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EXECUTIVE SUMMARY

Increased growth of aquatic vegetation, including the appearance of Eurasian watermilfoil, in the Kawartha lakes during the 1970's had necessitated the use of both physical harvesting methods and of aquatic herbicides for weed control. The Canada - Ontario Policies for Rideau, Trent-Severn Corridor (CORTS) have designated Environment Canada as the lead agency in research on the possible effects of herbicide use on water quality in the system.

Our survey of Buckhorn Lake sediments in May, 1983, prior to the midsummer herbicide applications, showed the presence of 2,4-D residues. The fall survey of the same sites, only three months after the applications, found less 2,4-D in the sediment. The high spring values suggest significant inputs into the system by spring runoff, or an unusually high 2,4-D persistence from the 1982 additions. A study of 2,4-D disappearance from an experimental site showed extensive 2,4-D transport in the water. The appearance of 2,4-D in well water samples in the experimental area, although well below the minimum levels of drinking water standards, showed the possibility of ground water transport of the chemical.

ABSTRACT

Two sediment surveys in Buckhorn Lake revealed unexpectedly high residual 2,4-D concentrations in early May, but lower levels at the end of September, about three months after the seasonal applications in the lake. The higher spring values may indicate lower degradation rates in 1982, or 2,4-D inputs from land sources during the spring runoff. A study of 2,4-D disappearance in an experimental site showed extensive 2,4-D transport from applications elsewhere in the lake. Well water samples, obtained from the vicinity of the site during a two-week period in August, showed the presence of 2,4-D at concentrations well below the level recommended in drinking water standards.

INTRODUCTION

The Trent and Severn water systems, comprising several lakes, are an economically significant recreational resource of southern Ontario, providing many miles of waterways for pleasure boats, sport fishing, and extensive cottage development. During the 1970's, the growth of aquatic vegetation in many areas of the system, combined with an invasion of Eurasian watermilfoil, Myriophyllum spicatum , began to seriously affect navigation and the recreational uses of these waters. Surveys conducted by the Ontario Ministries of the Environment and Natural Resources have documented the extent of the problem in the Kawartha Lakes in the 1970's (1,2). Continuing concern for the preservation of these water systems and a recognition of their importance as a recreational resource is further shown in a joint review on possible problem areas by Environment Canada and the Ontario Ministry of Natural Resources (3). The review, and the resulting Canada - Ontario Policies for Rideau, Trent-Severn Corridor (CORTS), recognizes the need to monitor both the weed problem, and the possible effect of herbicide uses on water quality.

The project reported here was initiated to study the persistence and possible accumulation of 2,4-dichlorophenoxy acetic acid (2,4-D) in Buckhorn Lake sediments, and its persistence and movement in the water column in an experimental application.

EXPERIMENTAL

The Study Area.

The Trent is the largest river in Southern Ontario with a total drainage area of about 12,000 km^2 (4790 sq. miles). The Kawartha Lakes of the Trent water system lie along the southern edge of the Canadian Shield, and vary in character from deep mesotrophic lakes with rocky bottom to shallower water bodies with silty and organic-rich sediments and increasingly eutrophic character. Many of these lakes include flooded land (4). The Trent navigation system, completed in 1920, consists of several locks to bridge a difference of about 182 m from the summit in Balsam Lake to the Bay of Quinte. In addition to geographic factors, and land drainage from extensive cottage areas, the character of the lakes is influenced by human controls: the water levels are kept high during the summer and fall vacation seasons, but are allowed to drop in the winter in anticipation of the spring floods. A map of the area is given in Figure 1.

Buckhorn Lake, with a surface area of about 32 km^2 and a mean depth of 2.3 m, represents an intermediate size, depth, and degree of eutrophication among the Kawartha Lakes. In the

surveys referred to above, it was found to be one of the lakes with excessive weed growth, and about 85% of the lake's area contained impenetrable beds of vegetation. At the time of the surveys, milfoil was recognized as one of the dominant plants in the system.

From the mid 1970's to the present, both mechanical harvesting and chemical control have been used in these waters to keep navigation channels open and to clear limited areas, predominantly around cottages, for swimming and other recreational uses. Aqua Kleen, a commercial formulation containing 20% of butoxyethanol ester (BEE) of 2,4-D on clay pellets, has been the herbicide most commonly used for milfoil control. The use of Aqua Kleen in Buckhorn Lake, estimated from the permits issued by the Ontario Ministry of the Environment and subsequent reports of actual use, amounted to about 940 kg in 1983 (5). Additional, but unknown quantities, of the chemical may enter the lake with runoff from cottage lawns and from farmland.

Sediment Sampling.

Sediment cores were collected at 13 locations in Buckhorn Lake on May 26, 1983. The core sites included nearshore areas around marinas and cottages, and mid-lake sediment along a north-south transect in the SW portion of the lake. The cores

were obtained by forcing a long 5 cm diameter plexiglass tube into the sediment. The core length varied from about 25 to over 50 cm depending on the bottom conditions: the soft black sediment appeared to sit on a hard layer containing much woody material that the corer could not penetrate. After extrusion from the tube, samples of about 50 mL each were removed from the core to represent the top, mid depth, and the bottom of the core. These samples were placed in screw-cap jars and kept on ice until returned to the laboratory. The samples were then stored in a walk-in freezer (-20^{o}C) until analysis.

The May sampling sites were revisited on September 29, 1983, and surface sediment samples were collected with an Ekman dredge. These samples were handled the same way as the core samples above.

Experimental 2,4-D Application.

The experimental site was a canal between the shore and an island with cottages and year-round residences in the eastern end of Scollard Bay. The location of the approximately 10X50 m treatment area, and of seven buoys designating the main sampling sites, are shown in Figure 2. On July 11, 1983, 4.5 kg Aqua Kleen was applied to the surface of the designated area, by hand-broadcasting from a canoe. Water and surface sediment samples were collected at the pre-designated stations across the

treated area as well as in the bay outside the channel daily during the first week, then at 1, 2, 4, 6, 8 and 10 weeks. The water samples were taken from just under the surface and transferred into 1 L brown bottles containing 2 grams each of Amberlite XAD-2 and XAD-7 ion exchange resins (Rohm & Haas Co.). The samples were kept on ice until they reached the laboratory where they were acidified with about 4 mL of concentrated H_2SO_4, and stored at $4^{\circ}C$ until analysis. The sediment samples were collected with an Ekman dredge and were handled as those obtained in the lake-wide survey.

Well water samples.

As part of our efforts to establish background noise levels in the 2,4-D analysis, tap water samples were collected from a residence next to the treatment site and from a nearby marina and cottage area. These were handled the same way as the water samples described above.

Analysis of Samples.

The determination of 2,4-D in the water and sediment samples consisted of the following steps:

Water samples:

* physical separation of resin beads from water,
* extraction with ethyl ether,

* reduction of volume,
* derivatization with diazomethane, and
* gas chromatography.

Sediment samples:

* extraction with 0.1 M Na_3PO_4 solution,
* extraction of acidified extract with ethyl ether,
* plus the last three steps of above.

The details of the methods have been reported earlier (6,7). The detection limits of the method were about 0.01 ug/g dry sediment and about 0.01 ug/L in the water samples.

RESULTS

Sediment surveys.

Buckhorn Lake sediments from the May cores and the September surface samples were generally very soft, black oozy masses with a high organic content (an average of 43% ignition loss from dry sediment samples from one core). Chips of wood and fine roots were frequently noted throughout the sediment column.

The results of the two sediment surveys are presented graphically in Figure 3. Four of the sampling sites were located in nearshore waters near extensive cottage developments (West shore approaching the town of Buckhorn, and off Emerald Isle). The site near Fox Island was between the main navigation channels. Seven sites were chosen along a north-south transect shown. The most striking feature of the data is the variation between the May and September results. The high concentrations found in the spring samples, assuming that they were residues from the 1982 herbicide applications, indicate a significant degree of persistence of the chemical. The much lower concentration levels observed in the fall, however, appear to indicate less persistence, especially since the herbicide use during the summer of 1983 was similar to that in the previous year.

As shown by the bar graphs, the concentrations were highest in the nearshore sediments. The site farthest downstream, just north of Hall Point, produced the highest concentrations in both

surveys. The concentrations in the sediment along the transect, as shown in Figure 4, were lower but still detectable about 2.8 km from the shore.

The vertical distribution of 2,4-D in the May sediment cores, shown in Figure 5, indicates a fairly homogeneous distribution in the sediment column. It was this observation that led to the use of the Ekman dredge in the September survey.

Experimental application of 2,4-D

The average 2,4-D concentrations in the water from the seven sampling sites are shown to decrease rapidly for about six weeks following the treatment (Figures 6 and 7). Concentration distributions in the treated channel and outside the treated area are shown in Figure 8. The appearance of 2,4-D in the small catchment area south of the channel, and in the more open waters of Scollard Bay indicate effective transport of the chemical. The possibility of outside sources was considered but could not be substantiated by the data. It is worth noting here that the Scollard Bay samples were collected about 100 m from the treated channel, while the nearest known milfoil treatment occurred in the opposite end of the bay, over 1000 m from the sampling site.

The 2,4-D concentrations in the sediment, shown in Figure 9, diminished more slowly, and were still above detectable levels ten weeks after the treatment. The variations among sampling sites were very large, due mainly to extreme variations of the

bottom from muddy to sandy or rocky within the small experimental site. This variation may have originated from dumping by a local building contractor or the home owners along the channel. The station-to-station distribution of the concentrations, given in Figure 10, is a further evidence of effective transport of the chemical.

The 2,4-D concentrations in the sediment at the last sampling date, that is 10 weeks after application, were similar to those obtained in the lakewide sampling in September, and corresponded to the lowest values observed in the May samples.

Well water samples were collected on August 8 as tap water from one of the residences on the island adjacent to the treatment area, as well as from the Emerald Isle marina and a neighbouring cottage, about 0.3 km north of the treatment channel. The 2,4-D concentrations in the marina and cottage samples were about 0.5 ug/L, while the well water at the island residence contained 4.5 ug/L. Additional well water samples collected from the cottages two weeks later did not contain detectable 2,4-D concentrations. Ontario Ministry of the Environment officials, alerted to the findings of the first analyses, sampled the well waters of island residents during the two week period and found intermediate 2,4-D concentrations (about 0.5 ug/L).

CONCLUSIONS

The results of the two sediment surveys are not compatible with known patterns of herbicide applications, which take place during the milfoil growing season, i.e. June and July. In a closed system, the fall concentrations, only 2 to 3 months after the 2,4-D applications, should be higher than the spring results, obtained just before another round of herbicide use, and about 10 months after last year's use. The summer of 1983 was exceptionally warm. The high seasonal temperatures may have increased degradation rates of the 2,4-D in the lake. Buckhorn Lake is obviously not a closed system, and the high 2,4-D concentrations in the spring sediment samples could also be produced by its movement downriver from Pigeon and Chemong Lakes, or by spring runoff from land. The results of the sediment survey along the North-South transect in the lake suggest nearshore inputs within Buckhorn Lake. Whichever source was responsible for the high spring concentrations, they do indicate a significant degree of persistence and widespread distribution in the system. Recognition of the predominant sources would also be needed before the low fall concentrations could be reliably ascribed to either degradation or to transport processes.

The results obtained in the experimental 2,4-D application site indicated the existence of effective transport mechanisms in Scollard Bay, and probably represented short-term variations in the herbicide concentrations in at least that section of the bay.

Prevailing westerly winds may indeed trap 2,4-D in Scollard Bay, and after several years' of its use may account for the relative absence of milfoil in most of the bay.

The detection of 2,4-D in the well waters of the experimental area showed the possibility of groundwater transport of the chemical. Although the highest observed concentration of 4.5 ug/L is well below the 100 ug/L recommended in drinking water standards, the observation indicates the need for a more thorough survey. Such a survey has indeed been planned by the Ontario Ministry of the Environment to take place during the 1984 herbicide application season.

References:

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3. Canada - Ontario Policies for Rideau, Trent-Severn Corridor. Joint Publ. of Environment Canada and the Ontario Ministry of Natural Resources, April, 1982. 32 p.

4. Chapman, L.J. and D.F. Putnam, The Physiography of Southern Ontario. Univ. of Toronto Press, 1966. 386 p.

5. Curry, Catherine, Pesticides Control Section, Ontario Ministry of the Environment. Personal communucation.

6. Scott, B.F., E. Nagy, J. Hart, B.K. Afghan, New extraction/GC technique finds traces of water pollutants. Industrial Res. & Development, April 1982, p.130-135.

7. Scott, B.F., D.S. Painter, E. Nagy, B.J. Dutka, W.D. Taylor, Fate and effects of 2,4-D formulations as herbicides in aquatic ecosystems. Part 1. Unpubl. Manuscript Series, National Water Research Institute, Burlington, Ont. May 1981, 73 p.

Figure 1

The Trent River system.

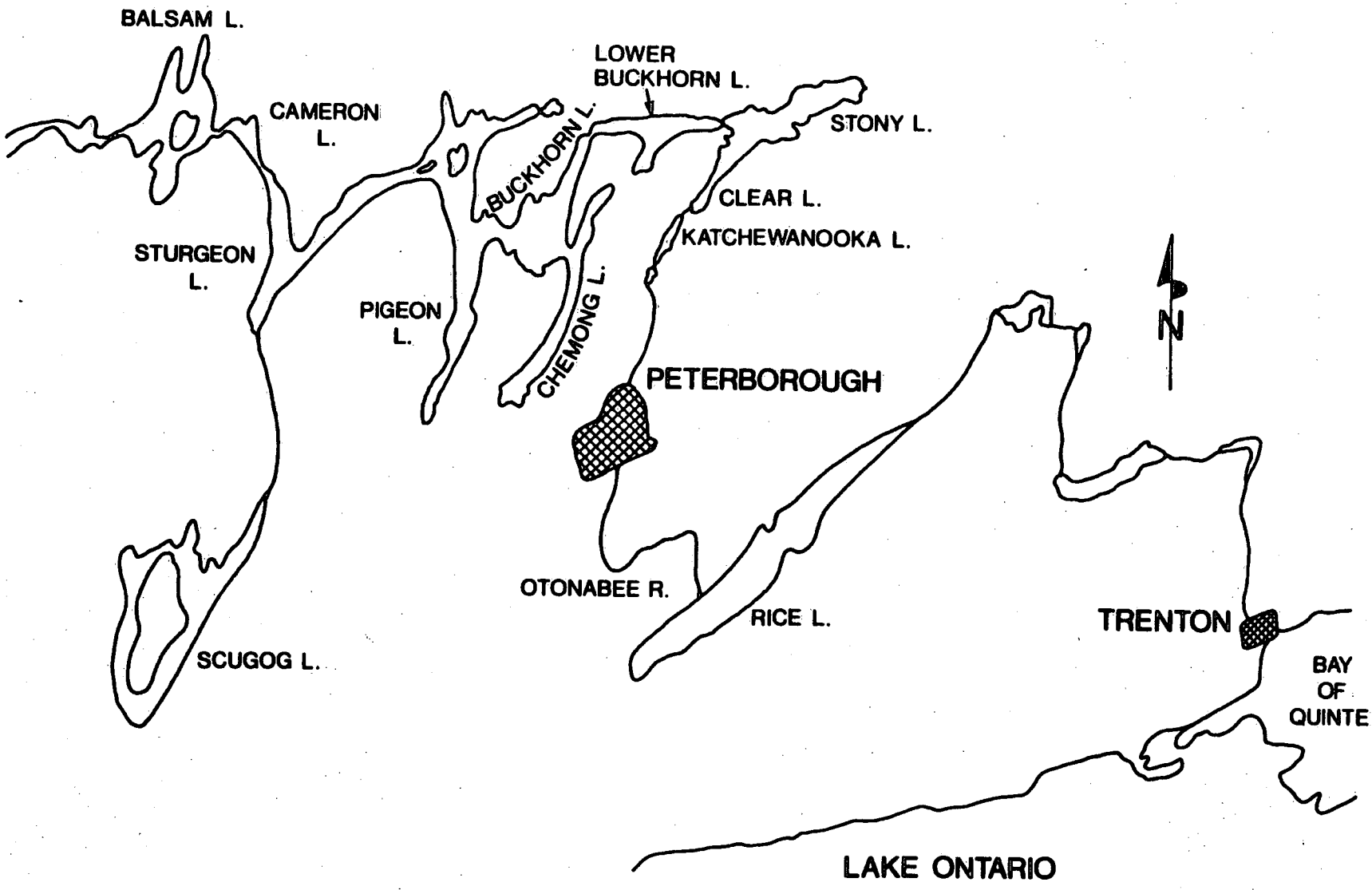

BALSAM L.
CAMERON L.
LOWER BUCKHORN L.
BUCKHORN L.
STONY L.
CLEAR L.
KATCHEWANOOKA L.
STURGEON L.
PIGEON L.
CHEMONG L.
N
PETERBOROUGH
OTONABEE R.
RICE L.
TRENTON
BAY OF QUINTE
SCUGOG L.
LAKE ONTARIO

Figure 2

The Site of Experimental 2,4-D Treatment.

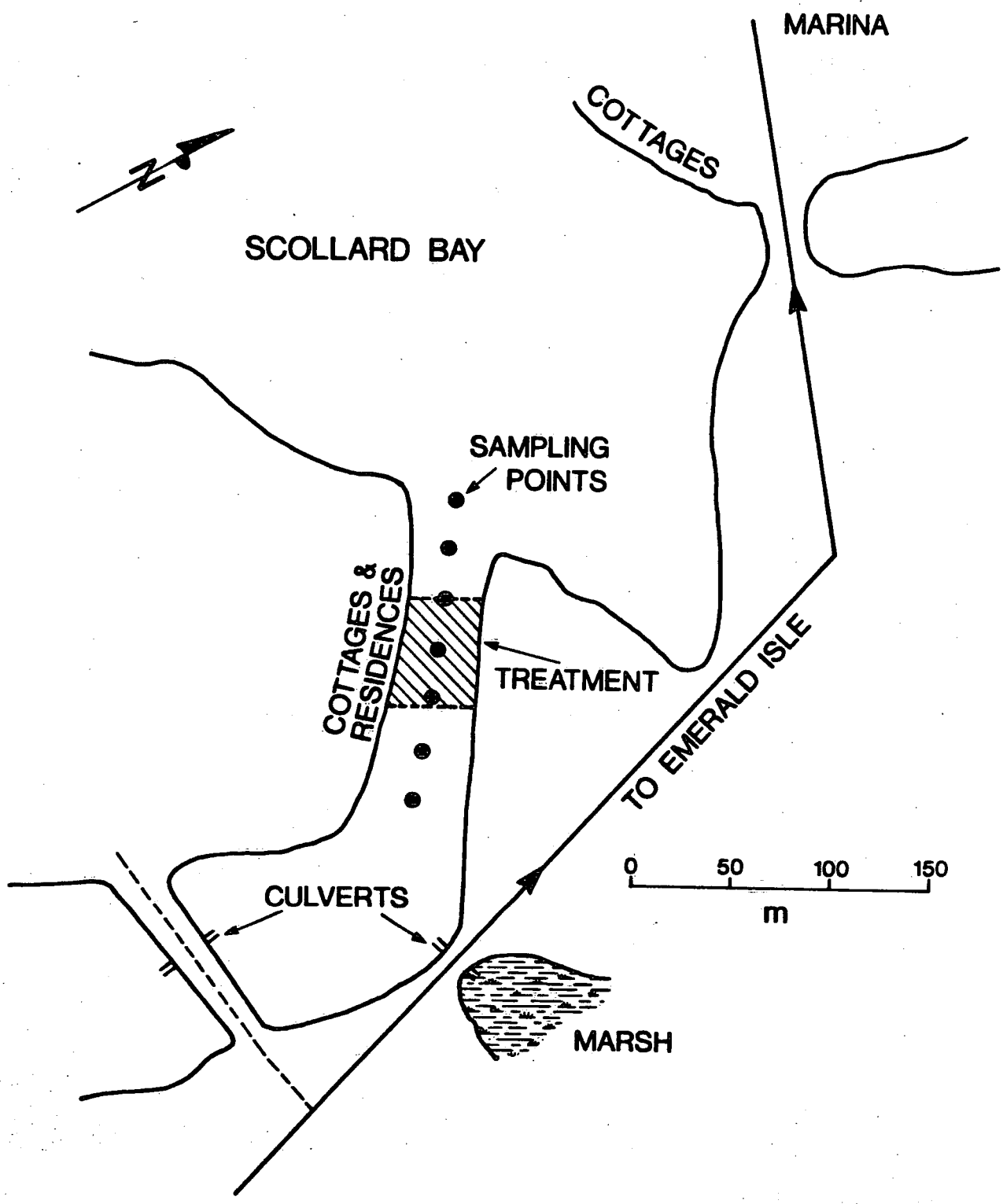

MARINA
COTTAGES
N
SCOLLARD BAY
SAMPLING
POINTS
COTTAGES &
RESIDENCES
TREATMENT
TO EMERALD ISLE
0
50
100
150
m
CULVERTS
MARSH

Figure 3

Sampling Sites and Results of the

1983 Buckhorn Lake Sediment Surveys.

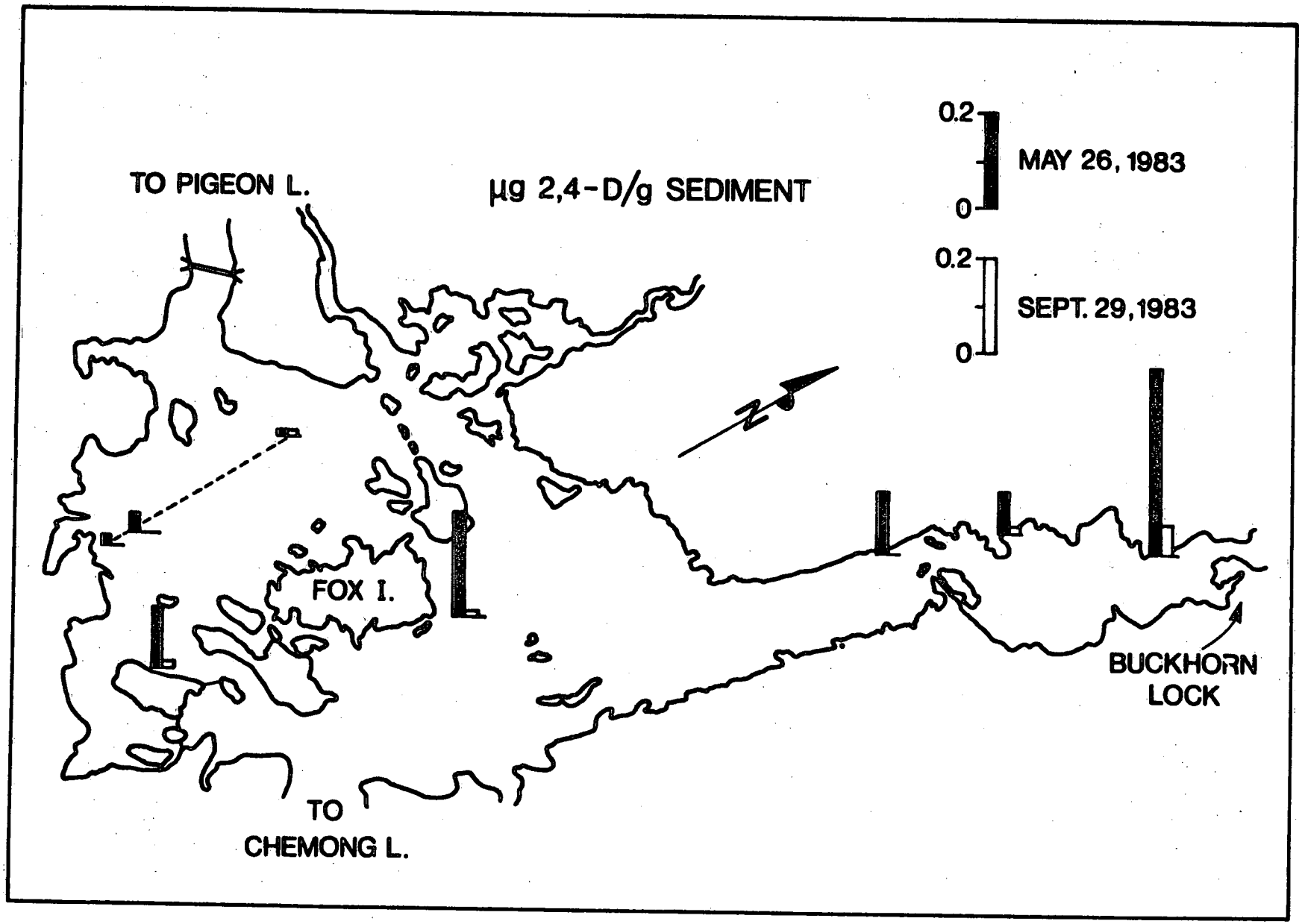

TO PIGEON L.
µg 2,4-D/g SEDIMENT
0.2
0
MAY 26, 1983
0.2
0
SEPT. 29, 1983
FOX I.
BUCKHORN
LOCK
TO
CHEMONG L.

Figure 4

2,4-D in Buckhorn Lake Sediments

Along South-to-North Transect.

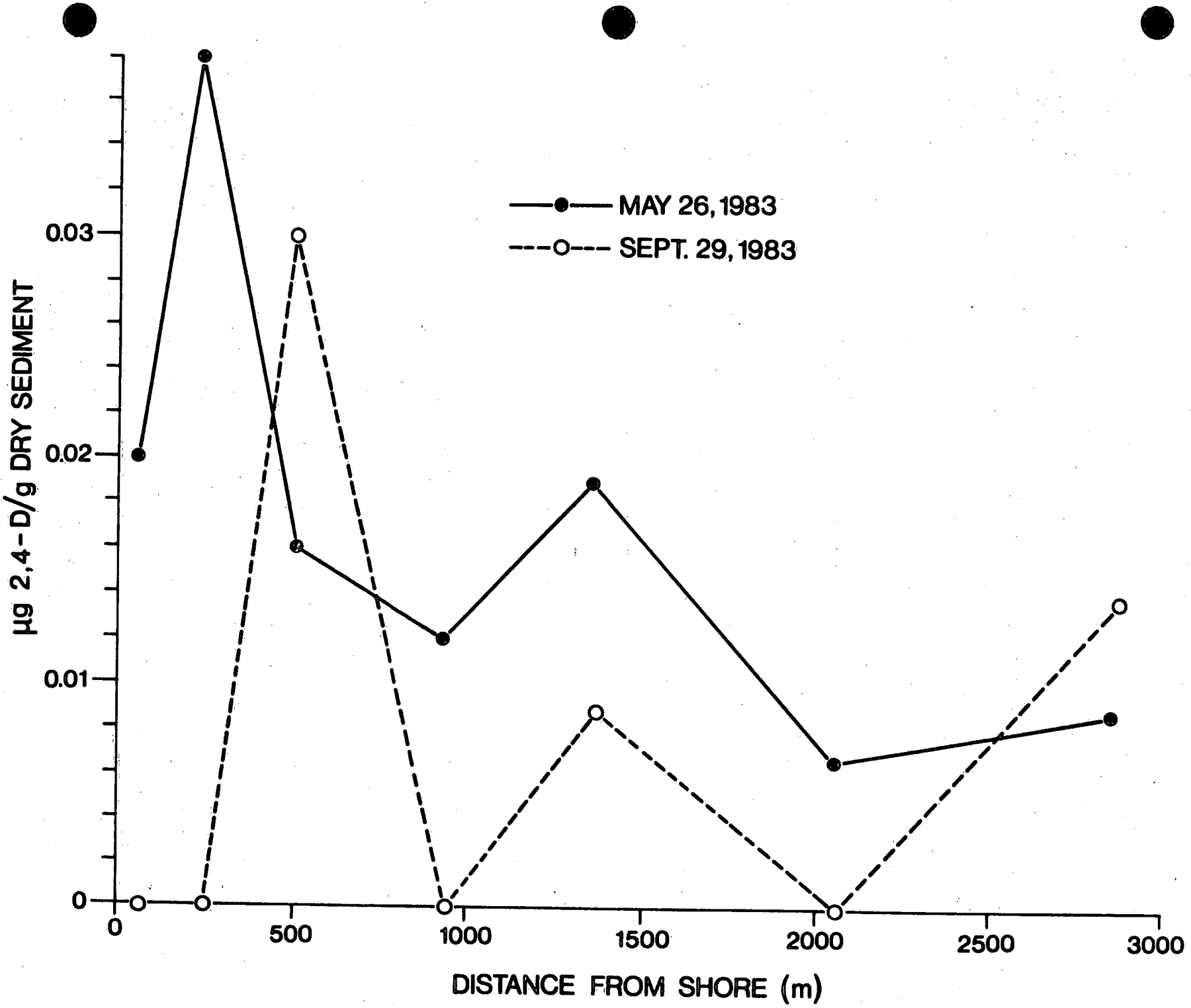

MAY 26, 1983
SEPT. 29, 1983
µg 2,4-D/g DRY SEDIMENT
0.03
0.02
0.01
0
0
500
1000
1500
2000
2500
3000
DISTANCE FROM SHORE (m)

Figure 5

2,4-D Distribution in Sediment Cores.

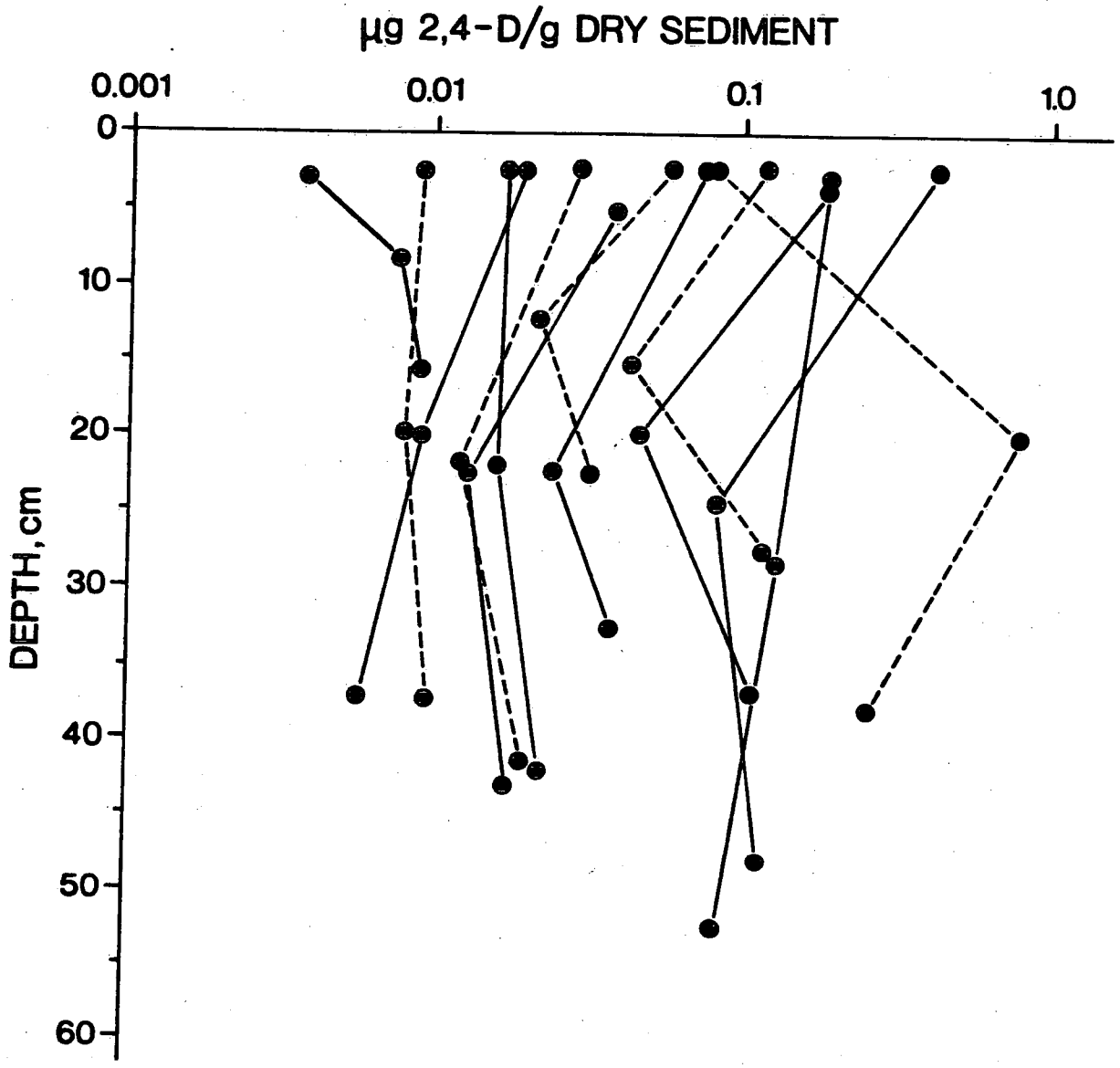

µg 2,4-D/g DRY SEDIMENT
0.001
0.01
0.1
1.0
0
10
20
30
40
50
60
DEPTH, cm

Figure 6

2,4-D in Water at Experimental Site -

Short-term Variation.

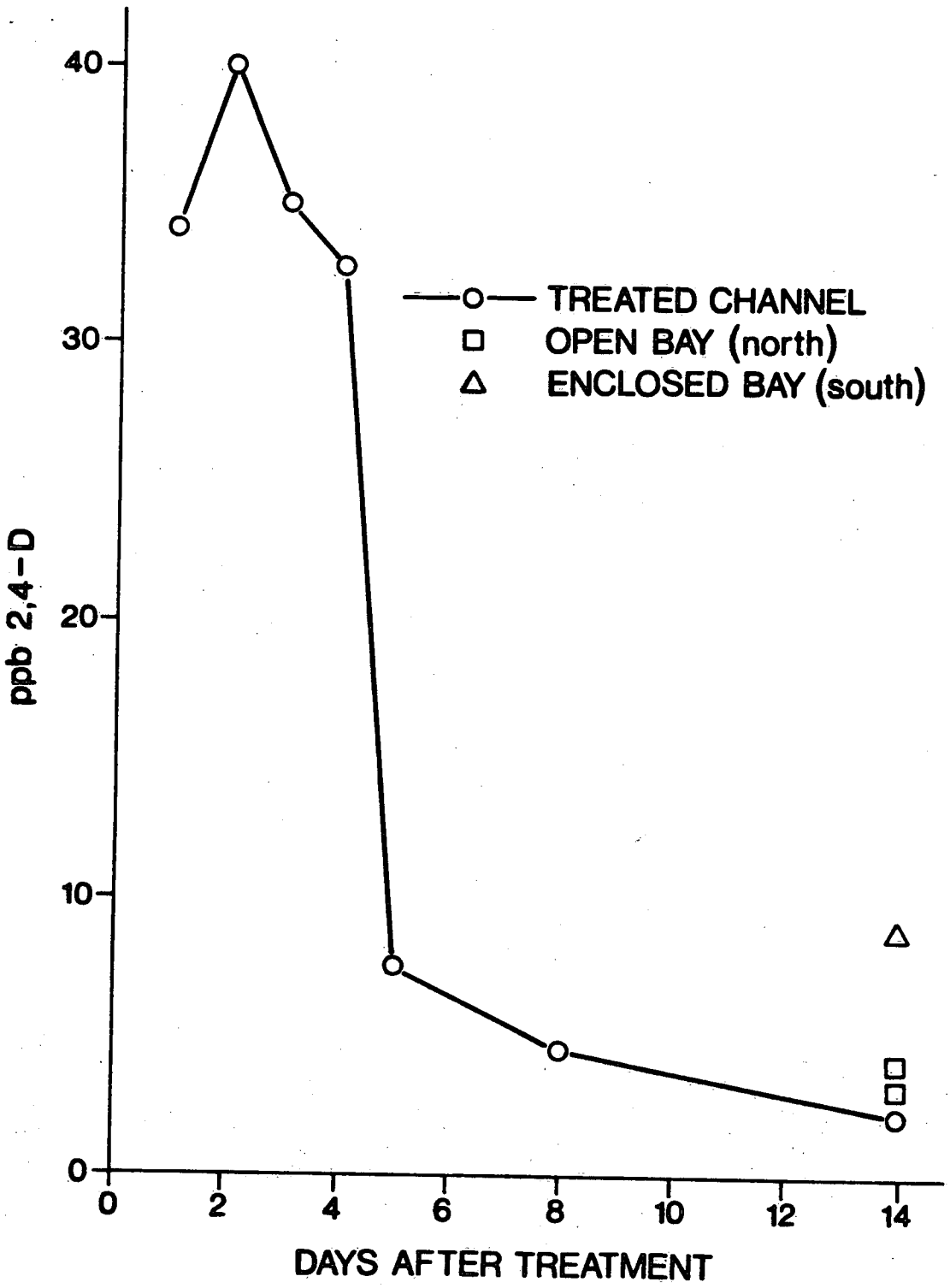

40
30
20
10
0
ppb 2,4-D
0
2
4
6
8
10
12
14
DAYS AFTER TREATMENT
TREATED CHANNEL
OPEN BAY (north)
ENCLOSED BAY (south)

Figure 7

2,4-D in Water at Experimental Site -

Long-term Variation.

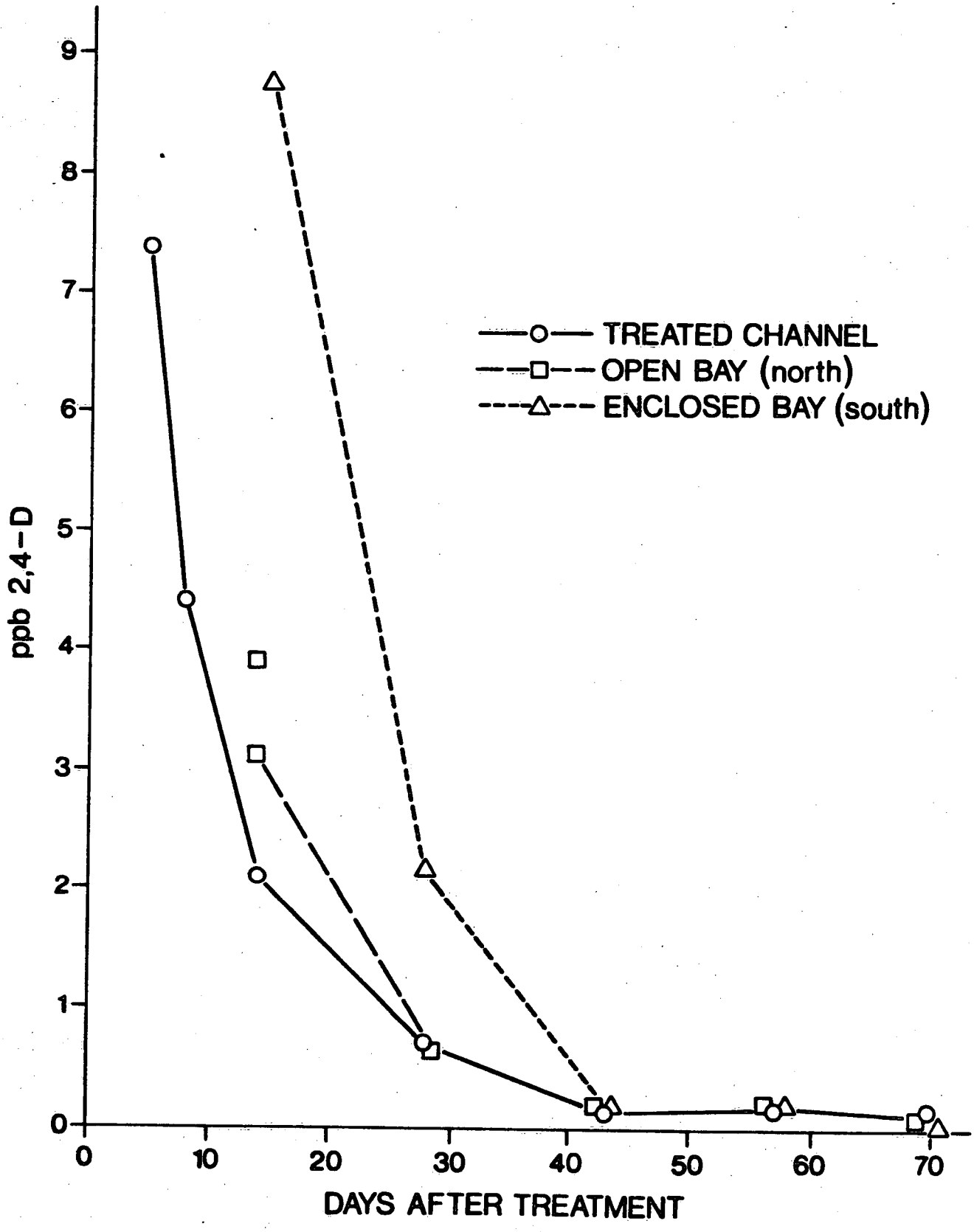

9
8
7
6
5
4
3
2
1
0
ppb 2,4-D
0
10
20
30
40
50
60
70
DAYS AFTER TREATMENT
TREATED CHANNEL
OPEN BAY (north)
ENCLOSED BAY (south)

Figure 8

2,4-D in Water at Experimental Site -

Variation Within Treated Area and in Adjacent Waters.

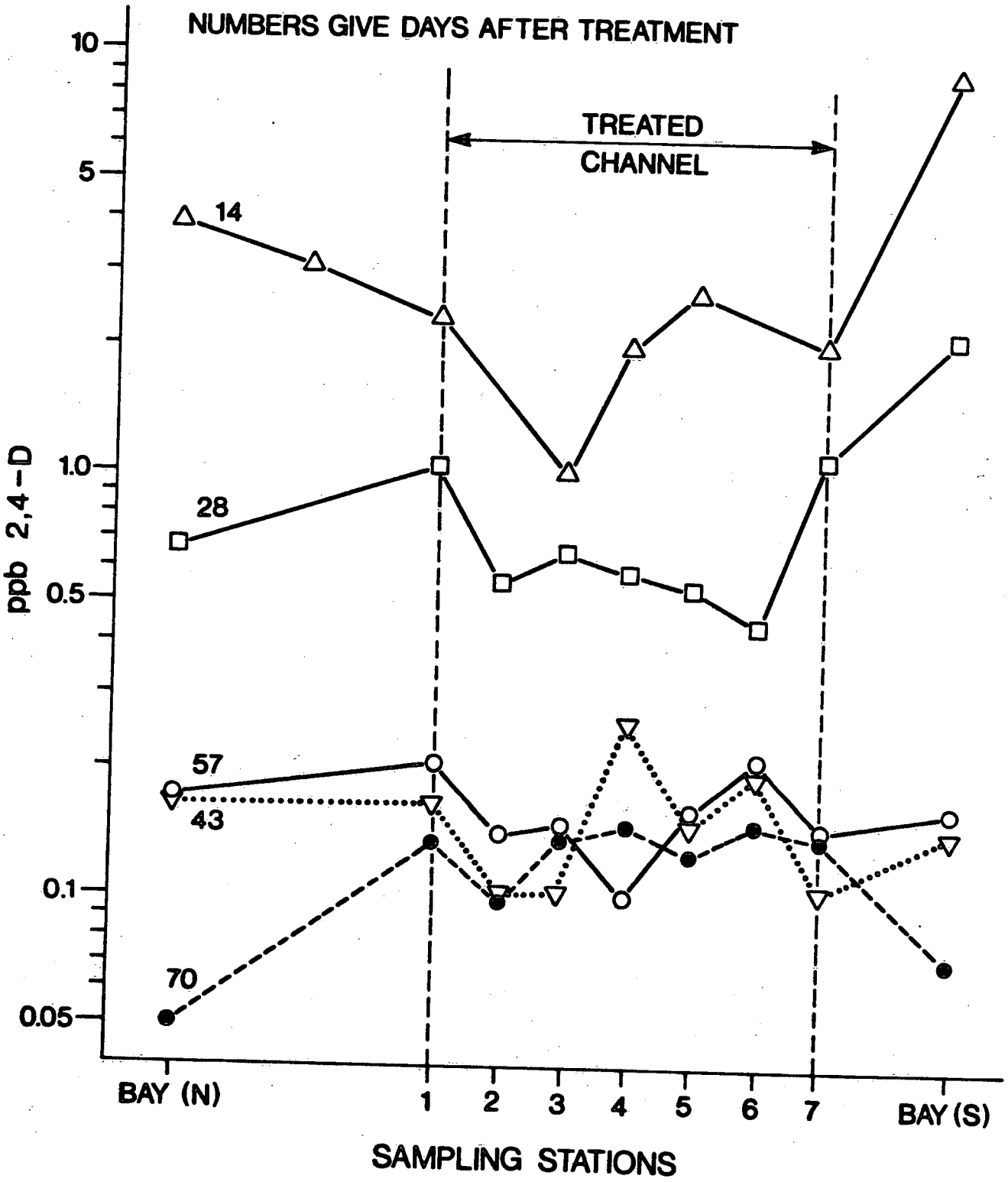

NUMBERS GIVE DAYS AFTER TREATMENT
TREATED
CHANNEL
14
28
57
43
70
10
5
1.0
0.5
0.1
0.05
ppb 2,4-D
BAY (N)
1
2
3
4
5
6
7
BAY (S)
SAMPLING STATIONS

Figure 9

2,4-D in Sediment in Treated Channel.

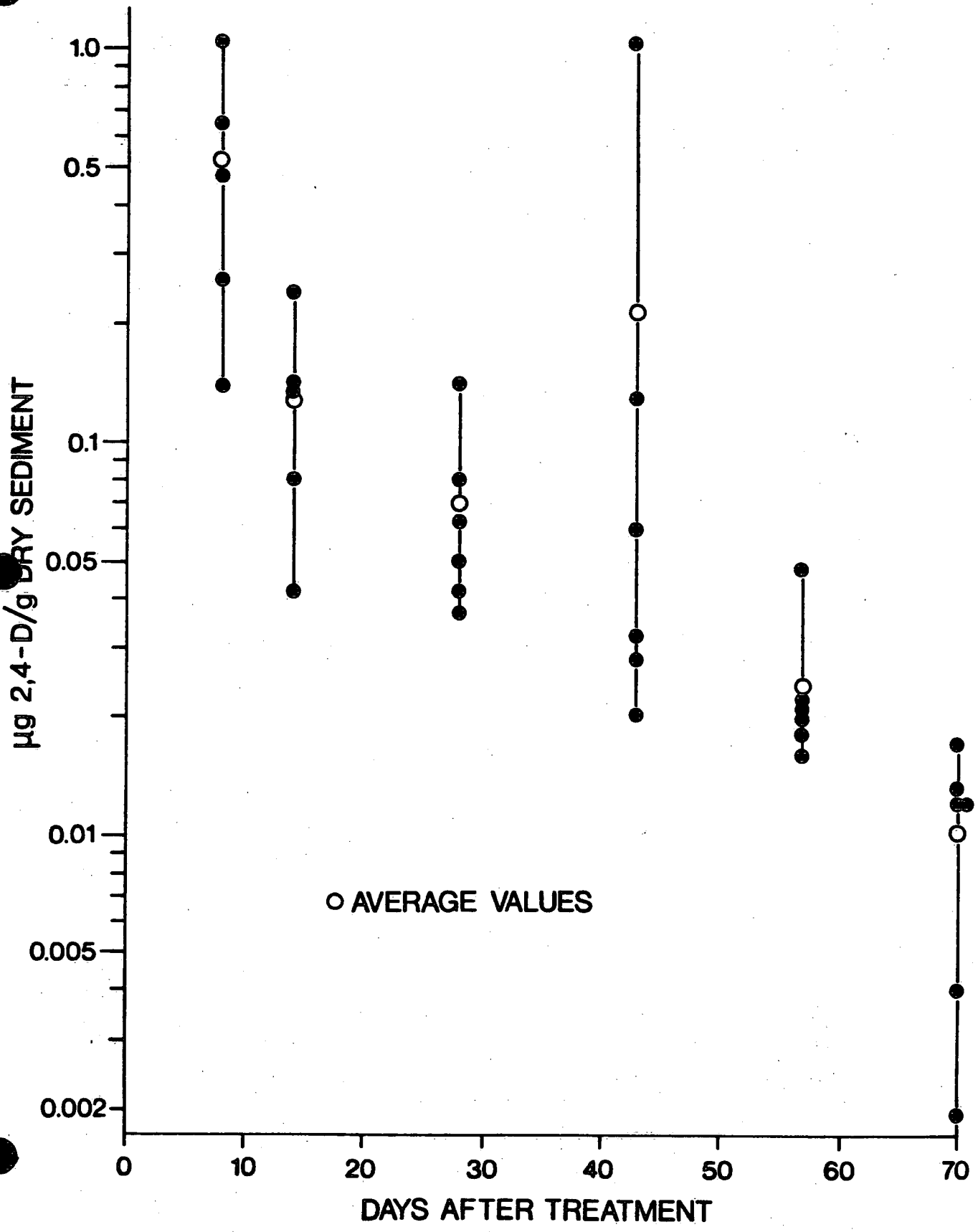
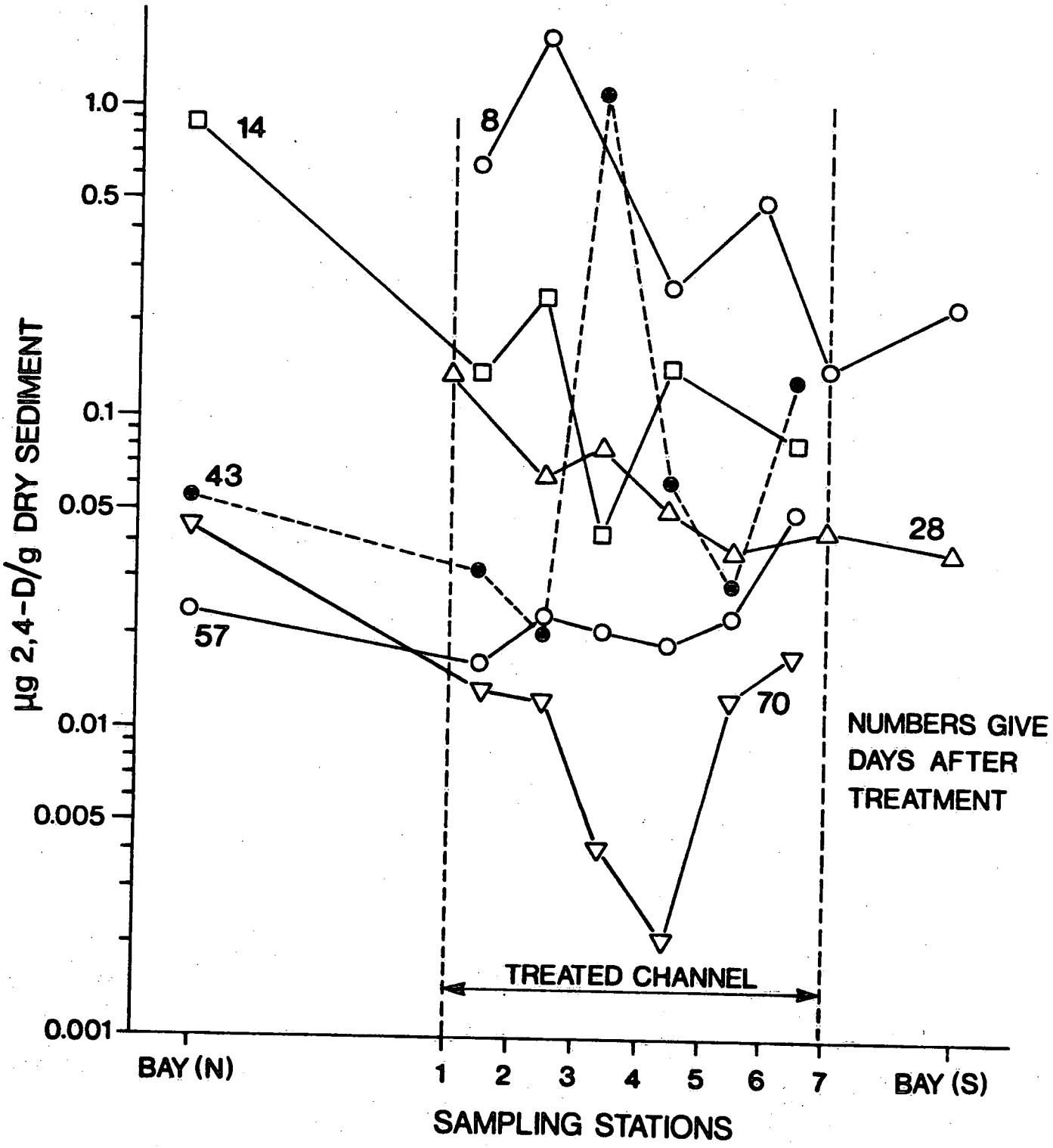

1.0
0.5
0.1
0.05
0.01
0.005
0.002
µg 2,4-D/g DRY SEDIMENT
o AVERAGE VALUES
0
10
20
30
40
50
60
70
DAYS AFTER TREATMENT

Figure 10

2,4-D in Sediment at Experimental Site -

Variation Within Treated Area and Adjacent Locations.


1.0
0.5
0.1
0.05
0.01
0.005
0.001
µg 2,4-D/g DRY SEDIMENT
14
8
43
28
57
70
NUMBERS GIVE DAYS AFTER TREATMENT
TREATED CHANNEL
BAY (N)
1
2
3
4
5
6
7
BAY (S)
SAMPLING STATIONS