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INVESTIGATIONS ON CONCENTRATIONS, DISTRIBUTIONS, AND FATES OF HEAVY METAL WASTES IN PARTS OF LONG ISLAND SOUND

By Peter Dehlinger, W. F. Fitzgerald, D. F. Paskausky, R. W. Garvine,
W. F. Bohlen, S. Y. Feng, A. J. Nalwalk, R. J. Szechtman,
C. D. Hunt, D. L. Murphy, C. E. Perkins, and G. M. Ruddy

Final Report Submitted To The Office of Sea Grant Programs
National Oceanic And Atmospheric Administration
Rockville, Maryland 20852



By The University of Connecticut
Marine Sciences Institute
Groton, Connecticut 06340

October 1974

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FINAL REPORT

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CHAPTER I

THE OVERALL PROGRAM

by

Peter Dehlinger, W. F. Fitzgerald, D. F. Paskausky,
R. W. Garvine, W. F. Bohlen, and S. Y. Feng

SUMMARY

A two-year investigation was conducted on heavy metal wastes in Long Island Sound, with emphasis on the eastern Sound and the Connecticut coast. The program consisted of five integrated projects with the ultimate objective being to determine a preliminary budget of these wastes. The projects were concerned with the concentrations, distributions, and fates of heavy metals in the water column, water circulation patterns and water renewal times in the Sound, the structure and outflow of the Connecticut River into the Sound, the transport of suspended materials in the Sound, and the uptake of metals in oysters at various locations along the Connecticut coast. These studies have resulted in significant new findings regarding heavy metals in the Sound, although considerably more work is clearly required before budgets of the metals can be fully understood.

The study involved collecting data aboard ships in the eastern Sound and reoccupying stations as needed to determine natural variability, establishing and monitoring oyster cultures at control stations along the Connecticut coast, conducting standard laboratory analyses and developing such new techniques as were needed to obtain required accuracies, making theoretical and other analyses and determining computer models where needed, and designing, constructing, and testing new field instrumentation.

The following indicates the more significant findings which have resulted from this investigation.

1. A preliminary model for budgets of Cu and Zn in eastern Long Island Sound has been constructed which identifies the important sources and sinks and provides estimates of the mass transfer of the metals. The model shows good agreement between input and output of these metals in Long Island Sound, and suggests a steady state for the amounts of these metals in the water column. Significant removal of the metal appears to occur through biological and geochemical processes and by rapid water renewal in the eastern Sound.
2. A net water movement which results in a rapid flushing of the eastern Sound was determined on the basis of current meter measurements over semi-diurnal tidal cycles, from surface and bottom drifter data, and from following the plume of

Connecticut River water in the Sound. A net circulation may involve a predominantly counterclockwise horizontal gyre in the eastern Sound which also includes vertical components of motion. The net inflow into the Sound appears to center in the lower two-thirds of the water column at the Race, with the net outflow apparently occurring in the shallower eastern passages to the south of the Race. Water renewal times in the eastern Sound appear to be on the order of a week. This rapid renewal time is consistent with the observed low metal concentrations in the eastern Sound.

3. The outflow of the Connecticut River into Long Island Sound has been determined in terms of its physical characteristics for different tidal cycles and discharge levels. The nature of the plume boundary was studied intensively in the field and was shown to exhibit typical frontal dynamics; its physical characteristics were further analyzed theoretically. The plume itself consists of a layer of mixed river and Sound water that is a few meters thick and has sharp frontal boundaries, involving downwelling on both sides of the front. The location of the plume in the Sound shows considerable variation, some of which can be predicted.
4. Investigations have shown that suspended materials in the Sound, consisting primarily of silica and various types of clays, are consistently higher near the bottom than the surface in the eastern Sound. Concentrations of the suspended materials are characterized by slow variations, except that they increase markedly during storms. The eastern Sound appears not to be a sink for suspended sediments.
5. It appears that, in view of the high flushing rate, the eastern Sound is not likely to be a sink for heavy metals or other pollutants. This tentative conclusion may be modified if metals are taken up by sedimentary processes in the eastern Sound.
6. Large fraction of Cu and possibly other metals brought into the Sound from the Connecticut River appear to be organically associated. Hg in the coastal and river waters also appears to be organically associated.
7. A new laboratory technique was developed which permits measuring mercury in sea water with about two orders of magnitude greater sensitivity than could be obtained previously.

8. A two-year study of the uptake of total heavy metals in oysters was made at control stations along the Connecticut coast. None of the concentrations of metals were dangerous for human consumption. However, the amounts of the metals has increased over the past 29 years, ranging to nearly 200%. The highest concentrations of Zn, Cu, Cd, and Mn observed occurred in oysters near the mouth of the Housatonic River. The highest concentration of Hg was observed in oysters at the most easterly control station.

INTRODUCTION

Long Island Sound is a major natural resource of the states of Connecticut and New York and also of the nation. The Sound is surrounded by a large human population which has placed varied and extensive demands on its waters. The principal users of the Sound include commercial fishermen, commercial shippers, the power-generating industry, and recreationalists. However, a more prevalent use of the Sound has been to make it a sink into which a variety of waste materials are dumped, particularly municipal sewage (in various stages of treatment) and industrial effluents, but also runoff from streets during storms, runoff of fertilizers and other wastes from farm lands, and materials that have been dredged from nearby rivers and harbors.

The varied uses of the Sound involve many conflicting interests. The effect of these uses, particularly those involving the introduction of pollutants and the dredging and dumping of dredged materials, have placed such severe environmental stresses on the Sound that there is now concern about its healthy preservation. The dumping of pollutants and dredge spoils affects not only the marine life in the Sound and its estuaries, but also those fish outside the Sound which are, in one way or another, dependent upon the Sound (and its estuaries and wetlands) during parts of their life cycles.

Because of the increasing pollution levels, it has become clear that the Sound, as it now exists, could deteriorate to an irreversible extent. What is needed is a management program directed toward the general welfare which will ensure preservation and endorse adequate utilization. Toward this end, the New England River Basins Commission was authorized in 1971 to develop a Regional Plan for the Sound. The Plan, which will be completed in early 1975, is expected to develop significant management concepts for

the Sound to the year 1990 and possibly thereafter. The Plan does not, it should be noted, provide funds in support of research which would either enhance the development of resources in the Sound or procure new basic information needed for effective management.

Principal types of information needed about the Sound include new base-line data and new knowledge regarding processes which could be applied to bring about improved utilization, preservation, and resource development. Knowledge of concentrations and distributions of pollutants in the Sound, and their fates, is a significant part of this problem.

In this regard, the University of Connecticut initiated a program to determine budgets of heavy metal wastes in Long Island Sound. This program was conducted from April 1, 1972 to March 31, 1974 and consisted of varied projects in the eastern Sound and along the Connecticut coast. While the program was not conducted over a sufficient period of time to obtain all of the information sought it has nevertheless provided significant findings.

Chapter I of this report attempts to describe the overall program. Chapters II through VI concern specific projects (Projects 1 through 5) which comprised the investigations.

OBJECTIVES OF THE PROGRAM

A long-range program was planned initially to determine budgets of heavy metal wastes in Long Island Sound, with the objectives of understanding the fates of the metals throughout the Sound, determining net water movements and water renewal times in the entire Sound, and determining effects of metal uptakes on the biota (including the effects on various body functions and on the genetics of the animals).

The principal objectives of the two-year program conducted were to obtain or determine:

1. Base-line data for Hg, Pb, Cd, Cu, Zn, and certain other heavy metals in the water column and in oysters, and on distributions of suspended load materials in the eastern Sound.

2. Fates and budgets of selected metals in the eastern Sound.
3. Water renewal times, flushing rates, and predominant circulation patterns in the eastern Sound.
4. Physical features of the Connecticut River estuary and the nature of the discharge plume in the Sound.
5. A budget for suspended materials in the water column of the eastern Sound and the importance of storm effects on their concentrations.
6. Uptake of metals in oysters at control stations along the Connecticut coast.
7. Whether shellfish can be used as indicators of the amounts of heavy metals in local bays and estuaries.

These objectives have, in essence, been achieved in this program.

PROCEDURES

The program consisted of five interrelated and interacting projects. Each project was under the direction of a principal investigator, a faculty member at the University of Connecticut, who conducted the field and laboratory studies and obtained, reduced, and analyzed the data with the assistance of graduate students and technicians. The investigators coordinated their research with one another, which, on occasion, led to modifications in some of the projects. The program director was Dr. Peter Dehlinger. The five projects and their principal investigators were:

- Project 1. Heavy Metal Wastes in Eastern Long Island Sound - Trace Metal Speciation; Dr. W. F. Fitzgerald.
- Project 2. Circulation and Renewal of Waters in Eastern L.I.S.; Dr. D. F. Paskausky.
- Project 3. Connecticut River Discharge in L.I.S.; Dr. R. W. Garvine.
- Project 4. Suspended Material Transport in Eastern L.I.S.; Dr. W. F. Bohlen.

Project 5. Determinations of Heavy Metals in Shellfish in
L.I.S.; Dr. S. Y. Feng.

The individual projects involved field, laboratory, computer, and theoretical studies. Ship-board measurements were made in all but Project 5, the shellfish project. Airborne measurements were made in Projects 2 and 3. Extensive laboratory analyses were made in Projects 1, 4, and 5. Computer analyses were significant factors in Project 3.

In Projects 1 to 4, stations in the eastern Sound were established at critical locations and reoccupied at specified intervals to observe variations over monthly and seasonal periods and, in some instances, following storms. In Project 1, to determine concentrations of heavy metals in the water column, approximately six field stations in the eastern Sound were each occupied about 7 times, with water samples obtained at four to five depths. Contamination of samples was minimized by using carefully controlled conditions.

In Project 2, on circulation and water renewal times, current and salinity measurements were made from an anchored ship at four different depths over periods of 14 hours or longer, each at selected stations in several of the eastern passages of the Sound, with subsequent reoccupation to estimate seasonal variations. These measurements provided data on current speed and direction at fixed locations and depths. Surface and bottom drifters were released from helicopters and airplanes at numerous sites and different times in the eastern Sound. From the returned drifter data, information was obtained on net movements of surface and near-bottom waters.

Investigations in Project 3, on the outflow path of Connecticut River water in the Sound, involved making continuous measurements aboard ship of surface-water salinity and temperature. These measurements were made at different times in the tidal cycle, in different seasons, and for different rates of river discharge. The measurements provided information on the nature of the plume boundaries in the lower river and its spacial and temporal distributions in the Sound. A series of aerial photographs were also made which provided pictures of the plume boundaries under a variety of outflow conditions.

In Project 4, on suspended load characteristics, ship-board measurements were made at 11 stations which were reoccupied on a monthly basis to determine seasonal variations in suspended materials. At each station water samples were obtained at three depths,

providing information on total suspended solids within the water column. Salinity and temperature profiles of the water column were also obtained at each station.

Physical properties of the water column were monitored on a continuous basis at a NOMAD buoy (Navy Oceanographic and Meteorological Automatic Data), on loan to the Marine Sciences Institute by the U. S. Navy Underwater Systems Center. The buoy was moored in the middle of the Sound south of the Connecticut River. It continuously recorded wind speed and direction, air and surface-water temperature, and salinity and current speed and direction in the surface waters. A separate instrument package also recorded near bottom (depth 130') current speed and direction, salinity, and temperature. These measurements were particularly significant during storms, when transport is high.

In Project 5, on the uptake of heavy metals in shellfish, six control stations were set up so as to cover the entire Connecticut coast. The stations were in Norwalk harbor, Bridgeport harbor, the Housatonic River (near Devon), New Haven harbor, the Thames River (at New London), and the Mystic River harbor (at Noank). Oysters from each station were sampled at monthly intervals for further analyses in the laboratory.

Laboratory methods used to analyze samples usually involved standard procedures, with refinements where needed. An exception involved the development of a modified method for determining trace quantities of chemical fractions of mercury in the marine environment. It was also established, as a result of our determinations of lead in sea water, as well as those of workers at other laboratories, that laboratory contaminations are usually so high that trace quantities of lead reported in the literature cannot, in general, be considered reliable. (Since this program has been completed, the Marine Sciences Institute has constructed an ultra-clean laboratory for determinations of heavy metals in the marine environment.)

An IBM-360/65 computer at the University was used to develop models for predicting general circulation patterns in the eastern Sound.

Equipment and instrumentation development was undertaken as needed. Instrumenting the NOMAD buoy involved extensive development, construction, and testing of instrument packages in the surface waters and near the bottom. In the river plume project, a ship-borne flow system was constructed which provided continuous underway measurements of salinity and temperature of surface waters while the ship proceeded at maximum speed (about 10 kn).

RESULTS AND DISCUSSION

This section discusses the principal overall results of the program; the following chapters describe results of the individual projects.

Concentrations of Pb, Hg, Cd, Cu, Zn, and Ni were measured in the water column of eastern Long Island Sound. The measurements of Pb were found to have insufficient accuracies to be useable, and only a few measurements of Hg were obtained. Concentrations of Cu, Zn, and Cd were observed to be only slightly higher in the eastern Sound than in the adjacent Block Island Sound, which can be taken as representative of concentrations on the continental shelf. These measurements thus indicate that the eastern Sound does not contain anomalously large concentrations of these metals.

The concentrations and distributions of Cu, Zn, Ni, and Cd are considerably lower in the waters of the eastern Sound than would be expected for the amounts brought in from industrial, municipal, and other sources. This fact suggests that either the waters of the eastern Sound are renewed within a short time period, i.e., that there are substantial net flows in the water movements, or that the metals are rapidly removed to sediments in the vicinity of the source area. A preliminary budget for Cu and Zn in the Sound indicates that sedimentary removal of these metals is substantial, and the physical oceanographic data indicate the eastern Sound is flushed rapidly.

The rapid flushing was determined from current-meter observations (Project 2) over semi-diurnal tidal cycles within the eastern passages of the Sound and by surface and bottom drifter data. These results show that there is a net inflow of water into the Sound (Fig. 1) at the Race (a deep channel at the northern portion of the eastern passages) and a net outflow near Plum Island (shallow water channels along the southern part of the passages). Water is generally transported into the Sound at the Race, principally over the lower two-thirds of the water column, for periods about twice as long during flood tide as during ebb tide. The net outflow at the more southerly shallow passages is spread over a wider area but appears to approximately balance the inflow. These current measurements suggest the presence of a net counter-clockwise (horizontal) gyre, and the drifter data suggest a vertical gyre, in the eastern Sound, with the net water movement being a combination of the two. The net motion appears to result in water renewal times of approximately one week in the eastern Sound.

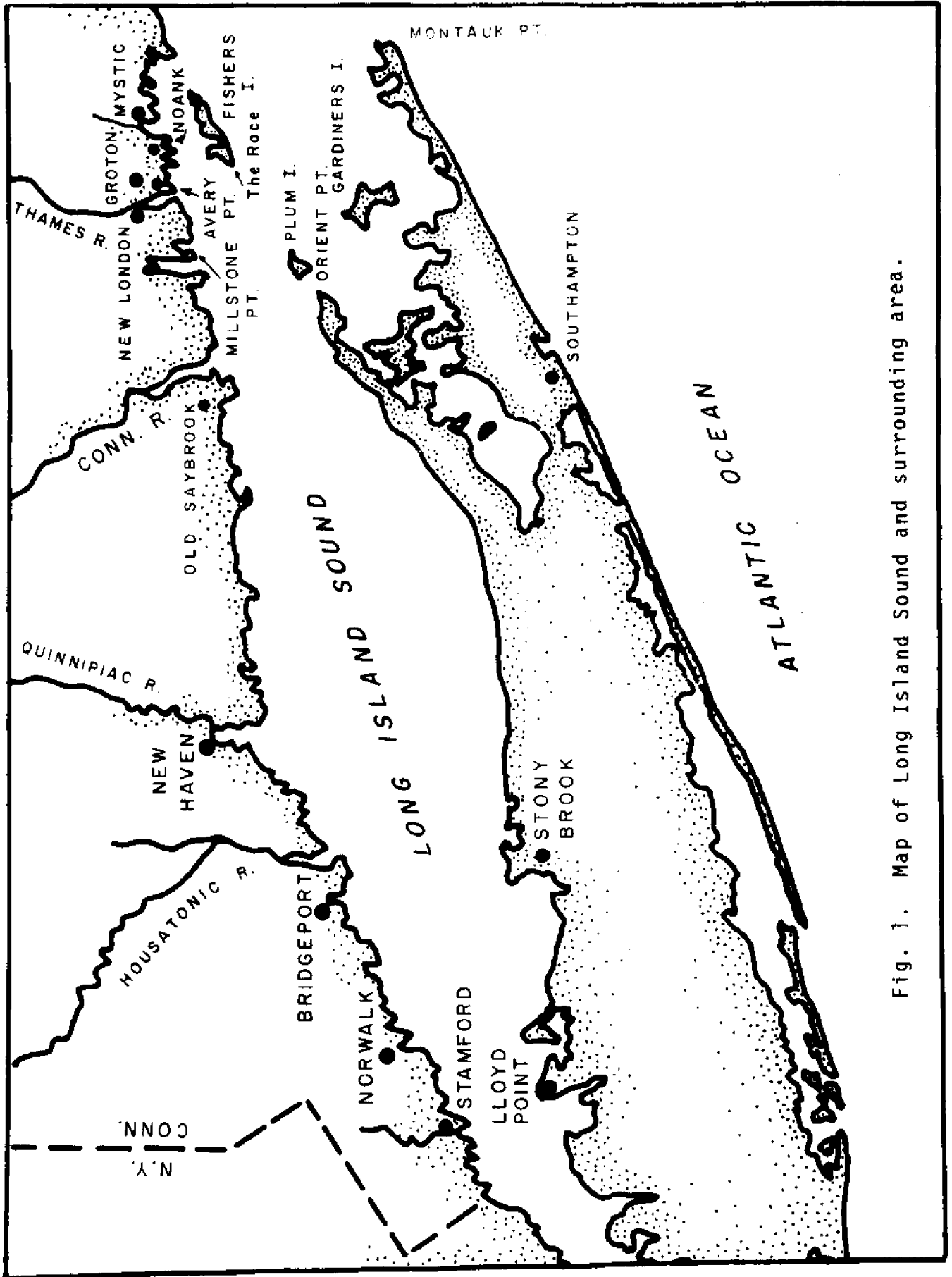


Fig. 1. Map of Long Island Sound and surrounding area.

where clearly these circulation patterns are superimposed upon predominantly oscillatory tidal motions. Drifter data in the central Sound, by contrast, suggest that prevalent winds essentially determine the net circulation patterns. Salinity measurements made in conjunction with the water current measurements substantiated the inference of a net inflow from the more saline continental shelf and net outflow from the less saline Sound.

The rapid flushing rate in the eastern Sound has been also verified as a result of mapping the plume of the Connecticut River in the eastern Sound (Project 3). The plume, which was found to be bounded by sharp fronts, is readily identifiable from salinity contrasts and color boundaries (observed on aerial photographs); it has thicknesses of a few meters. The plume consists of mixed river and Sound waters and its location varies greatly in response to tidal motion in the eastern Sound. The front of the plume is characterized by a downwelling on both sides of the boundary, exhibiting characteristic frontal dynamics. During flood tide the plume extends westward along the Connecticut coast to distances as much as 10 miles from the mouth, and during ebb tide it usually extends southeasterly, approximately in the direction of Plum Island, but deviates markedly on occasion. While the location of the plume cannot be predicted with reliability, the plume excursions verified the previously mentioned rapid flushing rates in the eastern Sound.

Estimates were made of the inputs of Cu and Zn into Long Island Sound from industrial and domestic sources and of the amounts of these metals leaving the Sound. Combining these estimates with measurements of Cu and Zn in the water column of the eastern Sound has made it possible to develop a preliminary model for the distribution and fluxes of Cu and Zn in the Sound. The principal sources of these metals have been identified as industrial and municipal wastes; the principal sinks for the metals appear to be biological and geochemical sediments, although more precise data on volume transport from the East River inflow is needed to further quantify the role of sediment removal processes; mass transfer of the metals has also been estimated. On the basis of the model, approximately 90% of the Cu and Zn annually entering the Sound is removed as sediment. The input of Cu and Zn from the Connecticut River appears to be comparable to the amounts annually flushed from the Sound.

Concentrations of suspended materials in the water column of the eastern Sound were found to be characterized by slow variations, which were sharply modified by storms and other intense meteorological events. Concentrations, which averaged from 15 mg/l near the Connecticut River to less than 5 mg/l in the deeper

waters of the Sound, were found to be consistently higher near the bottom than the surface. The highest average concentrations in the Sound occurred in March. The suspended materials consisted of various types of sands and clays (which were identified) and some organic matter.

There is, as yet, not enough information to know whether the Sound acts as a sink for heavy metals and other pollutants. On the basis of the rapid water renewal times and the low metal concentrations, it appears that the eastern Sound is not a sink for heavy metals. This would imply that the Sound is not a sink for other pollutants. For suspended materials it also does not appear to be a sink. However, some metals appear to be taken up by sediments, in biological or geochemical processes, and additional work is required to quantify this sediment uptake.

Large fractions of the Cu and Cd, and possibly Zn and Ni, brought into the Sound by the Connecticut River appear to be organically associated. From 50% to 60% of the Hg obtained from coastal and river waters in the eastern Sound was observed to be organically associated. A laboratory technique using cold-trap preconcentration for the determination of Hg was developed during the program that increased the sensitivity over conventional mercury analysis in sea water by about two orders of magnitude.

The uptake of heavy metals by oysters in the Sound was investigated by determining the total heavy metals in oysters at six control stations along the Connecticut coast (between Norwalk on the west and Noank on the east). The highest observed concentrations of Zn, Cu, Cd, and Mn occurred in Bridgeport harbor and in the Housatonic River, while medium to low concentrations occurred at Norwalk, New Haven, and New London harbors, and at Noank (near the mouth of the Mystic River). This pattern of distributions seems to be associated with the centers of industrial and municipal developments along the coast. However, Hg concentrations in oysters were found to be highest in the Noank station, which is unexpected and not yet explained; this station is the one most remote from industrial centers.

During the past 29 years, Zn in the oysters from central Long Island Sound has increased approximately 180%, while Cu and Mn have increased approximately 50%. Observed enrichment factors in the oysters are: Zn, 305,800; Cu, 33,000; Cd, 10,200; Mn, 4,100 (estimated); and Hg, 1,100. These values closely parallel the known rank order of divalent ion-ligand complexes. It was also observed from an experiment at the Noank station that accumulations of Hg and the elimination of Zn, Cu, Cd, and Mn appear to occur

simultaneously in oysters, the processes probably being governed by the chemical composition of the water mass rather than resulting from biological needs. Observed differential rates of attrition in Zn, Cu, and Cd, as well as Mn in the Bridgeport transplants suggest the presence of different binding mechanisms and degree of lability of bonds formed with organic ligands. This view is further supported by the presence of highly significant inter-element correlations detected among Cu, Zn, and Cd.

The instrumentation packages which were designed and developed for continuously measuring meteorological and oceanographic variables at the NOMAD buoy (Navy Oceanographic and Meteorological Automatic Data), located south of the Connecticut River, were constructed and tested. Meteorological instruments on the buoy recorded wind speed and direction, air temperature, and humidity. These data were originally telemetered to land, but later in the program were recorded at the buoy. A shallow-water instrument package was used to measure water current speed and direction, temperature, and particulate matter (with a modified nephelometer). A near-bottom package measured current speed and direction and also temperature. Attempts were made to include a nephelometer in the bottom package, but the effort was discontinued. Recordings have been made at the buoy, although numerous operational difficulties, owing to the corrosive nature of the marine environment, have not been fully overcome. (The buoy is continuing to record after the termination of the Sea Grant program; its principal application is to provide continuous recordings, which are of greatest interest during storm conditions.)

CHAPTER II

A PRELIMINARY BUDGET FOR Cu AND Zn
IN LONG ISLAND SOUND

by

W. F. Fitzgerald, R. J. Szechtman and
C. D. Hunt

INTRODUCTION

During the past two years, we have studied the fate of several heavy metals in the waters of eastern Long Island Sound. The immediate objectives of this work were (1) to initiate the determinations of the amounts, distribution, and seasonal variability of Cu, Zn, Pb, Cd, Hg, and Ni as associated with flow through the eastern passages of Long Island Sound and with inflow from the Connecticut River, and (2) to determine a preliminary budget of these metals in the Sound.

A summary of our measurements for Cu, Zn, Ni, and Cd in the waters of the eastern Sound appears in Table 1. Additional data for the concentrations of these metals in coastal waters, which were obtained in other relevant or comparable investigations, have also been included. The results for Pb measurements are not summarized because we are not yet satisfied with the accuracy of our measuring technique for Pb in sea water. At present, too few Hg measurements are available in the Sound to include in this tabulation. In the Appendix, our analytical methodology is briefly described and the raw experimental data for these metals are presented.

With respect to the variability of these metals in the eastern Sound, we found that seasonal variations in metal concentrations (notably Cu) are not pronounced and that concentrations and distributions of Cu, Cd, Zn, Ni, and perhaps Hg and Pb are comparable to other well-flushed continental shelf regions of the eastern United States.

In addition to our investigations, other workers have been gathering information relating to the fate of heavy metals in Long Island Sound. Our work has been complemented by (1) recent studies of the heavy metal distribution in the sediments throughout Long Island Sound (Sandy Hook Marine Laboratory of the National Marine Fisheries Service), (2) additional data on metal concentrations and determinations of sedimentation rates from several cores in the central Sound by workers at Yale University (Thomson *et al.*, 1974, in press), (3) data on metal concentrations from sewage treatment plants bordering the Sound (Mytelka *et al.*, 1973), as well as flow data from sewage outfalls compiled by the Interstate Sanitation Commission (1973), and (4) the analyses of metal concentrations in the rivers and harbors of Connecticut (Department of Environmental Protection, State of Connecticut).

Table 1

A Summary of Recent Determinations of Cu, Zn, Ni, and Cd in
Eastern Long Island Sound and in Other Coastal Waters

TRACE METAL

<u>STUDY</u>	<u>DATE</u>	<u>Cu</u> (<u>µg/kg</u>)	<u>Zn</u> (<u>µg/kg</u>)	<u>Ni</u> (<u>µg/kg</u>)	<u>Cd</u> (<u>µg/kg</u>)
Long Island Sound	10/73	0.8 - 4.0 (av. 1.8)	0.8 - 6.4 (av. 3.0)	1.0 - 2.0 (av. 1.7)	
	3/72-4/72	1.0 - 8.7 (av. 2.5)			
	2/73	0.8 - 2.6 (av. 1.0)			<0.01 - 0.6 (av. 0.2)
Block Island Sound	5/72	0.6 - 2.5 (av. 1.3)			0.03 - 0.4
Long Island Sound (Turekian)	1964			1.9 - 27	
Gulf of Maine (Spencer & Brewer)	9/66-10/67	2.0 - 4.0	2.5 - 6.9	1.3 - 2.0	
Eastern Continental Shelf - nearshore (Windom & Smith)	2/71		1.2 - 8.0	0.5 - 2.0	0.02 - 0.19
Straits of Dover (Dutton <u>et al</u>)	5/71-6/71	1.0 - 2.0	2.0 - 8.0	1.0 - 2.0	
British Isles Coastal Waters (Preston <u>et al</u>)	1969 1970	0.7 - 2.8 0.9 - 2.7	3.0 - 20.0 4.9 - 11.1	0.3 - 1.4 0.9 - 3.1	<0.01 - 0.6
Bristol Channel (Abdullah <u>et al</u>)	3/70-4/71	1.0 - 4.7	3.5 - 21.4		

These investigations allow the development of a preliminary model for the fate of two heavy metals, Cu and Zn, in Long Island Sound. The model is an input-output box for the sources, sinks, and routes of the reactive forms* of Cu and Zn in the Sound. The flow budget requires that the quantities of Cu and Zn entering the Sound per unit time from the major sources (land runoff, sewage effluents, East River inflow) must equal the amounts of Cu and Zn which leave the Sound through the eastern passages, enter the sediments or increase in the waters of the Sound per unit time. Thus the balance is simply:

Major Sources of Cu and Zn = Major Sinks for Cu and Zn

Land Runoff (Rivers)	Sediment
East River Inflow	Outflow to Continental shelf via Eastern Passages
Sewage Treatment Plant Effluent	Long Island Sound Water

The metal fluxes for Cu and Zn associated with these reservoirs are summarized in Tables 2 to 5, and the final model appears in Table 6.

The available data for the concentrations of Ni, Cd, and Hg are insufficient to use even in a preliminary budget. These metals, for example, are not measured in the effluent from sewage treatment plants. The determinations of Pb obtained in the waters of the eastern Sound may be too high. It has been clearly demonstrated (IDOE/NSF "Pb in Sea Water Workshop", Pasadena, California, September 1973) that extraordinary care must be exercised in order to measure Pb accurately in sea water. Further studies of the amounts and distribution of Pb in the Sound are necessary before attempting to calculate a Pb budget.

DATA PRESENTATION: TABLES 2 TO 5

Although these tables are designed to be self-explanatory, additional comments regarding the estimates and calculations are necessary.

* The measurements of Cu and Zn in the various waters do not generally include the amounts of these metals strongly bound within the stable structure of particulate matter, such as clays.

Table 2

Estimate of Annual Inputs of Cu and Zn into Long Island Sound from Land Runoff

Land Runoff Route*	Average		Average		Annual	
	Annual Flow ¹ (m ³ /sec)	Metal Concentrations ² Cu(μg/l)	Zn(μg/l)	Cu Input (10 ⁷ gm/yr)	Zn Input (10 ⁷ gm/yr)	
Connecticut River	576	3	8	6.0	14.5	
Thames River**	83	3	8	.8	2.1	
Housatonic River	106	40	44	13.4	14.7	
Other Surface Inflow***	<u>50</u>	21	26	<u>3.3</u>	<u>4.1</u>	
	815			~24X10 ⁷ gm/yr	~36X10 ⁷ gm/yr	

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* Excluding the effluent from sewage treatment plants emptying directly into Long Island Sound.

** Metal concentrations assumed to be the same as Connecticut River.

*** Metal inputs estimated by simply using the mean of the concentrations found for Cu and Zn in the Housatonic and Connecticut Rivers.

1. Water Resources Conditions in Connecticut, USGS, 1969-1972.

2. Connecticut River data from Fitzgerald et al (1973) and Hunt (1973); Housatonic River Data from Connecticut Department of Environmental Protection.

Table 3

Regional Breakdown of Effluents from Sewage Treatment Plants Bordering Long Island Sound

	<u>Eastern Sound¹</u>		<u>Central Sound²</u>		<u>Western Sound²</u>			
	New Haven to Groton		New Haven to Norwalk	Suffolk County	Norwalk to Greenwich	Westchester County	Nassau County	Total Flow
Primary (M.G.D)	3.37		63.5	1.2	23.9	42.5		134.5
Secondary (M.G.D.)	3.97		55.2	2.7	8.5		15.7	85.4

1. Long Island Water Quality Report (1974).

2. Interstate Sanitation Commission Report (1973).

Table 4

Estimate of Annual Inputs of Cu and Zn into Long Island Sound from Sewage Treatment Plants

Source	Effluent Flow to L.I.S. (M.G.D.) ² (m ³ /sec)	Average Metal		Annual Cu Input (10 ⁷ gm/yr)	Annual Zn Input (10 ⁷ gm/yr)
		Cu	Zn (mg/l) ¹		
Primary	134.5	0.47	1.34	8.7	24.2
Secondary	85.4	0.17	0.15	2.1	1.6
				$\sim 11 \times 10^7$ gm/yr	$\sim 26 \times 10^7$ gm/yr

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1. Mytelka et al (1973)

2. Interstate Sanitation Commission Report 1973.

Table 5

Estimate of the Flux of Cu and Zn in the East River
and at the Eastern Passages of Long Island Sound

Source	Average Annual Flow ¹ (m ³ /sec)	Average Metal ⁴ Concentrations		Annual Cu Flux (10 ³ gm/yr)	Annual Zn Flux (10 ³ gm/yr)
		Cu (μg/l)	Zn (μg/l)		
East River ²	1100	20	29	69	100
Eastern Passages ³ (Fishers Island Sound, the Race, and Plum Gut)	-1900	2.0±1.0	2.9±1.8	-12	-17.3

1. Estimate from Riley (1956).
2. Average metal concentrations estimated using the average phosphate concentrations in the East River and the Cu/P and Zn/P ratio found in eastern Long Island Sound.
3. Net outward flows (indicated by minus sign) estimated to be equal to the net flow from the East River plus land runoff (ca. 800 m³/sec; Table 1).
4. Average concentrations in eastern Long Island Sound from Fitzgerald et al (1973); Hunt (1973).

Table 2

The category entitled "other surface outflow" was assigned concentrations of Cu and Zn that were midway between the average quantities of Cu and Zn which we measured in the relatively clean Connecticut River over the year from March 1972 to February 1973 (Fitzgerald *et al*, 1973; Hunt, 1973) and the metal data for an obviously contaminated river, the Housatonic, provided by the Connecticut Department of Environmental Protection. This averaging method is a reasonable approximation of the unknown surface inflow metal concentrations.

Table 4

It was necessary to obtain a working average for the concentrations of Cu and Zn associated with both primary and secondary sewage treatment plants. This average was derived by determining the mean concentration from the metal analyses for sewage treatment plants as compiled by Mytelka *et al*, 1973. Their data are presented in a frequency distribution format. Thus, actual average metal concentrations could not be obtained, and these values in Table 4 should be considered as representative. A compilation of the metal measurements for the individual sewage treatment plants could be more usefully incorporated into the model.

Table 5

There are three important approximations employed in our estimate of the flux of Cu and Zn in the East River and at the passages of the eastern Sound. We used Riley's (1956) estimate of the net volume transport per second for the inflow to the Sound from the East River. More precise water transport measurements in the East River are needed.

Since no measurements of the Cu and Zn concentrations in the East River are presently available, we have estimated the dissolved metal concentrations to be proportional to the phosphate concentration. The average phosphate concentrations in the western Sound are approximately ten times those in the eastern Sound (Sandy Hook Marine Laboratory data provided by Mr. Andrew Draxler). Thus, we have assumed that the East River metal concentrations will be approximately ten times the average concentrations of Cu and Zn found in eastern Long Island Sound.

Finally, the estimation of net flow of water through the eastern passages follows the procedure used by Riley (1956).

That is, the net outflow must equal the inflow (East River plus land runoff), with precipitation assumed to be equivalent to water loss by evaporation. A more precise estimate of the mass transfer of metals at the eastern entrances to Long Island Sound will require more precise water volume transport measurements.

DISCUSSION

The preliminary budget/model for describing the fate of Cu and Zn in Long Island Sound is presented in Table 6. It is evident that the agreement between the total amounts of Cu and Zn associated with the various sources and sinks is quite favorable. Indeed the agreement for the mass balance is of the order of the analytical error associated with most trace metal measurements in sea water. The metal budget may be even more satisfactory because our assumptions tend to preclude a balance by overestimating the metal flux to the sediments and underestimating the metal input.

The flux of Cu and Zn to the sediments was determined by (1) using an average sedimentation rate of 0.5 cm/yr* from the measurements of Thomson et al. (1974) in two cores from central Long Island Sound; and (2) by averaging the Cu and Zn data for the sediments throughout the Sound as measured and reported in an interim form by the Sandy Hook Marine Laboratory. This averaging technique may overestimate the metal flux to the sediments, because the sedimentation rate in the eastern third of the Sound is probably <0.5 cm/yr and the chemical analyses for metals in sediments often include the metal fractions (e.g., metals structurally bound to clay minerals) not always measured in water. Conversely, the input of Cu and Zn to the Sound may be underestimated because the metal fractions ("environmentally inactive or slowly active") representing metals that are structurally bound in clays or very strongly associated with organic or detrital materials are probably not measured in most water analyses.

In view of these assumptions, we can be confident that the budget is qualitatively correct. Moreover, even at this preliminary stage, the model reveals several interesting features concerning the fate of Cu and Zn in the Sound and perhaps other estuaries.

* The sedimentation rates obtained from Pb²¹⁰ dating of two cores in the Sound were 0.45 cm/yr and 0.64 cm/yr.

Table 6
Preliminary Budget of Cu and Zn in Long Island Sound

<u>Sources</u>	Annual Metal Flux		Reference
	Cu (10 ⁷ gm/yr)	Zn	
Land Runoff	24	36	Table 2
Sewage Treatment Plants	11	26	Table 4
East River Input	<u>69</u>	<u>100</u>	Table 5
Total	104	172	
 <u>Sinks</u>			
Outflow through Eastern Passages	12	17	Table 5
Sediment	123	198	Thomson, <u>et al.</u> (1974) in press and Sandy Hook Marine Laboratory (1973)
	<u> </u>	<u> </u>	
Total	135	215	

The good agreement between sources and sinks (excluding the water column) suggests that Cu and Zn concentrations in the waters of the Sound may not be rapidly changing. A steady-state appears to be in operation, with the metal concentrations inhibited from rapid increase in the Sound waters by the rapid and substantial sedimentation which removes large quantities of the metals from the waters. It is clear that removal of Cu and Zn to the sediments by either biological or geochemical routes is a very significant process in Long Island Sound.

These data indicate that as much as 90% of the Cu and Zn which enters the Sound may end up in the sediments. Moreover, the magnitude of the sedimentary metal removal in the Sound suggests this mechanism is a means of buffering the concentrations of metals in coastal waters. That is, metal concentrations in even highly contaminated water may not become very large if sedimentation processes are significant. The compilation of world-wide Cu and Zn data (Table 1) suggests that the rather limited concentration range observed may result from significant near shore removal of Cu and Zn through sedimentation.

Most of the Cu and Zn input represents contamination resulting from industrial or domestic activities. At least 80% of this metal input represents metal increases over pre-industrial fluxes. The amounts of Cu and Zn flushed from the Sound each year are of the same order as the Cu and Zn input from the Connecticut River, i.e., about 10% of the total Cu and Zn introduced annually leaves the Sound.

As indicated, the significance of the above estimates for the various yearly metal fluxes in the Sound relies in large measure on Riley's (1956) net water transport approximations. Thus, the sediments of Long Island Sound appear to represent a significant sink for Cu, Zn, and other metals. However, if more precise volume transport data were available for the East River inflow and for the eastern passages of the Sound, the relative importance of sedimentary removal processes could be more quantitatively ascertained. For example, an increase in volume transport of a factor of two for the East River and through the eastern passes would yield a model indicating significant metal removal to the sediments, but about 20% of the yearly metal input would remain in the waters of the Sound. If the volume transport is 10 times (an upper limit) greater than Riley's estimate, sedimentation would account for only about 25% of the annual metal input. Accurate data on net inflow and outflow of water for the Sound are clearly required to develop a detailed model.

In summary, a preliminary model for the distribution and fluxes of Cu and Zn in Long Island Sound has been developed. The important sources and sinks have been identified and mass transfer of metal estimated. The calculated balance between input and output of Cu and Zn to Long Island Sound shows favorable agreement. The model suggests a steady-state for the quantities of metal in the water column and the time invariance is apparently maintained by a significant removal to the sediments. The model indicates that about 90% of the Cu and Zn entering the Sound annually is removed either biologically or geochemically to the sediment. More than 80% of the Cu and Zn input appears to be anthropogenic in origin (e.g., sewage treatment plant effluent; East River input). The amounts of Cu and Zn flushed from the Sound each year are comparable to the inputs of these metals from the major river, the Connecticut.

In order to develop a more precise and quantified model for the heavy metal budgets in Long Island Sound it would be necessary to have (1) metal concentrations and flow data for the East River; (2) volume transport measurements for the eastern passages of the Sound; (3) a more precise estimate of the sedimentation rate (metal flux) in the eastern Sound, and (4) measurements of the distribution and fractionations of metals between dissolved and particulate phases in the waters of Long Island Sound and environs.

ACKNOWLEDGMENTS

This investigation required the cooperation of several regulatory agencies and laboratories as well as the assistance of persons who provided us with metal and nutrient data in useable format. We acknowledge gratefully the help of Dr. A. Mytelka, Interstate Sanitation Commission; Mr. Roy Anderson and Ms. Pam Bergman of the Connecticut Department of Environmental Protection; and Messrs. Robert N. Reed and Andrew Draxler of the Sandy Hook Marine Laboratory, National Marine Fisheries Service, U. S. Dept. of Commerce.

APPENDIX

Sampling Stations

The sampling stations in the control volume network designed for the heavy metal budget study in eastern Long Island Sound are located at the following sites: the Race, Plum Gut, the mid-channel buoy off the Connecticut River, the Connecticut River, and Fishers Island Sound. All stations were occupied and water samples were collected during the following cruises: March 29, April 19, April 26 and October 13, 1972. During August 21, 1972 samples were obtained at the mid-Sound station and on February 22, 1973, the Race and mid-Sound stations were occupied. On May 12, 1972, four stations were sampled in Block Island Sound and a control station taken at the Race. Metal data from the latter survey provided information for the average amounts of heavy metals present in Block Island Sound (taken to be representative of the continental shelf) during the spring months.

A 14-hour sampling station was maintained at Plum Gut on June 6, 1972. The resultant data enabled us to assess the effect of tidal variations on metal concentrations and to combine metal measurements with volume transport determinations.

Two extensive surveys of the Connecticut River-Long Island Sound interface were carried out on August 21, 1972 and February 22, 1973.

Analytical Procedures

The water sampling for our heavy metal determinations was conducted under carefully controlled conditions. Water samples were usually collected at four of five depths using a PVC water sampler* with a Teflon^R-coated, stainless steel closing spring. The hydrowire was plastic coated and the hydroweight encased in fiberglass. The depths were selected on the basis of a preliminary temperature profile taken with a bathythermograph.

Following collection and transfer, the water samples were, in general, immediately acidified with a concentrated hydrochloric acid (HCl) to yield a final pH of ca. 3 in the water samples.

* Manufactured by General Oceanics, Inc., Miami, Florida

The collections were stored in acid (HCl) cleaned 8 or 10 liter linear polyethylene or polypropylene bottles. The samples were later filtered under a positive flow nitrogen atmosphere using polypropylene plastic filter holders and 0.45 μ membrane filters (Nuclepore^R).

Experiments and control samples indicate that, with the exception of Pb, we experienced no serious amounts of metal contamination during sampling handling or analytical procedures. There is no blank contribution from Hg, and the contamination associated with Cu and Cd measurements is quite small. Using anodic stripping voltammetry, we determined that approximately 0.060 μ g Cu/l and 0.010 μ g Cd/l were the average quantities of contamination associated with the collection, handling, and analysis of these metals. The anodic stripping data for Cu and Cd have been corrected accordingly. Unfortunately, rather high concentrations of Cd were occasionally observed (see Table A-2, for example). We have not yet ascertained whether such instances of unusually high Cd concentrations are real or simple contamination artifacts occasionally associated with some step in our analytical procedures.

We have conducted experimental checks to test for potential contamination associated with the determination in sea water of Cu, Zn, and Ni by atomic absorption spectrophotometry (AAS). The precision of analysis (coefficient of variation) for these metals at 1 μ g/l in sea water is approximately 10% using the AAS procedure. We could not detect evidence of contamination for Cu, Zn, and Ni within these precision limits.

Analytical Techniques

As indicated, the metal concentrations were established using two analytical techniques, anodic stripping analysis and atomic absorption spectrophotometry.

Anodic Stripping Analysis. Measurements of Pb, Cu, and Cd were made by direct stripping voltammetry of the natural water samples. The concentrations were determined by the method of standard additions. Spike concentrations of 10^{-5} or 10^{-6} M were prepared by appropriate dilution of 10^{-1} M CuCl_2 and 10^{-1} M CdCl_2 stock solutions. These stock solutions were made using freeze-dried analytical grade compounds, properly weighed, dissolved and made up to 1 liter with deionized water. Over the concentration

range found in coastal sea water the precision of analysis, expressed as a coefficient of variation, is 10% for Cu and 15% for Cd.

In addition to standard analyses of acidified filtered sea water and river water, gross measurements of various metal fractions were made. Earlier studies (Fitzgerald, 1970) have demonstrated that anodic stripping analysis can be combined with a technique for the destruction of dissolved organic matter (photo-oxidation with ultra-violet radiation) and an acidification procedure to obtain measurements of the trace-metal fractions in natural waters.

The procedure consists simply of direct analysis for Cu, Pb, and Cd by stripping voltammetry of an untreated water sample. This yields the concentration of free metal. An aliquot is photo-oxidized for a sufficient time to insure complete degradation of the dissolved organic matter (carbon) and reanalyzed. This gives the total amount of the metal present. The total metal minus free metal equals the metal associated with naturally occurring organic material. Analysis of aliquots acidified to ca. pH 3 provides information for the amounts of Cu and Pb sequestered by moderately stable weakly acidic ligands. These determinations were conducted during our Connecticut River/Long Island Sound boundary investigation, and the results are also included in this Appendix. Additional details regarding these studies can be found in Hunt (1973).

Atomic Absorption Spectrophotometry. The atomic absorption spectroscopic method for total metal analysis of Zn, Cu, Ni, Pb, Co, and Cd employed in this study has been described by Brewer et al (1969). This technique requires a preconcentration step involving the chelation of these metals with an organic sequestering agent and then the extraction of the metal chelates formed into an organic solvent. Ammonium pyrrolidine dithio-carbamate (APDC) was used as the chelating agent while methyl isobutyl ketone (MIBK) was the solvent. The method of standard additions, using four 400 g aliquots, allows us to determine a reagent blank and to determine the metal concentrations of the natural water samples. As noted above, the precision of analysis (coefficient of variation) found in this study and in previous investigations employing this technique is ca. 10% for Cu, Zn, and Ni at coastal water concentrations ($\geq 1 \mu\text{g/l}$).

EXPERIMENTAL RESULTS

We have determined the amounts of Cu and Cd, using anodic stripping voltammetry, in approximately 200 water samples from the several cruises. We have complete sets of metal data for these elements from our control volume network for the cruises of March 29, April 19, and April 26, 1972. Moreover, we have data from all of the stations occupied in Block Island Sound for these heavy metals. In addition, we have a most interesting set of measurements for Cu and Cd that were obtained on a Connecticut River survey which took place on August 21, 1972, and on February 22, 1973. A complete set of measurements for Cu, Zn, and Ni by atomic absorption spectrophotometry is available for the October 13, 1972 control volume survey.

These metal data which served in our development of a preliminary budget for Cu and Zn in Long Island Sound are presented in the following Tables.

Table A-1
Concentrations of Cu, Cd, Zn, and Ni at the Race*

Station Data						
Depth (ft)	Salinity (‰)	Temp (°C)	Metal Concentration (µg/l)			
			Cu	Cd	Zn	Ni
29 March 1972						
0	30.026	3.80	4.7	0.3		
74	30.564	3.71	6.0	0.3		
124	30.812	3.71	1.7			
174	30.937	3.72	4.8			
224	31.133	3.71				
274	31.183	3.70	8.7			
19 April 1972						
0		5.85		0.4		
24	28.554		1.6			
48	28.889		2.1			
97	29.370	3.35				
145	29.542					
242	30.074	4.20	4.0	0.2		
26 April 1972						
0	28.733	5.70	2.9			
34	29.646	6.00				
51	29.824	5.45				
106	30.118	5.40	1.0			
159	30.158					
212	30.779	5.08	1.8			
12 May 1972 (41°14.6'N, 72°03.8'W)						
0	28.605	7.50	1.2	0.4		
10	28.639	7.80				
34	28.619	7.45	2.0	0.4		
107	29.234	7.30				
122	29.873			0.2		
13 October 1972						
0	30.290	16.60	5.0		6.4	1.0
75	30.097		1.2		2.2	1.2
150	30.256	16.7	0.8		2.2	1.3
225	30.325	16.72	0.7		1.2	1.2
250	30.650	16.70	0.7		3.3	0.9
278	30.714	16.7	0.7		1.1	1.3

*Located at 41°14.3'N, 72°04.5'W

Table A-1 (continued)

<u>Depth</u> <u>(ft)</u>	<u>Salinity</u> <u>(0/00)</u>	<u>Temp</u> <u>(°C)</u>	<u>Metal Concentration (µg/l)</u>			
			<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>
22 February 1973						
0	28.224		2.6	0.1		
15	28.329					
53	28.684		0.7			
105	28.885					
157	29.527					
210	29.579		0.8	0.1		

Table A-2

Concentrations of Cu, Cd, Zn, and Ni at Plum Gut*

Depth (ft)	Salinity (‰)	Temp (°C)	Metal Concentration (µg/l)			
			Cu	Cd	Zn	Ni
29 March 1972						
0		4.00				
19	28.968	3.70	4.0			
69	28.996	3.60	1.9			
119	29.031	3.55				
169	29.108	3.70	2.1			
219	29.372	3.50	2.8			
19 April 1972						
0		4.5		2.7		
17	28.367		2.5	0.3		
43	28.747		2.6			
84	28.572		4.6	0.2		
130	28.837		1.6			
173	28.799		4.7	0.2		
26 April 1972						
0	26.950	6.65	2.5			
0	27.650	6.50	2.1			
24	28.296	5.46	1.7			
48	28.405	5.45	2.2			
96	29.096	5.35				
143	29.217	5.31	1.6			
13 October 1972						
0	29.441	16.9	1.4		2.1	1.0
25	29.277		2.3		1.4	1.0
75	29.383	16.80	1.3		1.4	0.9
150	29.408	16.82	1.3		1.3	0.8
225	29.524	16.70	1.9		1.9	0.6

*Located at 41°10.9'N, 72°13.8'W

Table A-2a

Time Study at Plum Gut: June 6, 1972

Cu Concentration ($\mu\text{g/l}$) and Salinity ($^{\circ}/\text{oo}$) Versus Time

<u>Depth (ft.)</u>	<u>1200</u>	<u>1400</u>	<u>1600</u>	<u>1800</u>	<u>2000</u>	<u>2200</u>	<u>2400</u>
Surface							
Cu ($\mu\text{g/l}$)	4.6	2.1	2.2	2.1	2.2	3.2	4.0
S ($^{\circ}/\text{oo}$)	25.816	27.286	27.551	27.300	26.797	26.860	25.766
35							
Cu ($\mu\text{g/l}$)	3.8	3.0	1.8	2.1	3.6	2.0	26.352
S ($^{\circ}/\text{oo}$)	26.573	27.565	28.203	28.801	29.122	28.461	
70							
Cu ($\mu\text{g/l}$)	2.4	1.8	2.1	2.3	1.8	1.8	28.038
S ($^{\circ}/\text{oo}$)	27.482	28.618	28.591	29.172	29.738	29.141	
105							
Cu ($\mu\text{g/l}$)	1.7		1.8	1.6	1.2	1.4	2.1
S ($^{\circ}/\text{oo}$)	28.858	28.999	28.650	29.623	29.792	29.319	28.567

Table A-3

Concentrations of Cu, Cd, Zn and Ni in Fishers Island Sound*

Station Data

<u>Depth</u> <u>(ft)</u>	<u>Salinity</u> <u>(‰)</u>	<u>Temp</u> <u>(°C)</u>	<u>Metal Concentration (µg/l)</u>			
			<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>
29 March 1972						
0		4.87				
3	28.794	5.85				
19	29.636	4.50				
44	29.707	4.10		0.3		
69	29.738	4.15				
19 April 1972						
0	29.592	6.60	1.3			
14	29.627	5.76				
42	29.694	5.70		0.3		
61	30.063	6.22	1.9			
85	30.214	7.28	1.9			
26 April 1972						
0	29.221	6.82	1.8			
16	28.818			0.2		
48	29.821					
13 October 1972						
0	30.234	16.65	1.4		1.9	1.4
11	30.215	16.6	1.0		3.6	1.5
36	30.254	15.4	1.2		3.9	
61	30.237	15.5	1.1		6.7	1.7

*Located at 41°17.7'N, 72°00.0'W

Table A-4

Concentrations of Cu, Cd, Zn and Ni at the Mid-Sound Station*

Station Data

Depth (ft)	Salinity (‰)	Temp (°C)	Metal Concentration (µg/l)			
			Cu	Cd	Zn	Ni
29 March 1972						
0		4.28		0.04		
37	28.713	3.55	2.4	0.03		
87	29.230	3.70	2.8			
137	29.676	3.55	4.8			
19 April 1972						
0	22.908	5.60				
10	25.644	6.05	2.0			
22	27.623	5.00				
43	27.931		1.5			
87	28.076	4.72	1.5	0.3		
130	28.155	4.65				
26 April 1972						
0	25.981	6.40	2.6			
48	27.474	5.92	2.1	0.6		
96	28.510	5.50	3.4			
144	28.911	5.21	1.6	0.4		
21 August 1972* (41°12'N, 71°19'W)						
0	28.984		1.6	0.07		
13	29.079		1.0			
28	29.526					
57	29.604		0.7			
86	30.065		0.3			
13 October 1972						
0	28.019	16.58	4.0		5.1	3.5
20	28.241	16.25				
70	29.542	17.12	1.8			1.2
145	29.669	16.85	1.8		4.2	
22 February 1973						
0	24.748		1.1	0.1		
45	26.748		1.5	0.07		
90	28.114		1.2	0.06		
113	28.537		1.0	0.04		
135	28.949		1.1	<0.01		

* Located at 41°11.3'N, 72°22.5'W except where noted

Table A-5

Concentrations of Cu, Cd, Zn and Ni at the Connecticut River Station*

Station Data

<u>Depth</u> <u>(ft)</u>	<u>Salinity</u> <u>(‰)</u>	<u>Temp</u> <u>(°C)</u>	<u>Metal Concentration (µg/l)</u>			
			<u>Cu</u>	<u>Cd</u>	<u>Zn</u>	<u>Ni</u>
29 March 1972						
0	1.487	4.30	1.8	0.3		
7	27.194	3.75	2.6			
14	28.495	4.05	7.7			
19 April 1972						
0	0.075	7.60	4.4			
10	9.918		3.2	0.1		
20	22.771		3.9	1.1		
26 April 1972**						
0	18.732	7.60	3.2	0.3		
0	24.641	5.98	3.1			
0	23.757	6.68	2.9	0.3		
0	25.039	6.22	3.4	0.2		
0	00.937	6.95	7.4			
0	00.064	6.98	11.0			
13 October 1972						
0	16.731	15.9	1.5		9.3	0.8
11	29.426	15.91	2.4		8.0	1.4
19	29.443	17.22	5.9		8.5	1.9

* Located at 41°16.7'N, 72°20.5"W

** Surface samples between Mid-Sound Station and Connecticut River Station

Table A-5a

Concentrations of Cu and Cd at the Connecticut River/Long Island Sound Boundary*

August 21, 1972

Sample	Depth (ft)	Salinity (‰)	Acidified Cu ($\mu\text{g/l}$)		Raw	Acidified Cd ($\mu\text{g/l}$)	
			Unfiltered	Filtered		Unfiltered	Filtered
RA-1	0	0.899	5.2	3.1		0.2	
RA-2	10	0.975	4.4	3.0		0.04	
RB-1	0	10.556	3.7	3.6		0.4	0.2
RB-2	4	4.927	4.6	3.7	0.2	0.02	0.3
RB-3	9	9.717	3.2	3.4	0.2	0.1	0.05
RC-1	0	10.548	3.4	3.6		0.2	0.1
RC-2	7	25.815	1.7			0.1	0.2
RC-3	12	27.235	1.8	1.7		0.1	
RD-1	0	12.734	3.3	4.3		0.1	
RD-2	0	19.969	3.1	2.0		0.2	
RD-3	16	26.652	2.0	1.0		0.2	
RE-1	0	27.883	1.6	2.0	0.2	0.3	
RE-2	10	27.892	2.0	2.0	0.2	0.1	
RE-3	20	28.314	2.5	1.4	0.2	0.1	

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*See Hunt (1973).

Table A-5b

Concentrations of Cu and Cd at the Connecticut River/Long Island Sound Boundary*

February 22, 1973

Sample	Depth (ft)	Salinity (o/oo)	Cu ($\mu\text{g/l}$)		Cd ($\mu\text{g/l}$)	
			Raw	Acidified filtered	Raw	Acidified filtered
R1-S	0	0.274	0.5	5.1	0.3	0.2
R1-B	6	0.153	0.9	3.4	0.2	0.2
R2-S	0	1.041	0.9	3.0	0.2	0.1
R2-B	16	25.094	0.3	1.4	0.1	0.1
R3-S	0	26.468	1.6	3.4	0.1	0.1
R3-B	12	26.429	0.7	2.0	0.1	0.2
R4-S	0	7.083	0.8	2.7	0.10	0.08
R4-B	13	26.456		1.4		0.08
R5-S	0	23.702		0.5		0.07
R5-B	15	28.614		0.6		0.06

* See Hunt (1973)

Table A-6

Concentrations of Cu and Cd in Block Island Sound

Station Data

12 May 1972

Depth (ft)	Salinity (‰)	Temp (°C)	Metal Concentration (µg/l)	
			Cu	Cd
Station 2 (40°14.2'N, 71°57.8'W)				
0	29.999	7.45	1.6	0.1
19	30.087	8.08	1.9	
43	30.408	7.23	0.8	
67	31.204	7.23		
115	31.376		1.2	
163	31.406	7.40	0.7	0.05
Station 3 (41°10.9'N, 71°57.0'W)				
0	29.145	7.60	1.5	0.05
20	29.161	7.54	1.6	
45	29.288	7.37	1.0	0.07
70	29.469	7.30	1.1	0.08
Station 4 (41°09.4'N, 71°49.4'W)				
0	29.742	7.60	1.6	0.03
27	29.853	7.70	0.4	0.07
59	30.118	7.36		
73	30.238	7.31		
118	30.849	7.28	0.6	0.05
Station 5 (41°07.8'N, 71°42.4'W)				
0	30.718	7.85	1.3	0.1
28	31.236	7.82	1.8	0.05
61	31.596	7.35	0.7	
75	31.786	7.13	1.2	0.2
122	32.033	6.80	2.5	0.4

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CHAPTER III

CIRCULATION IN EASTERN
LONG ISLAND SOUND

by

D. F. Paskausky, A. J. Nalwalk, D. L. Murphy and
C. E. Perkins

INTRODUCTION

A study of the circulation in Long Island and Block Island Sounds has been underway at the University of Connecticut since 1970 (with support received from the University of Connecticut Research Foundation, the U. S. Naval Underwater Systems Center, the U. S. Army Corps of Engineers and the U. S. Coast Guard, as well as the Office of Sea Grant Programs). This report concerns that part of the study in eastern Long Island Sound which was supported by Sea Grant over a two-year period.

Two methods were used to obtain data on water circulation: (1) an Eulerian approach, involving anchored ships as a platform for current-meter measurements at selected locations; and (2) a Lagrangian approach, using surface and seabed drifters. Most of the current measurements were made during the first year of the program. Evidence for the existence of a cyclonic-loop circulation in eastern Long Island Sound, reported by Paskausky et al (1972), suggested that surface and seabed drifters would be the most feasible method for determining the extent of the loop. The major efforts of the second year was a drifter study. The area of study is shown in Fig. 1.

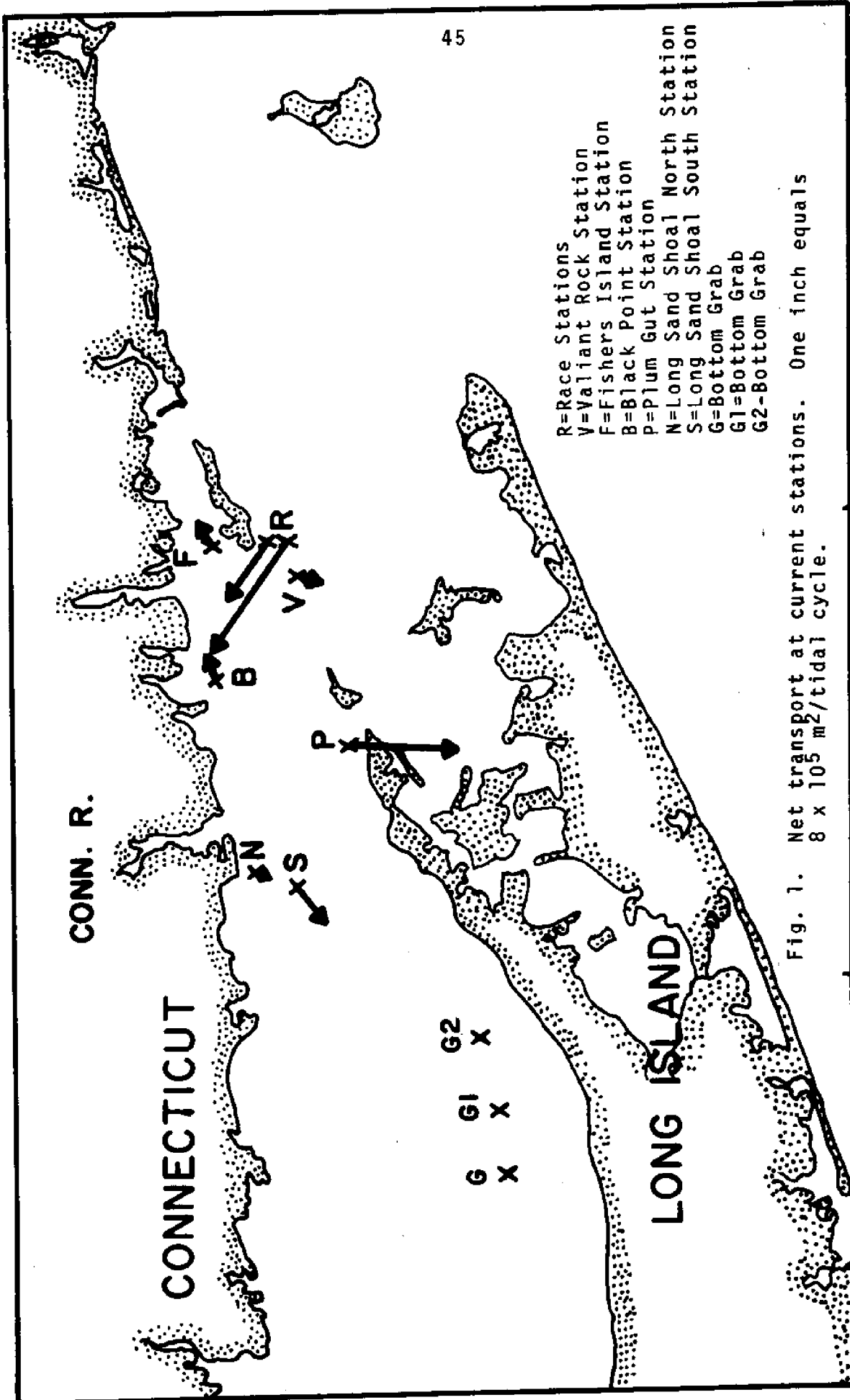
Current measurements in the eastern passages of Long Island Sound indicate that there is a net inflow of water over a tidal cycle in the deep channel of the Race, and a balancing outflow in the remainder of the passage between Orient Point and Fishers Island. These measurements and bottom samples taken in the eastern third of the Sound suggest the existence of a tidally driven counterclockwise gyre.

The drifter study supports the hypothesis that the circulation in the eastern third of the Sound is tidally influenced and that in the remainder of the Sound winds are the prime cause of net drift.

OBJECTIVES

The long term objectives of this project are to:

1. Make current measurements at the Race and Plum Gut in



to quantify the inflow.

2. Attempt to define the dimensions and persistence of the gyre based on data from bottom samples, current measurements, and use of sea bed drifters.
3. Determine the relative influence in all of Long Island Sound of tides, wind, and river inflow.

METHOD OF STUDY

Field Methods

1. Current measurements were made at selected locations at four depths (near-surface, 1/3, 2/3, near-bottom) over semi-diurnal tidal cycles, using three different types of current meters.
2. At all current stations water samples were taken hourly for salinity determinations at the four depths of current measurements.
3. At all current stations hourly bathythermograph casts were made and surface temperature was measured.
4. Weather data were observed.
5. Water samples were taken for other projects, as needed, in the Sea Grant program.
6. Bottom samples were obtained with a Petersen grab, as indicated in Fig. 1. Observations of grain size were made in the field only.
7. Surface and seabed drifters were launched from a helicopter on a grid of stations covering eastern Long Island Sound (packets of 5 bottom and 1 surface drifter were launched at each station).

Laboratory Methods

1. Salinity of the water samples was determined using an Industrial Instrument, Inc., RS-7B Induction Salinometer.

2. BT traces were reduced and read after preliminary checking in the field.

Equipment Used

The following lists the boats and special instrumentation used in the study:

1. R/V UConn (65 feet)
2. R/V T-441 (65 feet)
3. Boston Whaler (17 feet)
4. 202 Decca Radar
5. Bisset-Berman STD (self-contained)
6. Van Dorn water bottles
7. Bucket thermometers
8. Various types of instruments for weather measurements
9. Industrial Instrument Inc., RS-7B Induction Salinometer
10. Shallow-water bathythermograph (BT-200 ft)
11. Petersen grab sampler
12. Model CM2 Direct-Reading Current Rate and Direction current meter, a Savonius rotor current meter, and a ducted current meter
13. Surface and seabed drifters
14. Sikorsky H-3 helicopter

CURRENT MEASUREMENTS

Evidence for a two-layered flow at the eastern opening of Long Island Sound was given by Riley (1952, 1956, 1959, 1967). Nalwalk et al (1970) found in May 1970 that this two-layered

flow in the deep eastern channel of the Race consists of a predominant inflow in the lower two-thirds of the water column. Paskausky et al (1972) found that this net inflow at the eastern portion and a corresponding outflow in the western portion of the opening into Block Island Sound was tidally rather than river driven. Evidence indicates the presence of a cyclonic circulation pattern in eastern Long Island Sound which persists throughout all seasons.

Current measurements were made in an attempt to further delineate the cyclonic gyre. Hourly measurements were made near the surface, 1/3 depth, 2/3 depth, and near the bottom over a semi-diurnal tidal cycle at Plum Gut (41°10.3'N; 72°15.2'W) on 5 June 1972, in Fishers Island Sound (41°17.6'N; 72°01.2'W) on 7 June 1972, at Valiant Rock (41°12.9'N; 72°03.6'W) on 27 June 1972, near the Race (41°14.5'N; 72°00.6'W) in shallow water on 24 July 1972 (41°10.5'N; 72°15.7'W) on 17 January, 1973, and again at the Race (41°14.3'N; 72°00.2'W) in deeper water on 19 October 1972. Current measurements were made hourly during a tidal cycle just below the surface and above bottom south of Long Sand Shoals (41°13.4'N; 72°23.5'W) on 20 August 1973 and north of Long Sand Shoals (41°14.1'N; 72°24.0'W) on 23 August 1973. Measurements were made continuously over two tidal cycles near Black Point (41°16.4'N; 72°11.0'W) on 29-30 May 1974. A Savonius, a ducted, or a CM2 current meter was used to make the current measurements.

Fig. 2 shows the half-hourly current vectors at the four measured levels at Plum Gut on 5 June 1972 and at Valiant Rock on 27 June 1972, and hourly current vectors at the Race on 24 July 1972, 19 October 1972, and on 17 January 1973. The October Race station was located in 196 feet of water about one-quarter mile to the southwest of the July Race station. Single-point anchoring was used as the currents in the area of study are predominantly bi-directional. Fig. 2 (a, b, and c) indicates that there is a net transport of water into Long Island Sound at the Race, particularly in the lower two-thirds, since flood lasts approximately 6.5 hrs. and ebb lasts about 3 hrs. The magnitude of the flood-current vectors is also greater than those of the ebb. At Plum Gut there is a net transport out of the Sound, the ebb lasting about 6.5 hours and the flood about 5 hours. At Plum Gut the ebb vector magnitudes are greater than those of the flood and the duration differential is greatest in the upper layer. At Valiant Rock there is also a tendency to outflow in the upper layers. Thus, the inflow is restricted to the relatively narrow deep channel at the Race and the outflow

RACE JULY 24, 1972

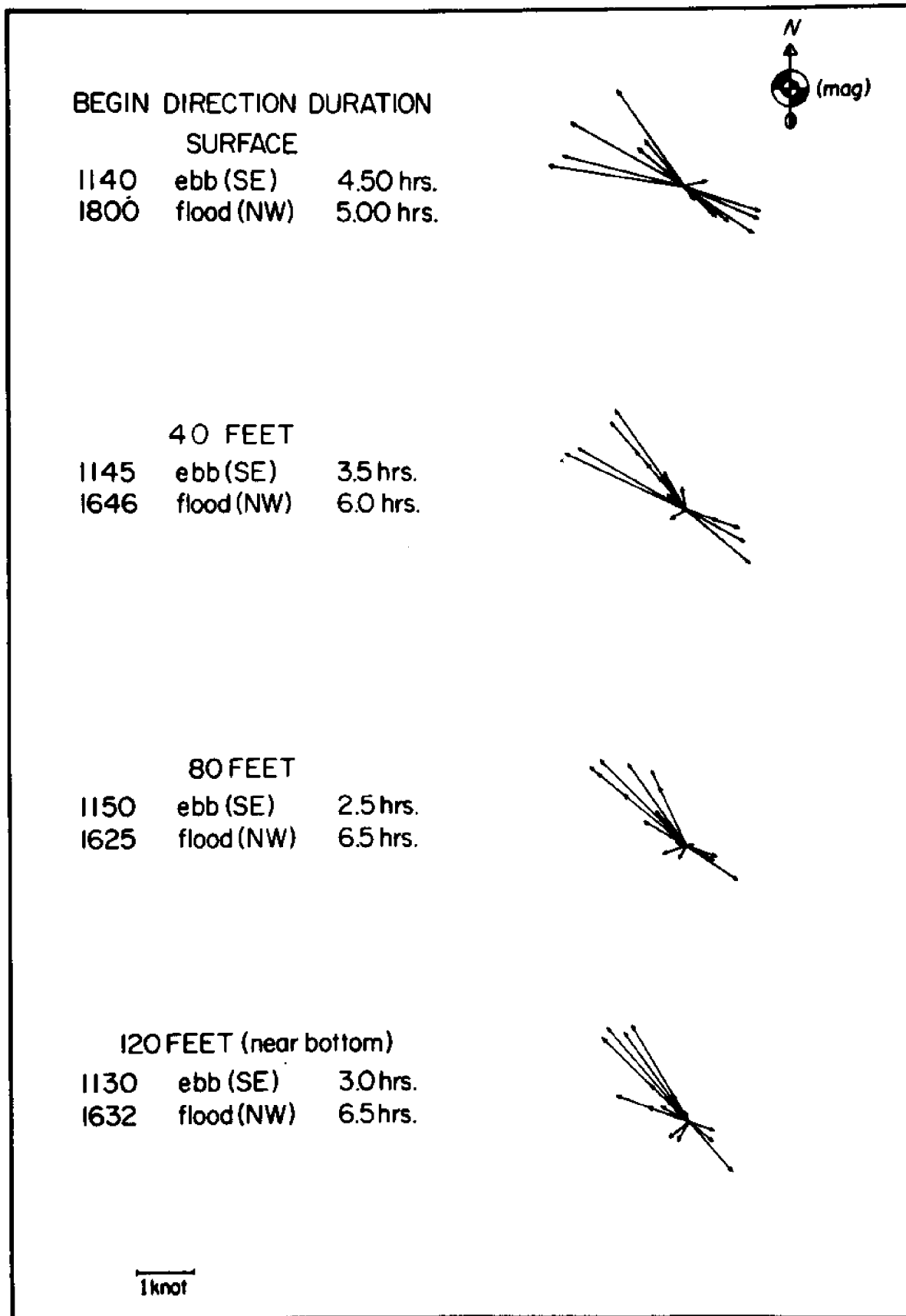


Fig. 2. Current magnitude, directions and duration of flood and ebb at:
a. The Race, July 24, 1972.

RACE OCT. 19, 1972

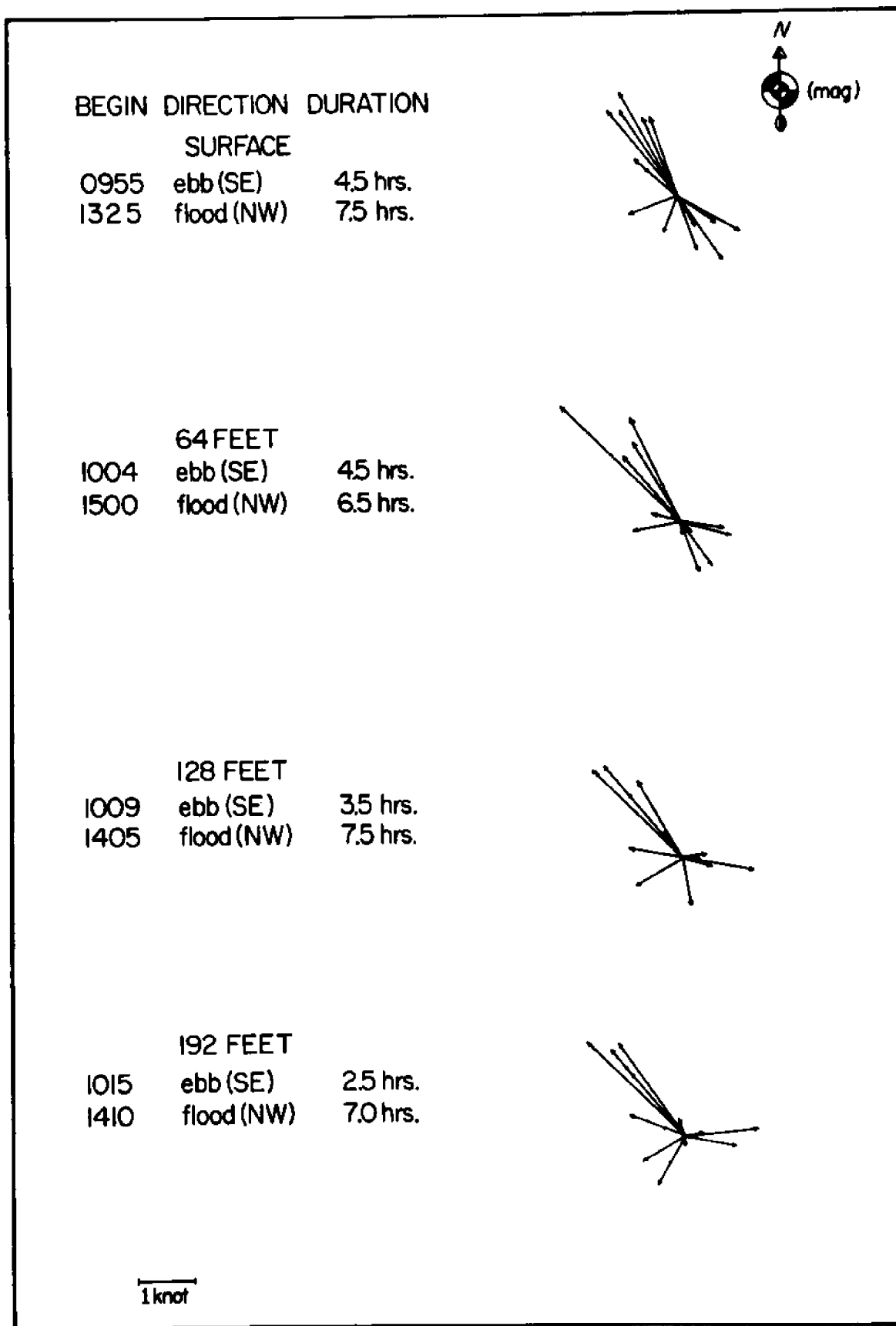


Fig. 2b. The Race, October 19, 1972.

THE RACE , JANUARY 17, 1973

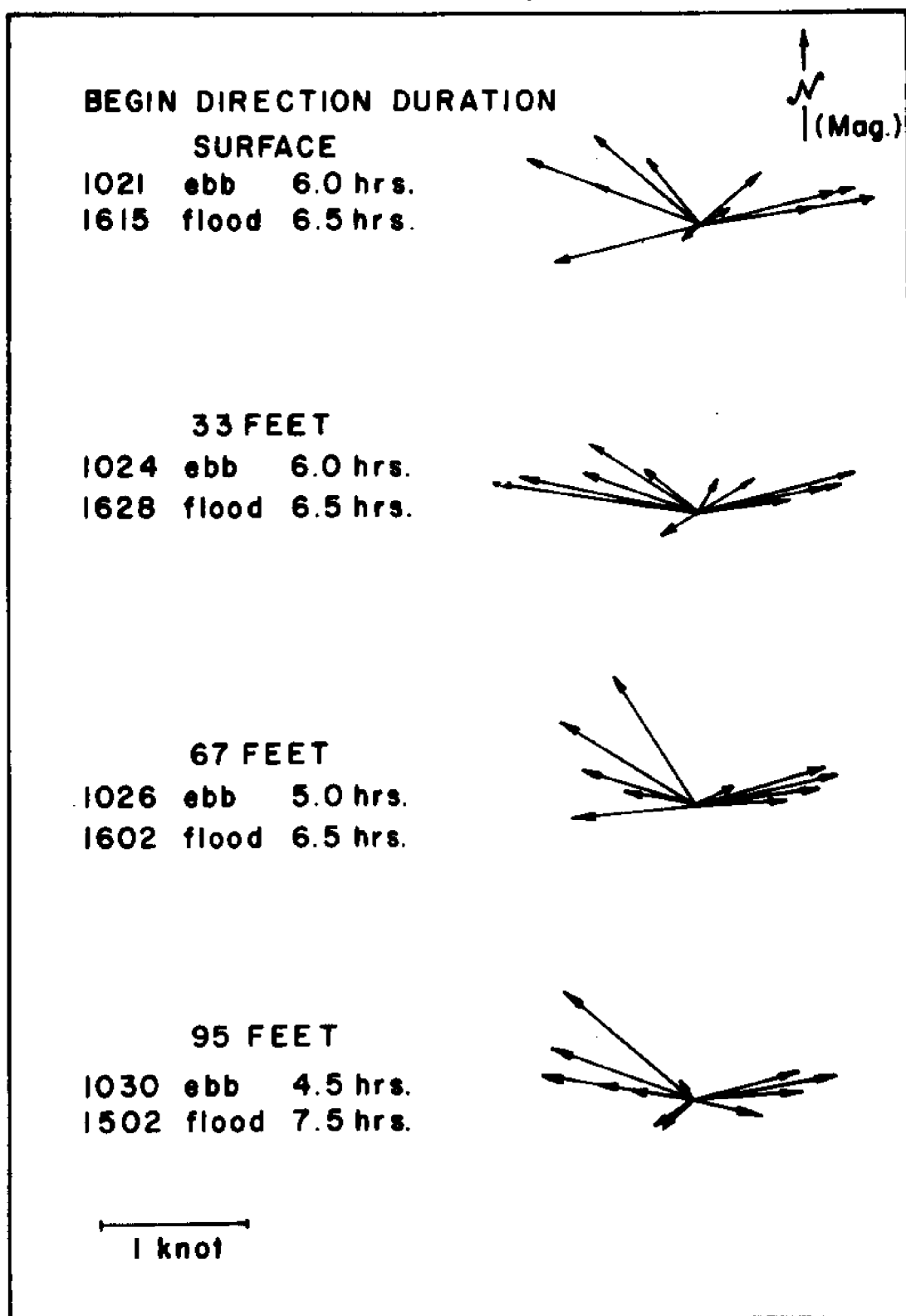


Fig. 2c. The Race, January 17, 1973.

PLUMGUT JUNE 5, 1972

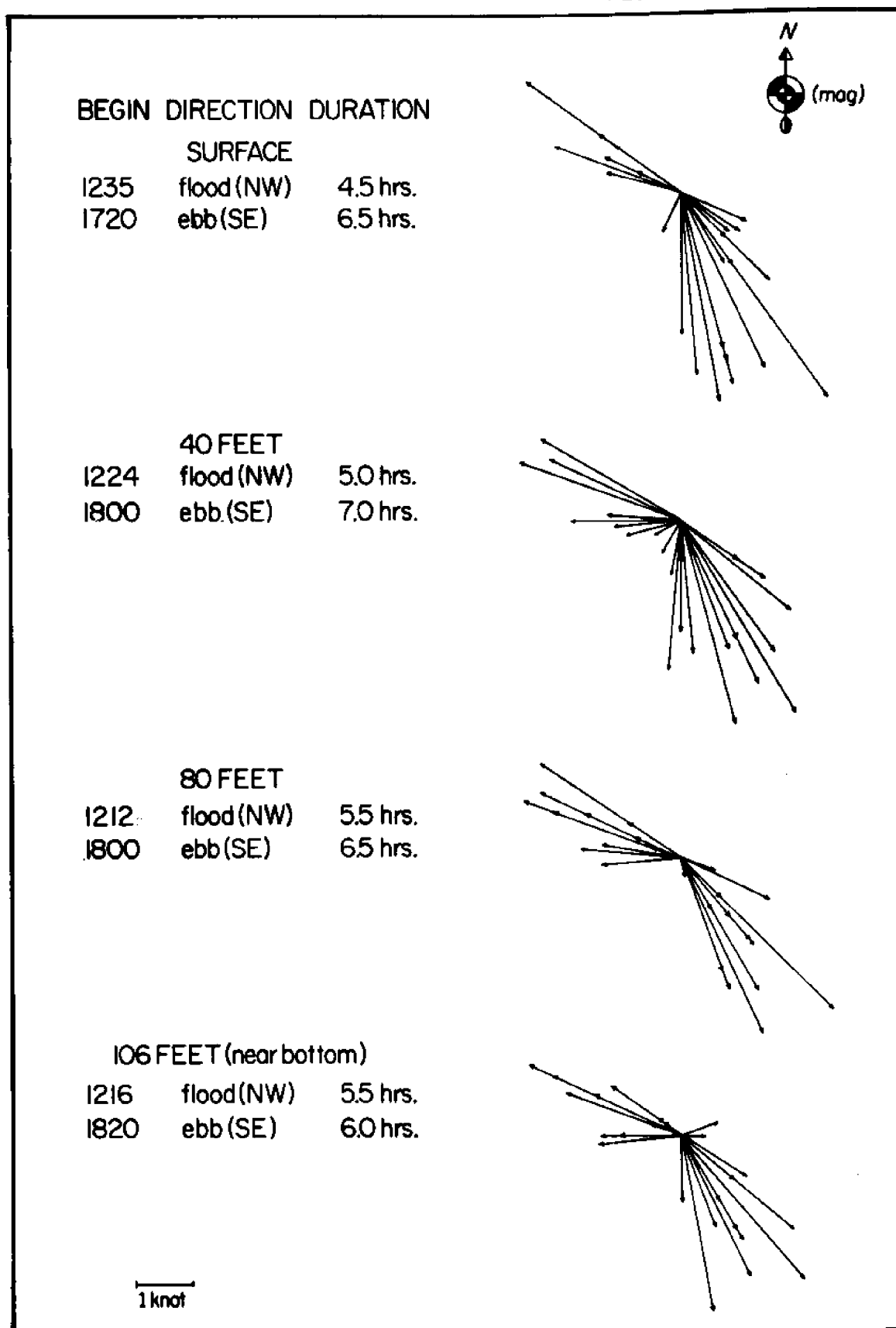


Fig. 2d. Plum Gut, June 5, 1972.

VALIANT ROCK JUNE 27, 1972

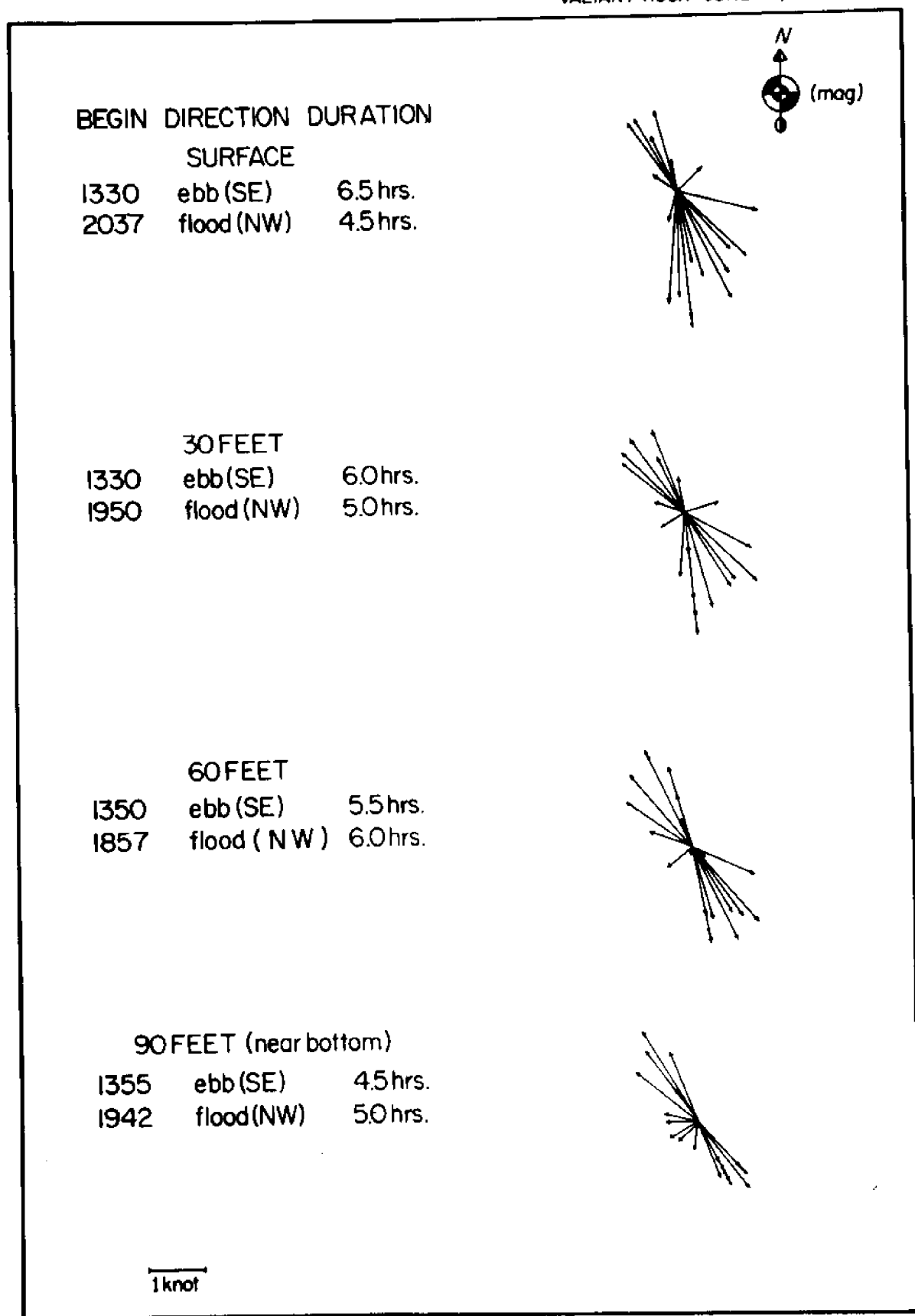


Fig. 2e. Valiant Rock, June 27, 1972.

FIS JUNE 7-8, 1972

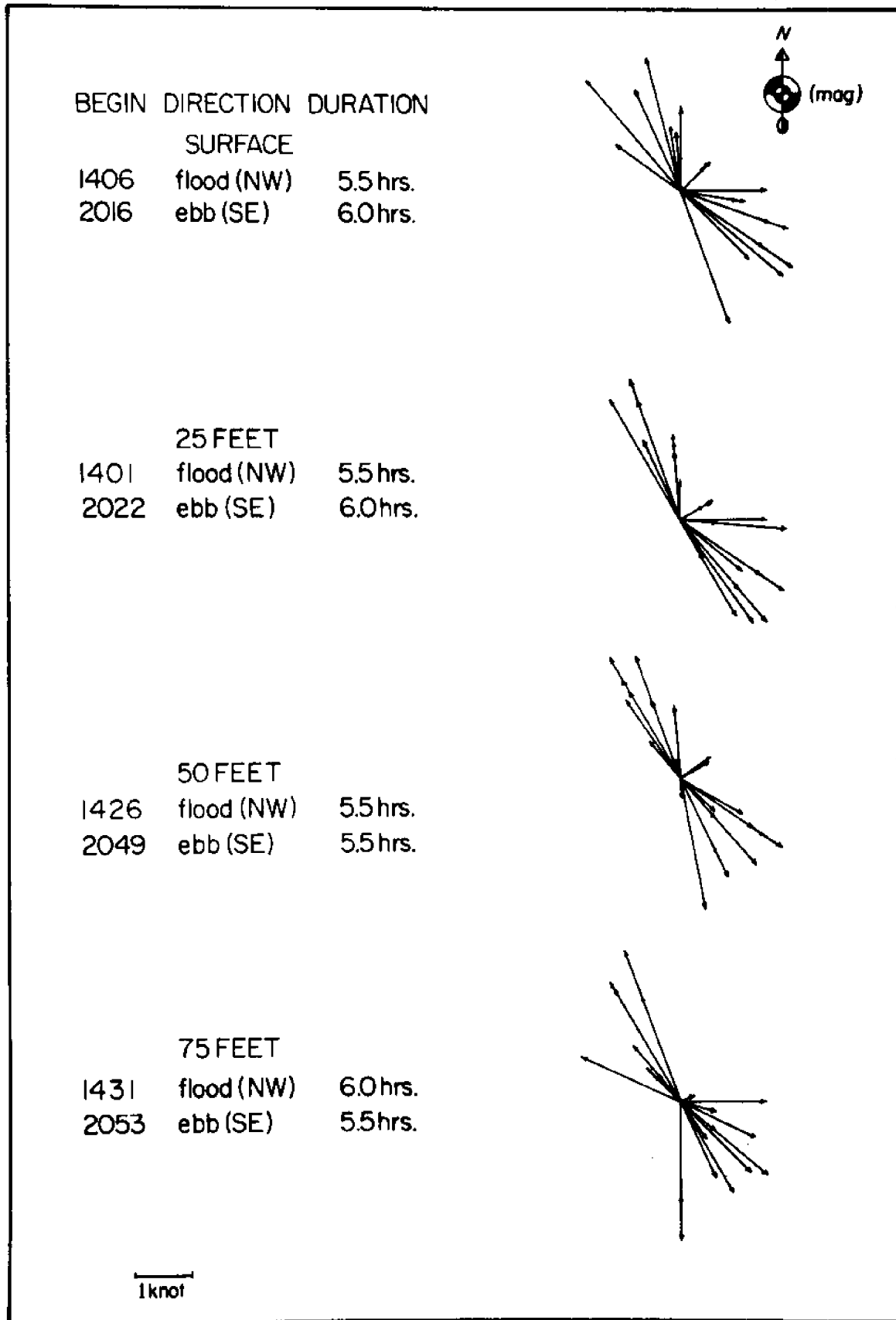


Fig. 2f. Fishers Island Sound, June 7, 1972.

appears to occur in the surface layer in the wider and shallower southwestern portion of the opening to Long Island Sound. During ebb the minimum salinity near the surface at the Race is $29.40^{\circ}/\text{oo}$ and the maximum near bottom is $31.14^{\circ}/\text{oo}$. During flood at the Race the minimum salinity is $30.18^{\circ}/\text{oo}$ and the maximum $31.53^{\circ}/\text{oo}$. During flood at Plum Gut the minimum salinity of $26.62^{\circ}/\text{oo}$ is at the surface, and the maximum of $29.21^{\circ}/\text{oo}$ is near the bottom. During ebb at Plum Gut the minimum salinity is $25.71^{\circ}/\text{oo}$ and the maximum $29.79^{\circ}/\text{oo}$. The magnitude and direction of the current, the temperature, and salinity at each station shown in Fig. 2 are tabulated in the Appendix. Care should be taken in interpreting magnitudes of velocities presented in the Appendix as they are uncalibrated; they were intended to show relative flow during flood and ebb tides.

The net inflow at the Race and outflow at Plum Gut suggests a tidally generated counterclockwise circulation or gyre in eastern Long Island Sound.

On 16 August 1972 bottom samples were taken at stations G, G1 and G2 shown in Fig. 1. The bottom samples at stations G and G1 were silty mud, similar to the type of bottom found in western Long Island Sound, and the bottom sample at station G2 was well sorted sand similar to the type of bottom found in the eastern Sound. This change of bottom from mud to sand suggests that the gyre persistently penetrates as far west as $72^{\circ}35'W$. Surface and seabed drifter results reported by Hollman and Sandberg (1972), and the persistence of Long Sand Shoal, provide further evidence in support of the existence of the gyre. Bathymetry and tides seem to be the principal causes of this gyre in the eastern Sound which probably exists year-round since the two-layered flow at the Race was observed to exist in July and October and January and also was observed by Nalwalk *et al* (1970) in May 1970. One attempt to simultaneously occupy a station at the Race and at Plum Gut was aborted due to failure of current meters.

To obtain a more complete picture of the transport in the eastern Sound, our data obtained on projects supported by the Army Corps of Engineers and the Naval Underwater System Center have been included in the following analysis.

To convert the raw current vector data into a form useful in computing net drift or transport, N-S and E-W components were plotted versus time as shown for the Black Point station in Fig. 3. The net transport per unit layer thickness, per unit

BLACK POINT TIDAL COMPONENTS

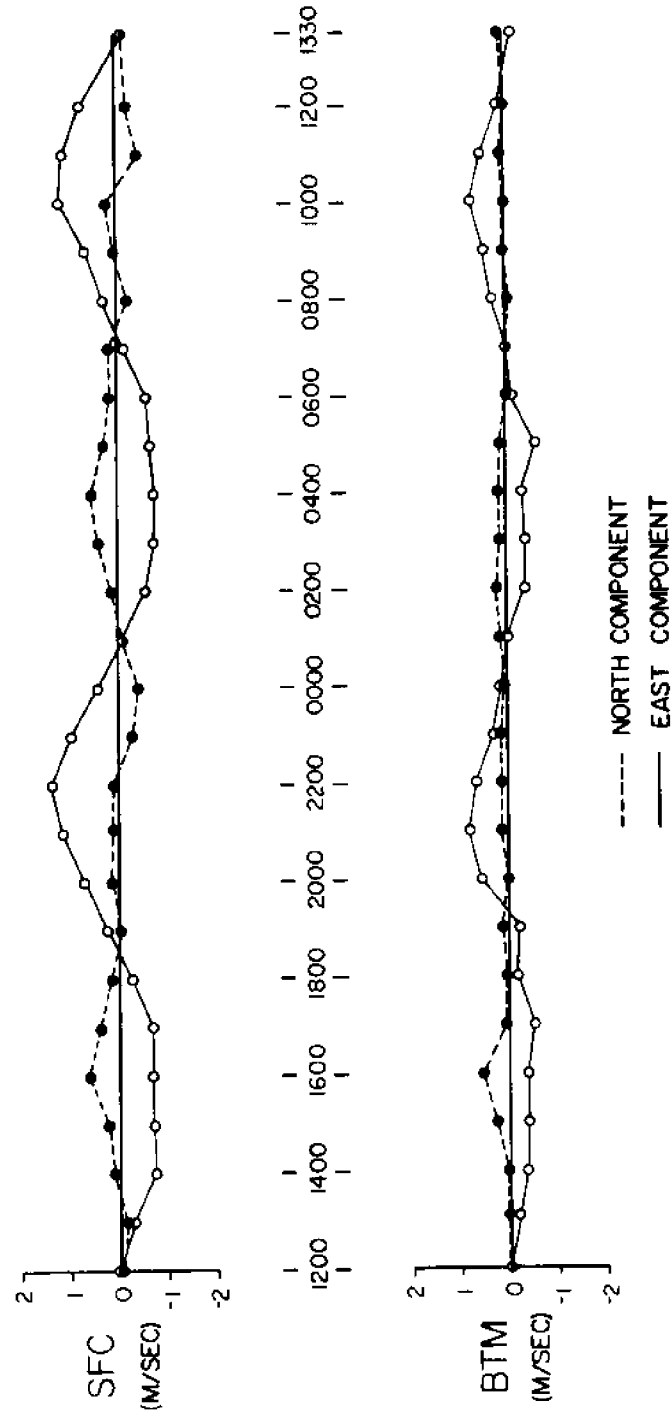


Fig. 3. Magnetic vector components of transport over two tidal cycles at the Black Point current station.

Table 1 Tidal Cycle Transport

STATION (and current meter type)	DEPTH (m)	FLOOD		EBB	
		(m/half-cycle) East	(m/half-cycle) North	(m/half-cycle) East	(m/half-cycle) North
Plum Gut 6/5/72 (Ducted)	2.4 12.2 24.4 32.3	-11628 -15480 -19368 -17424	5112 4752 7704 7636	9324 7344 11376 12384	-28512 -29628 -21996 -15588
Fishers Island Sound 6/7/72 (Ducted)	2.4 7.6 15.2 22.9	- 7416 - 5796 - 7956 - 8820	16200 18720 18216 15840	17208 14364 7956 8748	-12384 -13896 -13896 -13248
Valiant Rock 6/27/72 (Savonius)	2.4 9.1 18.3 27.3	- 4068 - 6336 - 7992 - 7092	10080 7524 10368 5832	3456 4140 4860 3060	-17928 -16200 -10296 - 7884
Race 7/24/72 (Savonius)	2.4 12.2 24.4 36.6	-12132 -12708 -13068 -12096	7524 12132 14724 10836	7740 4896 2880 2124	- 4824 - 2628 - 1800 - 1692
Race 10/19/72 (Savonius)	2.4 19.5 39.0 58.5	-12384 -12492 -15552 -15228	15120 14004 13968 13968	4500 4068 3852 2736	- 6192 - 3960 - 2412 - 1836

Table 1 (continued)

STATION (and current meter type)	DEPTH (m)	FLOOD		EBB	
		(m/half-cycle) ↑East	North	(m/half-cycle) ↑East	North
Long Sand Shoals South 8/20/73 (Savonius and ducted)	2.4	-19980	1548	5076	- 6264
	8.5	-18180	1404	6804	- 7056
	17.1	-15804	1188	9576	- 4356
	23.8	-11844	0	8424	- 4176
Long Sand Shoals North 8/23/73 (Savonius and ducted)	1.8	- 9972	3564	4428	-10944
	4.3	- 7524	2016	4248	- 6912
Black Point Cycle 1 5/29/74 (Ducted)	2.4	-11376	5004	17316	- 1080
	18.3	- 7596	3924	8460	2052
Black Point Cycle 2 5/30/74 (Ducted)	2.4	-12024	5976	14004	1872
	18.3	- 6084	2700	7344	396

width, per half tidal cycle (for ebb and for flood) was found graphically by summing the area under the component curves between zeros. The depths at which the currents were measured and the transport at each level (in m/half-cycle) are given in Table 1.

To visualize the net transport in the total water column at the stations where current measurements were taken, a simple vertical integration was accomplished by multiplying the transport given in Table 1 by the layer thickness, which was assumed to be midway between depths of measurements, e.g., at Valiant Rock the surface thickness was 5.8 m, the 1/3-depth-layer thickness was 8.0 m, the 2/3-depth-layer thickness 9.1 m, and the bottom-layer-thickness 9.0 m. The vertically integrated components of transport (in m^2 /half-cycle) for ebb and flood were added to give net transport components per cycle and then vectorially combined to give the transport vectors shown in Fig. 1. This figure shows strong evidence for a cyclonic tidally driven net drift loop (the gyre) in the eastern Sound, but does not indicate the extent of penetration into the central Sound. Since the net transport has weakened by the time it reaches Long Sand Shoal, the original estimate of westward penetration to 72°35'W by Paskausky *et al* (1972) appears reasonable. At least west of that longitude other factors, such as prevailing winds and storms, may dominate the circulation pattern.

DRIFTER STUDY

A U. S. Coast Guard H-3 helicopter was the platform for a synoptic "launch" of drifter packets at 50 stations in Long Island and Block Island Sound during a half tidal cycle on 18 June 1973, as described by Paskausky *et al* (1974). Earlier drifter studies in Long Island Sound (Larkin and Riley, 1967; Gross and Bumpus, 1972; Hollman and Sandberg, 1972) were conducted in a few selected areas only. Our helicopter launch included the entire area of the loop current described in the previous section. At each station shown in Figs. 4 to 6, a packet of five weighted (seabed or bottom) and one unweighted (surface) drifters was dropped. A Bunny Lik (a salt block for rabbits) and a rubber band were used as the mechanism to keep the drifters together until they reached bottom. The salt lick dissolved in about 50 minutes (a static test was made in a bucket of sea water). The number of the drifter, when found, was returned to us for a reward.

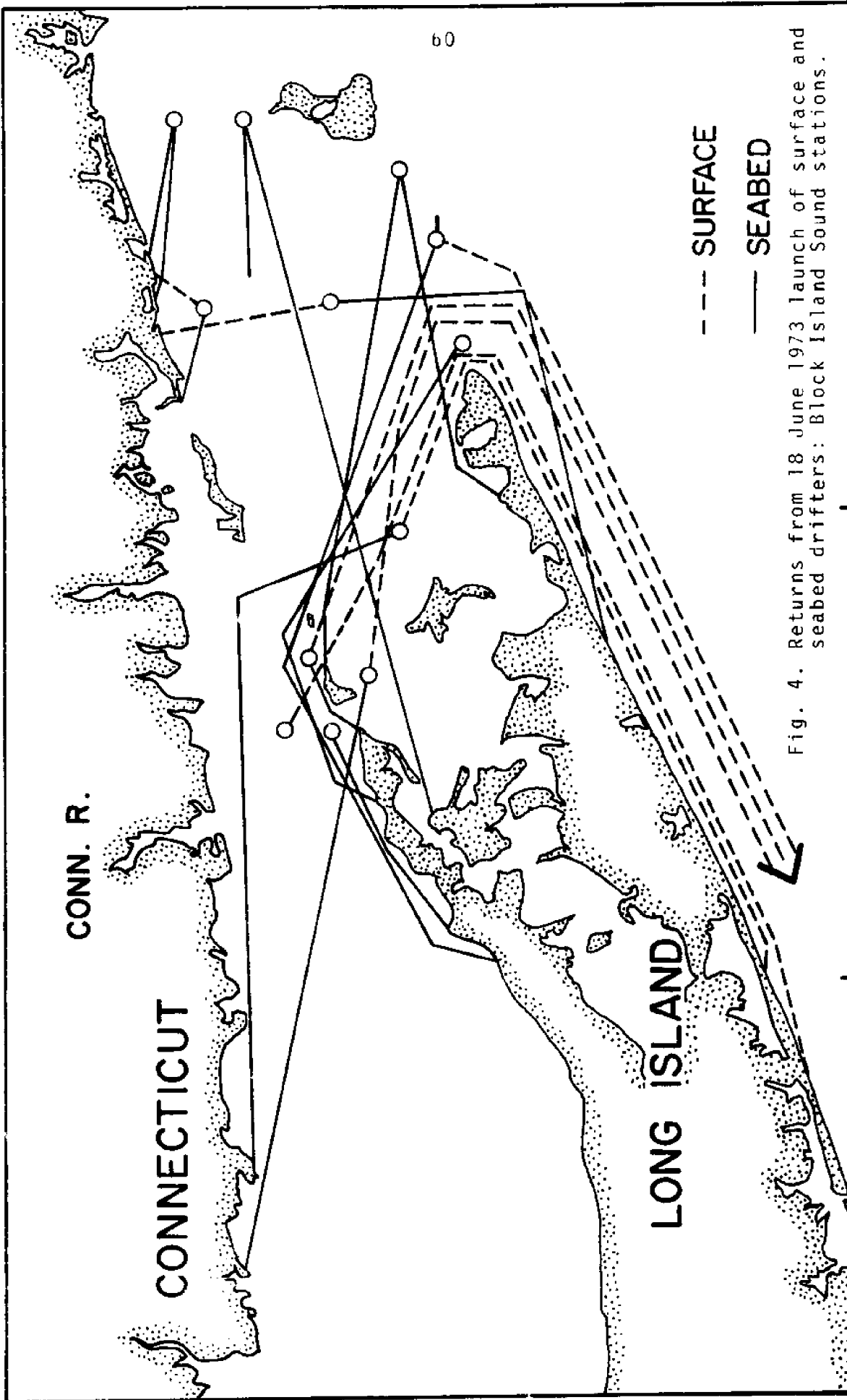


Fig. 4. Returns from 18 June 1973 launch of surface and seabed drifters: Block Island Sound stations.

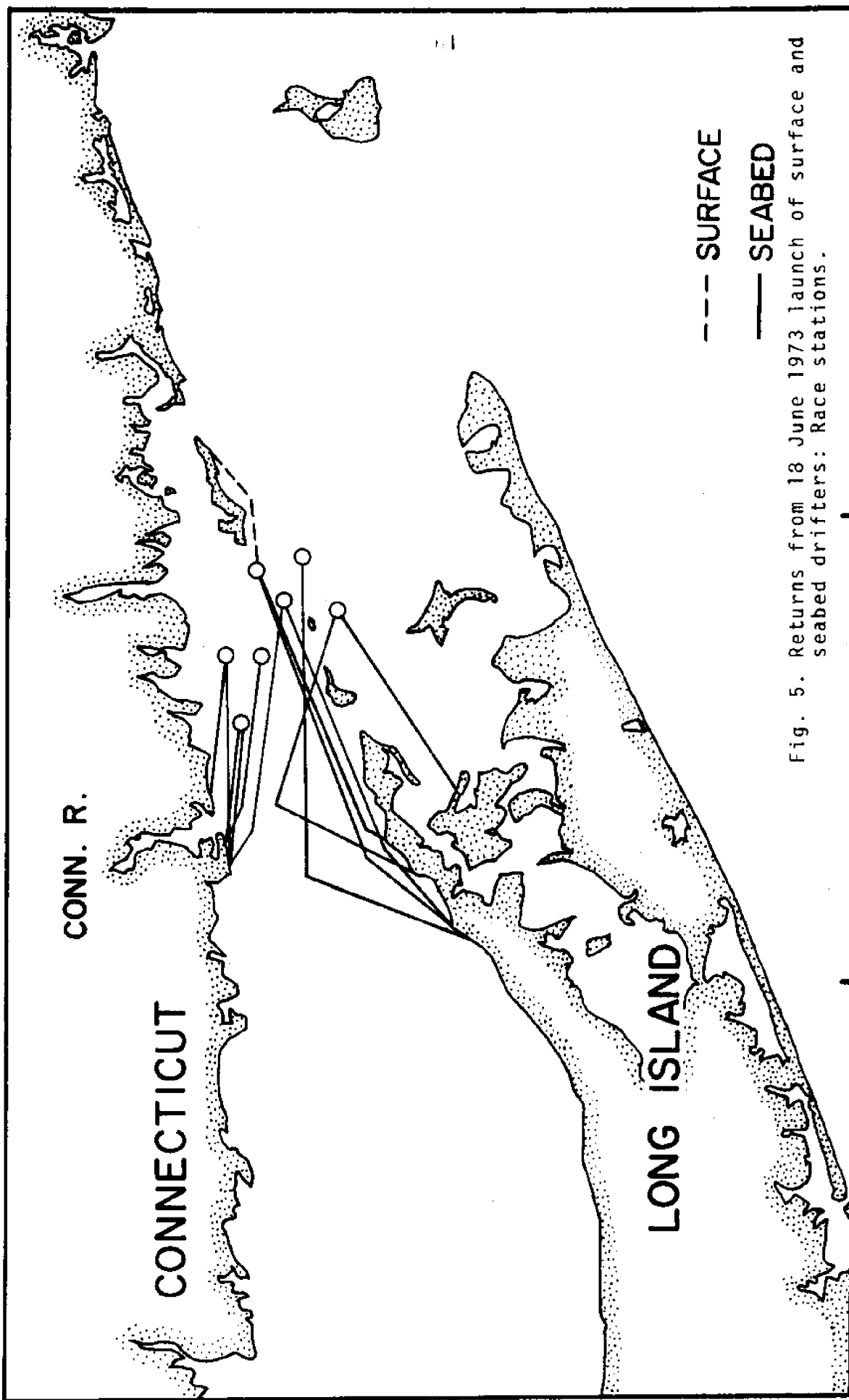
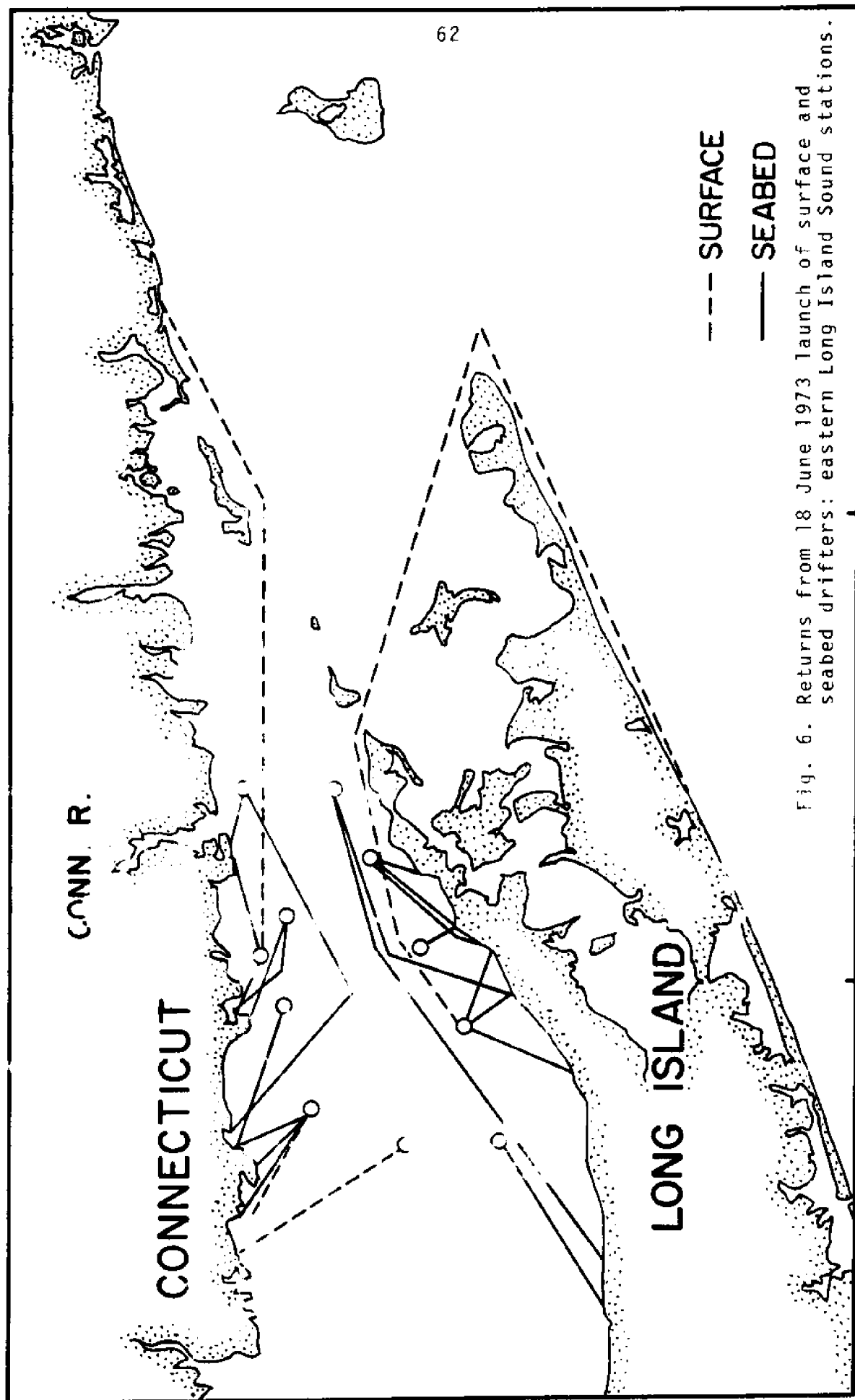


Fig. 5. Returns from 18 June 1973 launch of surface and seabed drifters: Race stations.



Returns from the 30 stations east of $72^{\circ}35'W$ longitude are shown in Figs. 4 to 6 (surface drifter returns are indicated by dashed lines and seabed drifter returns by solid lines). Lines ending at sea represent drifters found by draggers (fishermen). Fig. 4 shows a net bottom drift from Block Island toward Long Island Sound and a net surface drift near Plum Island out of Long Island Sound. Fig. 6 shows a continued westward bottom drift, further collaborating the surface drift out of Long Island Sound, which is indicated in Fig. 4. The two westward moving surface drifters indicated in Fig. 6 may be due to the surfacing of the bottom westward drift because of changes in bathymetry (the bottom becomes shallower westward from the Race). The drifter returns suggest a net westward drift at the bottom, balanced by an eastward surface drift in Block Island and eastern Long Island Sounds.

CONCLUSIONS

The drifter data and the current measurements in Block Island and eastern Long Island Sounds indicate that there is a distinct influx of bottom water and a balancing outflow on the surface in the eastern passages of Long Island Sound for all seasons. The current measurements suggest a horizontal gyre and the drifters suggest a vertical gyre. The circulation is probably a combination of the two since the westward penetration of the effect is greater than the distance that tidal velocities could carry waters during flood periods.

This program on circulation studies in eastern Long Island Sound has had some side benefits, in that support for a study of the net drift in all of Long Island Sound for all seasons has been provided by the U. S. Army Corps of Engineers, using a modification of the storm-surge model of Lake Erie developed by Paskausky and Murphy (1973). Net drift in the Sound predicted for a period of a week for prevailing northeasterly winds during March, as reported by Brumbach (1965), was in agreement with drifter returns at the New Haven Dump Site, as reported by Nalwalk et al (1974). This predicted circulation reinforces the tentative conclusion that prevailing winds are responsible for the net drift in the central Sound.

MOVIE

A super 8 movie (Helicopter Launching of Surface and Seabed Drifters) has been produced, in conjunction with a U. S. Coast Guard helicopter over-flight described by Paskausky et al (1974). Acknowledgment was made in the movie to all contracts which have supported drifter studies by the authors in Long Island and Block Island Sound. A description of the content of the movie is listed below.

Helicopter landing and simulated drifter find.
Title, authors, and acknowledgments.
Demonstration of drifters.
Assembly of packets (shows Bunny Lik).
Landing gear on helicopter.
Take-off from Trumbull Airport, Groton, Connecticut.
Logging numbers before launch (with double check).
Launch:

regular film speed, throw out packets, then
falling packet.

in water having survived impact (2 drops).

slow motion, falling through air and strikes water -
settles into water.

falling through air, strikes water, zoom misses
packet in water.

helicopter returns to airport and land.

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APPENDIX

Temperature, salinity, and current direction and speed at the current stations shown in Fig. 1. Note that the current magnitudes are not calibrated.

PLUM GUT

05 June, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
2100	SURF	13.5	27.48	165	3.5
	40	12.3	29.73	165	3.8
	80	11.6	29.54	155	3.3
	106	11.6	29.65	155	2.8
2200	SURF	13.9	26.86	175	3.3
	40	12.7	28.46	185	2.7
	80	11.8	29.14	160	2.5
	106	11.7	29.32	150	2.0
2300	SURF	13.9	25.71	155	3.5
	40	11.7	27.06	160	2.4
	80	11.7	29.04	140	1.3
	106	11.7	29.17	130	1.2
2400	SURF	14.9	25.77	180	0.2
	40	13.5	26.35	180	1.0
	80	12.2	28.04	150	1.1
	106	11.9	28.57	030	0.8

06 June, 1972

0100	SURF	14.4	25.81	220	0.0
	40	13.7	26.42	190	1.0
	80	12.8	27.41	290	0.5
	106	11.8	29.22	280	1.2
0200	SURF	14.4	NA	280	0.0
	40	14.9	NA	295	0.8
	80	13.5	NA	295	1.0
	106	11.8	NA	270	1.1

FISHERS ISLAND SOUND

07 June, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
1200	SURF	13.1	28.24	NA	NA
	25	12.5	29.13	NA	NA
	50	12.3	29.29	NA	NA
	75	12.3	29.30	NA	NA
1300	SURF	13.4	27.65	100	1.00
	25	12.8	28.74	090	1.50
	50	12.3	29.23	120	1.30
	75	12.2	29.49	120	1.10
1353	SURF	13.6	28.01	340	1.10
	25	12.8	28.87	350	1.00
	50	12.4	29.21	045	0.57
	75	12.2	29.55	110	0.57
1500	SURF	13.4	28.17	305	1.40
	25	12.8	28.73	335	1.60
	50	12.5	29.06	325	1.70
	75	12.2	29.31	340	2.00
1600	SURF	13.4	28.73	345	2.40
	25	12.9	28.97	340	2.70
	50	12.7	29.00	330	2.50
	75	12.7	29.02	340	2.90
1655	SURF	12.8	29.11	320	2.60
	25	12.8	29.09	330	2.50
	50	12.8	29.09	340	2.40
	75	12.8	29.09	330	2.30
1805	SURF	13.2	29.07	350	1.80
	25	13.0	29.20	350	1.90
	50	12.8	29.54	335	2.00
	75	12.8	29.65	330	2.40
1900	SURF	13.0	29.37	350	1.20
	25	13.0	29.40	355	1.20
	50	12.9	29.65	340	1.40
	75	12.8	29.76	320	1.30
2000	SURF	12.9	29.07	070	0.54
	25	12.9	29.43	340	0.32
	50	12.9	29.80	340	0.78
	75	12.9	29.93	320	0.58

FISHERS ISLAND SOUND

07 June, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
2055	SURF	13.3	27.89	140	1.60
	25	12.9	29.47	130	1.60
	50	12.8	29.74	160	1.10
	75	12.8	29.82	145	0.80
2155	SURF	13.7	25.97	145	2.50
	25	13.2	28.88	135	2.50
	50	12.9	29.27	205	2.20
	75	12.8	29.64	180	1.80
2255	SURF	13.7	26.45	125	2.40
	25	12.9	29.11	125	2.20
	50	12.9	29.27	125	2.20
	75	12.9	29.38	130	2.00
2356	SURF	13.3	26.38	130	2.30
	25	12.8	29.10	140	2.30
	50	12.4	29.20	140	2.10
	75	12.4	29.33	135	1.80

08 June, 1972

0100	SURF	12.8	27.14	110	2.00
	25	12.3	29.19	140	1.60
	50	12.2	29.41	140	1.80
	75	12.1	29.56	150	1.90
0200	SURF	12.8	29.59	100	1.10
	25	12.3	29.09	150	0.84
	50	12.2	29.43	135	0.84
	75	12.2	29.54	130	0.74
0240	SURF	12.7	NA	345	0.52
	25	12.4	NA	045	0.58
	50	12.3	NA	045	0.48
	75	12.2	NA	115	0.42

VALIANT ROCK

27 June, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
1320	SURF	14.2	29.10	NA	NA
	30	13.8	29.17	NA	NA
	60	13.1	29.52	NA	NA
	90	13.0	30.34	NA	NA
1415	SURF	NA	28.87	155	1.40
	30	NA	29.01	150	1.80
	60	NA	29.07	140	1.50
	90	NA	29.54	155	1.00
1535	SURF	NA	29.02	175	1.90
	30	NA	29.04	170	1.60
	60	NA	29.09	160	1.60
	90	NA	29.22	155	1.20
1600	SURF	NA	28.77	175	2.30
	30	NA	28.88	165	1.80
	60	NA	28.96	155	1.90
	90	NA	29.44	140	1.30
1700	SURF	15.0	28.38	175	2.30
	30	14.3	29.76	175	1.90
	60	14.3	28.96	170	1.20
	90	14.3	29.00	180	1.10
1805	SURF	15.8	26.96	165	1.60
	30	15.2	27.74	185	1.20
	60	14.3	29.04	185	0.11
	90	14.3	29.15	181	0.06
1910	SURF	15.2	27.28	190	0.67
	30	15.2	27.71	195	0.53
	60	14.7	28.63	280	0.57
	90	14.4	28.96	230	0.43
2000	SURF	15.3	27.36	205	0.35
	30	14.8	28.17	270	0.60
	60	14.5	28.87	295	1.10
	90	14.1	29.37	285	0.64
2100	SURF	14.8	27.88	325	1.80
	30	14.4	29.01	315	1.70
	60	14.1	29.07	325	1.80
	90	13.8	29.65	325	1.60

VALIANT ROCK

27 June, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
2200	SURF	14.2	29.18	340	1.60
	30	14.2	29.21	340	1.70
	60	14.2	29.23	330	1.90
	90	13.5	29.89	330	1.90
2300	SURF	14.2	29.15	345	1.60
	30	14.2	29.19	340	1.70
	60	13.6	29.26	345	1.50
	90	13.4	29.88	325	0.65
2400	SURF	14.1	29.25	335	1.10
	30	14.1	29.23	335	1.10
	60	13.5	29.46	345	0.90
	90	13.3	30.04	270	0.66

28 June, 1972

0100	SURF	14.2	29.12	045	0.59
	30	14.2	29.15	075	0.58
	60	13.7	29.30	135	0.22
	90	13.2	30.26	190	0.56
0200	SURF	14.5	28.86	135	1.70
	30	14.5	28.97	135	1.80
	60	14.3	29.07	130	1.70
	90	13.5	28.90	140	1.10

RACE

24 July, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
1000	SURF	17.8	30.42	310	1.10
	40	16.2	30.68	320	1.10
	80	15.5	31.15	320	0.80
	120	15.1	31.26	315	0.90
1100	SURF	17.8	30.50	080	0.38
	40	17.2	30.52	310	0.12
	80	17.3	30.66	290	0.20
	120	15.5	30.81	180	0.01
1200	SURF	17.8	29.80	125	0.90
	40	16.2	30.84	115	0.90
	80	14.4	31.49	130	1.40
	120	14.2	31.50	140	1.20
1300	SURF	16.6	30.19	110	1.40
	40	15.7	30.88	130	1.50
	80	15.2	31.13	110	0.60
	120	14.9	31.14	110	0.50
1400	SURF	17.5	29.46	125	1.50
	40	15.2	30.54	110	1.00
	80	14.5	31.30	085	0.15
	120	14.4	31.35	340	0.22
1500	SURF	18.0	29.10	130	1.00
	40	15.6	30.45	350	0.36
	80	15.1	30.92	250	0.46
	120	14.7	31.26	230	0.45
1600	SURF	18.2	29.68	145	0.27
	40	15.0	30.51	310	0.35
	80	15.1	30.93	300	0.90
	120	14.9	31.19	300	0.60
1700	SURF	18.5	29.91	310	0.30
	40	16.7	30.46	320	0.74
	80	15.1	30.57	310	1.40
	120	14.6	31.27	290	1.30
1800	SURF	18.5	29.77	310	0.34
	40	17.2	29.97	330	0.85
	80	16.1	30.46	325	1.80
	120	15.2	31.15	330	2.00

RACE

24 July, 1972

<u>TIME</u>	<u>DEPTH</u> <u>(ft)</u>	<u>TEMP.</u> <u>(°C)</u>	<u>SALINITY</u> <u>(ppt)</u>	<u>CURRENT</u>	
				<u>DIRECTION</u> <u>(Degrees Mag)</u>	<u>SPEED</u> <u>(Kts)</u>
1900	SURF	17.1	30.69	280	2.30
	40	15.8	30.90	305	2.20
	80	15.8	31.15	330	2.10
	120	15.0	31.42	315	2.10
2000	SURF	17.7	30.18	300	2.30
	40	17.5	30.70	300	2.20
	80	15.7	31.30	310	2.00
	120	15.2	31.39	325	1.90
2100	SURF	17.8	30.43	325	2.10
	40	17.3	30.99	325	2.20
	80	14.8	31.48	335	1.50
	120	14.5	30.46	330	0.50
2200	SURF	17.7	30.42	320	1.10
	40	16.1	31.10	320	1.40
	80	15.7	31.26	335	1.20
	120	14.9	31.53	290	0.75
2300	SURF	17.8	30.11	135	0.75
	40	17.7	30.64	240	0.32
	80	17.1	30.72	210	0.27
	120	16.1	31.15	130	0.65

RACE

19 October, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
0815	SURF	14.0	31.53	315	1.10
	64	14.0	31.58	305	0.60
	128	14.0	31.63	305	0.48
	192	14.0	31.65	315	0.24
0900	SURF	13.3	31.25	200	0.72
	64	13.3	31.54	305	0.19
	128	13.3	31.56	325	0.26
	192	13.3	31.61	290	0.40
1000	SURF	14.0	30.72	145	1.40
	64	14.0	31.55	100	0.70
	128	14.0	31.55	105	0.60
	192	14.1	31.61	100	0.90
1100	SURF	13.6	31.03	125	0.80
	64	14.0	31.05	105	0.90
	128	13.9	31.37	100	1.30
	192	13.9	31.69	085	1.30
1200	SURF	13.1	31.04	120	1.30
	64	13.2	31.07	145	1.00
	128	13.3	31.38	170	0.90
	192	13.4	31.52	210	1.00
1300	SURF	14.5	31.14	150	0.70
	64	14.6	31.15	170	0.25
	128	14.7	31.23	090	0.26
	192	14.7	31.34	180	0.20
1400	SURF	14.0	31.19	250	0.90
	64	14.1	31.21	160	1.00
	128	14.1	31.22	240	1.00
	192	14.1	31.29	240	0.80
1500	SURF	13.8	31.15	310	1.00
	64	13.8	31.20	280	0.80
	128	13.8	31.22	280	1.00
	192	13.8	31.25	290	1.10
1600	SURF	14.7	30.95	335	1.60
	64	14.8	31.01	335	2.10
	128	14.9	31.21	320	2.20
	192	14.9	31.25	325	2.10

RACE

19 October, 1972

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
1700	SURF	14.3	31.06	340	1.50
	64	14.3	31.10	330	1.70
	128	14.2	31.21	330	1.70
	192	14.2	31.31	320	2.10
1800	SURF	14.1	31.22	330	2.20
	64	14.3	31.23	315	2.10
	128	14.2	31.51	315	2.20
	192	14.2	31.53	315	2.40
1900	SURF	13.7	31.65	320	2.00
	64	13.8	31.64	315	2.10
	128	13.8	31.65	315	2.10
	192	13.9	31.68	320	1.70
2000	SURF	14.1	31.66	325	1.80
	64	14.3	31.65	320	1.60
	128	14.3	31.68	320	1.60
	192	14.3	31.68	320	1.40
2100	SURF	13.7	31.61	310	0.70
	64	13.8	31.66	285	0.53
	128	13.9	31.73	325	0.58
	192	13.9	31.73	340	0.36

RACE

17 January, 1973

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
1100	SURF	5.3	30.98	080	0.84
	33	5.4		080	0.63
	67	5.8	31.26	085	0.59
	95	5.7	31.25	100	0.45
1200	SURF	5.1	30.48	080	1.21
	33	5.1	31.02	075	1.12
	67	5.3	31.05	077	0.98
	95	5.3	31.32	079	0.92
1300	SURF	4.8	30.05	078	1.01
	33	5.1	30.11	078	0.94
	67	5.3	31.26	080	0.78
	95	5.3	31.38	083	0.69
1400	SURF	5.0	30.18	078	1.14
	33	5.3	30.44	078	0.98
	67	5.6	30.65	073	0.84
	95	5.7	31.20	075	0.65
1500	SURF	5.0	30.24	050	0.51
	33	5.0	30.35	057	0.45
	67	5.4	30.52	062	0.25
	95	5.6	30.90	315	0.06
1600	SURF	4.9	30.10	055	0.16
	33	5.0	30.25	028	0.25
	67	5.6	30.40	320	0.10
	95	5.6	31.01	235	0.35
1700	SURF	4.6	30.19	233	0.10
	33	4.8	30.36	240	0.29
	67	5.3	30.78	280	0.53
	95	5.4	31.30	278	0.49
1800	SURF	4.3	30.27	290	0.78
	33	4.6	30.43	290	0.76
	67	5.3	30.93	265	0.88
	95	5.4	31.51	278	1.07
1900	SURF	4.8	30.53	255	1.01
	33	5.2	30.95	282	1.27
	67	5.4	31.31	327	1.04
	95	5.4	31.46	310	1.19

RACE

17 January, 1973

TIME	DEPTH (ft)	TEMP. (°C)	SALINITY (ppt)	CURRENT	
				DIRECTION (Degrees Mag)	SPEED (Kts)
2000	SURF	5.3	31.08	290	1.27
	33	5.4	31.39	280	1.35
	67	5.5	31.45	302	1.12
	95	5.6	31.44	290	1.04
2100	SURF	5.4	31.18	310	0.94
	33	5.8	31.39	305	0.88
	67	5.9	31.54	288	0.80
	95	5.9	31.54	278	0.67
2200	SURF	5.2	31.24	320	0.55
	33	5.6	31.24	309	0.47
	67	5.8	31.41	285	0.37
	95	5.8	31.63	225	0.27

CHAPTER IV

PHYSICAL FEATURES OF THE CONNECTICUT RIVER ESTUARY
and
DISCHARGE PLUME IN LONG ISLAND SOUND

by

Richard W. Garvine

INTRODUCTION

Salinity and temperature are physical properties of primary importance to estuarine ecosystems. Their mean levels and the nature of their variations in time and space largely set the character of a particular estuary. Since their distribution is determined by the mixing dynamics of the estuary, knowledge of their variation is often indicative of the distribution of such other important quantities as dissolved oxygen, nutrients, and heavy metals. An understanding of the manner in which the salinity and temperature distribution is controlled would enable one to make valid predictions of the consequences to an estuary of such human enterprises as the upstream diversion of river flow or the conversion near the mouth of tidal energy into electric power.

This chapter deals with the estuary of the Connecticut River, New England's largest river. Its mean discharge of fresh water, $560 \text{ m}^3/\text{sec}$, is comparable to major rivers of the Atlantic coastal plain of the United States, such as the Hudson and the Delaware. In contrast to the valleys of these rivers, however, the lower valley of the Connecticut is tightly constricted by hills of crystalline bedrock. Consequently, it serves as only a long narrow conduit to tidal currents induced by the rise and fall of adjacent waters in Long Island Sound. Thus, despite its North American Indian name, which translates to "long tidal river", in reference to the penetration of tidal currents nearly 100 km upstream, the Connecticut supports relatively little tidal volume flux because of its smaller cross-sectional area. Its ratio of tidal inflow volume to fresh water flow volume during the flood portion of a tidal cycle is about 0.5 for mean conditions, compared to ratios of 10 and 140 for the Hudson and Delaware Rivers (Ketchum, 1951). Largely because of its relatively low tidal volume flux, the Connecticut River estuary, during mean conditions, falls into the Type 4 (salt-wedge) class of Hansen and Rattray (1966). As such, it is unique among major rivers of the United States east coast and is comparable in general character to that stem of the Mississippi River within its delta which exits at South Pass (Wright and Coleman, 1971).

Despite its unusual character, the Connecticut River estuary did not receive attention in the published literature until recently. Meade (1966) examined unpublished data obtained in the

1930's and showed the relation of the salinity structure within the estuary to stream flow and wind. Measurements were available, beginning 5.3 km above the mouth and further upstream (see Fig. 1). During times of discharge above the mean, Meade showed that this portion of the river was nearly free of salt at all depths, even during flood tide. For discharge levels well below the mean, salt water from Long Island Sound penetrated upstream in appreciable amounts nearly 20 km above the mouth. Even then the isohaline slope was relatively small, of the order 10^{-3} , and vertical stratification remained pronounced.

Garvine (1974) studied the discharge plume of the Connecticut in Long Island Sound for discharge levels above the mean. During such times the mixing region between fresh and salt water was found to be almost entirely beyond the mouth. The plume contained appreciably diluted sea water with a typical surface area of 50 km² and depth of 1-2 m. As the body of the plume was swept down the Sound with the strong tidal currents, its offshore boundary formed a front where fluid properties changed abruptly. The structure and motion at this frontal boundary was studied in detail by Garvine and Monk (1974).

EXPERIMENTAL PROCEDURES

Surface observations were made from the R/V Sea Hoss, a 40 foot cruiser. Position was determined by radar and was accurate to within 0.2 nautical miles (400 m). A shipboard system was constructed to pump sea water through a rigid pipe from a depth of 0.5 m while underway. Water from the pump was passed to a catch basin containing sensing elements for a Hydrolab TC-2 conductivity meter and Martek Instruments TMS thermistor probe. The conductivity probe itself was compensated for temperature change so that its output was proportional to salinity, except for water of very low salinity. Errors of measurement were $\pm 0.50\text{‰}$ for salinity and $\pm 0.10^\circ\text{C}$ for temperature. Due to mixing in the catch basin the response time for the system was about 20 sec, so that only the larger scale features of interest were recorded. Vertical profiles at selected stations were obtained on other cruises, using the Hydrolab Surveyor Probe which contained both a conductivity probe and thermistor probe of the same general accuracy as described above.

The measurements spanned the extremes of tidal phase and stream flow, so that salinity and temperature transitions varied

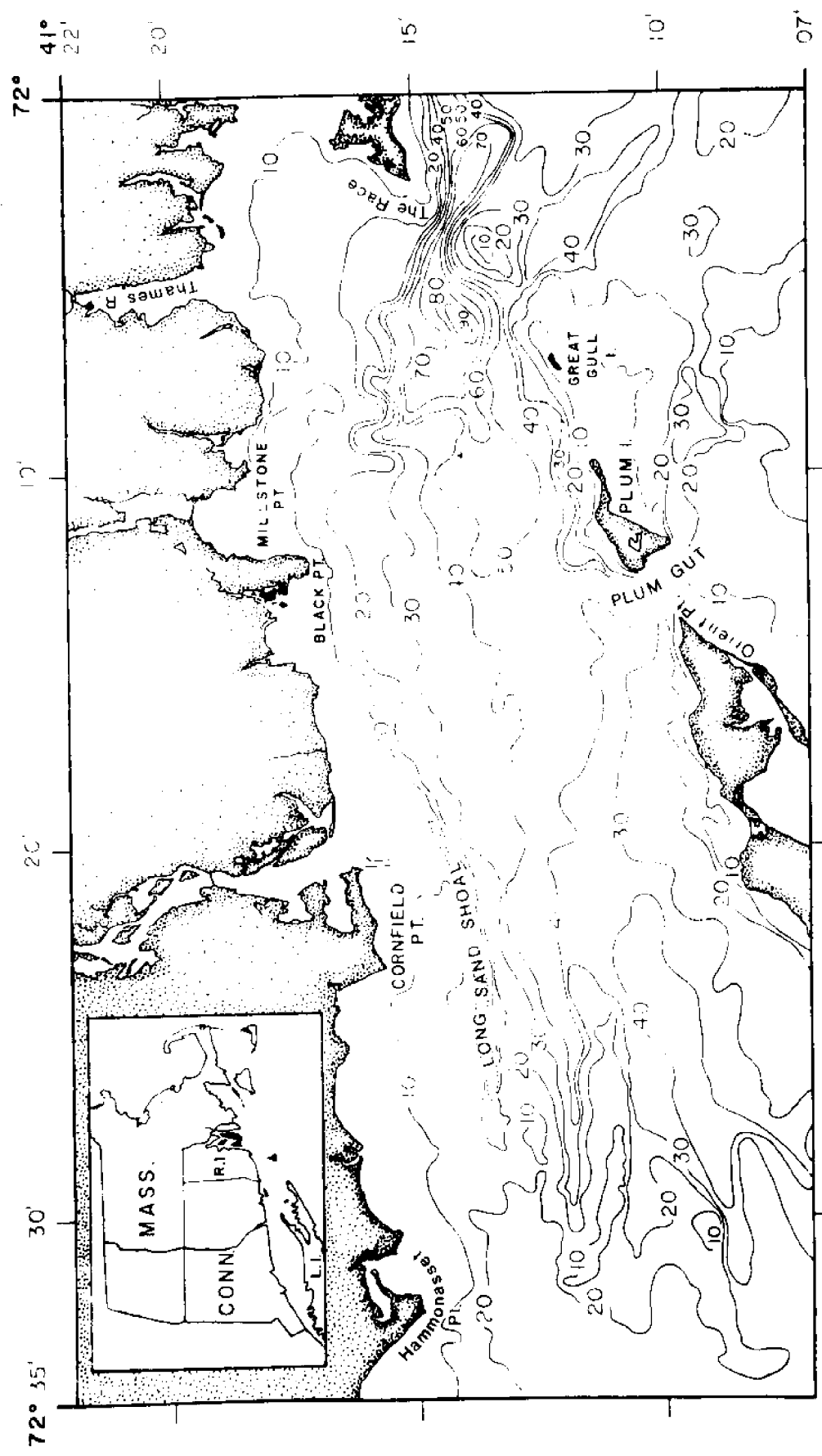


Fig. 1. The study area. Depth contours in meters.

in location from wholly within the river to wholly within the Sound. These two classes of distributions will be termed the riverine mode and plume mode, respectively.

THE DISTRIBUTION AND YEARLY CYCLE OF TEMPERATURE

In the estuarine zone distribution of properties is mainly controlled by the mixing of two distinct water masses: fresh water from upriver above the reach of salt intrusion and adjacent coastal sea water. We may regard each water mass as a reservoir within which properties vary slowly in time and space compared to the variations in the estuarine zone. In this case we may regard eastern Long Island Sound as a reservoir of water of salinity commonly about 28‰ and a temperature dependent mainly upon the time of year. We may view upstream river water as a reservoir of zero salinity and of a temperature determined also by the time of year due to varying temperature in the uplands. In the mixing region we find only levels of temperature and salinity that are between the extremes of these two variables.

The yearly cycle of temperature at 0.5 m depth is shown in Fig. 2 for both river and sound water. Temperatures were measured on seventeen different days in the course of the regular runs described above. In addition, results of similar measurements made available by Dr. W. F. Bohlen (Chapter V) on twenty-two different days are also shown. The combined data points span a time of 20 months, beginning in January 1972. Hand-fitted curves have been drawn through each set of temperatures. The yearly mean temperature for both water masses was about 12°C. River water reached a low value of about 1°C in February 1972, climbed to a high of about 25°C in August, and then fell again to a similar low in February 1973. By contrast, Long Island Sound water, because of its greater volume and depth, cooled to a winter low of only about 3°C in February, and then warmed in spring more slowly than the river. The two temperatures were about equal in early April, after which sound water was the cooler, reaching a summer peak of about 22°C in August 1972. During autumn, sound water cooled less rapidly than river water, so that in October the two temperatures were once again equal. Scatter of data points about the fitted curves is, of course, evident and reflects day to day variations in near surface temperature arising from changes in atmospheric temperature and solar isolation. The temperature difference shown in the upper part of Fig. 2 has the rough appearance of a sinusoid with a period of

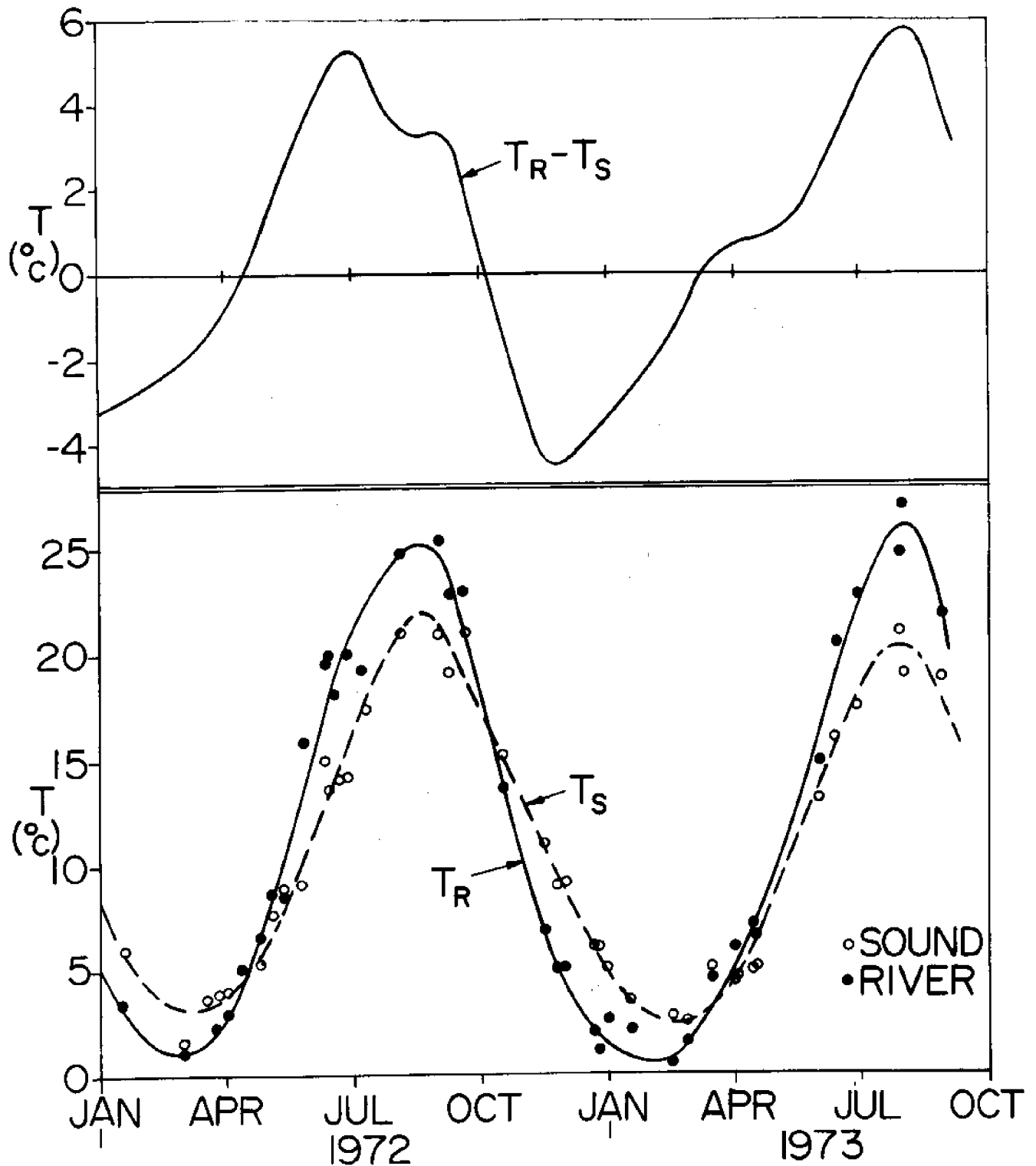


Fig. 2. Temperature measurements near the surface in Connecticut River water and Long Island Sound water. The hand-fitted curves labeled T_R and T_S denote river water and sound water temperatures, respectively. Their difference is plotted as the curve above.

one year and amplitude of about 5°C.

Since the estuarine mixing process involves turbulent flow, one would expect that the temperature transition between the two reservoir values should be well correlated with the salinity variations. To investigate the degree of correlation, pairs of values of salinity and temperature were selected at uniformly spaced intervals from the strip chart recordings for three separate runs made on November 22, November 28, and December 27, 1972 (see Table 1). On November 22 the transition zone was entirely within the river, while on November 28 and December 27 it was entirely within the Sound. Thus, the extremes of salinity distributions, from riverine to plume configurations, were tested. For each data set a least squares linear fit between temperature and salinity was determined. The correlation coefficients for the three cases were 0.97, 0.98, and 0.99, clearly showing that salinity and temperature variations in the estuarine zone are not independent. The linear relation between salinity and temperature together with the existence of well-defined reservoir values for each enables one to predict the temperature from the following linear equation:

$$T = T_R + (T_S - T_R)(S/S_m).$$

Here T is the temperature in the estuarine zone, T_S is the temperature of sound water, T_R the temperature of upstream river water, S the salinity in the estuarine zone, and S_m the maximum salinity, or salinity of the salt water reservoir. The root-mean-square error of this prediction was found to be a maximum of 7.6% of the magnitude of the temperature difference, $T_R - T_S$.

For purposes of prediction, values of T_S and T_R could be obtained from the fitted curves of Fig. 2. Then, if the distribution of salinity fraction S/S_m could be predicted, the temperature in the estuarine zone could be also.

THE DISTRIBUTION OF SALINITY

It is reasonable to postulate that the distribution of fresh and salt water, and hence the temperature and salinity, within the estuarine zone depends principally upon two parameters: tidal motion and river discharge.

Table 1. Tidal and river discharge data for twenty-one times of observation.

DATE	TIDAL PHASE*	MODE**	$\bar{Q}(\text{m}^3\text{s}^{-1})$	$V_t(\text{m}^3 \times 10^{-6})$	$V(\text{m}^3 \times 10^{-6})$	P
April 18, 1972	HSW	P1	1825	-9.3	32.1	4.02
April 21, 1972	LSW	P1	2815	10.1	69.8	5.35
April 21, 1972	HSW	P1	2725	-9.6	50.4	5.90
May 1, 1972	HSW	P1	1609	-7.7	26.8	3.86
May 1, 1972	LSW	P1	1613	11.3	49.1	3.00
May 22, 1972	LSW	P1	1390	11.2	41.2	2.41
June 12, 1972	HSW		942	-11.7	10.4	1.69
June 16, 1972	LSW	P1	673	13.1	28.7	1.04
Sept. 6, 1972	HSW	R	106	-14.9	-12.7	0.14
Sept. 6, 1972	mid-ebb	R	98	13.9	16.2	0.15
Oct. 3, 1972	HSW	R	120	-12.0	-9.4	0.19
Oct. 3, 1972	LSW	R	87	11.5	13.5	0.16
Nov. 22, 1972	HSW	R	1006	-19.7	2.7	1.03
Nov. 28, 1972	LSW	P1	1793	7.7	47.7	4.67
Dec. 20, 1972	HSW	R	581	-19.7	-7.2	0.57
Dec. 27, 1972	LSW	P1	540	11.5	18.1	0.52
Feb. 23, 1973	LSW	P1	537	12.0	26.1	1.06
March 30, 1973	LSW	P1	1220	11.0	40.0	2.37
April 13, 1973	LSW	P1	1130	10.1	32.7	2.22
July 29, 1973	HSW	R	298	-15.9	-10.1	0.33
July 29, 1973	LSW	R	236	13.9	19.7	0.38

* HSW denotes high slack water, LSW low slack water.

** P1 refers to a plume configuration, R to a riverine configuration.

The variations which tidal motion and stream flow produce in the salinity distributions are most compactly described in terms of similarity variables and other parameters introduced later. Better insight is afforded, however, by beginning with more descriptive aspects of the distributions. To that end, Figs. 3 and 4 should be examined.

Fig. 3a shows the salinity pattern in its riverine mode for high slack water within the river. The data were collected on July 29, 1973 when the river discharge was at a seasonal low level of about $250 \text{ m}^3/\text{sec}$. This small discharge, together with the further intrusion of offshore water into the mouth at high slack water, led to a salinity transition zone entirely within the river. The salinity was $10/00$ about 10.5 km upstream from the mouth (defined here as coincident with line M in Fig. 3) and increased rather uniformly in the downstream direction at a rate of about $1.3/00 \text{ km}$ until reaching a level of $15/00$. The salinity then rose abruptly to $23/00$ at a convergent surface front 3.5 km above the mouth. The front was similar in appearance to those studied by Garvine and Monk (1974). Thereafter the salinity again increased slowly, reaching an asymptotic value just below $28/00$ near the mouth. By the successive ebb tide (Fig. 3b), a portion of the salinity structure remained within the river which had been advected downstream about 6 km. Another portion moved out of the mouth and easterly with the ebb current in the Sound and there spread horizontally to form a small plume of about 18 km^2 area. The sharp frontal system between isohalines 15 and 23 was destroyed in the process.

In contrast to this riverine mode of salinity distribution, which prevails at discharge levels well below the mean, a plume mode exists for high levels. Fig. 4 shows distributions in the plume mode at low and high slack water for a discharge of $2800 \text{ m}^3/\text{sec}$, well above the mean and an order of magnitude larger than that of Fig. 3. Even for high slack water the transition occurs entirely beyond the mouth. The offshore boundary of the plume at both tidal stages was formed in large portion by a front which is indicated in the figure by the crowding of the isohalines. Change of tidal phase from low to high slack water completely reshaped the plume.

The distributions of Figs. 3 and 4 well illustrate the qualitative effects of tidal motion and fresh water discharge. They also serve as models for the two distinct salinity distributions, the riverine and plume modes. To investigate more quantitatively the nature of the salinity distribution and its variations, and recognizing that it appears in two major modes, two

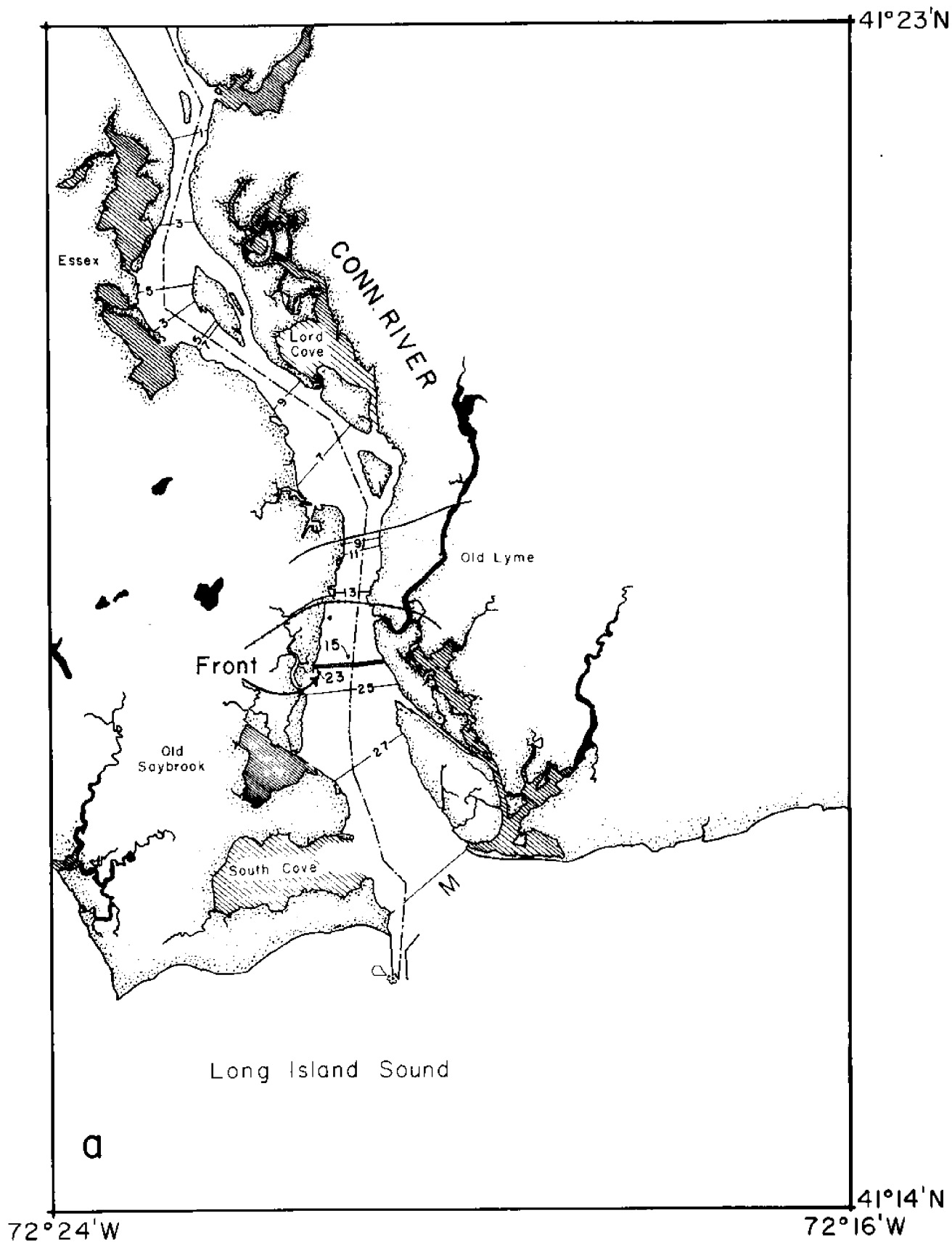


Fig. 3a. Isohalines in parts per mil at 0.5 m depth for July 29, 1973 at high slack water.

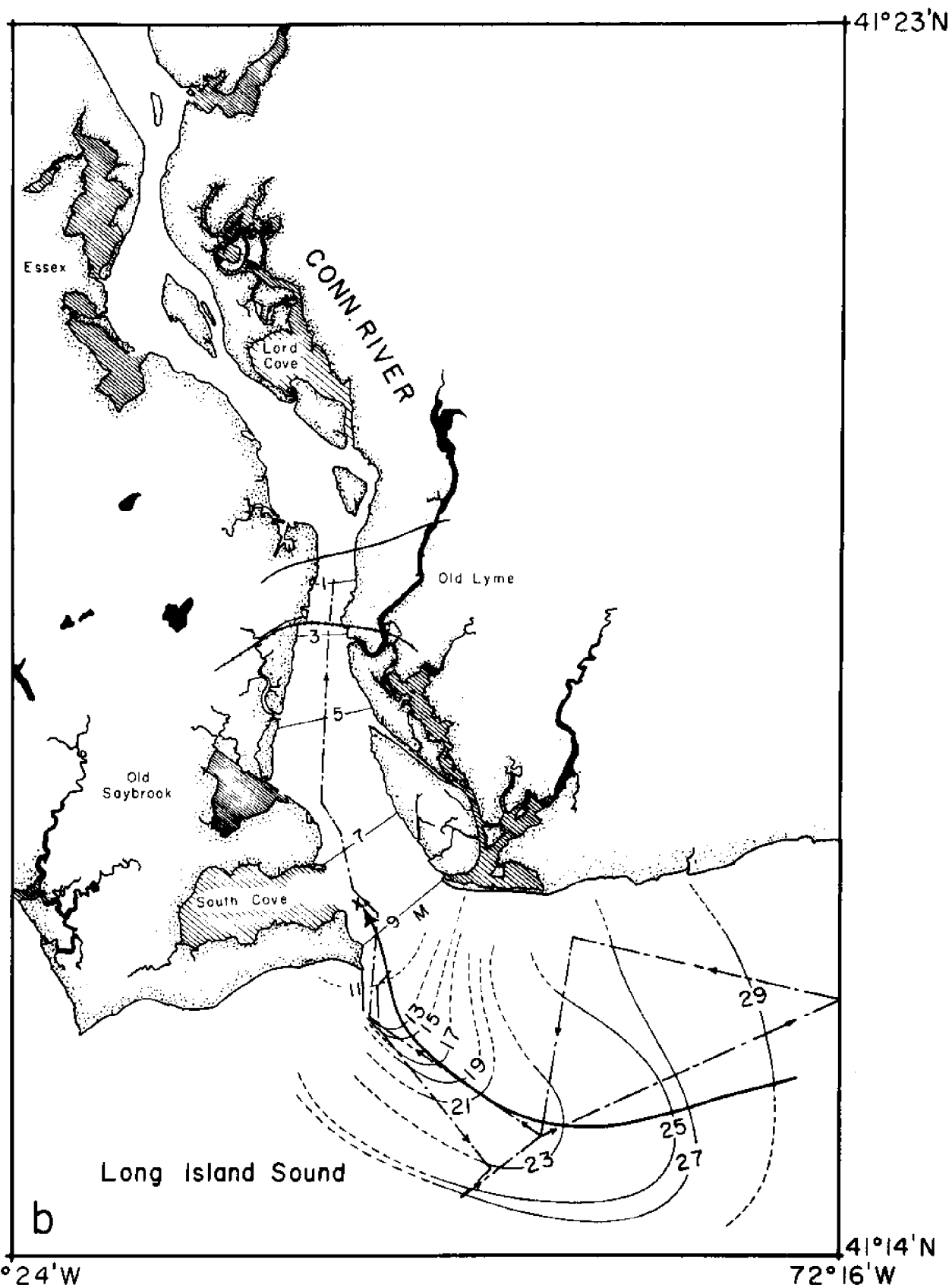


Fig. 3b. Isohalines in parts per mil at 0.5 m depth for July 29, 1973 at low slack water. The line with arrowheads denotes the shiptrack. The plume axis coordinate X is indicated.

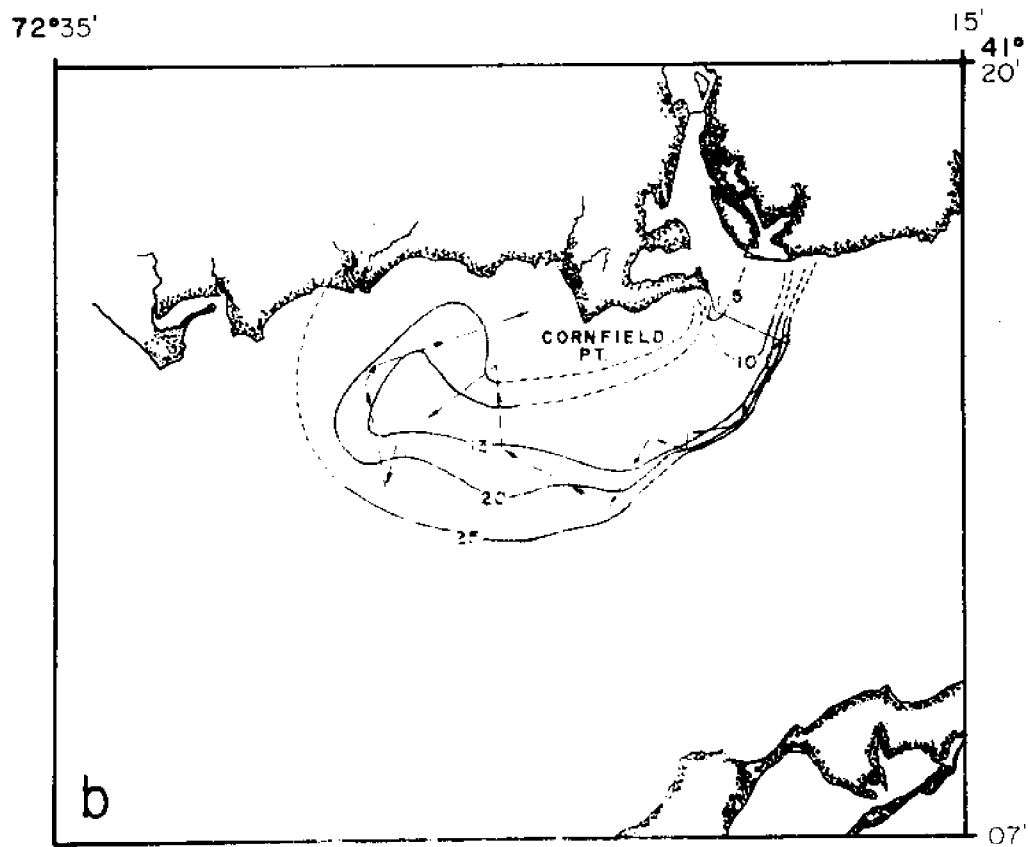
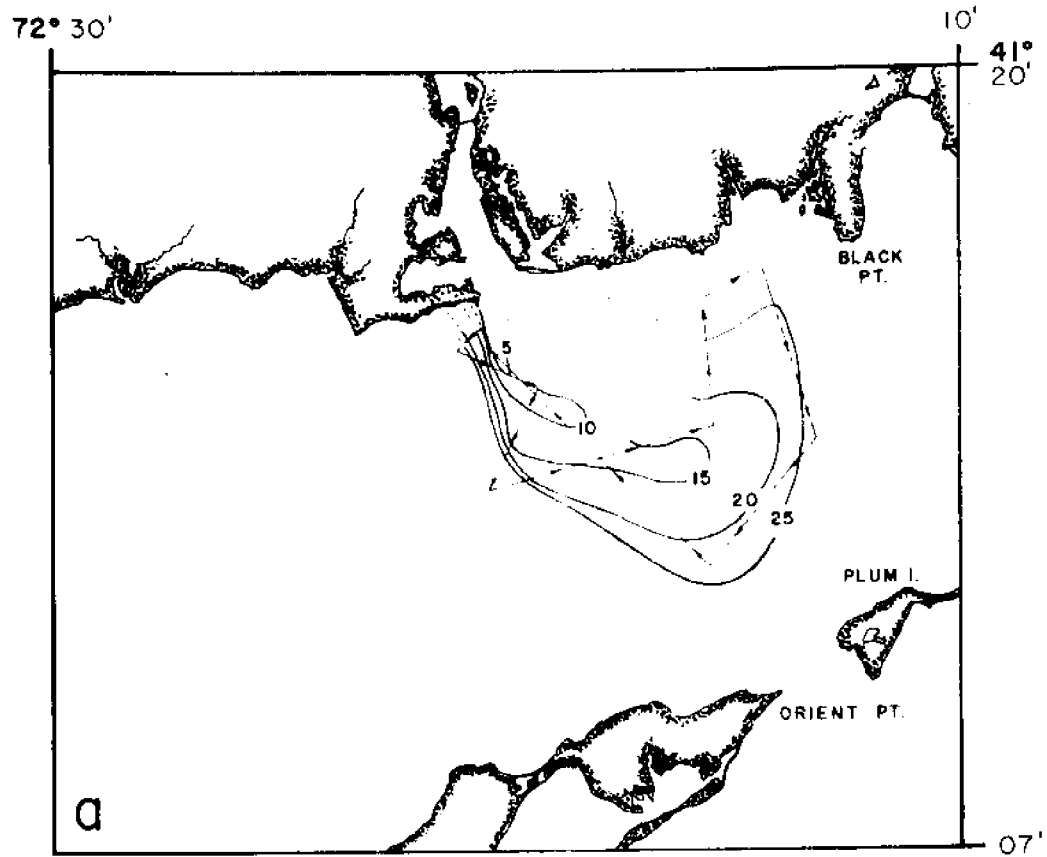


Fig. 4. Isohalines at 0.5 m depth on April 21, 1972 at a) low slack water and b) high slack water. From Garvine (1974), Fig. 12.

parameters are now introduced. The first is the total fresh water discharge volume at the mouth during a preceding tidal half-cycle, either ebb or flood, denoted by V . Changes in fresh water outflow from low to high slack water are accounted for directly in the computation of V (which is discussed fully in Garvine 1974). Here V is useful in quantifying distributions for the plume mode for which one would expect the total amount of fresh water in a given plume at high or low slack water to be the single most important parameter.

The second parameter which will be employed is the flow ratio P , defined by Hansen and Rattray (1966) as the ratio of the mean fresh water velocity downriver to the root-mean-square tidal velocity. This P is an index of the relative efficacy of tidal mixing within the river and is therefore of value principally in evaluating distributions of the riverine mode. In the present study velocity data were not obtained, but P was calculated by relating the two velocities to the mean river discharge for the preceding tidal half-cycle denoted by \bar{Q} , the semi-diurnal tidal half-period $T/2$, and the volume of water V_t , which enters (exits) the mouth during the flood (ebb) half-cycle. Ketchum (1951) estimated $|V_t|$ under mean conditions to be $12 \times 10^6 \text{ m}^3$. Estimates of V_t for other than mean conditions were made from tidal record data at New London following the method discussed in Garvine (1974). From these quantities P may be computed from:

$$P = \frac{2^{1/2}}{\pi} \left(\frac{\bar{Q}T}{|V_t|} \right).$$

For mean conditions in the Connecticut River estuary $\bar{Q} = 560 \text{ m}^3/\text{sec}$, $T = 12.4 \text{ h}$, and $V_t = 12 \times 10^6 \text{ m}^3$, so that $P = 0.93$. Considerably larger values of P correspond to diminished tidal mixing within the river and hence are typical of the plume mode. Considerably smaller values correspond to the riverine mode. Note that P does not account for variations in tidal phase, so that salinity distributions must be compared for the same tidal phase to judge the effectiveness of P .

Table 1 summarizes the twenty-one surveys of temperature and salinity made over the course of sixteen months beginning in April 1972. All surveys but one were completed at or near the time of slack tidal current and the tidal phase is indicated. The distributions are classified where appropriate into plume or riverine modes. Twelve cases were clearly of plume character,

as indicated in the table, while eight were riverine. One case, June 12, 1972, was of a hybrid sort. Its distribution was shown in Garvine 1974, Fig. 15. Brief study of the table will show that the plume mode appears at low slack water for the larger values of \bar{Q} . The estimated tidal volume flow at the mouth, V_t , is also listed. Negative values indicate that the volume of salt water offshore which flowed upstream during the flood half-cycle exceeded the volume of fresh water which flowed downstream during the same time.

In appraising horizontal salinity distributions for the riverine mode it is sufficient to examine only the variation in the direction of the stream, as cross-stream variations are generally quite limited at a given depth (see Meade [1966], Figs. 4, 5, and 8). However, for the plume mode, important variations occur horizontally in two directions. To compare different plumes and to relate plume distributions with those of the riverine mode, a plume axis is defined. It is the horizontal line normal to isohalines and marking the slowest descent in salinity approaching the mouth. We may define a curvilinear coordinate x measured along such a line, which increases positively toward the mouth. This coordinate may be continued upstream within the river; it then simply gives the upstream distance from the mouth (see Fig. 3b). For convenience x is set a zero at the mouth (line M). Using isohaline contours prepared from the measurements, then distributions of salinity with x could be determined. In plotting results the salinity fraction S/S_m , where S_m is the maximum salinity offshore, was used to normalize the data.

Let us now examine distribution features for the plume mode. A paramount feature is the horizontal area of a given plume at slack water. One would expect it to be controlled primarily by V . As a measure of the plume area we take the horizontal area bounded by the 15‰ or the 20‰ isohalines, the shoreline and line M. These areas are plotted in Fig. 5 against V . Points are plotted for all cases where any plume structure appeared, including that shown in Fig. 3b. A straight line least-squares fit was determined for both areas. For the 15‰ line the correlation coefficient was 0.77, while for 20‰ it was 0.72. Clearly, discharge volume does affect the plume area critically, but considerable variation remains. At any point on the 20‰ line the ratio of abscissa to ordinate has the dimension of length and should be a measure of the plume depth. Here it is about 1 m, characteristic of the plume depths reported in Garvine (1974).

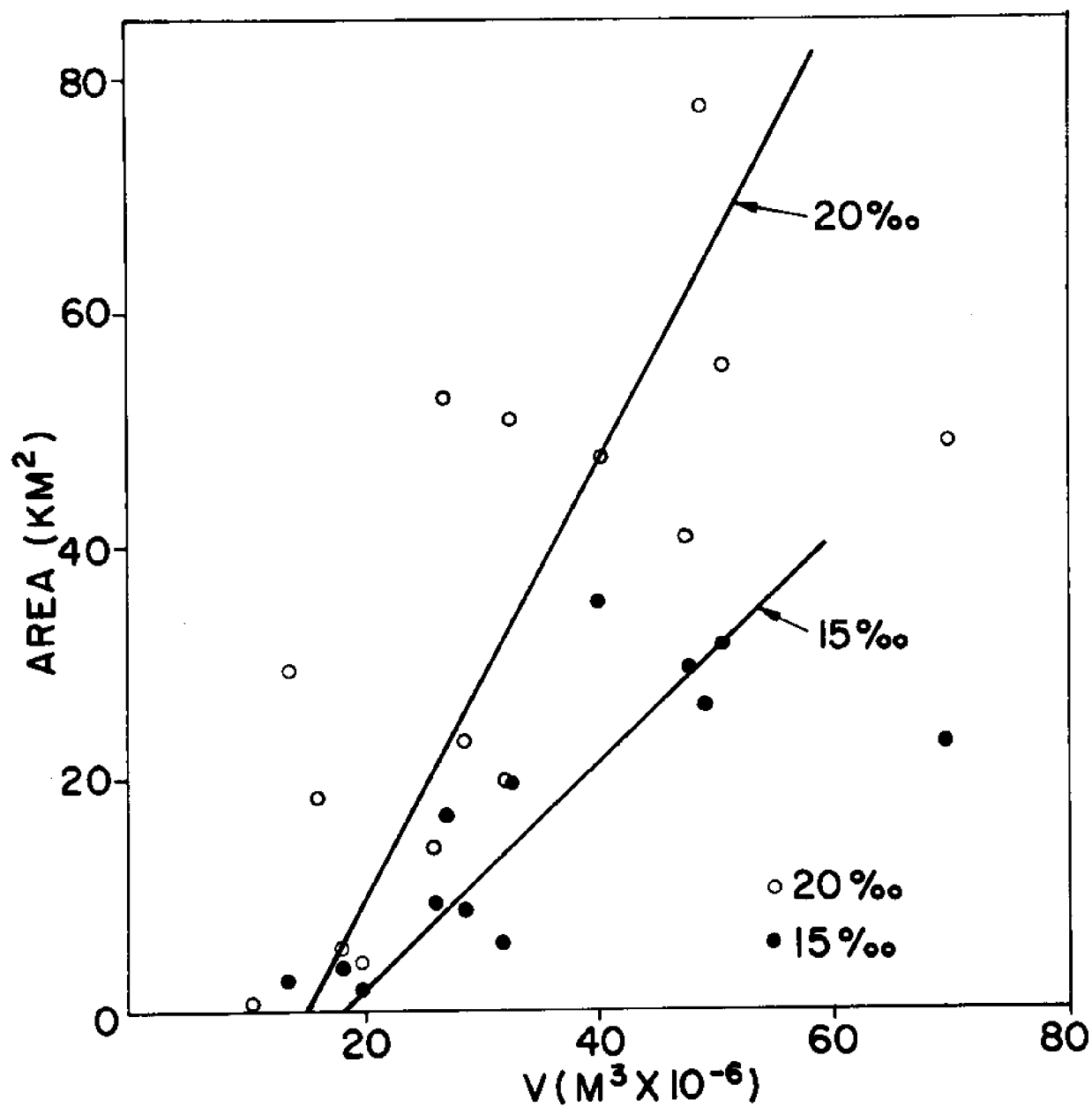


Fig. 5. Horizontal area of the plume bounded by the 15‰ and 20‰ isohalines at 0.5 m depth vs. volume of discharged fresh water for the preceding tidal half-cycle. Straight lines are least squares fits.

Besides the plume area behavior, the plume axial distribution of salinity is characteristic of the distribution as a whole. How is it affected by V ? Do the data suggest any similarity of forms for different levels of V ? To investigate these questions, let us postulate that the plume areas characterized by A_{20} , the area bounded by the 20‰ isohaline are related to V by,

$$V = \bar{D} A_{20},$$

where \bar{D} is a fixed characteristic plume depth. We further postulate that the axial coordinate, $-x_s$, for a given level of S/S_m (its distance from the mouth) varies from one plume at slack water to another as $(A_{20})^{1/2}$. Thus, we expect that $x_s = -\xi_s (V/\bar{D})^{1/2}$, where ξ_s is dimensionless and should be constant for a given salinity fraction.

These postulates may be tested by plotting S/S_m against $-x (\bar{D}/V)^{1/2} \equiv \xi_p$, a plume axis similarity coordinate. Such plots appear in Fig. 6, where a value of $\bar{D} = 1$ m has been assumed from the discussion above. The plots were made for the surveys identified as of the plume mode in Table 1. While use of ξ_p does not collapse the measured distributions to one curve by any means, it does reduce substantially the degree of scatter that would appear in a plot of S/S_m vs x . Furthermore, use of the coordinate ξ_p effectively removes any bias with V of the salinity distribution.

For the riverine mode, examination of the eight surveys so labeled in Table 1 indicated that more than one parameter would be needed in quantifying the salinity distribution, unlike the plume mode where only V was dominant. Both the parameter P measuring stream flow in relation to tidal flow, as well as the tidal phase, were involved. It was postulated that the upstream location x_s of a given value of salinity fraction S/S_m was related to S/S_m as follows:

$$x_s = F(S/S_m) + G(P) + H(t/T), \quad (1)$$

where F is some function of salinity fraction alone, G a function of P alone and H is the tidal variation with time t over tidal period T . If t is measured after the time of the preceding low slack water, then one may postulate that:

$$H = \frac{a}{2} \left[1 - \cos \left(\frac{2\pi t}{T} \right) \right],$$

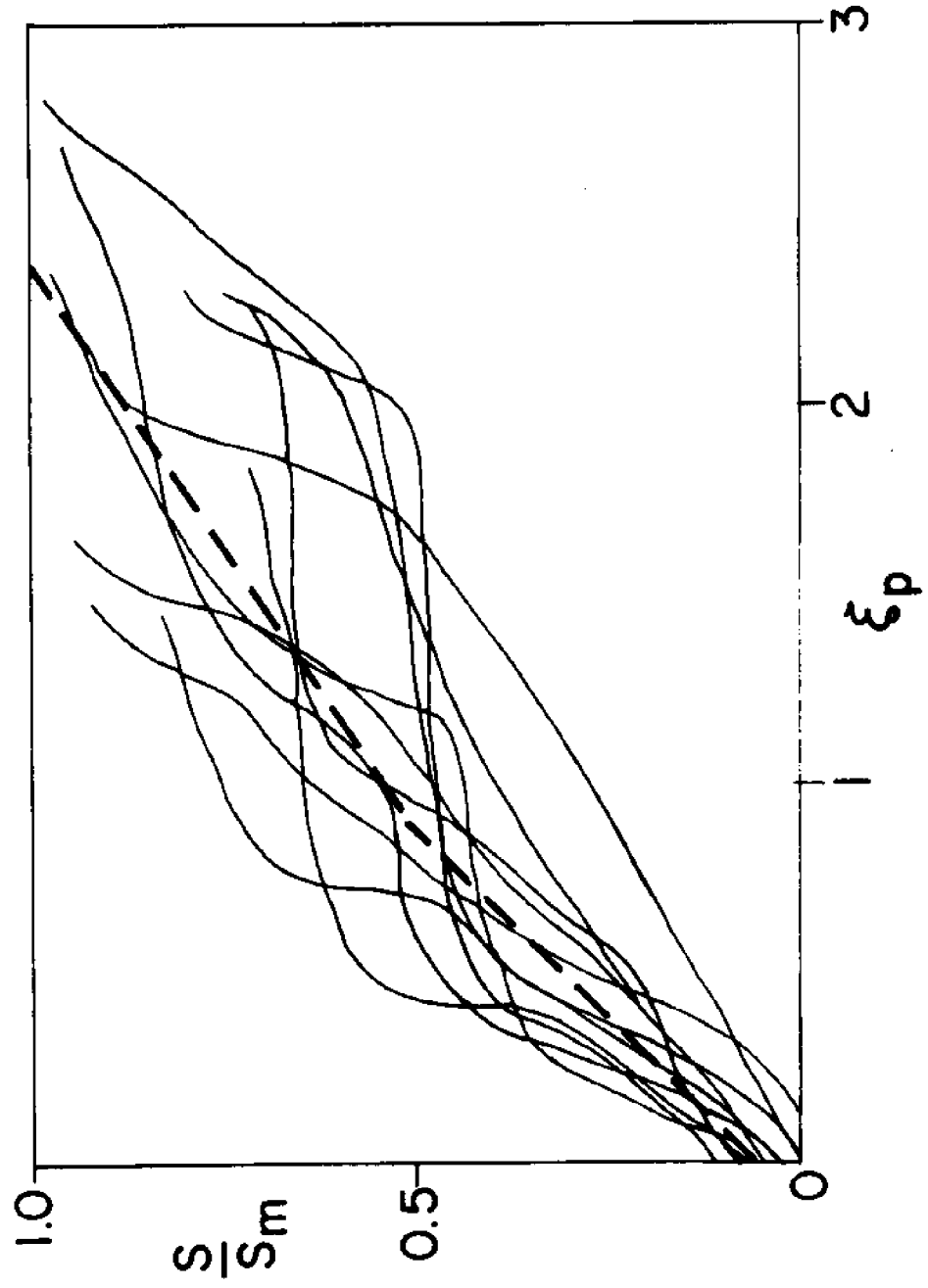


Fig. 6. Salinity fraction S/S_m vs. the similarity coordinate ξ_p for the plume mode. Dashed line segments indicate hand fitted means.

where $a \approx 6$ km from Fig. 3 and $T = 12.4$ h. By examining the eight surveys for fixed S/S_m and correcting for H the function $G(P)$ would be deduced. The data were well fitted by the relation $G(P) = 9.5 - 6P$ (for G in km) for $0.14 < P < 1.03$, the range of values for the riverine cases (see Table T). As one would expect, this indicates that for fixed tidal phase the location of a fixed salinity fraction moves downstream (decreasing x) with increasing P .

If the assumptions and deductions made above are meaningful, then a plot of $x - G - H$, where x is the location of a measured value of S/S_m , should appear for the eight riverine mode cases as nearly a single curve on a plot against S/S_m itself. To test the matter S/S_m was in fact plotted against:

$$\xi_R \equiv (G + H - x)/L,$$

where L is a fixed horizontal scaling length for the riverine mode salinity distribution. The raw data (see, for example, Fig. 3) showed that, for low values, S/S_m decreased nearly linearly with x at a rate such that S/S_m would change by unity in a distance of about 21.5 km. This value for L was chosen for convenience, since then, within the range of linear variation, equation 1 should reduce simply to $S/S_m = \xi_R$.

Fig. 7 shows the plots for the eight surveys. For $S/S_m < 0.4$ the curves bunch rather tightly around the heavy dashed line $S/S_m = \xi_R$ as anticipated. Published surface salinity distributions for three days at high slack water (Meade, 1966, Fig. 3) appear to fit within the scatter for this range also, but are not plotted here because of uncertainty in the appropriate values of V_t and S_m . For larger ξ_R (distance farther downstream or beyond the mouth), S/S_m for all but one curve increased much more rapidly. This sharper transition usually coincides in large part with a convergent frontal boundary, either within the river, such as that of Fig. 3a, or offshore of the mouth for ebb tide distributions. The mean location of this frontal transition is about where $\xi_R = 0.5$.

CONCLUDING REMARKS

Data collected over a period of sixteen months in the estuary of the Connecticut River enable a concise description of the horizontal distribution of temperature and salinity. The temperature distribution was found to be very highly correlated with the

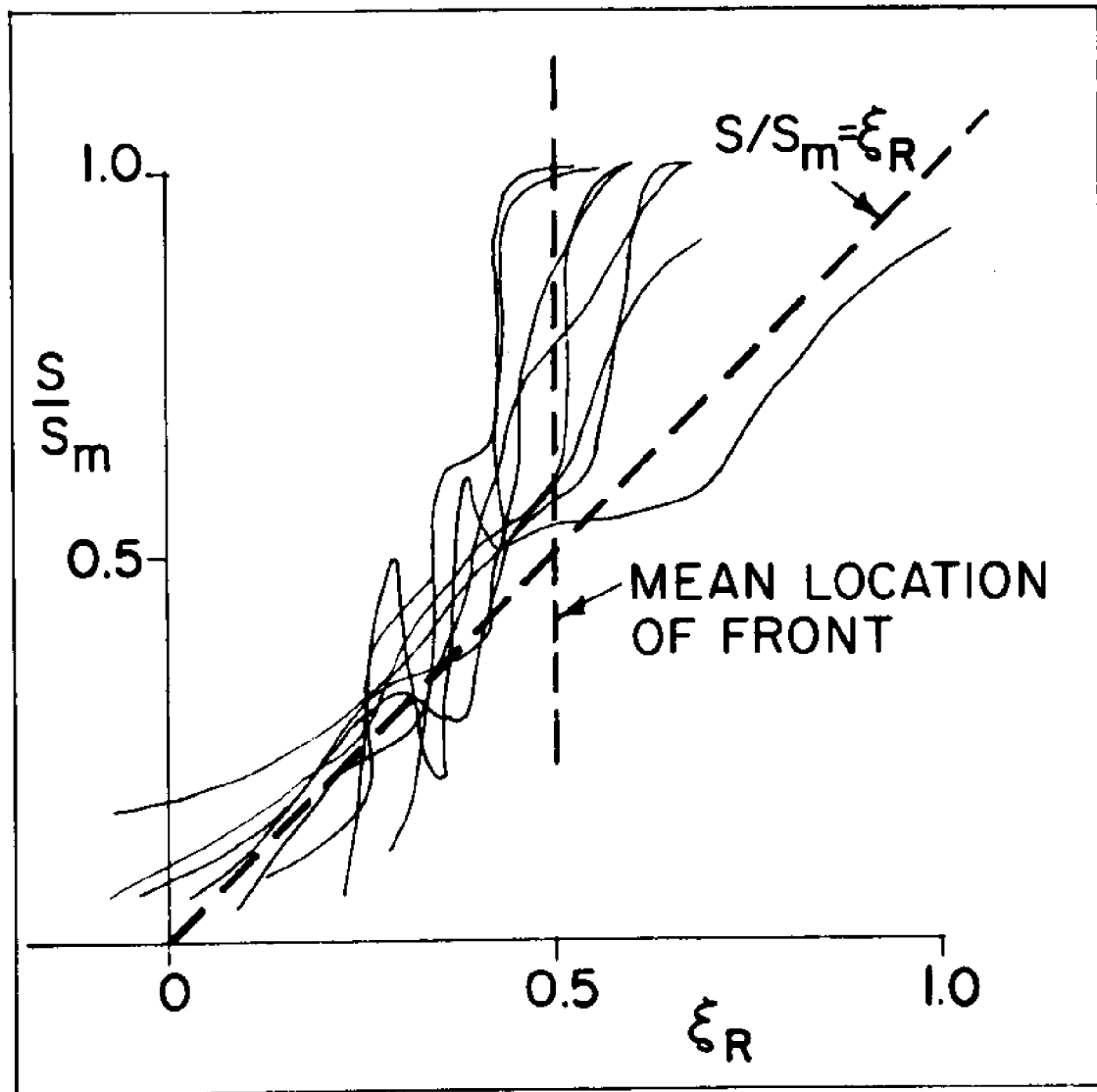


Fig. 7. Salinity fraction S/S_m vs. the similarity coordinate ξ_R for the riverine mode. Dashed line segments indicate hand fitted means.

salinity distribution. A simple linear relation between temperature and salinity permits the prediction of temperature distribution with good accuracy, given the salinity fraction distribution and the temperature of fresh and salt water masses. The yearly cycle of both temperature level and temperature contrast between fresh and salt water is predominantly seasonal.

The yearly cycle of salinity is not primarily seasonal, but varies principally with fresh water discharge. Although the latter does have a characteristic variation, high in spring and low in fall, unlike the temperature, large variations may occur on a time scale of a few days of as much as an order of magnitude. These variations are the result of heavy rain storms and floods.

The horizontal salinity distribution occurs predominantly in two modes, a riverine mode and a plume mode, corresponding to salinity transitions mostly within the river and those mostly within Long Island Sound. No systematic variations with wind stress were detected.

During the plume mode, plume area at slack water is fairly well correlated with V , the volume of fresh water discharged. The salinity distribution along the axis is reasonably well described using a coordinate scaled by $V^{1/2}$. Considerable variation remains, however, in particular plume shapes, as documented in Garvine (1974).

The salinity distribution for the riverine mode is well described using a horizontal coordinate ξ_R , which accounts for variations in tidal phase and in the ratio of stream flow to tidal flow characterized by P . The mean distribution consists of a linear variation with ξ_R for low values of salinity fraction and a rapid variation for larger values, which often arises from the presence of a convergent frontal boundary.

The major controlling parameters that govern the horizontal salinity, and hence temperature distribution, are V , P , and tidal phase. Thus, all depend upon variables which may be readily measured or even forecast, i.e., stream flow, tidal flow, and tidal phase.

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CHAPTER V

AN INVESTIGATION OF SUSPENDED MATERIAL CONCENTRATIONS
IN EASTERN LONG ISLAND SOUND

by

W. F. Bohlen

INTRODUCTION

The concentration of suspended materials in coastal waters is a complex function of river discharge, tidal state, regional geology, bathymetry, biological activity, and transient meteorological events. These factors serve to determine both the available supply of materials and the transport competence of the circulation field characteristic of the area. Quantitative predictions of the resultant distribution of materials requires specification of the relative importance of each of these factors within the selected study area and an ability to quantify the local mass transport system. Efforts to satisfy these requirements are hampered by an imperfect understanding of the mechanics governing sediment transport and turbulence, and a lack of comprehensive in situ observations of these parameters in coastal waters. As a result the extensive body of literature detailing material concentrations in estuaries (Schubel, 1969; Meade, 1968; Anderson, 1970) and on the adjacent continental shelf (Manheim et al, 1970; Buss and Rodolfo, 1972; Eittreim et al, 1969) is largely site specific and finds limited application within other areas.

In the spring of 1972 an intensive field investigation of suspended material transport was initiated in eastern Long Island Sound. This study was designed to complement a concurrent investigation of heavy metal transport (Fitzgerald et al, 1973) by providing quantitative measurements of material concentrations and the characteristic range of spatial and temporal variability. In addition, the primary factors controlling concentration levels were to be detailed in combination with long term observations of the mass transport field. The data bloc was to be sufficiently comprehensive to permit development of a quantitative material budget and to insure applicability of the results of this study to other similar coastal areas.

This chapter presents the results of the first two years of this investigation. Primary emphasis is placed on the characteristics of the field of suspended materials in the eastern Sound and the factors governing material concentrations. Subsequent reports will detail the composition of the suspended load, the character of the mass transport field, and the resultant material budget.

METHODS AND PROCEDURES

The Study Area

The circulation field in eastern Long Island Sound (Fig. 1), is dominated by the semi-diurnal (M_2) tide. Peak velocities exceed 200 cm/sec in the eastern passes, decreasing to approximately 125 cm/sec in the vicinity of the Connecticut River. Discharge from this river, representing more than 70% of the total fresh-water inflow into the Sound (Riley, 1956), produces persistent vertical and horizontal density gradients. This structure results in a two-layer transport system with observed bottom inflows proceeding to the north and west and surface outflow to the south and east (Hollman and Sandberg, 1972; Paskausky *et al*, 1972, and Chapter III of this report). Net drift in the system averages 10-15% of the peak tidal velocities with significant perturbations induced by variations in wind stress.

The average depth of the study area is approximately 30 m (Fig.1). A marked north-south asymmetry can be observed with extensive shoals and shallow water areas along the northern shore contrasting a rapid variation in depth along the southern shore. These depth contours are only weakly correlated with sediment type. Sediments throughout the area are primarily sands (>70%) with occasional lenses of silts and clays (Donahue and Tucker, 1970; Buzas, 1965).

The wind field characteristic of the eastern Sound varies seasonally, with winter months dominated by northwesterly winds while southwesterlies prevail during the summer. Occasional high energy easterly storms can occur throughout the year.

Sampling Routine

Suspended material characteristics have been detailed at eleven stations located on the periphery of the study area (Fig. 2). Station locations were selected to coincide with the major routes of sediment entry and egress. Sampling was conducted monthly with each survey being initiated approximately two hours after the beginning of the ebb tide in the Connecticut River. On the average, four hours were required to complete the field sampling.

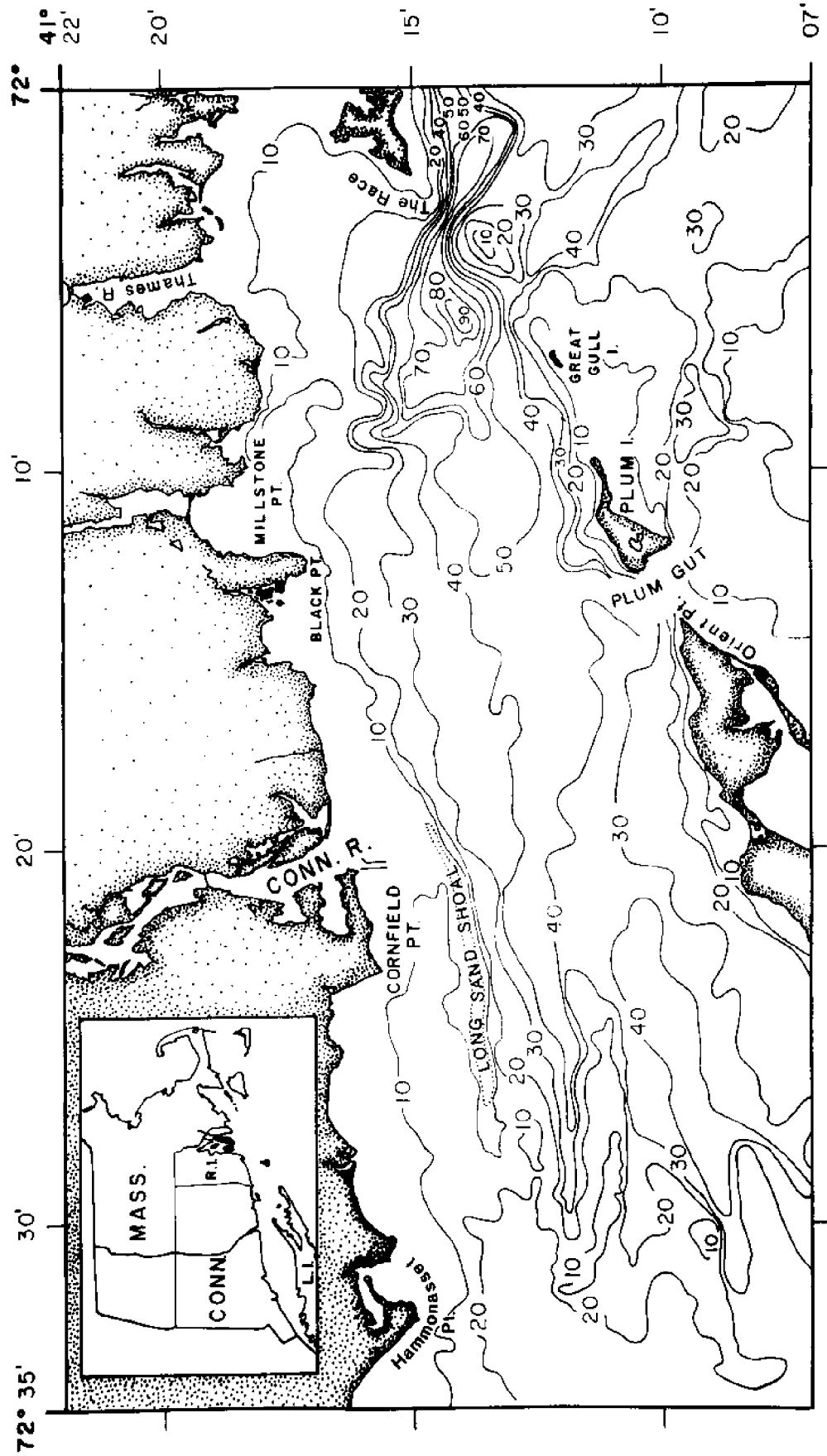


Fig. 1. Eastern Long Island Sound

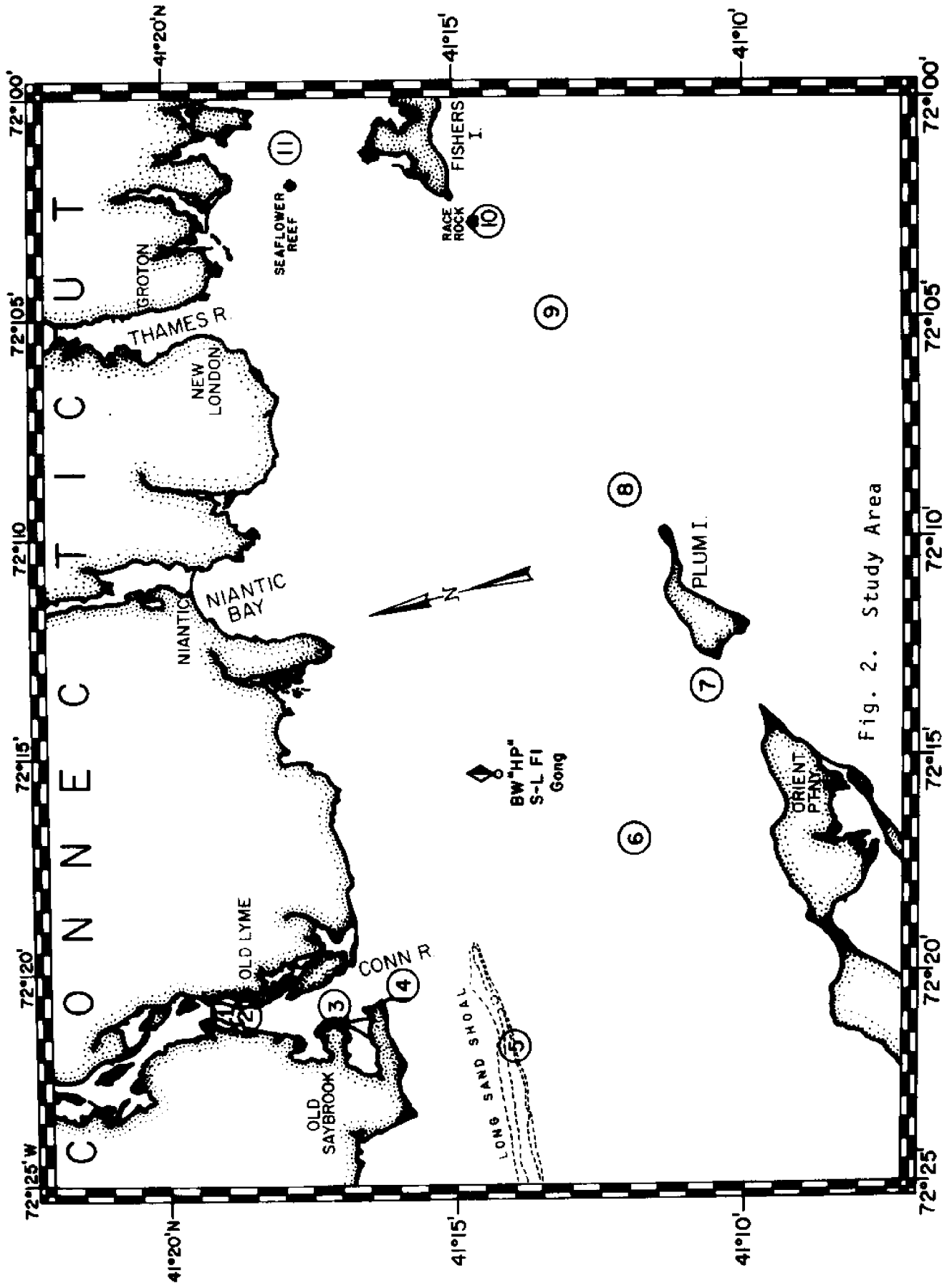


Fig. 2. Study Area

At each station three-liter drawn water samples were obtained at the surface and near bottom using a Van Dorn sampler. Glass bottles were used for sample storage. To complement each hydrocast the vertical profile of temperature and salinity was determined using an in situ temperature-conductivity probe. (Hydro-lab Corporation).

In addition to the routine monthly sampling a series of twelve hour observations were obtained at selected stations to determine the range of variation in suspended material concentrations over a tidal cycle.

Analytical Procedures

Water samples were returned to the laboratory and filtered within twenty-four hours using preweighed and dried silver membrane filters (47 mm, 0.45 μ). A cool room was used to store samples prior to filtration. No effort was made to inhibit bacterial activity. After careful removal of all salts, the filters were again dried and reweighed to determine the by-weight concentration of total suspended solids.

After weighing, selected filters were examined using X-ray diffraction techniques to determine the composition of suspended clay minerals. In addition, carbon-hydrogen-nitrogen analysis was used to determine the percentage of organic material retained on the filter.

Silver membrane filters were selected after an analysis of the resolution and repeatability afforded by the standard Millipore filter technique (Banse et al, 1963). Resultant tests indicated a random weight loss during filtration that was often sufficient to mask the low material concentrations found in the eastern Sound. Weight loss occurred during the initial stages of filtration and appeared to level off after filtration of 0.5 l. Maximum weight loss was approximately 0.5 mg. This indicates that accuracy could be increased using large volume samples. In these waters, however, this procedure increases filtration time sufficiently to permit particulate formation due to bacterial activity (Sheldon et al, 1967). As a result, an additional unknown source of error is introduced.

Although superior to Millipore filters, the silver filters also appear to display an occasional loss in weight following filtration, possibly as a result of precipitation of silver

chloride during sampling of high salinity waters (Gaudette and Anderson, 1970). Analysis of a group of filters to determine weight variations under conditions characteristic of the eastern Sound indicates that an average loss of 0.25 mg can be expected (Smith, 1974). This is believed to represent the major source of error within the sampling routine. The reported data are therefore considered representative of the field concentrations to within ± 0.25 mg/l.

RESULTS AND CONCLUSIONS

Suspended material concentrations in eastern Long Island Sound display a marked spatial and temporal variability. Concentration levels both within the lower Connecticut River (Fig. 3) and in the open Sound (Fig. 4) are characterized by persistent high frequency fluctuations. Although there is indication that periods of maximum concentration occur primarily during the spring and early winter months with minima during the late summer, the large variability tends to obscure the seasonal trends. The clear seasonal patterns observed in other portions of the Sound (Bohlen and Tramontano, 1974a; Riley, 1959) are only weakly evident in this area.

Concentrations decrease rapidly with distance from the Connecticut River. Levels in the lower river typically exceed those in the adjacent Sound by more than a factor of two. More significantly, variations in riverine material concentrations are, with few exceptions, weakly correlated with variations in the open Sound. Realizing that this feature may simply be a sampling artifact resulting from the difference between the response time of the river and that of the open Sound, it is tempting to hypothesize that the imperfect correlation implies that a major fraction of the suspended materials supplied by the river remains within the estuarine reach. A review of the known sedimentation rates (Bloom, 1967) and geomorphological characteristics of the lower Connecticut River supports this hypothesis.

Examination of the relationship between suspended material concentrations and salinity in the open Sound indicates that the simple linear variability observed along the adjacent continental shelf (Manheim *et al.*, 1970) is absent (Fig. 5). At a given salinity, material concentrations can vary by more than two orders of magnitude. Only during periods of extremely high discharge from

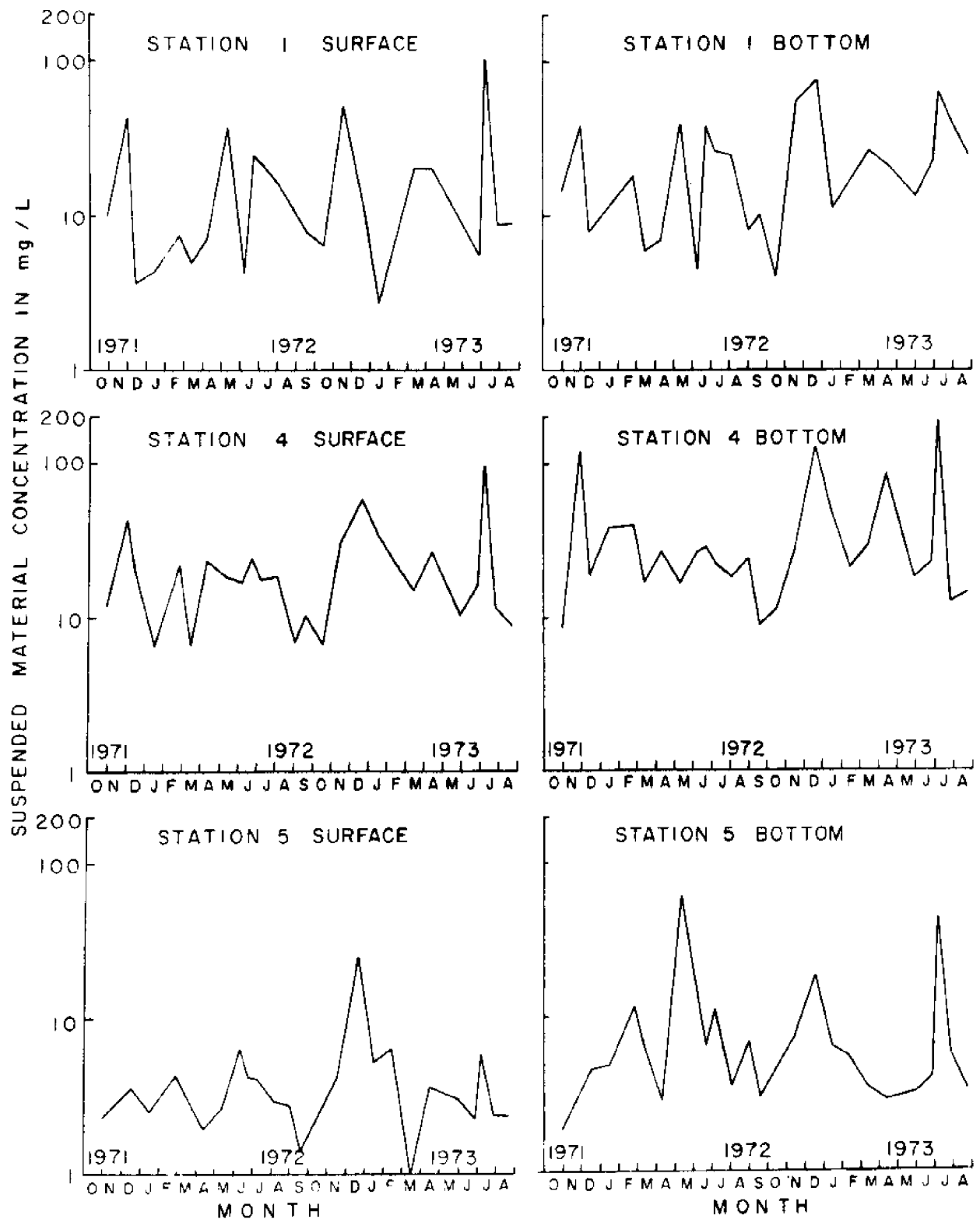


Fig. 3. Suspended Material Concentrations
Stations 1, 4 and 5

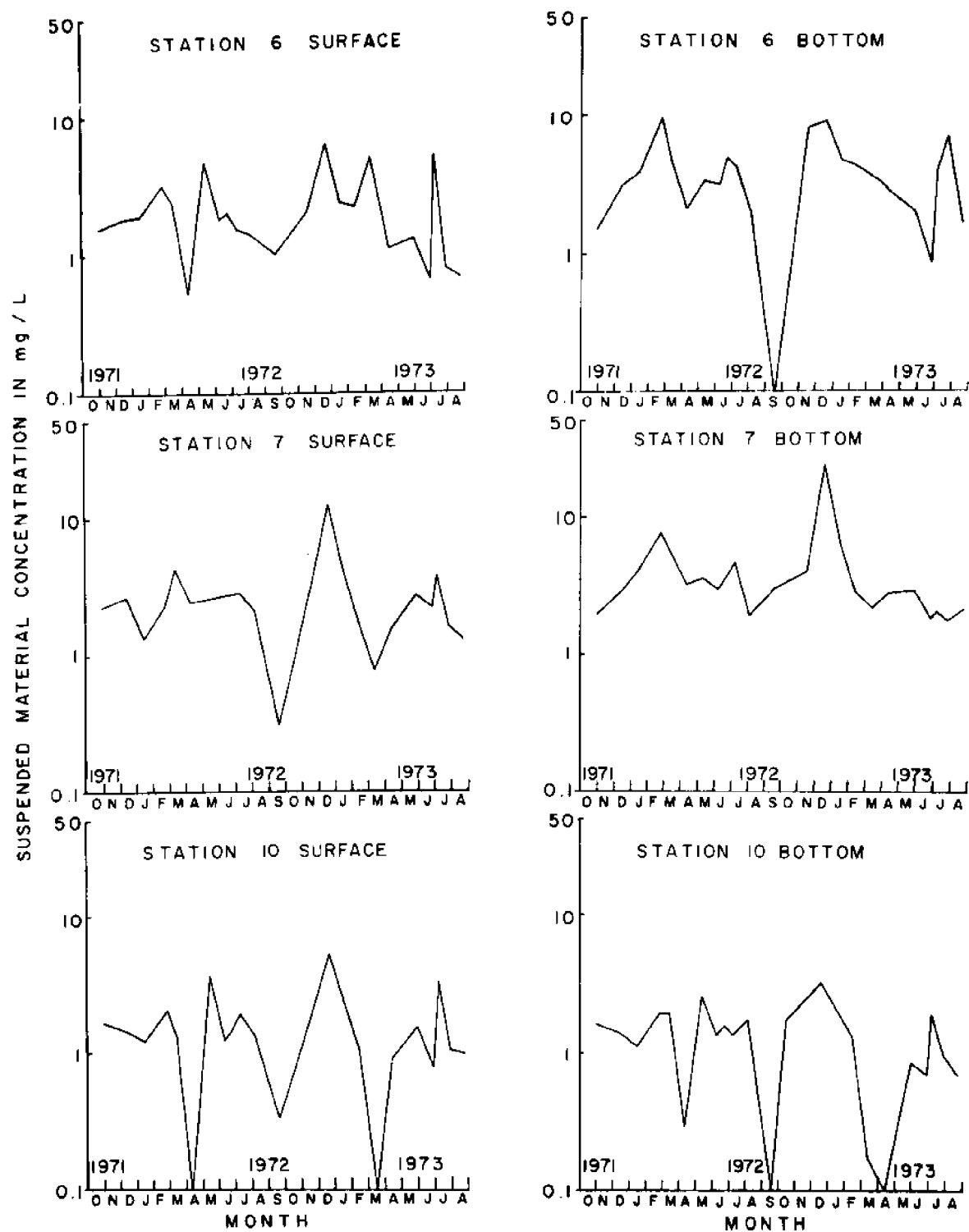


Fig. 4. Suspended Material Concentrations
Stations 6, 7 and 10

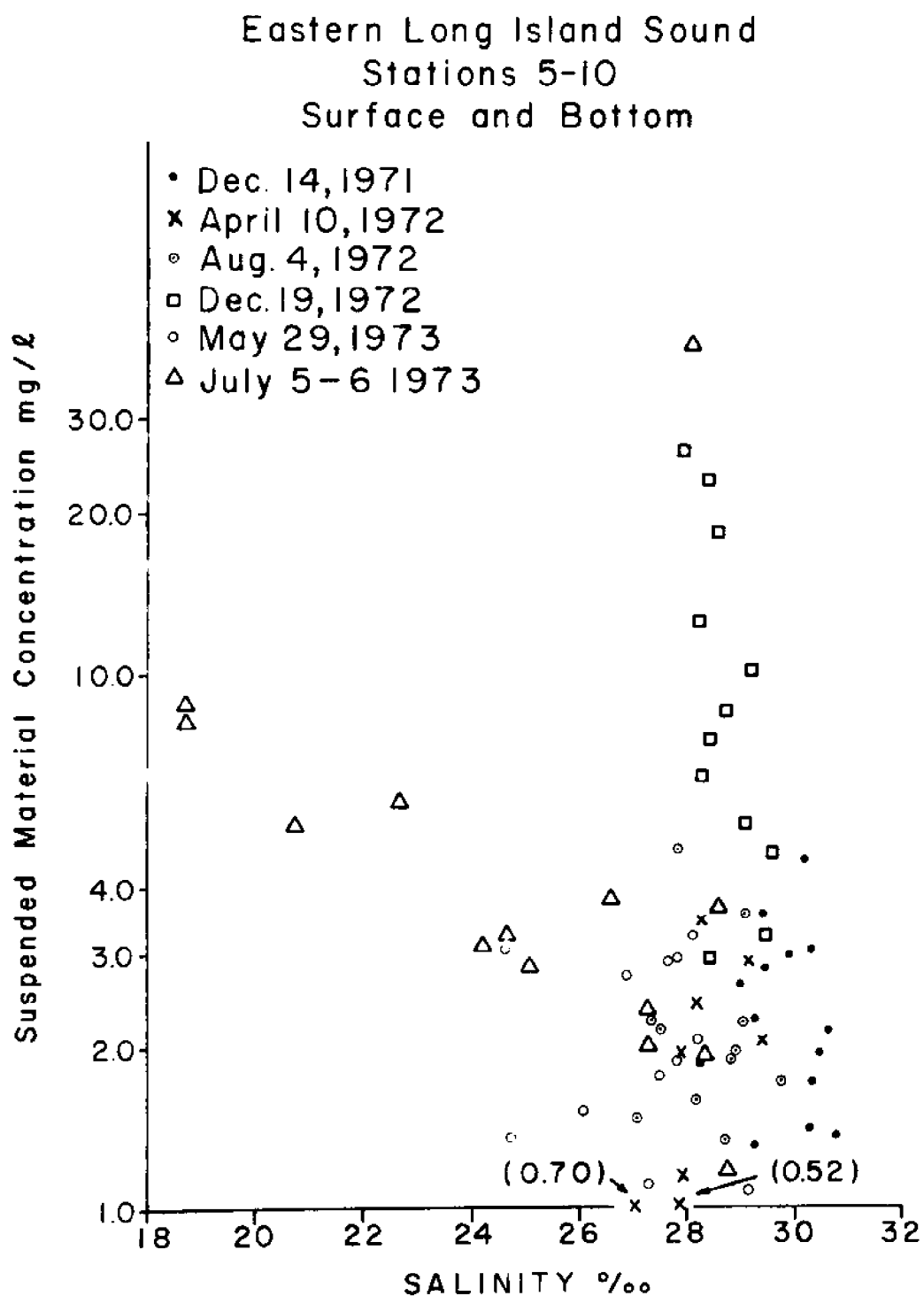


Fig. 5. The Relationship between Material Concentrations and Salinity: Eastern Long Island Sound

the Connecticut River (e.g., July 5 and 6, 1974) is there evidence of a uniform decrease in material concentrations with increasing salinity. Under these circumstances the river, representing the major supply of materials to the eastern Sound, is progressively mixed with the lower concentration waters from the adjacent shelf. The survey data indicate that this situation is a relatively infrequent occurrence.

The above characteristics are representative of a system in which material concentrations are governed by a combination of hydrodynamic, biological, and meteorological factors. Within this system no single factor is consistently dominant. As previously noted, the problem then becomes the specification of the range of conditions under which a given factor dominates and the concurrent degree of influence.

Factors Controlling Suspended Material Concentrations

Tidal State. Numerous investigations have shown that suspended material concentrations in coastal and estuarine waters will vary significantly over a tidal cycle (Schubel, 1971; Postma, 1967; Morton, 1967). Observations obtained within the eastern Sound indicate a similar range of variability, although qualitatively the behavior displayed during each of three survey periods was substantially different (Fig. 6).

During the November 1971 survey, near bottom concentrations varied by approximately ± 1.6 mg/l over a tidal cycle. Peak values were coincident with the time of maximum flood (westerly flow). A secondary peak is assumed to have occurred near maximum ebb. During the same period near surface concentrations varied by ± 1.5 mg/l with peak values occurring two hours after maximum ebb (easterly flow). The minor peak following maximum flood was similarly displaced in time. The patterns suggest that the variations in material concentration are primarily the result of an increase or decrease in the ability of the tidal stream to erode and transport sediments. Near surface concentrations are further perturbed by spatial variations in material supply. During the ebb the higher concentration, near-shore waters are transported to the south and east past the survey site resulting in the observed peak concentrations.

In the case of the June 1972 survey, near bottom concentrations varied over the tidal cycle by ± 1.75 mg/l with the peak values remaining coincident with the period of maximum flood and

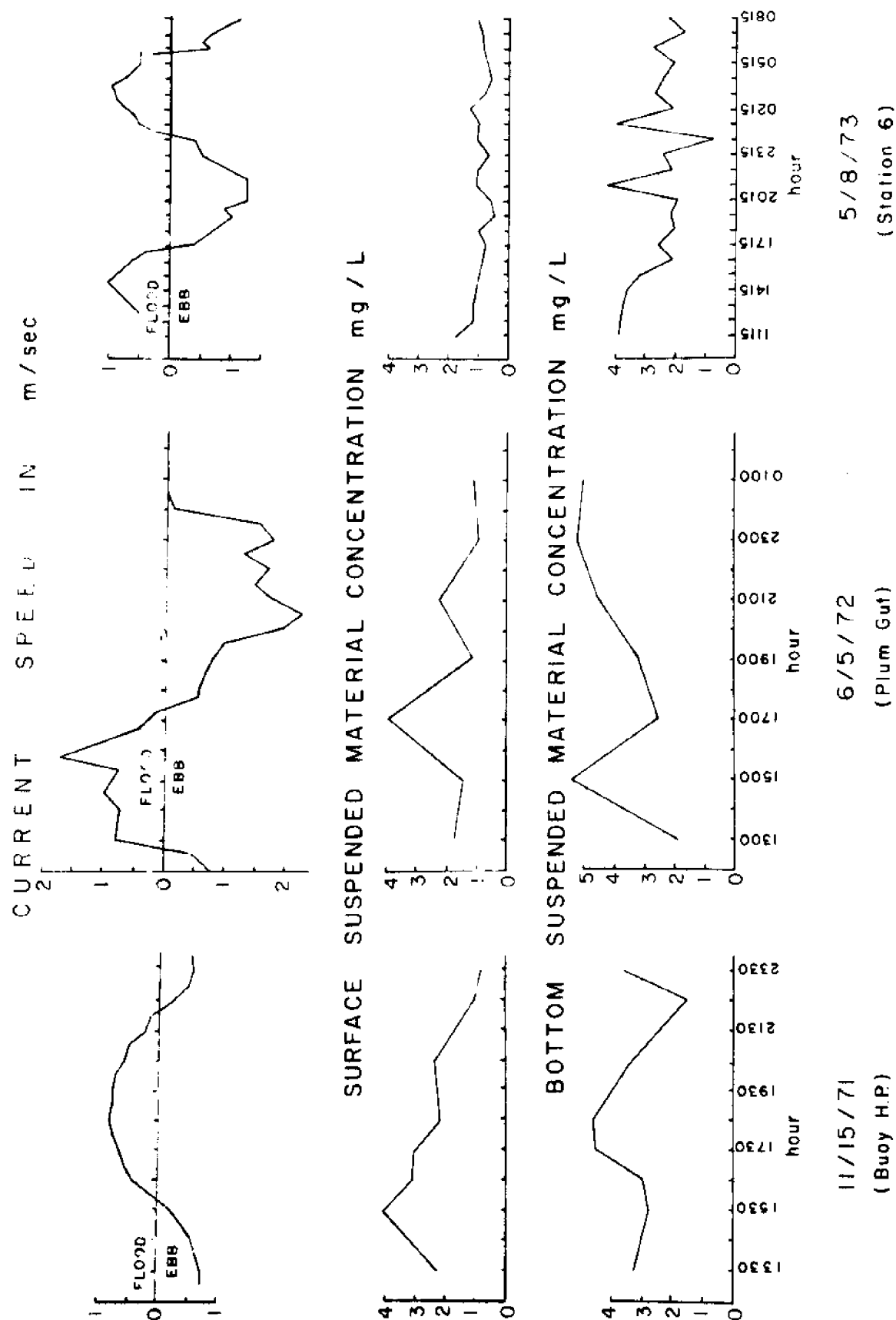


Fig. 6. Variations of Suspended Material Concentrations over a Tidal Cycle

ebb. Maximum concentrations were identical under both conditions. Near surface concentrations again varied by ± 1.5 mg/l, with maxima lagging the times of maximum velocity by approximately one hour. In contrast to the November survey, however, the peak values in this case occurred following maximum flood rather than maximum ebb. The difference is explained in terms of the characteristics of the respective station locations. The November survey occupied a mid-Sound location and, as indicated, received higher concentration near shore waters during the ebb. In June the survey site was located in the vicinity of Station 7 (Fig. 2) in Plum Gut. The observed near surface peak following the flood is the result of the intrusion of high concentration waters from Gardiners Bay, just to the south of Orient Point. The remaining variations in material concentrations are again primarily the result of variations in the competency of the tidal stream.

The tidal variations observed during May 1973 varied substantially in character from those of the preceding surveys. Near bottom concentrations varied by ± 2.0 mg/l but showed little correlation with the concurrent tidal velocities. Peak values occurred just before maximum flood and just after maximum ebb. The pattern, however, lacks consistency and does not appear to be repetitive. Near surface concentrations varied by less than ± 0.5 mg/l in a manner characteristic of a system in which the bulk of material in suspension is extremely fine grained with settling times far in excess of the tidal period. Similar patterns have been observed in Chesapeake Bay (Schubel, 1971) and Wadden Zee (Postma, 1967). The variant behavior again appears to be the result of differing physical conditions produced by the shift in station location. The May 1973 survey was conducted in the vicinity of Station 6 (Fig. 2), approximately 4 km southwest of the site of the November 1971 survey (buoy BW-HP). The resultant increase in water depth from 30 m to 50 m appears sufficient to isolate the near surface waters from bottom boundary layer effects. In addition, the near uniformity in material concentrations suggests that this location is removed from the area of direct river and nearshore influence. The variability in bottom concentrations appears to be the result of variations in competency and material supply. The aperiodic nature of the data seemingly results from the transport of masses of high concentration water past the station.

In summary, the tidal state must be taken into consideration in the evaluation of the factors governing material concentrations. Although particularly effective in shallow water areas,

tidal effects combine with other transport factors to persistently perturb concentration levels throughout the greater portion of the study area. The tidal stream serves to erode and suspend materials and represents the single most important mechanism for the distribution of sediments introduced by river inflows and by the action of shallow water wind waves. The tides exert a continuous influence in contrast to other factors governing material concentration.

Streamflow. Either through direct hypothesis or by implication, the majority of the available geological literature concerning marine sedimentation proceeds from the assumption that materials suspended in coastal waters are supplied primarily by river discharge. Plumes of sediment-laden waters adjoining the lower river are used as indicators of the transport routes between the river and the adjacent continental shelf. Upon investigation, however, it becomes apparent that selection of this factor is more often the result of familiarity produced by the large number of studies detailing the fluvial transport process rather than any quantitative comparison(s) between each of the factors capable of affecting material supplies. Such comparisons generally indicate complicated "cause and effect" relationships characterized by significant spatial and temporal variations.

In the open waters of the eastern Sound material concentrations (Fig. 4) are observed to be weakly correlated with volume discharge from the Connecticut River (Fig. 7). Concentrations are high during the spring months, coincident with the period of maximum discharge. Following the spring, maximum concentrations generally decrease to a minimum in the late summer, followed by a period of increasing concentrations leading to a second maximum in the early winter. At most stations the peak concentrations during the period of observation occurred during these winter maxima.

Although this pattern closely follows that displayed by the monthly average streamflow of the Connecticut River (Fig. 7), the numerous deviations from simple correlation, particularly during the winter months, suggest that material distributions in the eastern Sound may be sensitive to higher frequency fluctuations in streamflow and/or may represent the resultant of a variety of factors acting in combination with Connecticut River discharge. Although the low sampling rate characteristic of the data set precludes precise resolution of the high frequency response of the field of suspended materials, these hypotheses can, in part, be examined using the ensemble average of the data obtained at

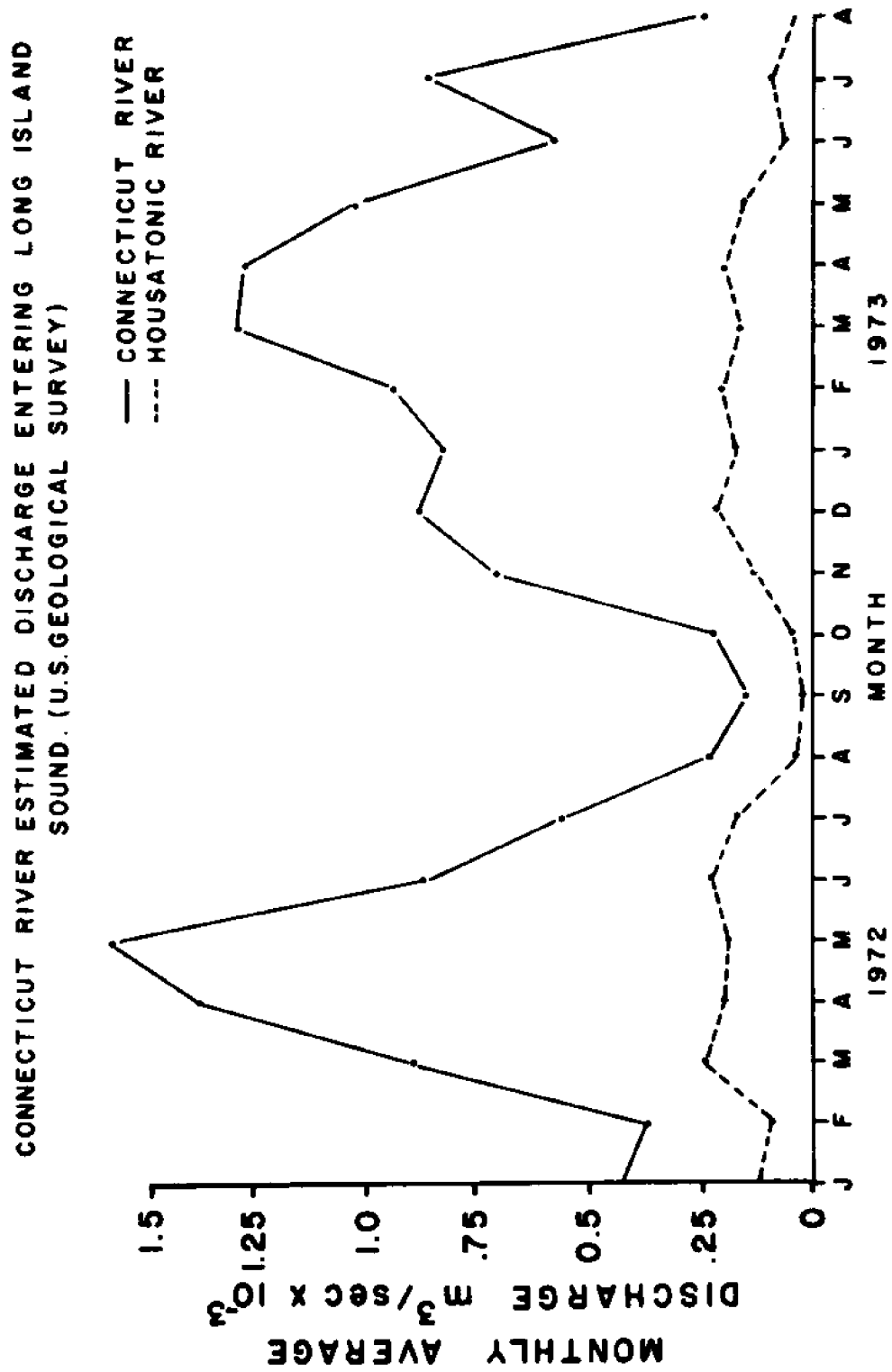


Fig. 7. Monthly Average - Connecticut River Discharge

each of the open Sound stations (Nos. 6, 7, 8, 9, 10). Applied to both material concentrations and salinity levels, this procedure minimizes the noise introduced by non-synoptic sampling of the tidal stream and reduces the effects of spatial variability that tends to obscure the temporal characteristics of the area. Ensemble averaging appears justified since each of the selected stations remains outside of the area of direct river influence, except during periods of extremely high discharge ($1400 \text{ m}^3/\text{sec}$). As a result, their respective material concentrations are determined primarily by large scale mixing processes. If it can be assumed that suspended material transport occurs in a manner similar to that of water mass properties then the same mixing processes that produce near-uniformity in the behavior of the density field in the eastern Sound should also result in similar uniformity in material distributions. Insofar as the assumption is correct, the behavior of the ensemble average is expected to be representative of the conditions characteristic of each station.

To complement the average salinity and concentration data (Fig. 8a, b) the average Connecticut River discharge for the four days preceding each survey was calculated and plotted on the cruise data. (Fig. 8c). This period was selected as being representative of the response time of the salinity field to variations in streamflow. Again applying the above assumptions concerning transport characteristics, materials supplied by the river discharge should therefore also vary in response to these antecedent conditions.

The ensemble averages clearly display the response of the concentration and salinity fields to the seasonal streamflow cycle and to aperiodic discharge events. Maximum concentrations occur during periods of low salinity and above average streamflow while progressive decreases in material concentrations during the summer months coincide with the period of decreasing streamflow and increasing salinity. Discharge anomalies observed in May 1972 and July 1973 produced a general decrease in the average salinity of the water column primarily through marked freshening of the surface waters. Although material concentrations in both cases were high, the July 1973 event resulted in a particularly prominent concentration anomaly. The high values observed during the winter of 1972-1973 were essentially uncorrelated with concurrent river discharge.

These data indicate that eastern Long Island Sound receives a steady supply of suspended materials from the Connecticut River. These materials in combination with those suspended by tidal

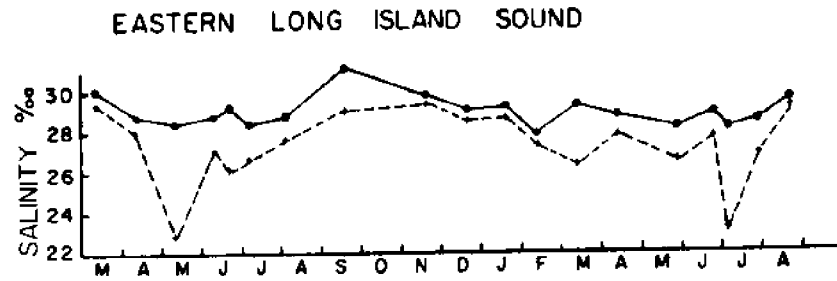


Fig. 8a.

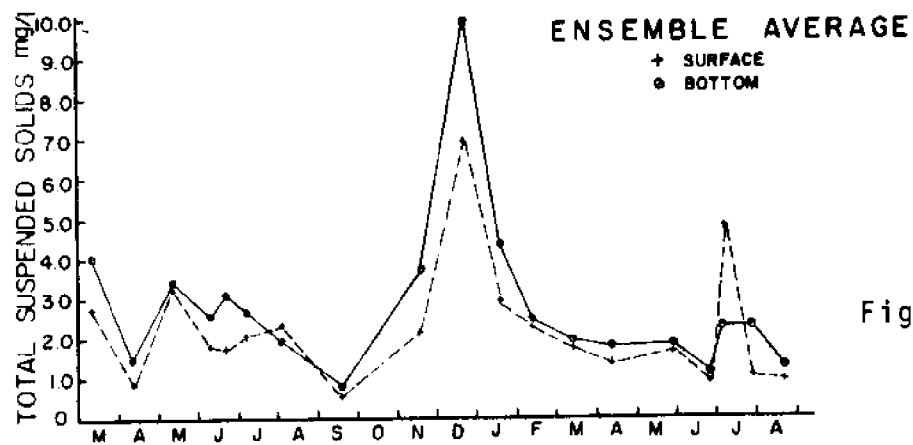


Fig. 8b.

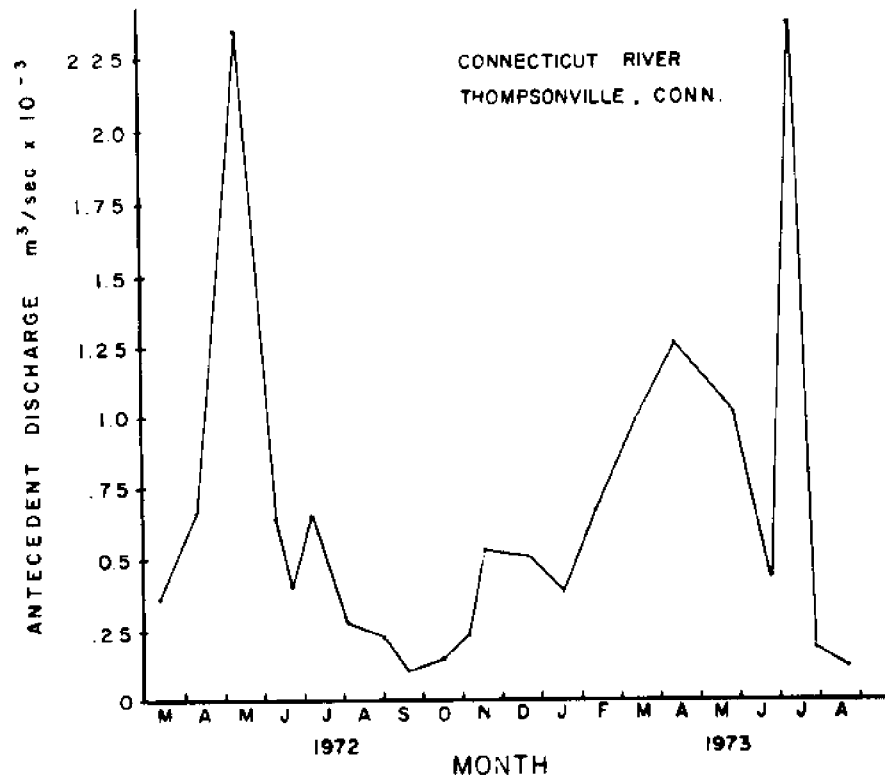


Fig. 8c.

Fig. 8a. Average Salinity
 Fig. 8b. Ensemble Average Material Concentration
 Fig. 8c. Antecedent Discharge Conditions

currents produce a persistent background concentration characterized by an evident seasonal variability throughout the study area. The close similarity between the salinity distributions and the background material concentrations implies that similar mixing processes govern both properties and that, therefore, the riverine materials and tidal scour products consist primarily of extremely fine grained sediments. In addition, the noted similarities can be used to predict the behavior of the background concentration levels and to develop quantitative estimates of the flux of riverine materials through the study area. Such calculations are presently in progress, using both these data and those obtained during 1972 to 1974 in central Long Island Sound (Bohlen and Tramontano, 1974a, b).

The behavior of the ensemble average indicates that the observed total material concentrations represent the resultant of a variety of factors acting in combination with river discharge rather than being simply the product of riverine supply. The significant departure from the expected background concentration during July 1973 shows the response of the material concentration field to high frequency fluctuations in streamflow to be effectively limited by the large volume and intense mixing characteristic of the eastern Sound except during extreme discharge events. The observed anomaly resulted from an event characterized by high concentration levels (Fig. 4) and large volume discharge (Fig. 9). The combination, produced by a rapid (~ 5 days) and large amplitude ($2352\text{m}^3/\text{sec}$) increase in discharge from a low base flow resulted in a marked alteration of the density field sufficient to inhibit vertical mixing within the open Sound. These conditions reduce the area's ability to assimilate large volumes of material and result in a prominent perturbation in concentration levels. Examination of the Connecticut River streamflow records indicates that such an extreme discharge condition occurred only once during the period of observation. Under more typical discharge conditions, such as those observed in May 1972 (Fig. 9), the response time of the material field to a fluctuation in streamflow is significantly increased. Using the discharge characteristics for the period preceding this cruise to set a lower limit on the event conditions required to affect significant short term perturbations in material concentrations indicates that a minimum increase of $1120\text{m}^3/\text{sec}$ must occur within a six day period. The maximum impact will result when this increase proceeds from a base flow below $560\text{m}^3/\text{sec}$. The streamflow records show that these conditions were satisfied only twice during the study period. The infrequent occurrence of significant streamflow events suggests that river discharge influences primarily the long-term background

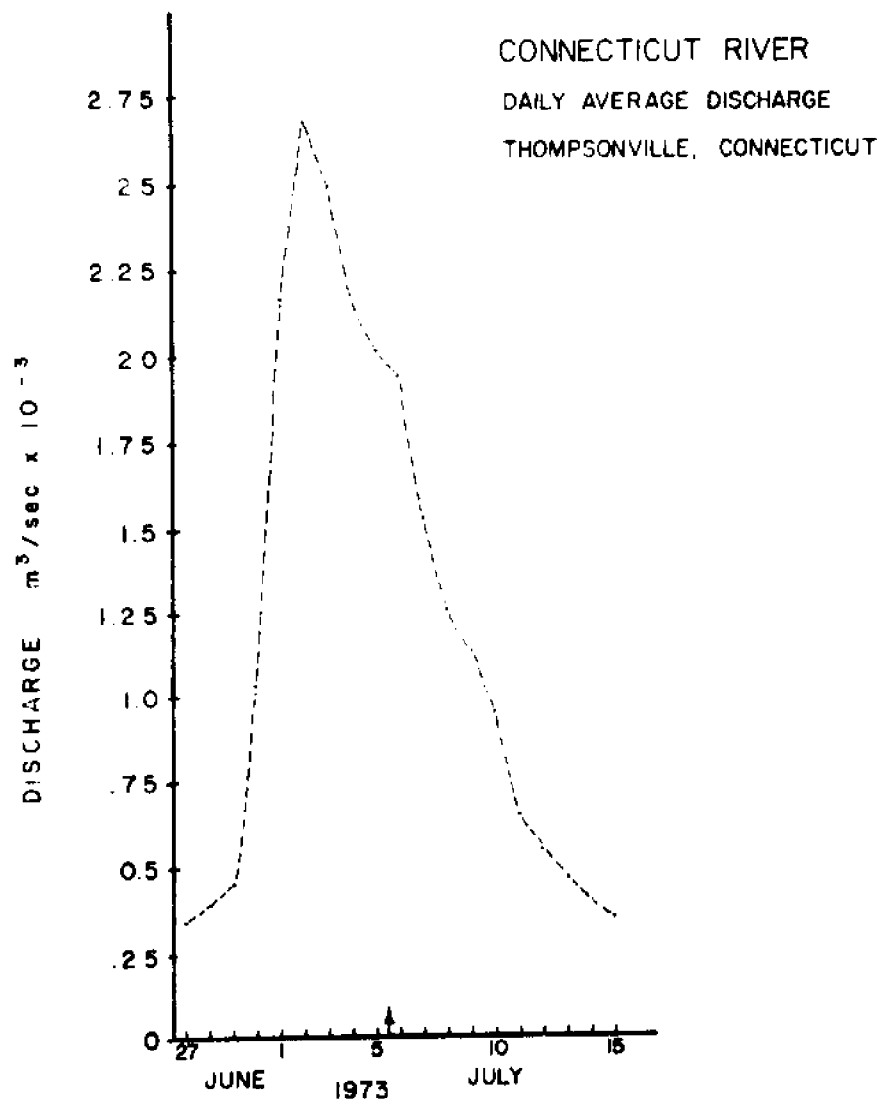
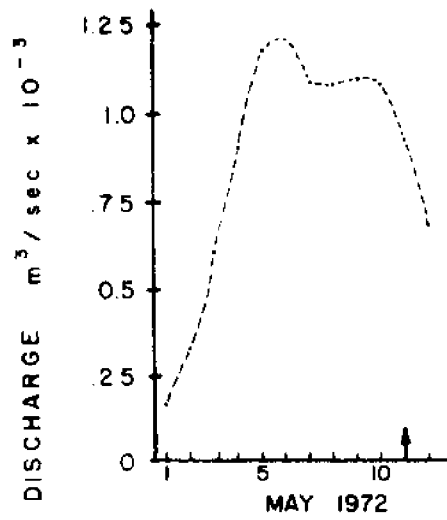


Fig. 9. Selected Daily Average Discharge of the Connecticut River:
May 1972, June-July 1973

concentrations, with other transport factors dominating the short term spatial and temporal variability.

Wind Stress. As noted above, the wind field characteristic of the eastern Sound displays a regular seasonal variability in both speed and direction. To investigate the relationship between these trends and the seasonal cycle in material concentrations, daily average wind stress levels were computed for the study period. The calculations employed hourly wind speed observations obtained at Millstone Point (Fig. 2). Data recorded at the 46 m level were corrected to the ten meter level, assuming a logarithmic velocity profile. The resultant wind stress was computed using:

$$t_o = \rho_a C$$

where ρ_a (Halpern, 1974)

$$C_{10} = \text{drag coefficient} = 1.3 \times 10^{-3}$$

and U_{10} = wind speed @ 10 m level.

The hourly values were then combined to determine the daily average wind stress levels (Fig. 10).

These data indicate that minimum wind stress occurs during the summer months, with maxima generally observed during the winter and early spring. During 1972 and 1973, extreme wind stress levels occurred in June, November, and December 1972, and in January, February, and March 1973. The June 1972 event, produced by the passage of hurricane Agnes, is not considered representative of summer conditions. The occurrence of high stress levels during the winter months closely coincides with the time of peak suspended material concentrations noted in the ensemble average (Fig. 8b). The absence of significant discharge events during this period suggests that the marked increase in material concentration over expected background levels is the result of variations in transport competence or material supply induced by surface wind stress. This "cause and effect" relationship was particularly evident during the event observed on December 19, 1972.

Connecticut River streamflow for the period preceding December 19 is characterized by near average volume discharge and

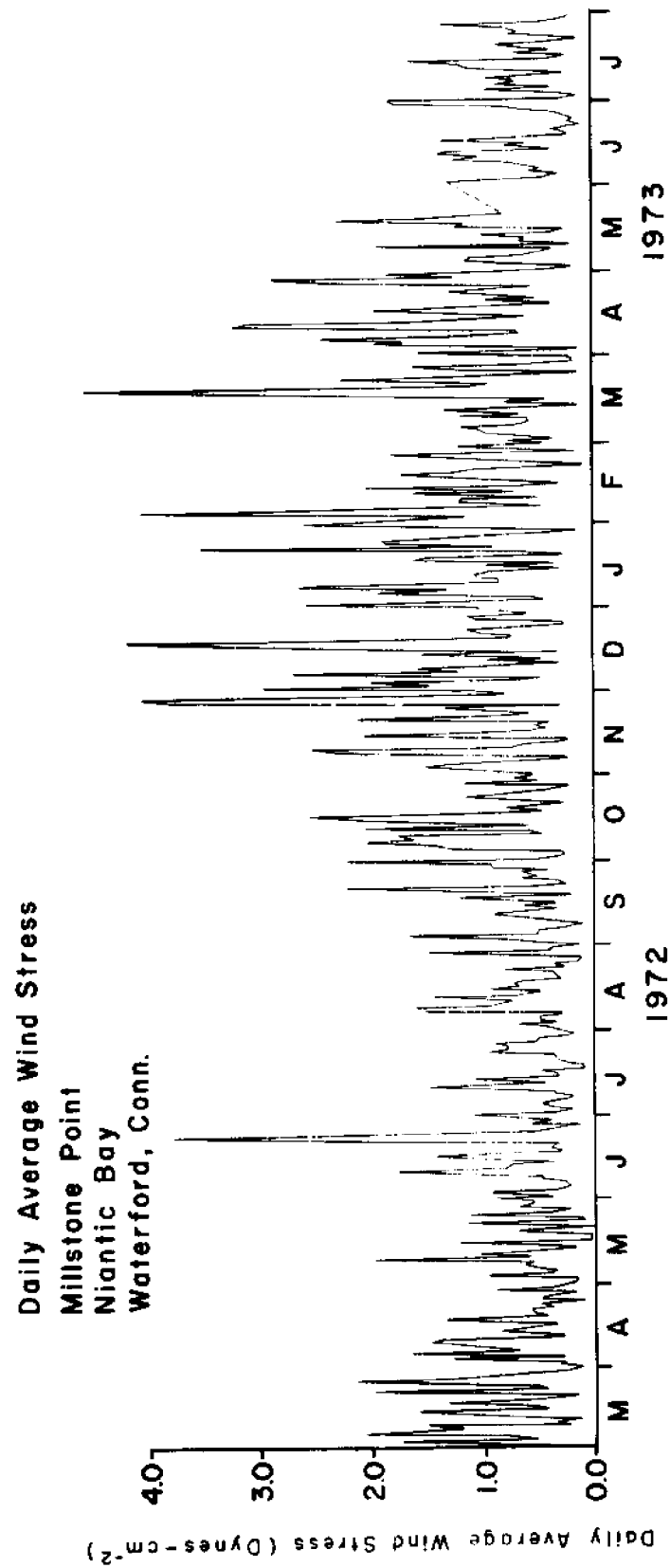


Fig. 10. Daily Average Wind Stress

generally falling stage (Fig. 11). A minor discharge event occurred 10 to 11 days before the survey. Based on the qualitative discussion in the previous section, this event is not considered capable of significantly perturbing material concentrations in the open Sound. In contrast, the winds during this period were extremely energetic and produced high stress levels (Fig. 10). Average winds exceeded 13m/sec for a period of four days preceding the survey. Wind direction varied from the northeast on the 15th through northwest on the 16th and 17th, to the southwest on the 18th (Fig. 12). In addition to perturbing material concentrations, this intense wind system served to modify the near bottom net drift field in the central Sound (R. B. Gordon, Yale University, personal communication) and was coincident with a period of extremely low tides (local observations).

Although the clear correlations during the winter months are evidence of cause and effect, the mechanics governing the coupling between wind stress and the material concentration field are not immediately apparent. Despite this fact it seems reasonable to assume that wind stress affects concentration levels primarily through the generation of wind waves and by alteration of the near surface mass transport field. These mechanisms are most effective in the shallow water, along the coastal margin and within the Connecticut River. The depth and limited fetch conditions characteristic of the eastern Sound (Fig. 1) generally preclude the generation of long waves sufficient to erode materials in the open water areas.

The materials eroded and suspended in the coastal areas will serve to perturb the concentration levels throughout the area if the erosion process persists for a sufficient period of time to permit widespread mixing of these sediments. Although this mixing time is expected to vary as a function of a number of variables, including wind direction and stress levels, examination of the survey data indicates that each of the concentration anomalies observed during the winter of 1972-1973 was associated with a wind stress event that persisted for more than 48 hours. Shorter duration events served simply to modify the local concentration levels. This observation explains in part why winter storms are more effective than similar high stress events occurring during other seasons. The latter events generally do not persist for more than 24 hours. During the period of observation approximately 75% of the storms with periods longer than 48 hours occurred during the late fall, winter, and early spring months.

In addition to providing sufficient duration for large scale mixing, winter storms dominated by northerly winds favor increased material supply and mixing in the eastern Sound. These

CONNECTICUT RIVER
DAILY AVERAGE DISCHARGE
THOMPSONVILLE, CONNECTICUT

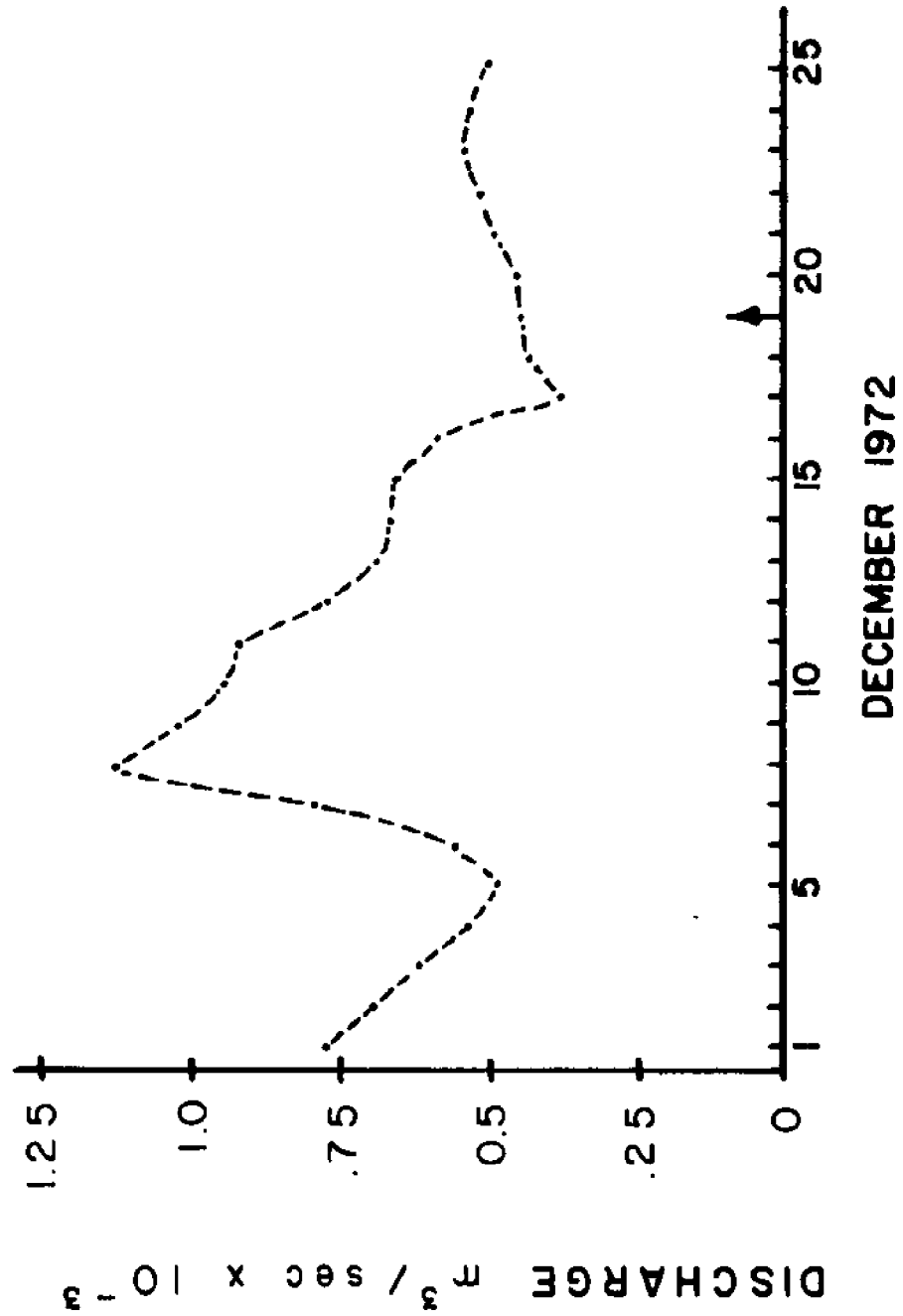


Fig. 11. Selected Daily Average Discharge of the Connecticut River:
December 1972

WIND VELOCITY

MILLSTONE POINT

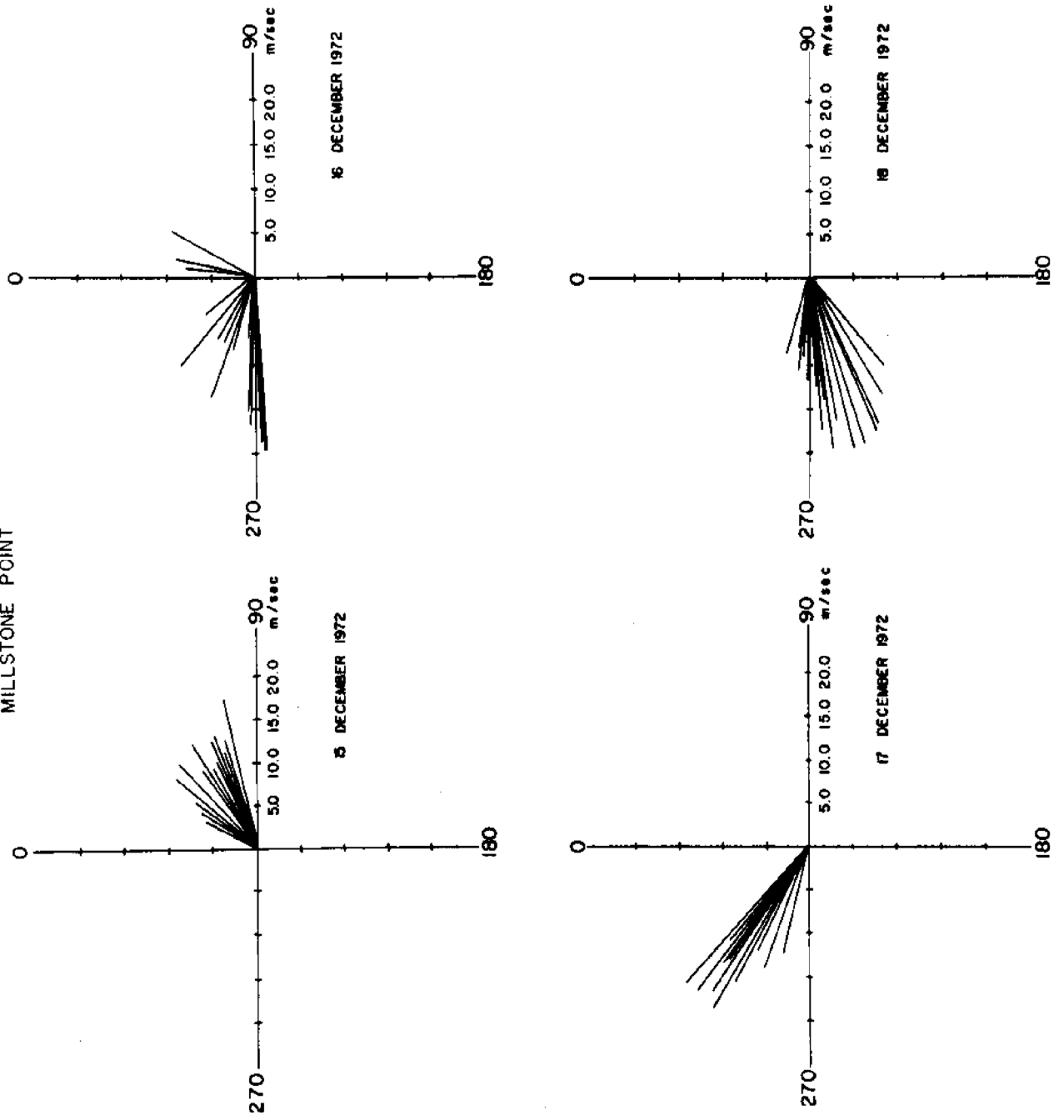


Fig. 12. Millstone Point Wind Velocity: 15-18 December 1972

winds, through generation of an upwelling cell along the northern shore and an increased exchange between the Connecticut River estuary and the adjacent Sound, can effectively reduce the time required to affect significant perturbations of the concentration field. The weak correlation between southerly storms and concentration anomalies suggests that these processes are essential elements of the wind induced transport system and that their reduction or reversal will significantly decrease the impact of wind stress events.

The above features suggest that the effectiveness of wind stress results from the combination of duration, direction, and stress level rather than any single factor. The optimum event characteristics are established by the bathymetry, orientation and mixing characteristics of the eastern Sound and the Connecticut River. These elements appear to favor high intensity northerly storms of moderate duration. Since these requirements are satisfied most frequently during the winter months, the concurrent material concentrations persistently display clear correlations with wind events.

Biological Influences. Biological activity serves to produce the bulk of the materials suspended in the eastern Sound. Analyses of particulate matter indicate a 30-40% loss in weight following combustion. The remaining ash consists primarily of diatom frustules, iron oxides, and shell fragments with inorganic mineral grains representing less than 10% of the total suspensoid (Meade, 1972). This supply represents the resultant of a variety of processes, including phytoplankton and zooplankton production, bacterial particulate formation, and the introduction of detrital materials from coastal marsh areas and the adjacent continental shelf. The combination results in a large background concentration of organic detritus characterized by seasonal variations in composition that produce only minor variations in concentration. Previous investigations have shown that the percentage of combustible organics in suspension varies seasonally within narrow limits and is essentially unrelated to the characteristic phytoplankton cycle (Riley, 1959). Similarly, material concentrations and organic content show only slight increase during the period of expected peak zooplankton production in August and September (Riley and Conover, 1956). This effective isolation indicates that the volume of detrital organic materials available to the eastern Sound is many times larger than the volume of plankton produced during the seasonal blooms. As a result, total material concentrations in this area vary primarily in response to the variety of transport factors rather than the seasonal biological cycle.

In addition to in situ production of particulate matter, material concentrations in coastal waters can also be perturbed by the resuspension of bottom sediments by deposit-feeders. Within areas characterized by organic rich silts and clays, this process very often dominates the near bottom concentration field particularly during periods of maximum benthic activity in the late summer (Rhoads and Young, 1970).

As previously indicated, eastern Long Island Sound sediments are dominated by sands and silts. These materials are similar to those observed in areas of Buzzards Bay that favor suspension feeders rather than deposit feeders. Within such areas bioturbation is expected to represent a minor influence on near bottom suspended material concentrations (Rhoads, 1973). The behavior of the concentration field in the eastern Sound seems thoroughly consistent with this observation. Although the open water distributions are characterized by persistent vertical gradients, the slight differences are often near the resolution limit of the analytical procedures and can generally be explained in terms of physical rather than biological influences. Also, these gradients fail to display any obvious seasonal trends. In particular there is no marked behavioral differences during the expected period of maximum benthic activity. As a result, it seems reasonable to conclude that bioturbation represents a minor contribution to the observed material distributions.

DISCUSSION

Suspended material concentrations in eastern Long Island Sound vary primarily in response to Connecticut River discharge and wind stress. Streamflow provides a continuous supply of fine grained materials that, in combination with locally produced organics and tidal scour products, results in a persistent background material concentration having regular seasonal variability. In contrast, the effects of wind stress are confined primarily to the winter months. These events serve to perturb concentration levels through the addition of materials eroded and suspended within shallow water areas and by modification of the nearshore and estuarine transport system. The resultant increase in material supply produces concentrations far in excess of expected background levels. Yearly maxima normally occur during this period. In addition to modifying the concentration levels, wind stress events may also serve to alter the composition of the materials in suspensions. Estimates of the volume of materials required to

produce the increase in concentration levels observed during the period of peak wind stress indicates that, in the absence of a marked alteration in the large scale transport field, the supplies available from the Connecticut River alone are insufficient. Although the paucity of data precludes quantitative analysis of the relationship between wind stress and residence times, it seems unreasonable to suppose that the volume deficiency of the Connecticut River supply will be offset by increased residence time induced by high wind stress. In fact, qualitatively, the dominant northwesterly winds would tend to favor increased surface water exchange between the Sound and the adjacent shelf, in apparent opposition to the required increase in residence time. A more reasonable construct would assume that the volume requirements are satisfied by the combination of riverine supplies and materials eroded and suspended along the shallow water coastal margins of the Sound. Satellite photographs obtained under high wind stress conditions (Fig. 13) clearly show that periods of peak wind stress result in increased turbidity within the shallow water areas. The increased material concentrations along the coastal margin are indicative of an increase in transport competence induced by the wind stress event. Given the relatively non-cohesive nature of the sediments in this area, this increase in competence should, in addition to perturbing concentration levels, also tend to increase the median grain size of the material in suspension. As a result, both suspended material concentrations and particle size distribution are expected to display a regular seasonal variability in response to the wind stress cycle.

A comparison between the characteristics of the concentration field in eastern Long Island Sound and those observed in other estuarine areas indicates a substantial difference in the relationship between the dominant transport factors. Within the typical estuary material concentrations are dominated by the combination of tidal state and river discharge with aperiodic perturbations induced by wind stress throughout the year (Schubel, 1971). Each of these factors serves both to erode and suspend, as well as to transport materials. In the eastern Sound tidal currents serve principally to determine the mixing characteristics of the area. Although tidal scour products represent a fraction of the materials in suspension, the primary function of the tides is to distribute the materials supplied by river discharge and coastal erosion. The resultant mixing, in combination with the large volume of the eastern Sound, effectively limits the response of the concentration field to high frequency variations in streamflow except during extreme discharge events.



Fig. 13. ERTS Satellite Photograph of Long Island Sound:
December 2, 1972

As a result, river discharge represents primarily a persistent material supply that dominates the low frequency variability of the concentration field. In the open waters of Sound streamflow does not directly represent a significant erosional force. second-order effects, produced by variations in the near bottom velocity structure following a streamflow-induced alteration of the density field, are not expected to produce significant amounts of suspended materials.

Wind stress dominates the high frequency variability of the concentration field. In contrast to other estuarine areas, however, its effectiveness is confined by the combination of bathymetry and mixing characteristics primarily to the winter months.

The noted variations in the characteristics of the concentration field in the eastern Sound suggest that this area is more nearly representative of a continental shelf than an estuary. Although there have been relatively few detailed studies of suspended material transport along the Atlantic Continental Shelf, this area is known to serve primarily as a sink for the variety of materials introduced by river discharge and coastal erosion. Distribution patterns are determined by the complex circulation field dominated by tidal currents and the combined effects of the density field and surface wind stress. In a similar fashion eastern Long Island Sound serves as a sink and a mixing area for the materials supplied by the Connecticut River, by shallow water erosion processes and by intrusions from the adjacent shelf. Material distributions in this area are governed by the same primary transport factors that dominate on the shelf and display seasonal variations in response similar to those displayed by the continental shelf circulation field. These observations suggest that the eastern Sound is more properly viewed as a coastal embayment rather than an estuary. Within this area the variety of materials supplied are thoroughly mixed, serving to establish the eastern boundary conditions for the remaining portions of the Sound. The weak vertical gradients imply that both eastern and western transport will occur with the ultimate routes and rates determined by the net drift field. Quantitative estimates of the resultant flux of material remain to be determined.

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CHAPTER VI

Zn, Cu, Cd, Mn, AND Hg IN OYSTERS
ALONG THE CONNECTICUT COAST

by

S. Y. Feng and G. M. Ruddy

INTRODUCTION

The propensity of bivalve molluscs to accumulate water-borne contaminants, e.g., viruses, bacteria, toxic algae, hydrocarbon, heavy metals, pesticides and related compounds from the environment, is well known. Among the various species of shellfish examined regarding contaminants, the oyster is probably the best known example in terms of the kinds of contaminants being concentrated, as well as being of historical interest. For example, as early as 1898 the greening in Crassostrea virginica relaid in English waters was ascribed to the presence of copper in the tissues by Boyce and Herdman. Although the mechanism of accumulation and the functional significance of heavy metals in shellfish remain to be explored, shellfish have been used occasionally as environmental monitors which are able to integrate dilute water-borne contaminants present in the environment over an extended period of time. Consequently the concentration of metals may reach several orders of magnitude higher in shellfish than in the environment in which they have been maintained. Thus, the shellfish is also known as the biological amplifier.

In Connecticut the major oyster producing areas are located in the western end of Long Island Sound (New Haven and west) where major population centers and industries of the state also exist. It is conceivable that the continued operation of this fishery depends on the maintenance of adequate water qualities and is extremely vulnerable to both domestic and industrial pollutions. The immediate objectives of this project were (1) to establish six shellfish monitoring stations on the north shore of Long Island Sound and (2) to identify and quantify selected metals (Pb, Zn, Cu, Cd, Hg and Mn) sequestered in the tissues of oysters maintained at the monitoring stations.

MATERIALS AND METHODS

Field Stations. Six stations were established along the north shore of Long Island Sound. These stations were located at (1) Norwalk Harbor (Northeast Utilities Company pier), (2) Bridgeport (Pleasure Beach Bridge), (3) Housatonic River, below Devon, (4) New Haven Harbor (Coast Guard Station finger pier), (5) New London Harbor (U.S. Navy Underwater Systems Center pier)

and (6) Noank (the University of Connecticut Marine Sciences Institute pier). These sites were selected on the basis of reflecting population densities as well as degrees of industrialization.

Source of Oysters. The oysters used as biological monitors were obtained as yearlings from a Norwalk oyster bed through the courtesy of Blume Brothers Oyster Company in June 1972. The use of a single stock of oysters was designed to minimize possible variations due to different locations from which the oysters were obtained. Approximately 3,500 oysters were obtained and briefly held in trays at the National Marine Fisheries Service Laboratory pier in Milford Harbor prior to being transferred to the six monitoring stations. At each station 500-600 oysters were placed in round plastic trays and suspended about two feet off the bottom.

Another group of about 500 oysters from an oyster bed of Blume Brothers Oyster Company in Bridgeport located about 2.5 miles south of the monitoring station at Pleasure Beach Bridge, which was referred to as the Bridgeport import, was transplanted to Noank in August 1973. This portion of our study was designed to ascertain whether attrition of metals occurs in oysters from a high metal input area when they were transplanted to Noank, an area of relatively low metal burden.

Procedures. A base sample of 25 oysters was taken in June, 1972. Thereafter at monthly intervals ten oysters were sampled from each station; the sampling was terminated in April, 1974. Beginning in September 1973, the Bridgeport import was similarly sampled. A base sample was obtained in August prior to being transplanted to Noank.

At the laboratory 10 oysters from each monitoring station were divided into three groups, shucked, and the pooled meats from each group were homogenized in a glass tissue grinder and lyophilized. For the Bridgeport import 10 oysters were dissected each month. The adductor muscle, gills, mantle, and visceral mass were pooled separately, weighed, homogenized, lyophilized, and reweighed again.

Zn, Cu, Cd, Mn, and Pb were determined on 0.4 gram of the freeze-dried tissue, which were digested in 10 ml of concentrated nitric acid and diluted to a volume of 25 ml with deionized water, as recommended in the Perkin-Elmer Analytical Methods for Atomic Absorption Spectrophotometry. The analyses were made on a Perkin-Elmer Model 290B atomic absorption spectrophotometer.

For Hg analysis, the Model 290B unit was modified to operate in the flameless mode with a Perkin-Elmer mercury analysis

system (Hatch and Ott, 1968). Two-tenths gram freeze-dried samples were prepared according to the procedure outline for fish samples in the Instruction of Mercury Analysis System (Perkin-Elmer 303-3119). To determine the effect of wet ashing time on the yield of mercury, four portions of 0.2 gram freeze-dried oyster and hard clam tissues, each with triplicate samples, were subject to 6, 12, 24 and 48-hr wet ashing at 50°C. The results of mercury yield are presented in Table 1. In general there is a tendency to lose Hg as the wet ashing is prolonged beyond 6 hours. Furthermore the standard deviation of means derived from triplicate samples also appears to increase with ashing time. Based upon these considerations, the 6-hr wet ashing time for oyster and clam tissues was selected.

Statistical Analysis. For determining the significance of the mean concentrations of metals in oysters from different stations and among different tissues, the Student-Newman-Keuls multiple range test (Sokal and Rohlf, 1969) was employed. The Pearson product moment correlation coefficient (r) was calculated to determine whether interelement correlations exist in oysters maintained at various stations.

RESULTS

The average heavy metal concentrations of the oyster samples pooled on seasonal basis from July 1972 to April 1974 are summarized in Tables 2 to 6. At the Housatonic River station, sampling was discontinued in July 1972 due to excessive mortalities in oysters induced by freshwater run-off. Oysters at New Haven Harbor station were exhausted in October 1973 and those at New London Harbor as well as at the Noank station were depleted in January 1974. New oysters were reintroduced into these stations for replenishment, with the exception of Housatonic River stations. The results obtained from these reintroduced oysters were not included in the discussion of the overall results because of inadequate times of observation.

1. Temporal and spatial distribution of Cd, Cu, Hg, Mn, and Zn recovered from oysters maintained at the six monitoring stations along the Connecticut coast.

Mercury. Of the five metals detected, Hg was found to be the least concentrated in the oyster tissue (Tables 2 and 7). While no discernible seasonal variations in the concentration of Hg were noted, there was a distinct trend indicating that the amount of Hg increased from west to east along the north shore

Table 1. Effect of time of wet ashing on the yield of mercury in freeze-dried Crassostrea virginica and Mercenaria mercenaria tissues.

Species	Digestion Time (hr.)			
	6	12	24	48
<u>Crassostrea virginica</u>	0.180±0.005*	0.135±0.015	0.132±0.013	0.101±0.014
<u>Mercenaria mercenaria</u>	0.098±0.004	0.102±0.018	0.115±0.014	0.073±0.016

*Expressed as mean ug Hg/gm freeze-dried tissues ± 1. S. D.

Table 2. Mercury concentrations* in Crassostrea virginica maintained in trays at Norwalk Harbor, Bridgeport, Housatonic River, New Haven Harbor, New London Harbor, and Noank, Connecticut (June 1972 to March 1974).

Date	Norwalk Harbor	Bridgeport	Housatonic River	New Haven Harbor	New London Harbor	Noank
June 72	0.265+0.043					
July-Sept.	0.293+0.063	0.388+0.220	0.472+0.079	0.532+0.065	0.448+0.046	0.562+0.069
Oct.-Dec.	0.236+0.033	0.220+0.130	0.289+0.118	0.382+0.094	0.258+0.050	0.708+0.198
Jan.-Mar. 73	0.299+0.111	0.234+0.034	0.359+0.079	0.413+0.066	0.377+0.050	0.662+0.109
Apr.-June	0.336+0.035	0.256+0.023	0.365+0.058	0.518+0.037	0.373+0.063	0.658+0.078
July-Sept.	0.284+0.056	0.241+0.056		0.510+0.088	0.434+0.071	0.795+0.189
Oct.-Dec.	0.209+0.057	0.152+0.048			0.303+0.076	0.628+0.069
Jan.-Mar. 74	0.286+0.014	0.174+0.055				

*Expressed as mean ug Hg/gm \pm 1 S. D.

of Long Island Sound. The mean mercury concentration was highest in oysters from Noank (0.676 ppm) and New Haven Harbor (0.475 ppm), intermediate in those from Housatonic River and New London Harbor (0.367 ppm) and lowest in the oysters from Norwalk Harbor (0.275 ppm) and Bridgeport (0.240 ppm), the two westernmost stations. The Student-Newman-Keuls test indicates that the means of these three levels are significantly different (Table 7, $P < 0.05$). It was surprising to learn that oysters at Noank, being remote from major industrial and population centers, exhibited the highest level of Hg in all the stations examined.

Cadmium. Table 3 depicts Cd concentrations found in oysters held at the six stations. There was a steady increase in Cd concentrations of the Bridgeport and Housatonic River oysters with time. After an initial rapid rise during the first year, the Cd level appeared to be reaching a plateau which was ca. 10 times the level of the base sample (9.24 ppm). In New Haven Harbor for the 15-month period following the initial introduction of Norwalk oysters, no sample analyzed had Cd content greater than that of the base sample. A similar decrease in the Cd concentration occurred in New London Harbor and Noank oysters during the first 12 months; samples taken during the ensuing 6-month period, however, showed a slightly higher level of Cd than the previous months at these two stations. At Norwalk Harbor, from July to September 1972, the amount of Cd in oysters decreased; in the following 18 months, the Cd content fluctuated within the narrow limits of 9.06 to 12.01 ppm, except during April to June 1973 when a level of 16.94 ppm Cd was found in the samples. Statistically the mean concentrations of Cd at New Haven Harbor, Noank, New London Harbor, and Norwalk Harbor are not significantly different, but these levels are significantly lower than the mean concentrations at Housatonic River and Bridgeport (Table 7).

Manganese. Results of Mn determinations are presented in Tables 4 and 7. Mn levels in oysters taken from New London Harbor and Noank were significantly lower than the base sample from Norwalk ($P < 0.05$); a reduction of approximately 50% of the original Mn concentration (23.48 ppm) was noted. The data also suggest that this apparent attrition of Mn from the oysters was accomplished within three months after the initial transplantation. Depletion of Mn also existed in the oysters maintained at Bridgeport and New Haven Harbor. Mn in the oysters held at Housatonic River reached the highest level in six months after being exposed to the environment; the concentration of Mn remained generally higher than that at other stations during the 12-month period. Oysters from Norwalk Harbor had the next highest concentration of Mn. It was further noted that variations

Table 3. Cadmium concentrations* in *Crassostrea virginica* maintained in trays at Norwalk Harbor, Bridgeport, Housatonic River, New Haven Harbor, New London Harbor, and Noank, Connecticut (June, 1972 to March, 1974).

Date	Norwalk Harbor	Bridgeport	Housatonic River	New Haven Harbor	New London Harbor	Noank
June 72	9.24+1.19					
July-Sept.	7.24+2.36	25.30+ 8.28	23.06+14.13	7.20+2.15	6.30+1.43	5.93+1.34
Oct.-Dec.	12.01+1.74	44.00+ 6.40	49.20+ 3.42	5.30+0.66	6.40+1.64	6.80+2.93
Jan.-Mar. 73	10.67+1.66	53.20+ 5.60	61.65+ 6.97	4.60+1.27	7.60+2.56	5.27+1.44
Apr.-June	16.94+2.07	77.70+ 4.16	84.01+18.33	8.51+1.97	8.81+2.89	8.00+2.13
July-Sept.	11.91+3.37	106.80+13.54		7.90+0.73	11.33+2.15	11.10+2.88
Oct.-Dec.	11.74+2.12	88.24+14.98			10.75+2.72	11.36+2.65
Jan.-Mar. 74	9.06+3.74	93.49+ 9.98				

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*Expressed as mean ug Cd/gm \pm 1 S. D.

Table 4. Manganese concentrations* in Crassostrea virginica maintained in trays at Norwalk Harbor, Bridgeport, Housatonic River, New Haven Harbor, New London Harbor, and Noank, Connecticut (June 1972 to March 1974).

June 72	23.48±4.42							
July-Sept.	16.57±4.17	17.92±5.73	23.90±11.93	12.76±7.12	10.45±5.31	13.18±7.11		
Oct.-Dec.	25.62±5.98	19.07±4.23	28.20± 9.34	17.30±3.22	14.75±1.59	15.22±3.13		
Jan.-Mar. 73	19.51±3.85	13.73±1.79	29.60± 9.39	13.40±1.44	14.21±1.58	13.02±1.50		
Apr.-June	22.87±9.04	10.90±7.06	24.39±19.96	10.04±5.21	4.16±3.46	4.10±2.46		
July-Sept.	21.33±6.59	28.30±5.02		23.32±6.64	9.20±3.12	13.80±4.25		
Oct.-Dec.	13.98±2.22	12.02±3.00			9.67±1.92	14.40±1.80		
Jan.-Mar. 74	8.22±1.54	7.00±1.84						140

*Expressed as mean ug Mn/gm ± 1 S. D.

Table 5. Copper concentrations* in Crassostrea virginica maintained in trays at Norwalk Harbor, Bridgeport, Housatonic River, New Haven Harbor, New London Harbor, and Noank, Connecticut June 1972 to March 1974).

Date	Norwalk Harbor	Bridgeport	Housatonic River	New Haven Harbor	New London Harbor	Noank
June 72	374± 50					
July-Sept.	305± 83	1388± 355	743±370	282± 65	341± 71	243± 86
Oct.-Dec.	514± 95	1886± 300	1536±168	214± 37	380±117	361± 76
Jan.-Mar. 73	715±113	2603± 432	2418±485	288± 26	392± 88	450±145
Apr.-June	693± 89	3135± 603	3028±309	404±103	494±129	452±145
July-Sept.	520±147	4304± 886		475± 52	657± 96	613±141
Oct.-Dec.	373± 50	3399± 874		497±117	586±136	592±174
Jan-Mar. 74	495±103	4001±1102		551±143	527± 85	475± 58

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*Expressed as mean ug Cu/gm ± 1 S. D.

Table 6. Zinc concentrations* in *Crassostrea virginica* maintained in trays at Norwalk Harbor, Bridgeport, Housatonic River, New Haven Harbor, New London Harbor, and Noank, Connecticut (June 1972 to March 1974).

Date	Norwalk Harbor	Bridgeport	Housatonic River	New Haven Harbor	New London Harbor	Noank
June 72	4425± 620					
July-Sept.	3895± 496	6341± 941	5540±2084	4835± 783	6212±1148	4593± 873
Oct.-Dec.	5653±1093	8515±1289	10986±1145	4742± 547	8677±1474	6208±1388
Jan-Mar. 73	7864± 825	11198±1145	15948±3154	6240± 635	9458±1620	6635±1284
Apr.-June	7657±1262	12229±1782	13495±2483	6705±1206	9679±1533	7019±1072
July-Sept.	5608±1368	14045±2050		7106± 413	11652±1932	8751±1360
Oct.-Dec.	4247± 538	10524± 779		7654±1161	12521±1909	9451±2676
Jan-Mar. 74	4926± 746	10698±1136		7441± 893		

*Expressed as mean ug Zn/gm ± 1 S. D.

Table 7. Multiple comparisons among means of Zn, Cu, Mn, Cd and Hg from oysters maintained at Norwalk Harbor (Hw.), Bridgeport (Bd.), Housatonic River (Ho.), New Haven Harbor (N. H.), New London (N. L.) and Noank (No.) from June 1972 to March 1974, using the Student-Newman-Keuls Test.

Station						
	Nw.	N.H.	No.	N.L	Bd.	No.
Zn	5550±1543*	5894±1027	7183±1897	9702±2300	10493±2483	10922±4115
Cu	335±100	463±156	480±130	504±157	1880±895	3013±1119
Mn	10±4	12±5	15±8	16±6	20±9	27±6
						143
Cd	7±2	8±3	9±2	11±4	55±26	72±28
Hg	0.240±0.108	0.275±0.052	0.367±0.104	0.367±0.084	0.475±0.084	0.676±0.133

*Expressed as ug/gm freeze-dried tissues.

Underline denotes those ranges which are found to be not significant; ranges which are not underlined, are significant at $P < 0.05$.

observed in the Mn concentration of oysters could not be associated with seasons at all stations.

Copper. Accumulation of Cu characterizes the temporal distribution of this metal in the oysters from the six stations, although there are distinct variations in the rate of uptake by the oysters, which presumably reflects the concentration of Cu in the environment (Table 5). The greatest rate of the uptake was at Bridgeport and the Housatonic River; an increase of four to five times from the original concentration (374 ppm) was noted during the first six-month period. In New Haven Harbor, New London Harbor, and Noank, oysters showed little or no significant uptake of Cu for nine months. However, in all stations, oysters sampled during the second year contained more Cu than those sampled in the first year. In terms of overall concentration of Cu, oysters from Bridgeport and the Housatonic River had considerably greater Cu contents than those at the other four stations (Table 7, $P < 0.05$).

Zinc. Among the five metals studied, oysters appeared to have a special affinity for Zn, as seen by the high concentrations shown in Table 6. Zinc concentrations over 10,000 ppm were observed in oysters from Bridgeport, Housatonic River, and New London Harbor, which were significantly higher than the mean Zn concentrations detected in Norwalk, New Haven, and Noank (Table 7, $P < 0.05$). No apparent accumulation of Zn was seen in Norwalk Harbor oysters, whereas, in the Housatonic River, Bridgeport, New London Harbor, Noank, and New Haven Harbor, a steady increase of Zn concentrations was clearly discernible. The maximum Zn concentration recorded to date was 1.59% of the dry weight of oyster tissues in the Housatonic River.

II. Interelement correlations

In an attempt to understand the process of uptake of the five metals by the oysters relative to the geochemical behavior of these metals, correlation coefficients between various combinations of the metals were sought. There are ten possible combinations of inter-element correlations among the five metals investigated at each station. The results of the Pearson product moment correlation coefficients (r) for each station are summarized in Tables 8 to 13. The data indicate that as much as 50% or as few as 20% of the interelement correlation coefficients were found to be highly significant at these stations. From those which were statistically significant, it was revealed that the triad of Cu, Cd, and Zn interelement correlations was universally present in all the stations. However, at Norwalk Harbor additional significant interelement correlations between Cu-Hg and Zn-Hg were also discovered; the latter correlation

Table 8. Interelement correlations (r) in Crassostrea virginica maintained at Norwalk Harbor, Connecticut. (n=20).

	Mn	Cd	Zn	Hg
Cu	0.3381	0.6487***	0.9159***	0.4655*
Mn		0.3241	0.3439	0.1466
Cd			0.6112***	0.3169
Zn				0.5299**

Correlation significant: *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$

Table 9. Interelement correlation (r) in Crassostrea virginica maintained at Bridgeport, Connecticut. (n=22).

	Mn	Cd	Zn	Hg
Cu	-0.2048	0.9190***	0.8449***	-0.3984
Mn		-0.2087	-0.0746	0.2158
Cd			0.8189***	-0.4056
Zn				-0.3743

Correlation significant: ***, $P < 0.001$.

Table 10. Interelement correlation (r) in Crassostrea virginica maintained at Housatonic River, Connecticut. (n=12).

	Mn	Cd	Zn	Hg
Cu	-0.2431	0.9193***	0.8828***	-0.1302
Mn		-0.2689	-0.1150	0.3910
Cd			0.7824***	-0.2773
Zn				-0.2198

Correlation significant: ***, $P < 0.001$.

Table 11. Interelement correlation (r) in Crassostrea virginica maintained at New Haven Harbor, Connecticut. (n=15).

	Mn	Cd	Zn	Hg
Cu	0.3325	0.5846*	0.7654***	0.3215
Mn		0.1427	-0.0135	-0.2184
Cd			0.2784	0.1467
Zn				0.3390

Correlation significant: *, $P < 0.05$; ***, $P < 0.001$.

Table 12. Interelement correlation (r) in Crassostrea virginica maintained at New London Harbor, Connecticut. (n=18)

	Mn	Cd	Zn	Hg
Cu	-0.4850*	0.7000**	0.8054***	0.2077
Mn		-0.2794	-0.6233	-0.2691
Cd			0.5016*	0.1235
Zn				0.0249

Correlation significant: *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

Table 13. Interelement correlation (r) in Crassostrea virginica maintained at Noank, Connecticut. (n=19).

	Mn	Cd	Zn	Hg
Cu	0.0100	0.7543***	0.8228***	0.3810
Mn		0.2526	-0.1083	-0.0743
Cd			0.7867***	0.3888
Zn				0.5034*

Correlation significant: *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$

TABLE 14. Multiple comparisons among means of Zn, Cu, Mn, Cd, and Hg from adductor muscles, gill, visceral mass, and mantle of oysters maintained at Noank from August 1973 to April 1974, using the Student-Newman-Keuls Test.

Tissue				
	Adductor Muscle	Gill	Visceral Mass	Mantle
Zn	3285± 544*	<u>9225±1881</u>	<u>10921±2267</u>	13646±4543
	Adductor Muscle	Visceral Mass	Gill	Mantle
Cu	332±155	<u>918±274</u>	<u>936±238</u>	1450±170
	Adductor Muscle	Visceral Mass	Mantle	Gill
Mn	<u>6.442±3.508</u>	<u>10.162±4.428</u>	<u>10.875±4.062</u>	19.215±8.644
	Adductor Muscle	Gill	Mantle	Visceral Mass
Cd	<u>9.912±3.602</u>	<u>10.150±3.673</u>	<u>10.212±4.657</u>	<u>13.450±4.129</u>
	Visceral Mass	Adductor Muscle	Mantle	Gill
Hg	<u>0.640±0.412</u>	<u>0.738±0.364</u>	<u>0.788±0.452</u>	<u>0.882±0.469</u>

* Expressed as $\mu\text{g/gm}$ freeze-dried tissue ± 1 S.D.
 Underline denotes those ranges which are found to be not significant; ranges which are not underlined, are significant at $P < 0.05$.

TABLE 15. Comparison of heavy metal concentration in oysters from the Atlantic Coast, Long Island Sound, Georgia Coast, and Mobile Bay, Alabama (ppm wet weight).

Element	Mobile Bay ¹	Georgia Coast ²	Long Island ³ Sound	Atlantic ⁴ Coast
Zinc	665	2580	1036	1426
Copper	19.5	97.3	139	91.5
Cadmium	0.62	----	3.38	3.10
Manganese	----	34.7	2.10	4.30

¹ from Kopfler and Mayer (1973).

² from Windom and Smith (1972).

³ from the present study

⁴ from Pringle et al. (1968), Maine to North Carolina.

TABLE 16. Comparison of median concentrations of manganese, copper and zinc in oysters taken from central Long Island Sound during 1933-1935 and 1972-1974.

Element	1933-1935*		1972-1974**	
	Median	Range	Median	Range
Manganese	15***	8-50	23	5-44
Copper	1,000	400-3,000	1,500	200-5,000
Zinc	6,200	3500-14,000	11,000	3,500-19,000

* Data from Galtsoff (1964);

** Data from the present study;

*** Expressed as ug/gm dry weight.

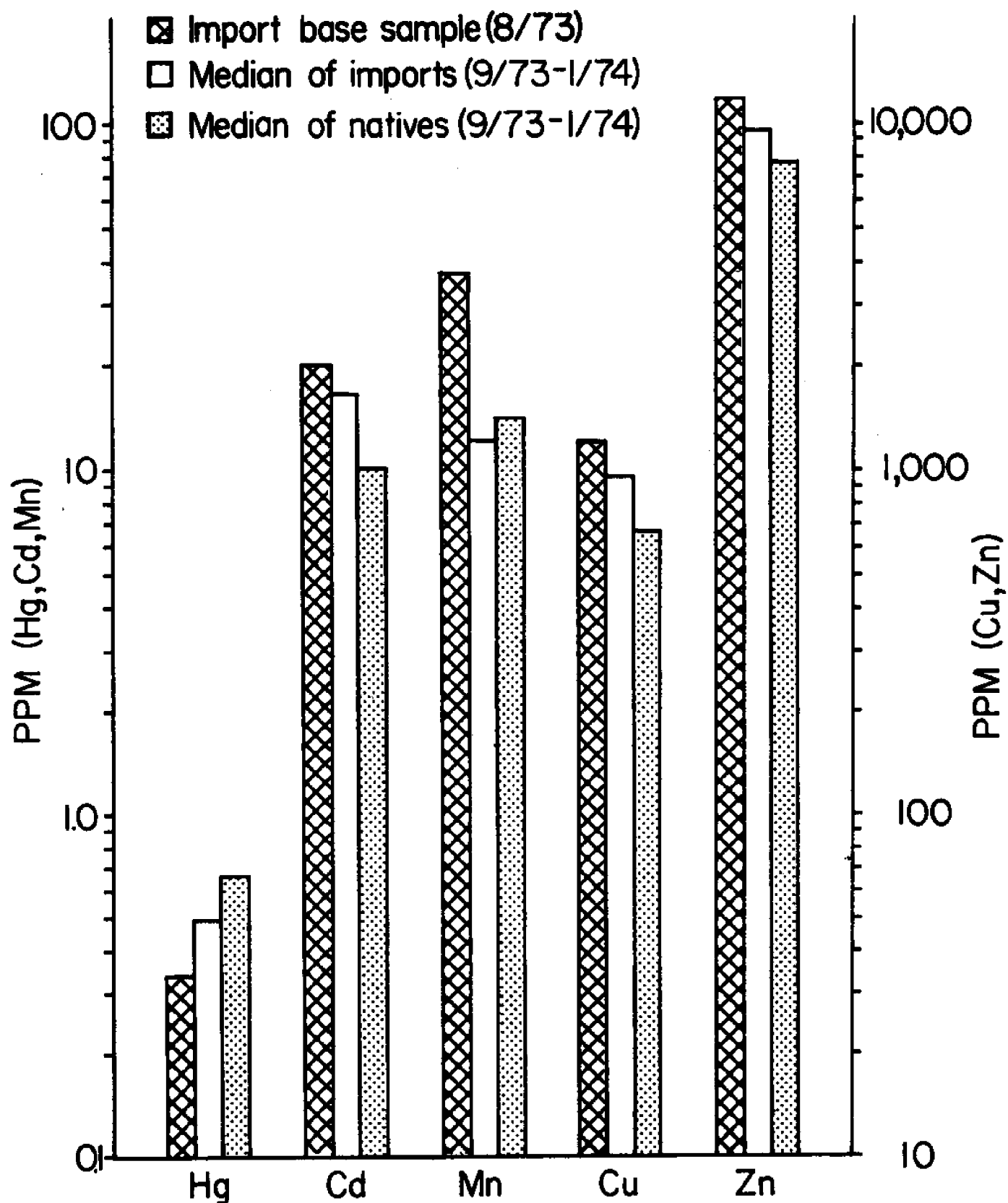


Fig. 1. Elimination and accumulation of heavy metals in Bridgeport imports maintained at Noank.

mantle. The mean concentrations of Zn and Cu in adductor muscle (8 samples) were 3,285 ppm and 332 ppm, respectively, whereas the corresponding concentrations in mantle were 13,646 ppm and 1,450 ppm. Intermediate concentrations of Zn and Cu were found in the gill and visceral mass; the concentrations between the two tissues were not significantly different.

DISCUSSION

The data on the spatial distribution of the five metals show considerable variations among stations but clearly indicate that Bridgeport and the Housatonic River are the foci of highest metal concentration along the Connecticut shore. New Haven Harbor, New London Harbor and Noank generally have the lowest concentration of most metals. Norwalk Harbor oysters tend to exhibit concentrations that are intermediate between the two extremes. Such a pattern of metal distributions, as anticipated, appears to be closely associated with the centers of industrial development along the coastal region of Connecticut. High concentrations of Co, Ni, and Ag in water samples from western Long Island Sound apparently associated with industrial effluent-laden rivers, have been reported by Turekian (1971).

Hg is the only element studied in our investigation that does not conform to the above-mentioned pattern of distribution. In fact, it is most concentrated in Noank and New Haven Harbor where the concentrations of other metals are generally the lowest. It is of interest to note that the total Hg concentration of Fishers Island Sound adjacent to Noank is the highest (0.078 ug/l) among the areas examined in the eastern Long Island Sound (Fitzgerald *et al.*, 1973). Clearly, further work is required to explain and identify the sources of Hg in Noank and eastern Long Island Sound in general.

To gain a broader perspective of metals concentrations in the oyster, data from Alabama, Georgia, Long Island Sound and the Atlantic coast from Maine to North Carolina are compared in Table 15. Zn in Connecticut oysters is seen to be in general agreement with concentrations reported for Maine to North Carolina by Pringle *et al.* (1968). The Atlantic coast and Long Island Sound oysters contain five times more Cu and Cd and twice as much Zn as the Mobile Bay oysters (Kopfler and Mayer, 1973). Furthermore, Zn concentrations in the northern oysters are one half times less and Mn 8 to 16 times less than in Georgia oysters (Windom and Smith, 1972). These variations encountered in east coast oysters probably reflect the degree of industrial pollution as well as geochemical composition of the water mass.

(Zu-Hg) was also observed in Noank oysters. In New London Harbor it was evident that Cu was the only element to exhibit a significant inverse correlation with Mn (Table 12).

III. Elimination and accumulation of metals in Bridgeport import maintained at Noank.

Attrition of metals, particularly Cd and Mn, has already been demonstrated in the oysters which have been transplanted from Norwalk to the three eastern stations, i.e., New Haven Harbor, New London Harbor, and Noank (Table 3 and 4). Further evidences were provided in this study to illustrate not only the attrition but also accumulation of heavy metals in the imported population at Noank. Changes in the concentrations of Hg, Cd, Mn, Cu, and Zn in the Bridgeport import as well as the Noank "native" during the first five-month period are shown in Fig. 1. During this period the transplants showed a 42% increase in Hg concentration above that of the base sample. At the end of eight months, the Hg content of the import was 205% of the original concentration, which approximated Hg content of the "native". Some interesting trends of attrition were also manifested in the import. Mn appeared to be the most labile of the metals investigated; its concentration decreased from 36.76 ppm to 12.33 ppm in five months, or a reduction of 66% of the original level, which was lower than that of the "native". During the same period similar trends of attrition of Zn, Cd, and Cu in the import were noted, but the rate of attrition of these three metals was approximately one-third of the rate of Mn depletion; the concentrations of Zn, Cd, and Cu were reduced, respectively, to 21%, 23% and 24% of the base sample.

IV. Distribution of metals in various oyster tissues.

An eight-month investigation of intraorganismal distributions of Hg, Cd, Mn, Cu, and Zn was conducted to ascertain whether different tissues exhibited special affinities for certain metals. Results on the tissue distribution of the five metals are shown in Table 14. While Hg and Cd were uniformly taken up by the adductor muscle, gill, mantle, and visceral mass ($P < 0.05$), there was a definite preferential uptake of Mn, Cu, and Zn by these tissues. In general, adductor muscles contained the least amount of the three metals and the mantle usually exhibited the highest concentration. However, this generalization did not seem to apply in the case of Mn; gill tissues contained significantly greater amounts of Mn (19.215 ppm) than the other three tissues ($P < 0.05$). Specifically, Zn and Cu concentrations were low in the adductor muscle, intermediate in the gill and visceral mass, and reached maxima in the

Perhaps the most revealing information derived from our study can be seen (Table 16) when these data are compared with those obtained by Galtsoff (1964) for the period 1933 to 1935. His samples were obtained from a commercial bed off Charles Island in central Long Island Sound. It is surprising to find that the orders of magnitude of Mn and Cu concentration are remarkably similar for the two periods, in spite of the difference in the sampling stations and in the analytical procedures employed in the two studies. Over the past 29 years, the median concentrations of Mn and Cu appear to have increased 50%, although the ranges remain essentially unchanged. Zn concentration has shown 177% increase over the years. Such changes are probably indicative of alterations in the environment presumably associated with anthropogenic activities.

There are at least three lines of evidence in our data which tend to support predilection of oysters for particular elements. Such evidences are manifested by (1) the presence of a significant interelement correlation among Cu, Cd, and Zn (Table 8-13), (2) the order of metal concentrations in oysters (Table 7), and the order of enrichment factors for the heavy metals investigated. The environment factor or concentration factor defined as

$$\frac{\text{ug element/gm wet weight tissues}}{\text{ug element/gm seawater}},$$

is frequently employed to express the accumulation of elements by organisms (see Goldberg, 1965). In the marine biosphere the concentration factors for metals are known to be closely related to the stability of complexes formed by divalent ions with ligands. According to Schubert (1954), the order of stability of the complex appears to increase with increasing basicity of the metal ion and is summarized as follows: $\text{Pd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Fe} > \text{Cd} > \text{Mn} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Ra}$. In our study the concentration factors for the oysters are: Zn, 305,800; Cu, 33,000; Cd, 10,200; Mn, 4,000 (?); and Hg, 1,100, which closely parallel the rank order of the above series. However, it should be pointed out here that not all molluscs studied showed similar patterns. For example, Brooks and Rumsby (1965) could not confirm this trend in New Zealand scallop, mussel, and oyster. They suggested that direct ingestion of particulate matter laden with heavy metals and adhesion of sediment on the gills could obscure the direct coordination bonds with suitable organic ligands. In our study, evidences for stability of Zn, Cu, and Cd complexes are further shown by the significant interelement correlation of the triad (Tables 8 to 13) and slow attrition rates of these metals in Bridgeport transplants maintained at Noank (21% to 24% decrease in concentrations in five months). Moreover, the relative lack

of stability of the Mn complex can be correlated with its high attrition rate (66% in five months).

Although the available data suggest that Zn is readily taken up by oysters, it appears to be only weakly bound to soluble oyster macromolecules. It has been demonstrated by Wolfe (1970) and Coombs (1972) in a series of in vitro experiments that 90% to 96% of the Zn is readily removed from extracted Crassostrea virginica and Ostrea edulis proteins by dialysis without apparently affecting the alkaline phosphatase of C. virginica, a zinc metalloenzyme. Romeril (1971) has reported that approximately 90% of ^{65}Zn is removed in the homogenates of C. angulata and O. edulis by dialysis against EDTA solution and deionized water in 7 days. Cu on the other hand is more firmly bound, only 43% of the metal is dialysable in O. edulis; no such information is available for the American oysters. The differential dialysability of Zn and Cu coupled with the lack of interelement correlations (except with Ca) has led Coombs (1972) to conclude that in O. edulis, the English oyster, different binding sites are involved in the uptake of Zn and Cu. No such inference regarding the binding site of these metals in the American oyster could be drawn at present for the lack of information.

In as far as the uptake of Zn, Cu, Mn, Cd, and Hg by various tissues is concerned, it is worthy to note that with minor exceptions, high concentrations are invariably associated with gill and mantle tissues which are known to be mucus-producing epithelia and in close contact with the sea water. The results, therefore, seem to support the contention that mucus sheet is the site for binding of polyvalent ions (Korringa, 1952).

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