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WATER QUALITY EFFECTS OF LEAD FROM RECREATIONAL BOATING

by

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ABSTRACT

The temporal and spatial variations in the lead concentration of a fresh water-recreational lake were determined, and the results compared with daily records of lake volume, residence time and number of boats launched. In addition, laboratory studies were carried out to establish the influence of sediment-water inter- actions on the lead concentration of the lake water. The variation in the lead concentration in the main body of the lake was found to correlate with the lake volume. This fact, together with the laboratory studies and calculations based on a plug flow model, suggests that sediment-water interactions are significant in controlling the lead concentration in the main body of the lake. On the other hand, boating was found to be important in controlling the lead concentration in the boat dock area. The water in this area is subjected to both poor mixing and heavy boat traffic.

With the goal of providing experimental evidence concerning the origin and transport mechanisms of lead in fresh water lakes with very low lead levels, we have observed the long-term variations of the lead concentrations of a local lake, and have attempted to identify those factors which control these variations. These results should also be of value in the development of models concerned with the behavior of heavy metals in natural water systems.

The lake studied was Turlock Lake located in eastern Stanislaus County in the San Joaquin Valley of California. It is a man-made lake, and its waters are used for irrigation by the Turlock Irrigation District. It covers an area of 1.42×10^7 m^2 and has an average depth of 4.3 m. The lake is fed by a single canal which carries water from a snow-fed reservoir in the foothills of the Sierra Nevada Mountains. Except for a slight contribution from rainfall and runoff in winter, this canal is the only source of lake water. Water flows out of the lake into an irrigation canal at the western end. The north shore is occupied by a state park which includes boat launching facilities. (See Figure 1.) The rest of the lake is surrounded by range land.

Turlock Lake is ideal for this type of study for several reasons. It has a single well-defined source of water and a single outlet. The lake volume, rates of inflow and outflow

are controlled and measured daily by the Turlock Irrigation District. The area surrounding the lake is sparsely populated, and hence the effects of industry and urbanization on water composition are negligible. The lack of rainfall in summer rules out contributions from runoff. Finally, a daily record of the number of boats launched is kept by the California Department of Parks and Recreation.

The work described in this paper includes the weekly measurement of the lead concentration in the water of Turlock Lake at three sampling stations, and a corresponding laboratory study of water in contact with Turlock Lake sediment. In addition, we will discuss the contributions of boating activity to lead levels in the lake water.

Experimental

Lake Water Analysis

Our procedure was to take samples for lead analysis at weekly intervals at three stations: at the mouth of the inlet canal where water enters the lake, at the outlet, and at the boat dock next to the boat launching ramp. The locations of the stations are shown in Figure 1. Samples were taken from the shore or boat dock and were stored in polyethylene bottles which had been presoaked in lake water to minimize adsorptive losses (Batley and Gardner, 1977). Lead analyses were accomplished within 2 to 3 hours of collection with a Perkin-Elmer Model-103 Atomic Absorption Spectrophotometer equipped with an HGA-2100

graphite furnace and a high intensity lead hollow cathode lamp.
Milli-Q water was used throughout and blanks were run on all
reagents. Teflon ware, prerinsed with the water to be analyzed,
was used. All samples were gravity filtered with S and S #589
fine porosity filter paper to remove suspended solids. The
filtration system was flushed several times with lake water
before a sample was collected for analysis. Experiments showed
that the filtration process neither added nor removed lead from
the sample. Several samples were filtered using 0.45 μm millipore
filters, and these gave results identical to those given by
samples filtered with the filter paper.

The pH of Turlock Lake water falls in the range 6.0 to 6.8.
The data of Subraramanian et. al. (1978), show that in this pH range
the rate of absorptive loss of lead on the container wall might
be significant, whereas no losses were observed by them at a
pH of 1.6. We checked our procedure for losses on the container
walls in two ways. In one method duplicate samples were taken.
One was filtered and acidified with nitric acid to a pH of
1.6 immediately after sampling. The other sample was treated
in the usual way. That is, it was filtered in the
laboratory 1-2 hours after sampling, and not acidified.
Analysis of the two samples gave identical results. (See
Table 1.) Thus, there was no significant loss of lead onto the
container walls for our unacidified samples during the interval
between sampling and analysis. In a second method

a pre-treated sample bottle was filled with a solution containing 10 ppb lead in milli-Q water. The lead concentration remained unchanged for several days.

It is well known that the determination of lead concentrations at the $\mu g/\ell$ level is subject to relatively large error (Patterson and Settle, 1976; Dybczynski et. al., 1978). In view of this fact, a sample of Turlock Lake water was collected and analyzed according to the stringent procedures of Patterson and Settle (1976). An identical sample was analyzed by our procedure and the results agreed to within a factor of two. Such agreement is quite acceptable, especially in view of a recent International Atomic Energy Agency Intercomparison Test in which water samples containing trace levels of various elements including lead (16 $\mu g/\ell$) were sent to independent laboratories for analyses. The greatest error in analysis occurred for lead. The average of the lead concentrations reported by 24 laboratories showed a deviation from the true value of 85% (Dybczynski et. al., 1978).

Occasional samples were analyzed for species other than lead. The analytical methods used were those described in Standard Methods (APHA, AWWA, WPCF, 1976). Chloride (Cl^-) was determined by the Mercuric Nitrate Method. Dissolved oxygen was measured using the Azide Modification of the Iodometric Method. An Ultraviolet-Spectrophotometric method was used in the determination of nitrate (NO_3^-). Total phosphate was determined by persulfate digestion followed by the vanadomolybdophosphoric acid colorimetric method.

Laboratory Studies of Water Sediment Interactions

In one set of experiments lake sediment was placed in contact with each of four aqueous phases and the system allowed to come to equilibrium. The four aqueous phases were: a) milli-Q water, b) milli-Q water containing 10 ppb of lead as $PbNO_3$, c) Turlock Lake water, and d) Turlock Lake water containing an additional 10 ppb of lead introduced as $PbNO_3$.

In each of the above experiments 750 ml of the aqueous phase and 100.0 g of dry sediment were placed in 1-liter teflon bottles which had been pre-treated by washing, pre-soaking in a 10 ppb lead solution and washing again. Control experiments showed that the bottles themselves did not affect the lead concentration of solutions stored in them. The sediment and aqueous phase were left in contact without shaking for one week in a constant temperature bath at 24.9°C, and the aqueous phase was then analyzed for lead using the atomic absorption spectrophotometer described above. Prior to analysis the aqueous phase was filtered through a 0.45 micron filter using an all-plastic "Antilia" filtration system made by Schleicher and Schuell. Lead absorption by the filtration apparatus was maintained at an insignificant level by pre-rinsing with the solution to be analyzed.

Measurements of exchangeable lead were carried out by placing 5.00 g of sediment, 5.0 ml of 0.100 $\underline{M}$ EDTA solution and

45.0 ml of water in a teflon bottle and shaking periodically for 24 hours. The temperature was maintained at 25°C. The EDTA solution was then filtered using the "Antilia" apparatus mentioned previously, and analyzed by atomic absorption spectrophotometry. In experiments involving EDTA all labware was pre-soaked in EDTA and blanks were again run on the filtration system, the teflon bottles and reagents.

Both the lake sediment and shore soil, taken 54 meters from the high-water line were analyzed for total lead. In these analyses the sample was dissolved in hot aqua regia and the resulting solution filtered. The filtrate was extracted with a dithizone-carbon tetrachloride solution according to the procedure in Standard Methods (APHA, AWWA, WPCF, 1976). The carbon tetrachloride solution, containing lead dithizonate, was then extracted with a 1% nitric acid water solution. Under these conditions lead was quantitatively transferred to the aqueous phase which was then analyzed by atomic absorption spectrophotometry. The precision of this procedure was greater than that obtained in the procedure in which the carbon tetrachloride solution was analyzed directly by atomic absorption spectrophotometry.

Results   Table 2 shows the ranges of concentrations of various chemical species observed in Turlock Lake water during the summer months. In addition, the dissolved oxygen concentration was typically at or near saturation. The water is clearly low in dissolved solids, and its composition is similar to that reported for the waters of some Sierra Nevada springs by Garrels and MacKenzie (1967).

Water samples were analyzed for lead at weekly intervals during the periods: June 15 to August 31, 1976; October 14 to December 12, 1976; March 2 to April 18, 1977; and June 8 to September 21, 1977. The data are shown in Figures 2, 3, 4, 5.

During the time of this study, the flow conditions in the lake varied. In the summers (Figures 2 and 3), water flowed continuously through the lake. The fluctuations in lake volume shown in Figures 2 and 3 arise from changing irrigation demands.

During the interval October 14, 1976 to December 12, 1976 (Figure 6), no water was released from the lake, although some was fed into it during the first part of the interval and the lake volume increased.

During the period March 2, 1977 to April 18, 1977, periods of zero outflow and nonzero inflow occurred (Figure 7), and these account for the periods of increasing volume.

In general, the lead levels at the inlet and outlet seldom exceeded 2.0 ppb. The highest observed levels were obtained at the boat dock. A brief summary of the main features of the data follows.

THE SUMMER DATA. During both summers (Figures 2 and 3), the concentration of lead was consistently higher at the outlet than at the inlet. Since water was flowing continuously through the lake at these times, the implication is that lead was introduced into the water as it passed through the lake. Another interesting feature is the apparent correlation between

the lake volume and the outlet lead concentration during both summers, Figures 12 and 13. The correlation is especially good for the summer of 1977. In 1976, the minima and maxima in the lead concentration and volume curves are somewhat shifted with respect to one another.

FALL AND SPRING DATA (Figures 4, 5, 6 and 7) These data differ from the summer data in several respects. In some instances the inlet lead concentration is larger than that at the outlet. This may arise from differences in flow conditions caused by the periods of zero outflow. Secondly, the outlet lead concentrations do not show as good a correlation with lake volume, (Figures 6 and 7) as they do in the summer.

Discussion

Influence of Boats: An obvious potential contributor of lead to the water is boating. Histograms were prepared of the total number of boats launched per-unit-volume of lake water over a one-week period. "Boats-per-unit-volume" was used to compensate for fluctuation in lake volume. The number of boats used in the calculation was the total number of all types of boats launched. This includes a very minor contribution from sailboats. The histograms appear in Figures 4, 5, 8, and 9. An examination of Figures 8 and 9 shows that during both summers a maximum in the boat concentration occurs during the July 4th weekend. In fact, the largest number of boat launchings per week in both summers was 420, and occurred during the July 4th week.

These maxima in boat concentrations correlate with the maxima
in lead level concentration at the boat dock, Figures 8 and 9.
A correlation between boat concentration and lead concentration
at the boat dock also exists in the data obtained in the Fall
of 1976, Figure 4. The correlation between boats launched and
boat dock lead concentration is even more evident if the absolute
numbers of boats launched, rather then boat concentration is
plotted versus lead concentration as in Figures 10 and 11. It
is significant too, that the greatest lead concentrations at
the boat dock, and the greatest fluctuations in these values
occurred during the summer of 1977 when the boat concentrations
were higher than at any other period during this study. This
is especially evident during the July 4th week. In 1976 the
boat concentration during this period was 0.015 boats-per-acre-ft
and the lead concentration was 1.2 ppb, whereas, in 1977, a year
of extreme drought conditions, the corresponding values were
0.032 boats-per-acre-ft and 4.0 ppb, respectively.

The behavior of the inlet and outlet lead concentrations
is quite different from that of the boat dock and shows no
correlation with boat concentration.

Plug Flow Model: As mentioned previously, during both
summers, water flowed continuously through the lake, and the
lead concentration was always higher at the outlet than at the
inlet. In view of this, the summer data were treated in terms
of a simple plug flow model. The average monthly residence

times of the water in the lake were calculated by dividing the
average monthly volume by the average monthly rate of outflow.
The results are shown in Table 3.

It will be noticed that the lowest residence times occurred
in the summer months when irrigation water usage was at a
maximum. The average residence times during the summers of
1976 and 1977 were 8 and 9 days, respectively.

The residence times represent the times required for the
total lake volume to flow out of the lake, and their average
value was reasonably close to the seven-day interval between
our sampling times. To calculate the increase in lead
concentration in a given volume of water as it passed through
the lake, we subtracted the inlet lead concentration at the
beginning of a seven-day interval from the outlet lead
concentration at the end of that interval. This difference
will be referred to as $\Delta(Pb)$. Thus, $\Delta(Pb)$ represents, roughly,
the change in lead concentration for an average plug of water
as it traverses the lake.

The plug-flow model could only be applied to data gathered
in the summers since only at these times did conditions
approximate a flow system.

Values of $\Delta(Pb)$ are shown in Figures 8 and 9 and they
range from 1 to 0 ppb. They show the same general behavior as
the lead concentrations at the dock except that they are shifted
in time. Especially significant are the maxima which appear

after the boat concentration maxima of the week of July 4th.

Although the temporal variations of $\Delta(Pb)$ and the boat concentrations appear to correlate with one another their absolute values do not. As mentioned previously, the boat concentrations in the summer of 1977 were nearly twice as great as in the summer of 1976. The doubling of the boat concentration is not reflected in the $\Delta(Pb)$ values; the range of these values was roughly the same for both summers.

To further investigate a possible relationship between the $\Delta(Pb)$ values and boating activity, a calculation was made to determine if the observed $\Delta(Pb)$ values were consistant with the number of boats using the lake. The calculation was based on the assumption that $\Delta(Pb)$, the rise in the lead level of the lake water, came entirely from the combustion of gasoline and that all of the lead in the exhaust gases was absorbed by the water. The calculation was made using some typical average data: $\Delta(Pb) = 0.5$ ppb, lake volume = 25,000 acre-feet (3.1×10^{10} liters), and the lead content of gasoline was taken to be 0.66 g of lead per liter of gasoline (Wheeler, et. al., 1978). The result is that approximately 6.0×10^3 gallons of gasoline would have to be burned in order to obtain the observed $\Delta(Pb)$. If we make the further assumption, based on a survey of local boating authorities, that each motorboat on Turlock Lake uses an average of ten gallons of gasoline and that the residence time of the

water is seven days, we obtain the result that 600 motorboats
must be launched in a seven-day interval to give $\Delta(Pb)$ = 0.5 ppb.
The maximum number of boats launched in a one-week interval
during our study was 420. This occurred only once during each
summer. The average weekly number of boats launched during
each summer was about 300. Thus, the increase in the lead
level of the water as it passed through the lake was greater,
by at least a factor of two, than would be expected on the basis
of the number of boats launched. This factor is probably much
larger since this calculation is based on the assumption that
all of the lead in the gasoline is absorbed by the water.
English et. al. (1963), in experiments designed to measure
pollutional effects of outboard motors, found that only 9 to
31% of the total lead in gasoline appeared in the exhaust water.

In summary then, the data suggest that boating is the main
contributor to aqueous lead at the boat dock. This is reasonable
since the dock area is the area of greatest boating activity.
All boats launched must pass through this area, and fueling
facilities are located there as well. The latter fact makes
the potential for gasoline spills there greater than elsewhere
in the lake. Furthermore, the dock is located in a cove
somewhat isolated from the main body of the lake and the water
in this area is probably not well mixed with that of the rest
of the lake. Thus, any impact of boating on water composition
should be most apparent in the dock area.

The relative contribution of boating to the lead concentration in the main body of the lake is less clear. The variation of the $\Delta(Pb)$ values calculated from the plug flow model show some correlation with boat concentration, but their absolute values do not. This latter discrepancy could be due to a deficiency in the plug flow model. It could also be indicative of other lead-controlling processes.

The Influence of Sediment-Water Interactions

A great deal of experimental evidence shows that sediment in contact with water can act as both a source and a sink for lead and other heavy metals (Jackson, et. al., 1978; Khalid, et. al., 1978; Lu and Chen, 1977; Ramanoorthy and Rust, 1978; Reece, et. al., 1978). Sediment-water interactions may also be playing a role in determining the lead level in the main body of Turlock Lake. Evidence for this comes from several sources. First of all, as we pointed out above, a correlation exists between the outlet-lead concentration and the lake volume, during both summers, Figures 12 and 13. One explanation for this behavior is that as the volume of the lake increases, previously dry soil, richer in exchangeable lead than the original sediment, comes into contact with lake water and migration of lead from this soil into the water occurs.

Equilibration Studies   Further information about sediment-water interactions in Turlock Lake were obtained in experiments in which lake sediment was equilibrated at 25°C with four different aqueous phases: milli-Q water, milli-Q water containing 10 ppb lead, Turlock Lake water, and Turlock Lake water containing 10 ppb lead. The results are shown in Table 5.

The experiments are conveniently divided into two groups: those involving milli-Q water (a and b in Table 5) and those involving lake water (c and d in Table 5). In both groups the equilibrium concentration of dissolved lead in the aqueous phase is independent of the initial lead concentration of the aqueous phase. The sediment appears to act as a lead buffer. It maintains a constant lead concentration in the aqueous phase by either adsorbing or desorbing lead.

This ability of the sediment to either adsorb or desorb lead could explain why the lake lead concentrations react to both volume increases and volume decreases. Volume increases cause the lead level to rise due to the desorption of lead from freshly covered soil, while the decreases in lead concentration accompanying volume decreases could be due to adsorption of lead by permanently submerged sediment.

Another interesting aspect of these data is that the equilibrium lead concentrations are essentially independent of whether milli-Q water or lake water is used. This implies that Turlock Lake water does not contain significant amounts of dissolved substances capable of influencing the solubility of lead, and that the effect of complexation reactions on the distribution of lead in the lake is minimal.

Summary

The lead concentration of Turlock Lake water measured at the inlet, outlet and boat dock fluctuates during the year. Comparison of lead concentrations measured at the inlet and outlet shows that, during two consecutive summers, the lead concentration increases as water flows through the lake. Furthermore, the fluctuations in outlet lead concentrations during the summers correlate with fluctuations in lake volume.

The application of a simple plug flow model to the water in the main body of the lake leads to the conclusion that boating cannot be the sole contributor to the lead concentration in this part of the lake, and that sediment-water interactions are probably significant. This latter observation is suggested by the observed correlation between outlet-lead concentration and lake volume, and also by laboratory experiments. In equilibration studies involving lake

sediment and an aqueous phase, the equilibrium aqueous lead concentration was found to be independent of the initial lead concentration of the aqueous phase, and of whether the aqueous phase solvent was Turlock Lake water or milli-Q water. This implies two things: a) that the sediment in contact with water is capable of either adsorbing or desorbing lead, and thus of regulating the lead concentration of the aqueous phase, and b) that the influence of complexation reactions on the equilibrium lead concentration is minimal. Extraction by EDTA shows that dry soil on the lake shore has a higher amount of exchangeable lead than the dried lake sediment.

In the boat dock area of the lake, which is subject to poor mixing and possible fuel spills, the impact of boating is apparent.

Acknowledgments

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TABLE 1

Typical Results of Experimental Checks for
Absorptive Losses on Container Walls.

Station	ppb of Pb
Inlet	$0.38 \pm 0.15 (0.36 \pm 0.20)$
Boat dock	$1.3 \pm 0.4 (1.1 \pm 0.48)$
Outlet	$0.91 \pm 0.25 (0.72 \pm 0.38)$

Values in parentheses were obtained with samples
filtered and acidified immediately after the sample
was taken. The other values were obtained with
samples filtered in the laboratory, 1-2 hours after
sampling, and not acidified.

TABLE 2

Chemical Characteristics of Turlock Lake Water

pH	6.0 - 6.8
Alkalinity, mg/l $CaCO_3$	15.5 - 16.6
Conductivity, μmho/cm	22.2 - 24.0
COD, mg/l	4.75 - 8.96
PO_4^{3-}, mg/l	0.15 - 0.05
NO_3^-, mg/l	0.00 - 0.70
Cl^-, mg/l	0.6 - 0.8

The above ranges of values were obtained during the summer months.

TABLE 3

Residence Times For Water In Turlock Lake

Month	Average Volume acre-feet	Average Outflow (acre-feet)/day	Average Residence time, days
June '76	23,122	3015.	7.67
July '76	21,912	3722.	5.89
Aug. '76	28,085	2941.	9.55
Sept.'76	14,166	1801.	7.87
Oct. '76	15,530	944.8	16.4
Nov. '76	25,064	0	∞
Dec. '76	24,370	0	∞
Mar. '77	25,967	455.0	57.1
Apr. '77	18,738	550.0	34.1
May '77	12,245	283.0	43.3
June '77	12,054	1036.	11.6
July '77	9,843	1279.	7.70
Aug. '77	7,556	988.0	7.65

TABLE 4

Characteristics of Shore-soil and Lake Sediment

Exchangeable Pb by EDTA Extration

    i)   Sediment 0.9 ± 0.2 µg Pb/g sediment

   ii)   Shore soil 1.5 ± 0.1 µg Pb/g soil

Lead concentration of sediment   21. ppm

Lead concentration of shore soil   18 ppm

TABLE 5

Results of experiments in which sediment was
equilibrated with various aqueous phases.

Initial Aqueous Phase	Equilibrium lead concentration of aqueous phase, ppb
a) milli-Q water	1.1±0.1
b) 10 ppb lead in milli-Q water	1.4±0.3
c) Turlock Lake water	1.3±0.6
d) 10 ppb lead in Turlock Lake water	1.6±0.8

FIGURE CAPTION

1. A map of Turlock Lake, showing the three sampling stations used in this study.

2. Lead concentrations and lake volume during summer 1976. $\bigcirc$, lead concentration at outlet; $\bullet$, lead concentration at inlet; $\triangle$ lead concentration at boat dock. Heavy line shows lake volume.

3. Lead concentrations and lake volume during summer 1977. $\bigcirc$, outlet concentration; $\bullet$, inlet concentration; $\triangle$, boat dock concentration. Heavy line shows lake volume.

4. Lead concentrations and boats per-unit-volume during fall 1976. $\bigcirc$, outlet concentration; $\bullet$, inlet concentration; $\triangle$, boat dock concentration. This histogram shows the number of boats per-acre-foot in the lake.

5. Lead concentrations and boats per-unit-volume during spring 1977. $\bigcirc$, outlet cocnetration; $\bullet$, inlet concentration; $\triangle$, boat dock concentration. The histogram shows the number of boats per-acre-foot in the lake.

6. Lead concentrations and lake volume during fall 1976. $\bigcirc$, outlet concentration; $\bullet$, inlet concentration. Heavy line shows lake volume. During this entire period, no water was released from the lake.

7. Lead concentrations and lake volume during spring 1977. $\bigcirc$, outlet concentration; $\bullet$, inlet concentration. Heavy line shows lake volume. The intervals labelled "Z.O." are periods of zero outflow from the lake.

8. A comparison of $\Delta(Pb)$ and the lead concentration at the boat dock with the number of boats per-unit-volume during summer 1976. $\triangle$, boat dock lead concentration; $\bigcirc$, $\Delta(Pb)$ values from plug-flow model. The histogram shows the number of boats per-unit-volume.

9. A comparison of $\Delta(Pb)$ and the lead concentration at the boat dock with the number of boats per-unit-volume during summer 1977. △, boat dock lead concentration; ◯, $\Delta(Pb)$ values from plug-flow model. The histogram shows the number of boats per-unit-volume.

10. A comparison of the lead concentration at the boat dock, (circles), and the total number of boats launched, (histogram), during summer 1976.

11. A comparison of the lead concentration at the boat dock, (circles), and the total number of boats launched, (histogram), during the summer 1977.

12. A comparison of the outlet lead concentration, (cirlces), and the lake volume (heavy line) during summer 1976. A correlation exists, although the two curves are shifted in time.

13. A comparison of the outlet lead concentration, (circles), and the lake volume, (heavy line), during summer 1977.

Boat Dock
Sampling Station

TURLOCK LAKE STATE PARK

N

Outlet Canal

Outlet
Sampling
Station

Inlet
Sampling
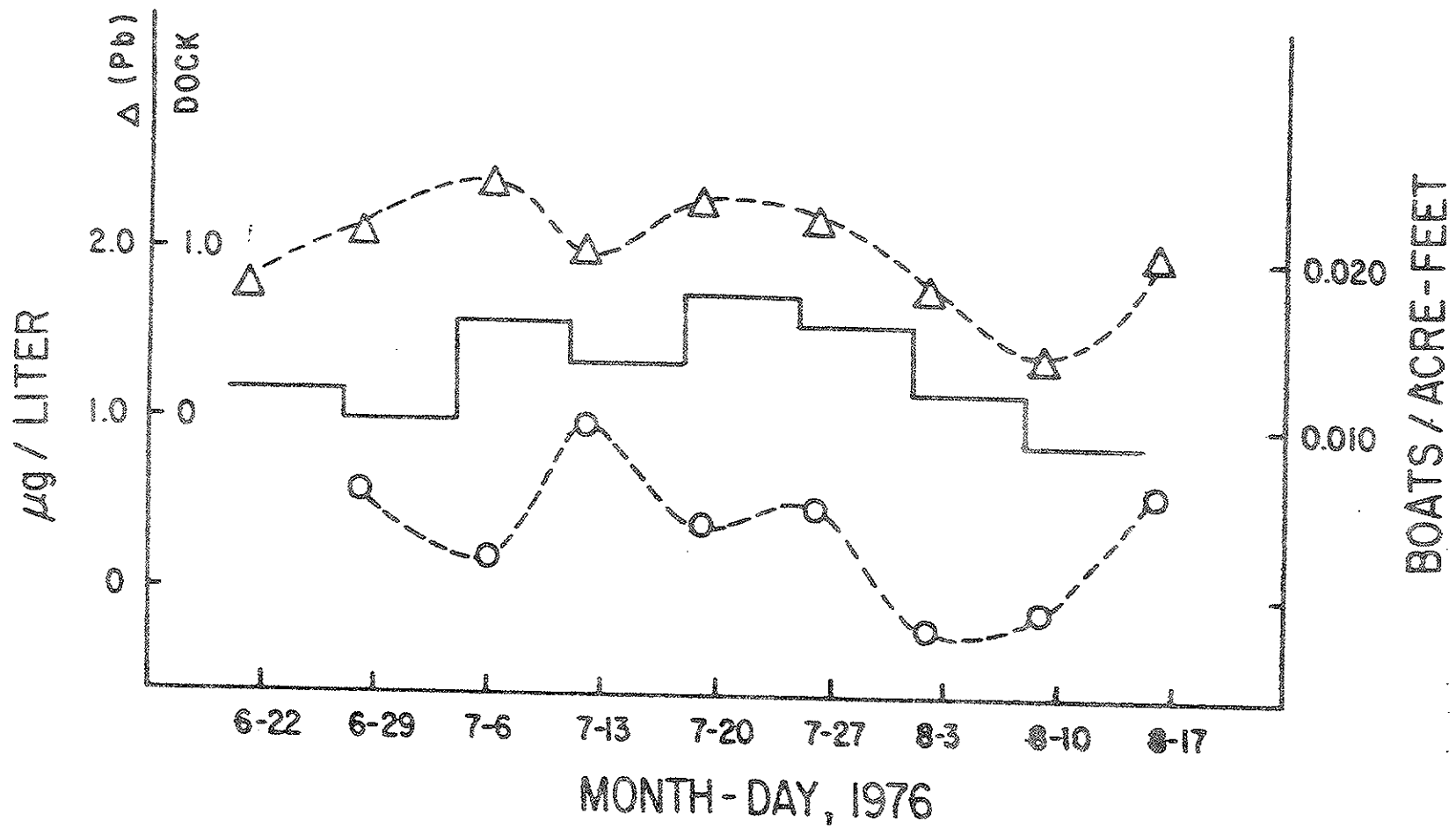Station

Inlet Canal
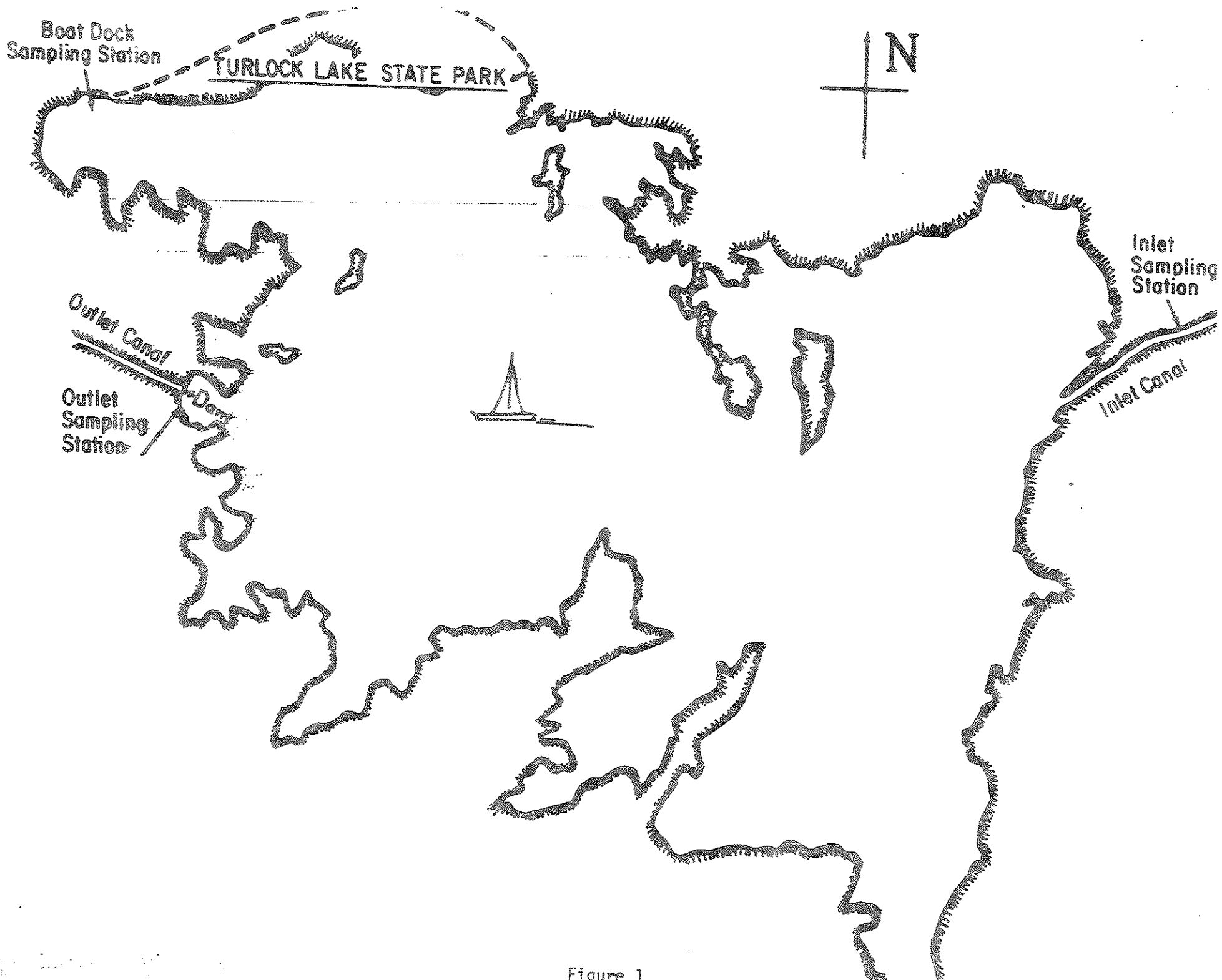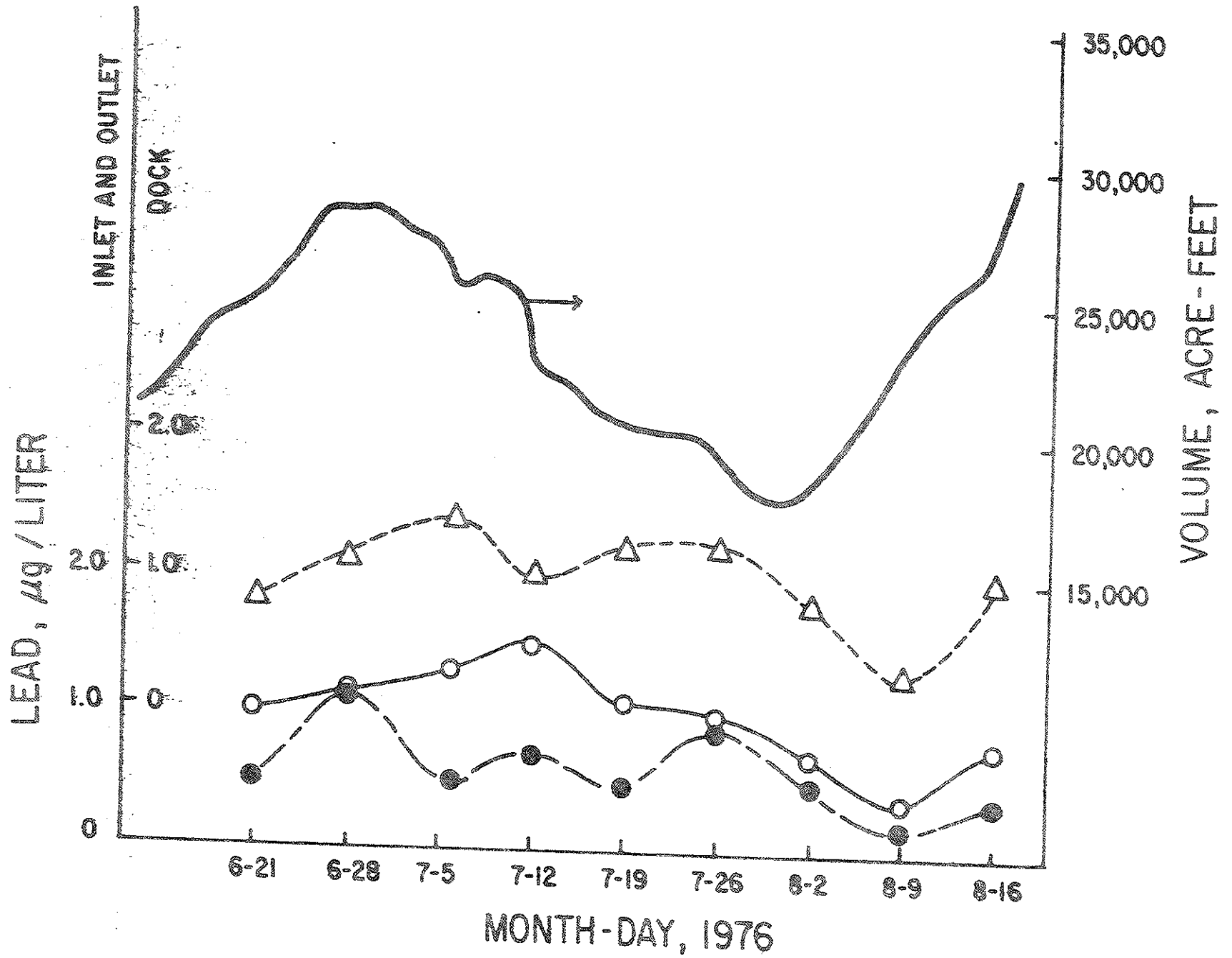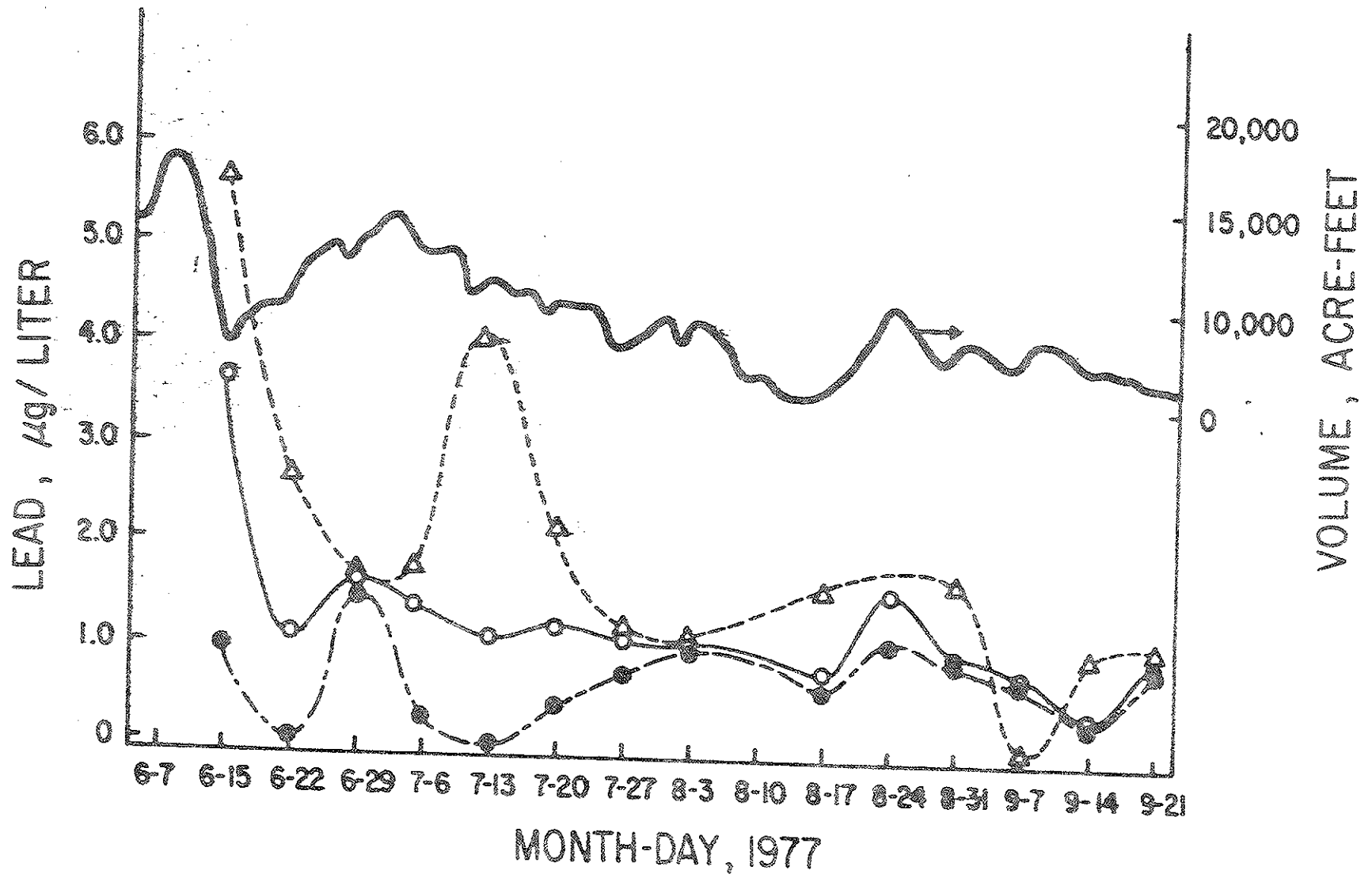
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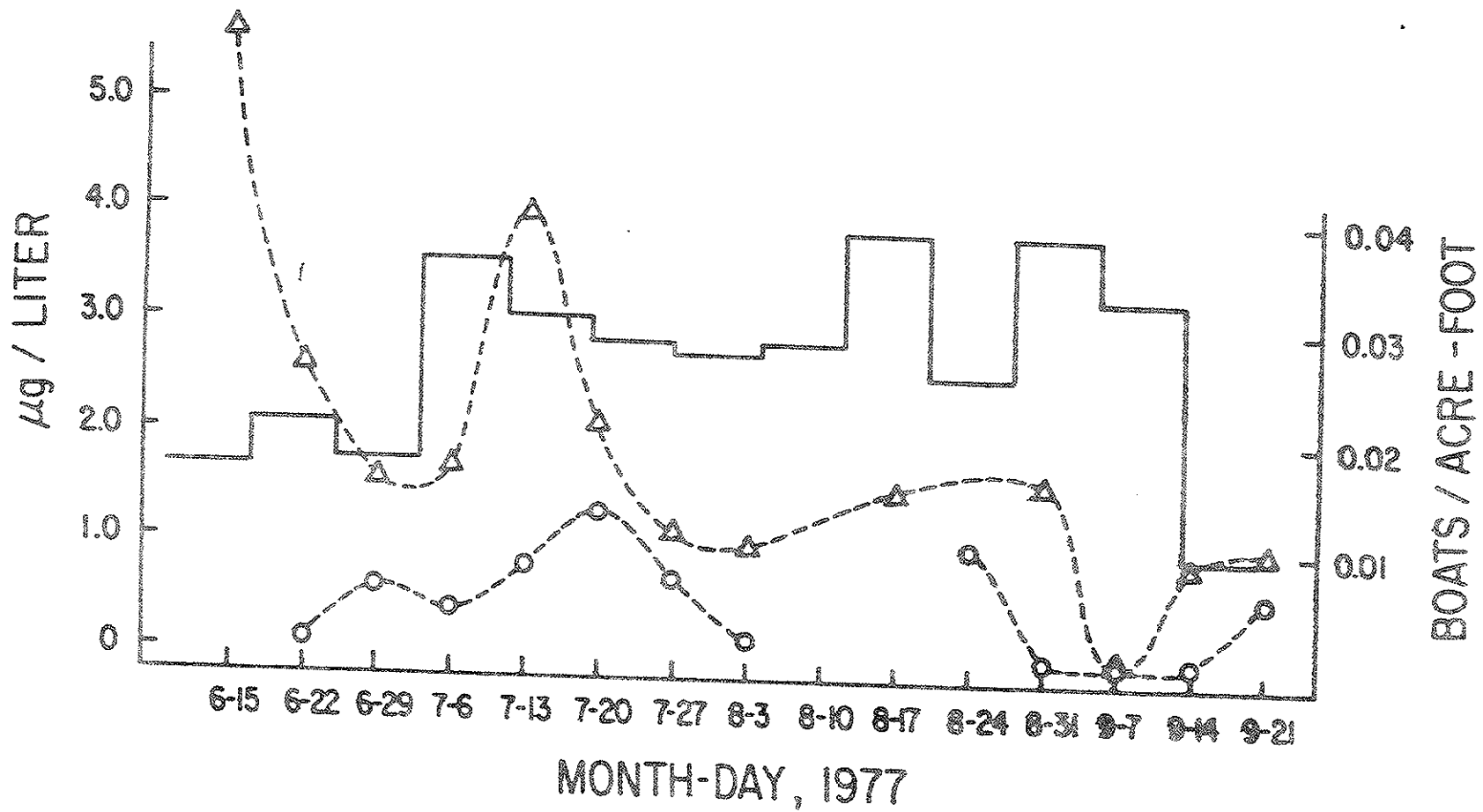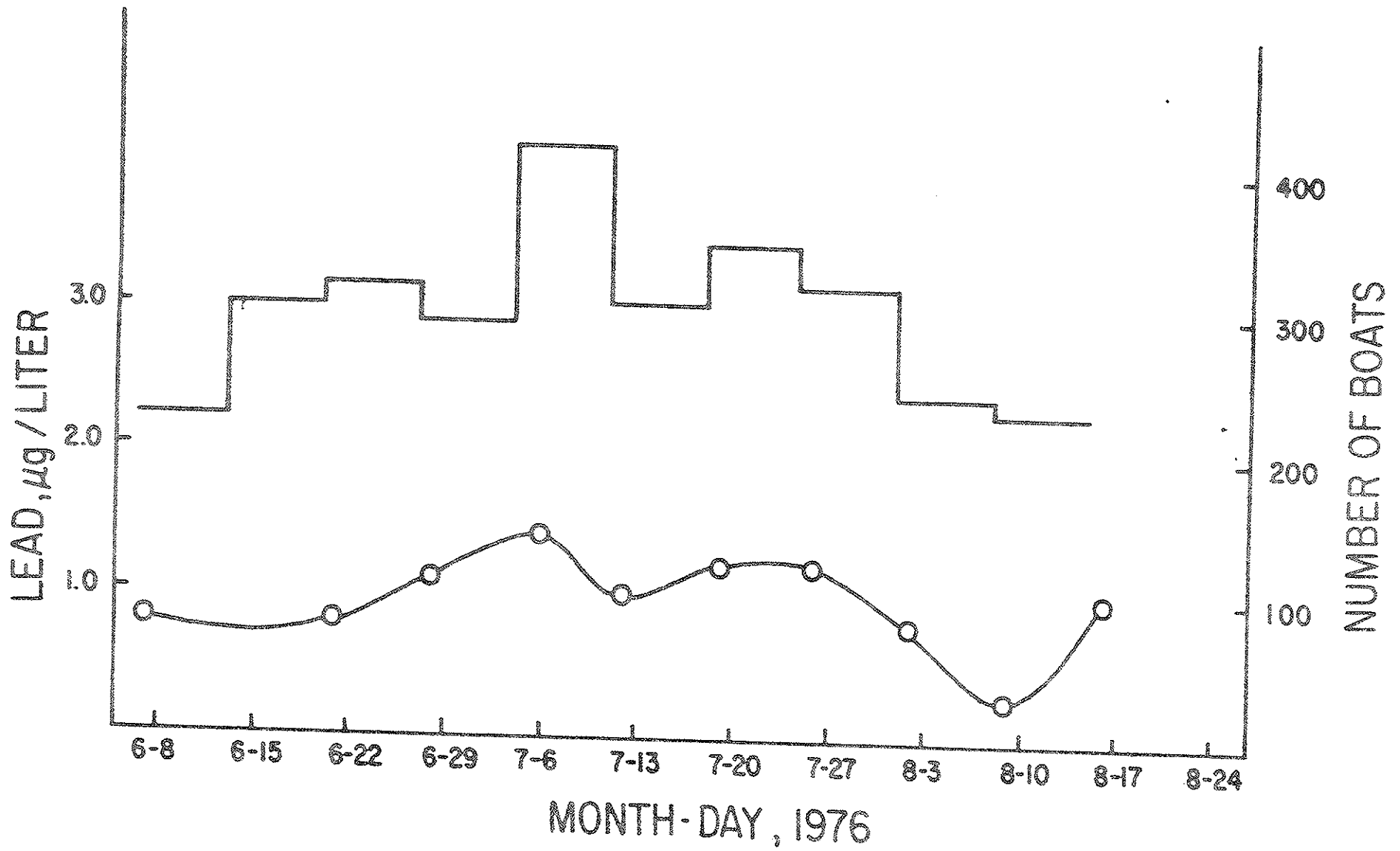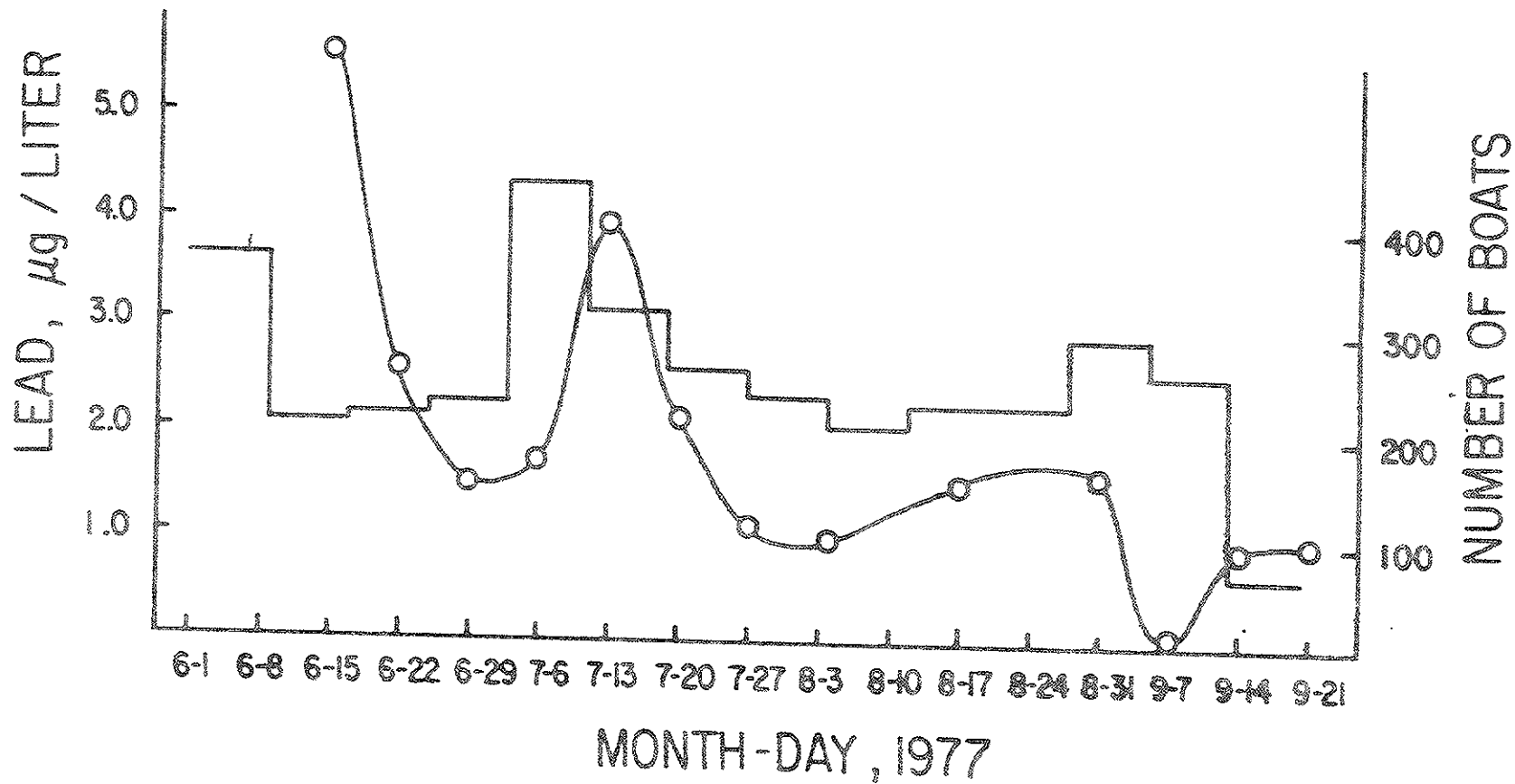
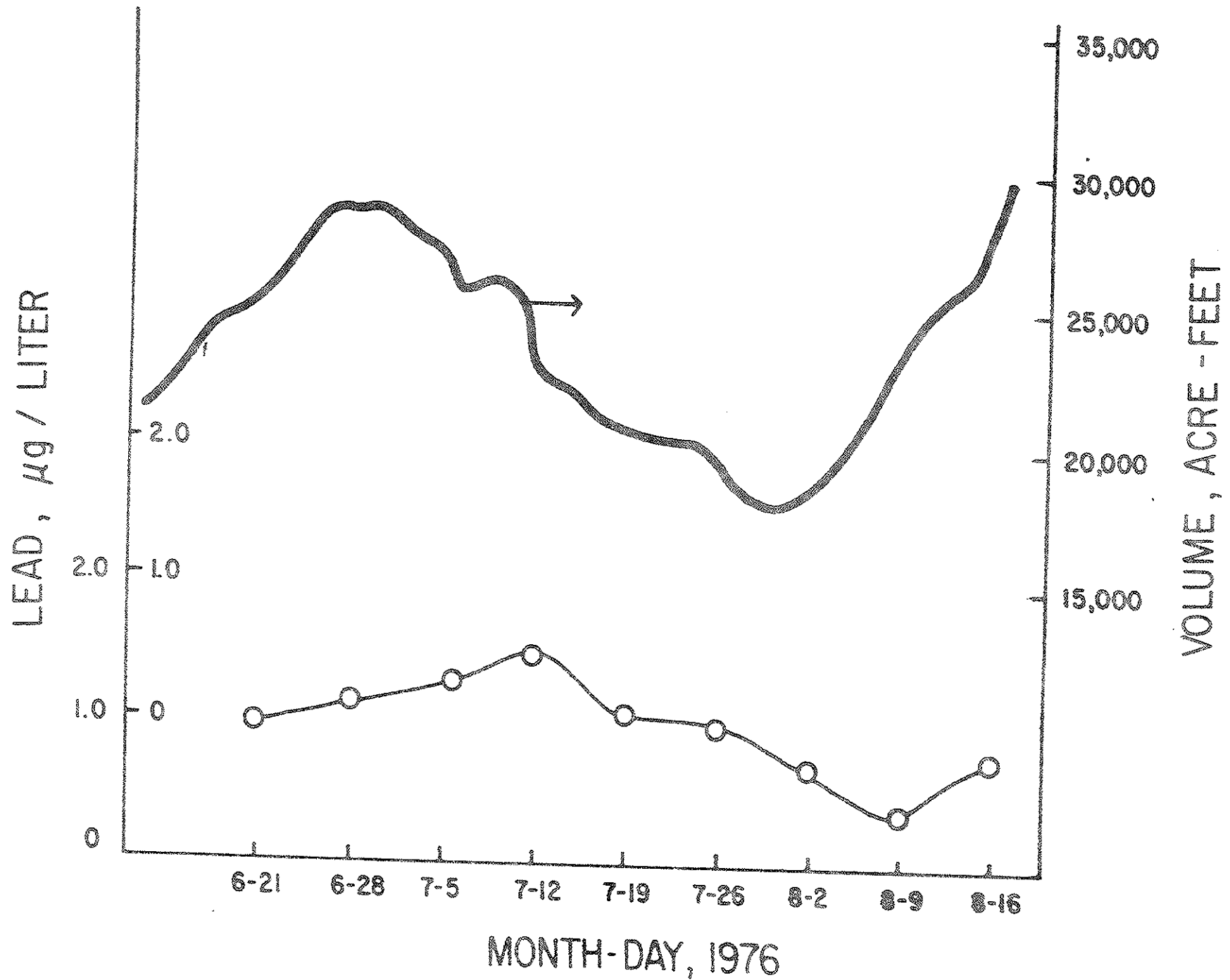Figure 2

Figure 3
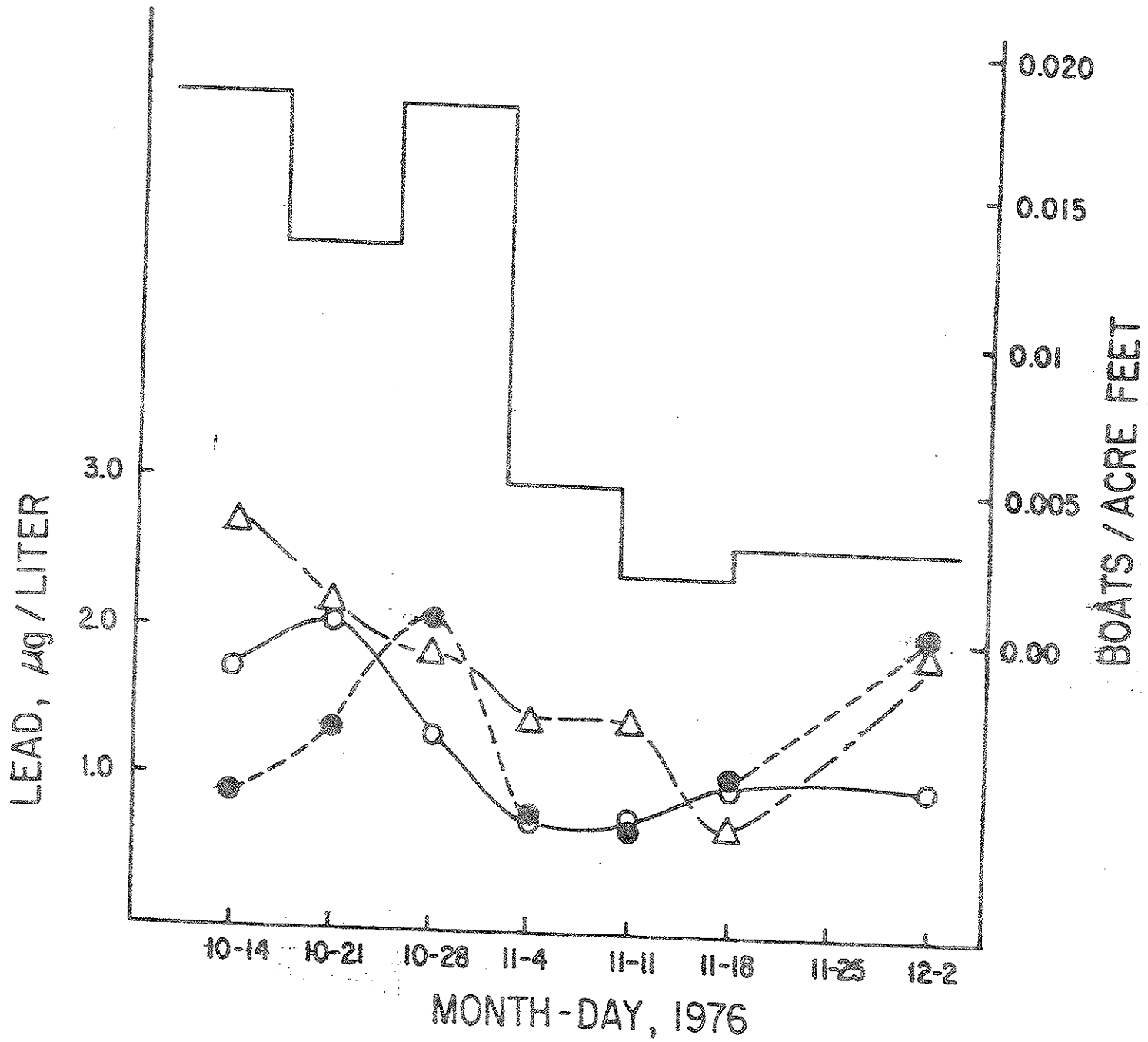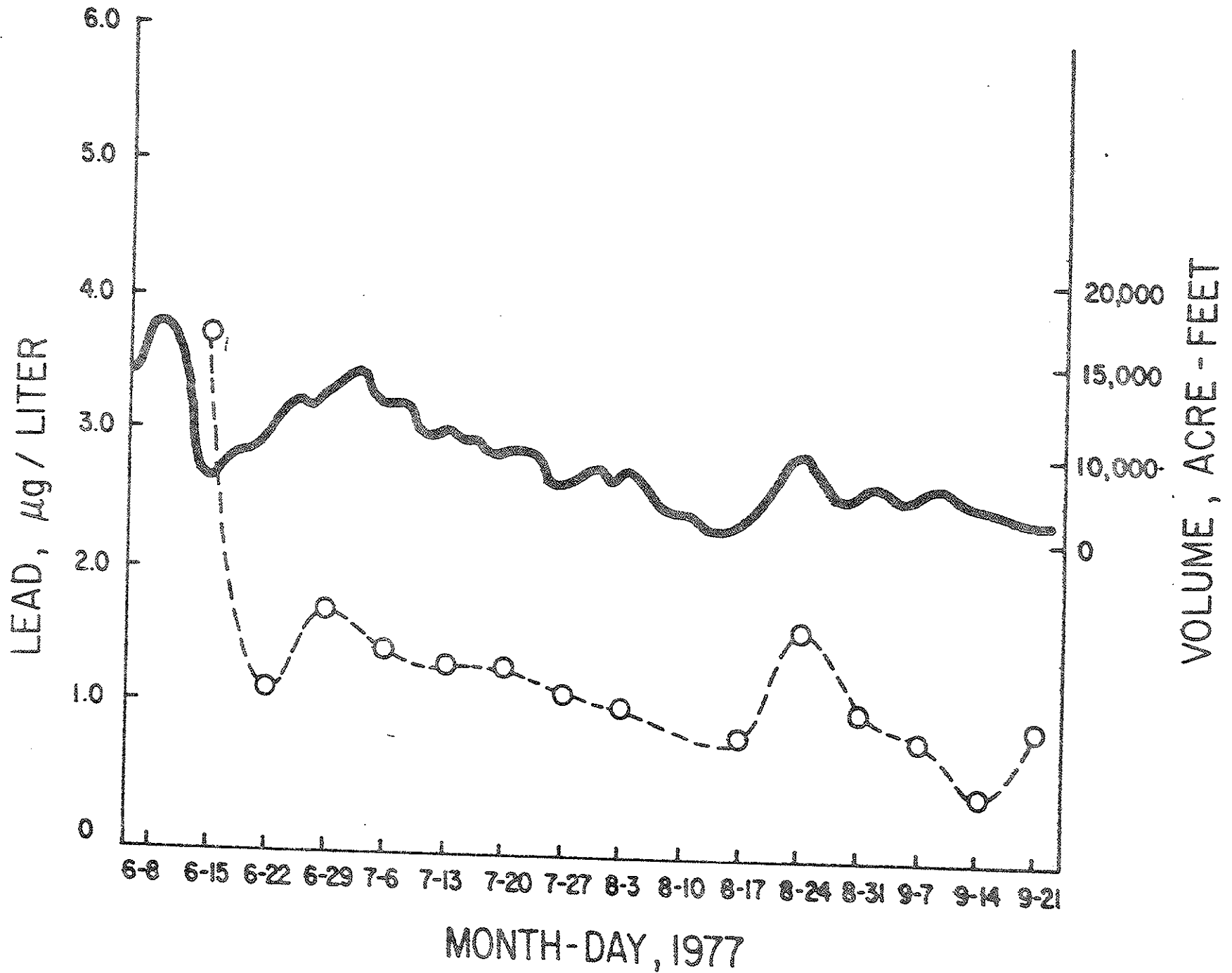
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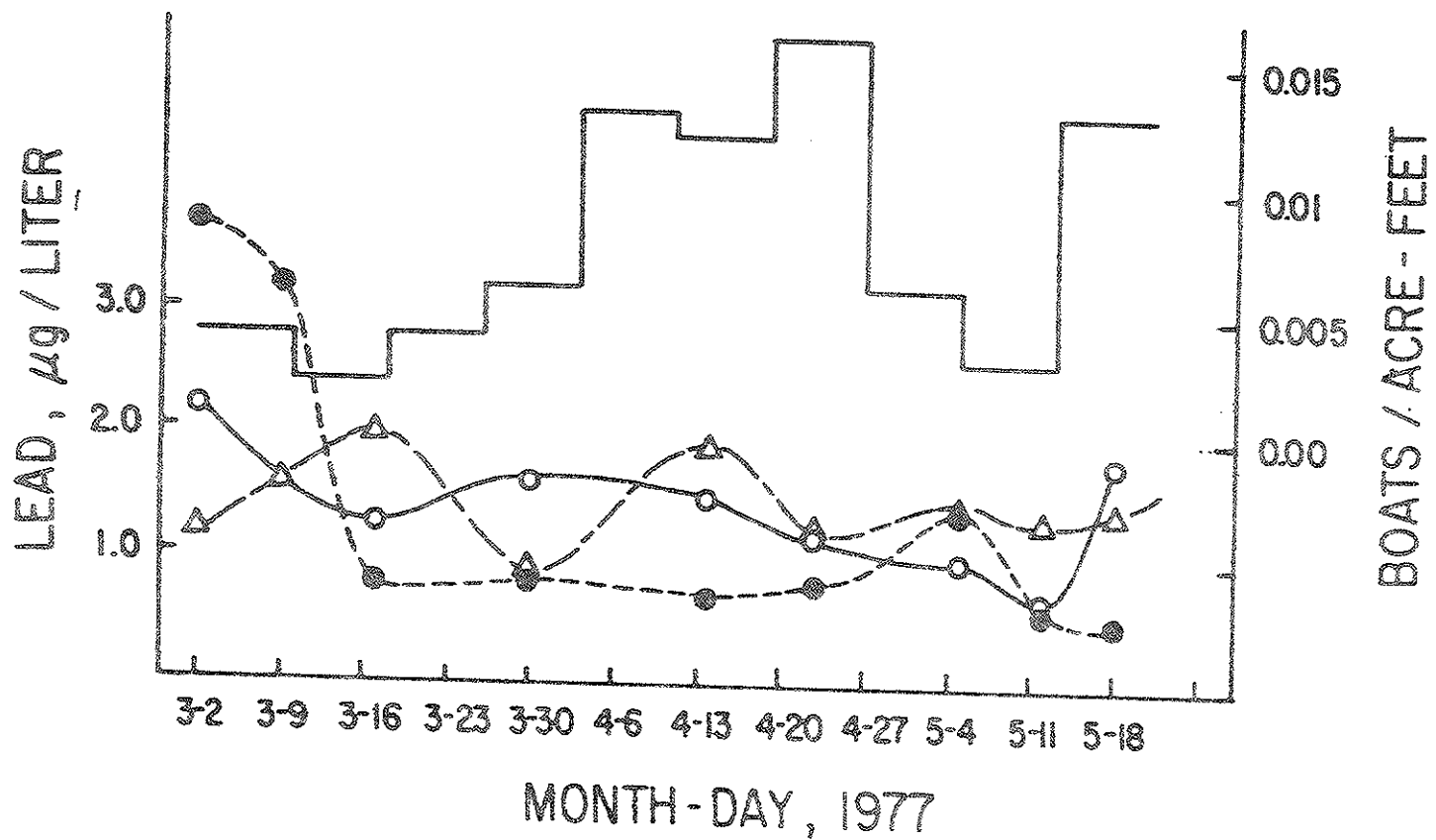
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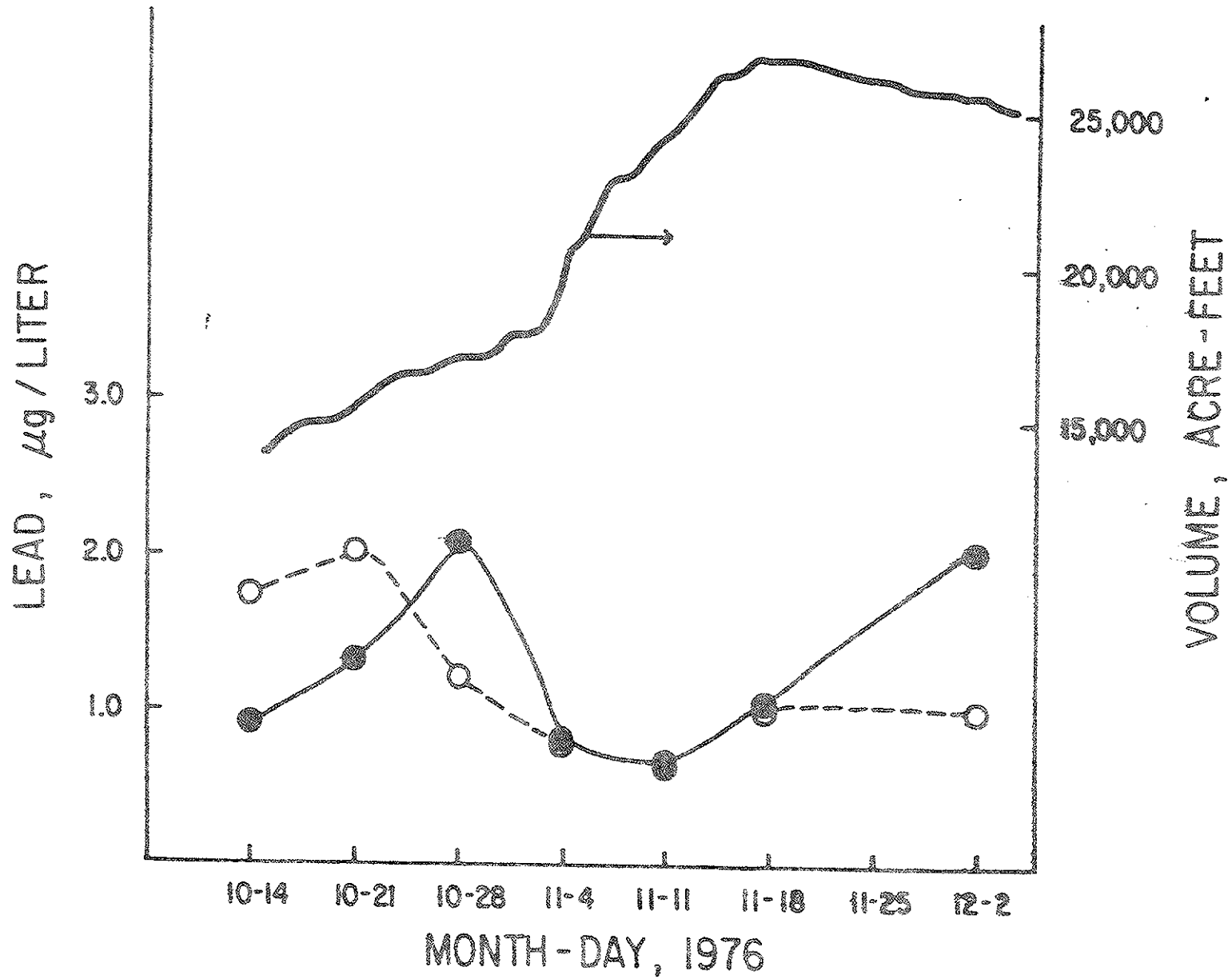
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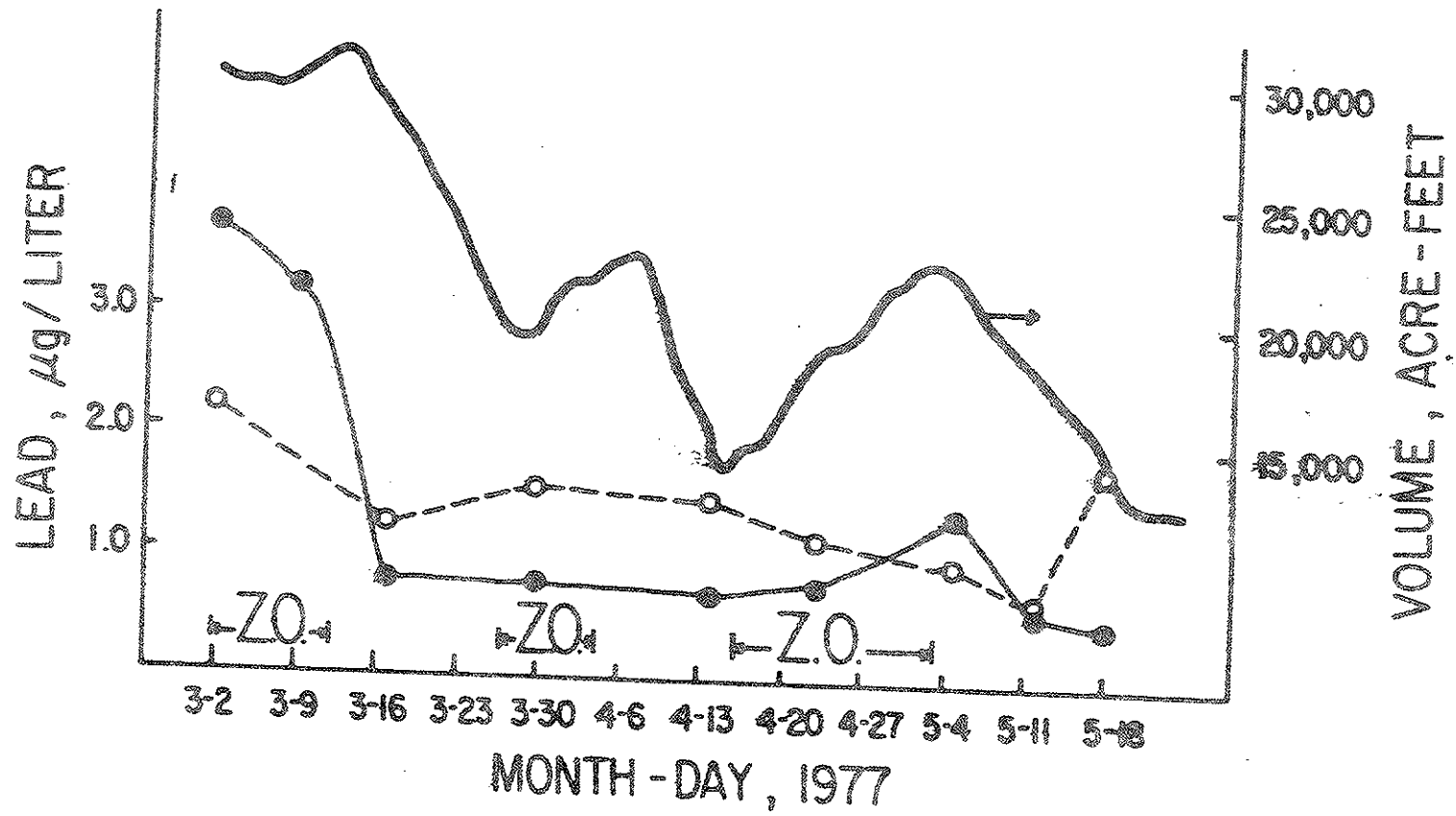
Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13