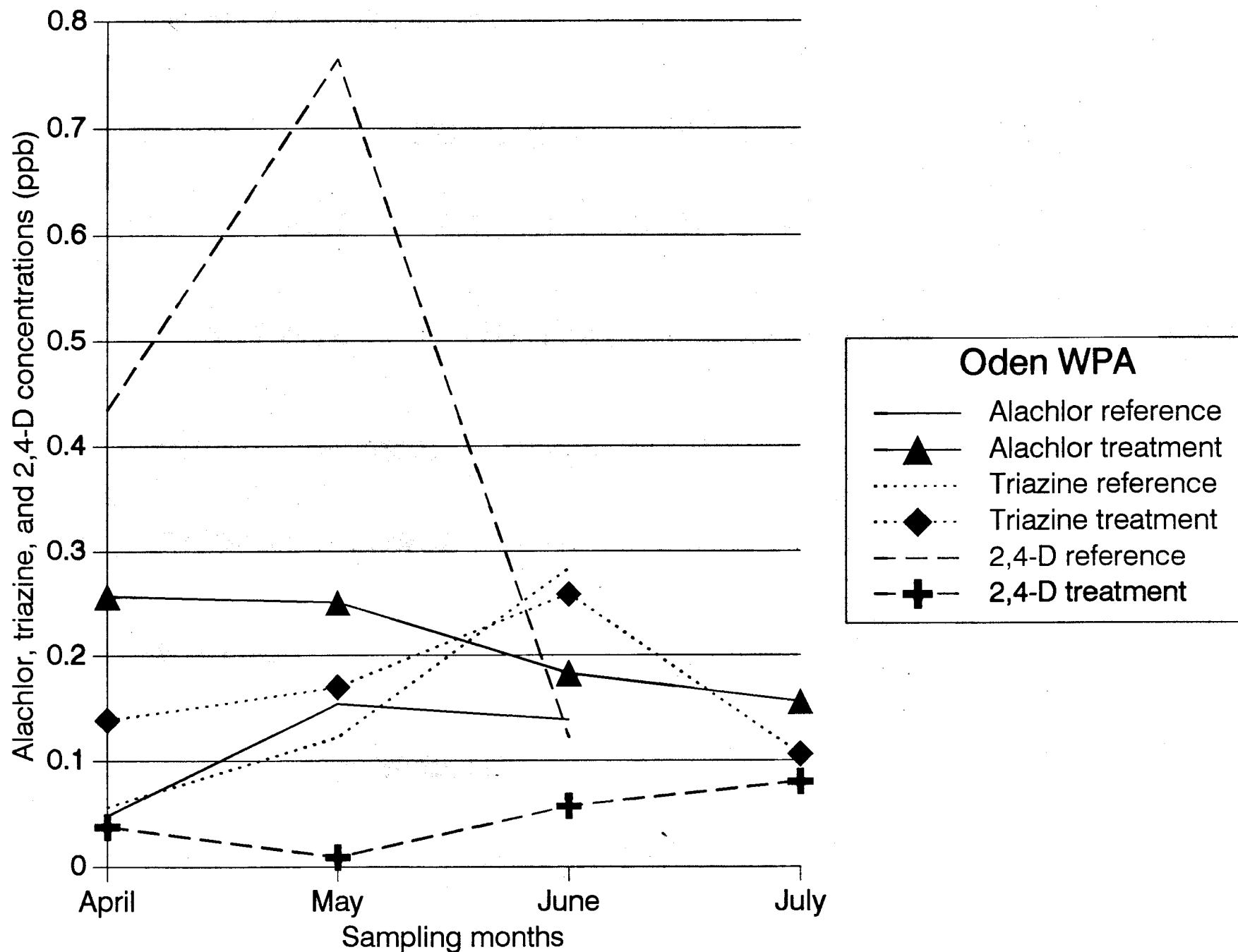


Figure 18. Surface water alachlor, triazine and 2,4-D concentrations (ppb) in a "reference" and "treatment" wetland on Oden WPA, Minnesota, April - July, 1992.

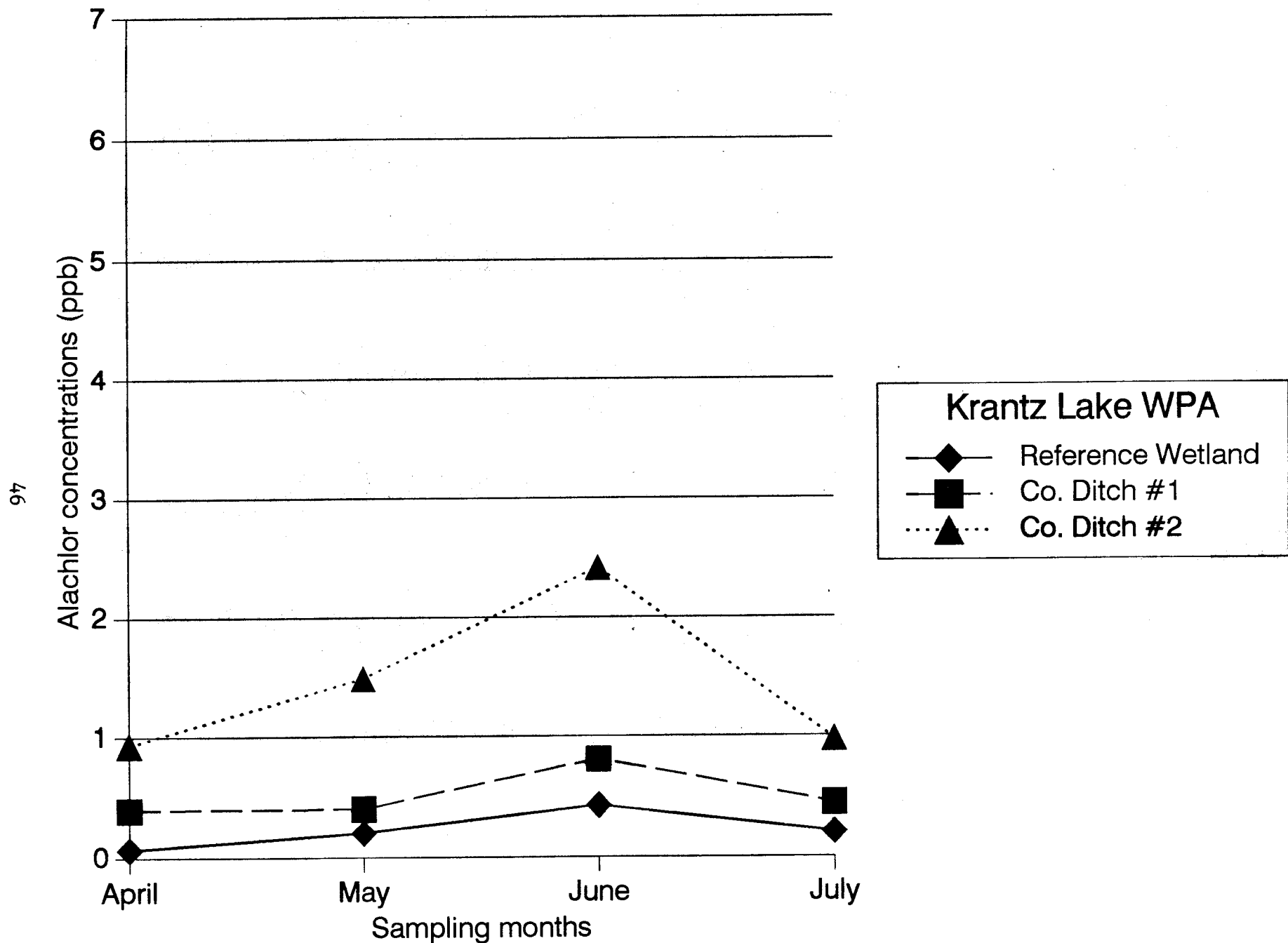


Figure 19. Surface water alachlor concentrations (ppb) in a "reference" wetland and two "treatment" county ditches on Krantz Lake WPA, Minnesota, April - July, 1992.

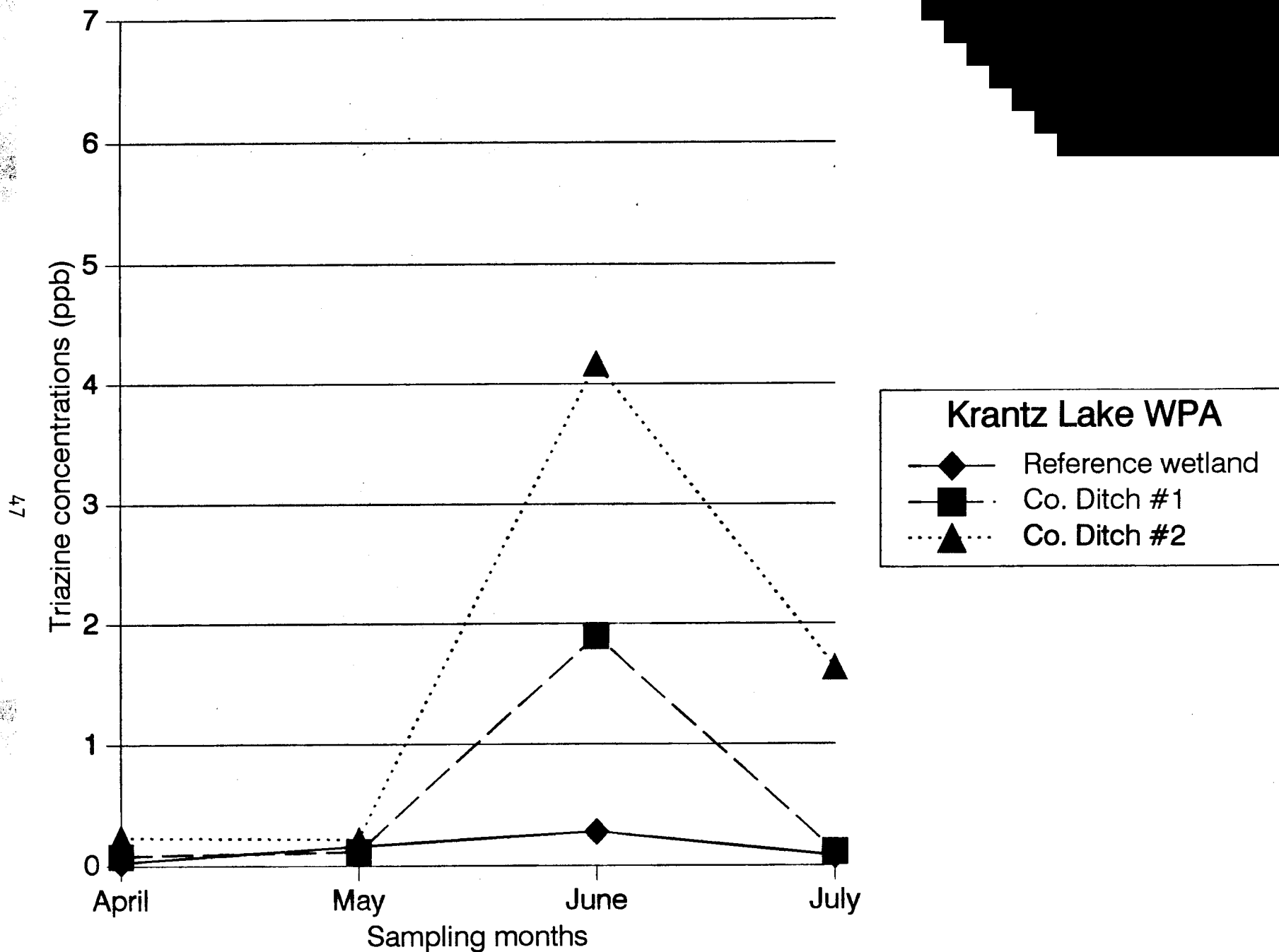


Figure 20. Surface water triazine concentrations (ppb) in a "reference" wetland and two "treatment" county ditches on Krantz Lake WPA, Minnesota, April - July, 1992.

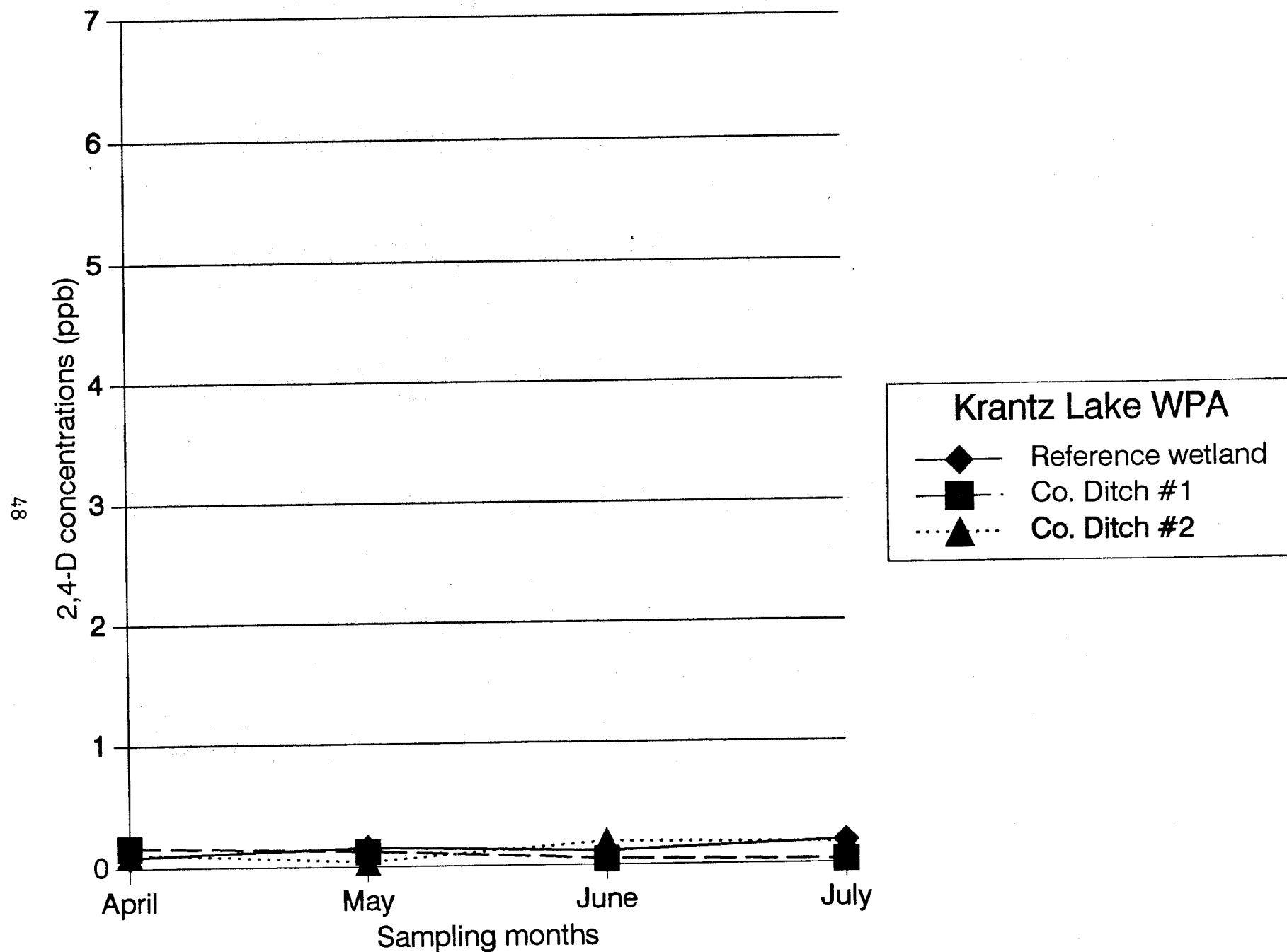


Figure 21. Surface water 2,4-D concentrations (ppb) in a "reference" wetland and two "treatment" county ditches on Krantz Lake WPA, Minnesota, April - July, 1992.

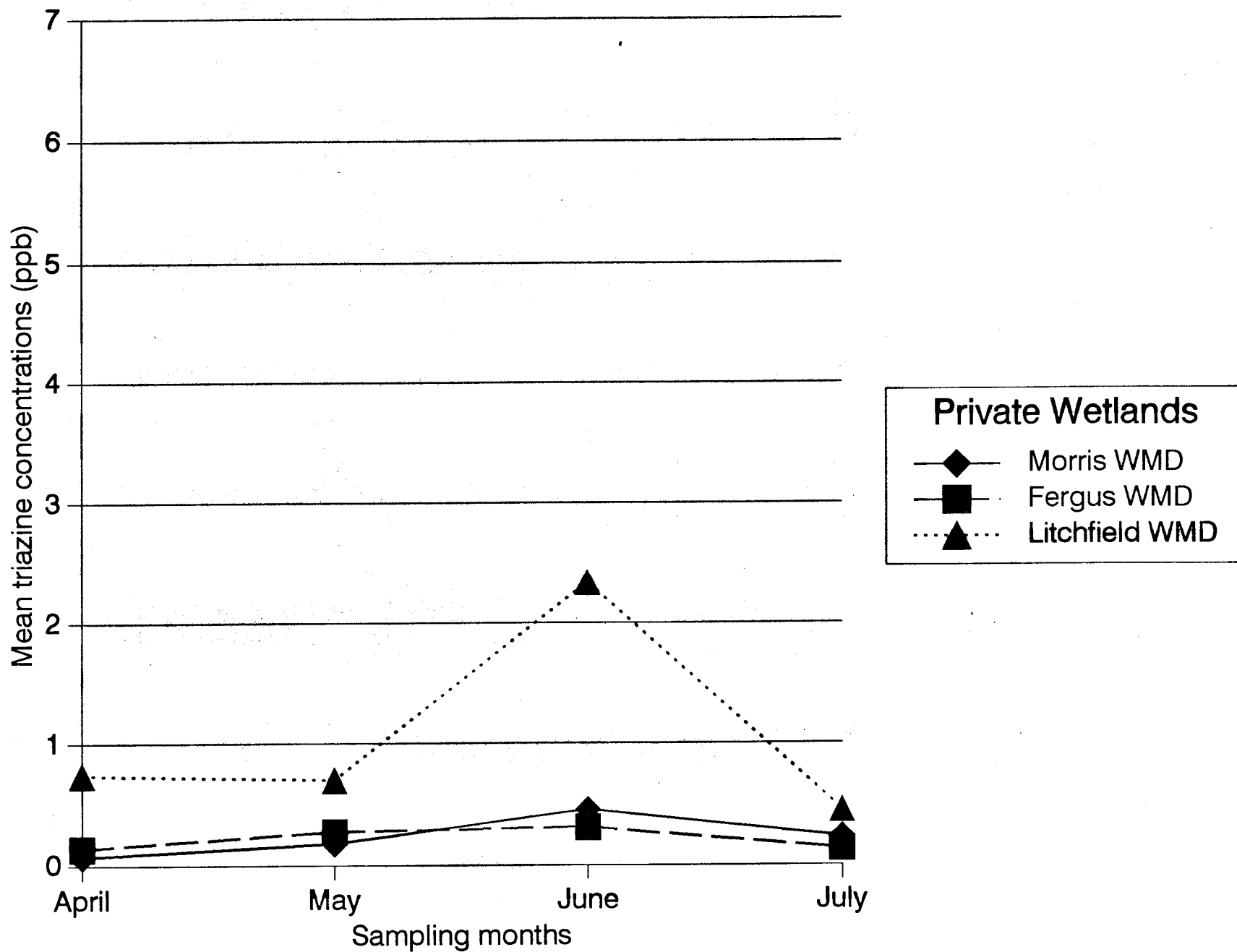


Figure 22. Mean monthly surface water triazine concentrations (ppb) in privately owned wetlands within Morris, Fergus Falls, and Litchfield WMDs, Minnesota, April - July, 1992.

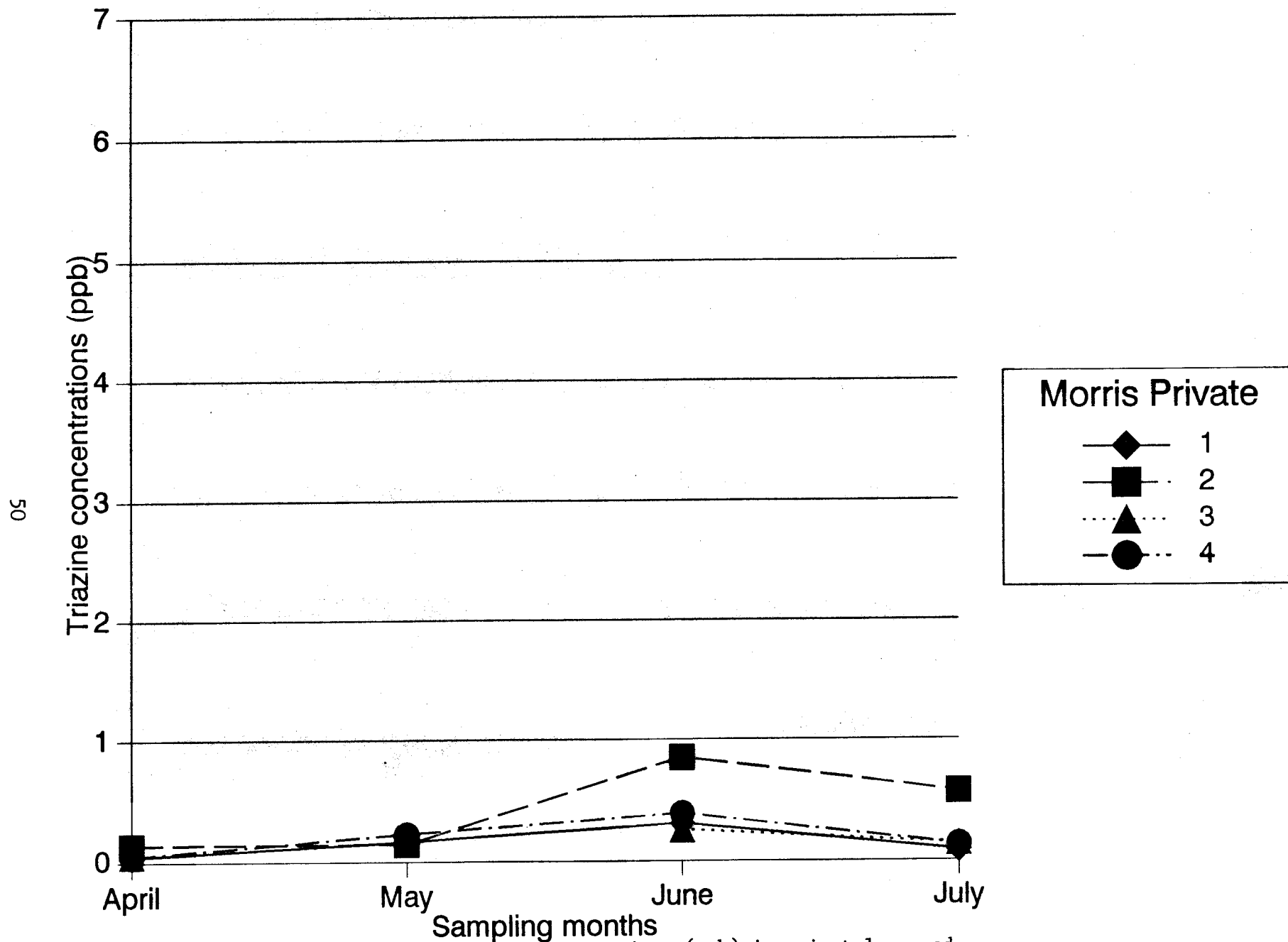


Figure 23. Surface water triazine concentrations (ppb) in privately owned wetlands within Morris WMD, Minnesota, April - July, 1992.

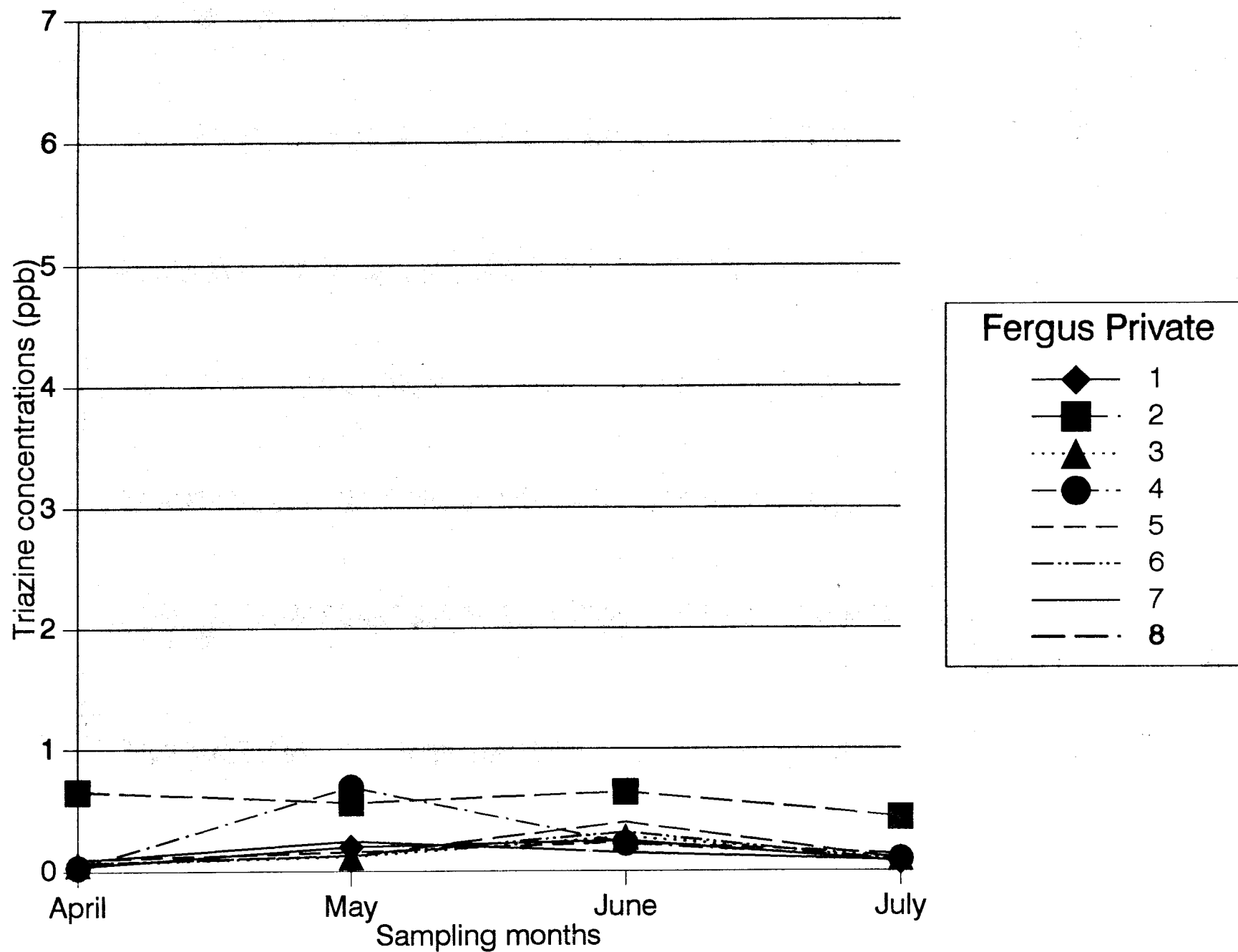


Figure 24. Surface water triazine concentrations (ppb) in privately owned wetlands within Fergus Falls WMD, Minnesota, April - July, 1992.

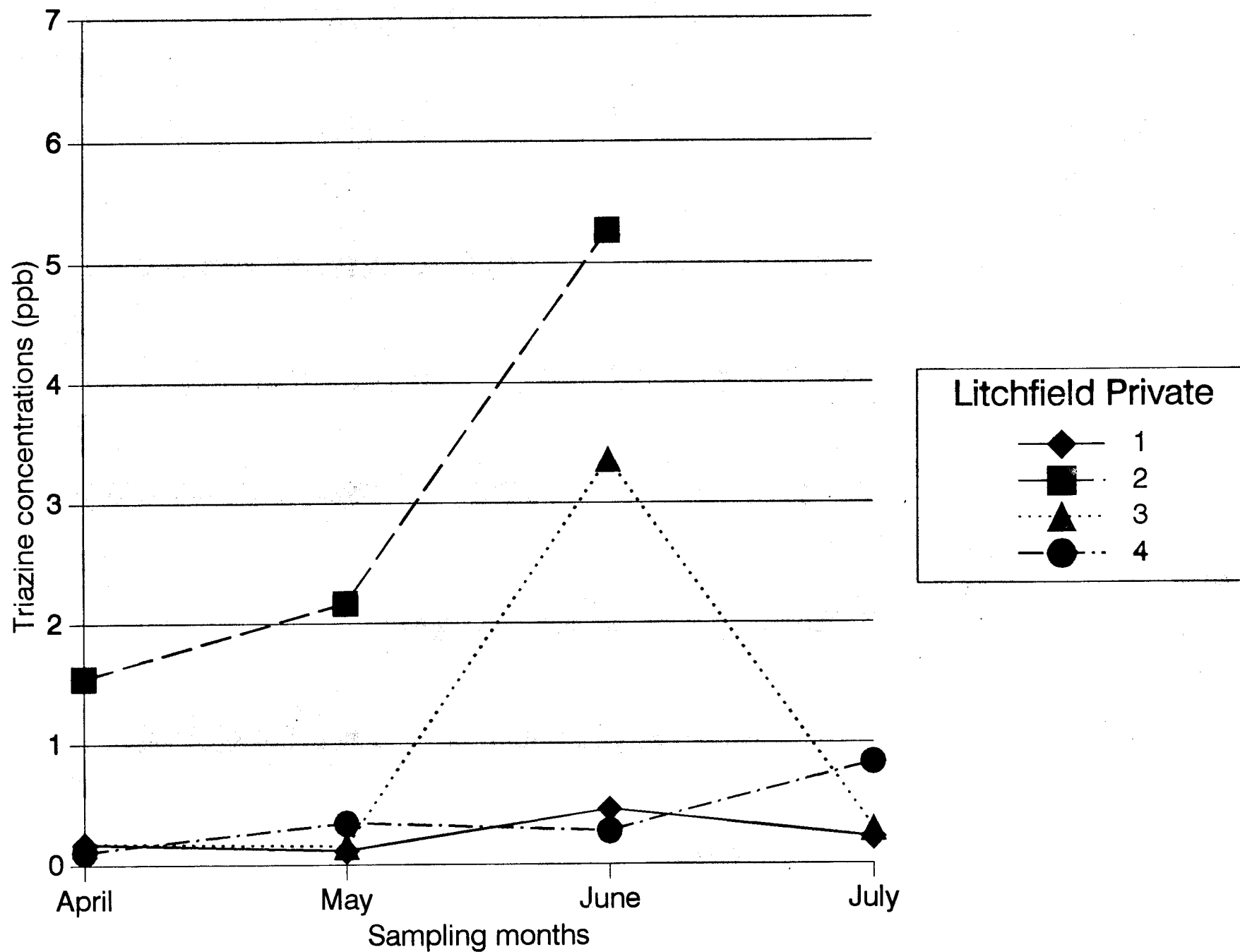


Figure 25. Surface water triazine concentrations (ppb) in privately owned wetlands within Litchfield WMD, Minnesota, April - July, 1992.

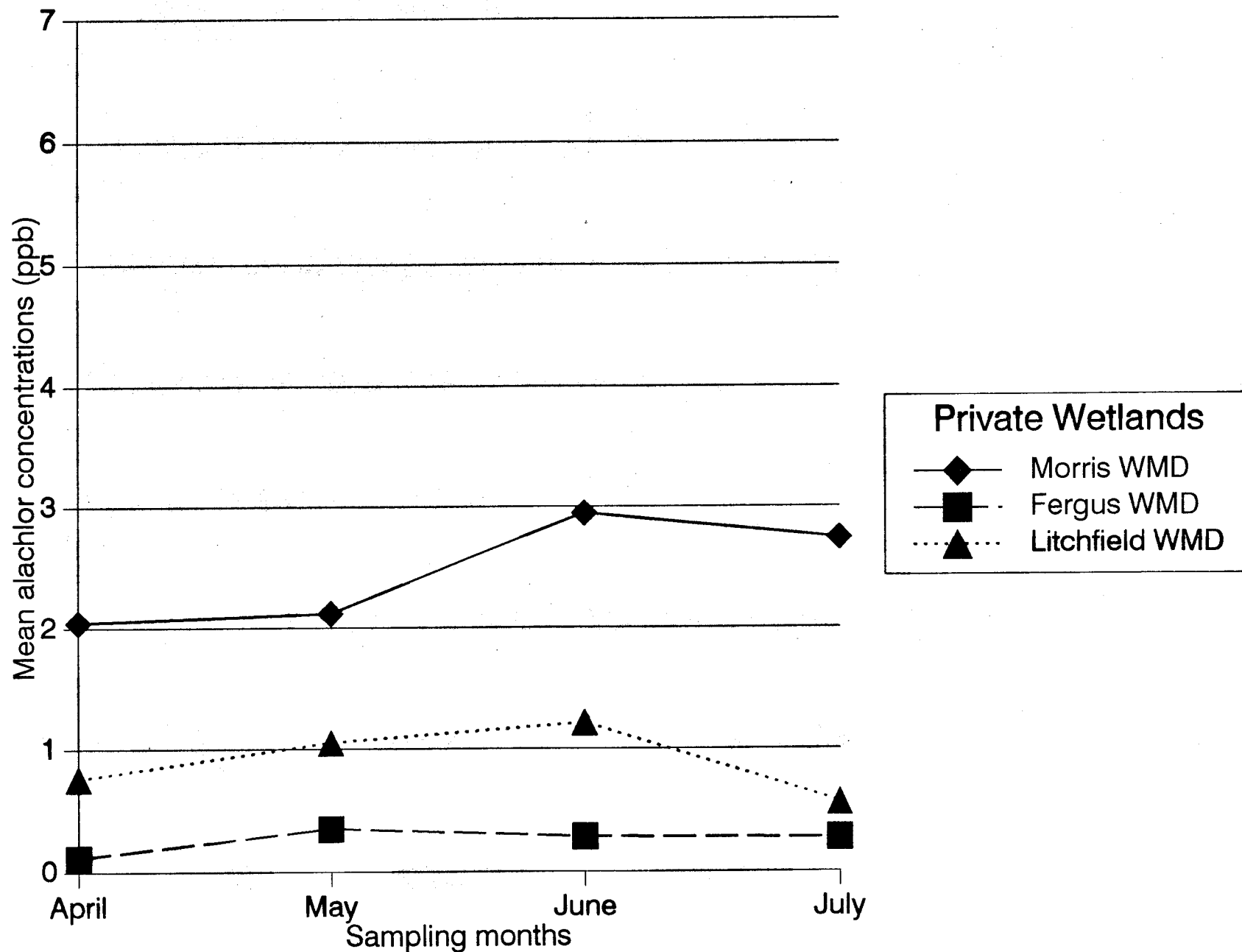


Figure 26. Mean monthly surface water alachlor concentrations (ppb) in privately owned wetlands within Morris, Fergus Falls, and Litchfield WMDs, Minnesota, April - July, 1992.

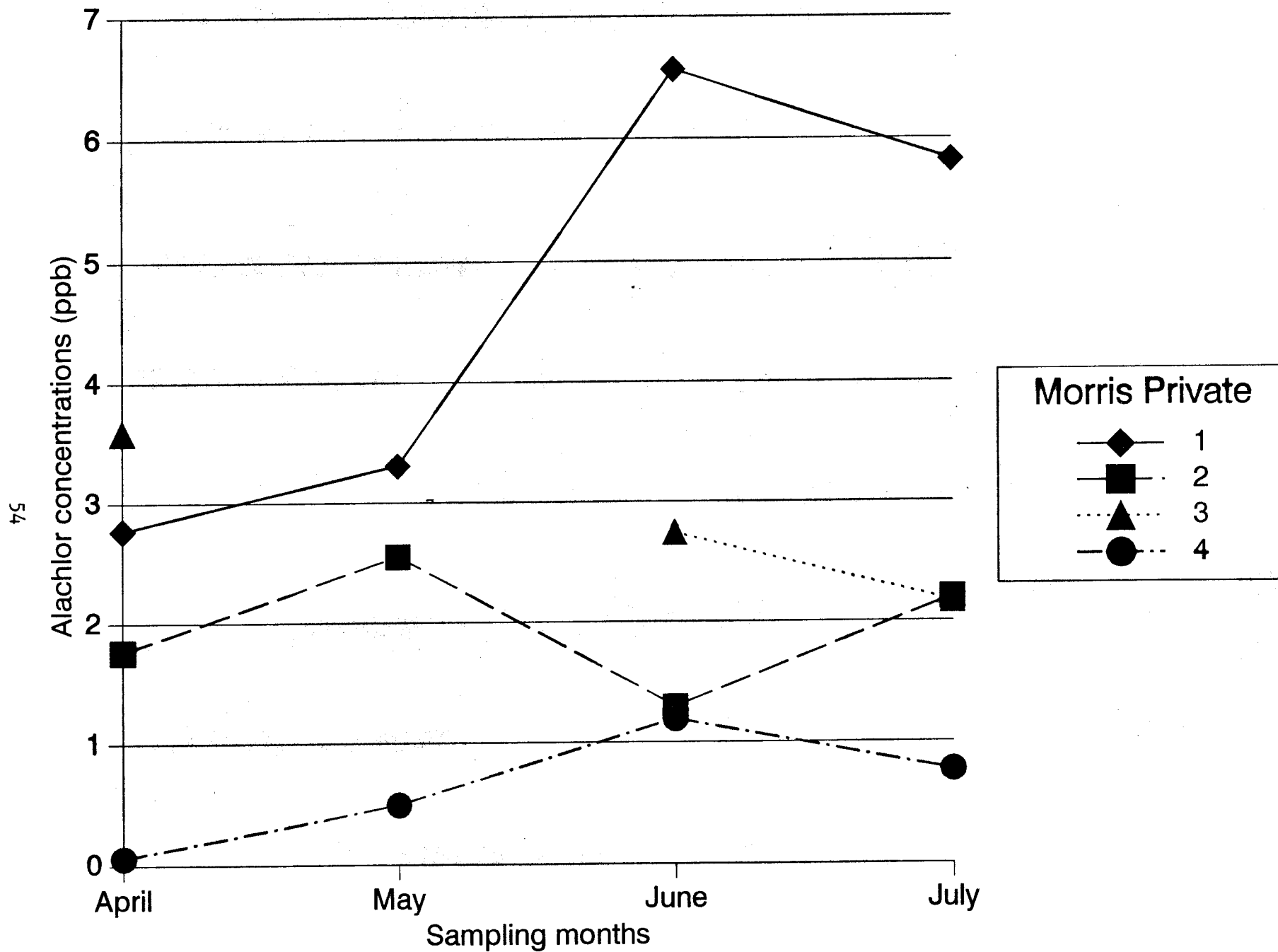


Figure 27. Surface water alachlor concentrations (ppb) in privately owned wetlands within Morris WMD, Minnesota, April - July, 1992.

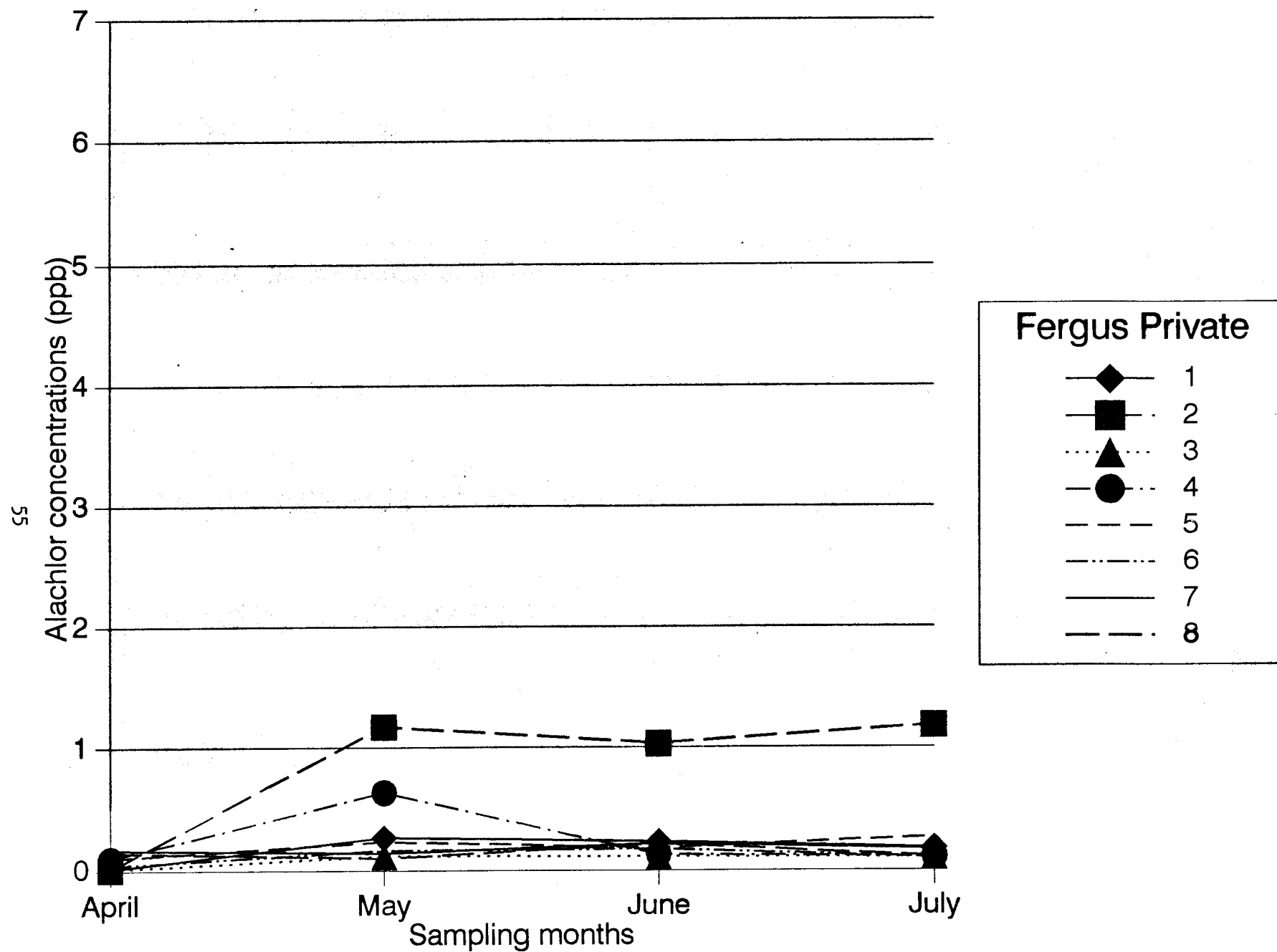


Figure 28. Surface water alachlor concentrations (ppb) in privately owned wetlands within Fergus Falls WMD, Minnesota, April - July, 1992.

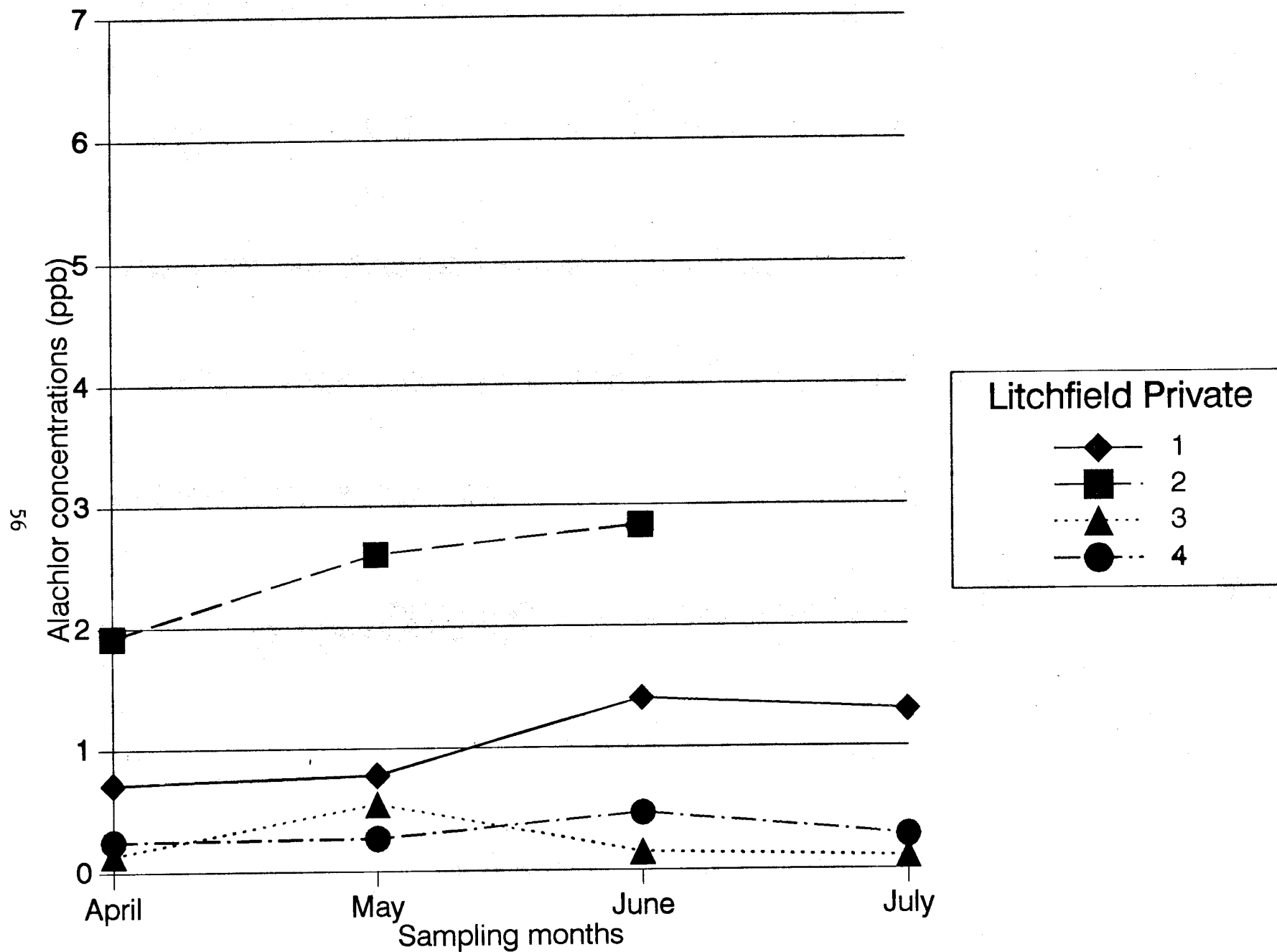


Figure 29. Surface water alachlor concentrations (ppb) in privately owned wetlands within Litchfield WMD, Minnesota, April - July, 1992.

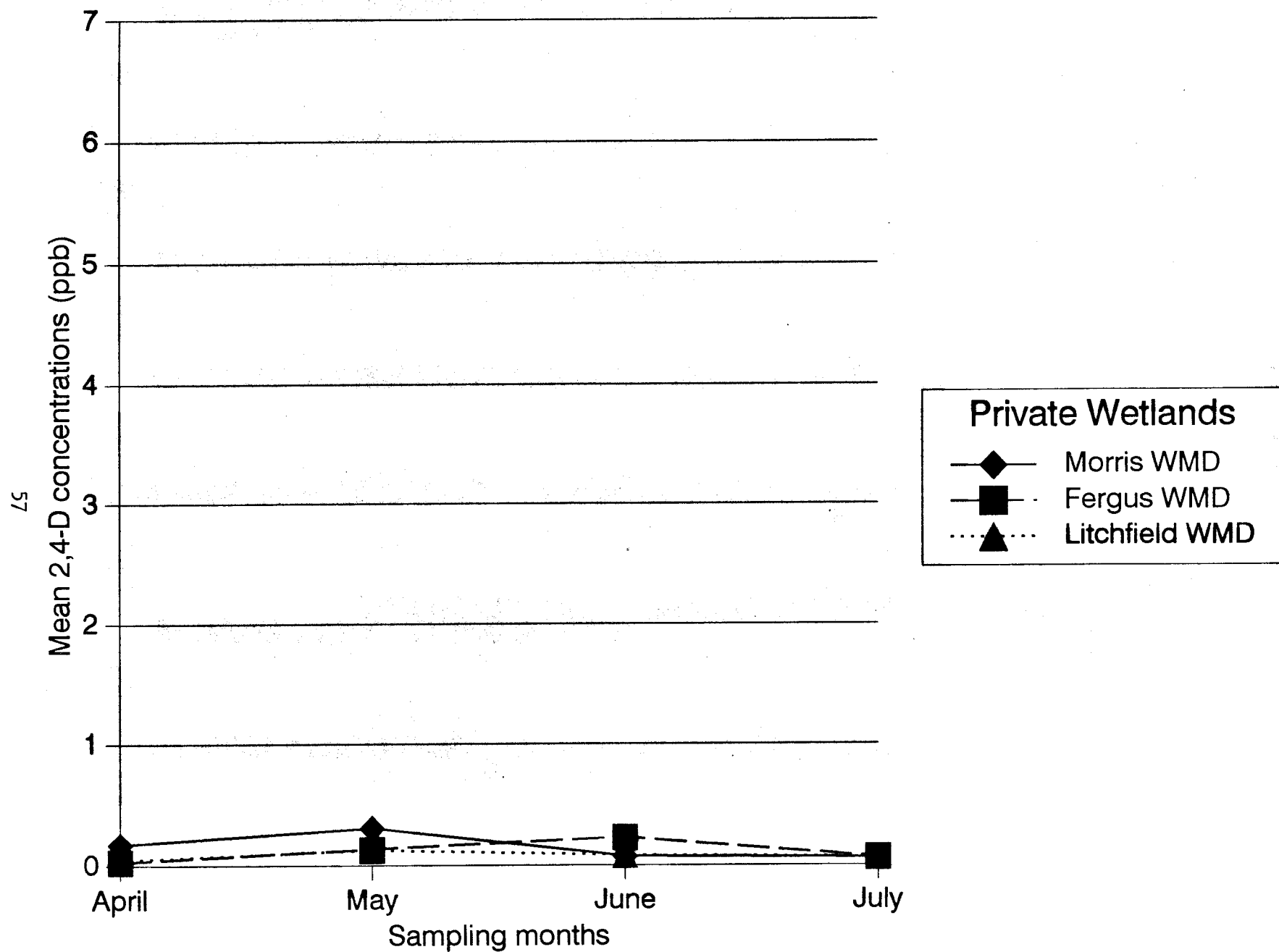


Figure 30. Mean monthly surface water 2,4-D concentrations (ppb) in privately owned wetlands within Morris, Fergus Falls, and Litchfield WMDs, Minnesota, April - July, 1992.

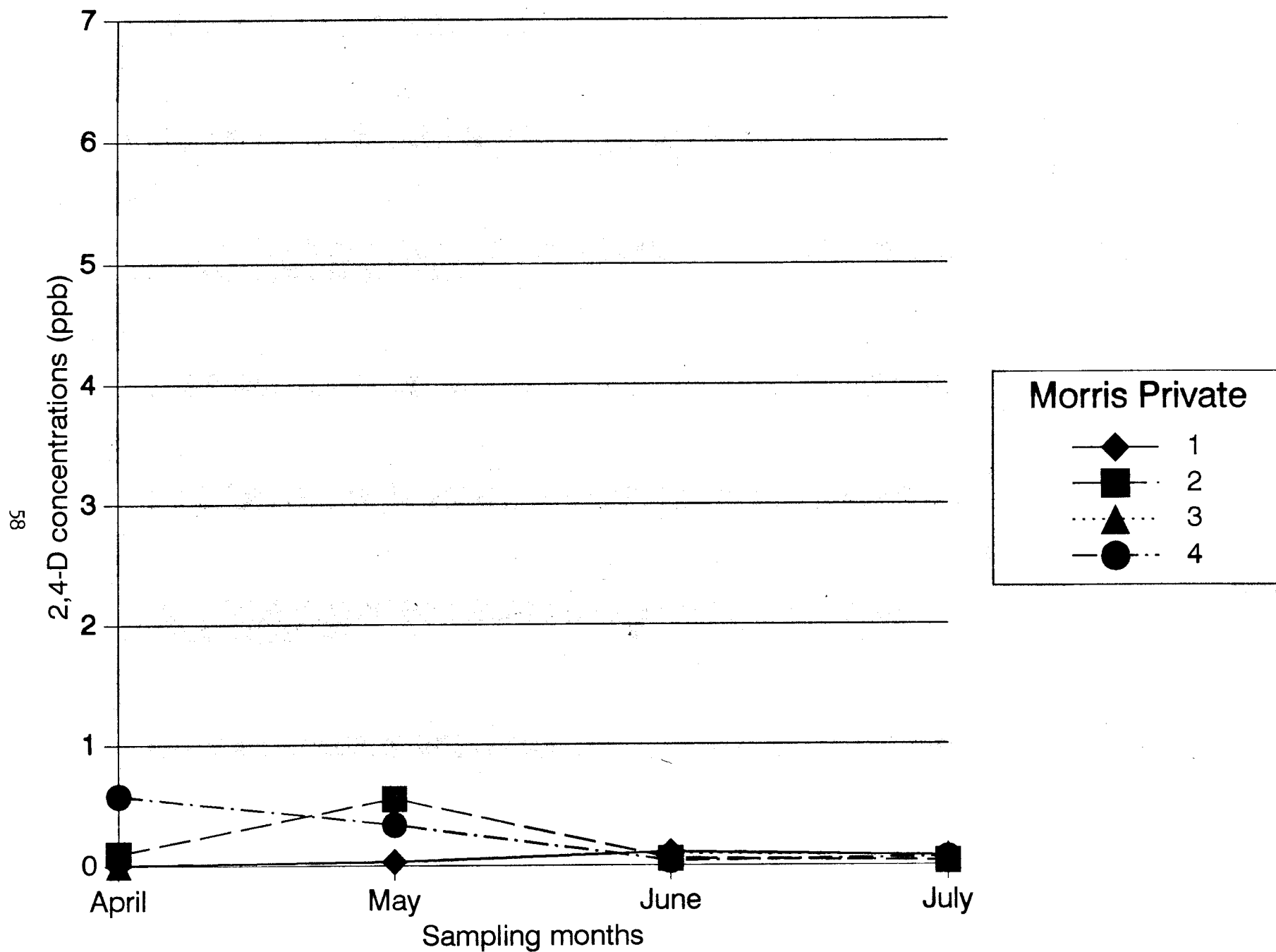


Figure 31. Surface water 2,4-D concentrations (ppb) in privately owned wetlands within Morris WMD, Minnesota, April - July, 1992.

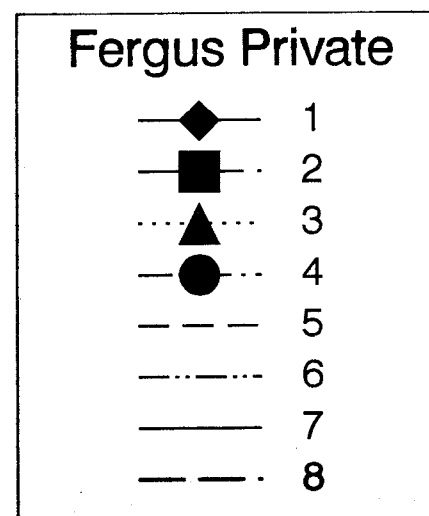
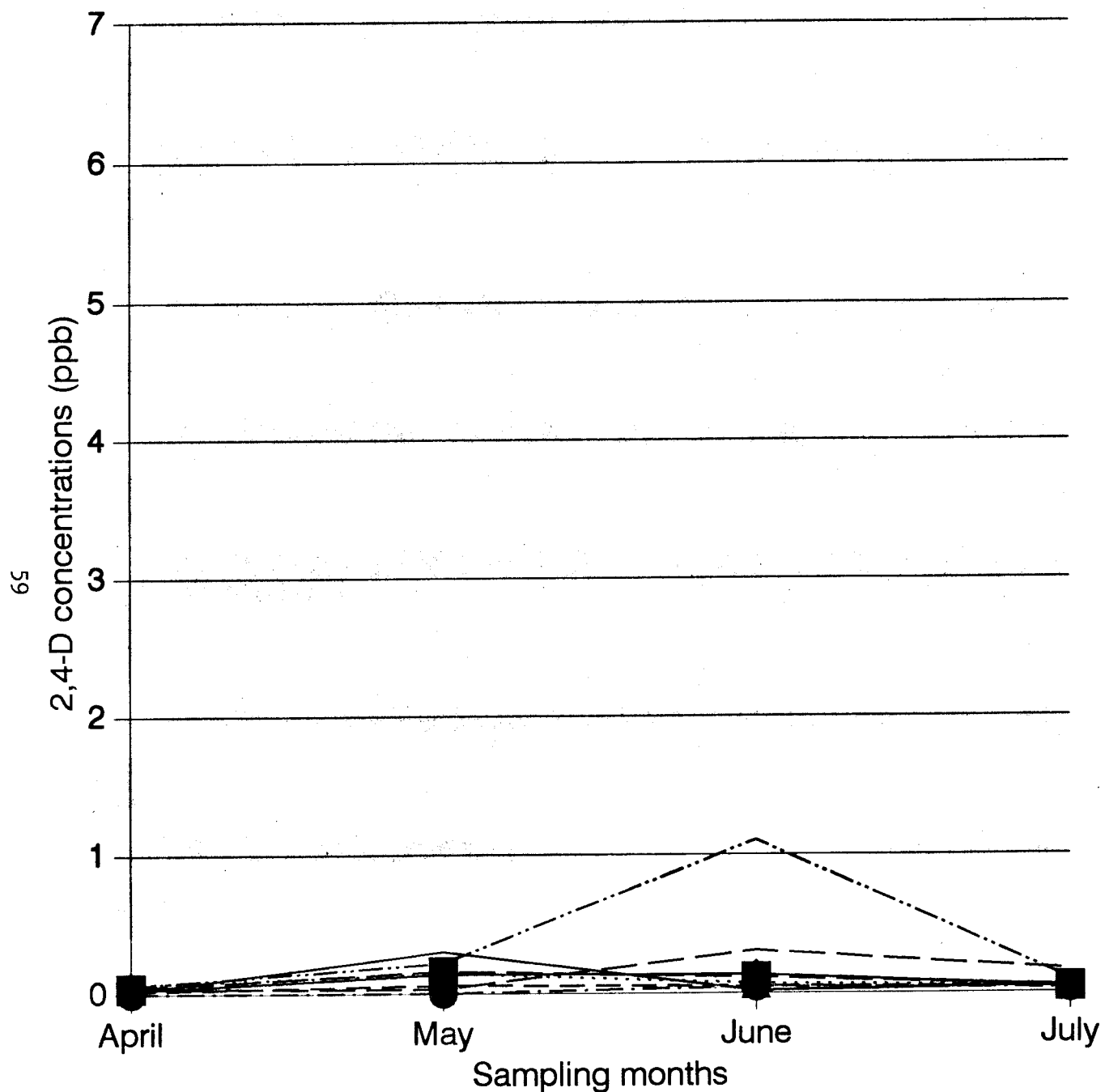


Figure 32. Surface water 2,4-D concentrations (ppb) in privately owned wetlands within Fergus Falls WMD, Minnesota, April - July, 1992.

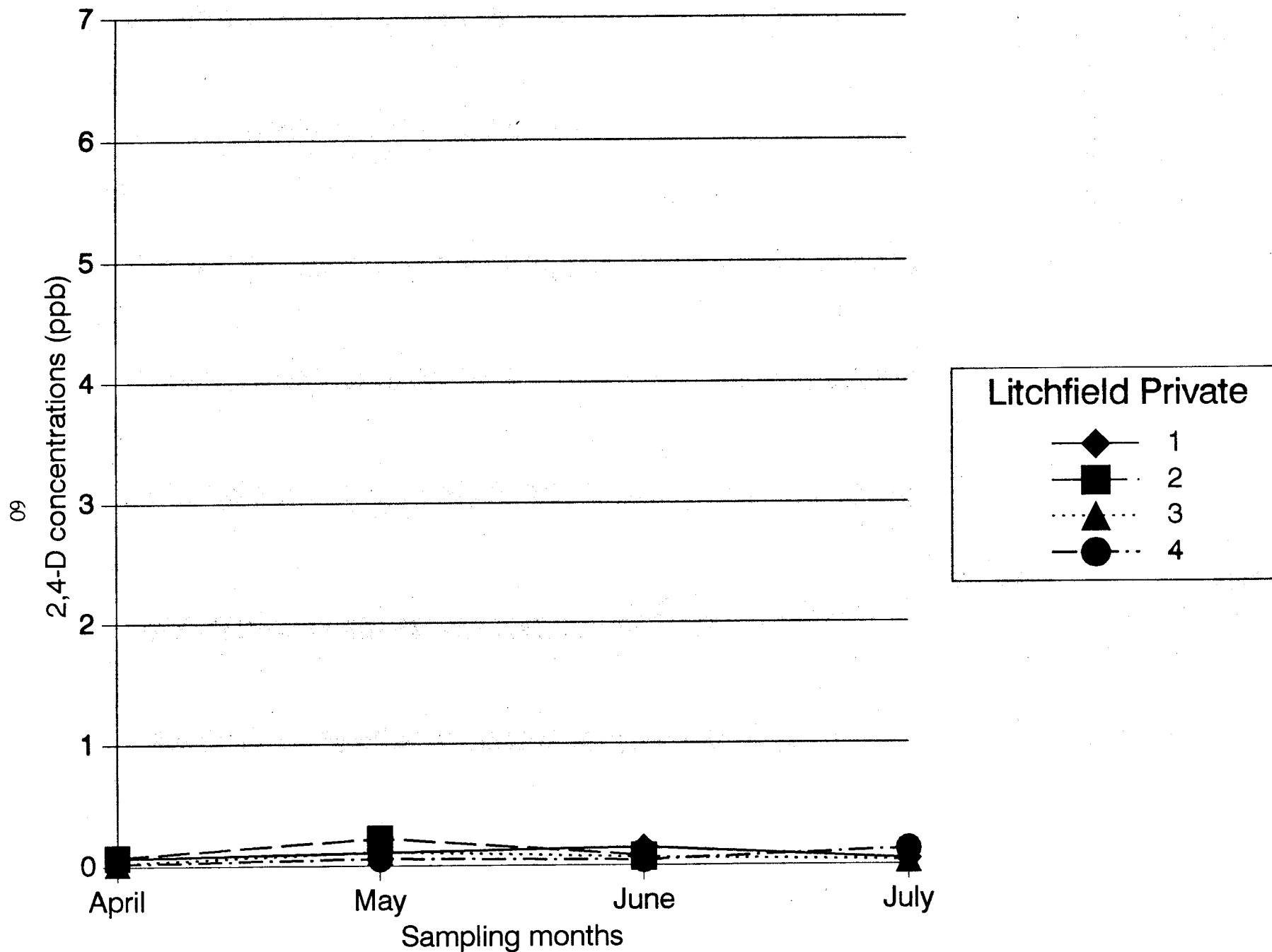


Figure 33. Surface water 2,4-D concentrations (ppb) in privately owned wetlands within Litchfield WMD, Minnesota, April - July, 1992.

REFERENCES

- Allmaras, R.R. and R.H. Dowdy. 1985. Conservation tillage systems and their adoption in the United States. *Soil Tillage Res.* 5:197-222.
- Baker, D.B. 1988. Sediment, nutrient and pesticide transport in selected lower Great Lakes tributaries. EPA-905/4-88-001. Great Lakes Natl. Program Off. U.S. Environmental Protection Agency, Chicago. IL.
- Bartonek, J.C. and J.J. Hickey. 1969. Food habits of canvasbacks, redheads, and lesser scaup in Manitoba. *Condor* 71:280-90.
- Buhl, K.J. and N.L. Faerber. 1989. Acute toxicity of selected herbicides and surfactants to larvae of midge *Chironomus riparius*. *Arch. Environ. Contam. Toxicol.* 18:530-536.
- Butler, G.L., T.R. Deason, J.C. O'Kelley. 1975. The effect of atrazine, 2,4-D, methoxychlor, carbaryl and diazinon on the growth of planktonic algae. *Brit. Phycol. J.* 10:371-376.
- Canadian Water Quality Guidelines. 1987. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environment Ministers.
- deNoyelles, F. W.D. Kettle, and D.E. Sinn. 1982. The responses of phytoplankton communities in experimental ponds to atrazine, the most heavily used pesticide in the United States. *Ecology* 63(5):1285-1293.
- Frank R., G.J. Sirons. 1979. Atrazine: Its use in corn production and its loss to stream waters in southern Ontario, 1975-77. *Science Total Environ.* 12:233-239.
- Frank, R., H.E. Braun, M. Holdrinet, G.J. Sirons and B.D. Ripley. 1978. Monitoring stream water for pesticides in eleven agricultural watersheds in Southern Ontario, Canada, 1974-1977 (Project 4). International Joint Commission Technical Report, Windsor, Ontario.
- Frank, R., B.S. Clegg, N.K. Patni. 1991. Dissipation of cyanazine and metolachlor on a clay loam soil, Ontario, Canada, 1987-1990. *Arch. Environ. Contam. Toxicol.* 21:253-262.
- Grue, C.E., L.R. DeWeese, P. Mineau, G.A. Swanson, J.R. Foster, P.M. Arnold, J.N. Huckins, P.J. Sheehan, W.K. Marshall, A.P. Ludden. 1986. Potential impacts of agricultural chemicals on waterfowl and other wildlife inhabiting prairie wetlands: an evaluation of research needs and approaches. Pages 357-383 in *Impacts of Agricultural Chemicals*. Trans. 51st N.A. Wildl. & Nat. Res. Conf.

- Hamilton, P.B., G.S. Jackson, N.K. Kaushik, K.R. Solomon. 1987. The impact of atrazine on lake periphyton communities, including carbon uptake dynamics using track autoradiography. *Environ. Pollut.* 46:83-103.
- Hartman, W.A. and D.B. Martin. 1985. Effects of four agricultural pesticides on *Daphnia pulex*, *Lemna minor*, and *Potamogeton pectinatus*. *Bull. Environ. Contam. Toxicol.* 35:646-651.
- Johnson, B.T. 1986. Potential impact of selected agricultural chemical contaminants on a northern prairie wetland: a microcosm evaluation. *Environ. Toxicol. & Chem.* 5:473-485.
- Krapu, G.. 1974. Foods of breeding pintails in North Dakota. *J. Wildl. Manage.* 38(3):408-417.
- Martin, D.B. and W.A. Hartman. 1987. The effect of cultivation on sediment composition in prairie pothole wetlands. *Water, Air and Soil Pollution* 34:45-53.
- Martin, D.B. 1985. Accumulation of sediment, nutrients, and cesium-137 in prairie potholes in cultivated and noncultivated watersheds. Pages 274-275 in Perspectives on nonpoint source pollution. Proceedings of a national conference. U.S. Environmental Protection Agency. Washington, D.C. 1985.
- Minnesota Agriculture Statistics 1991. Minnesota Agricultural Statistics Service 1991. Minnesota Department of Agriculture, St. Paul.
- Murkin, H.R. 1983. Responses of aquatic macroinvertebrates to prolonged flooding of marsh habitat. Ph.D. diss., Utah State Univ., Logan.
- Murkin, H.R. and B.D.J. Batt. 1987. The interactions of vertebrates and invertebrates in peatlands. *Mem. Entomol. Soc. Can.* 140:15-30.
- Nations, B.K. 1992. Pesticides in Iowa precipitation. 1992. *Iowa Conservationist*. July/August:42-43.
- Ruelle, R. 1981. A survey of chlorinated phenoxy herbicide residues in sediments of waterfowl production areas in Minnesota. U.S. Fish and Wildlife Service, RIFO, IL. 16 pp.
- Sather, J.H. and R.D. Smith. 1984. An overview of major wetland functions and values. U.S. Fish and Wildlife Service. FWS/OBS-84/18. 68 pp.
- Sethunathan, N., R. Siddaramappa, K.P. Rajaram, S. Barik. and P.A. Wahid. 1977. Parathion residues in soil and water. *Residue Rev.* 68:91-122.
- Sheenan, P.K., A. Baril, P. Mineau, D.K. Smith, and W.K. Marshall. 1987. The impact of pesticides on the ecology of prairie-nesting ducks. Unpublished report. Canadian Wildlife Service.

Sugden, L.G. 1973. Feeding ecology of pintail, gadwall, American widgeon and lesser scaup ducklings in southern Alberta. Can. Wildl. Serv. Rep. Ser. 24. 45 pp.

Swanson, G.A. and H.F. Duebbert. 1989. Wetland habitats of waterfowl in the prairie pothole region. Pages 229-267 in A. Van der Valk, ed. Northern Prairie Wetlands. Iowa State University Press. 400 p.

Swanson, G.A., G.L. Krapu, and Jerome R. Serie. 1979. Foods of laying female dabbling ducks on the breeding grounds. Pages 47-57 in T.A. Brookhout, ed. Waterfowl and wetlands - and integrated review. Proc. 1977 Symps., Madison, WI, NC Sect., The Wildlife Society. LaCrosse Printing Co., Inc., LaCrosse, WI. 147 p.

Taraldson, J.E. and T.J. Norberg-King. 1990. New method for determining effluent toxicity using duckweed (*Lemna minor*). Environ. Toxicol. & Chem. 9:761-767.

Thurman, E.M., D.A. Goolsby, M.T. Meyer, D.W. Kolpin. 1991. Herbicides in surface waters of the Midwestern United States: the effect of spring flush. Environ. Sci. Technol. 25:1794-1796.

U.S. Department of Agriculture. 1992. Agricultural Chemical Usage: 1991 Field Crops Summary. National Agricultural Statistics Service and Economic Research Service. 150 pp.

U.S. Fish and Wildlife Service, Region 3. Pesticide Use Report: 1990. Office of Environmental Contaminants and Office of Refuge Biology.

U.S. Fish and Wildlife Service. 1992. Wetland Management District Briefing Document. Minnesota Waterfowl and Wetland Management Complex.

Voights, D.K. 1976. Aquatic invertebrate abundance in relation to changing marsh vegetation. Amer. Midl. Nat. 95: 313-22.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields - a review. J. Environ. Qual. 7:459-472.

Weber, J.B., P.J. Shea, H.J. Streck. 1980. An evaluation of nonpoint sources of pesticide pollution in runoff. In Overcash, M.R., J.M. Davidson (eds.) Environmental impact of nonpoint source pollution. Ann Arbor Science, Ann Arbor, MI. Pp. 69-98.