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PARTICULATE ORGANIC CARBON IN SAN FRANCISCO BAY, CALIFORNIA,

1971-1977

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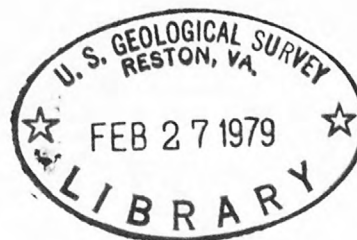
U. S. GEOLOGICAL SURVEY

Open-File Report 79-512

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Prepared as part of continuing

San Francisco Bay estuarine study



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March 1979

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By Laurence E. Schemel and Lee A. Dedini

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UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

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OPEN-FILE REPORT

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Abstract

The organic-carbon content of suspended particulate matter is determined by wet oxidation and analysis of the resulting CO₂ with an infrared analyzer. Modifications of methods and improved designs of apparatus are presented.

Results of particulate organic carbon (POC) analyses from 1971 through 1977 show that concentrations in North San Francisco Bay (estuary) typically decrease from the delta of the Sacramento and San Joaquin rivers to Golden Gate (seaward). Median winter (November through February) concentrations decrease from 85 to 30 µg-at./L seaward. During March through October, median concentrations are higher and ranges are wider. Concentrations frequently exceed 250 µg-at./L in the upper estuary.

POC concentrations in South San Francisco Bay are highest at the southern reach. POC is more abundant during March through October than during winter, but POC is not as abundant in South San Francisco Bay as it is in the estuary.

Introduction

The organic carbon content of suspended particulate matter (SPM) in estuarine waters can be measured by a modification of the dissolved organic carbon method described by Menzel and Vaccaro (1964). In this procedure, SPM is collected on a glass-fiber filter, then oxidized in a sealed glass ampule. The carbon dioxide resulting from the oxidation of the organic carbon fraction is measured by flushing the gaseous contents of the ampule through an infrared analyzer. This method is routinely used in our studies of San Francisco Bay (1971 to present) and has been progressively improved and modified to meet specific requirements. The present apparatus and method are presented here with results from San Francisco Bay.

Method

The description below is abbreviated in order to highlight modifications in procedure and apparatus. Some additional details are described by Strickland and Parsons (1972). The reader should refer to the manufacturer's manuals for operation of instruments mentioned below (Table 1). Similar apparatus and instruction manuals are available from Oceanography International Corporation (College Station, Texas)^{1/}.

Sample collection and preparation

Glass-fiber filters and glass ampules are baked in a muffle furnace to remove organic carbon contamination. Filters are baked for 1 hour at 450°C. Ampules are capped with aluminum foil, then baked for 4 hours at 550°C.

^{1/} The mention of brand names is for identification purposes and does not constitute endorsement by the U. S. Geological Survey.

SPM is collected on the filters under pressure or low vacuum (approx. 10 psi). The filter is folded, then inserted into an ampule. The aluminum cap is replaced and the sample is frozen until it can be sealed. Sample volume is an important factor. An appropriate volume must be filtered so that the organic carbon content is within the measurement range of the analysis. Typically, 100 to 250 mL is sufficient in San Francisco Bay, while 1000 mL is necessary in the ocean.

Potassium persulfate (0.2 g) and 0.01N phosphoric acid (10 ml) solution are added to each ampule just before it is sealed. A capillary tube is inserted and CO₂-free nitrogen gas is bubbled through the ampule contents to remove inorganic carbon. After approximately 5 minutes, the ampule is sealed with a micro-torch. Ampules are autoclaved in a pressure vessel for 12 to 16 hours (overnight) at 150°C. After the sample is autoclaved, it can be stored indefinitely.

Standard preparation

Ampules containing standard concentrations of sucrose are processed in the same manner as samples. Sucrose solutions are prepared by diluting a 1.25 g-at./L stock solution with 0.01N phosphoric acid solution. Aliquots (10 mL) of each concentration are transferred to ampules containing oxidant and sealed immediately. A typical set of particulate organic carbon (POC) standards includes a reagent blank and five or six sucrose concentrations ranging to 75 µg-at. of carbon per ampule.

Analytical procedure

POC in the ampules is oxidized to a stoichiometric amount of carbon dioxide. After an ampule is broken, the flow of nitrogen gas (200 mL/min) purges the carbon dioxide from the solution (Fig. 1). Water vapor is removed from the gas stream by magnesium perchlorate in the drying tubes, and the infrared analyzer (IRA) measures the relative concentration of carbon dioxide in the gas stream. The signal from the IRA is recorded on the analog chart and the peak area is automatically computed. Each sample requires approximately 5 minutes for analysis.

The breaking of the ampule and purging of the carbon dioxide are critical procedures, which prompted the design of the ampule breaking assembly (Fig. 2). The four-way valve (in the bypass position) allows an ampule to be placed in the breaking assembly without interrupting the gas flow to the IRA. The base of the ampule is seated in the clamp. The clamp is tightened until the "O" ring is slightly compressed between the ampule shoulder and the plastic block. The location of the "O" ring seal at the ampule shoulder has considerable advantage, because an ampule will rarely crack or shatter below the color-break line on its neck.

Samples are analyzed in the following manner. The cutter tube is withdrawn to its limit and the purge tube is inserted to the ampule top. The cutter tube and purge tube fittings are slightly tightened. The four-way valve is switched; residual carbon dioxide is flushed from the ampule breaking assembly and the integrator establishes a base line. The purge tube is then withdrawn beyond the cutters and the cutter-tube

fitting is loosened. The next steps, breaking of the ampule, and insertion of the purge tube, must be performed in a continuous and rapid sequence. The cutters are lowered to the top of the ampule, which is then broken by direct pressure of the cutters and a twisting action. The cutter tube is quickly withdrawn to its limit; the purge tube is inserted to the bottom of the ampule, and the fittings are tightened. Withdrawal of the cutter tube is necessary to minimize dead volume in the assembly.

When the ampule is broken, the pressure of the contained carbon dioxide is released, causing a rapid signal increase at the beginning of the peak (Fig. 3). Purging of the gas from the liquid phase, however, is a slower process and the eluted peak is skewed as a consequence. If too much time elapses between breaking and insertion of the purge tube into the liquid phase, a double peak will be eluted. The relative shapes of sample and standard peaks must be the same; therefore, double peaks give inaccurate results. This limitation is imposed by the inherent nonlinearity of the infrared analyzer.

To reduce analysis time and to conserve dessicant, the entire peak is not eluted. Rather, the integrator calculates the peak area until the IRA signal decreases to a predetermined level (about 2 percent of full scale). The cut-off point is reproducibly detected by a comparator device, which transmits a command to the integrator (Fig. 4). The area of the remaining portion is small in relation to the integrated area and does not noticeably affect the shape of the standard curve or incur other significant errors.

Standardization and data reduction

The IRA does not respond linearly to increases in the carbon dioxide concentration and becomes more nonlinear with increasing concentration.

Since increasing concentrations result in less signal per unit concentration increase, there exists a practical limit where the analyzer is incapable of detecting rather large changes. The near-linear low-concentration range of the analyzer must be used in order to relate peak-area to an amount of carbon dioxide. In this range, the small differences in relative peak shape are less important.

Two variables, the amount of carbon in the most concentrated samples and the range of the infrared analyzer, must be optimized. The volume of water filtered must be sufficiently large to minimize sampling errors (constitute a representative sample), but may be decreased when other parameters (i.e., chlorophyll a fluorescence, etc.) suggest that more or fewer phytoplankton are present. The range of the IRA is most directly related to the path length of the (sample and reference) cells. Shorter cell lengths increase the range of the analysis, but decrease the sensitivity.

The standard curve relates nominal peak areas (integrator counts) to amounts of carbon (Fig. 5). With 5-inch cells, the range of the POC analysis was limited to approximately 250 $\mu\text{g-at./L}$ for a 250-mL sample. After the cell lengths were decreased to 1.25 inches (in April, 1977), the range was extended to 300 $\mu\text{g-at./L}$ (250-mL sample) with better linearity and reproducibility. A recent modification (January, 1978) allows the sample volume to be decreased to 100 mL, in effect extending the measurement range to 750 $\mu\text{g-at./L}$.

The standard curve is approximated by a second-order function within the measurement range shown in Fig. 5. The expression cannot be used to calculated concentrations significantly higher than the most concentrated

standard because of the increasing nonlinearity of the curve. Therefore, such results must be reported as being greater than the highest standard. This is apparent in the results reported below.

Replicate sucrose standards agree within 2 percent. With the current sampling and ampule-sealing procedures, we estimate the accuracy of the analysis to be approximately ± 5 percent of value.

POC in San Francisco Bay

The presence of SPM is readily observable in San Francisco Bay. During winter and spring, fresh-water discharge from the delta of the Sacramento and San Joaquin rivers (Fig. 6) supplies massive amounts of SPM (mostly lithogenic) to North Bay (Conomos and Peterson, 1977), and the turbid water often penetrates the northern reach of South Bay (Carlson and McCulloch, 1974). The delta discharge has important effects on the abundance and circulation of SPM throughout the year. Circulation resulting from the delta discharge (estuarine circulation) maintains a turbidity maximum in the upper estuary, its actual location being a function of the discharge rate (Peterson et al., 1975a). Phytoplankton, living particles, are similarly trapped in the upper estuary, and, under conditions of increased insolation and decreased discharge rate, grow to produce a maximum (Peterson et al., 1975b). In situ production by phytoplankton and delta discharge have been identified as sources of POC in North Bay (Spiker and Schemel, in press).

The sources of POC in South Bay have not been well defined. Local streams and the Delta discharge are not capable of maintaining high SPM concentrations in the South Bay. The sectional volume of the South Bay decreases southward, increasing the effectiveness of local sources in

influencing the water quality. In particular, substantial sewage inflows in the southern half of South Bay are a major factor determining nutrient concentrations (McCulloch et al., 1970), and they also influence, directly or indirectly, the dissolved organic carbon concentrations (Schemel, 1971). Data collected during 1976-1977 do not show excessive POC abundance, even in the southernmost reach of South Bay (Schemel et al., in press). Stable carbon isotope ratios of South Bay POC indicate that, in situ-grown phytoplankton, resuspended bottom sediments, and unidentifiable land-derived matter are major sources (Spiker and Schemel, in press).

In addition to the effects of major seasonal events, large variations in chlorophyll a fluorescence and turbidity occur over short distances (100 m or less) in San Francisco Bay (Schemel, 1975). These variations are primarily due to tide- and wind-induced (turbulent) mixing. Coincident variations in POC probably exist, but would be difficult to quantify. Variations on this scale have the effect of increasing the range of POC, which is encountered at any location or salinity. All of the above factors contribute to the observed POC distributions in the Bay, making interpretation difficult, except where one process obviously dominates. Other processes, which may influence POC distributions in the Bay, are discussed by Head (1975) and Biggs and Flemer (1972).

Results

Particulate organic carbon samples were collected at permanent sampling locations in San Francisco Bay (Fig. 6). Water was pumped from the 2-m depth with a low-capacity in situ pump and salinity, temperature, and other parameters were simultaneously measured at the time the sample was collected (Schemel and Dedini, in press). Results

presented here are from bimonthly cruises, 1971-1977; numerical values are compiled by Smith et al. (1979).

Results are separated into three seasonal groups. The winter period (November through February), with normally increasing and highest delta discharge rates and low water temperatures, is least favorable for in situ production by phytoplankton. Decreasing delta discharge and increasing water temperature and insolation typify the spring period (March through June). During the summer period (July through October), delta discharge is lowest and water temperature is highest.

South Bay results are presented with respect to distance from Golden Gate. North Bay results are related to salinity in an attempt to normalize some effects of differing delta discharge rates and tides during the different sampling times. POC concentrations exceeding the measurement range (250 $\mu\text{g-at./L}$) are represented as solid circles.

North Bay POC decreases with increasing salinity (seaward) during winter (Fig. 7). The range of values also decreases seaward. Delta and low-salinity POC ranges between low values (20 $\mu\text{g-at./L}$) and values higher than the measurement range. The median value of approximately 95 percent of the delta samples is about 85 $\mu\text{g-at./L}$. The range of values at mid- to high-salinity is about 30 $\mu\text{g-at./L}$. The median value decreases from about 55 $\mu\text{g-at./L}$ at mid-salinity to about 30 $\mu\text{g-at./L}$ seaward.

POC in North Bay is more concentrated and the range is wider during spring (Fig. 8). A large number of the samples landward are higher than the measurement range and median values are higher than in winter. The range of landward values is over 200 $\mu\text{g-at./L}$. The median value at high salinity is about 50 $\mu\text{g-at./L}$ with a range of over 100 $\mu\text{g-at./L}$.

The spring distribution is similar to that during winter in that concentration and range appear to decrease seaward.

Summer POC median values and ranges in North Bay are similar to those during spring (Fig. 9). The lowest and highest concentrations occur during summer and spring.

South Bay POC concentrations increase southward during winter (Fig. 10). The median value for the northern reach is about 40 $\mu\text{g-at./L}$ and the range is 50 $\mu\text{g-at./L}$ or less. The range of values in the southernmost reach exceeds 200 $\mu\text{g-at./L}$. Spring and summer POC concentrations also increase southward (Fig. 11, 12). The range in the northern reach increases (winter to spring) to over 100 $\mu\text{g-at./L}$, with a median value of about 60 $\mu\text{g-at./L}$. South Bay ranges and median values are slightly higher in spring than in summer. The winter to spring-summer POC increase in South Bay is less than that in North Bay. During spring and summer, POC is more concentrated in North Bay.

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Table 1. Manufacturers of instruments and equipment^{1/}

<u>Item</u>	<u>Model</u>	<u>Manufacturer</u>
Infrared analyzer	865	Beckman Instruments, Fullerton, CA
Recorder	SR	E. H. Sargent & Co., Chicago, IL
Integrator	Minigrator	Spectra-physics, Santa Clara, CA
Tube fittings	Swagelok	Crawford Fitting Co., Solon, OH
4-way valve	SS-43YF2	Whitey Research Tool Co., Emeryville, CA

^{1/}The mention of brand names is for identification purposes and does not constitute endorsement by the U. S. Geological Survey.

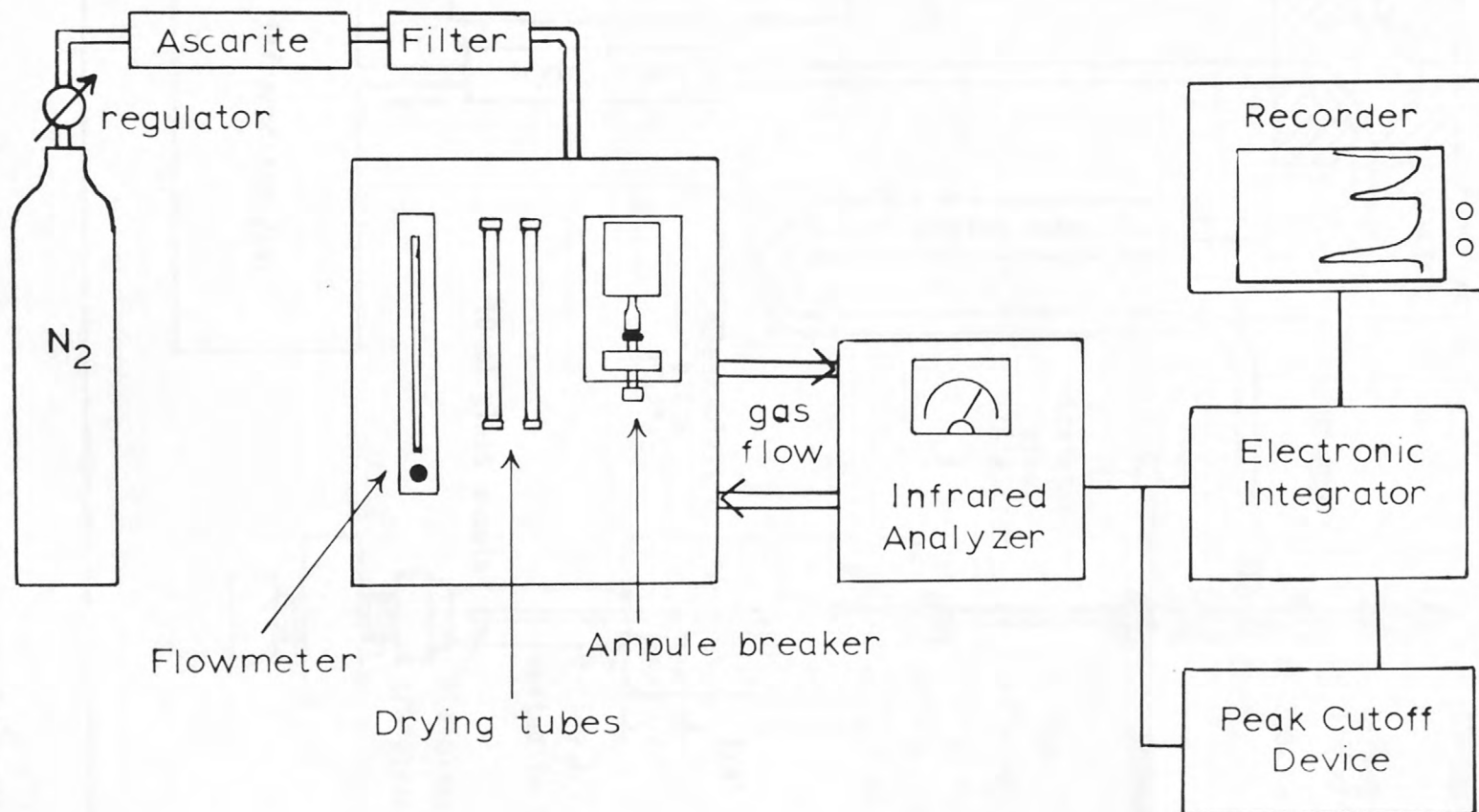


Figure 1. Particulate organic carbon analyzer.

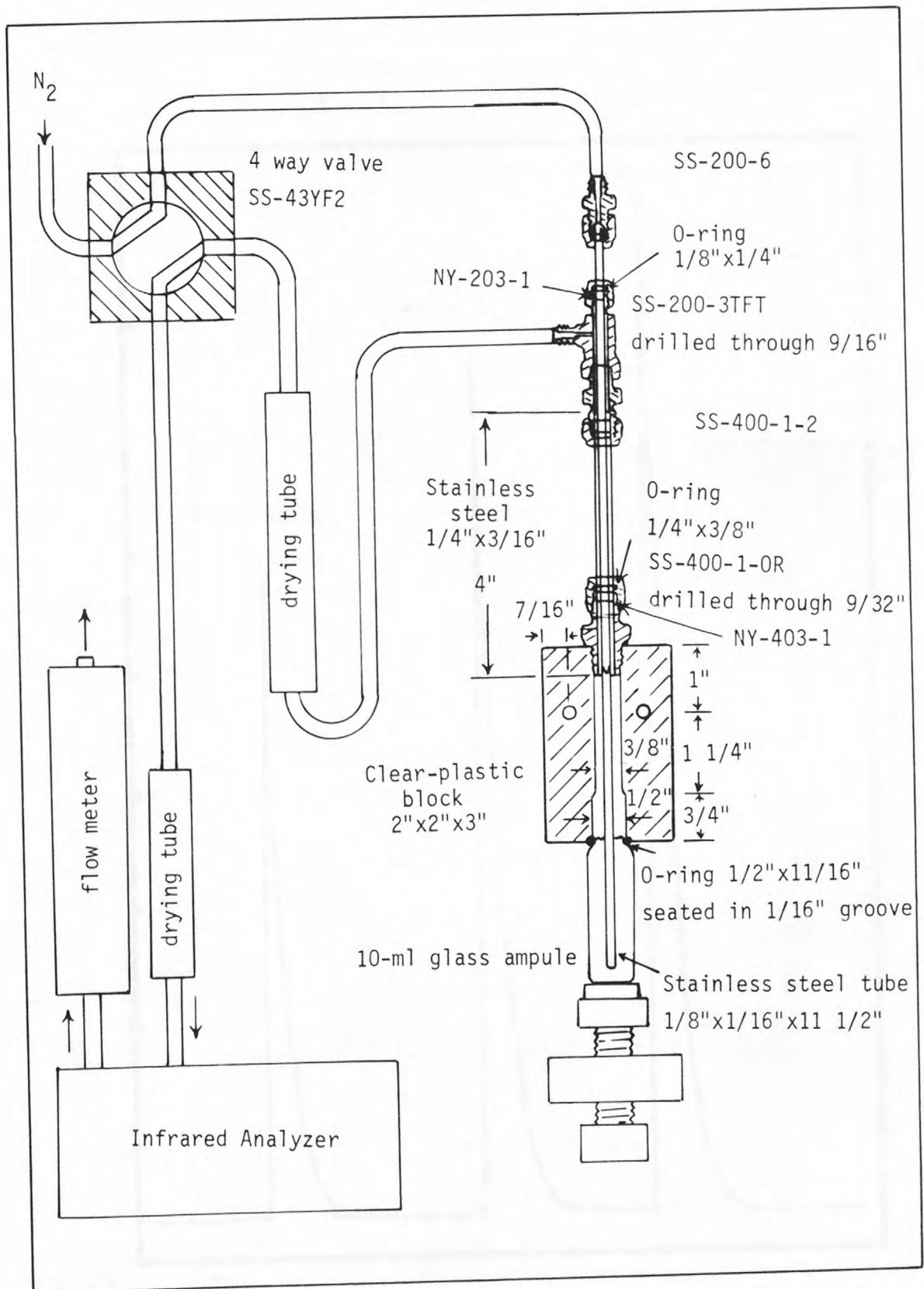


Figure 2. Gas flow diagram and details of ampule breaking assembly.

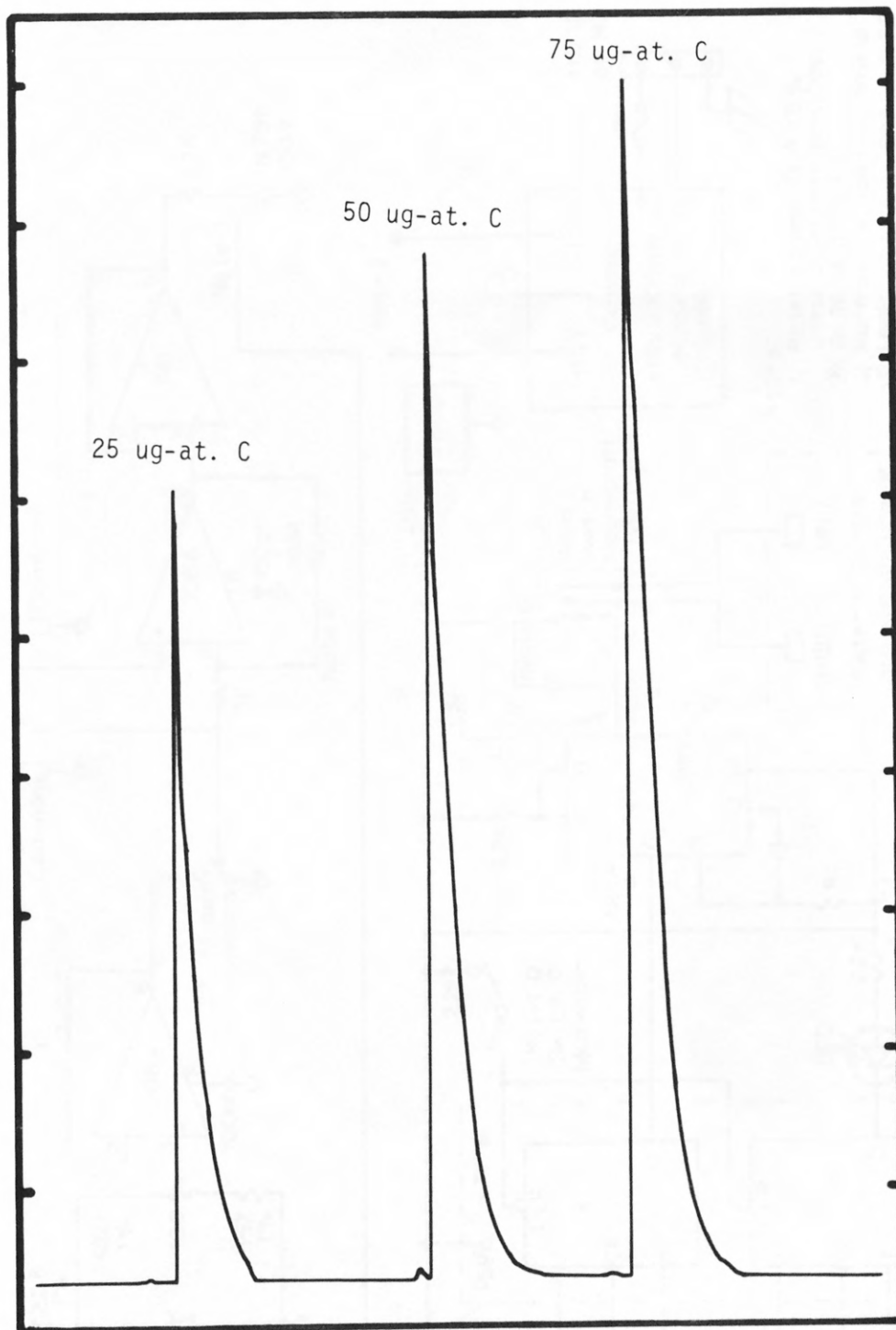


Figure 3. Typical peaks resulting from analyses of POC standards.

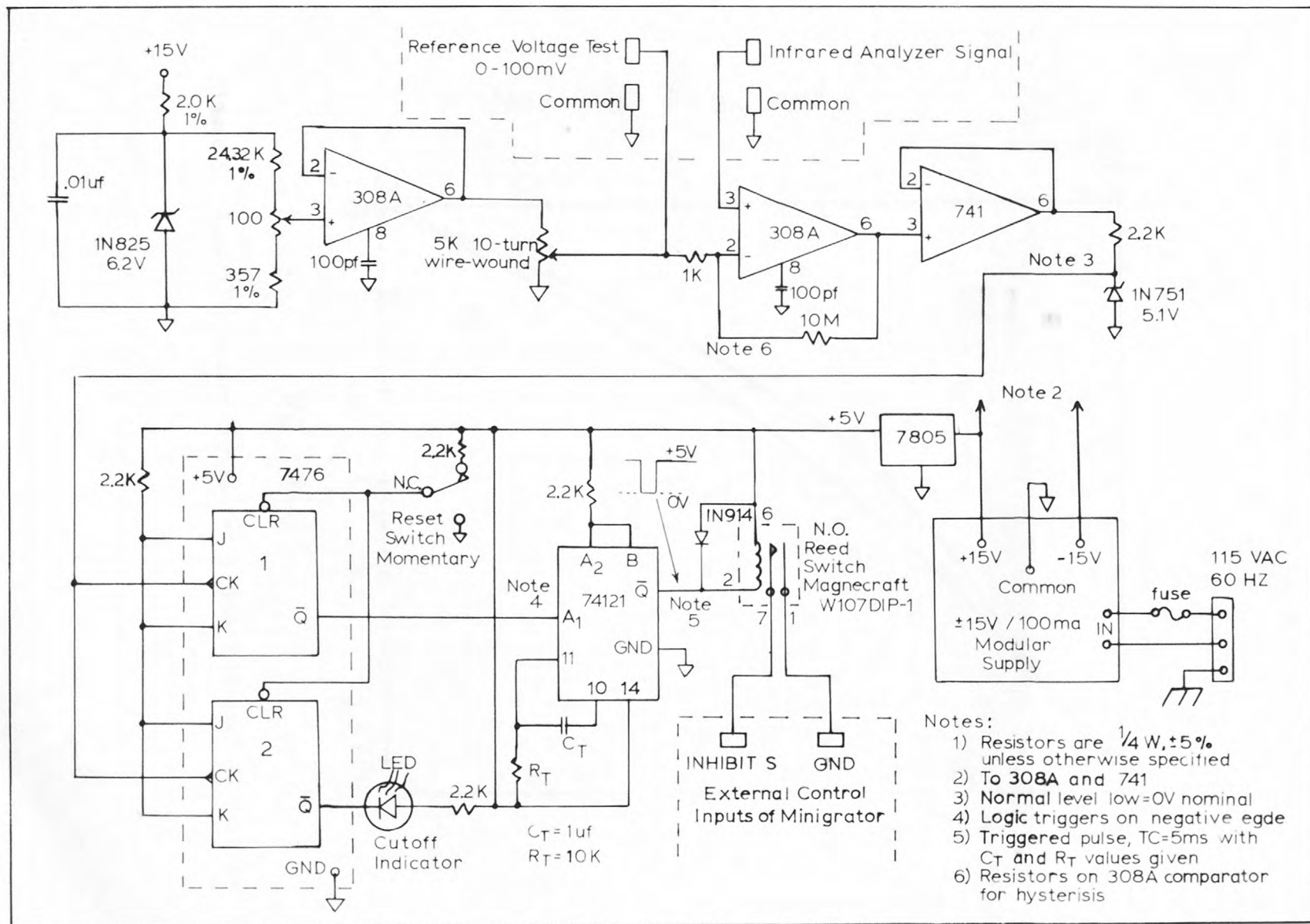


Figure 4. Schematic diagram of peak cut-off device.

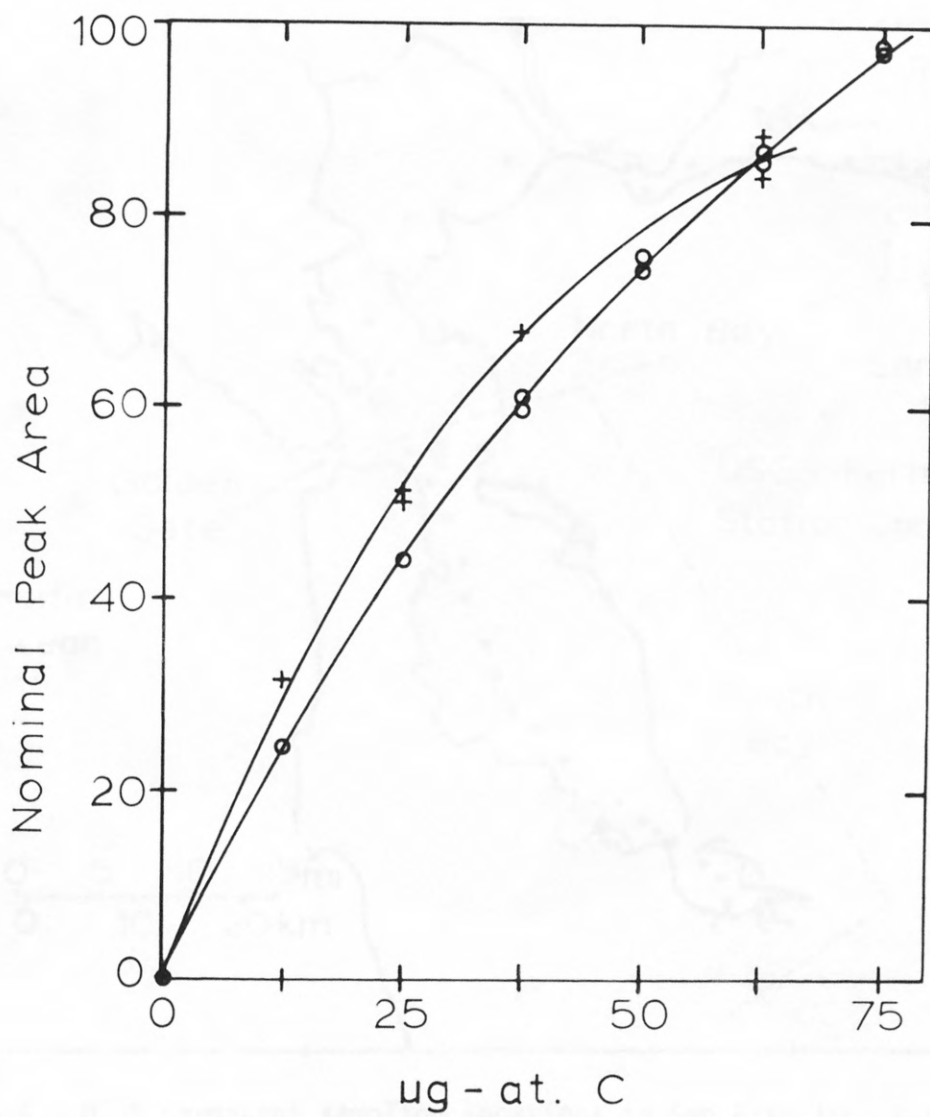


Figure 5. Typical standard curves for 5- and 1.25-inch IRA cells.

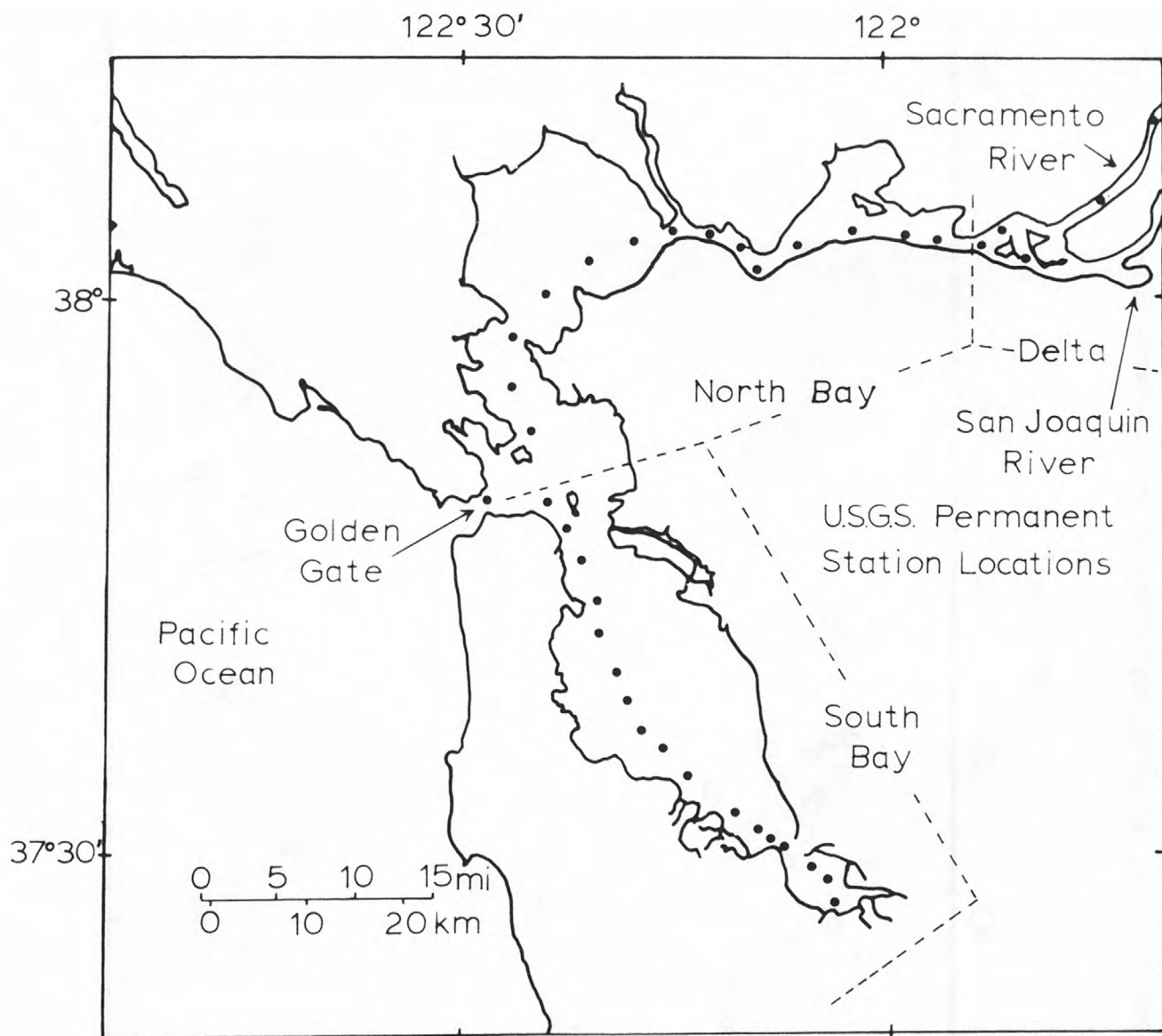


Figure 6. USGS permanent sampling locations in San Francisco Bay.

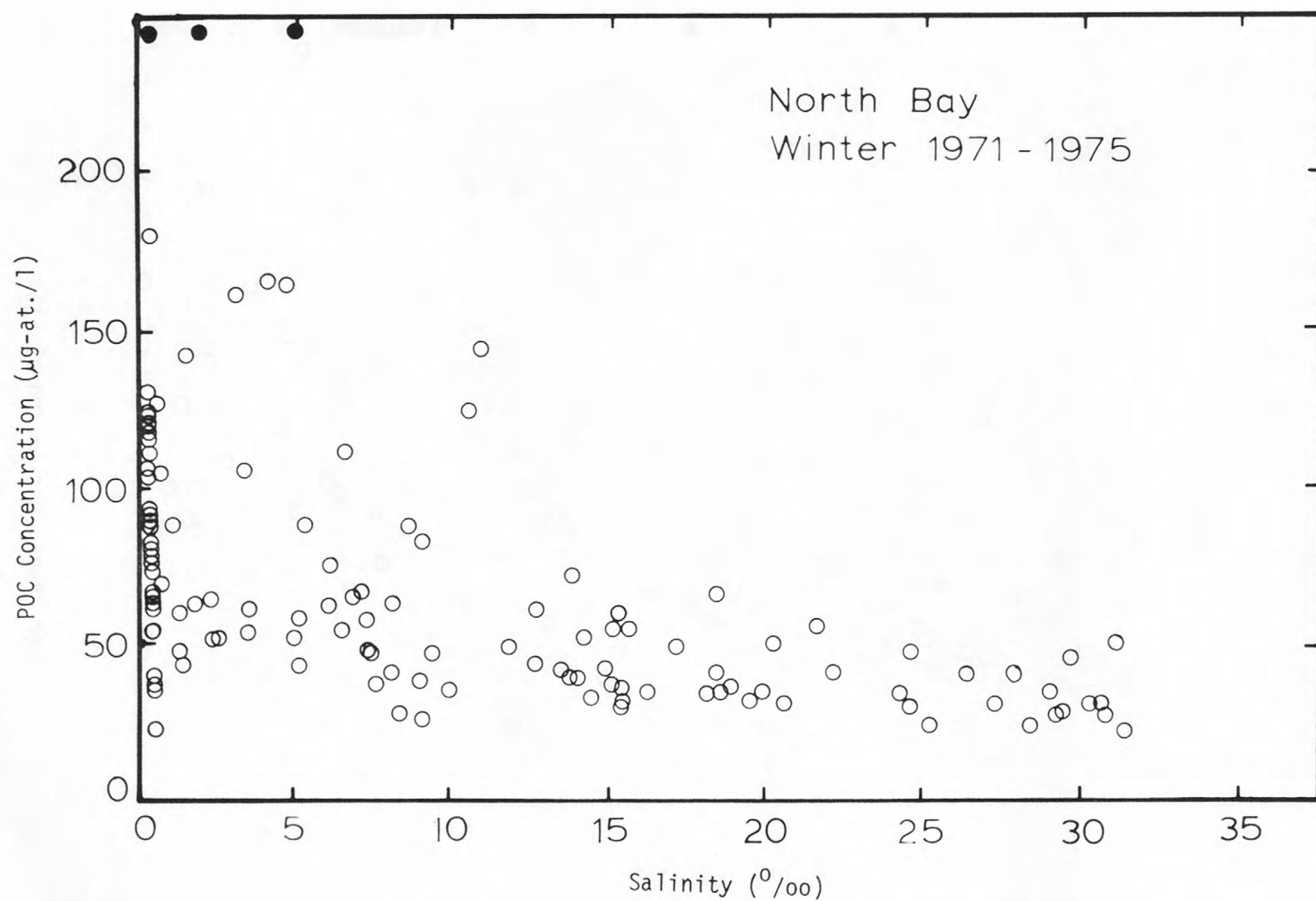


Figure 7. Distribution of POC in North San Francisco Bay, November-February, 1971-1975.

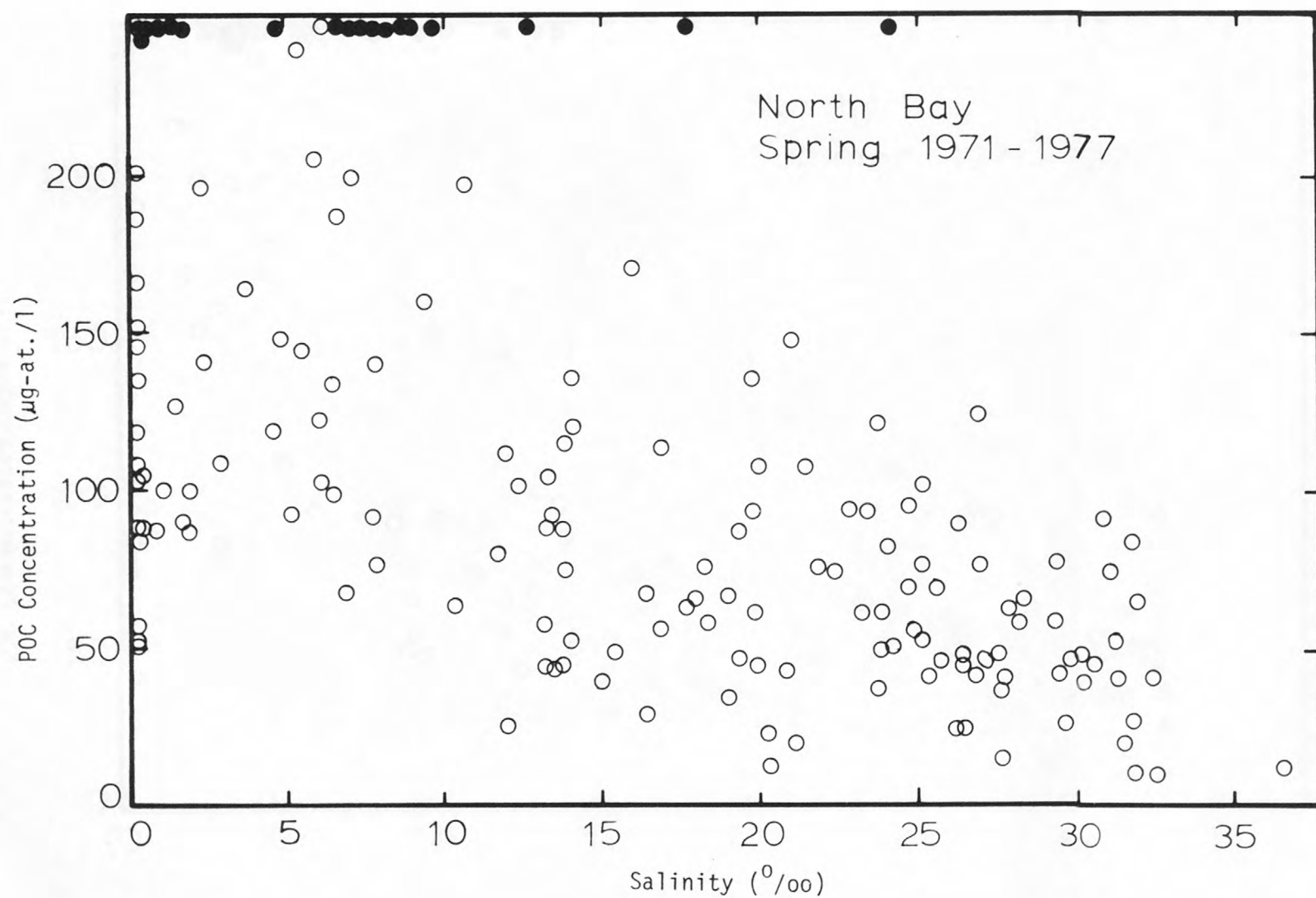


Figure 8. Distribution of POC in North San Francisco Bay, March-June, 1971-1977.

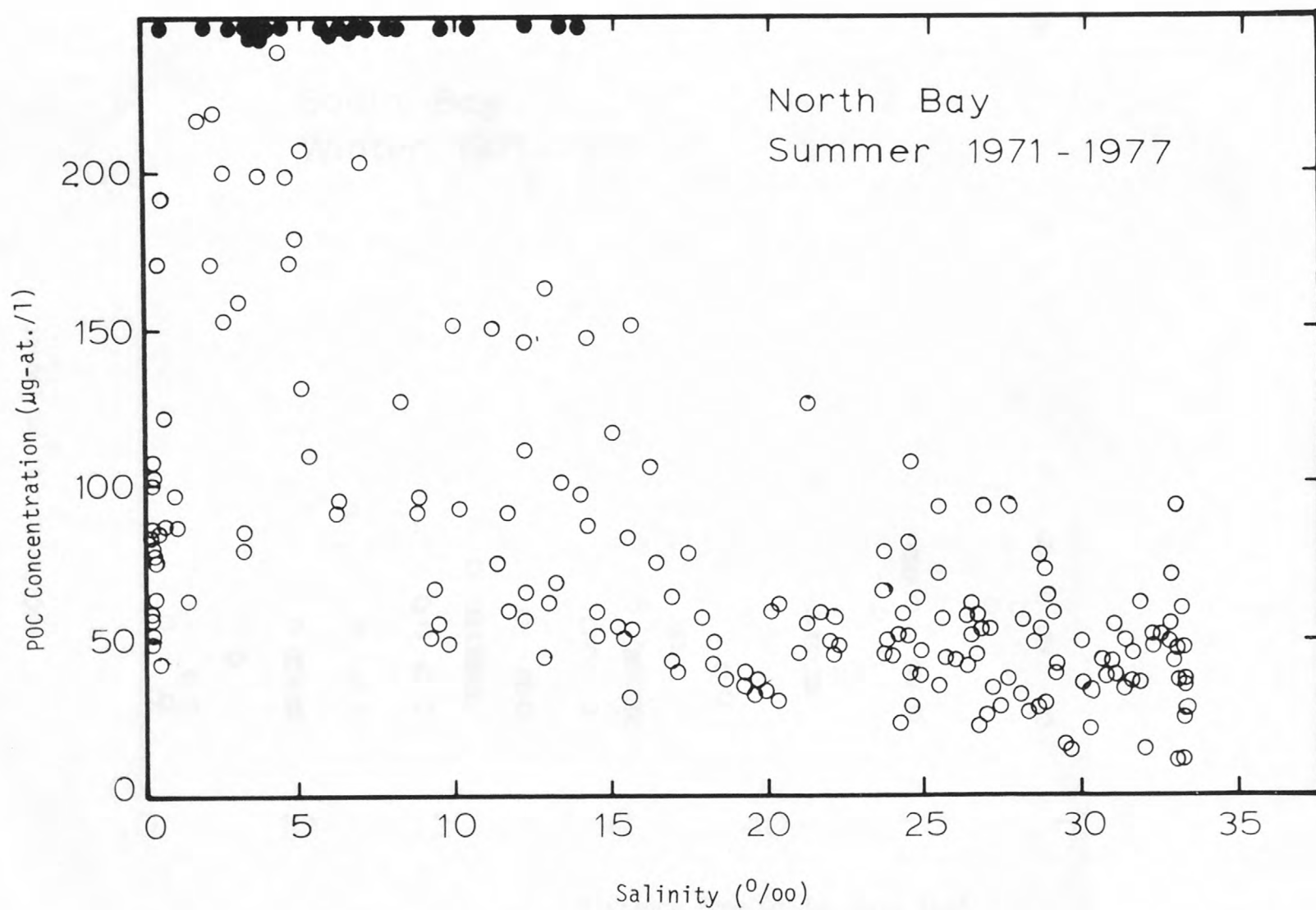


Figure 9. Distribution of POC in North San Francisco Bay, July-October, 1971-1977.

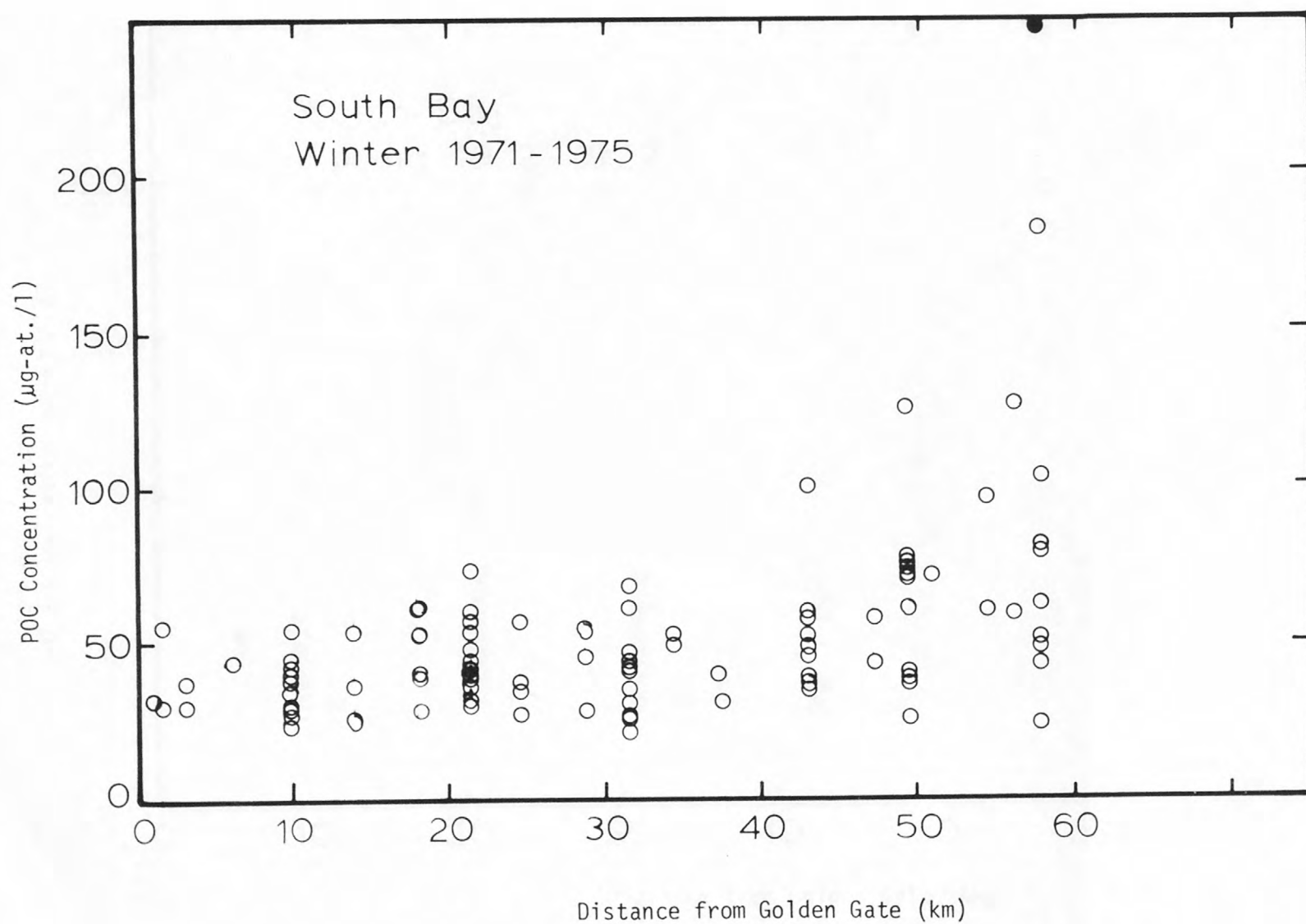


Figure 10. Distribution of POC in South San Francisco Bay, November-February, 1971-1975.

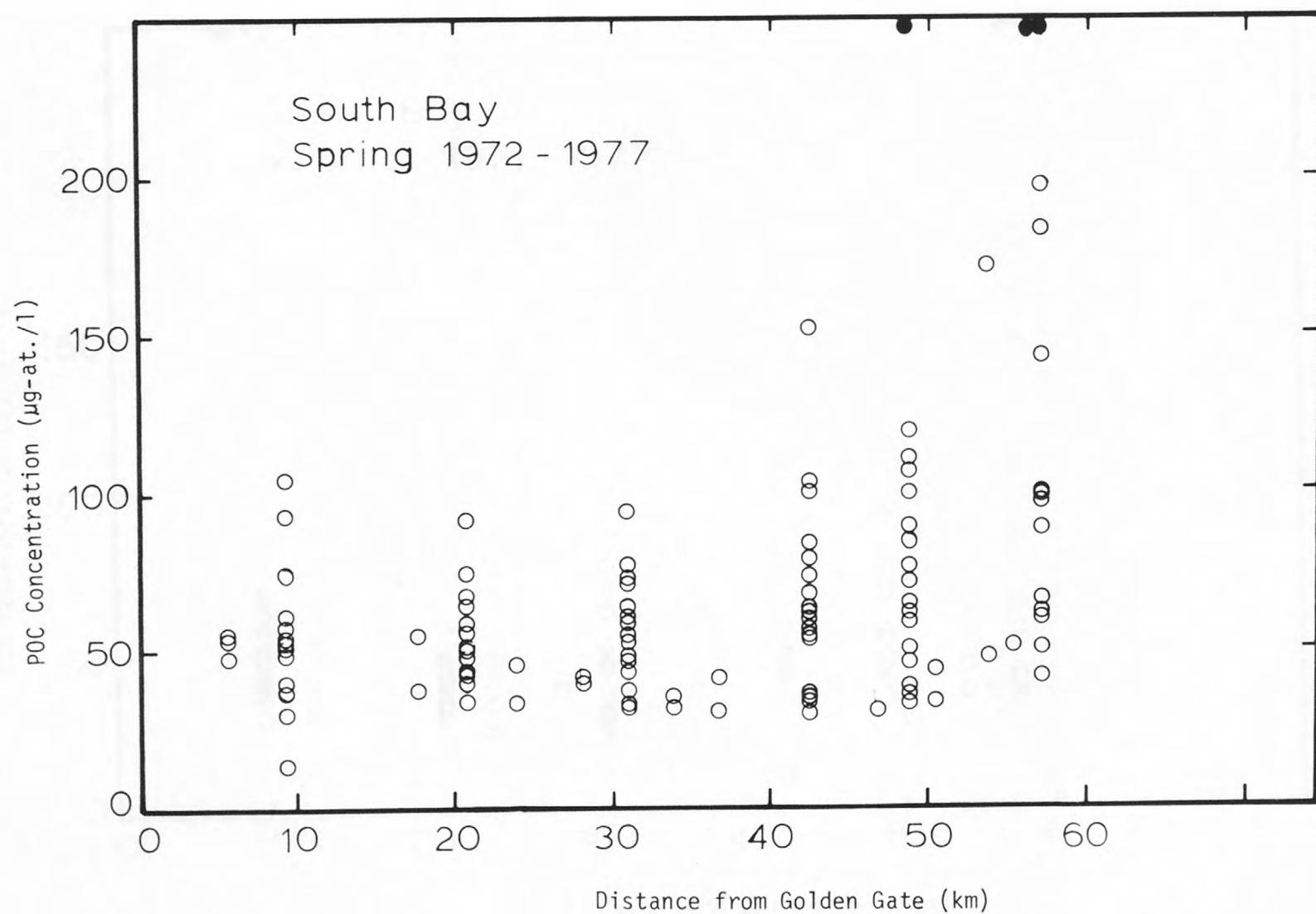


Figure 11. Distribution of POC in South San Francisco Bay, March-June, 1972-1977.

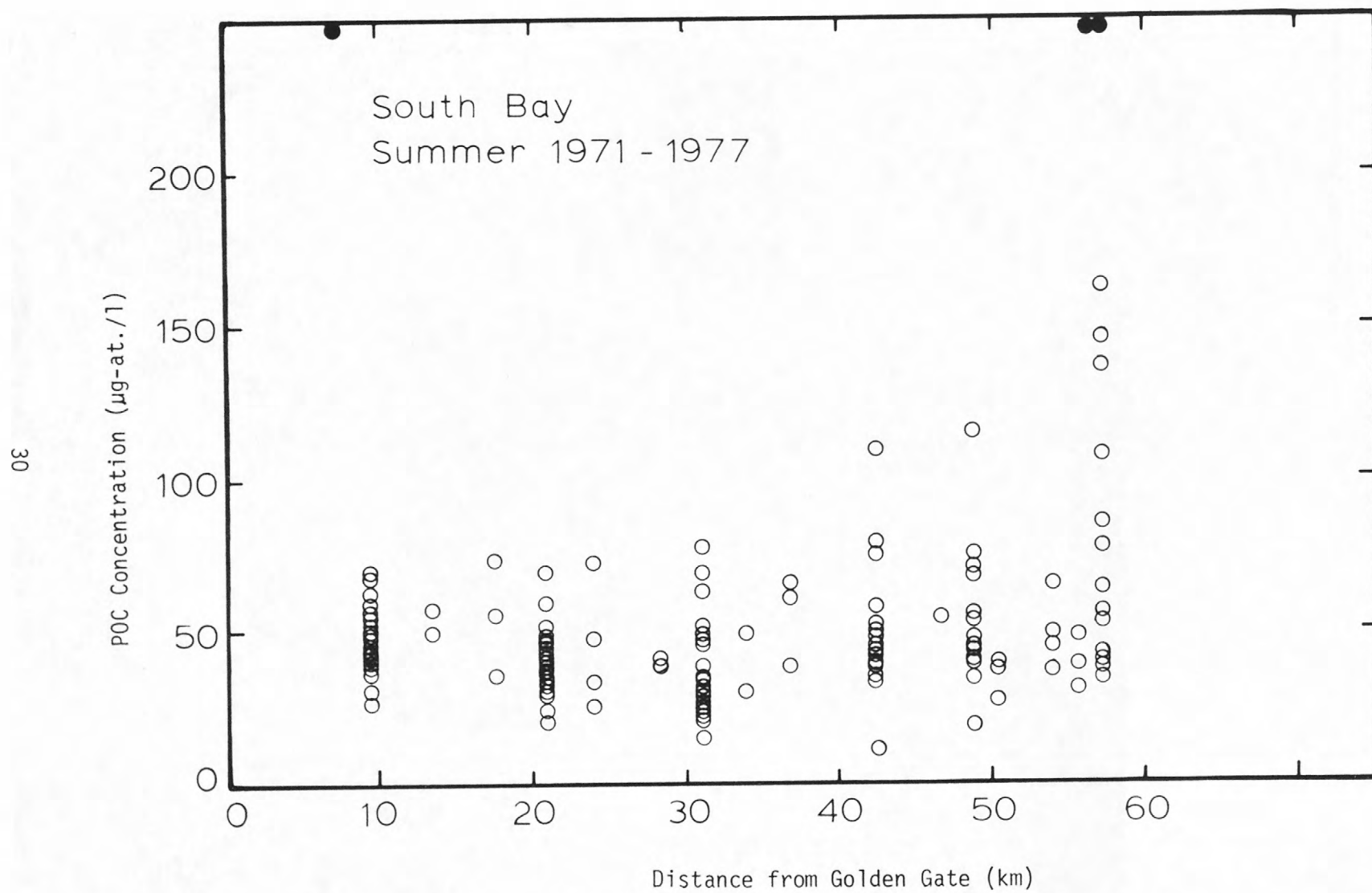


Figure 12. Distribution of POC in South San Francisco Bay, July-October, 1971-1977.



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