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HEAVY METALS IN THE WATER AND SEDIMENT OF LAKES IN WESTERN MASSACHUSETTS I. ARSENIC

Lawrence N. Kuzminski

Gibson Stine

*Progress Report for Division of Water Pollution
Control, Massachusetts Water Resources Commission.*

Contract Number 15-051454.



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OF LAKES IN WESTERN MASSACHUSETTS

I. ARSENIC

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by

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PREFACE

This progress report is the first in a series of detailed progress reports prepared for the Division of Water Pollution Control, Massachusetts Water Resources Commission, Contract Number 15-51454, "Impact of Heavy Metals on the Aquatic Biota of Massachusetts Waters."

The report focuses on the levels of arsenic currently found in several lakes in western Massachusetts. The research presented herein was conducted by the authors from January to September, 1973. The authors are, respectively, Assistant Professor and Graduate Research Assistant, Department of Civil Engineering, University of Massachusetts, Amherst.

This report will be brought to the attention of various agencies, organizations, companies, industries, and individuals interested in the preservation of our natural resources.

ACKNOWLEDGEMENTS

Our sincere thanks is due to the Perkin-Elmer Corporation of Norwalk, Connecticut, for their help with analytical difficulties.

ABSTRACT

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Seventeen lakes in western Massachusetts were surveyed to determine arsenic levels in the water and sediments. Background levels of 0.20 to 0.91 $\mu\text{g/l}$ As and 1.1 to 9.4 mg/kg As dry weight were determined, respectively. Four of the lakes had histories of sodium arsenite treatment and exhibited levels one to two orders of magnitude greater than background. Three lakes indicated arsenic levels about five times greater than "natural", presumably due to industrial and heavy residential and highway land uses, though no definite relationship was ascertained. All lakes showed excellent correlation between water and sediment levels, suggesting similar chemistries for the lakes surveyed.

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INTRODUCTION

ARSENIC IN THE WATER AND SEDIMENT OF LAKES IN WESTERN MASSACHUSETTS

INTRODUCTION

Over the past fifty years, sodium arsenite has been widely used to control the growth of aquatic plants in lakes, ponds, and reservoirs (Surber, 1950). The long range effects of such treatments on these bodies of water are largely unknown, though the U.S. Public Health Service has limited the concentration of arsenic in drinking water to 10 $\mu\text{g}/\text{l}$ As because of the known toxic and carcinogenic effects to man (U.S.P.H.S., 1962). Both the known effects to man and the possible impacts on the aquatic environment have also moved the state of Massachusetts to ban the use of sodium arsenite as an aquatic herbicide (Hood, 1973).

This study was undertaken to provide much needed information relating to the long term effects of sodium arsenite treatment. The project was basically broken down into three parts. Part I consisted of an in depth literature survey concerning arsenic in the aquatic environment. Part II of the study consisted of collecting water and sediment samples from lakes in western Massachusetts, and Part III concerned the analysis of these samples. All three phases of the study are reported herein.

LITERATURE REVIEW

LITERATURE REVIEW

Sources of Arsenic in the Environment. As a trace element, arsenic is considered fairly abundant. The earth's crust contains an average of 1 mg/kg As dry weight, though concentrations of up to 20,000 mg/kg may be found in geothermal areas (Wedpohl, 1969). In the aquatic environment, background arsenic levels will be greatly influenced by the geological formations underlying the lake, as well as the chemical composition of the water and the lake biota. It is therefore very difficult to define a typical natural level. Rain water has been reported to contain as much as 14 $\mu\text{g/l}$ As, and tap water 0.4 $\mu\text{g/l}$ (Smith, 1969; Angino, 1970). The generally accepted range for lake water is 1-5 $\mu\text{g/l}$ As. In Massachusetts, lake sediments have been shown to contain 0 to 30 mg/kg As dry weight, though the higher levels were achieved in a highly industrialized lake (Isaac and Delaney, 1972). These findings compare favorably with those of Ruch, et. al. (1970) and Edgington and Callender (1970) for Lake Michigan.

Data is scarce concerning the arsenic levels naturally occurring in lake biota. Two surveys concerning Great Lakes fish report average concentrations under 0.05 mg/kg As wet weight for non-industrialized areas (Lucas, et. al. 1970; Uthe and Bligh, 1971), and Reay (1972) suggests a natural level for aquatic plants to be less than 12 mg/kg As dry weight.

To these background levels are of course added the arsenic reintroduced into the environment by the activities of man. Known for a long time as a poison, arsenic is also used in dyes, glass and metal alloy manufacture, wood preservatives, flypaper, soap, germicides, detergents, pesticides, and herbicides (Jenkins, 1972). The manufacture, the use, and the disposal of these products may all contribute to increased arsenic levels. The last three items are particularly

important because of their past or present widespread use. Detergents contain from 70 to 80 mg/kg of arsenate in conjunction with the phosphate buffer, and wash-water concentrations range from 5 to 100 $\mu\text{g/l}$ As (Anonymous, Chemical and Engineering News, 1970; Harris, et. al., 1971; Pattison, 1970). Lead arsenate was widely used as a pesticide on tobacco crops, apple trees, and vineyards until the introduction of organic pesticides in the 1940's, and Paris Green (copper acetoarsenite) was used to control mosquitoes until around 1950 (Jenkins, 1972). Both of these arsenicals have contributed to increased levels of arsenic in the soil and in nearby lakes (Lisella, et. al., 1972).

Sodium arsenite is a non-selective herbicide, and is generally used to control aquatic plants. Its widespread use can be attributed to its low cost, \$3/acre for sodium arsenite vs. \$100/acre for an organic herbicide such as 2,4-D or 2,4,5-T, and its ease of application (Surber, 1950). In general practice, sodium arsenite in liquid form is distributed by a submerged nozzle to obtain a final concentration of 4 to 8 mg/l As_2O_3 in the upper two and a half feet of water (Lawrence, 1957). Both the high concentrations employed and its widespread use indicate that this arsenical is the major source of arsenic in the aquatic environment. Though treatment of lake water with sodium arsenite will be of primary concern in this study, one cannot neglect the possible inputs from domestic wastewater, industrial wastewater and air pollution, and agricultural runoff, as well as other activities of man.

The Fate of Arsenic in the Aquatic Environment. The chemistry of arsenic in aquatic environments is very complex. Oxidation-reduction, precipitation, ligand-exchange, and adsorption reactions all take place, with four oxidation states being stable (+5, +3, 0, -3). The thermodynamic data (Table 1) and

Table 1

Free Energies of Formation for Arsenic Species at 25°C and 1 atm.

<u>Species</u>	<u>State</u>	<u>G_f⁰</u>	<u>Reference</u>
H ₃ AsO ₄	aq.	-184.0 kcal/mole	Reguson & Gavos (1972)
H ₂ AsO ₄ ⁻	aq.	-181.0	"
HAsO ₄ ⁻²	aq.	-171.5	"
AsO ₄ ⁻³	aq.	-155.8	"
H ₃ AsO ₃	aq.	-154.4	"
H ₂ AsO ₃ ⁻	aq.	-144.1	"
HAsO ₃ ⁻²	aq.	-125.3	"
AsO ₂ ⁻	aq.	- 83.7	Garrels and Christ (1965)

resulting Eh-pH diagram (Figure 1) supplied by Ferguson and Gavis (1972) indicate a popular mechanism, however, is the co-precipitation of arsenate with metal ions, particularly hydrous iron oxides. Ferric arsenate is very insoluble and thus may accumulate in lake sediments (Onishi and Sandell, 1955). Arsenite may also be removed by this mechanism or by co-precipitation with metal sulfides, if oxidation to arsenate is incomplete (Ferguson and Gavis, 1972). In very severe reducing conditions sometimes occurring in lake sediments, the ferric arsenate may be reduced causing the evolution of arsine gas. This gas is soluble in water, and thus the arsenic is recycled.

Aquatic biota also play an important role in the removal of arsenic from the lake water. Plants, fish, and other organisms are known to accumulate arsenic, though there is no evidence of its concentration upward through the food chain (Mullison, 1970). In lake sediments, fungi, yeast, and bacteria are believed to methylate arsenic to derivatives to arsine gas, thus reintroducing the element into the overlying water in another manner.

From all of the above considerations, a local cycle for arsenic in a typical lake can now be postulated (Figure 2). This diagram clearly shows that the ultimate sink for arsenic introduced into the aquatic environment is the sediment though there will be a residual in the water and contamination of the biota. All three areas of the aquatic environment may eventually establish equilibrium

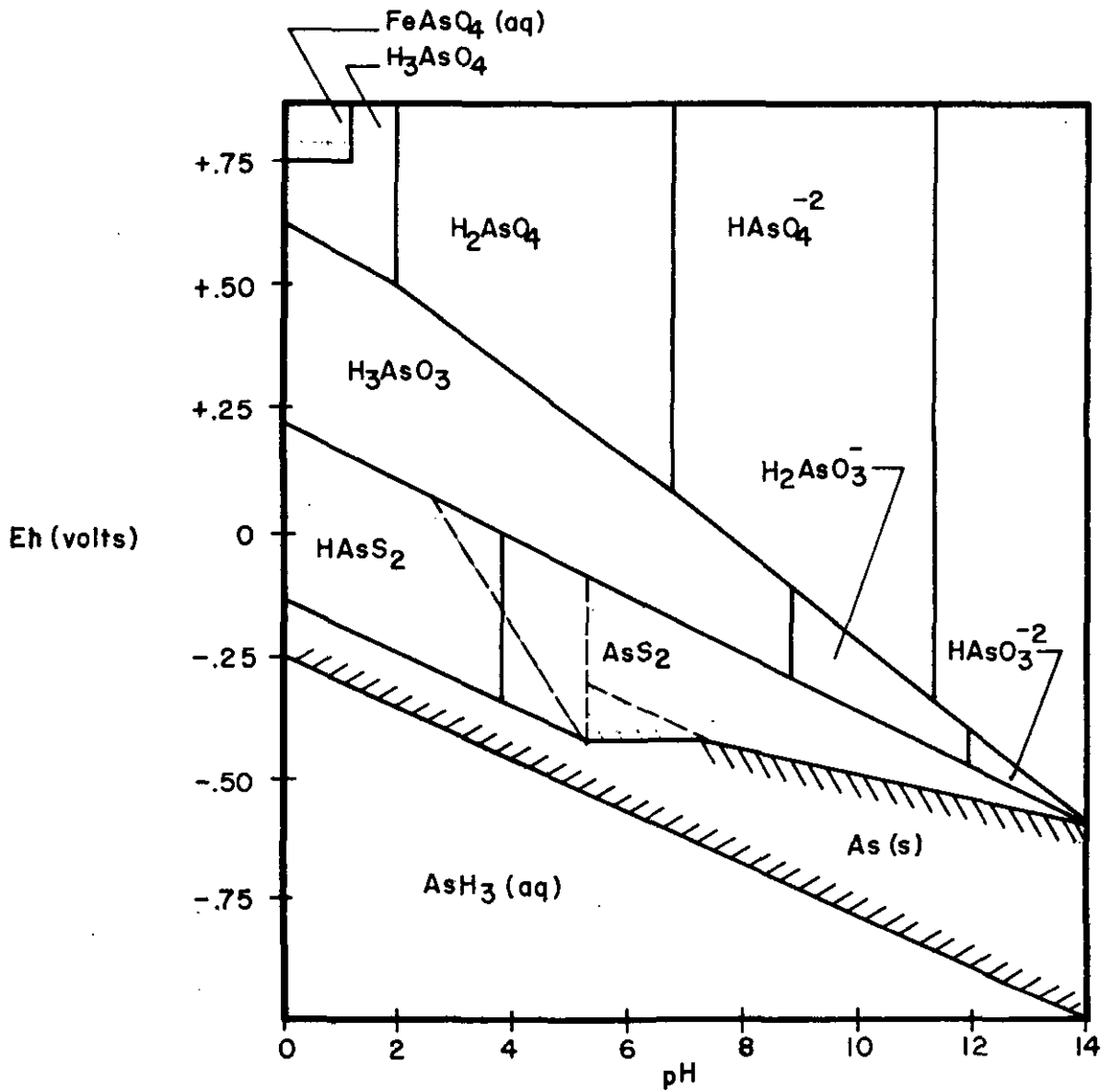
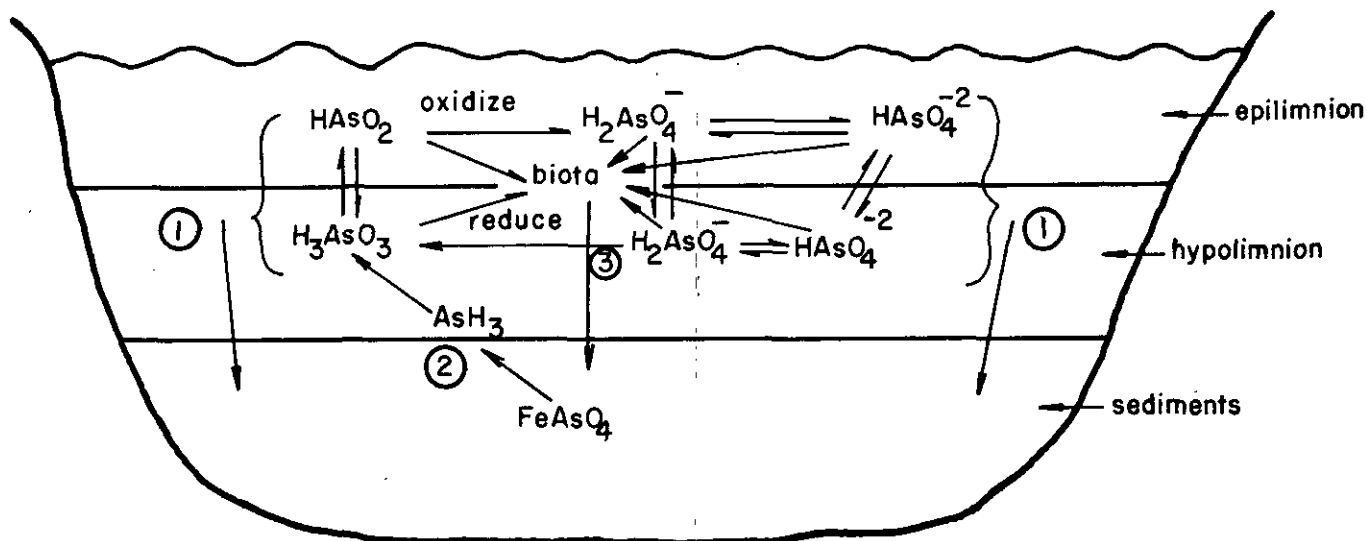


FIGURE 1

Eh vs. pH for arsenic in H_2O
[As] = .00001 mole/l
[S] = .001 mole/l

Reproduced from Ferguson and Gavis (1972)



- ① adsorption or coprecipitation
- ② reduction or biomethylation
- ③ death

FIGURE 2
Arsenic Cycle in a Typical Lake

concentrations of arsenic, and each area's content will affect the others' levels. Other important factors influencing these concentrations are the water chemistry, types of biota, and geochemistry for the environment. The levels that are found in the water, sediment, and biota of lakes treated with sodium arsenite will be presented in the next section.

Past Surveys. The majority of studies dealing with arsenic concentrations in ponds, lakes, and reservoirs have been concerned with the levels achieved after treatment with sodium arsenite. No long term studies of these levels have been done, and unfortunately, arsenic concentrations prior to treatment were usually not measured. In general, the results of these past surveys indicate that after sodium arsenite application:

- the level of arsenic in the lake water decreases rapidly and is almost undetectable after six months,
- there is a rapid increase in the levels of arsenic in the lake biota, and
- there is a slower rise in the sediment concentrations.

Specifically, Lawrence (1957) treated six ponds with 4 mg/l sodium arsenite (as As_2O_3) and found an average of 3 mg/l after one day, 1.5 mg/l after two days, 0.4 mg/l after 24 days, and 0.06 mg/l after six months (all in the top 2-1/2 feet of water). A laboratory study done by Surber and Meehan (1930) used aquaria to show that arsenic concentrations in the water decreased faster when the iron concentration in the water was higher, thus supporting one removal mechanism mentioned previously. A third study reported by Dupree (1960) indicates that repeated dosing of sodium arsenite in lakes results in a slower decline of water concentrations as well as a higher final level.

This same study also showed that arsenic levels in the sediments gradually increased after treatment, ranging from 14 to 54 mg/kg As_2O_3 dry weight in the six treated lakes several months after the second 4 mg/l dosage. Concentrations in plankton peaked at 3700 to 7200 mg/kg As_2O_3 dry weight after a thirty day period, and then declined to half this value after 76 days. Arsenic levels in the digestive tracts of sunfish seined from these lakes ranged from 2.1 to 6.6 mg/kg As_2O_3 wet weight after 76 days, though only trace amounts were present in the flesh of these fish. Other studies concerning the uptake of arsenic by fish in lakes treated with sodium arsenite were done by Ullman, et. al. (1930).

Though not directly concerned with sodium arsenite treatment, a survey by Reay (1972) reports on the uptake of arsenic by aquatic plants in an arsenic-enriched geothermal area. Concentrations ranging from 30-650 mg/kg As_2O_3 dry weight were reported for aquatic plants, with uncontaminated levels for the area suggested as 12 mg/kg. Corresponding water and sediment concentrations ranged from 30-70 $\mu g/l$ As_2O_3 and 7-550 mg/kg dry weight, respectively. The data collected by Fish (1963) from lakes in a similar area nearby showed a smaller range: 20-70 mg/kg As_2O_3 dry weight for a particular species of aquatic plant, and 17-54 mg/kg dry weight for the lake sediment.

In conclusion, then, we see that these past surveys confirm several of the mechanisms involving the fate of arsenic in aquatic environments. One last unanswered question involves the effect of sodium arsenite treatment on the aquatic eco-system.

Effects of Sodium Arsenite Treatment. Concern about the effects of sodium arsenite treatment dates aback to before 1930, at which time the herbicide was widely used to control aquatic vegetation in fisheries ponds. Primary interest

at this time focused on fish growth and mortality, and several studies were conducted. From field investigations, Wiebe (1929) concluded that the exposure of 7 mg/l As_2O_3 of sodium arsenite for up to six days had no "harmful" effect on eight species of fingerlings after three months, and that a much longer exposure to 2 mg/l was likewise harmless. A more recent study, however, showed that goldfish indicated impaired behavior at a water concentration of 0.1 mg/l As_2O_3 , somewhat below the lethal concentration for 1% of the fish (Weir and Hine, 1970).

Returning to the earlier studies, since the direct effects of sodium arsenite treatment on the fish population were considered insignificant, attention was turned to the aquatic organisms that the fish feed on. Surber (1930) suggested from field studies that a treatment of 1.7 to 2.0 mg/l As_2O_3 would not kill any of the important food organisms. This assertion was then confirmed with extensive laboratory studies utilizing aquaria and including approximately nineteen species of aquatic organisms (Surber and Meehan, 1930).

A recent review by Mullison (1970) reports that sodium arsenite treatment at 8 mg/l As_2O_3 had a drastic effect on the aquatic community metabolism, as evidenced by the diurnal O_2 curve. Uptake by the plants was rapid, and death occurred within five days. Aquatic organisms showed great variations in their sensitivity to the chemical, from no effect to total eradication, and the survival and growth of young fish declined. Cowell (1963) concluded that phytoplankton were generally insensitive to treatment at 4 mg/l As_2O_3 , though drastic reductions in zooplankton occurred. Field investigations by Lawrence (1957) concurred, and noted that though recovery of the phytoplankton population began two months after treatment, it was not complete for almost a year. In addition, this study reported that plankton populations increased slightly a few days after treatment along with the phosphorous content of the water, presumably due to the substitution

of arsenate for phosphate in the sediments, an arsenic removal mechanism mentioned previously.

Though the above biological effects of sodium arsenite treatment have been shown to occur, the reasons are not fully understood. Only a handful of studies concerning this topic have been conducted, and none have dealt directly with the aquatic ecosystem. In general, it is known that arsenate is about sixty times less toxic to aquatic organisms (and to man) than is arsenite (Ferguson and Gavis, 1972). But the popular theory explaining arsenic toxicity concerns the inhibition of enzymes involved with the phosphate uptake system of organisms by arsenate (Blum, 1966; Rothstein, 1963). This apparent discrepancy may be resolved by postulating the reduction of arsenate to arsenite by the organism, and is supported in studies by Glazer (1968).

The past studies found in the literature may thus be divided into several categories: 1) general surveys to determine arsenic levels present in lake water and sediment, 2) short range studies dealing with concentrations found in lake water, sediment, and biota as a result of sodium arsenite treatment, 3) short range studies concerned with the effects of such treatment on the biota, and 4) surveys of the long range accumulation of arsenic in arsenic-rich aquatic environments. A major shortcoming of these past studies is that the long range results and biological effects of sodium arsenite treatment have not been looked into. Both the short range studies and the arsenic cycle postulated earlier indicate what to expect, but confirming field data is warranted.

SCOPE OF THE STUDY

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This particular study was undertaken to provide some of the missing data, specifically, the long term results of sodium arsenite treatment. Water and sediment samples from seventeen lakes in western Massachusetts were collected and analyzed to determine their arsenic content. Four of these lakes were known to have histories of treatment with sodium arsenite, and the remainder had never been treated (Boschetti, 1973; Coleman, 1973; Coughlin, 1973; Hood, 1973). Treatments varied in number, dosage, and date. The untreated lakes also presented a wide spectrum with respect to man's industrial, agricultural, and residential activities, and ranged from practically untouched to heavily polluted. Appendix III contains an extensive review of the characteristics of each lake, and this data is summarized in Tables 2 and 3.

Samples of lake biota were not collected for the primary reason that previous surveys and the cycle of arsenic indicate that the lake sediment is the ultimate sink for arsenic. Thus sediment samples would provide the best basis for determining whether or not a relationship exists between sodium arsenite treatment and arsenic levels in the aquatic environment. Water concentrations were of interest because of their relationship to sediment concentrations and because of the effect on aquatic biota. It is of course difficult to establish an exact correlation between treatment history, sediment concentrations and arsenic levels in the water because of the varying geological, chemical, and biological factors for each lake. A rough correlation was hoped for.

Secondary results of this study will also include a comparison of the arsenic levels found with values in the literature to determine if the aquatic ecosystem might be affected. In addition, much needed background data will be supplied, and it will also be possible to speculate on the effect of man's activities with respect to the other possible sources of arsenic mentioned earlier.

Table 2

Summary of Pond Uses

Pond	Industrial	Cooling Water	Flood Control	Hunting	Boating	Swimming	Water Skiing	Fishing	Ice Skating	Ice Fishing	Camping	Aesthetics	Residential	Farming	Municipal	Highway	Industrial	Park	Swamp	Vacant	Sodium Arsenite Treatment?	
L. Metacomet				1	3	1		1		1			7									Yes
Indian Lake ¹													8		9							No
Prindle Lake ¹													2						6			Yes
Shaw Pond				3				3					3						8			Yes
Center Pond	2				2	2	23		1	1			7						3			No
Cranberry Pond							3											9				No
Borrow Pit Pond ²																						No
Pelham Lake ¹													1	1								No
North Pond				1	3		2			3								9				No
Cheshire Res. ²				3			33	3					3	2				1	3			No
Silver Lake	3	3											3		6	3			3			No
Pontoosuc L.						2	24		2				9	1								No
Stockbridge Bowl	1			3	2	22	2	2	1	1			8	1								Yes
Guilder Pond							1		2									9				No
Upper Spectacle				2					2	2								9				No
Big Benton Pond				1	3	2	2						7						3			No
West Lake			2	2	2	2			2										9			No

* Pond Use: 1=light, 2=moderate, 3=heavy,4-excessive

** Land Development: 0=0-9% 5=50-59%
 1=10-19% 6=60-69%
 2=20-29% 7=70-79%
 3=30-39% 8=80-89%
 4=40-49% 9=90-100%

Notes: 1. no pond use data available
 2. no data available

Source: McCann and Daly, 1972a, 1972b, 1973.

Table 3
Summary of Arsenic Treatments¹

<u>Lake</u>	<u>Year</u>	<u>Dosage</u> ²	<u>Concentration</u>	
			<u>top 2-1/2'</u>	<u>fully mixed</u>
L. Metacomet	1970	200 lb/acre	28 mg/l	7 mg/l
Prindle L.	1957	52	7.8	3.2
Shaw Pond	1969	270	39	5.2
Stockbridge Bowl	1960	6	0.9	0.08
	1961	59	8.7	0.81
	1967	32	4.8	0.45
	1968	32	4.8	0.45
	1969	86	12.6	1.2
Total		215		

- Notes - 1. Sodium Arsenite, expressed as As_2O_3
2. Dosage, in lb/acre, appears to be the most logical method to compare treatments with arsenic levels in the lake sediment. The other two columns are included only for comparison purposes and to postulate biological effects.

Analytical Determination of Arsenic. From three to ten samples of water and sediment were collected at each lake, the number and locations being chosen to achieve a representative picture of the particular lake. Water samples were collected at the surface using one-quart polyethylene bottles, and sediment samples were collected with an Eckman dredge. At locations where the lake was believed to be stratified (judging from the temperature of the sediment), depth water samples were also taken, again utilizing the Eckman dredge. Sample storage and preparation techniques are described in detail in Appendix I.

An in-depth literature search revealed numerous methods for the determination of arsenic (see Bibliography). None of these methods was deemed totally acceptable, though some were definitely better than others. The final decision was to use flameless atomic absorption spectrophotometry (AAS) with the heated graphite atomizer (HGA) (Fernandez and Manning, 1971a). It was felt that the excellent detection limit ($<.02$ mg/l As) was an adequate trade-off with the potential interference from salts and other background absorption experienced with the determination of arsenic by AAS. Analyses were thus run on a Perkin-Elmer model 303 atomic absorption spectrophotometer and a model HGA-70 graphite furnace. Appendix I contains the operating conditions.

Results of the analyses of the samples unfortunately indicated that the effects of background absorption were much greater than expected (see Figure I-1, Appendix I). The noise level was particularly high as was the absorption during the drying and charring programs due to the evaporation of the nitric acid in the samples. The greatest problem, however, was the molecular absorption due to the furnace glow during atomization. Apparently, the light from the furnace was much more intense than that from the arsenic hollow cathode lamp and totally overrode the optics of the AAS. Since measurement of the sample absorbance occurs

during this last program, the values obtained are at best questionable. Perkin-Elmer went so far as to say that the combination of the above three effects renders the data worthless (Slavin, 1973). The concentrations obtained using our instrument support this contention; they were two to three orders of magnitude greater than expected from past surveys.

Several instrument accessories are needed to correct the above problems. The much more intense arsenic electrodeless discharge lamp (EDL) would eliminate both the noise problem and a majority of the background absorption during atomization. A deuterium background corrector is necessary to eliminate the remainder of this absorption, and will also cut out the nitric acid signal as well as the absorption from any interfering elements in the sample matrix (Kahn, 1968). Theoretically, only the absorption due to arsenic is measured. Since it was not feasible for us to obtain these accessories, Perkin-Elmer agreed to analyze a limited number of samples using their equipment: a model 305 AAS with the above accessories and a model HGA-2000 graphite furnace. To obtain representative data that would serve the purposes of this study, equally weighted composites of the water and sediment samples were prepared by taking 1 ml from each of the original samples, and then analyzed at Perkin-Elmer using the particular instruments cited.

The limited time at Perkin-Elmer unfortunately made it impossible to perform a complete statistical analysis of the analytical method. A simplified analysis is presented in Appendix II, though, as well as other statistical handling of the data collected.

RESULTS

RESULTS

The concentrations of arsenic determined for the composite water and sediment samples for each lake are listed in Table 4. For the purpose of discussion, the lakes may be clearly divided into three groups:

<u>Treated</u>	<u>Not Treated</u>	
	<u>High Background</u>	<u>Low Background</u>
Lake Metacomet	Indian Lake	Center Pond
Prindle Lake	Silver Lake	Cranberry Pond
Shaw Pond	Pontoosuc Lake	Borrow Pit Pond
		Pelham Lake
		North Pond
		Cheshire Res.
		Guilder Pond
		Upper Spectacle
		West Lake
		Big Benton Pond

The treated lakes generally had water concentrations between 10 and 20 $\mu\text{g/l}$ As and sediment levels from 150-200 mg/kg As dry weight. Lakes with low background levels ranged from 1-10 mg/kg for the sediment, and water concentrations were less than 1 $\mu\text{g/l}$ As. The high background level lakes had corresponding values of 10-40 mg/kg and 1-4 $\mu\text{g/l}$ As.

The size of the 95% confidence intervals varied with each sample's analysis, and depends on the sample aliquot and the dilution factor (see Appendix II). Variations between lakes should be analyzed with these values in mind.

A linear regression was performed to compare water and sediment levels in all of the lakes. The calculated correlation coefficient, +.946, indicates that

Table 4
Arsenic Levels

<u>Lake</u>	<u>Water Samples¹</u>		<u>Sediment Samples²</u>	
	<u>Concentration</u> <u>($\mu\text{g}/\text{l}$)</u>	<u>95% Confidence</u> <u>($\mu\text{g}/\text{l}$)</u>	<u>Concentration</u> <u>(mg/kg)</u>	<u>95% Confidence</u> <u>(mg/kg)</u>
Metacomet	12.3	$\pm .44$	151	± 21
Indian Lake	3.76	$\pm .18$	39	± 2
Prindle Lake	11.6	$\pm .44$	196	± 21
Shaw Pond	10.9	$\pm .44$	211	± 21
Center Pond	0.64	$\pm .18$	2.4	$\pm .44$
Cranberry Pond	0.76	$\pm .18$	1.7	$\pm .44$
Borrow Pit Pond	0.76	$\pm .18$	1.1	$\pm .44$
Pelham Lake	0.38	$\pm .18$	4.6	$\pm .44$
North Pond	0.31	$\pm .18$	6.1	$\pm .44$
Cheshire Reservoir	0.91	$\pm .18$	9.4	$\pm .44$
Silver Lake	0.64	$\pm .18$	20	± 2.2
Pontoosuc Lake	2.3	$\pm .44$	6.1	$\pm .44$
Stockbridge Bowl	17.1	$\pm .88$	176	± 21
Guilder Pond	0.20	$\pm .18$	6.6	$\pm .44$
Upper Spectacle Pond	0.36	$\pm .18$	3.1	$\pm .44$
West Lake	0.69	$\pm .18$	2.1	$\pm .44$
Big Benton Pond	0.87	$\pm .18$	1.2	$\pm .44$

Notes: ¹Water concentrations expressed as $\mu\text{g As}/\text{l}$.

²Sediment concentrations expressed as $\text{mg As}/\text{kg}$ dry sediment passing through a No. 30 sieve.

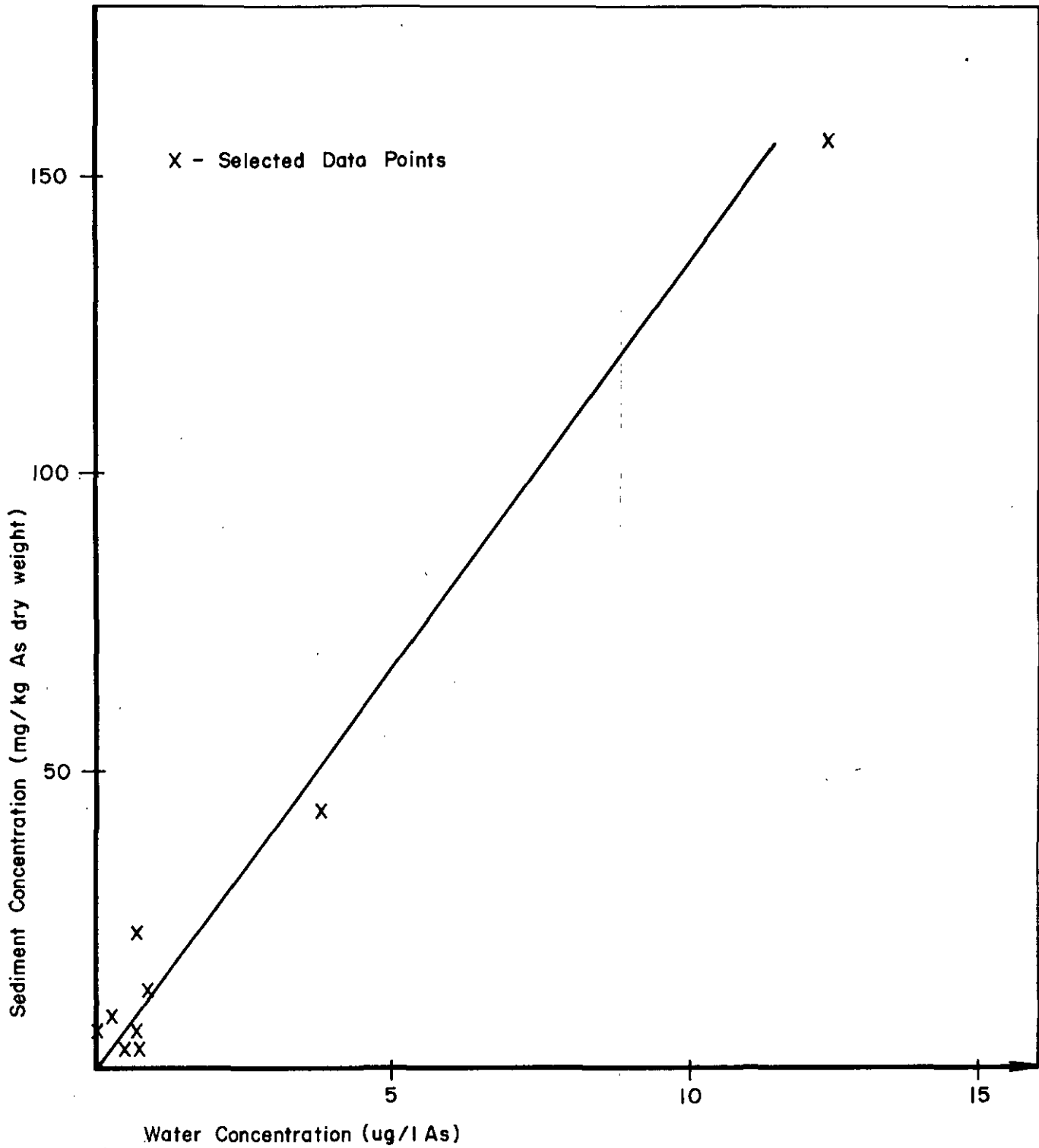


FIGURE 3
Sediment - Water
Linear Regression Curve

DISCUSSION

DISCUSSION

The strong correlation between water and sediment levels of arsenic indicates that there is a chemical relationship between the two phases, as described in the previously presented arsenic cycle. The high correlation coefficient and resulting linearity also suggest a similarity between the lakes with respect to the aquatic chemistry of arsenic. Furthermore, since concentrations in the sediment are from 10 to 20,000 times the corresponding water concentrations, the sediment does appear to be the final fate for arsenic. Biological interplay was, of course, not studied in this project.

Several of the lakes in this survey were also considered by Isaac and Delaney (1972). Only sediment samples were analyzed in the latter survey, and the results compare favorably with this study:

<u>Lake</u>	<u>This Study</u>	<u>Isaac and Delaney</u>
Cranberry Pond	1.7 mg/kg As	1.9 mg/kg; mean of two samples
Silver Lake	20	17; mean of 5 samples range; 11-28 mg/kg
Big Benton Pond	1.2	1.5; mean of two samples

In the study by Isaac and Delaney, analyses were done by the Standard Methods approved Gutzeit method (Standard Methods, APHA, 1971). The favorable comparison of this data with the previous study suggests that AAS with the HGA could be approved also.

Let us now consider the specific groups of lakes mentioned earlier.

Treated Lakes. The arsenic levels present in the four lakes with treatment histories clearly show the result of sodium arsenite treatment. Both water and sediment concentrations are from 10 to 100 times greater than expected (and determined) background levels. Direct comparison of these values to levels

reported in the literature is not really possible, though, since none of the studies found was long term in scope. Two conclusions may be drawn, however. The arsenic levels in the lake waters are well below the 100 $\mu\text{g/l As}_2\text{O}_3$ (76 $\mu\text{g/l As}$) limit causing impaired behavior of goldfish (Weir and Hine, 1970). Additionally, though these concentrations are above the U.S.P.H.S. recommended level (10 $\mu\text{g/l As}$) for drinking water, none of these lakes would be rejected as a drinking water source on the basis of arsenic content (U.S.P.H.S., 1962). Also noteworthy of mention is that the water and sediment levels in the treated lakes are well below the levels reported in a geothermal area, up to a factor of 5 (Reay, 1972). This difference is probably due to the continuous source of arsenic in a geothermal area and the likely lower level of arsenic dosage by sodium arsenite treatment.

The various uses of these lakes appear to have no effect on the arsenic levels (Table 2). It thus appears that sodium arsenite treatment greatly overshadows the effects from these uses, as expected. There does, however, appear to be an excellent correlation between arsenic dosage and the arsenic levels in the sediments (Table 3). Excepting Prindle Lake, the greater the dosage (lb/acre) was, the greater the sediment arsenic level. The deviation by Prindle Lake can best be explained by unreported treatments. This lake is privately owned by its residents, and Mr. John Panchuck, President of the Prindle Lake Association, remembers numerous other treatments having been made, though he has no records. Thus the dosage reported for Prindle Lake is incorrect; considering the above correlation, 230-250 lb/acre would be a good estimate.

Considering other correlations, it is difficult to establish a relationship between the treatment dates and the arsenic levels in the sediments, due to

variations in lake chemistries, biota, and dosages. Whether or not the levels have achieved equilibrium is likewise hard to prove, though the sediment level-dosage correlation mentioned above would tend to support this idea.

The treatment histories may also be used to postulate the biological effects of the initial applications. Comparison with literature values indicates that if conventional methods of application were followed (top 2-1/2 feet), a drastic reduction in the zooplankton population would have occurred in all cases except the 1960 Stockbridge Bowl treatment (Cowell, 1963). The effect on the fish population is questionable, since none of the studies considered such high concentrations.

In making the above conclusions, one must keep in mind the precision of the analysis. All relationships still hold reasonably well when values are stretched to their 95% confidence intervals. Variations in lake chemistry and biota must also be considered, even though all lakes appear to be similar.

Lakes With High Background Levels. Indian Lake, Silver Lake, and Pontoosuc Lake all had arsenic levels in their water and/or sediment that were about five times higher than anticipated background or "natural" levels. In searching for an explanation, it should be noted that these values could in fact be natural - due to different water chemistry and biota or to geological formations containing above average arsenic levels. Assuming, though, that these lakes are similar to the others studied, there must be some other source of the arsenic contamination.

Considering the lake uses and the land development around the lakes (Table 2), two possible sources of arsenic for Indian Lake are residential and highway in nature. Silver Lake is also surrounded by roads, and is additionally highly industrialized. Pontoosuc Lake is primarily residential in nature. Many of the

sources of arsenic mentioned earlier in this paper were industrial, residential, and highway in nature. Stating the source of contamination, however, would only be speculation, since low background lakes also have these pond uses and land developments. And, as mentioned earlier, there may be no true contamination. It can only be stated that these pond uses appear to have some effect on this group of lakes' arsenic levels.

Lakes With Low Background Levels. Of the ten lakes with low background levels of arsenic, four appear to offer estimates for a "true" natural level of arsenic in western Massachusetts lakes: Cranberry Pond, Guildler Pond, Upper Spectacle Pond, and West Lake. Land development around all four lakes is either vacant or park, and pond uses are generally light or non-polluting. Mean levels for water and sediment from these lakes are $0.50 \mu\text{g/l}$ and 3.4 mg/kg As , respectively.

The other lakes in this grouping have varying amounts of human interference. The highest water and sediment concentrations come from Cheshire Reservoir, which incidently is the only lake whose surrounding land development includes agriculture. Whether or not this use is a contributing factor is again only speculation, though it does offer an answer. Big Benton Pond and Center Pond, while having much residential development and moderate pond use, report sediment levels less than the "true" natural level and water concentrations somewhat higher than the corresponding "natural" level. Thus, in this case, there appears to be no concentration - land development relationship.

Any of the lakes with low background levels would fit the range of natural values mentioned earlier in this paper; thus the mean levels of $0.50 \mu\text{g/l}$ and 3.4 mg/kg As should not be taken as absolute—they are only an estimate from the basis of pond use and land development.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS AND RECOMMENDATIONS

This study, with respect to its original goals, has in general turned out well. The results of sodium arsenite treatment were clearly shown, as well as the sediment-water concentrations correlation. This study also provided confirming field data as to one fate of arsenic in the aquatic ecosystem - the sediments. Much needed background data was supplied, indicating natural levels of 0.2 to 0.9 $\mu\text{g/l}$ As in the water and 1.1 to 9.4 mg/kg As dry weight in the sediment of lakes in western Massachusetts. The relationship of arsenic levels to land use was not clearly indicated, however. Data concerning the arsenic content of industrial and domestic discharges as well as fuels is needed for confirmation.

The major recommendation is that the study be continued. Biological data is sadly lacking, especially with respect to arsenic levels in the biota. Their role in the arsenic cycle should first be studied from field data, both in background lakes and in treated lakes. A follow-up study should involve laboratory determinations of the biological uptake of arsenic. All levels of the food chain should be studied.

As mentioned earlier, other removal mechanisms also need to be studied in greater depth. For example, chemical removal rates could be studied in both the laboratory and the field. The influence of iron concentrations in the water and phosphorous levels in the sediment would be especially interesting.

A final recommendation, without which the study could not be continued, is that the AAS deuterium background corrector and arsenic EDL be purchased. It is a modest investment for such a potentially enlightening study.

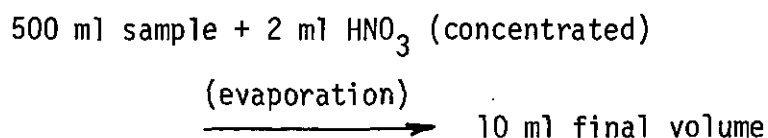
APPENDIX I - EXPERIMENTAL PROCEDURE

Appendix I - Experimental Procedure

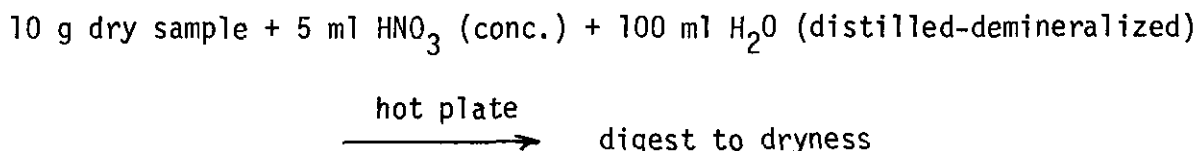
1. Sample Storage. Water samples were acidified at the time of collection with 5 ml concentrated nitric acid for preservation during storage (Standard Methods, APHA, 1971; EPA, 1971). Sediment samples were stored in 1-quart polyethylene bottles until preparation for analysis.

2. Sample Preparation.

a) Water samples - Because of the low levels of arsenic naturally occurring in lake waters, the samples were concentrated 50:1 by evaporation on a temperature-controlled hot plate:



b) Sediment samples - The samples were dried to constant weight at 60-70°C (48 hours)¹, pulverized using a mortar and pestle, and passed through a No. 30 sieve to eliminate stones and twigs. 10.0 g of the sample was then weighed out on a triple beam balance and digested on a hot plate as follows:



This procedure was repeated once to ensure complete digestion. The residue was then wetted with 2 ml concentrated HNO₃ and distilled-demineralized water, filtered through a No. 42 Whatman filter, and brought up to 100 ml with distilled-demineralized water (Isaac and Delaney, 1972):

¹The time of drying necessary to achieve constant weight was determined experimentally with 100 g (wet) aliquots of a representative sediment (triplicate analyses). The drying curve is shown below.

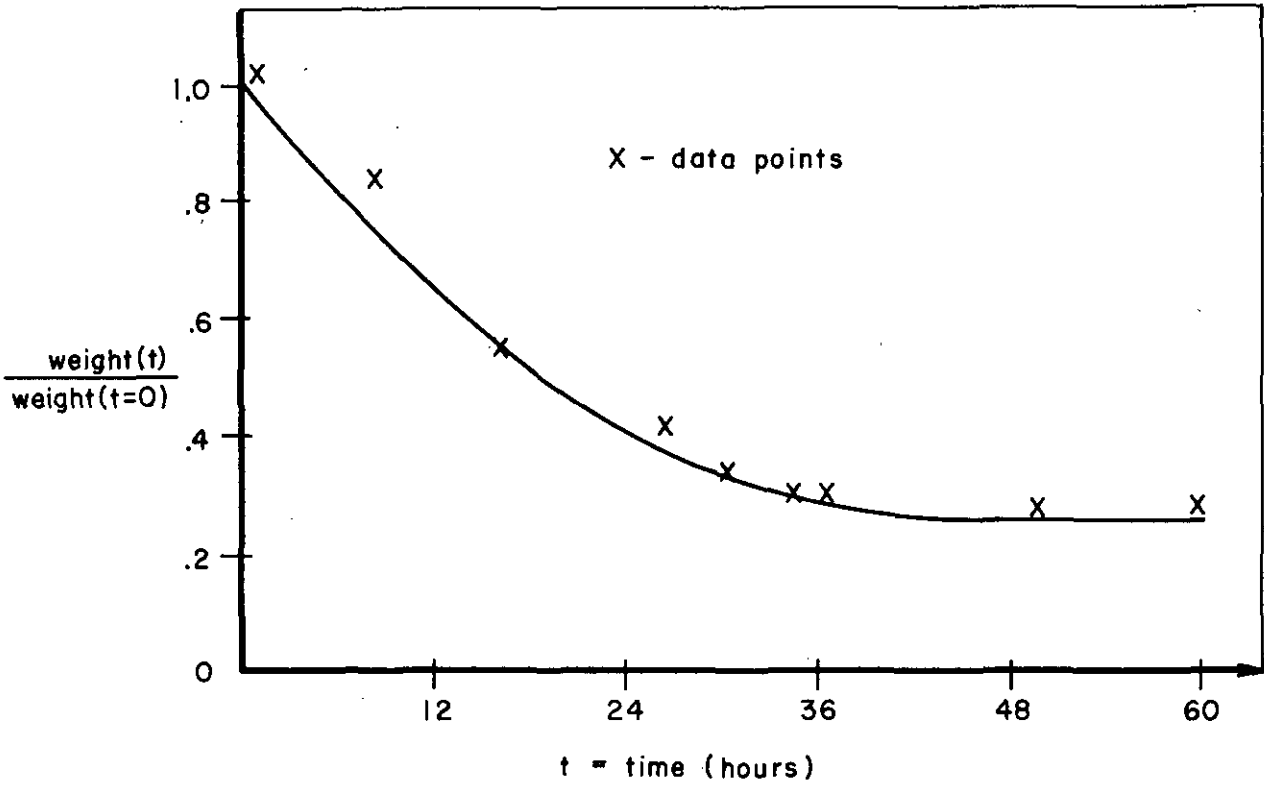


FIGURE I-1
Sediment Drying Curve

$$\frac{1 \text{ mg As}}{10 \text{ g dry sediment}} = \frac{1 \text{ mg As}}{100 \text{ ml filtrate}}$$

$$1 \text{ mg/kg As dry weight} = 100 \text{ mg/l (filtrate)}$$

3. Sample Analysis. All 250 or so samples were initially analyzed in our laboratory with the Perkin-Elmer 303 AAS and HGA-70. The following operating conditions were used (Barnett, 1973):

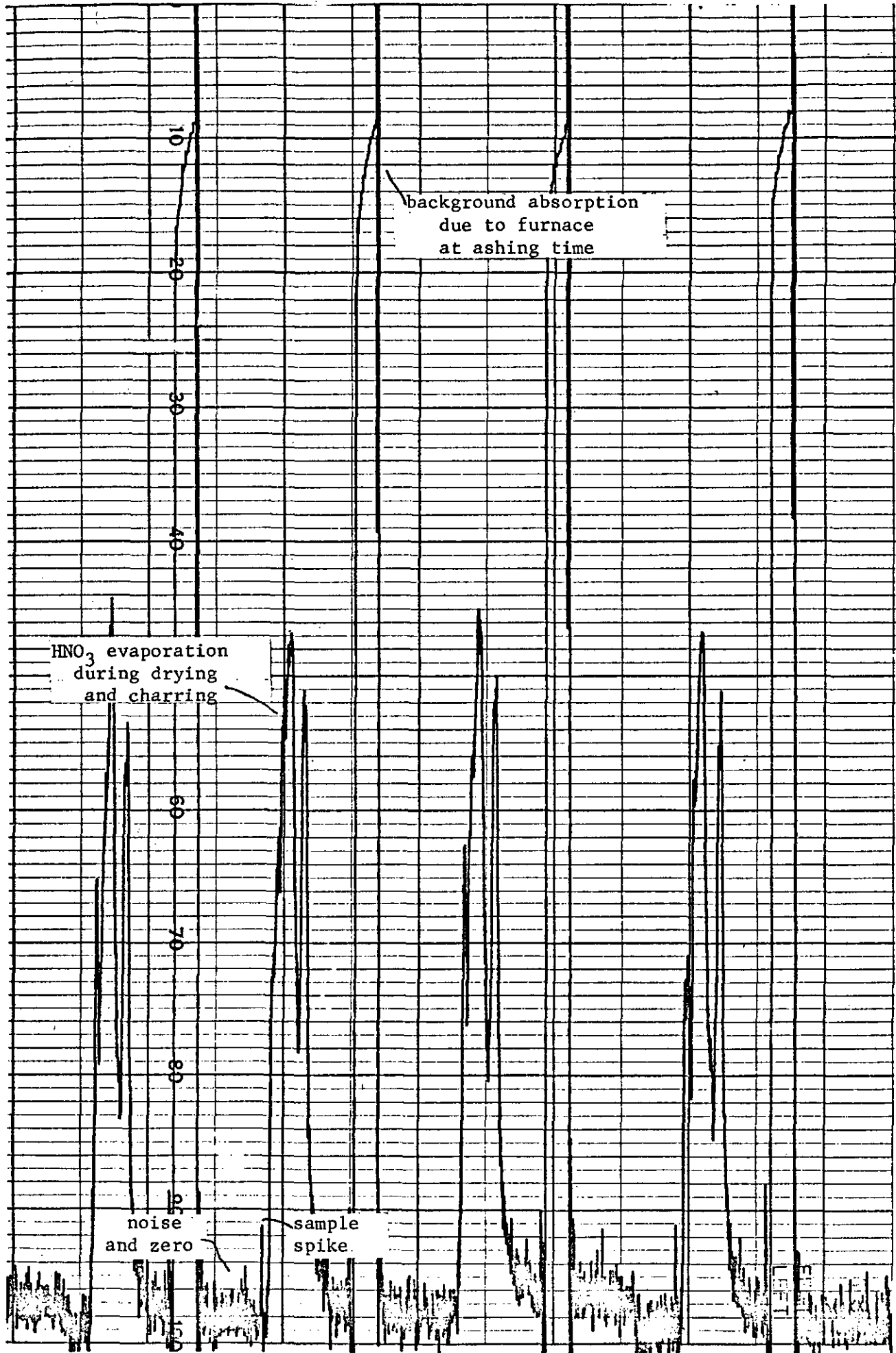
- 20 l aliquots
- AAS settings
 - wavelength = 1937 A
 - slit = 5²
 - filter out
 - lamp current = 20 milliamps
- HGA settings
 - program 4: dry @ 100⁰C for 20 seconds
 - char @ 325⁰C for 30 seconds
 - atomize @ 2500⁰C for 15 seconds
- Texas Instruments chart recorder @ 0.75 in/min.

A sample of the chart recorder tracing is supplied as Figure I-2. This tracing clearly shows the noise and background absorption problems mentioned in the text.

At Perkin-Elmer, a model 305B AAS with deuterium background compensation and electrodeless discharge lamp (EDL) was used with an HGA-2000 graphite furnace.

²Recommended slit setting for the determination of arsenic by AAS is 4. For excessive noise encountered with weak lamps, as with arsenic's hollow cathode lamp, one larger step (5) is suggested as remedy (Perkin-Elmer, 1971).

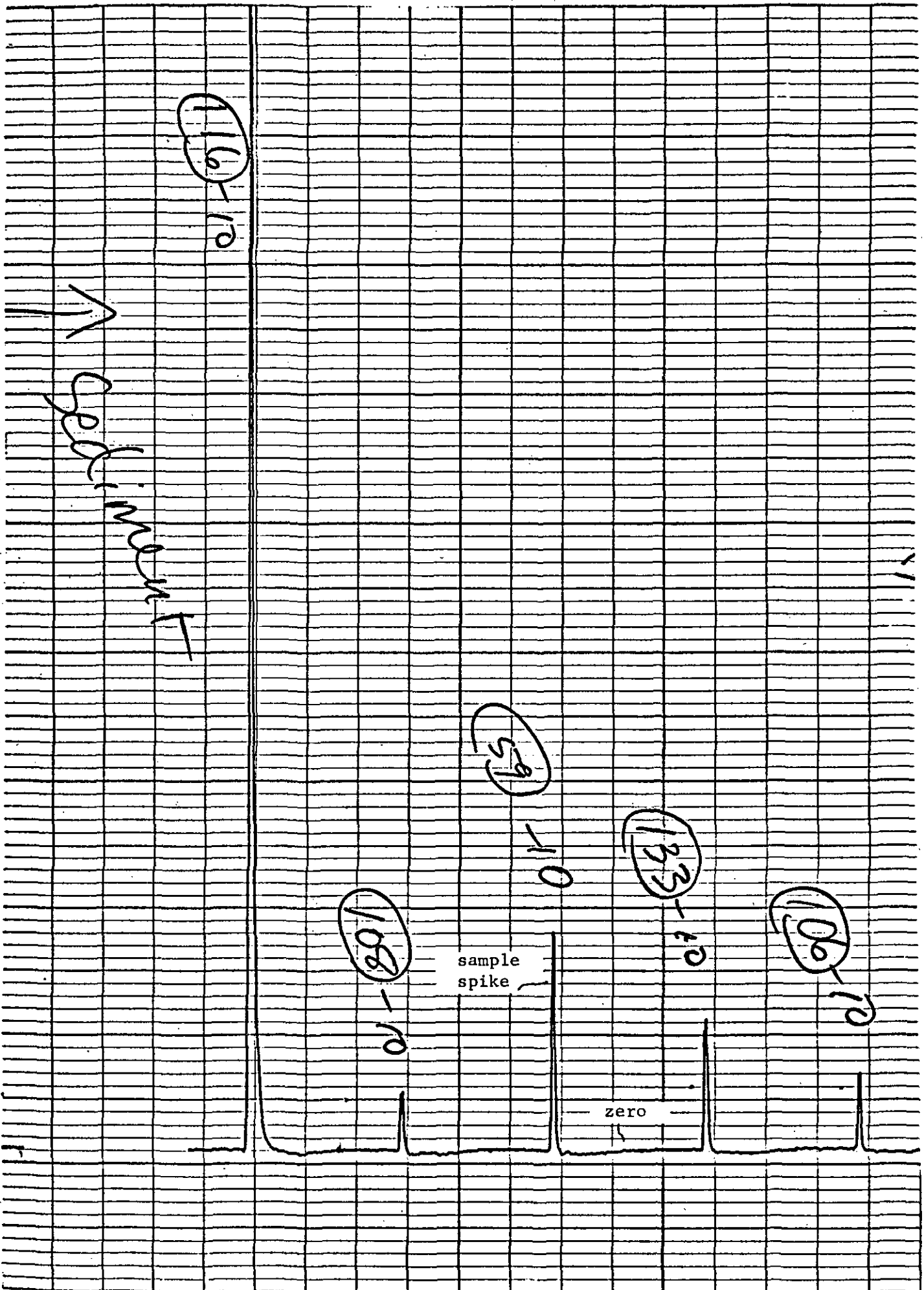
Figure I-2 Sample Tracing UMass



The operating conditions were (Slavin, 1973):

- 10,20, and 50 μ l aliquots
- AAS settings
 - wavelength = 1937 A
 - slit = 4
 - filter out
 - lamp power = 8.5 watts
- HGA settings
 - dry @ 125⁰C for 20 seconds
 - char @ 300⁰C for 40 seconds
 - atomize @ 2700⁰C for 15 seconds

The much improved chart recorder tracing is shown in Figure I-3.



APPENDIX II - STATISTICAL ANALYSIS OF THE DATA

Appendix II - Statistical Analysis of the Data

1. Precision of the Analysis. Atomic absorption spectrophotometry with the graphite furnace is particularly sensitive to operator technique as well as the complexity of the matrix that the element of interest is in. This is especially true of the instrumentation in our laboratory (303 AAS and HGA-70), though the setup at Perkin-Elmer exhibited excellent reproducibility. The limited time in Norwalk unfortunately made a determination of the standard deviation impossible, but the precision of the analysis may be estimated in another way, using the calibration data (Holman, 1971; Velz, 1970).

A linear regression was applied to the calibration data obtained at Perkin-Elmer, and the standard error of estimate (s_e) of the data was calculated:

$$s_e = \sqrt{\frac{\sum(y_o - y)^2}{N}}$$

y_o = the value of absorbance expected for a particular concentration

y = the value of absorbance actually recorded

N = number of calibration points obtained

The standard error of estimate may next be used to calculate the 95% confidence intervals for the calibration curve, which will subsequently be used for the actual sample determinations:

$$\bar{y}$$

\bar{y} = mean value of absorbance obtained for the sample

n = number of replicate determinations of the sample

For my calibration data,

$$s_e = 0.004 \text{ absorbance unit, and}$$

$$95\% \text{ confidence interval} = \pm 0.01008 \text{ absorbance unit for a single sample}$$

determination. This value translates to 0.44 ng As, and the actual concentration

range depends on the sample aliquot and the dilution factor. Calculations result in the following table:

Table II-1 - 95% Confidence Intervals

<u>Sediment Samples</u>		<u>Water Samples</u>	
<u>Dilution</u>	<u>95% Confidence</u>	<u>Aliquot</u>	<u>95% Confidence</u>
0	+0.44 mg/kg	10 µl	+ 0.88 µg/l
1:25	2.2	20	0.44
1:25	21	50	0.18

2. Other Statistical Analyses. Linear regressions were also performed to compare arsenic concentrations determined in our laboratory to those determined at Perkin-Elmer, and to compare sediment and water levels of arsenic. The correlation coefficient, r, is used to determine if a relationship does indeed exist. In comparing 17 data points, r must be greater than 0.75 if one desires to be 99.73% sure that a relationship exists.

(Velz, 1970):

$$r = \frac{(\sum (x-\bar{x})(y-\bar{y}))}{(\sum (x-\bar{x})^2 \cdot \sum (y-\bar{y})^2)^{1/2}}$$

x = concentration

\bar{x} = mean of concentrations

y = corresponding absorbance

\bar{y} = mean of absorbances

The values of r presented below indicate that there is no relationship between the data obtained in our laboratory and the data collected at Perkin-Elmer, again showing the worthlessness of the original data. The calibration and water sediment correlations are strong, however.

Table II-2 - Correlation Coefficients

<u>Correlation</u>	<u>r</u>
arsenic levels in the composite water samples (UMass vs. Perkin-Elmer)	0.521
arsenic levels in the composite sediment samples (UMass vs. Perkin-Elmer)	0.092
composite samples, water vs. sediment (Perkin-Elmer)	0.946
Calibration Curve	0.999

APPENDIX III - LAKES DATA

Lake Metacomet

1. Background Data (McCann and Daly, 1972b).

location - Belchertown, Hampshire County

2.5 miles NW from center of town

size - 74 acres

mean depth = 10'

maximum depth = 18'

limnology - natural pond

eutrophic

abundant vegetation

pond use - light hunting, swimming, fishing, and ice fishing; heavy boating

land development - residential, 70-80%

2. Sodium Arsenite Treatment - 3700 gallons in 1970

4# As_2O_3 per gallon

3. Sampling Locations (see map)

#1 - 100' from inlet, depth = 10'

#2 - 100' from large willow tree, depth = 5'

#3 - 100' from island, depth = 14'

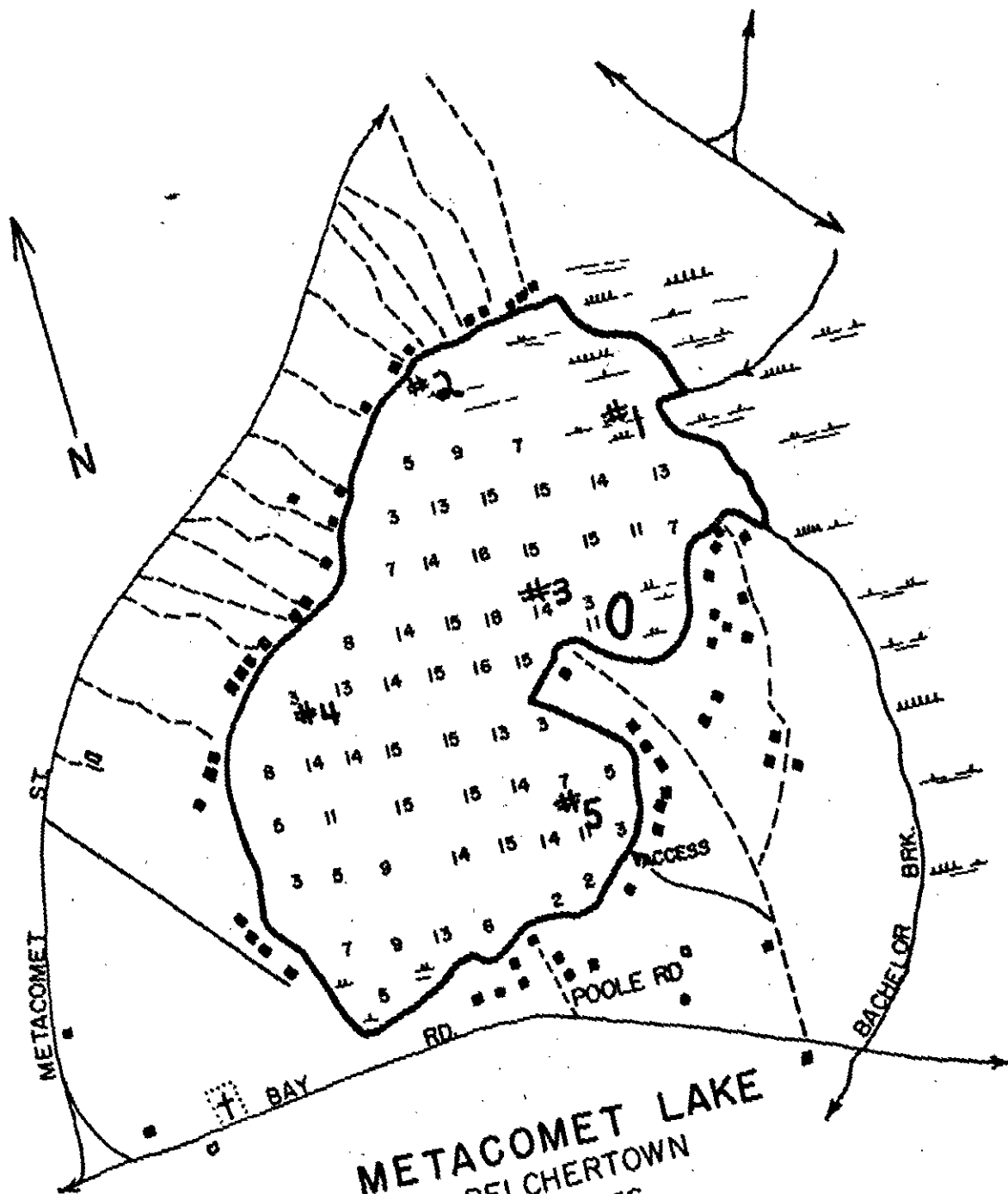
#4 - 150' from point, depth = 13'

#5 - 50' from access, depth = 3'

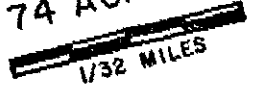
4. Arsenic Levels (composites)

Water - 12.3 $\mu\text{g}/\text{l}$ As

sediment - 151 mg/kg dry weight As



METACOMET LAKE
 BELCHERTOWN
 74 ACRES



Indian Lake

1. Background Data (McCann and Daly, 1973)

Location - Worcester, Worcester County

2.0 miles N from town center

size - 190 acres

mean depth = 8'

maximum depth = 15'

limnology - enhanced pond

eutrophic

common vegetation

land development - residential, 80-90%

highway, 90-100%

2. Sodium Arsenite Treatment - None

3. Sampling Locations (see map)

#1 - 50' from island, depth = 1'

#2 - 150' from bridge, depth = 4'

#3 - 30' from cove, depth = 6'

#4 - 100' from beach, depth = 7'

#5 - midway between cove and lighthouse, depth = 12'

#6 - 300' from lighthouse, depth = 13'

#7 - 30' from lighthouse, depth = 8'

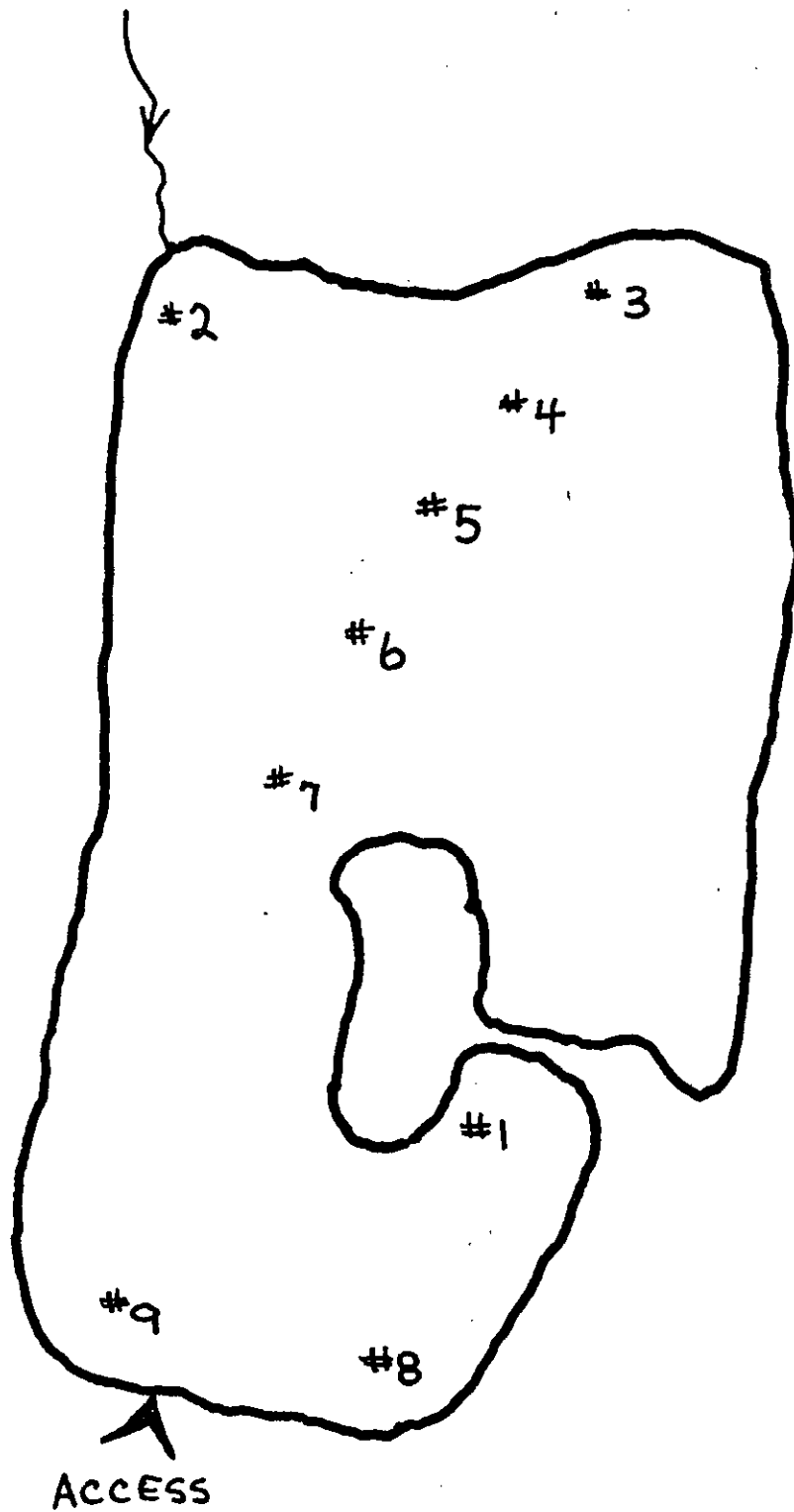
#8 - 20' from highway, depth = 5'

#9 - 30' from access ramp, depth = 6'

4. Arsenic Levels (Composites)

water - 3.76 $\mu\text{g/l}$ As

sediment - 39 mg/kg dry weight As



INDIAN LAKE

Prindle Lake

1. Background Data (McCann and Daly, 1973)

location - Charlton, Worcester County

size - 71 acres

meant depth = 8'

limnology - enhanced pond

eutrophic

land development - residential, 20-30%

vacant, 60-70%

2. Sodium Arsenite Treatment - 930 gallons in 1957 4# As_2O_3 per gallon

3. Sampling Locations (see map)

#1 - center of cove, depth = 6'

#2 - 50' off point, depth = 5'

#3 - center of cove, depth = 5'

#4 - mouth of large cove, depth = 6'

#5 - 150' from shore, depth = 5'

#6 - 40' from shore, depth = 4'

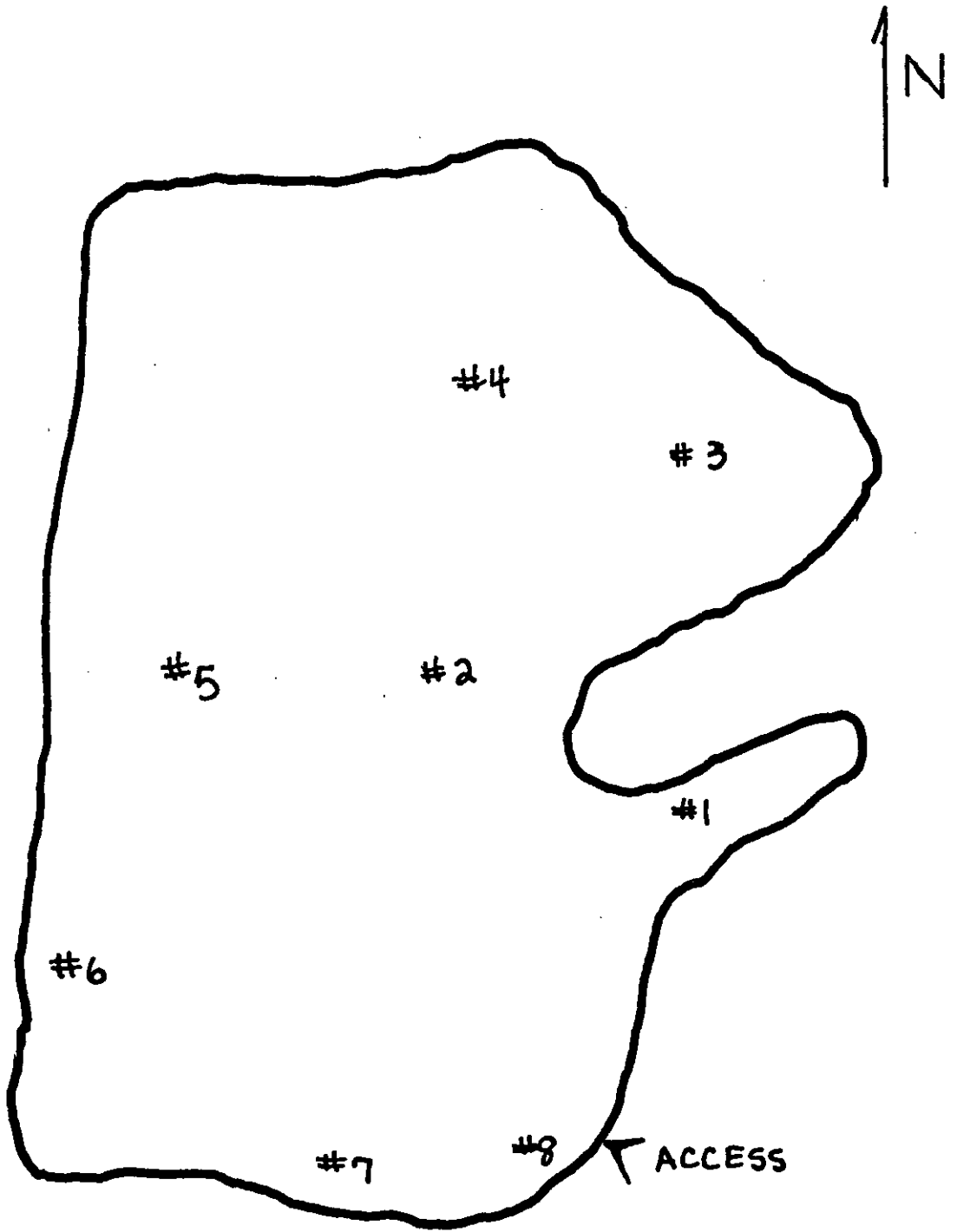
#7 - 25' from shore, depth = 5'

#8 - 3' from shore, depth = 1'

4. Arsenic Levels (Composites)

Water - 11.6 $\mu\text{g/l}$ As

Sediment - 196 mg/kg As dry weight



PRINDLE LAKE

Shaw Pond

1. Background Data (McCann and Daly, 1972a)

location - Becket, Berkshire County

0.5 mile SE from center of town

size - 100 acres

mean depth = 13'

maximum depth = 19'

limnology - enhanced pond

eutrophic

abundant vegetation

pond use - heavy hunting and fishing

land development - residential, 30-40%

vacant, 60-70%

2. Sodium Arsenite Treatment - 6670 gallons in 1969

4# As_2O_3 per gallon

3. Sampling Locations (see map)

#1 - 10' from shore, depth = 3'

#2 - middle of lake, depth = 9'

#3 - 50' from shore, depth = 9'

#4 - middle, depth = 14'

#5 - 100' from N shore, depth = 15'

#6 - 100' from outlet, depth = 13'

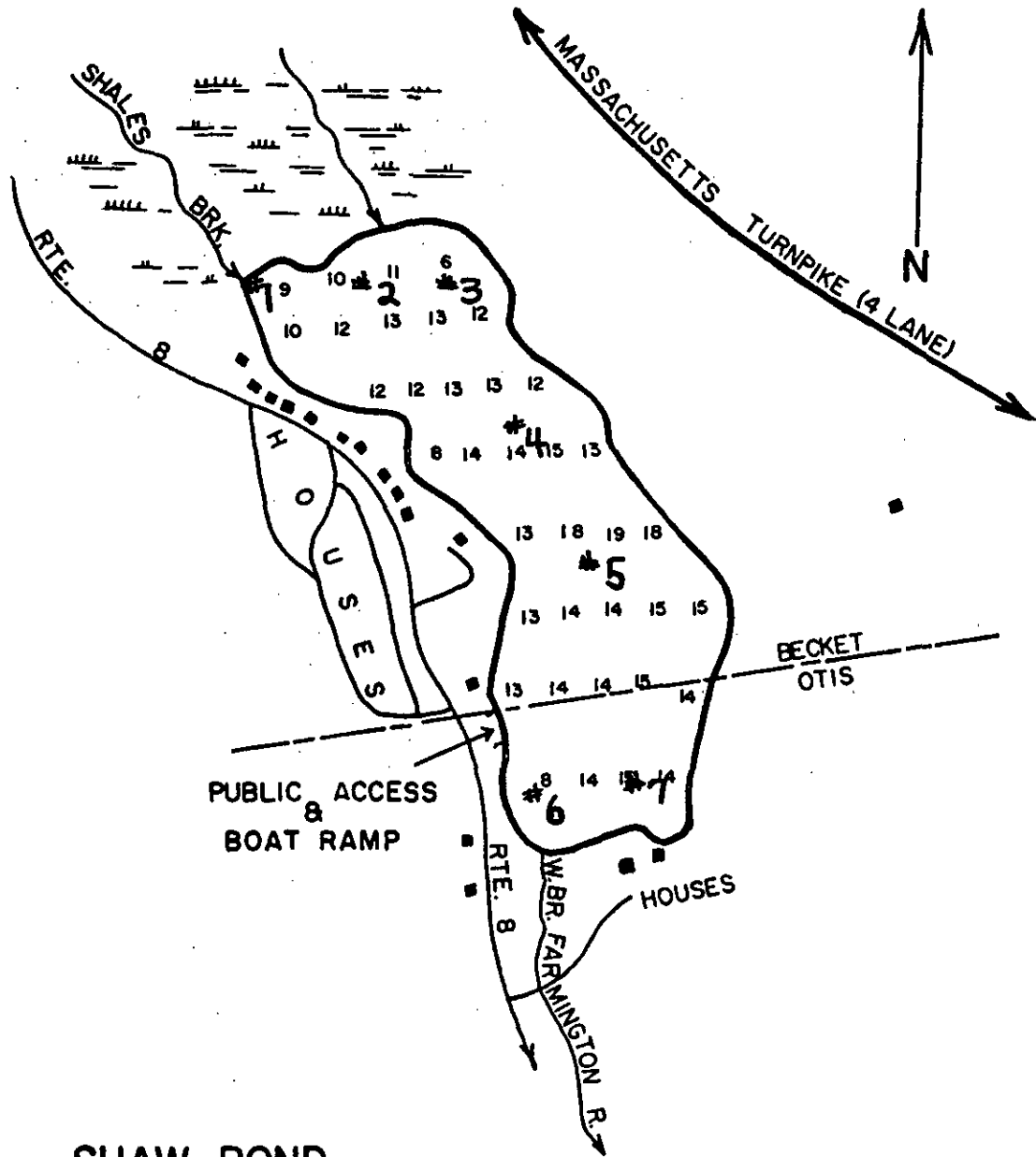
#7 - 30' from shore, depth = 4'

#8 - 50' from boat ramp, depth = 8'

4. Arsenic Levels (Composites)

water - 10.9 $\mu\text{g}/\text{l}$ As

sediment - 211 mg/kg As dry weight



SHAW POND
 BECKET
 100 ACRES



1/16 MILES

Center Pond

1. Background Data (McCann and Daly, 1972a)

location - Becket, Berkshire County

0.4 mile N from center of town

size - 125 acres

mean depth = 8'

maximum depth = 14'

liminology - enhanced pond

eutrophic

scant vegetation

pond use - light camping

moderate industry, boating, swimming, and water skiing

heavy fishing

land development - residential, 70-80%

vacant - 30-40%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - center of cove, depth = 5'

#2 - 25' from outlet, depth = 5'

#3 - middle, depth = 14'

#4 - middle, depth = 11'

#5 - middle, depth = 13'

#6 - middle, depth = 13'

#7 - 30' from shore, depth = 10'

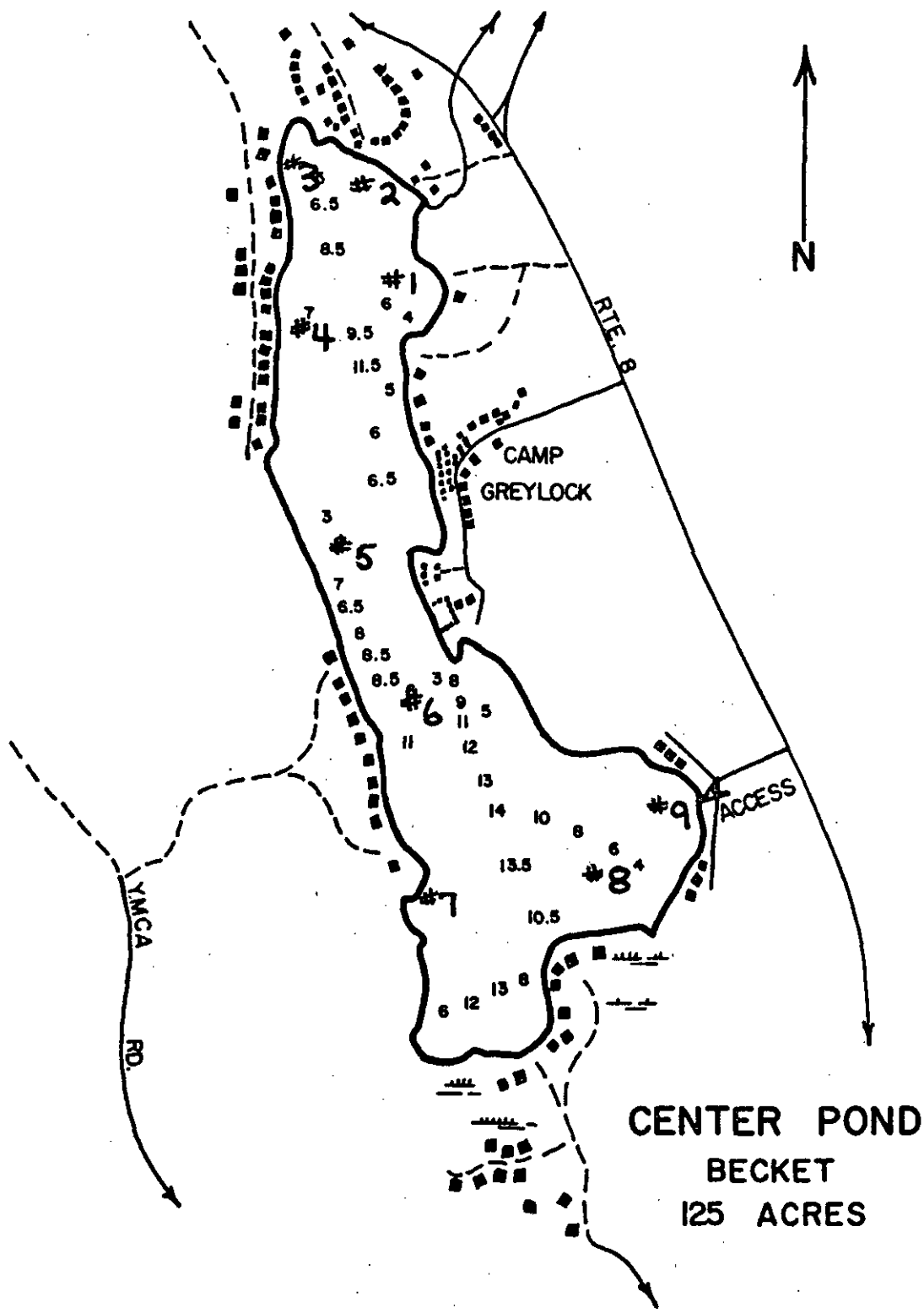
#8 - 25' from shore, depth = 4'

#9 - 50' from shore, depth = 8'

4. Arsenic Levels (composites)

water - 0.64 $\mu\text{g}/\text{l}$ As

sediment - 2.4 mg/kg As dry weight



**CENTER POND
BECKET
125 ACRES**

Cranberry Pond

1. Background Data (McCann and Daly, 1972a)

location - Sunderland, Franklin County

3.6 miles NE from center of town

size - 24 acres

mean depth = 4'

maximum depth = 26'

limnology - enhanced pond

eutrophic

common vegetation

pond use - heavy fishing

land development - park, 90-100%

2. Sodium Arsenite Treatment - none

3. Sampling locations (see map)

#1 - 10' from tree stump in water, depth = 4'

#2 - middle of deep area, depth = 18'

#3 - 50' from W shore, depth = 5'

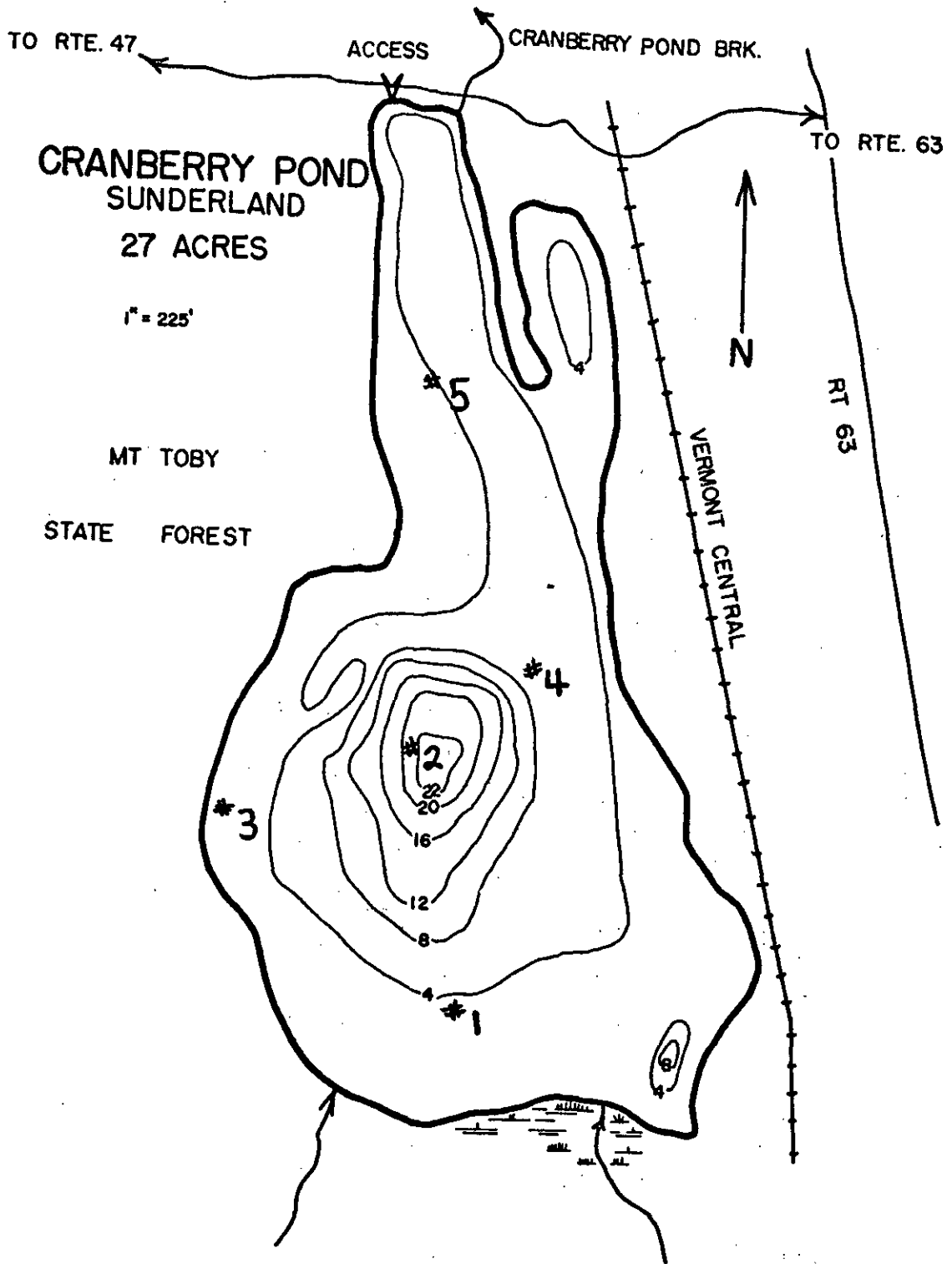
#4 - 30' from E shore, depth = 6'

#5 - 50' from W shore, depth = 6'

4. Arsenic Levels (composites)

water - 0.76 $\mu\text{g/l}$ As

sediment - 1.7 mg/kg As dry weight



Borrow Pit Pond

1. Background Data (McCann and Daly, 1972a)

location - Whately, Franklin County

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 50' from E shore, depth = 7'

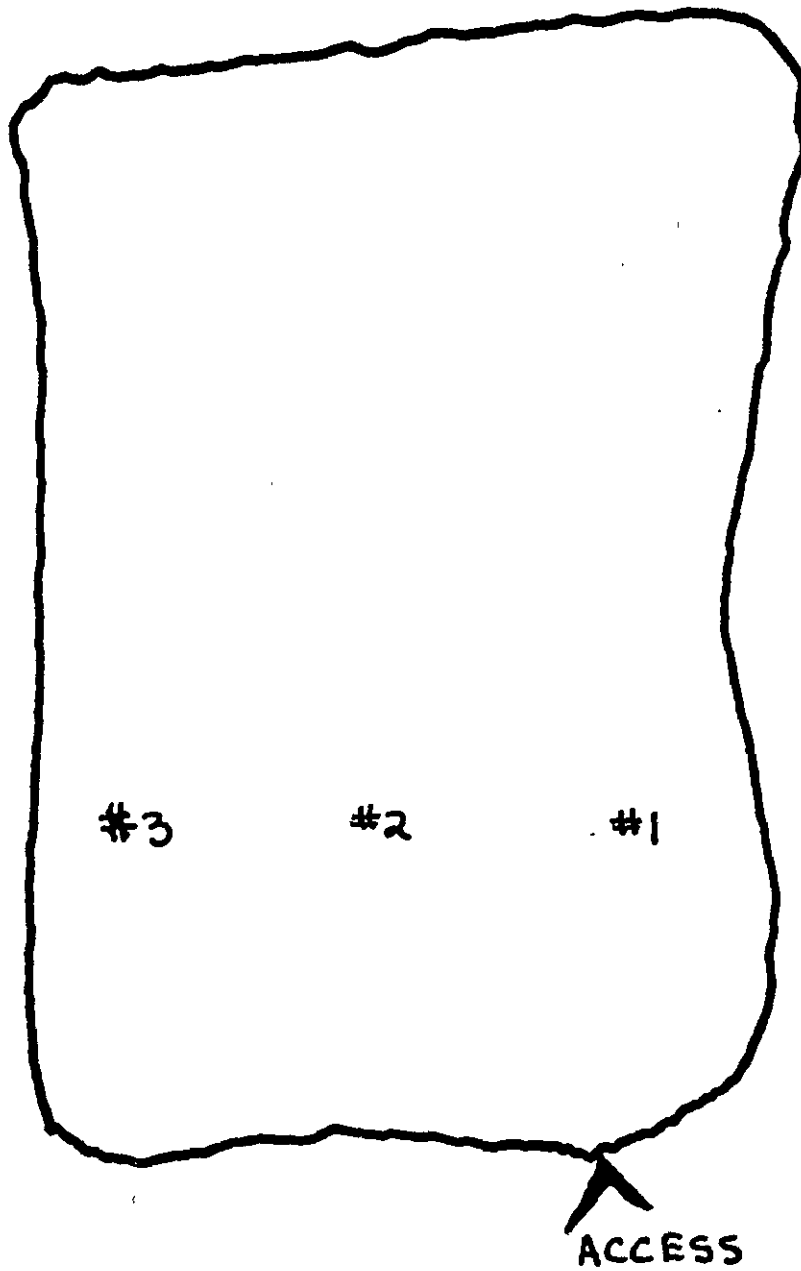
#2 - 150' from E shore, depth = 7'

#3 - 300' from E shore, depth = 7'

4. Arsenic Levels (composites)

water - 0.76 $\mu\text{g/l}$ As

sediment - 1.1 mg/kg As dry weight



BORROW PIT POND

Pelham Lake

1. Background Data (McCann and Daly, 1972a)

location - Rowe, Franklin County

0.7 mile NE from center of town

size - 71 acres

mean depth = 5'

maximum depth = 8'

limnology - artificial pond

eutrophic

common vegetation

land development - residential, 10-20%

municipal, 10-20%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 50' from shore, depth = 7'

#2 - center of pond, depth = 8'

#3 - 50' from point, depth = 3'

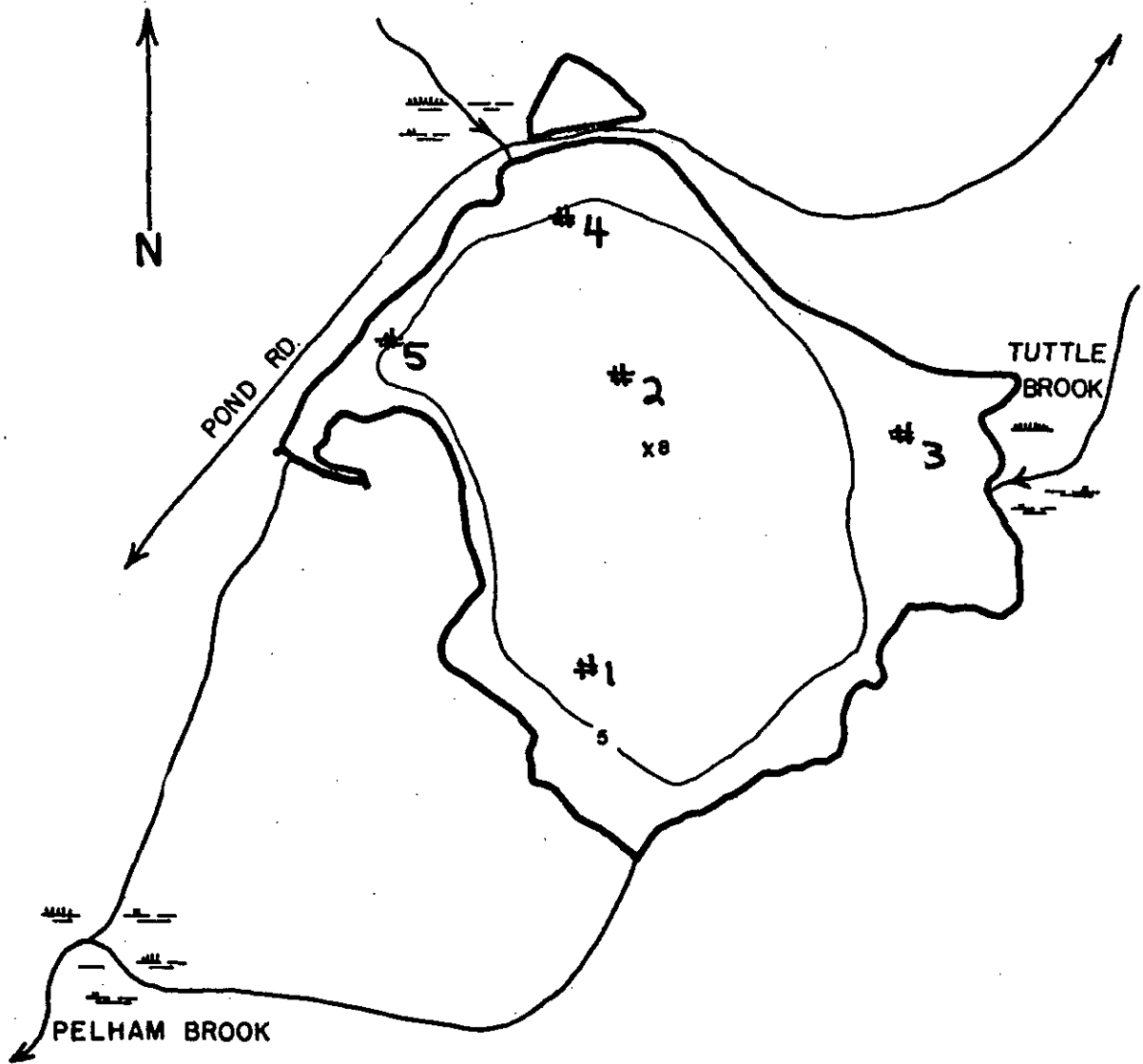
#4 - 50' from inlet, depth = 5'

#5 - 125' from dam, depth = 12'

4. Arsenic Levels (composites)

water - 0.38 $\mu\text{g}/\text{l}$ As

sediment - 4.6 mg/kg As dry weight



PELHAM LAKE
ROWE
71 ACRES



North Pond

1. Background Data (McCann and Daly, 1972a)

location - Florida, Berkshire County

2.4 miles SW from town center

size - 18 acres

mean depth = 13'

maximum depth = 28'

limnology - natural pond

oligotrophic

scant vegetation

pond use - light boating

moderate fishing

heavy swimming and camping

land development - park, 90-100%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 100' from swim area, depth = 27'; depth water sample also taken at 22'

#2 - 75' from W shore, depth = 10'

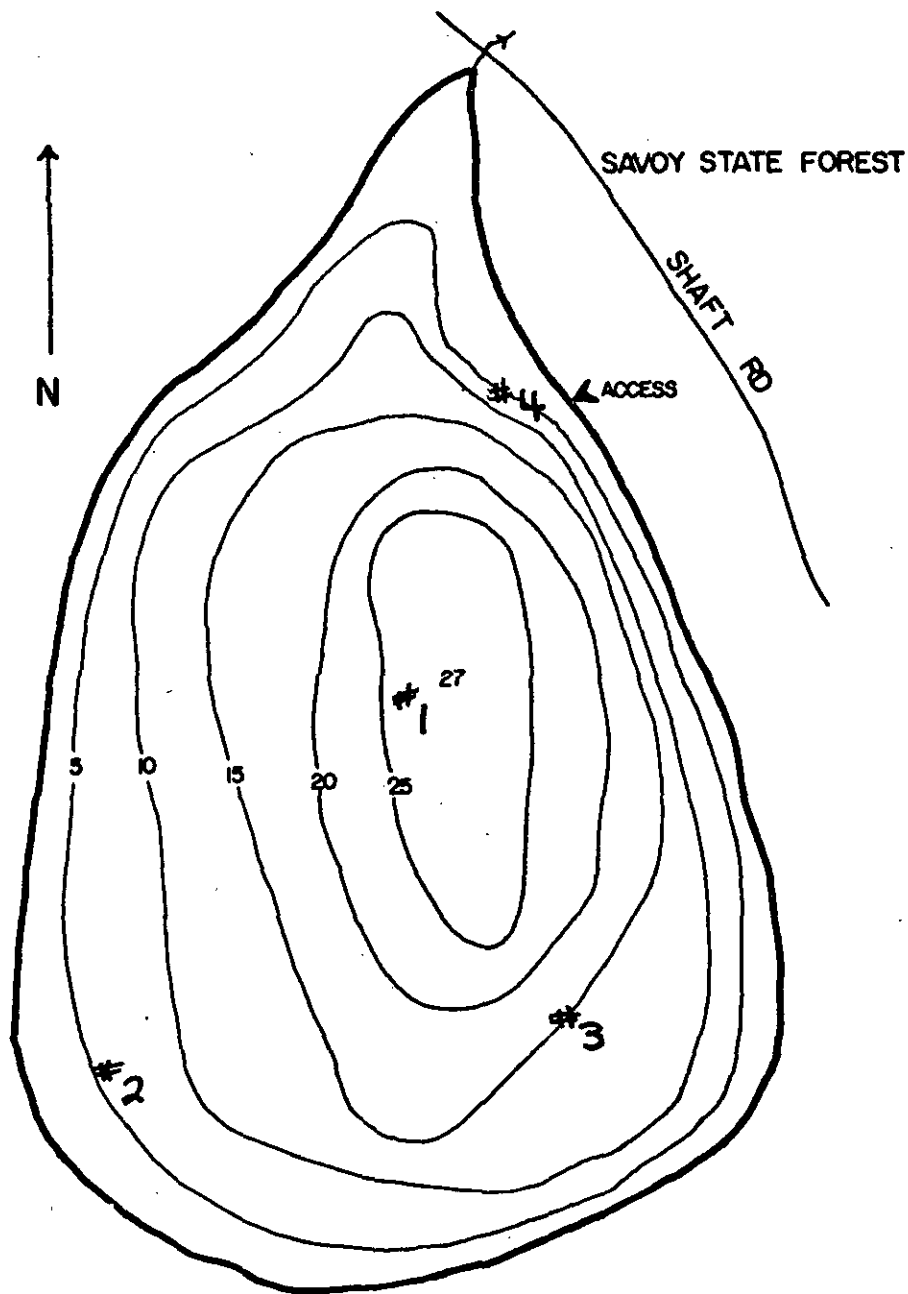
#3 - 150' from large rock, depth = 21'; depth water sample also taken at 17'

#4 - 50' from boat launch, depth = 8'

4. Arsenic Levels (composites)

water - 0.31 $\mu\text{g}/\text{l}$ As

sediment - 6.1 mg/kg As dry weight



NORTH POND
FLORIDA
18 ACRES

Cheshire Reservoir

1. Background Data (McCann and Daly, 1972a)

location - Cheshire, Berkshire County

0.5 mile S from center of town

size - 418 acres

mean depth = 7'

maximum depth = 9'

limnology - artificial pond

eutrophic

abundant vegetation

pond use - moderate industry

heavy boating, water skiing, fishing, and ice fishing

land development - residential, 30-40%

farming, 20-30%

park, 10-20%

swamp, 30-40%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map).

#1 - 20' from railroad bridge, depth = 8'

#2 - 100' from twin willow trees, depth = 7'

#3 - 200' from boat house, depth = 10'

#4 - 20' from abandoned building, depth = 7'

#5 - 500' from abandoned building, depth = 10'

#6 - 100' from shore, depth = 9'

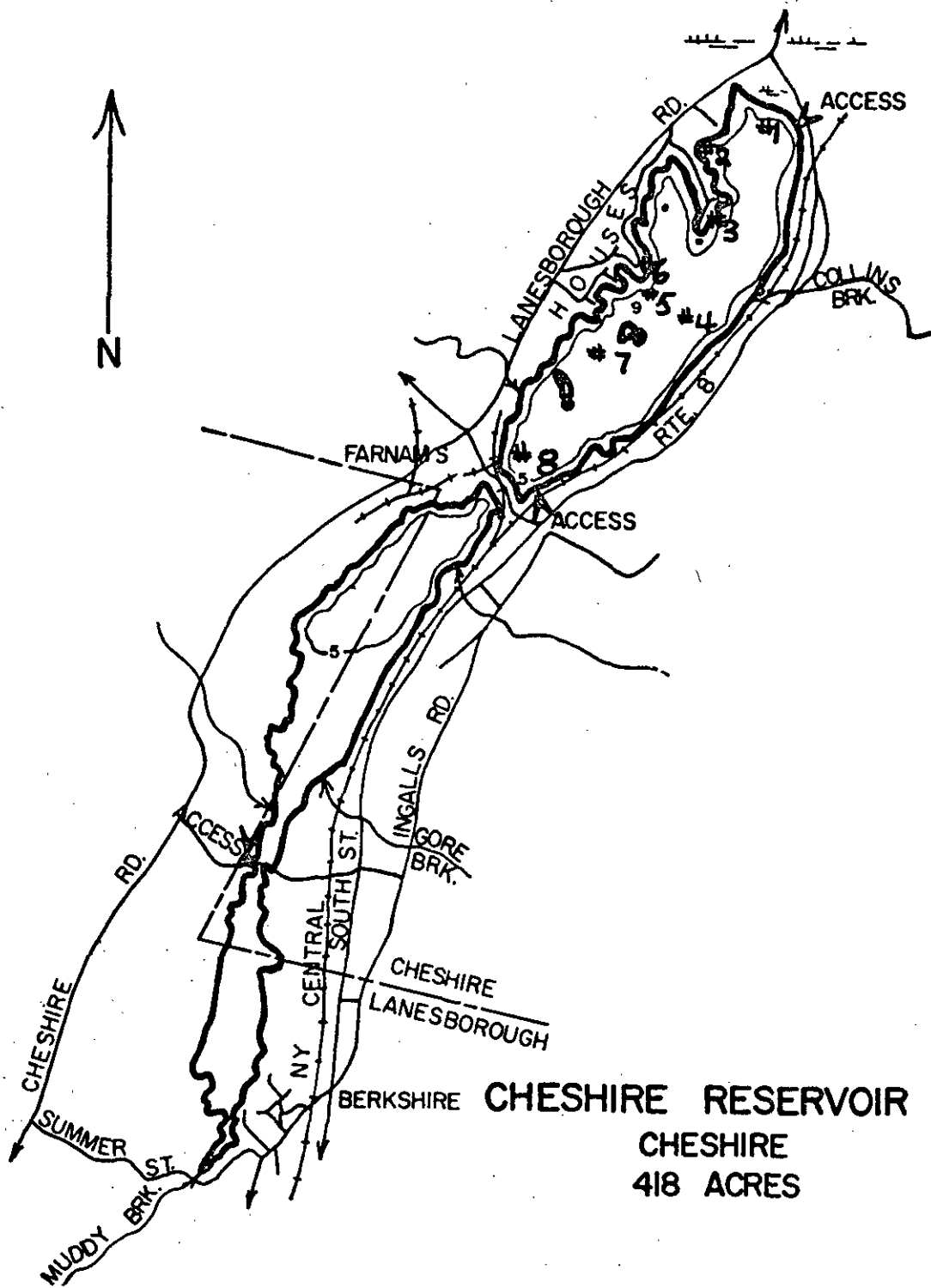
#7 - 200' from largest island, depth = 9'

#8 - 10' from access ramp, depth = 2'

4. Arsenic Levels (composites)

water - 0.91 $\mu\text{g/l}$ As

sediment - 9.4 mg/kg As dry weight



CHESHIRE RESERVOIR
CHESHIRE
418 ACRES

Silver Lake

1. Background Data (McCann and Daly, 1972a)

Location - Pittsfield, Berkshire County

0.7 mile NE from town center

size - 24 acres

limnology - kettlehole pond

eutrophic

scant vegetation

heavily polluted

pond use - heavy industry and cooling uses

land development - residential, 30-40%

highway, 60-70%

industry, 30-40%

vacant, 30-40%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 150' from stack, depth = 20'

#2 - 200' SW from building in lake, depth = 17'

#3 - 75' from N shore, depth = 23'

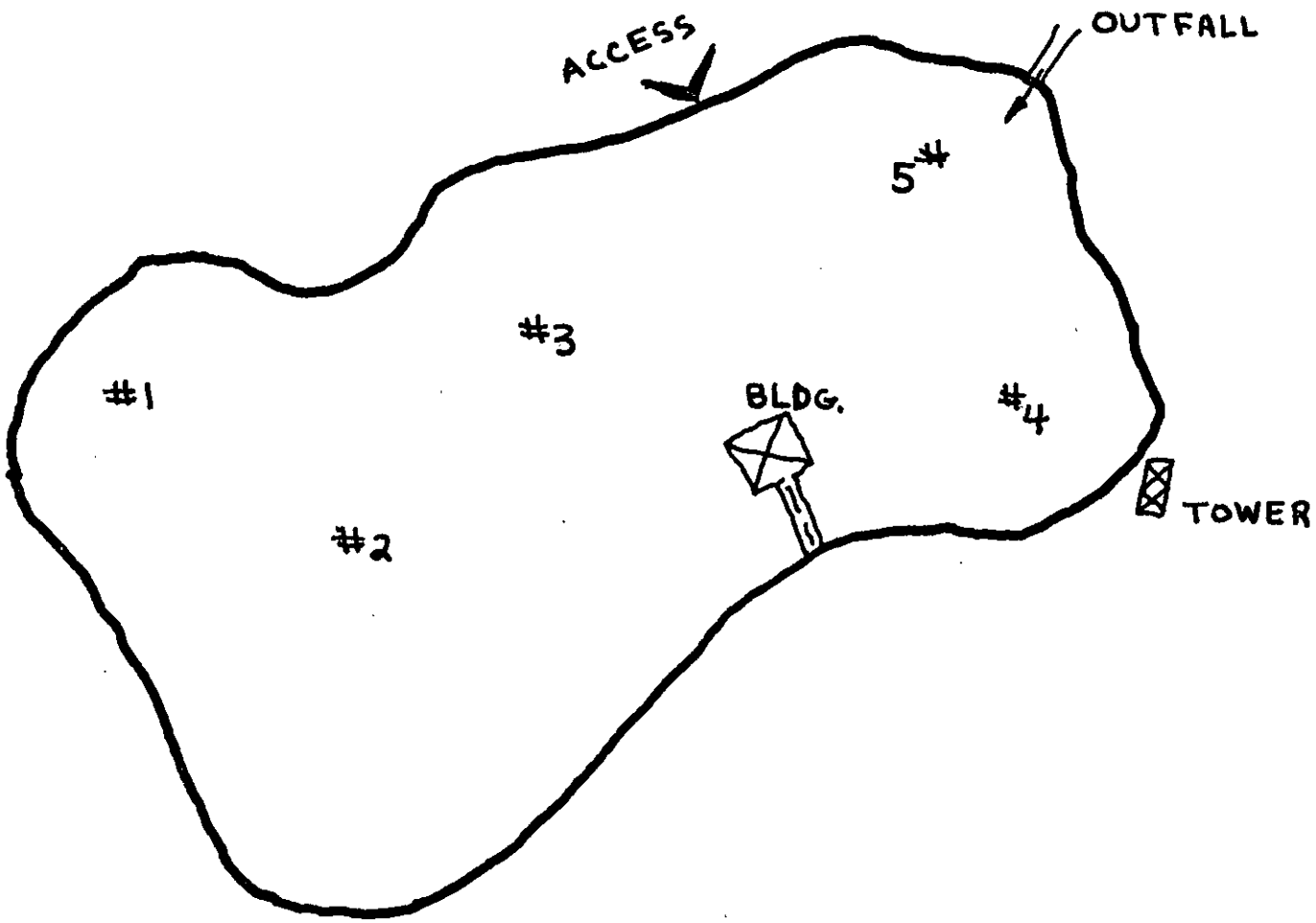
#4 - 100' from high tension tower, depth = 25'

#5 - 100' from outfall, depth = 15'

4. Arsenic Levels (composites)

water - 0.64 $\mu\text{g}/\text{l}$ As

sediment - 20.0 mg/kg As dry weight



SILVER LAKE

Pontoosuc Lake

1. Background Data (McCann and Daly, 1972a)

Location - Lanesborough, Berkshire County

1.4 miles SW from center of town

size - 480 acres

mean depth = 15'

maximum depth = 36'

limnology - enhanced pond

eutrophic

abundant vegetation

pond use - moderate swimming, water skiing, and camping, excessive fishing

land development - residential, 90-100%

municipal, 10-20%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 100' from white house, depth = 6'

#2 - 200' from point, depth = 8'

#3 - 500' from large island, depth = 32'; depth water sample taken at 20'

#4 - 200' from highway culvert, depth = 6'

#5 - 150' from large island, depth = 12'

#6 - 20' from white house on E shore, depth = 8'

#7 - 15' from marker, depth = 8'

#8 - 100' from island, depth = 14'

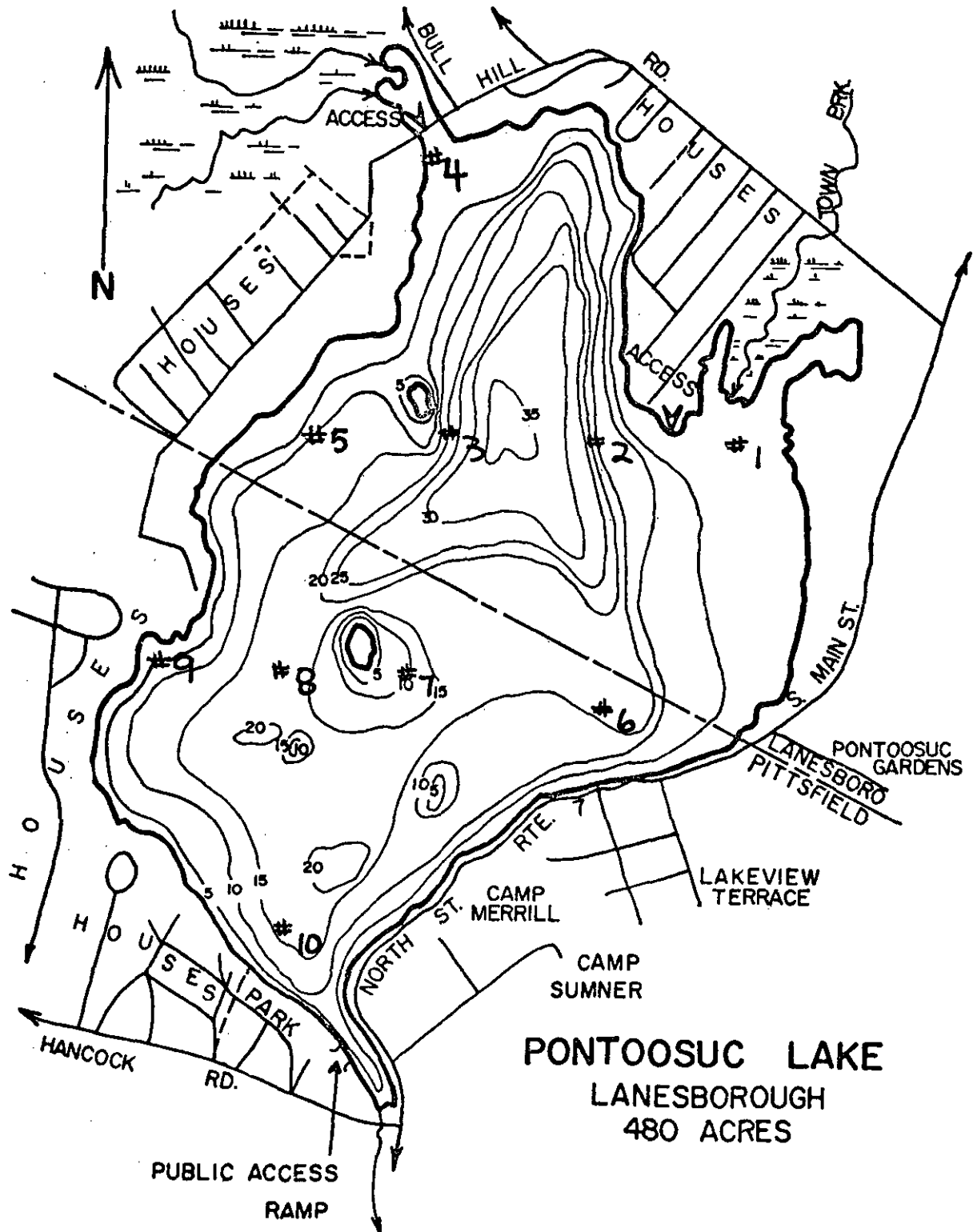
#9 - 200' from barn, depth = 16'; water sample taken at 15'

#10 - 10' from boat launch, depth = 2'

4. Arsenic Levels (composites)

water - 2.3 µg/l As

sediment - 6.1 mg/kg As dry weight



PONTOOSUC LAKE
LANESBOROUGH
480 ACRES

Stockbridge Bowl

1. Background Data (McCann and Daly, 1972a)

location - Stockbridge, Berkshire County

3.6 miles N of town center

size - 372 acres

mean depth = 27'

maximum depth = 53'

limnology - natural pond

eutrophic

common vegetation

pond use - light flood control, camping, moderate swimming, water skiing,
fishing, ice fishing, and skating; heavy boating

land development - residential, 80-90%

municipal, 10-20%

2. Sodium Arsenite Treatment - 1960, 1100 gallons @ 2# As_2O_3 /gal.

1961, 5500 gallons @ 4# As_2O_3 /gal.

1967, 3000 gallons "

1968, 3000 gallons "

1969, 8000 gallons "

3. Sampling Locations (see map)

#1 - 20' from W shore, depth = 4'

#2 - 75' E of island, depth = 28'; water sample taken at 25'

#3 - 40' off E shore, depth = 16'

#4 - middle, depth = 37'

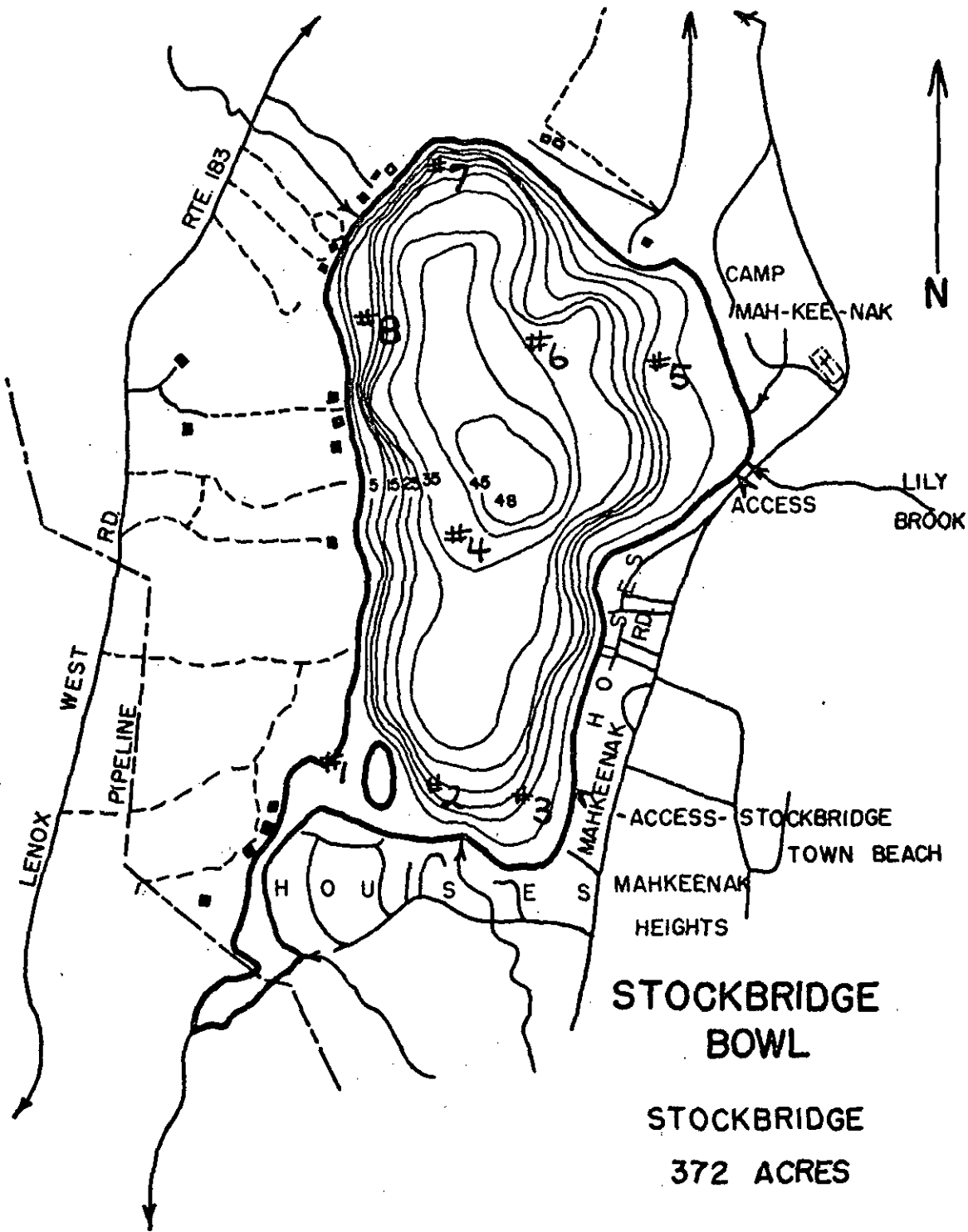
#5 - 105' off E shore, depth = 12'

#6 - halfway, depth = 37'; water sample taken at 30'

#7 - 25' from shore, depth = 20'

#8 - 10' off boat ramp, depth = 3'

4. Arsenic Levels (composites) - water, 17.1 $\mu g/l$ As
sediment, 176 mg/kg As dry weight

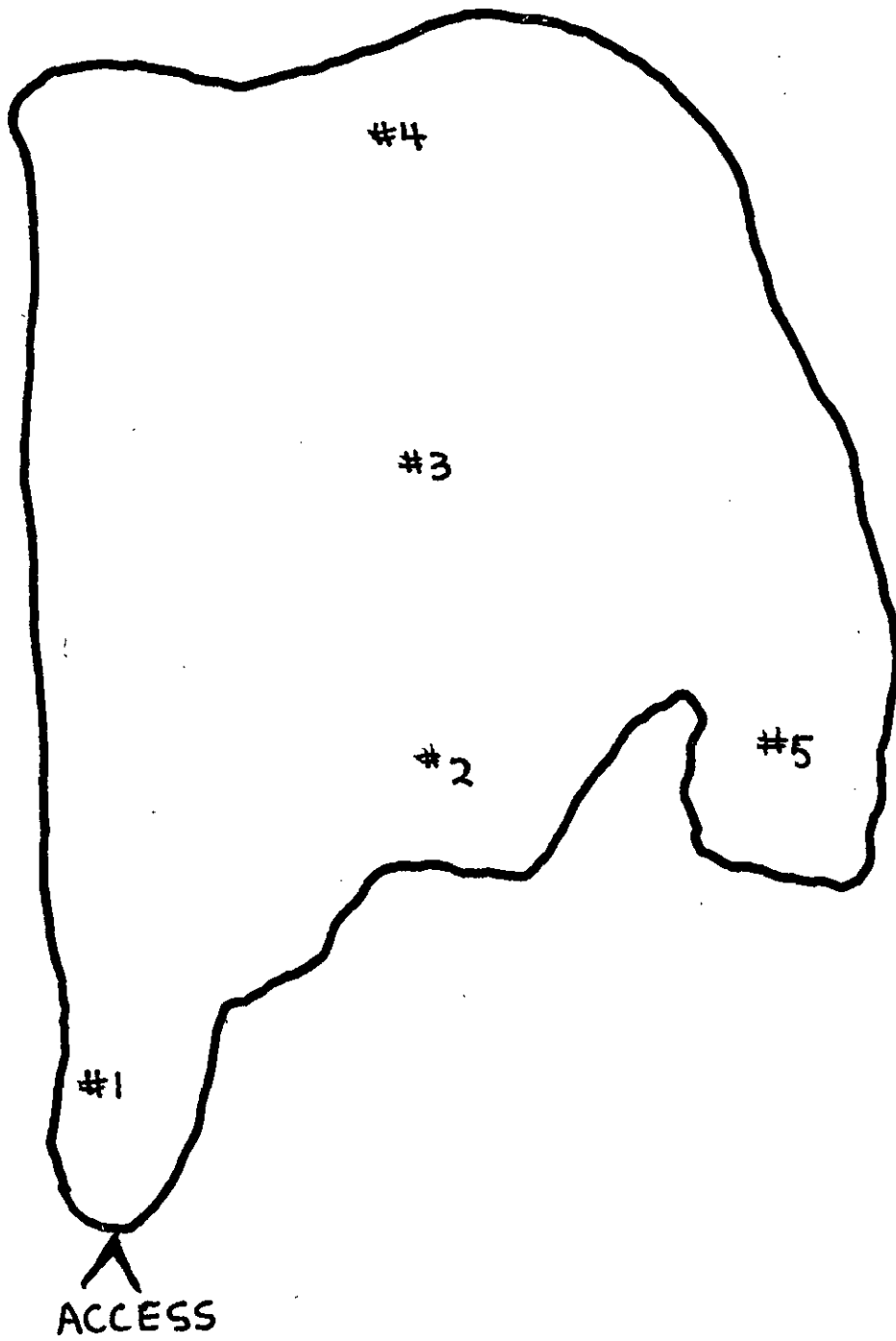


STOCKBRIDGE BOWL

**STOCKBRIDGE
372 ACRES**

Guilder Pond

1. Background Data (McCann and Daly, 1972a)
 - location - Mount Washington, Berkshire County
 - 1.0 mile NE from center of town
 - size - 15 acres
 - limnology - artificial pond
 - eutrophic
 - scant vegetation
 - pond use - light fishing, moderate camping
 - land development - 90-100% park
2. Sodium Arsenite Treatment - none
3. Sampling Locations (see map)
 - #1 - 5' from shore, depth = 4'
 - #2 - midway, depth = 3'
 - #3 - middle of pond, depth = 4'
 - #4 - 25' from shore, depth = 3'
 - #5 - 40' radius in cove, depth = 3'
4. Arsenic Levels (composites)
 - water - 0.20 $\mu\text{g}/\text{l}$ As
 - sediment - 6.6 mg/kg As dry weight



GUILDER POND

Upper Spectacle Pond

1. Background Data (McCann and Daly, 1972a)

Location - Sandisfield, Berkshire County

5.0 miles NE from town center

size - 72 acres

maximum depth = 32'

Limnology - enhanced pond

eutrophic

common vegetation

pond use - moderate boating and camping

land development - 90-100% park

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - midway between island and W shore, depth = 6'

#2 - middle of cove, depth = 3'

#3 - middle of lake, depth = 10'

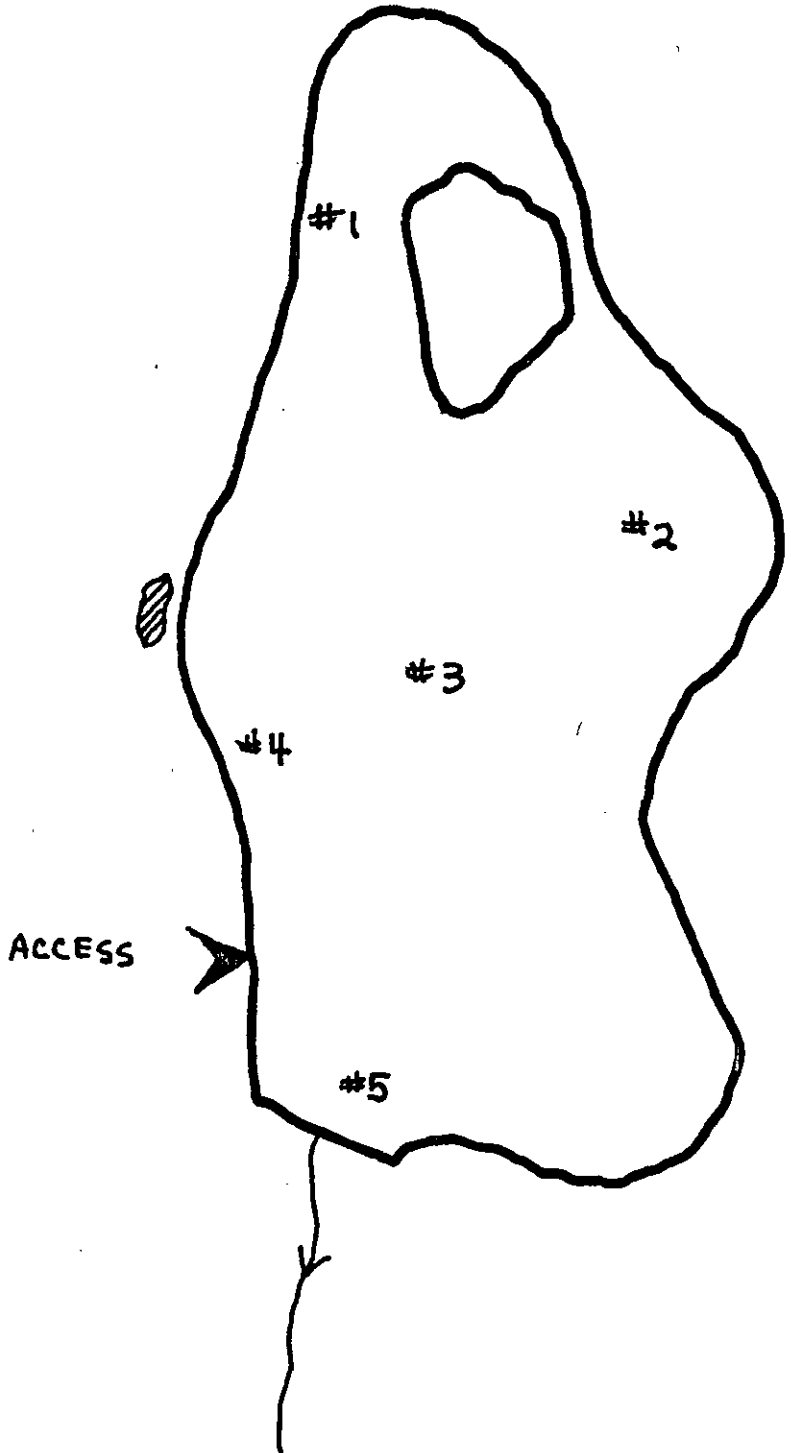
#4 - 50' from shore, depth = 16'; depth water sample taken at 14'

#5 - 40' from outlet, depth = 13'

4. Arsenic Levels (composites)

water - 0.36 $\mu\text{g/l}$ As

sediment - 3.3 mg/kg As dry weight



UPPER SPECTACLE POND

West Lake

1. Background Data (McCann and Daly, 1972a)

location - Sandisfield, Berkshire County

1.8 miles NW from town center

size - 60 acres

mean depth = 8'

maximum depth = 16'

limnology - enhanced pond

eutrophic

common vegetation

pond use - moderate flood control, boating, swimming, fishing and camping

land development - 90-100%

2. Sodium Arsenite Treatment - none

3. Sampling Locations (see map)

#1 - 100' from inlet, depth = 7'

#2 - 300' from fallen tree, depth = 15'

#3 - 40' from dam, depth = 14'

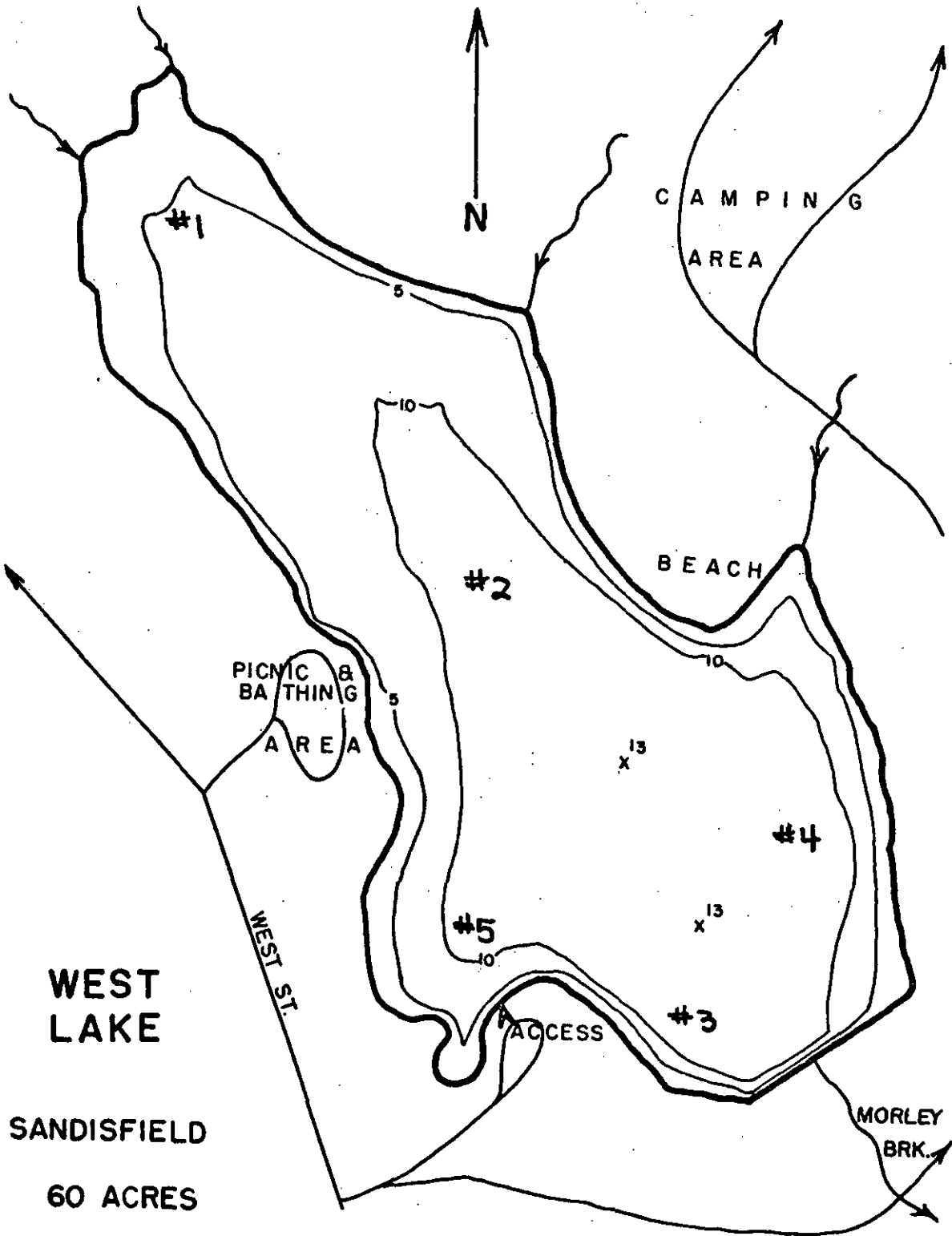
#4 - 30' from shore, depth = 9'

#5 - 20' from access, depth = 2'

4. Arsenic Levels (composites)

water - 0.69 $\mu\text{g/l}$ As

sediment - 2.1 mg/kg As dry weight



Big Benton Pond

1. Background Data (McCann and Daly, 1972a)

location - Otis, Berkshire County

2.5 miles E of center of town

size - 331 acres

mean depth = 16'

maximum depth = 32'

limnology - natural pond

oligotrophic

abundant vegetation

pond use - light boating, moderate fishing and ice fishing, heavy swimming

land development - residential, 70-80%

swamp, 30-40%

2. Sodium Arsenite Treatment - none

3. Sampling Locations

#1 - 25' from island and W shore, depth = 5'

#2 - midway between islands, depth = 25'

#3 - 75' W of big island, depth = 21'; depth water sample taken at 18'

#4 - 10' off docks, depth = 3'

#5 - 25' from N shore, middle of cove, depth = 3'

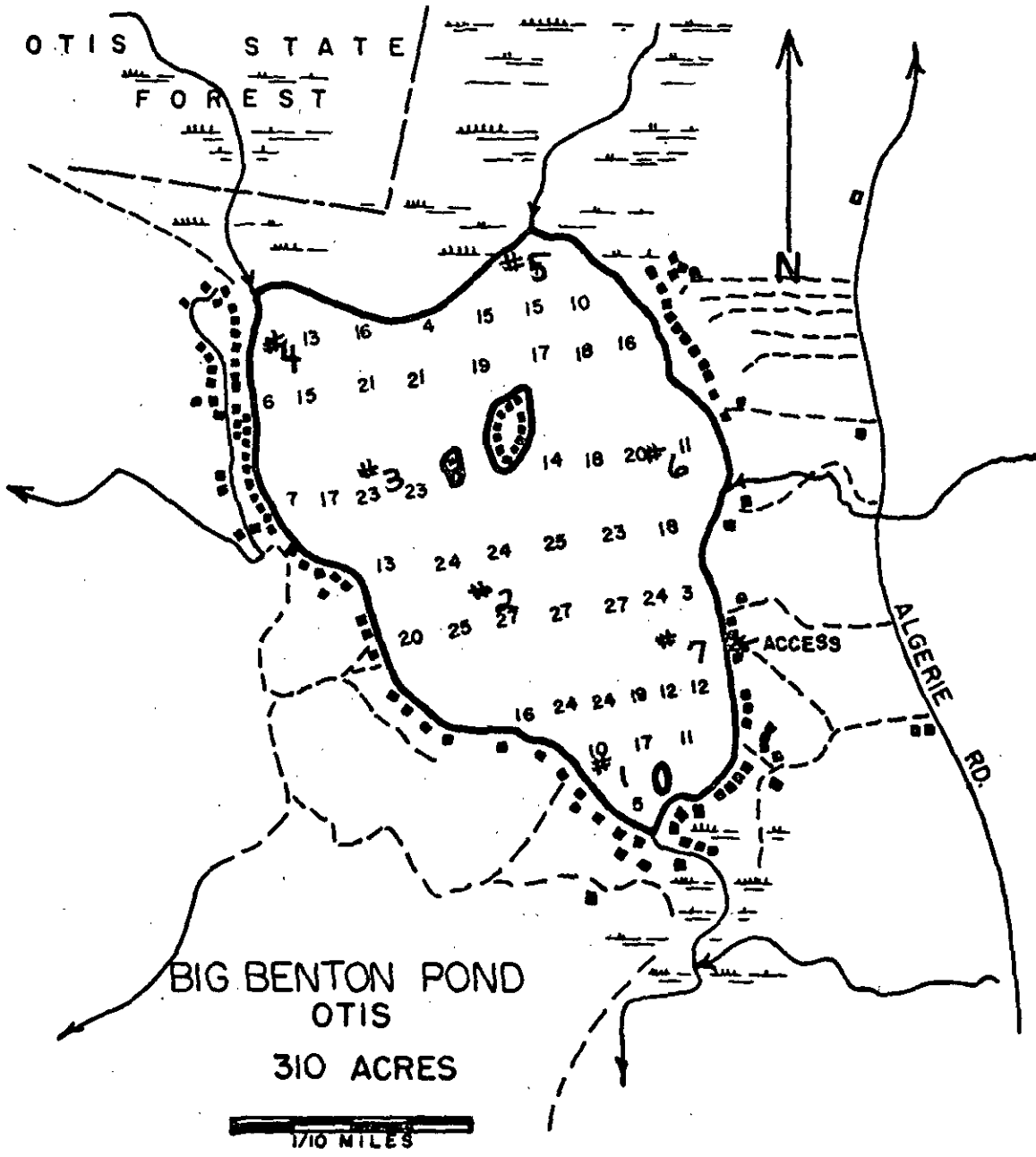
#6 - middle of cove, depth = 3'

#7 - 20' off access, depth = 2'

4. Arsenic Levels (composites)

water - 0.87 $\mu\text{g/l}$ As

sediment - 1.2 mg/kg As dry weight



BIBLIOGRAPHY

Bibliography

American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater, 13th edition, 1971.

Angino, E. E., "Arsenic in Detergents: Possible Danger and Pollution Hazard," Science, April 17, 1970, pp. 389-390.

Anonymous, "Chemical Quality of Waters in Broward County, Florida," Florida Geological Survey Report of Investigation No. 51, 1968, pp. 45-48.

----, "Detergent Enzymes, Arsenic Pose Health Problems", Chemical and Engineering News, February 23, 1970, pp. 13-14.

Ayres, Gilbert H., Quantitative Chemical Analysis, Harper and Row, New York, c. 1958.

Barnett, William B., "Acid Interferences in Atomic Absorption Spectrometry", Analytical Chemistry, April, 1972, pp. 695-698.

----, "Determination of As and Se with the HGA", Atomic Absorption Application Study No. 523, Perkin-Elmer, 1973.

Bird, Marjorie L., F. Challenger, P. T. Charlton, and J. O. Smith, "Studies on Biological Methylation-the Action of Moulds on Inorganic and Organic Compounds of Arsenic", Journal of Biochemistry, Vol. 43 (1948), pp. 78-83.

Blume, J. J., "Phosphate Uptake by Phosphate-Starved Euglena", Journal of General Physiology, Vol. 49 (1966), pp. 1125-1137.

Boschetti, Mario M., Massachusetts Department of Public Health, personal communication June 14, 1973.

Chapman, A. Chaston, "On the Presence of Compounds of Arsenic in Marine Crustaceans and Shellfish", Analyst, Vol. 51 (1926), pp. 548-563.

Chu, Richard C., George P. Barron, and Paul A. W. Baumgarner, "Arsenic Determination at Sub-microgram Levels by Arsine Evolution and Flameless Atomic Absorption Spectrophotometric Technique", Analytical Chemistry, July, 1972, pp. 1476-1479.

Coleman, S., Allied Biological Control Corporation, Wellesley Hills, Mass., personal communication June 18, 1973.

Coughlin, Paul, Northeast Weed and Brush Control, Spencer, Mass., personal communication June 18, 1973.

Cowell, Bruce C., "The Effects of Sodium Arsenite and Silvex on the Plankton Populations in Farm Ponds", Transactions of the American Fisheries Society, Vol. 94 (1963), pp. 371-377.

Dupree, Harry K., "The Arsenic Content of Water, Plankton, Soil, and Fish from Ponds Treated with Sodium Arsenite for Weed Control", Proceedings of the Southeast Association of Fish and Game Commissions, Vol. 14 (1960), pp. 132-137.

Edgington, David N. and Edward Callender, "Minor Element Geochemistry of Lake Michigan Ferromanganese Nodules", Earth and Planetary Science Letters, Vol. 8 (1970), pp. 97-100.

Ediger, Richard, analytical chemist at Perkin-Elmer Corp., Norwalk, Conn., personal communications on numerous occasions, August, 1973.

Environmental Protection Agency (EPA), Methods for Chemical Analysis of Water and Wastes, U.S. Government Printing Office, 1971.

Ferguson, John F. and Gerome Gavis, "A Review of the Arsenic Cycle in Natural Waters", Water Research, Vol. 6 (1972), pp. 1259-1274.

Fernandez, F. J. and D. C. Manning, "Atomic Absorption Analyses of Metal Pollutants in Water Using a Heated Graphite Atomizer", Atomic Absorption Newsletter, May-June, 1971, pp. 65-69, (a).

----, "The Determination of ARsenic at Sub-microgram Levels by Atomic Absorption Spectrophotometry", Atomic Absorption Newsletter, July-August, 1971, pp. 86-88, (b).

Fish, G. R., "Observations on Excessive Weed Growth in Two Lakes in New Zealand", New Zealand Journal of Botany, 1963, pp. 410-418.

Foess, G. W. and T. H. Feng, "Bottom Deposits", Journal of the Water Pollution Control Federation, June, 1971, pp. 1257-1266.

Garrels, R. M. and C. L. Christ, Solutions, Minerals, and Equilibria, Harper and Row, New York, c. 1965.

Glazer, A. N., "Inhibition of 'Serine' Esterases by Phenyl-Arsonic Acids", Journal of Biological Chemistry, July, 1968, pp. 3693-3701.

Hamilton, E. I., M. J. Minski, and J. J. Cleary, "The Loss of Elements During the Decomposition of Biological Materials with Special Reference on Arsenic, Sodium, Strontium, and Zinc", Analyst, April, 1967, pp. 257-259.

Harris, A. J., K. J. Roberts, and A. E. Christie, "Effects of Detergents on Water Supplies", Journal of the American Water Works Association, December, 1971, pp. 795-799.

Holak, Walter, "Gas Sampling Technique for Arsenic Determination by Atomic Absorption Spectrophotometry", Analytical Chemistry, October, 1969, pp. 1712-1713.

Holman, J. P., Experimental Methods for Engineers, 2nd edition, McGraw-Hill, New York, c. 1971, pp. 33-77.

Hood, Stan, Massachusetts Department of Natural Resources, personal communication June 25, 1973.

Isaac, Russell A. and John Delaney, Toxic Element Survey Progress Report No. 1 (and related data), Mass. Water Resources Commission, Division of Water Pollution Control, Publication No. 6108, April, 1972.

Jenkins, Dale W., "The Toxic Metals in Your Future-and Your Past", Smithsonian, April, 1972, pp. 62-69.

Johnson, David L., "Simultaneous Determination of Arsenate and Phosphate in Natural Waters", Environmental Science and Technology, May, 1971, pp. 411-414.

Kahn, Herbert L., "A Background Compensation System for Atomic Absorption", Atomic Absorption Newsletter, March-April, 1968, pp. 40-43.

Kahn, Herbert L., George E. Peterson, and Jane E. Shallis, "Atomic Absorption Microsampling with the 'Sampling Boat' Technique", Atomic Absorption Newsletter, March-April, 1968, pp. 35-40.

Kirkbright, G. F., M. Sargent, and T. S. West, "The Determination of Arsenic and Selenium by Atomic Absorption Spectroscopy in a Nitrogen-Separated Air Acetylene Flame", Atomic Absorption Newsletter, March-April, 1969, pp. 34-347.

Kopp, John F. and Robert C. Kroner, "A Direct- Reading Spectrochemical Procedure for the Measurement of Nineteen Minor Elements in Natural Water", Applied Spectroscopy, May, 1965, pp. 155-159.

Lawrence, J. M., "Recent Investigations on the Use of Sodium Arsenite as an Algicide and its Effects on Fish Production in Ponds", Proceedings of the Southeast Association of Fish and Game Commissions, 1957, pp. 281-287.

Lisella, Frank S., Keith R. Long, and Harold G. Scott, "Health Aspects of Arsenicals in the Environment", Journal of Environmental Health, March-April, 1972, pp. 511-518.

Lucas, Henry F., David N. Edgington, and Peter J. Colby, "Concentrations of Trace Elements in Great Lakes Fishes", Journal of the Fisheries Research Board of Canada, April, 1970, pp. 677-684.

Lunde, G., "Activation Analysis of Trace Elements in Fishmeal", Journal of Food Science and Agriculture, August, 1968, pp. 432-434.

----, "Analysis of Arsenic and Selenium in Marine Raw Materials", Journal of Food Science and Agriculture, May, 1970, pp. 242-247.

McCann, James A. and Leo M. Daly, An Inventory of the Ponds, Lakes and Reservoirs of Massachusetts - Berkshire and Franklin Counties, University of Massachusetts Water Resources Research Center Publication No. 10-2, 1972, (a).

- , . . . - Hampden and Hampshire Counties, Publication No. 10-4, 1972, (b).

-----, . . . - Worcester County, Publication No. 10-3, 1973.

Mullison, W. R., "Effects of Herbicides on Water and Its Inhabitants", Weed Science, November, 1970, pp. 738-750.

Onishi, Hiroshi and E. B. Sandell, "Geochemistry of Arsenic", Geochim Cosmochim Acta, 1955, pp. 25-33.

Pattison, E. Scott, "Arsenic and Water Pollution Hazard", Science, Vol. 170 (1970), p. 870.

Perkin-Elmer Corporation, Analytical Methods for Atomic Absorption Spectrophotometry, 1970.

-----, Analytical Methods for Atomic Absorption Spectrophotometry with the Heated Graphite Atomizer HGA-70, 1971.

-----, Instructions for Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer, 1966.

Portmann, J. E. and J. P. Riley, "Determination of ARsenic in Sea Water, Marine Plants, and Silicate and Carbonate Sediments", Analytica Chimica Acta, 1964, pp. 509-519.

Reay, P. F., "The Accumulation of Arsenic from Arsenic-Rich Natural Waters by Aquatic Plants", Journal of Applied Ecology, 1972, pp. 557-565.

Ronk, Richard J., "Heavy Metals in United States Fish", 36th North American Wildlife Conference, 1971, pp. 133-138.

Rothstein, Aser, "Interactions of Arsenate with the Phosphate Transporting System of Yeast", Journal of General Physiology, 1963, pp. 1075-1085.

Ruch, R. R., E. Joyce Kennedy, and Neil F. Shimp, Distribution of Arsenic in Unconsolidated Sediments from Southern Lake Michigan, Illinois Environmental Geology Notes No. 37, 1970.

Sanders, Herman O., "Toxicities of Some Herbicides to Six Species of Freshwater Crustaceans", Journal of the Water Pollution Control Federation, August, 1970, pp. 1544-1550.

Slavin, Sabina, Perkin-Elmer Corp., Norwalk, Conn., personal communication during visit for analyses August 22, 1973.

Smith, Ralph G., "Occurrence of Trace Elements in Water", Trace Substances in Environmental Health-3, Proceedings of University of Missouri Conference, 1969, pp. 158-162.

Sugawara, Ken and Satoru Kanamori, "The Spectrophotometric Determination of Trace Amounts of Arsenate and Arsenite in Natural Waters with Special Reference to Phosphate Determination", Bulletin of the Chemical Society of Japan, September, 1964, pp. 1358-1363.

Surber, Eugene W., "Control of Aquatic Growths in Impounding Reservoirs", Journal of the American Water Works Association, August, 1950, pp. 735-740.

----, "Sodium Arsenite for Controlling Submerged Vegetation in Fish Ponds", Transactions of the American Fisheries Society, Vol. 61 (1930), pp. 143-419.

Surber, Eugene W. and O. L. Meehan, "Lethal Concentrations of Arsenic for Certain Aquatic Organisms", Transactions of the American Fisheries Society, Vol. 61 (1930), pp. 225-239.

Ullman, William W., Robert W. Schaefer, and Wallace W. Sanderson, "Arsenic Accumulation by Fish in Lakes Treated with Sodium Arsenite", Journal of the Water Pollution Control Federation, April 1961, pp. 416-418.

Uthe, J. F. and E. G. Bligh, "Preliminary Survey of Heavy Metal Contamination of Canadian Freshwater Fish", Journal of the Fisheries Research Board of Canada, May, 1971, pp. 786-788.

U. S. Public Health Service, Drinking Water Standards, U. S. Government Printing Office, 1962.

Vaskovsky, V. E., O. D. Korotchenko, and V. S. Levin, "Arsenic in the Lipid Extracts of Marine Invertebrates", Comprehensive Biochemical Physiology, Vol. 41B (1972), pp. 777-784.

Velz, Clarence J., Applied Stream Sanitation, Wiley-Interscience, New York, c. 1970, pp. 508-593.

Wedepohl, Handbook of Geochemistry, Vol. 2, Chapter 33-"Natural Sources of Arsenic", Springer-Verlag, Berlin, 1969.

Weir, Patricia and Charles H. Hine, "Effects of Various Metals in the Behavior of conditioned Goldfish", Archives of Environmental Health, January, 1970, pp. 45-51.

Whitnack, Gerald C. and Richard G. Brophy, "A Rapid and Highly Sensitive Single-Sweep Polarographic Method of Analysis for Arsenic (III) in Drinking Water", Analytica Chimica Acta, Vol. 48 (1969), pp. 123-127.

Wiebe, A. H., "Notes on the Exposure of Young Fish to Varying Concentrations of Arsenic", Transactions of the American Fisheries Society, Vol. 60 (1929), pp. 270-278.

Wiebe, A. H., E. G. Gross, and D. H. Slaughter, "The Arsenic Content of Large-Mouth Black Bass Fingerlings", Transactions of the American Fisheries Society, Vol. 61 (1930), pp. 150-163.