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# ENVIRONMENTAL STUDIES OF PORT VALDEZ

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# ENVIRONMENTAL STUDIES

## OF PORT VALDEZ

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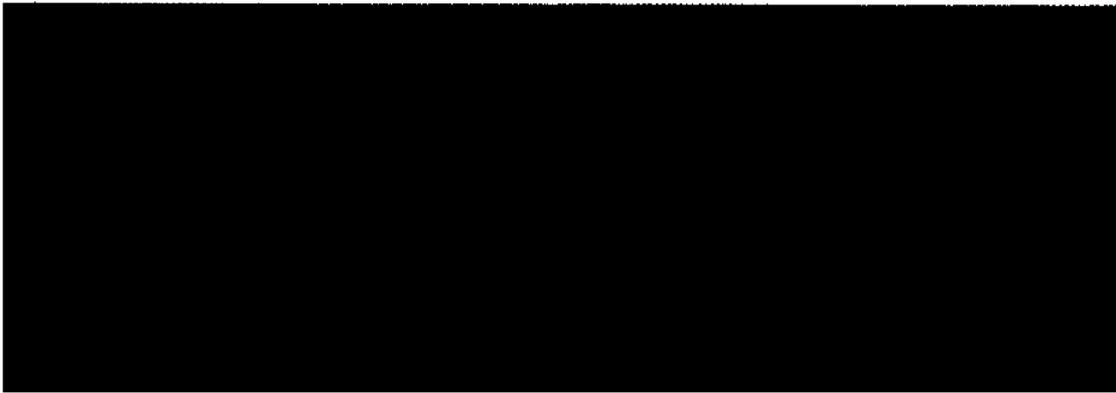
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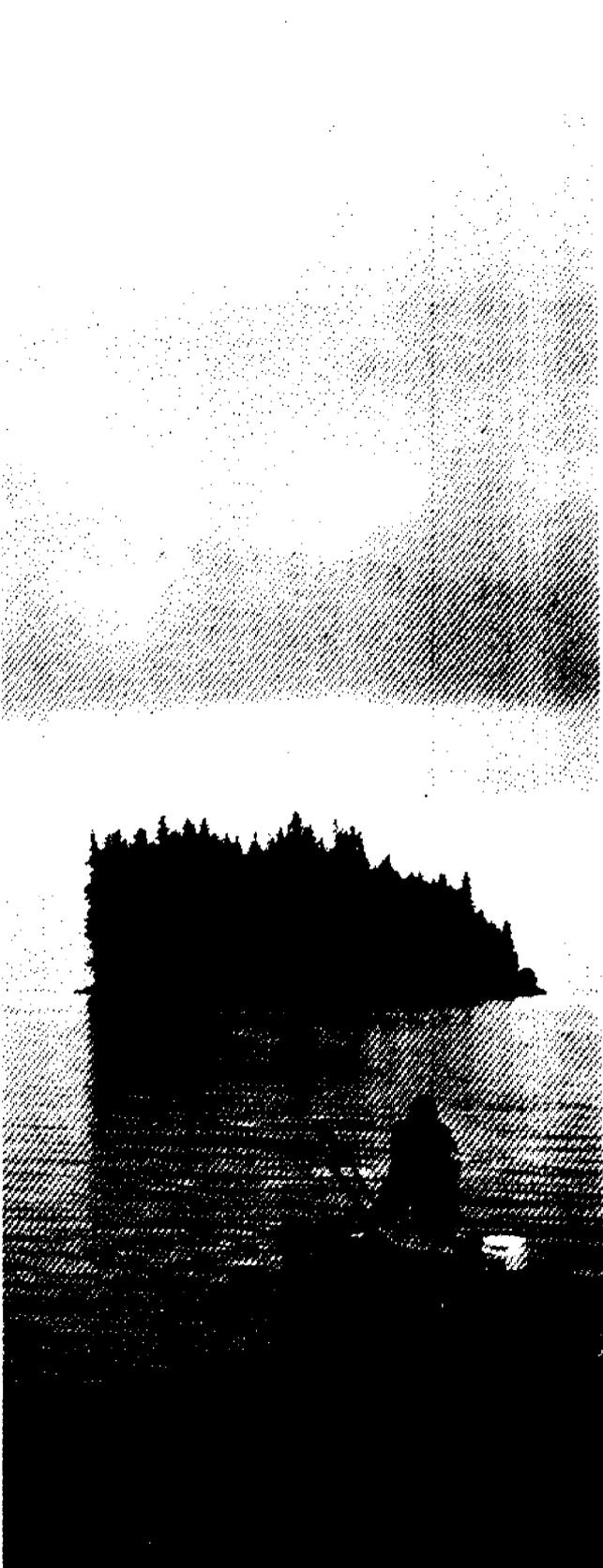
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Discharge of wastes into the intricately balanced marine ecosystem without significant disruption requires an accurate identification of the amounts and kinds of wastes, delineation of processes affecting their dispersal in the receiving waters, an understanding of their geochemical and biological transfer in the ocean, a determination of their effect on living organisms, and knowledge of their rates of ultimate decomposition or sites of deposition. These complex problems do not lend themselves to an exact solution but require a combination of experimentation and observation on the part of interdisciplinary scientists who are willing to estimate their conclusions, continuously taking a new look to test and verify their previous hypotheses. A short-term environmental evaluation of a waste discharge problem can be at best no more than preliminary. An intensive year's study such as the one reported here, however, does introduce a baseline perspective on which future testing and monitoring programs can be based in developing capability for predicting and regulating environmental effects.

A workshop on *Critical Problems of the Coastal Zone* held at Woods Hole Oceanographic Institution in May-June 1972 developed a philosophy concerning the discharge of wastes into the marine environment, published in summary as follows (Ketchum 1972):

*The aquatic ecosystem of the coastal zone has a finite assimilative capacity for a particular contaminant without significant deleterious effects. There are some who advocate that all waste discharge to a natural water system should be eliminated. This approach is neither technically feasible nor in the best interests of the public. The assimilative capacity of any particular part of the coastal zone is determined by such physical processes as currents and mixing, geomorphology, types of sediments, types of water chemistry, and biology. The "no waste discharge" approach ignores the fact that nature does provide for waste treatment without significant harm. The problem develops when man attempts to apply a certain waste load without giving consideration to the characteristics of the particular receiving area. Each region of the coastal zone should be considered on its own merit, its own uses and characteristics, and the contaminant load should be determined on a performance basis—an approach that requires a much better understanding of the aquatic ecosystem than exists today.*

It was on such a philosophy that the Valdez study was undertaken.

Initially the *Environmental Study of Port Valdez* was to be presented as a technical report of the Institute of Marine Science, University of Alaska, covering the work accomplished in a one-year study sponsored by the Alyeska Pipeline Service Company to provide a basis for determining the probable impact of treated ballast-water discharge on the waters of Port Valdez, Alaska. As the study developed, it became apparent that the significance of the approach and results to coastal zone management problems had broad general importance. Additional sponsorship for the project was then obtained through the National Sea Grant Program, the National Science Foundation through ship support, and with the aid of internal funds of the Institute of Marine Science to provide for a more complete study, the results to be more widely distributed in the form of this publication.

This study was directed toward obtaining a basic oceanographic understanding of Port Valdez and Valdez Narrows. The ultimate goal of such studies is to provide information which can be used in developing models to predict the effects of man's actions on the ecosystem and thus permit rational coastal management decisions.

Supplementary to this text, an 800-page *Data Volume I* has been published separately (IMS Occasional Publication 3A) in support of Chapters 1, 2, 4-7 and 9.

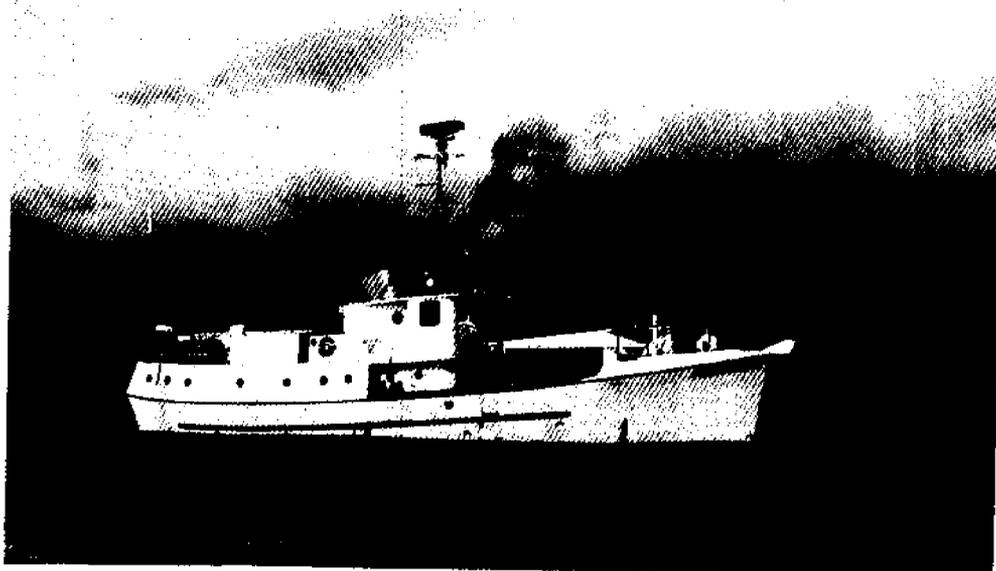
DONALD W. HOOD

Director  
Institute of Marine Science  
University of Alaska  
Fairbanks

1 July 1973

*...Port Valdez, a landlocked harbor with anchorage sufficient to accommodate the navies of the world. The temperature and depth of its waters are said to be such as to render it available as a harbor for ocean-going steamers during every day in the year...*

*Narratives of Explorations in Alaska  
Government Printing Office, Washington, D. C., 1900*



*Research Vessel Acona  
Institute of Marine Science  
University of Alaska*

The R/V Acona was built in Portland, Oregon, by the L. S. Baier Company and commissioned in 1961. At that time, the vessel was the first ship to be designed specifically for oceanographic research in America in more than 30 years. In 1969 she was extensively remodeled, adding five feet to her length and more than doubling her laboratory space. Owned by the Office of Naval Research, U. S. Navy, the Acona was assigned in 1964 to the Institute of Marine Science, University of Alaska, to support the oceanographic effort of the University. Although the prime vessel schedule and scientific programs are developed by the Institute of Marine Science, the Acona is part of the University National Oceanographic Laboratory System (UNOLS) and is thus available for use by the total oceanographic community of the United States.

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*Ship's Master in wheelhouse of R/V Acona*



*Port Valdez small boat harbor*

# ***Introduction***

by

D. W. Hood

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Ecological abuse through man's activities is no longer acceptable in a modern masterplan of quality survival. The dilemma of maintaining a satisfied society in a sound environment must look for rational solution in development of man's ability to accurately define and predictively monitor environmental tolerance levels in his managing for optimal but compatible utilization of natural resources.

As a first step in assessing potential stress to the marine environment by the addition of petroleum hydrocarbons, it is necessary to investigate the underlying stability and vitality limits of the natural system, considering not only its fragile aspects but its offsetting self-regulatory mechanisms as well.

## **Hydrocarbons: the world problem**

This topic has been the central theme of a recent book, *Impingement of Man on the Oceans* (Hood 1971), as well as that of several panel and workshop reviews: *Cleaning Our Environment - The Chemical Basis for Action* (ACS 1969); *Wastes Management Concepts for the Coastal Zone* (NAS-NAE 1970); *Marine Environmental Quality* (NAS 1971); *Man's Impact on the Global Environment* (SCEP 1970); *Environmental Quality* (CEQ 1971); *The Ecological Effects of Oil Pollution on Littoral Communities* (Cowell 1971); and *Baseline Studies of Pollutants in the Marine Environment and Research Recommendations* (IDOE 1972); and *The Water's Edge* (Ketchum 1972). Although many types of wastes are considered in these scholarly discussions, four groups are of primary importance to large-scale ocean contaminations: heavy metals, radioactive isotopes, chlorinated aromatic hydrocarbons, and petroleum. Of these, the introduction of petroleum into the environment has probably aroused the most public concern (Moss 1971). Petroleum is the raw material for the petrochemical industry and the major source of energy for society; the involvement of petroleum in the marine environment (SCEP 1970) is summarized below:

	metric tons/1969
World oil production (1969)	$1.82 \times 10^9$
Oil transport by tanker (1969)	$1.18 \times 10^9$
Injections into marine environment through man's activities	$2.6 \times 10^6$
Offshore oil production (seepage from wells)	$1.0 \times 10^5$
Tanker operations	$5.0 \times 10^5$
Other ship operation	$5.0 \times 10^5$
Accidental spills	$2.0 \times 10^5$
Deliberate dumping	$5.0 \times 10^5$
Refinery operations	$3.5 \times 10^5$
Industrial and automotive wastes	$4.5 \times 10^5$
Torrey Canyon discharge	$1.17 \times 10^5$
Santa Barbara blowout	$3.11 \times 10^3$
Atmospheric input from continents through vaporization of petroleum products	$9.0 \times 10^7$
Natural seepage into marine environment	$<1.0 \times 10^5$

Although the amount of petroleum reaching the marine environment is large, it must be placed in perspective by comparing it to the quantity of organic matter that occurs naturally in the sea (Ketchum 1972):

Primary productivity	$5 \times 10^{10}$ metric tons/yr
Dissolved organic matter	$3 \times 10^{12}$
Particulate detrital organic matter	$3 \times 10^{11}$
Living organic carbon	$7 \times 10^9$
Hydrocarbons	$3 \times 10^{11}$
Hydrocarbons produced by organisms	$1 \times 10^7$ metric tons/yr

Hydrocarbon compounds, some of them common to petroleum, are natural to the ocean system. Considering the whole ocean, the hydrocarbon quantities present are 100 times greater than the annual total world petroleum production, and the amount produced each year by the biota ( $1 \times 10^7$  metric tons) is several-fold greater than that injected into the ocean by man ( $2.6 \times 10^6$  metric tons). Many components found in petroleum, however, are not synthesized naturally, and many are toxic to marine organisms.

Crude oil contains about 350 different chemical compounds and as such is the most complex of the earth's raw materials. The physical and chemical properties of crude oil vary according to the source of the oil.

Experiments conducted in the past have indicated that toxicity is proportional to volatility and aromaticity. The most hazardous products are those containing high concentrations of aromatics. Low-molecular weight, highly volatile compounds are toxic but evaporate quickly in a typical spill situation and thus usually exert only little effect unless vigorously mixed in the water by wind or current action. All hydrocarbons are biodegraded, but the rate varies widely depending on the structure of the compound, organisms present, temperature, nutrients, and availability of oxygen.

Petroleum hydrocarbons have been found in marine biota under highly stressed environmental conditions; the effect of these retained compounds on the physiological processes of organisms has not been determined. A recent assessment of petroleum hydrocarbon contamination in the marine environment was obtained in a baseline study supported by the NSF Office for the International Decade of Oceanographic Exploration (IDOE 1972):

Collection data	HC concentration	Boiling range
Plankton — Louisiana coast (small tarballs in sample)	100 ppm (wet wt)	nC <sub>16</sub> -nC <sub>36</sub>
Seston, open ocean 2 samples North Atlantic 1 sample South Atlantic	0.3-20 ppm (wet wt)	nC <sub>16</sub> -nC <sub>28</sub>
<i>Sargassum</i> community (plants and animals), Sargasso Sea	1-34 ppm (wet wt)	
2 fish livers, Georges Bank	5 and 19 ppm	nC <sub>16</sub> -nC <sub>28</sub>
Water, Louisiana coast (1 sample)	0.63 µg/liter	nC <sub>16</sub> -nC <sub>34</sub>
Water, Gulf of Mexico (2 samples)	0.03, 30 µg/liter	nC <sub>1</sub> -nC <sub>3</sub>

### Crude Oil: the Alaskan scene

The discovery of a large oil field in Prudhoe Bay, Alaska, in 1969 was followed by a rapid succession of investigations on how best to distribute this oil throughout the market. The method proposed by the oil companies as most practical was a pipeline passing through the center of Alaska to Port Valdez, where the crude oil would be loaded into tankers and shipped to southern ports. The loading facility would be constructed on the south shore of Port Valdez near Jackson Point. Holding tanks, loading facilities, docks, and a ballast treatment plant to dilute ballast water of the tankers to less than 10 ppm before discharge into Port Valdez waters would be provided at this site. The planned operation would discharge a maximum of 800,000 barrels of ballast water containing less than 8 barrels of oil per day. Through process design, this oil would be in true solution or in finely divided suspended droplets. It would be discharged into the Port through a dispenser designed to assure optimal dispersal at a depth determined by oceanographic studies to provide the best mixing and transport in the Port waters.

The possible impact of this amount of oil discharged daily into Port Valdez waters is of great concern to many segments of society: the Alyeska Pipeline Service Company; those who use the Port for recreational purposes; fisheries interest, both in the Port and in Prince William Sound; the state and federal agencies responsible for environmental quality; and by others who have deep interest in maintaining healthy marine ecosystems. In order to obtain the information necessary to predict the possible effect of ballast water discharge and to provide a basis for monitoring these effects, the Alyeska Pipeline Service Company engaged the Institute of Marine Science, University of Alaska, to conduct a 1-year intensive oceanographic study of Port Valdez to observe its circulation; to measure dispersion at the outfall site; to compute the flushing rate; and to investigate the Port Valdez productivity regime, chemistry, benthic biology, and sedimentology. The following report is produced from data obtained during this preliminary background study.

### Port Valdez: the site

The fjord waters of Port Valdez form a 28-km northernmost projection of Prince William Sound, one of the largest tidal estuarine systems on the North American continent not presently influenced by coastal urbanization. The waters of Prince William Sound

connect with those of the rest of the world as shown in Figure A. About 3000 miles of predominantly primitive coastline encompass numerous islands and fjords in an area comparable in size to Puget Sound, Washington, yet populated by less than 5000 permanent inhabitants in the remote communities of Valdez, Cordova, Whittier and Tatitlek. Fringed from above by imposing glaciers, the deep narrow inlets of Prince William Sound are surrounded by precipitous mountains etched with perpendicular icy rivulets.

The town of Valdez, the only settlement on Port Valdez, was inundated by the Great Alaskan Earthquake of 1964 and rebuilt on higher ground approximately 9 km west of its original site on the north shore of the inlet. From historical prominence as the leading seaport for Interior Alaskan goldmining operations at the turn of the century, Valdez has shifted its economic base to commercial fishing and a seasonal tourist industry that boasts a heavy run of silver, pink and chum salmon during late summer months. A rich recreational resource framed in exotic surroundings guarantees Valdez continued success in attracting a wide range of tourists who arrive by the Alaska Marine Highway ferry system, excursion boats, airlines, and by surface vehicles down the scenic Richardson Highway.

Port Valdez opens to the southcentral Gulf of Alaska through Valdez Narrows and Prince William Sound. The renewable resources of Prince William Sound include prodigious but only partially exploited stocks of king, tanner and dungeness crabs; razor, butter and little-neck clams; scallops; and commercially important fish such as salmon, halibut, herring, flatfish, ocean perch, cod, and hake. Mammals are also represented substantially by species of seals, sea lions, sea otter and whales; bear and deer frequent the grassy beaches and fresh water streams. The local bird population is both diverse and abundant. At various times of the year the area is inhabited by over 130 avian species, about 60 of which contain tens of thousands of individuals, and another seven species have numbers in the millions. Prince William Sound is without a doubt a resource of unique dimension: a resplendent but reposing natural wealth as yet unassailed by unmanaged human use.

The Alaskan fjords typified by Port Valdez are *positive* estuaries, since they receive more fresh water by runoff and precipitation than is lost by evaporation (Pritchard 1952). The classical estuarine circulation of a seaward movement of a brackish surface layer and a landward movement of the deeper layers is exhibited. The theory of the circulation and structure of such fjords has been studied by Trites 1955; Tully 1958; Rattray 1967; Pickard 1967; Matthews and Rosenberg 1969; Quinlan 1970; Nebert 1972; and Matthews 1972. These authors have found that fjord circulation is nearly always sufficient for continuous, or at least frequent, renewal of the water within the fjord. Bottom waters in the Alaska fjords show a cyclic variation in their renewal. During the winter months, freezing air temperatures and limited fresh-water runoff cause a renewal of the entire water structure within the fjord. This is accomplished both by local thermocline conversion and by dense water inflow across the sill from outside. The result of these two processes is that the bottom waters are renewed each year during the winter. In addition, density flow may occur throughout the year in fjords with sufficient sill depth and under high tidal influence (Matthews 1972).

The Valdez area has a maritime climate partially altered by the surrounding mountains. The ocean moderates the climate, which is characterized by mild winters and cool summers, with many cloudy days and high precipitation.

Mean temperatures range from 7 to 13C during the summer months and from -10 to -4C during the winter months. A maximum daily temperature exceeding 20C occurs on the average of only four days per year and a minimum temperature lower than -18C occurs on the average of only fifteen days per year. The record minimum temperature is -34C.

The steep mountains on both sides of the fjord channel the wind into a general east-west direction with the wind prevailing from the southwest during the months of May through September and from the northwest during the remainder of the year.

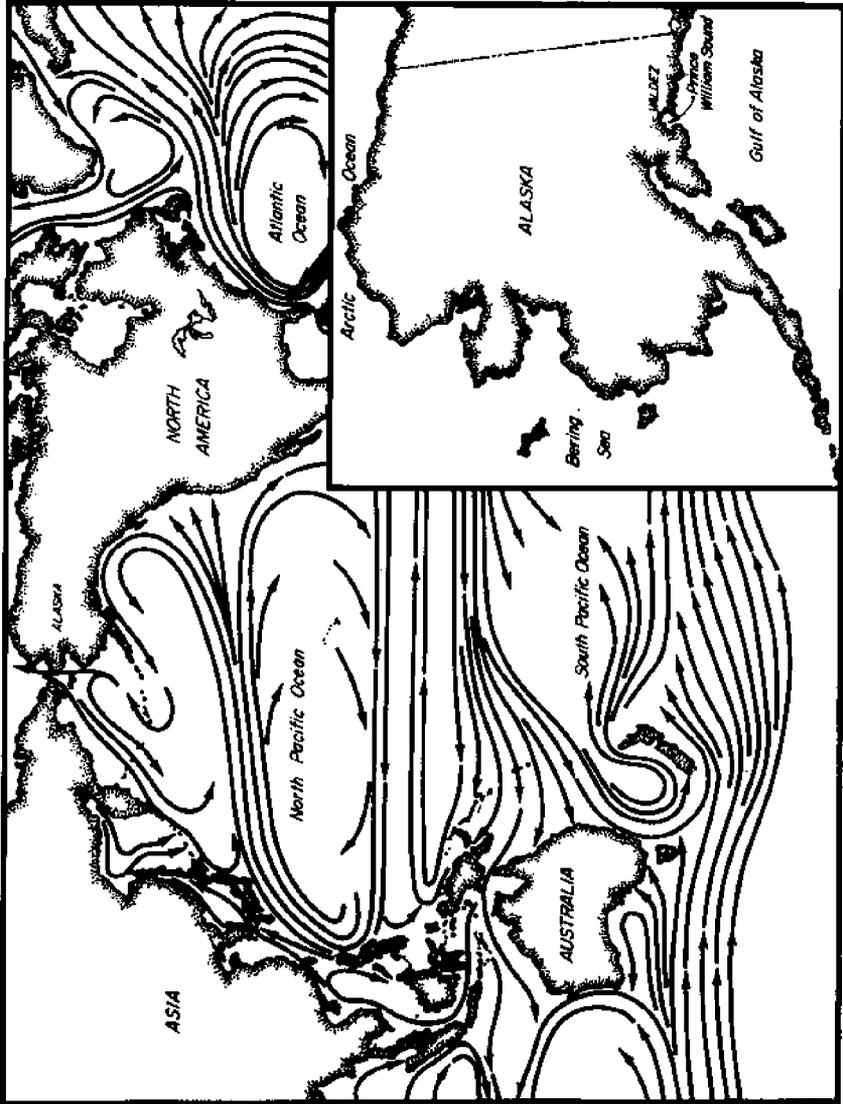
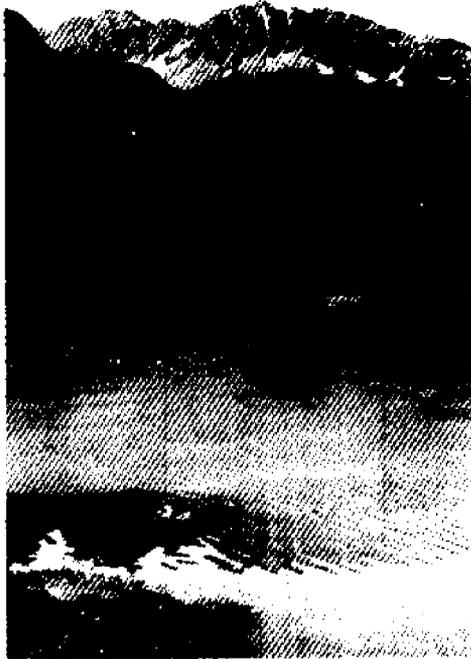


Figure A. Major currents of the Pacific Ocean (insert map shows location of study area).



hillside of proposed tank farm site

**JACKSON POINT**  
proposed pipeline terminus in Port Valdez

shoreline near proposed docking facility



The mean annual precipitation at Valdez is 158 cm (62 inches). August through November is the wettest period with almost one half the annual precipitation. Daily precipitation  $>0.25$  cm (0.1 inch) occurs during an average of 120 days per year, and a clear sky occurs only one day in six. A considerable portion of the precipitation occurs as moist dense snow resulting in a mean annual snowfall of 245 inches.

At present, there are only two known domestic waste discharges into the Valdez estuary—the outfall from the city waste treatment plant and the effluent from the septic tanks serving the State Ferry Terminal.

Waste-flows from the State Ferry Terminal septic tank have a chemical oxygen demand (COD) of less than 30 mg/liter, which indicates a quality that would have little biological or chemical effect on the estuary.

The waste discharge from the city of Valdez has an average daily flow (taken on a monthly basis) of between 90,000 and 255,000 gallons per day. The large flows are caused by groundwater infiltration, particularly during the spring and fall rainy seasons. Fortunately, groundwater infiltration to the sewers helps to dilute the waste before it reaches the estuary. Other sources of waste, such as outfalls from local fish processing or from ships using the port, are considered insignificant if controlled to avoid pollution of local areas such as the small boat harbor.

It appears that the effect of the total municipal waste discharge is not significant to the whole of Port Valdez. Local effects, however, were noticed during the fall sampling period. Samples obtained approximately 10 m from the outfall site at various depths showed COD values of 470 mg/liter at the bottom, 378 mg/liter at the 1.5 m depth, 165 mg/liter at the 0.75-m depth, and 50 mg/liter at the surface. The outfall at slack tide was overlain by about 2.1 m of water. There was only minor evidence of floating oils and scum in the vicinity. The data indicate that the high oxygen demand loads are near the bottom and could result in oxygen depletion in this local area.

A strong divergence of public attitude exists with respect to the future of Port Valdez and Prince William Sound. While interests at one end of the scale are adamant in protecting the area from further development altogether, there are others who favor exploitation to the degree that is economically feasible. As idyllic as total preservation may appear, the inevitability of Alaskan development dictates that Prince William Sound is soon destined to play its part in meeting a growing society's increasing demands for food, services and commodities. Alaska is a vast resource which many people feel can be utilized to best advantage by developing multiple uses compatible with a rationally determined degree of environmental maintenance. Accepting this middle approach of concerned development, it is necessary to gain a keen knowledge of how the natural environment functions, what stresses it can accept without significant change, and how changes imposed upon it may affect the various elements of the ecological system.

### **This project**

Work on this project was undertaken on 1 May 1971 under sponsorship of the Alyeska Pipeline Service Company. At a later date additional funds were obtained from the Sea Grant Program and the Institute of Marine Science, University of Alaska. The project was designed to obtain critical environmental data on Port Valdez, Valdez Narrows and the approaches to this system in Prince William Sound. Extent of the field study was limited to about a 15-month period compatible with the personnel, facilities and funds available. Emphasis was on acquisition of baseline data against which future monitoring could be based and assessment of the oceanographic features of this system essential in predicting the impact of future additions of contaminants, particularly as related to a crude oil tanker loading and ballast treatment facility. To reach these major goals, an integrated interdisciplinary approach was taken by the Institute of Marine Science, utilizing the *R/V Acona* as the major field facility and the laboratories at Fairbanks and aboard the *R/V Ursa Minor* moored in Valdez for the analytical work.

The major field work initiated in May 1971 was continued on an approximately bimonthly basis through April 1972 on cruises of approximately 10 days duration each. Stations were selected throughout the region indicated in Figure 2.1 and 2.2. Additional field work was undertaken to collect background geological data during the summer of 1972.

Geological studies with particular reference to sediment distribution, suspended sediments and correlation of sediment distribution with water circulation and types of benthic organisms present are described in Chapter 1.

Hydrographic stations shown in Figure 2.1 were occupied on six cruises during this study for measurement of salinity, temperature and oxygen at standard oceanographic depths. The dilution rate or dispersion of water in the vicinity of the ballast treatment outfall site at three locations near Jackson Point was determined by the use of rhodamine-B dye injected at depths of about 2.5, 15, 23 and 30 m (8, 50, 75 and 100 ft). In addition, current drogues and meters were used to the extent feasible for direct measurement of circulation in the fjord. From these studies, a general description of the circulation of the estuary, dilution rates at the outfall site, and rates of flushing into Prince William Sound were determined. This work is discussed in Chapters 2 and 3.

Chemical studies were made of pH, alkalinity, total carbon dioxide, oxygen and nutrients. These data were obtained in association with productivity stations and are described in Chapters 4 and 5.

Primary productivity measurements were made at selected stations on each cruise to determine the net photosynthesis occurring at the various depths related to the penetration of incident light. The phytoplankton species responsible for the photosynthesis were also determined at representative stations. Some identification was made of zooplankton species that comprise the secondary producers or phytoplankton grazers obtained in net hauls at the productivity station. The results of these studies are presented in Chapters 6, 7 and 8. The major benthic infaunal associations are identified and assessed in Chapter 9.

Hydrocarbon analysis of water, sediments and organisms of Port Valdez and measurements of the biodegradation information on the levels of hydrocarbons added to this system were studied to give background information on the levels of hydrocarbons present in the system and the ability of indigenous organisms present to decompose added quantities. The toxicity of Prudhoe Bay crude oil to the phytoplankton indigenous to Port Valdez was examined to determine the level of contamination which would be inhibitory to photosynthesis. The results of these studies are presented in Chapters 11 and 12.

The summary synthesizes the findings in an attempt to relate all sections of the report to the central question: what are the flushing rates, water distribution, chemistry, hydrocarbon content and living organisms occurring in Port Valdez at the present time, and how might these be affected by the expected crude oil additions to Port Valdez due to treated ballast-water effluent?

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# PART I

## THE PHYSICAL BASELINE



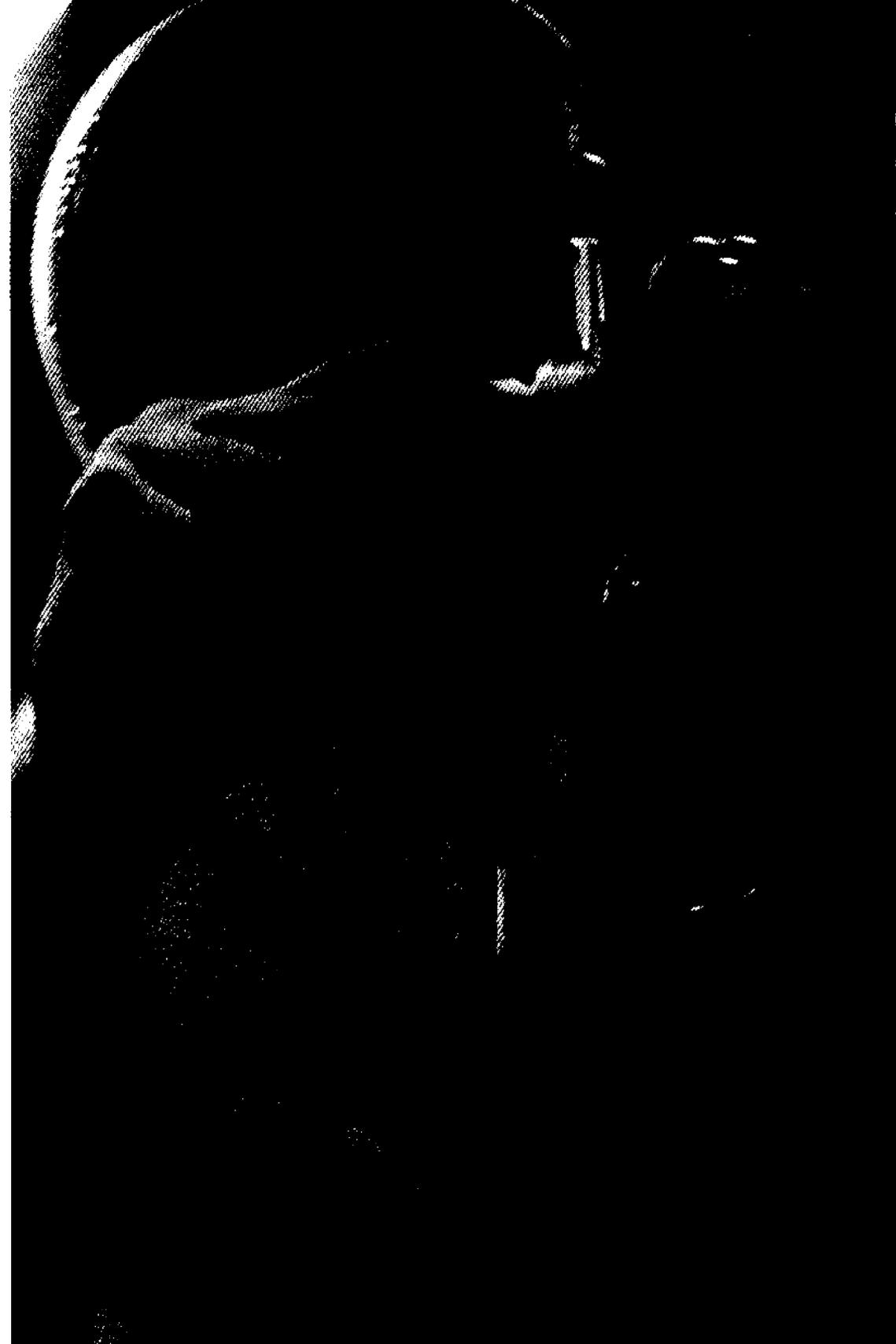
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# *Chapter 1*

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## GEOLOGICAL OCEANOGRAPHY





## 1. GEOLOGICAL OCEANOGRAPHY

by

G. D. Sharma and D. C. Burbank

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### 1.1 Introduction

#### 1.1.1 Location and area description

Located in the northeastern part of Prince William Sound (Figure 1.1), Port Valdez is a relatively deep, narrow, glaciated re-entrant or fjord indented in the high, rugged Chugach Mountains. Its main physiographic features are typical of an ice-sculptured landscape and show vividly the extensive glaciation and tectonism of the recent past. Port Valdez trends east-west approximately 21 km in length and 4.5 km in width. The axial alignment of the Port is the outcome of a strongly developed, steeply dipping foliation in the basement rocks. The fjord has steep rocky shores, the high-angle slope of which extends beneath the water to form a steep-walled, flat-bottomed trough with maximum depths of about 240 m (131 fathoms) (Figure 1.2). Near the mouth of the fjord, the Valdez Narrows form a nearly right-angle constriction (about 1.5 km wide) with two sills.

Near its head, Port Valdez is fed by the Lowe and Robe rivers and by the Valdez Glacier Stream. These waters have formed an extensive Valdez outwash delta upon which the town of Old Valdez was located. The new town of Valdez is located on an alluvial fan deposited by Mineral Creek. Both the Valdez outwash delta and the Mineral Creek alluvial fan consist of poorly consolidated alluvial and glacial deposits of silt, sand and gravel. Large tidal flats have formed at the seaward edge of these deltas because of the relatively high tidal range 5.5 m (18 ft) and the large amounts of fine sediments provided by the streams and rivers.

#### 1.1.2 Geological setting

The exposures in the vicinity of Port Valdez (the Valdez Group) consist primarily of gray or bluish-gray graywacke, argillite, and bluish-gray or black slate (Moffit 1954), which are metamorphosed derivatives of the muds and feldspathic sands (of variable proportions of quartz and feldspar) that were deposited during the late Mesozoic era. The closely folded beds exhibit varying degrees of metamorphism transforming slate and graywacke into phyllite and schist. Extensively fractured rocks are traversed by a complicated network of quartz veins which vary considerably in size.





The rugged shoreline of Port Valdez displays a remarkable uniform composition and structure. Exposures include interbedded, dark gray to black, hard, slaty shales and dark gray, hard, fine-grained shaly siltstones with quartz veins. The thin-bedded texture is accentuated in weathered sections exposed along the shoreline. The strike of the bedding in Port Valdez is east-west with an average dip of about  $55^\circ$  to the north; the fjord appears to lie on a monocline. The entire section exposed in Port Valdez consists of a network of complex fractures, the most important of which are oriented perpendicular to the strike. These structural features have strongly influenced the present north-south orientation of most streams entering Port Valdez.

During the ice ages glaciers moved from the higher areas of the Chugach Mountains into the Valdez area and thence west and southwestward into Prince William Sound. Glacial excavation of the lowlands resulted in generally irregular topography; however, ice-stream movement produced the channel-like depression of Port Valdez, the largest and deepest channel in the Prince William Sound area. The thickness of the ice flow in Port Valdez varied, although evidence of glaciation has been found as high as 975 m above sea level (Tarr and Martin 1914, p. 469).

During the recession of the glaciers, the channel was filled with morainal material that blanketed the steeply dipping bedrock. Three acoustic units - lower, middle and upper - were revealed on seismic records from Port Valdez (von Huene et al. 1967). The highly reflective lower unit represents the slate and graywacke basement rock of the Valdez Group and can be traced to its land exposure. The intermediate unit consists of unconsolidated glacial drift and marine sediments. The evenly bedded upper unit represents sediments deposited during post-glaciation and marine transgression. The total thickness of the intermediate and upper units in Port Valdez is estimated to be about 400 m (Figure 1.3).

### 1.1.3 Bathymetric features

Bathymetry is an integral and important part of geological and biological studies. The bottom topography exerts a significant influence on the nature and rate of sedimentation, the biological habitat and the hydrological circulation.

The salient bathymetric features in Port Valdez are extensive steep, rocky shores and deltaic deposits with tidal flats in the east (Figure 1.2). The gradient of delta deposits is significantly lower than that of the rocky shores. A submarine valley, here called the Valdez Channel, originates in the vicinity of Old Valdez and terminates about 3-4 km west near two topographic highs (submarine fans), the easternmost of which is named Valdez Fan II and the westernmost Valdez Fan I. Similar topographic highs are found south and southeast of the entrance to Shoup Bay. The southeast topographic high is named the Cliff Mine Fan. The bottom topography of the greater part of Port Valdez is remarkably flat, varying between 230-250 m (126-137 fathoms) in depth. At the mouth of the inlet there is a narrow constriction with two sills, the outer sill being the shallower (110-128 m or 60-70 fathoms) of the two. In general, the morphology of Port Valdez is typical of a glaciated fjord: a U-shaped valley with a flat bottom and a complex sill near its entrance.

### 1.1.4 Weather

The local terrain surrounding Port Valdez has a strong influence on the weather. The snow-covered Chugach Mountains feed glaciers which descend to within 8-16 km of Valdez. The rugged mountains extend from southeast of Valdez to north to west-southwest. Due to the configuration of these mountains, local winds are channeled into two distinct directions. Prevailing winds during winter (October-April) are from the northeast, and those in the summer (May-September) are from the west and southwest. The winds from the northeast are gusty and produce gales. Locally, down-slope winds commonly known as the *williwaw*

are caused by the rapid downhill flow of cold dense air formed at the top of the mountains. This flow occurs along the valleys or low cuts in the terrain. These air slides are weakened significantly after they reach sea level and dissipate rapidly with increasing distance from shore.

The dominance of cold dense air from the mountains results in a rise of barometric pressure and movement of clouds from north to south, followed by clearing skies. On the other hand, the advance of a Gulf of Alaska low into the region is accompanied by falling barometric pressure and increasing cloudiness (clouds moving from southeast to northwest) with precipitation.

The average mean temperature in Port Valdez varies from about -3C in January to about 16C in July. The coldest temperatures occur during the settling of cold air with no wind movement. The extreme continental climatic conditions are modified by the high mountains which block movement of cold arctic air into the region during winter. Summer temperatures, modified by snow fields and Port Valdez waters, seldom reach 30C.

Port Valdez is generally under a cloud cover, and only about 1 day in 6 can be classified as clear. The precipitation at Valdez averages about 152 cm/year. The dry month is June with an average precipitation of about 5 cm, whereas the maximum precipitation of over 23 cm occurs during September.

### 1.1.5 Cruise operations

A joint cruise for geological and biological sampling was conducted aboard the *R/V Acona* during 20-30 September 1971. Sixty-two stations were occupied, and bottom grabs were retrieved for biological and geological studies. Piston cores from selected stations (Figure 1.2) were taken for laboratory analysis, and water samples from various depths were collected at 19 stations for determination of the suspended sediment load. Sediment samples from 21 stations were obtained for determination of hydrocarbon content. Chemical parameters such as pH, Eh and temperature of sediments from grab and core samples were routinely measured on board ship.

Stations during the initial cruise (20-30 September 1971) were located uniformly throughout Port Valdez to provide full coverage of the area and to allow determination of lateral variations in sediment parameters that could be easily compared between adjacent stations. During the subsequent cruises of 20 March 1972 and 11-14 May 1972, station locations were chosen for specific study objectives such as deposition rates, sediment transport and deposition during various tectonic activities in the area, and formation of submarine fans. Station locations in Port Valdez and vicinity are shown in Figure 1.2.

Twelve gravity and piston cores were retrieved on 20 March 1972. Sampling was designed to study the sediment variations and depositions on the topographic highs in Port Valdez. A 4-day cruise during the period 11-14 May 1972 was conducted to obtain additional bottom grabs and gravity cores from topographic highs to determine rates of deposition in Port Valdez. A total of 24 piston and gravity cores and 14 bottom grab samples were retrieved for sediment analysis.

To supplement the suspended sediment sampling from aboard the *R/V Acona* in September 1971, suspended sediments were collected from a small boat at approximately 1-month intervals during the summer of 1972 (14-21 June, 5-14 July, 29 July-7 August, 31 August-5 September and 28-31 October). During these periods, sampling was conducted from a 14-ft speedboat that provided the capability to cover an extensive grid of surface stations throughout Port Valdez, the Narrows and Shoup Bay within 3-4 hours. Portable equipment was used to measure salinity and temperature to a depth of 13 m and light transmissibility down to 50 m. A hand-operated winch with a single messenger-triggered sample bottle was used for collecting suspended sediment and for measuring temperature at depth.

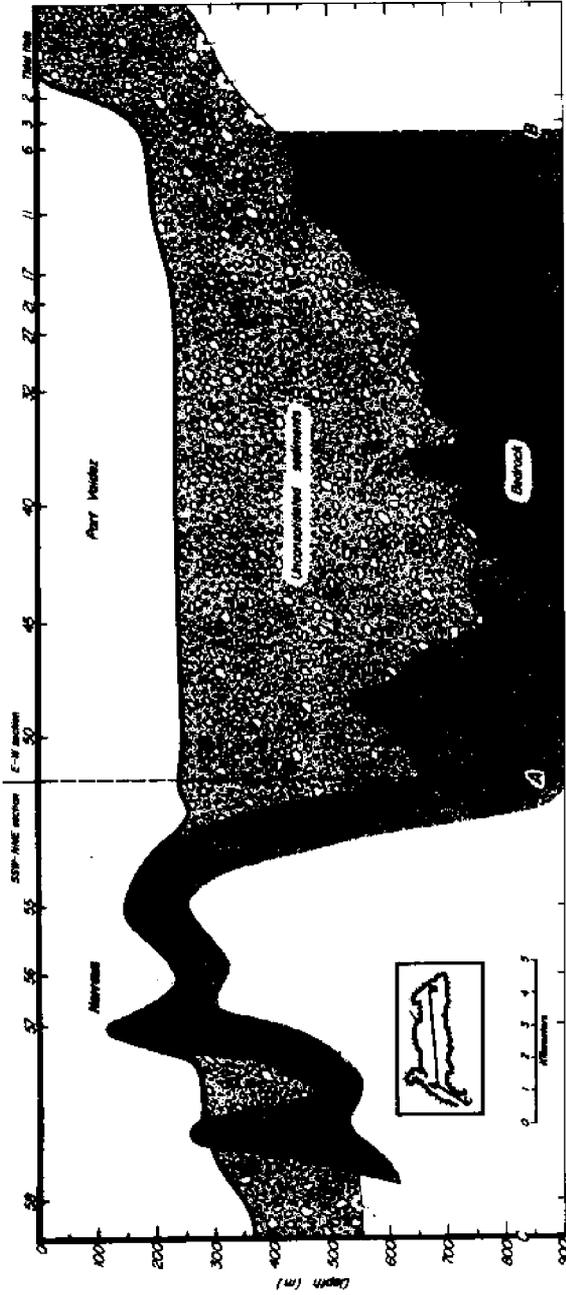


Figure 1.3 Vertical cross-section of Port Valdez and Valdez Narrows. The profile is based upon seismic records and bottom samples. Numbers at the top of the profile refer to core sampling locations, R/V *Aconaz* cruise 20-30 September 1971.

Suspended sediment samples, temperatures, and approximate water discharge rates of rivers and streams draining into Port Valdez and Shoup Bay were also obtained in order to better delineate sediment sources and their relative importance.

#### 1.1.6 Previous studies

Earlier investigations in Port Valdez and vicinity were confined to bathymetry, surface geology and seismic-reflection profiles. Little or no information was available concerning the bottom sediment distribution in Port Valdez. Pilot charts for navigation in the region were available from the U.S. Coast and Geodetic Survey (Charts Nos. 8515, 8517, 8519, 8520 and 8551). On the basis of these charts and additional soundings in Prince William Sound, the glacier movement and thickness of Pleistocene ice in the region had been described (Bean 1911; Tarr and Martin 1914). Reconnaissance was conducted of the exposed-surface geology and glaciology in Prince William Sound, (Grant and Higgins 1910, 1913; Moffit 1954) and the surface geology of Port Valdez was described in detail (Moffit 1954).

The aftermath of the devastating Great Alaskan Earthquake of 27 March 1964 necessitated extensive studies of bathymetric changes, coastal sediments and potential danger of sea waves generated by submarine slides or tsunamis. Plafker and Mayo (1965), Coulter and Migliaccio (1966) and Plafker (1969) studied the effects of the 1964 earthquake on Port Valdez and vicinity. A series of continuous seismic-reflection profiles of Port Valdez and Prince William Sound was obtained during the 1964 Kayak Expedition of the Scripps Institution of Oceanography (von Huene et al. 1967).

#### 1.1.7 Objectives

The study reported herein was conducted to obtain baseline geological parameters needed to synthesize ecological information on the Port Valdez environment. The results obtained from this and associated studies would serve as a reference basis for the evaluation of future development impact on the area. Geological data obtained in these studies would also be used to elucidate the benthic faunal distribution in Port Valdez. Aspects of geological investigations conducted in Port Valdez included bathymetry; sediment characteristics and distribution; sediment transport; and environment of deposition.

In describing the Port Valdez sediment distribution in this report, emphasis has been directed to the source, transport and various environments of the sediments deposited in the area. For meaningful inference, detailed descriptive analyses were made of core and suspended sediments, including those from rivers and streams, as well as routine study of bottom grab sediments. Both the lateral distribution of surficial bottom sediments and the subsurface sedimentation are discussed, including estimates of sediments contributed by various rivers and subaqueous slides.

### 1.2 Field Methods

#### 1.2.1 Grab sampling

Bottom surficial sediments were obtained during the September 1971 cruise by means of a modified van Veen grab sampler. Three sediment samples were collected at each station, and subsamples for analyses were obtained by inserting a 5-cm (outside diameter) tube into the top of the sediments to a depth of 15 cm. The Shipek bottom grab sampler was used during the May 1972 cruise, and representative sediment cuts were taken for further analysis.

### 1.2.2 Core sampling

A modified Ewing piston corer, fitted with a 5-cm (2 inch) o.d. core liner, was used to retrieve piston cores. Gravity cores, which generally gave less penetration but assured retrieval of undisturbed surficial layers of sediments, were taken using both a 5-cm (2 inch) o.d. corer and the small Phleger corer. The capped and sealed cores were transferred to the Fairbanks laboratory for further study.

### 1.2.3 Water sampling

Water samples from the surface and various depths were obtained by Nansen and Niskin bottle casts from aboard the ship. Additional sampling from a skiff necessitated use of a hand winch and an open-end water sampler triggered by a messenger.

### 1.2.4 Salinity and temperature measurements

A portable Beckman Model RSS-3 Salinometer was employed for measurements of temperature and salinity down to its depth capability of 13 m. Surface-water temperatures were determined with a partial immersion mercury thermometer. In the case of water samples obtained from depths >13 m, temperature was measured with a full immersion mercury thermometer contained within the open-end water sampler, and salinity measurements were made in the laboratory using a Bissett Berman Model 6230N inductive salinometer.

### 1.2.5 Light transmissibility determination

A Hydroproduct Model 410-BR Transmissometer was used to measure percent light transmissibility (through a 10-cm light pathlength) down to a depth of 50 m. The instrument was calibrated to read 100 percent transmission in clear water.

### 1.2.6 Water discharge estimation

Approximate estimates of water discharge of various rivers and streams were made by observing the velocity of water and the area of discharge of the stream. The stream velocity was measured by the movement of flottage in midstream, and the area of discharge was computed from the depth and breadth of the stream. These estimates are close to those reported in previous years by the U.S. Geological Survey and by the Institute of Water Resources at the University of Alaska (Carlson et al. 1969).

Suspended sediment samples from rivers and streams, sampled at the water surface approximately 0.6 m from the riverbank, were obtained at locations where the water was turbulent and flowing rapidly such that suspended sediments were in a fairly uniform suspension from bank to bank and from surface to bottom.

### 1.2.7 pH and Eh measurements

Instruments used to measure pH and Eh consisted of a Photovolt Digicord pH/Eh Meter, an Orion Model 404 Specific Ion Meter, and a battery-operated Instrumentation Laboratory Portomatic pH Meter. The measurements, checked and counterchecked by using different electrodes on each meter, were found to be stable and identical.

### 1.2.8 Bathymetry

The station depths were routinely recorded on board ship by use of a Ross Precision Depth Recorder. Various depth profiles were obtained to further delineate the bottom structures in the Narrows, and several traverses over topographic highs were made by the *Acona* to determine the configuration of submarine fans resulting from subaqueous slides.

## 1.3 Laboratory Methods

### 1.3.1 Textural analysis

Sedimentological analyses were carried out according to the methods of Folk (1961). Sediment samples were treated with  $H_2O_2$  to remove organics. Sand and gravel that had first been fractionated by wet-sieving was next dry-sieved, and pipette analyses were run on the silt and clay fraction. Sediment grain size parameters were computed using formulas described by Folk (1961).

### 1.3.2 Core analysis

Cores were brought to the laboratory, split lengthwise, photographed and described. Cuts were taken at various depths in each core, and size distribution analyses were performed to determine the textural variations within each core.

### 1.3.3 Organic carbon analysis

Sediment samples were finely ground, treated with HCl and dried at 40C. The carbonate-free powdered samples were dried again, and 50-100 mg of each sample was weighed and placed into a porcelain boat for combustion analysis. The samples were combusted with oxygen at 800C, and the total  $CO_2$  evolved was measured using a Beckman Model 315B Infrared Analyzer (Menzel and Vaccaro 1964).

### 1.3.4 X-ray diffraction analysis

Mineralogical composition and ratios of clay minerals ( $<4\mu$ -particle size) of selected samples from bottom grabs and cores were determined with a Norelco X-Ray Diffractometer. Relative amounts of clay minerals were computed from the relative peak heights of the X-ray diffractograms.

### 1.3.5 Measurement of suspended sediment load

One liter of water sample was filtered through preweighed 47-mm Millipore filter paper (HAWP 04700, HA 0.45- $\mu$  Millipore) which had been dried for 3 hours in a desiccator. The material retained on the filter paper was air-dried and then desiccated overnight prior to being weighed and reported in mg/liter.

## 1.4 Results

### *General bathymetry*

The general contoured bathymetry of Port Valdez and the Narrows shown in Figure 1.2 is based on data obtained from cruises conducted during this study, together with survey data provided by the Alyeska Pipeline Service Company.

## Surface sediments

### 1.4.1 Introductory remarks

Three major units of surficial deposits are recognized in Port Valdez (Figure 1.4). (1) The inshore sediments at the mouths of the Lowe River, Valdez Glacier Stream and Sawmill Creek, as well as the sediments in the Narrows, are mixtures of silt, sand and gravel. (2) An elongated narrow area extending west-northwest from the head of the inlet to Mineral Creek and Gold Creek is covered by fine to very fine silt. (3) The predominant unit covering the rest of Port Valdez consists of coarse clay.

Port Valdez sediments vary from poorly sorted to very poorly sorted (Figure 1.5); the finer sediments generally are better sorted. The size distribution of most sediments in the Port is positively skewed to very positively skewed (Figure 1.6) and mesokurtic to leptokurtic (Figure 1.7). (Field descriptions of individual samples and the results of size distribution analyses are listed in Data Vol. I: Tables 1.1 and 1.3).

The percent sand-gravel, silt and clay distribution in sediments of Port Valdez is shown in Figures 1.8-1.10 and tabulated in Data Vol. I: Table 1.4. Most sediments are silty clay or clayey silt (Figure 1.11). The uniformity of the depositional environment and the sediments within Port Valdez is further reflected by the scatter plots of various sediment parameters (Figures 1.12-1.15).

### 1.4.2 Eh and pH (of surface sediments)

During the *R/V Acona* cruise of 20-30 September 1971, the hydrogen ion concentration (pH) was measured at each sampling station about 5 cm below the sediment-water interface and ranged from 6.6 to 8.0 throughout the Port (Figure 1.16; also Data Vol. I: Tables 1.1 and 1.2). The general distribution of pH showed no obvious pattern and no relation to sediment size distribution.

The redox potential is a quantitative measure of the state of oxidation or reduction of a reversible oxidation-reduction system and is termed Eh with reference to a standard hydrogen cell. The Eh of samples collected during the September 1971 cruise was measured at a depth of approximately 5 cm at each station. Values ranged from +18 to +399 millivolts (mv) (Figure 1.17; also Data Vol. I: Table 1.1). Coarse sediments from shallow depths are generally characterized by potentials varying between +150 and +350 mv, whereas Eh variations in finer sediments from deeper water typically ranged from +50 to +150 mv. The western half of the Port was covered by a 2-mm layer of brown oxidized sediment. The variation of Eh with depth within the sediment was measured in greater detail during May 1972 cruise (Data Vol. I: Table 1.2). The Eh in the top 1-2 cm was consistently much higher (typically +350 to +450 mv) than that measured deeper in the sediment; below 2 cm the Eh values in the sediment decreased rapidly with sediment burial and stabilized at about 5 cm from the sediment-seawater interface.

It was noted that the Eh and pH values of the overlying waters were similar to those of the sediments close to the depositional interface. Due to various changes which took place in the sediments during the process of their retrieval and on-board measurement, the parameters of pH and Eh are described only semi-quantitatively at best. In support of the data obtained during earlier cruises, however, these measurements do indicate that highly oxidizing conditions prevail at the sediment-seawater interface and decrease appreciably with increasing depth in the sediment. The thin, highly oxidized layer prevalent in the western half of the Port is due perhaps to the oxygen-rich ocean water originating in the well-mixed shallow Prince William Sound region and carried into Port Valdez by tides. The boundary of the oxidation-reduction layer in Port Valdez lies beneath the sediment surface, thus forming an oxidizing environment at the sediment-seawater interface.

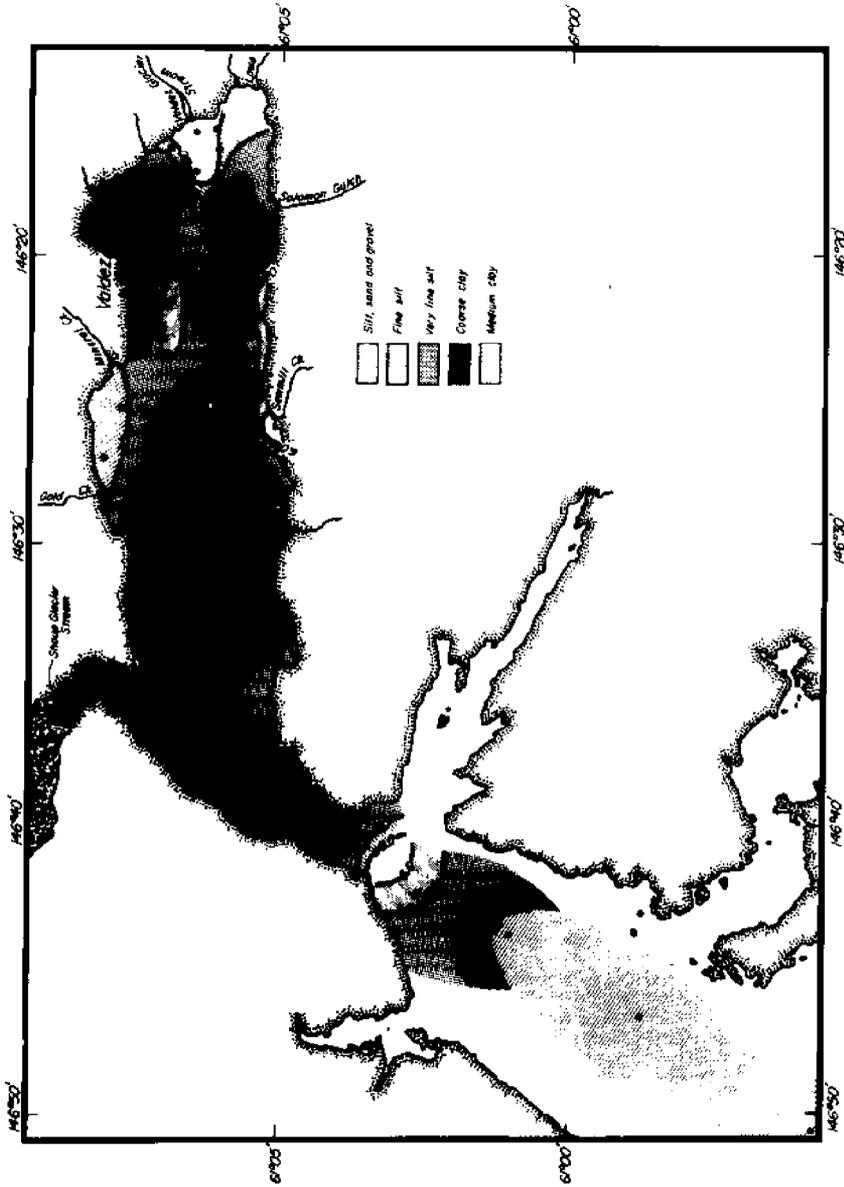


Figure 1.4 Mean size ( $M_z$ ) variation of surficial bottom sediments in Port Valdez.

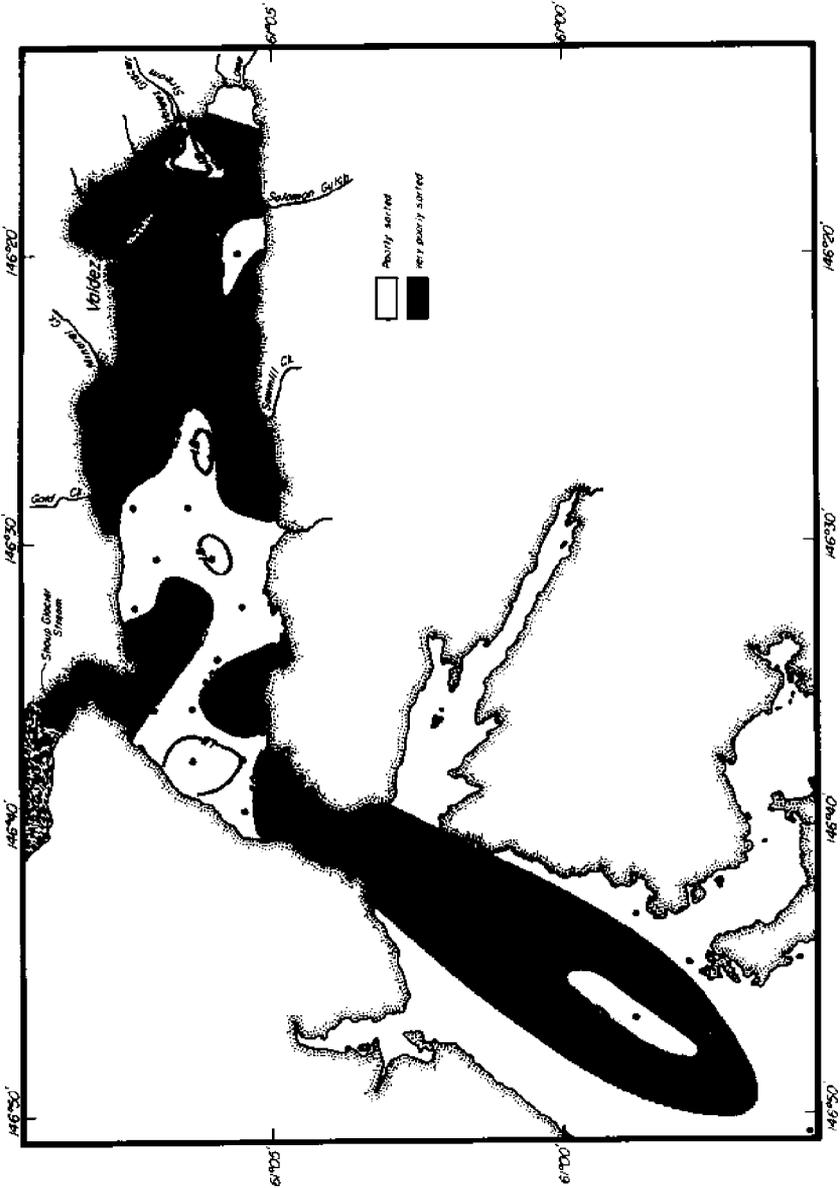


Figure 1.5 Sorting ( $\sigma_1$ ) in surficial bottom sediments in Port Valdez.



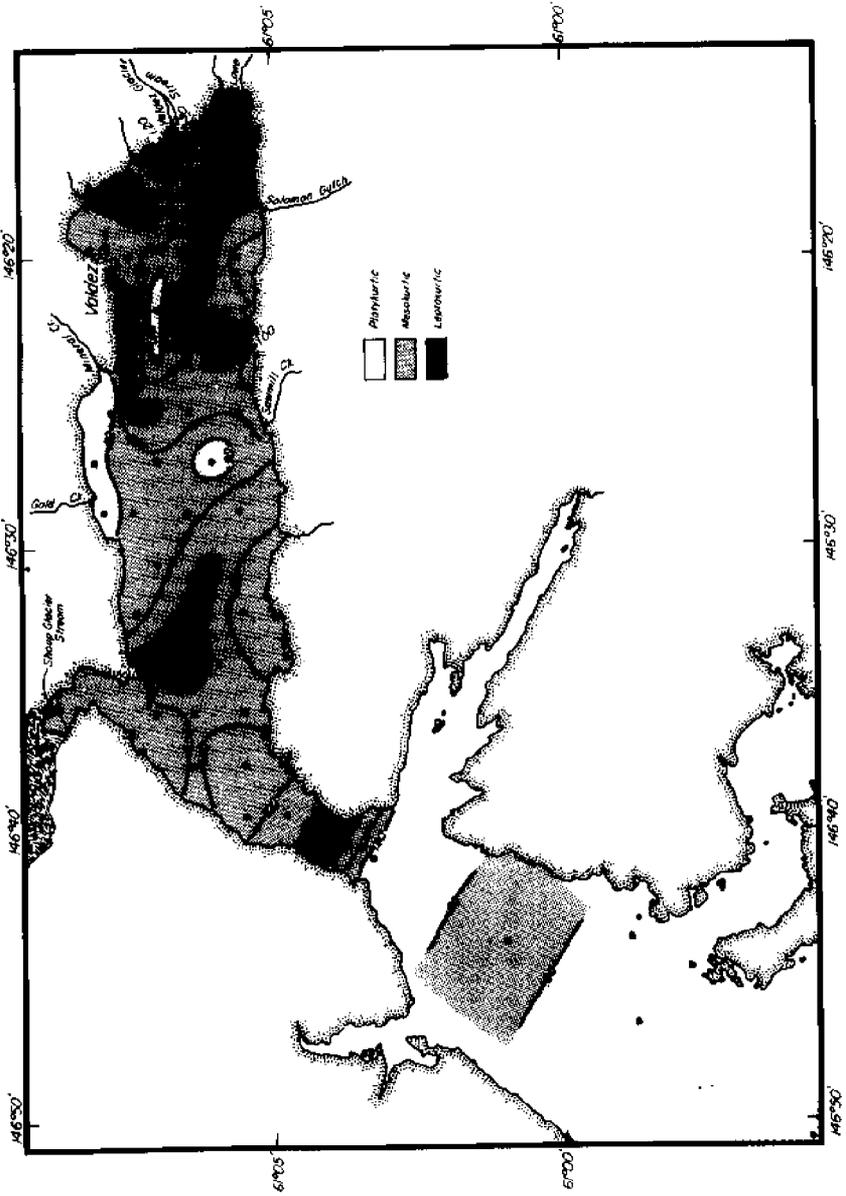


Figure 1.7 Kurtosis (K<sub>G</sub>) of surficial bottom sediments in Port Valdez.

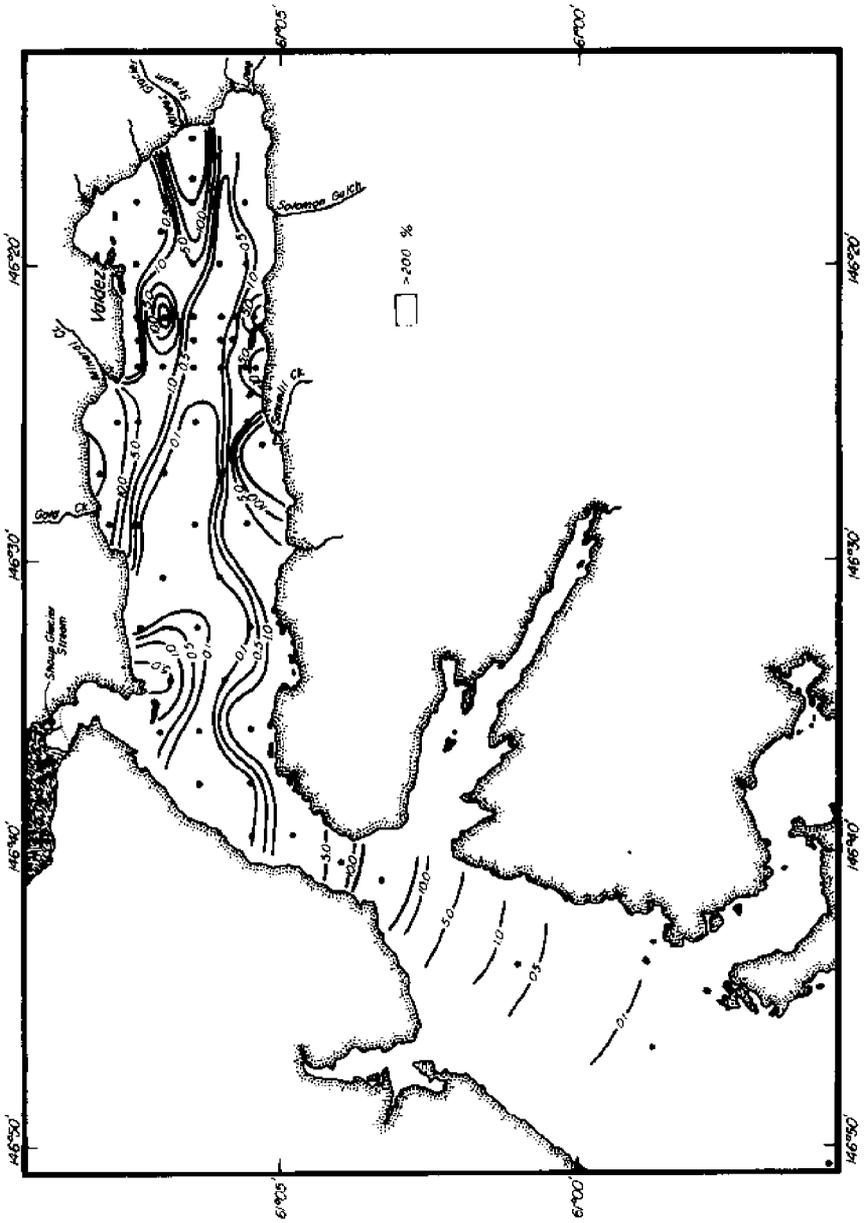


Figure 1.8 Weight percent sand-gravel in Port Valdez surficial bottom sediments.

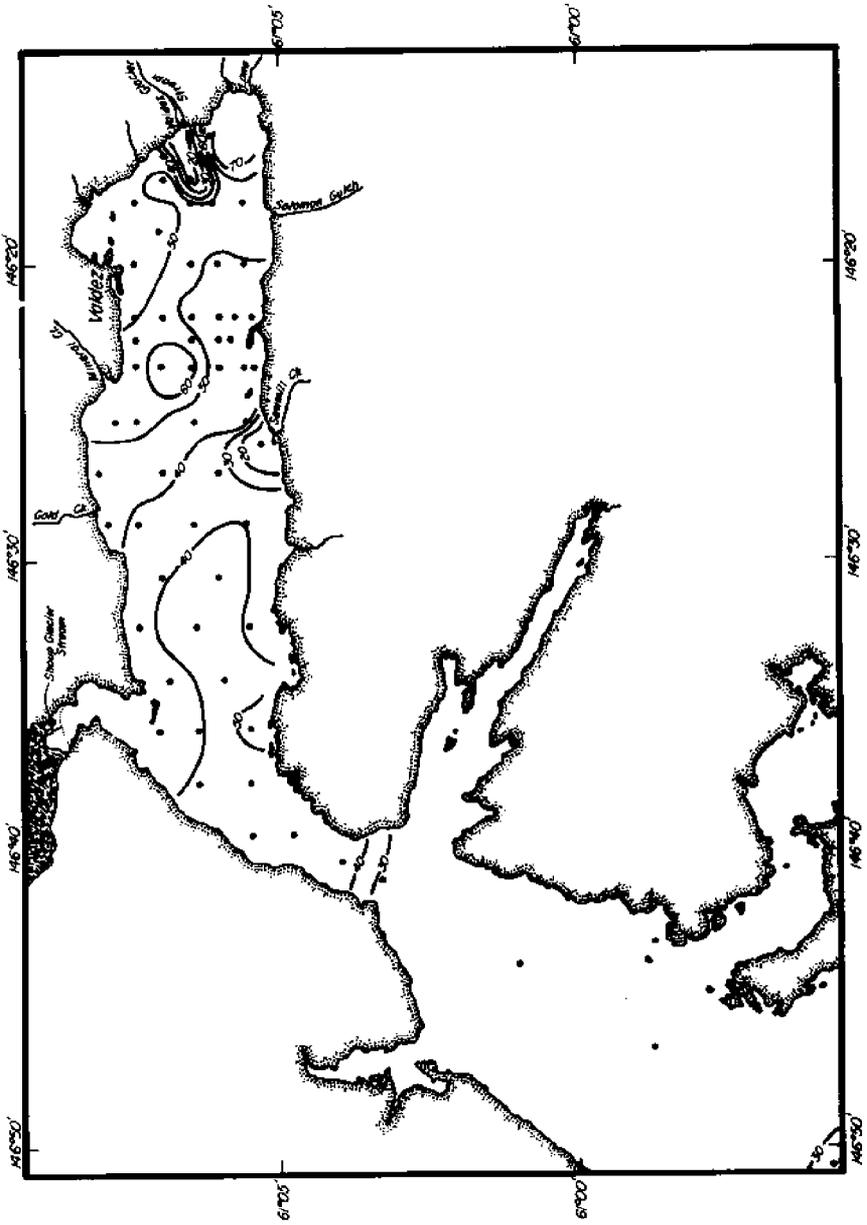


Figure 1.9 Weight percent silt in Port Valdez surficial bottom sediments.

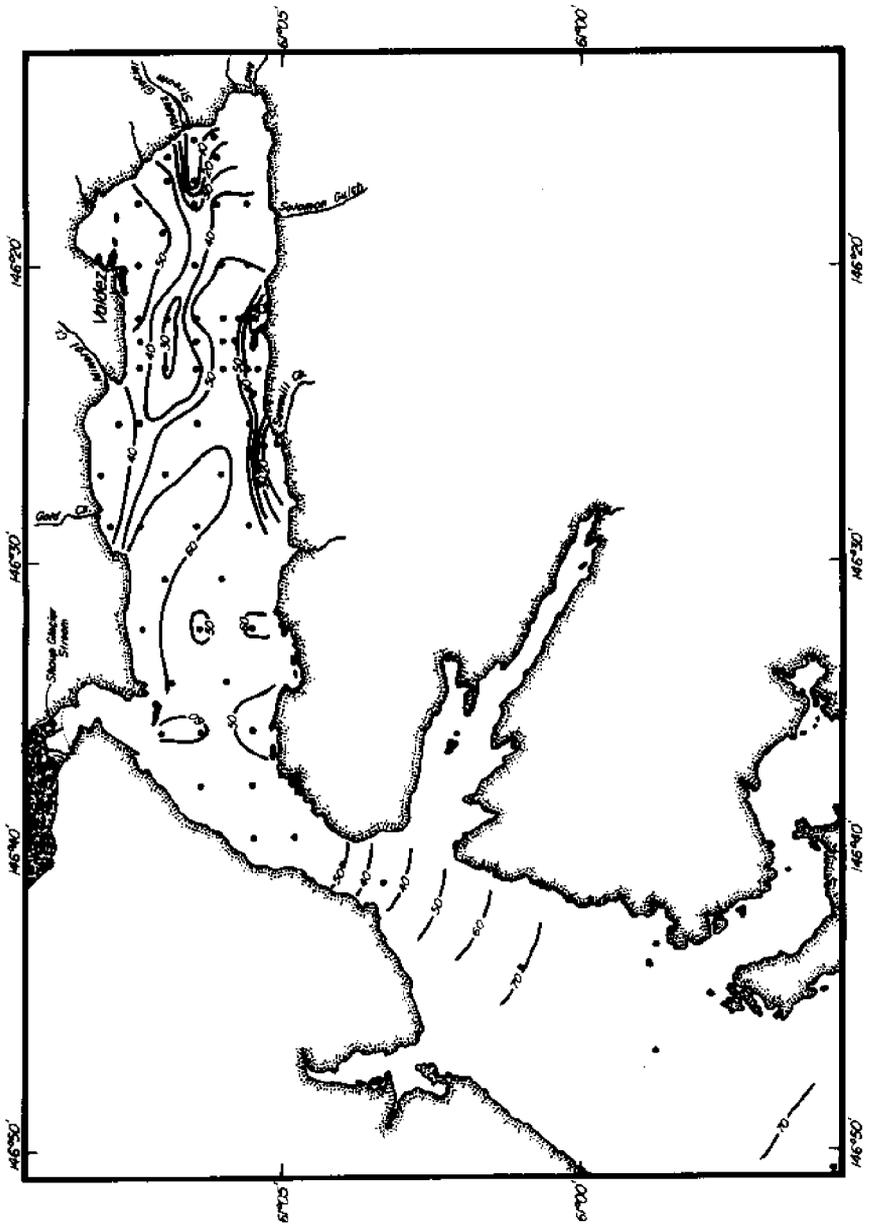


Figure 1.10 Weight percent clay in Port Valdez surficial bottom sediments.

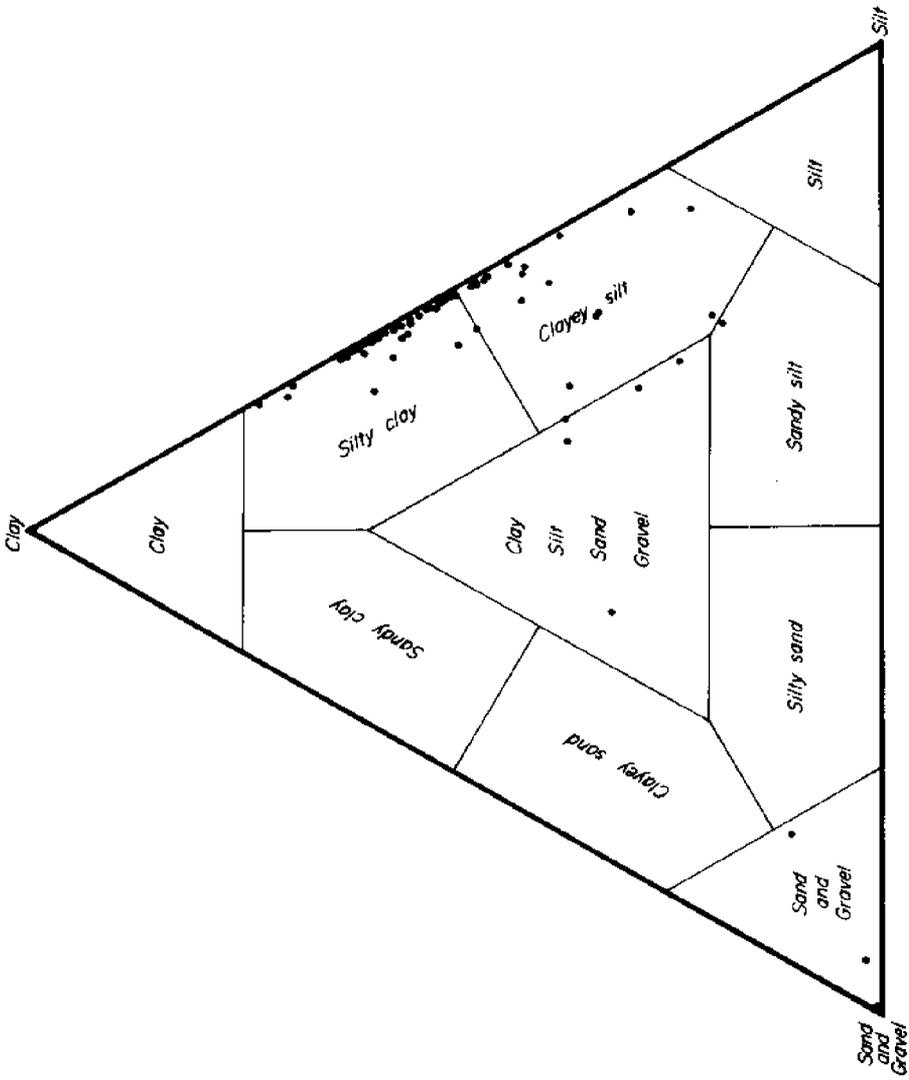
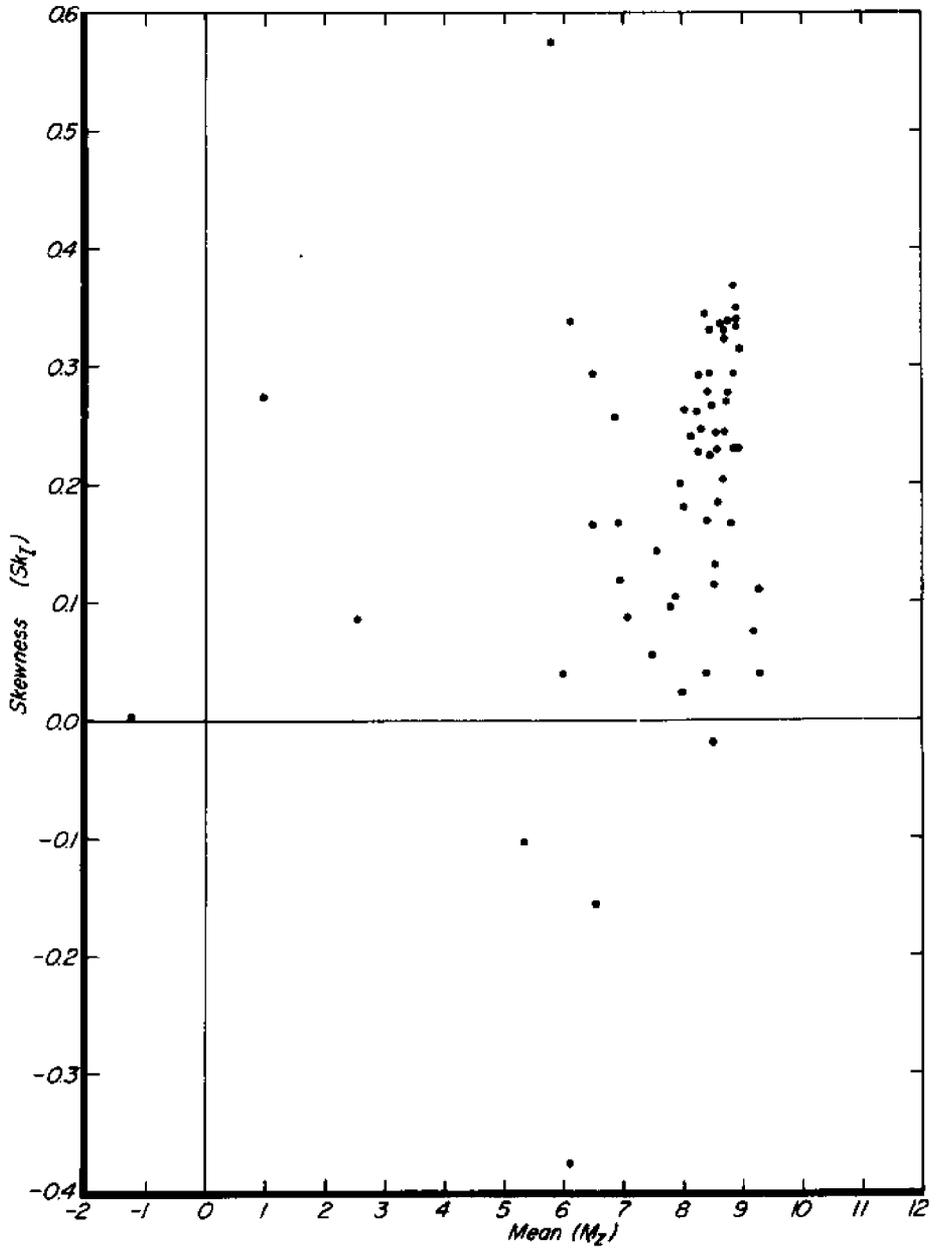


Figure 1.11 Gravel-sand, silt and clay contents of Port Valdez surficial bottom sediments.





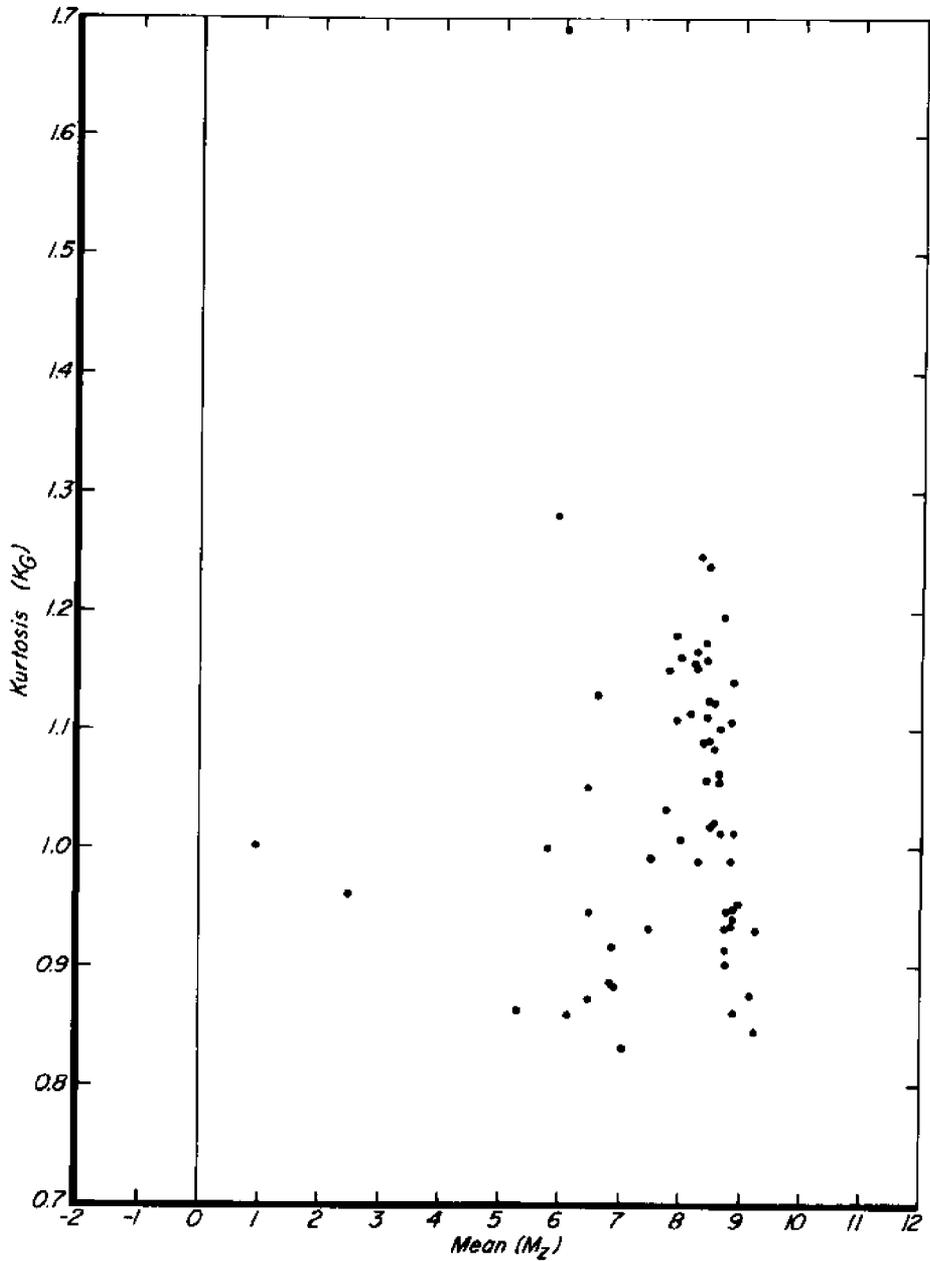


Figure 1.14 Mean size versus kurtosis for Port Valdez surficial bottom sediments.

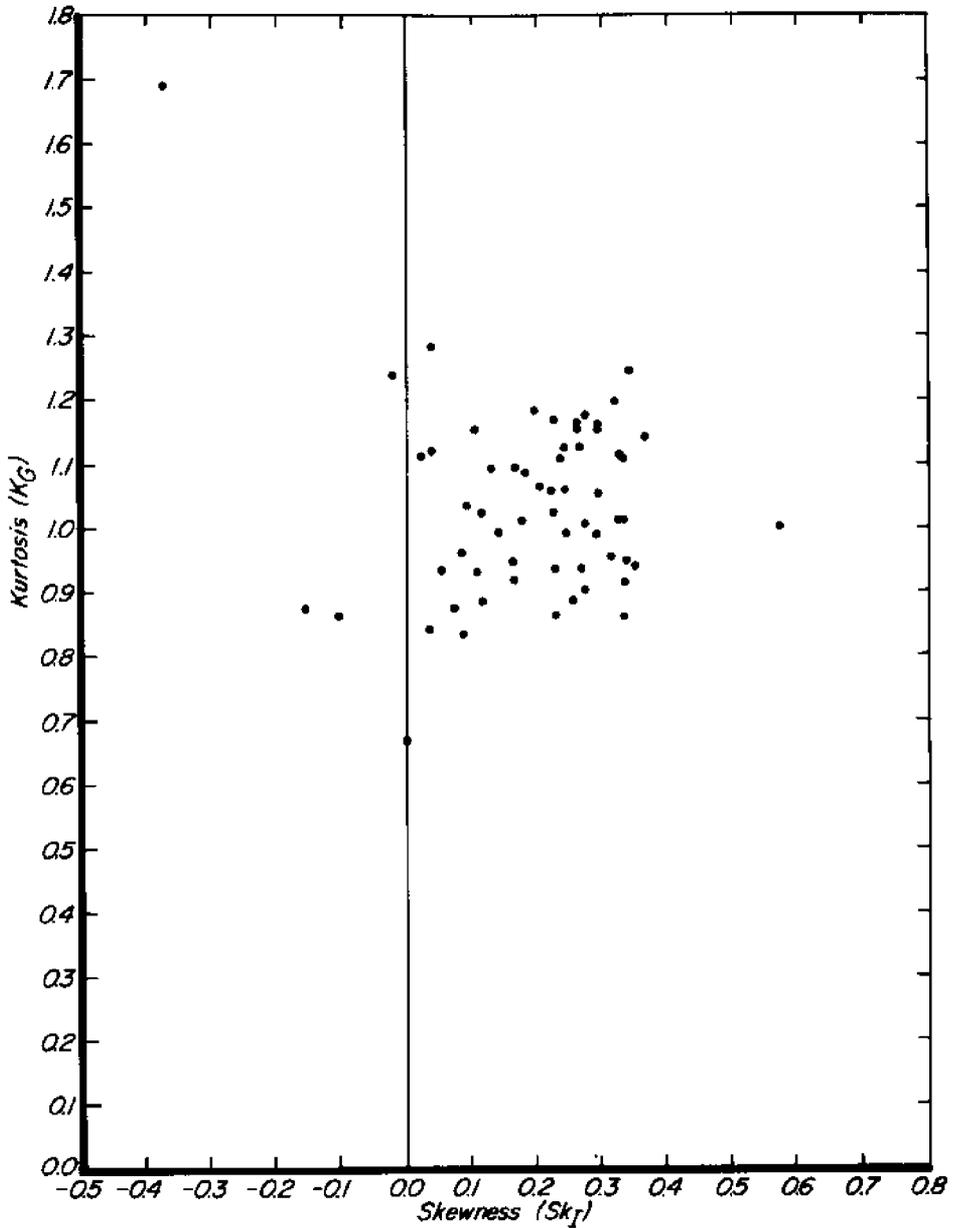


Figure 1.15 Skewness versus kurtosis for Port Valdez surficial bottom sediments.

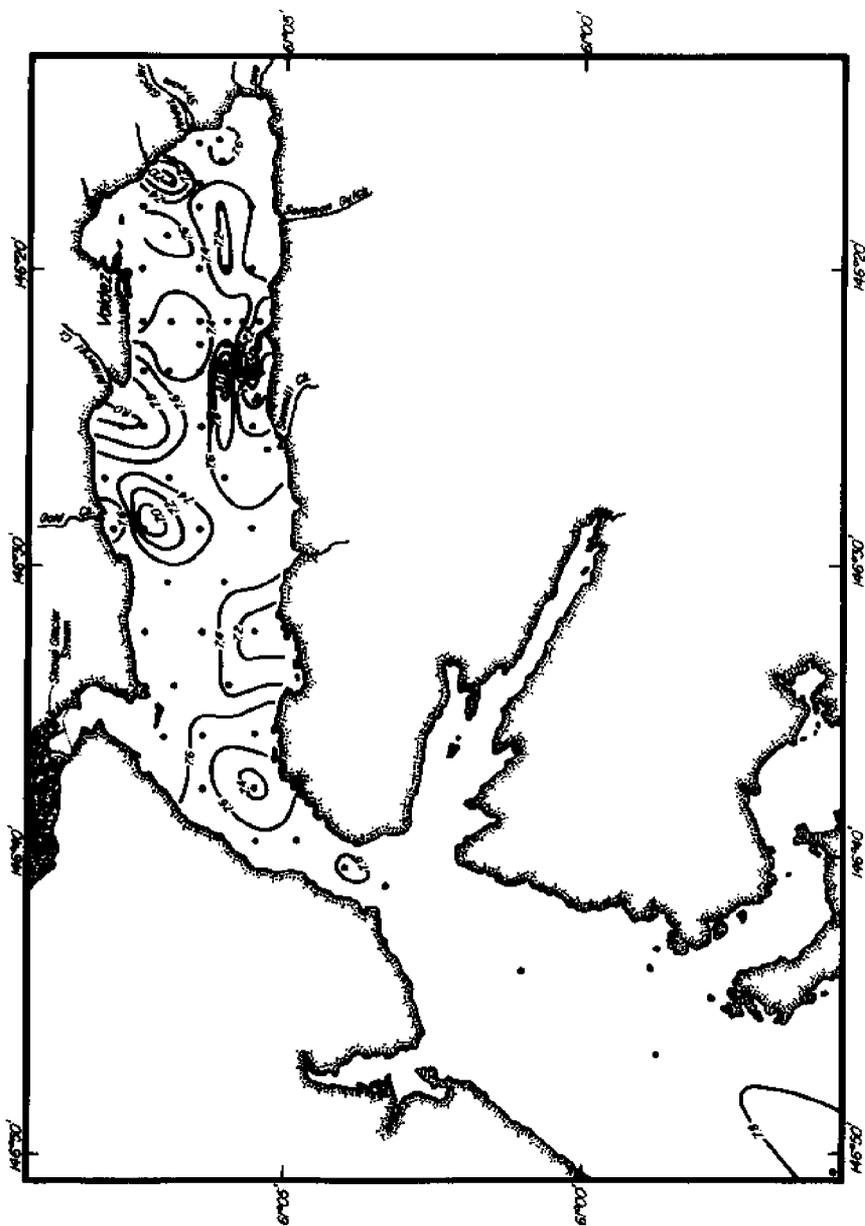


Figure 1.16 pH of Port Valdez surficial bottom sediments, 20-30 September 1971.

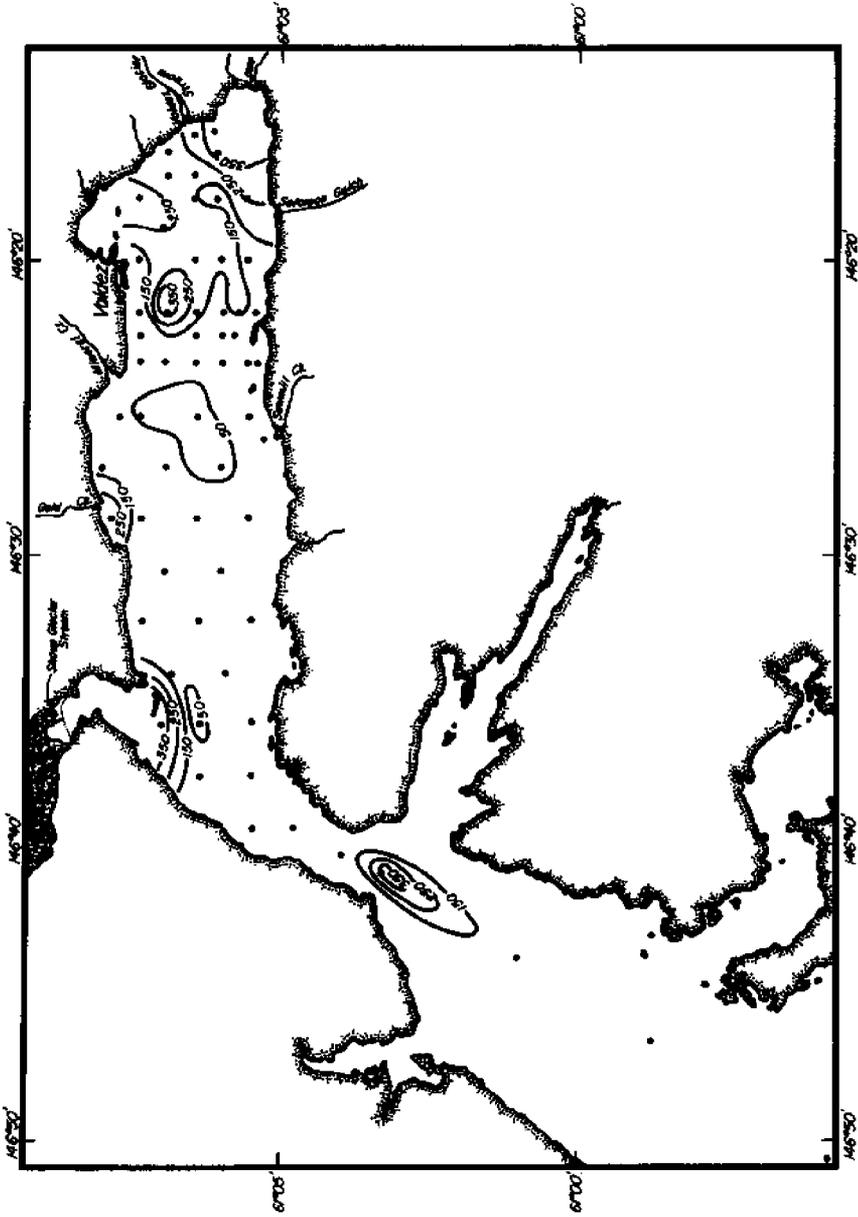


Figure 1.17 Eh (mv) of Port Valdez surficial bottom sediments, 20-30 September 1971.

The pH-Eh plot (Figure 1.18) suggests that the sediments from most stations in Port Valdez are similar to normal coastal marine sediments (Figure 1.19). The sediments were typically neutral to weakly alkaline throughout the Port, highly oxidizing at the surface and slightly oxidizing at depth.

#### 1.4.3 Organic carbon (in surface sediments)

The organic carbon in sediments of Port Valdez varied from 0.1 to 0.6 percent by weight (Figure 1.20 and Table 1.5). An increase in the clay fraction (material composed of particles  $<4\mu$  in size) was accompanied by an increase in the organic carbon in the sediments (Figure 1.21). The inverse relationship of organic carbon with Eh (Figure 1.22) is attributable perhaps to the function of chemical and bacterial oxidation of organic carbon in sediments. Bacterial oxidation may depend on the availability of oxygen and the benthic oxygen demand. The oxygen measurements in Port Valdez (see Data Vol. I, Section 4) were suggestive of well-oxygenated bottom water throughout the inlet. It appears, therefore, that sediment type (i.e., clay) is the primary factor controlling organic carbon accumulation in the sediments.

#### 1.4.4 Clay mineralogy (of surface sediments)

X-ray diffraction analysis of the clay ( $<4\mu$ ) fraction demonstrated a consistent suite of clay minerals throughout Port Valdez, predominantly chlorite and illite-mica; kaolinite and montmorillonite were not observed in the sediments. Semi-quantitative estimates were made of the relative abundance of illite, chlorite and quartz, based on comparison of their peak heights (10 Å, 7 Å and 4.26 Å, respectively; Figures 1.23-1.25 and Data Vol. I: Table 1.6). Low chlorite-quartz and illite-quartz ratios near the river mouths and an increase in the basin suggest relatively faster settling of quartz and resultant higher clay content with increase in distance from the source. The chlorite-illite ratio (Figure 1.25) suggests, however, that illite (more highly concentrated in the source sediments) appears to settle faster than chlorite, thus causing an increased chlorite-illite ratio farther out in the Port (Whitehouse et al. 1960). The clay mineral distribution patterns are interpreted as a combined result of input source and differential settling. Quartz and illite reflect their input because they settle more quickly. The distribution of chlorite is an outcome of slower settling and water circulation.

#### *Subsurface sediments*

##### 1.4.5 General remarks

Subsurface sediment studies, including determination of the growth patterns of various subaqueous slides, were initiated to supplement the study of the surface sediments and to elucidate the more recent history of sedimentation in Port Valdez.

According to Moffit's (1954) summary of the tectonic and sedimentary history of Port Valdez and adjacent region, the Port Valdez basin began to form during early Cretaceous time and attained its present morphology during late Eocene to Oligocene time. Von Huene et al. (1967), on the basis of seismic reflection profiles, inferred that most of the postorogenic basin fill consists of unconsolidated glacial sediments deposited probably during various ice ages (Figure 1.3) and is overlain by a relatively thin layer of marine transgressive sequence. Gravity and piston cores collected in Port Valdez during this investigation were taken from only the upper 1-3 m of the marine transgressive sequence and therefore represent only very recent sediments.



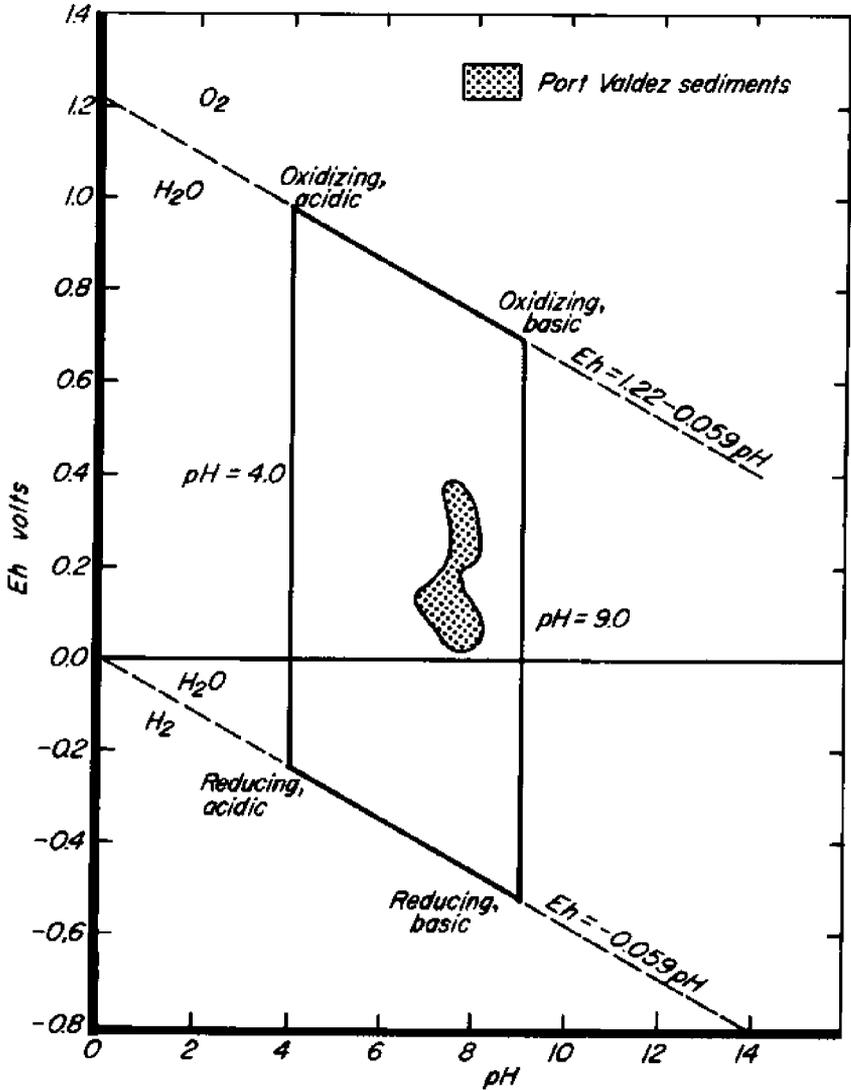


Figure 1.19 Environmental boundaries of Eh and pH (Figure 1.18) for Port Valdez surficial bottom sediments. The parallelogram outlines the usual limits of Eh and pH found in near-surface environments. Drawing adapted from Krauskopf (1967, p. 247).

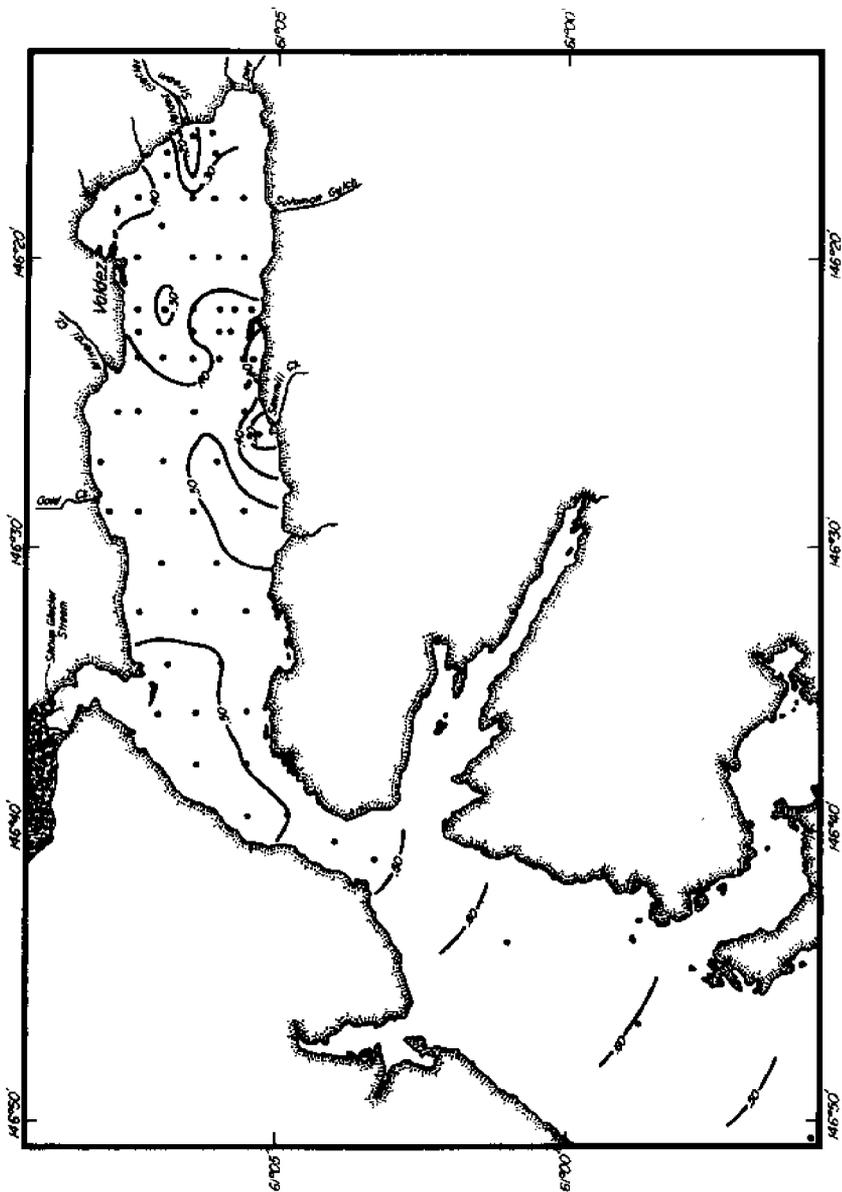


Figure 1.20 Weight percent organic carbon in Port Valdez surficial bottom sediments.

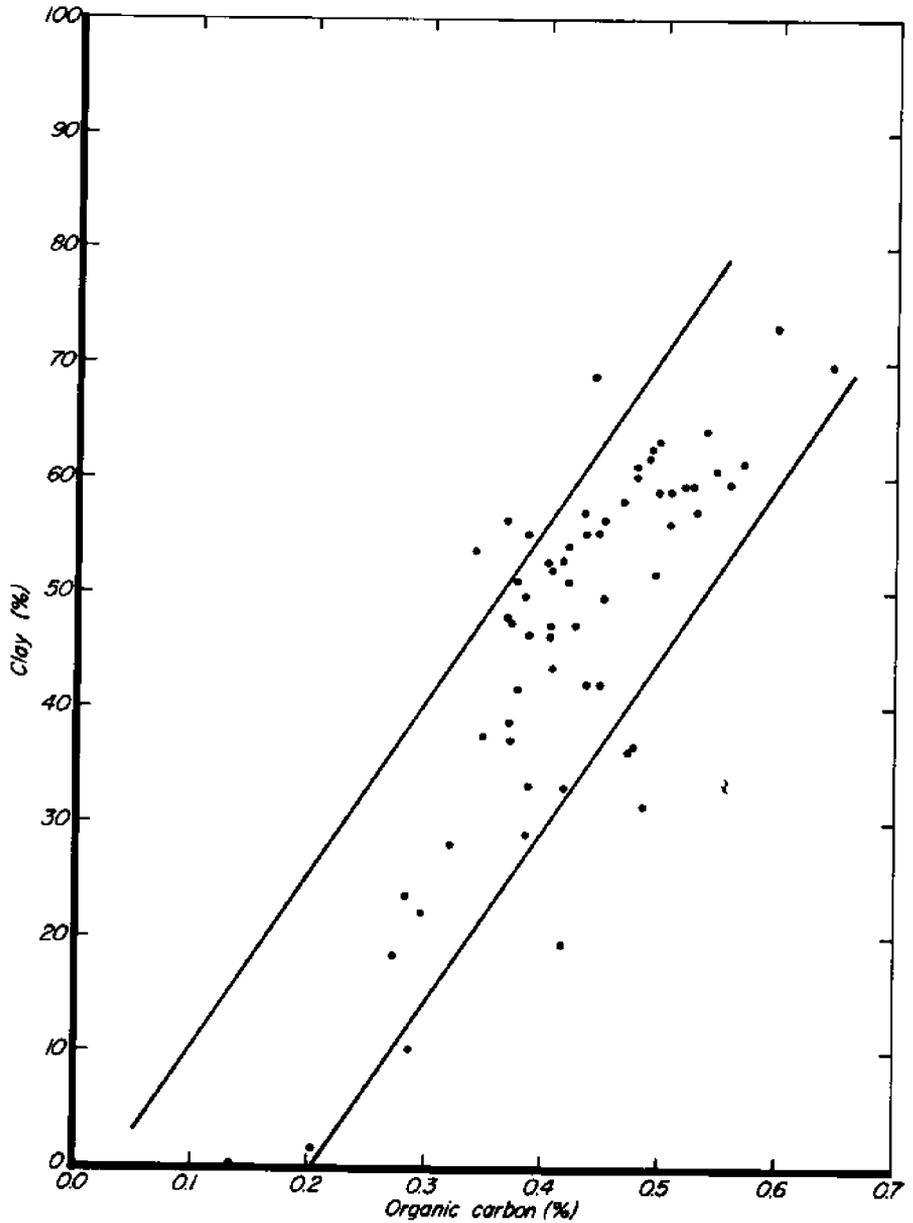


Figure 1.21 Weight percent organic carbon versus weight percent clay ( $<4\mu$ ) for Port Valdez surficial bottom sediments.

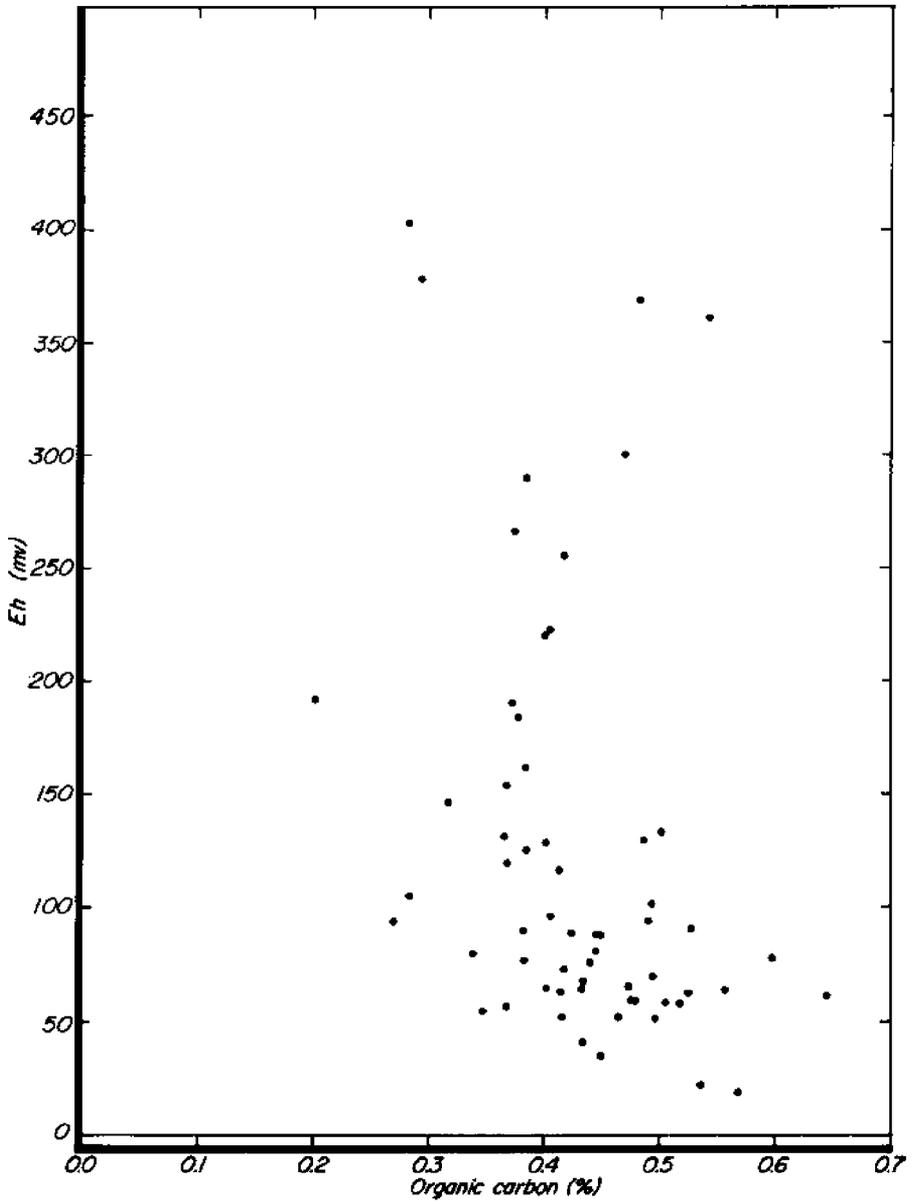


Figure 1.22 Weight percent organic carbon versus Eh (mv) for Port Valdez surficial bottom sediments.

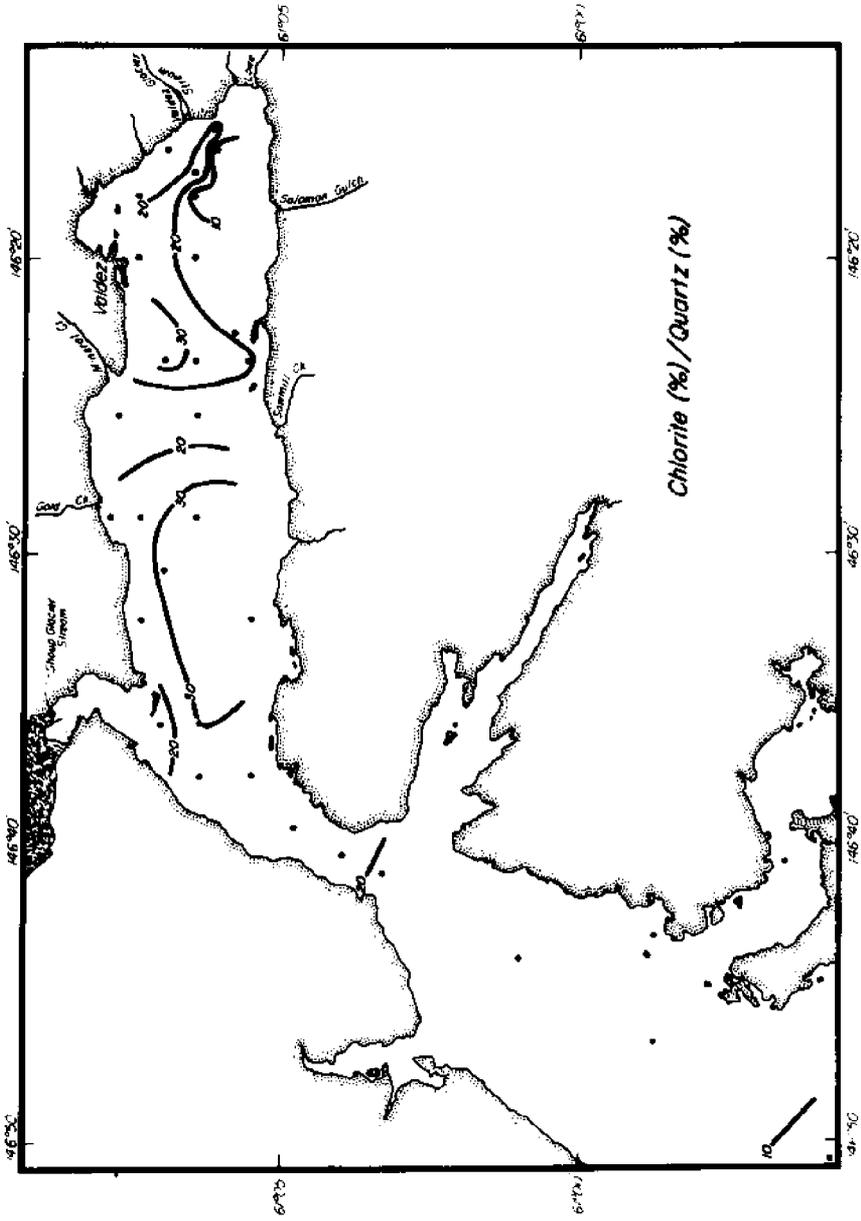


Figure 1.23 Variation in the chlorite-quartz peak height ratio in surficial bottom sediments in Port Valdez.

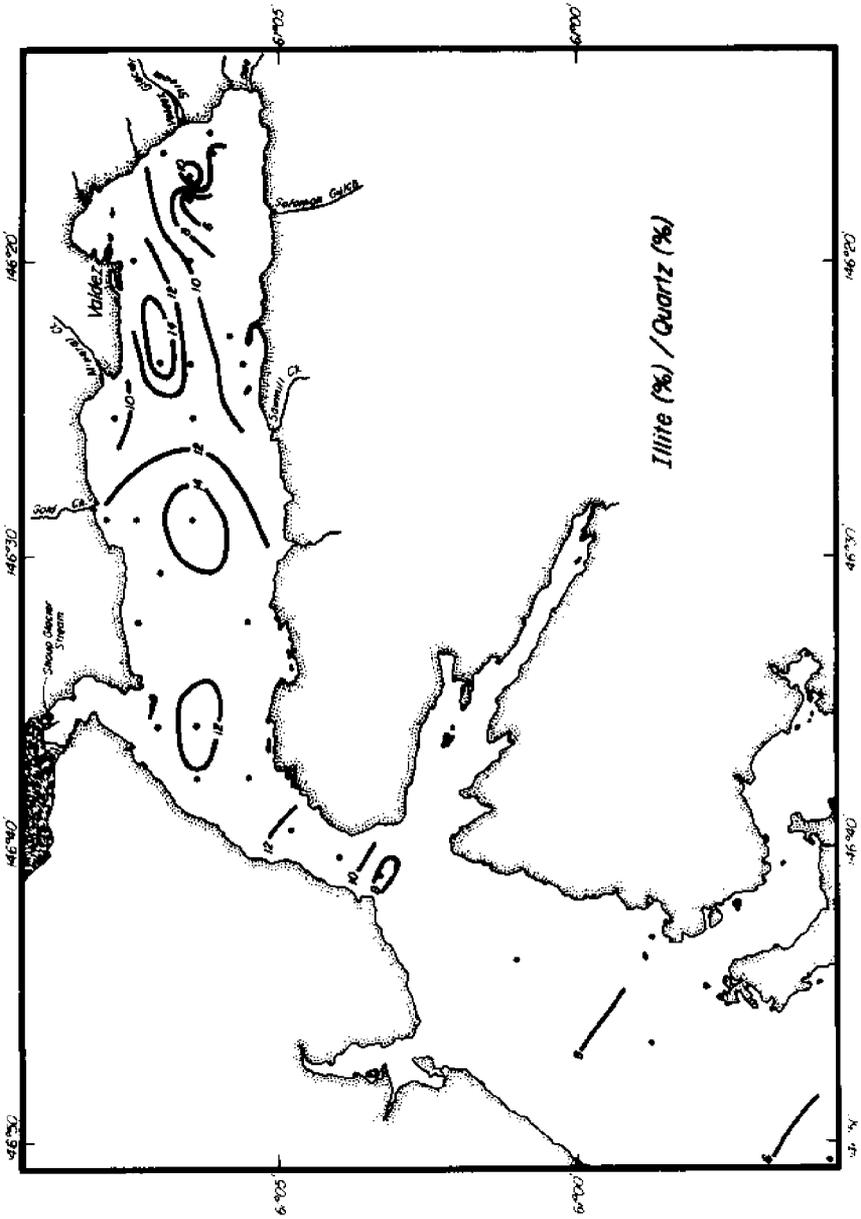


Figure 1.24 Variation in the illite-quartz peak height ratio in surficial bottom sediments in Port Valdez.

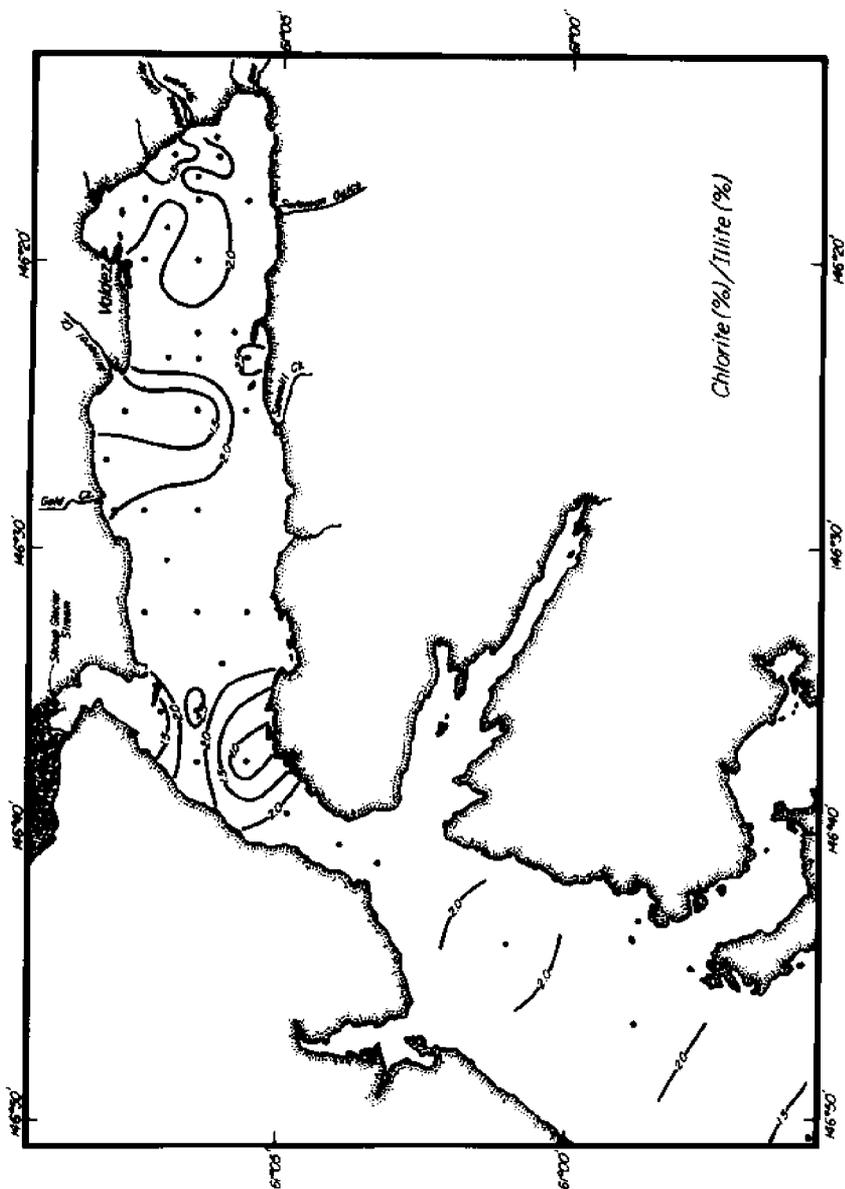


Figure 1.25 Variation in the chlorite-illite peak height ratio in surficial bottom sediments in Port Valdez.

Piston cores collected during the September 1971 cruise are shown in Figure 1.26. The small-diameter cores did not permit the study of structures within the sediments; however, the cores are described in Table 1.7 of Data Vol. 1, which also lists the size distributions of subsamples from various depths within these cores (Table 1.10). The mean size of most core sediments was in the range of medium sand to clay; some gravel also was observed in cores obtained from nearshore areas and topographic highs. The sands were moderately sorted, although silts and clays were very poorly sorted.

Sediments deposited near the delta were positively skewed and became negatively skewed near the Narrows; in Valdez Arm the core sediment skewness was nearly symmetrical. Throughout the core length, the sediments in general were progressively finer from east to west, with the exception of sediments from core PV-56 taken in the vicinity of the Narrows.

Both the visual appearance and the size distribution of sediments showed a characteristic uniform gradation in most of the cores from coarse sediments at the bottom to fine sediments at the top. Usually the graded bedding found in the cores was simple, although in some cases it was multiple. Parallel laminations were common. Graded sand and silt sections in most of the cores included fragments of clayey sediments generally varying from 1 to >5 cm in diameter. From the size of these clayey fragments and the thickness of the coarse-graded sediment layers in Port Valdez, it appeared that the underlying sediments had been eroded by rigorous currents and redeposited in the overlying sands and silts.

In general, all of Port Valdez was covered by a thin layer of clayey and silty sediments which unconformably overlaid coarse, graded sediments. The underlying sediments displayed an abrupt change in texture; for example, in core B-8A (Figure 1.32) the fine-grained sediments were overlain by gravel. In some areas, the thickness of the overlying fine sediments was <15 cm.

The bottom morphology of Port Valdez showed four distinct sedimentary topographic highs and a channel. The location and texture of sediments from these features were suggestive that these features are the result of submarine slumps and turbidity currents. The sediment grading observed in the cores is characteristic of sediments which have settled from a turbid suspension.

During the Great Alaskan Earthquake of 1964, approximately  $75 \times 10^6$  m<sup>3</sup> of gravel, sand and silt that had broken away from the head of the inlet was deposited in Port Valdez (Coulter and Migliaccio 1966). Additional sediments were supplied to the area as a result of slumping in the vicinity of Cliff Mine at the west end of the Port (Plafker and Mayo 1965). The appearance of muddy water at the surface soon after the collapse of docks near Old Valdez was witnessed by many observers. It appears that submarine slumps are generally followed by turbidity currents. In order to study the effects of the 1964 earthquake, piston and gravity cores were collected during March and May 1972 (Figures 1.27-1.32; also Data Vol. 1: Tables 1.8 and 1.9). Gravity coring was employed to retrieve undisturbed surficial sediments. The cores taken from the tops and around Valdez Fans I and II (see text 1.1.3 and Figure 1.2) exhibited distinctly the unconformity between the overlying fine sediments and the underlying graded bedding or gravel. An east-west core profile across Valdez Fans I and II is shown in Figure 1.31. In core B-2C (Figure 1.32), the overlying fine-grained sediments consisted of eight layers of cyclic sedimentation. The bottom of each layer contained somewhat coarser-grained sediments with a high content of wooden debris and graded upward into very fine-grained gray sediments. Thickness of the bottom cyclic layer was 7 cm, and the topmost (eighth) layer was 4 cm. Similar but less distinct cyclic sedimentation was observed also in certain other cores. It is suggested that the underlying graded sediments were deposited during the 1964 earthquake and that the overlying cyclic layers were deposited during each of the subsequent 8 years. In core B-2C the bottom sediments within each layer display the nature and accelerated rate of sedimentation characteristic in summer when river sediment discharge is at its peak.

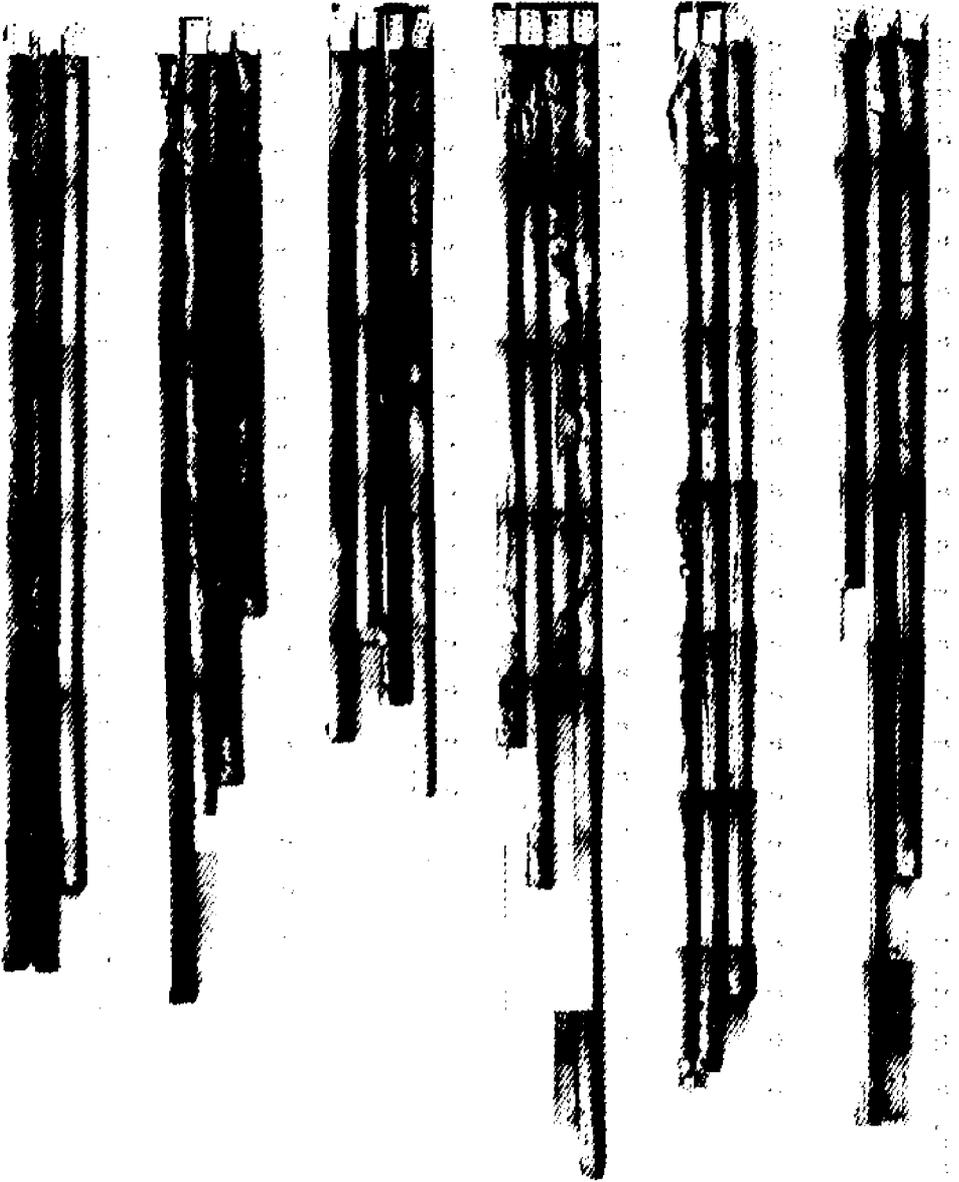
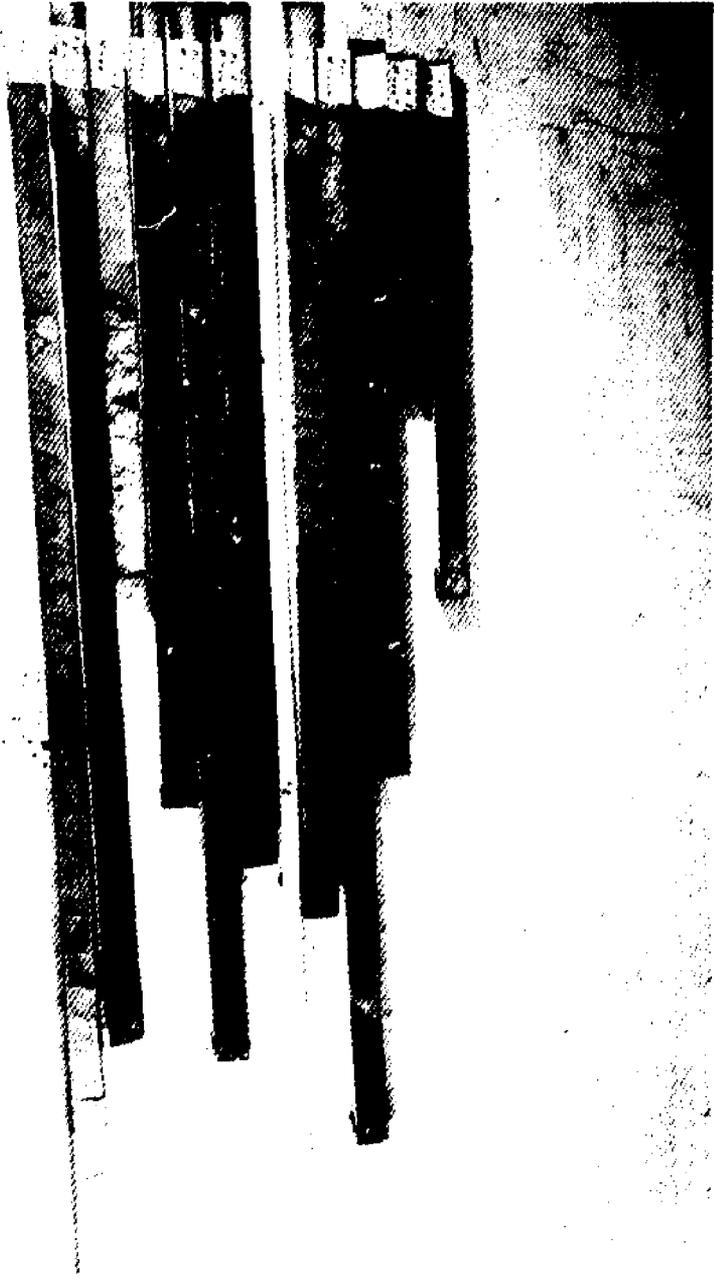


Figure 1.26 Photograph of cores retrieved in Port Valdez aboard the *R/V Acona*, 20-30 September 1971.



**Figure 1.27** Photograph of cores retrieved in Port Valdez aboard the *R/V Acona*, 20 March 1972.

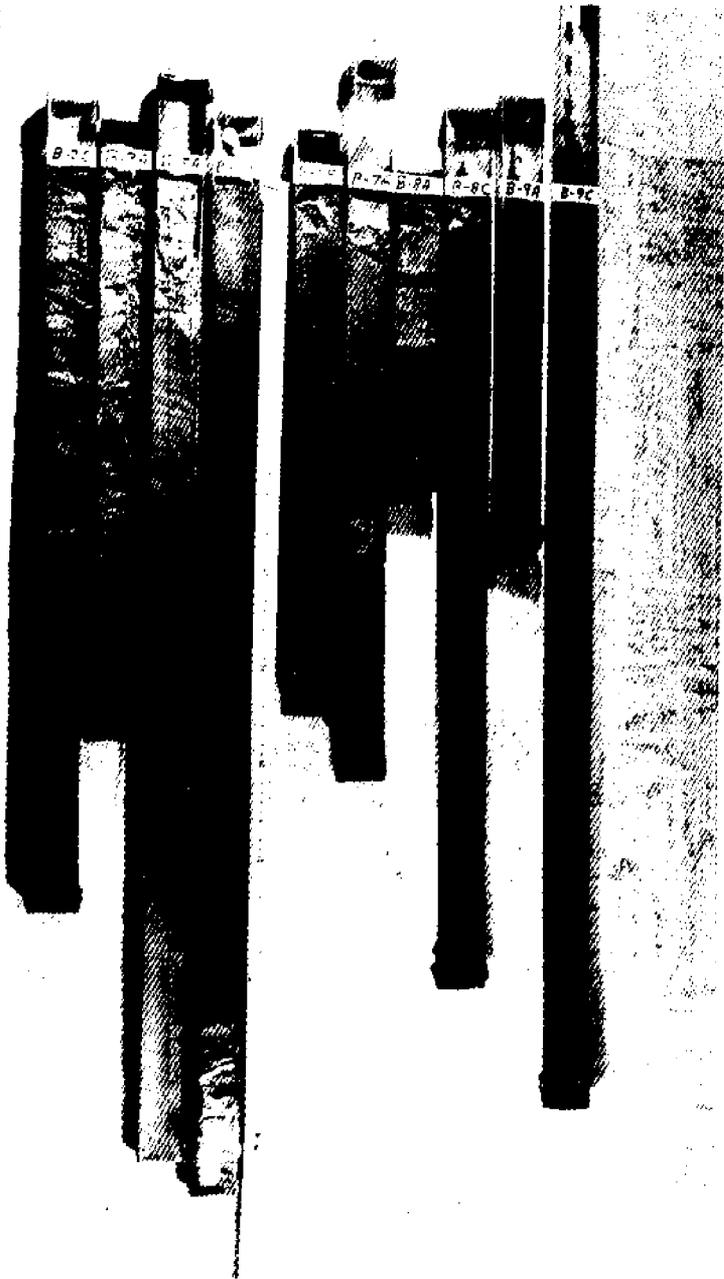


Figure 1.28 Photograph of cores retrieved in Port Valdez aboard the *R/V Acona*, 11-14 May 1972.



Figure 1.29 Photograph of cores retrieved in Port Valdez aboard the *R/V Acona*, 11-14 May 1972.

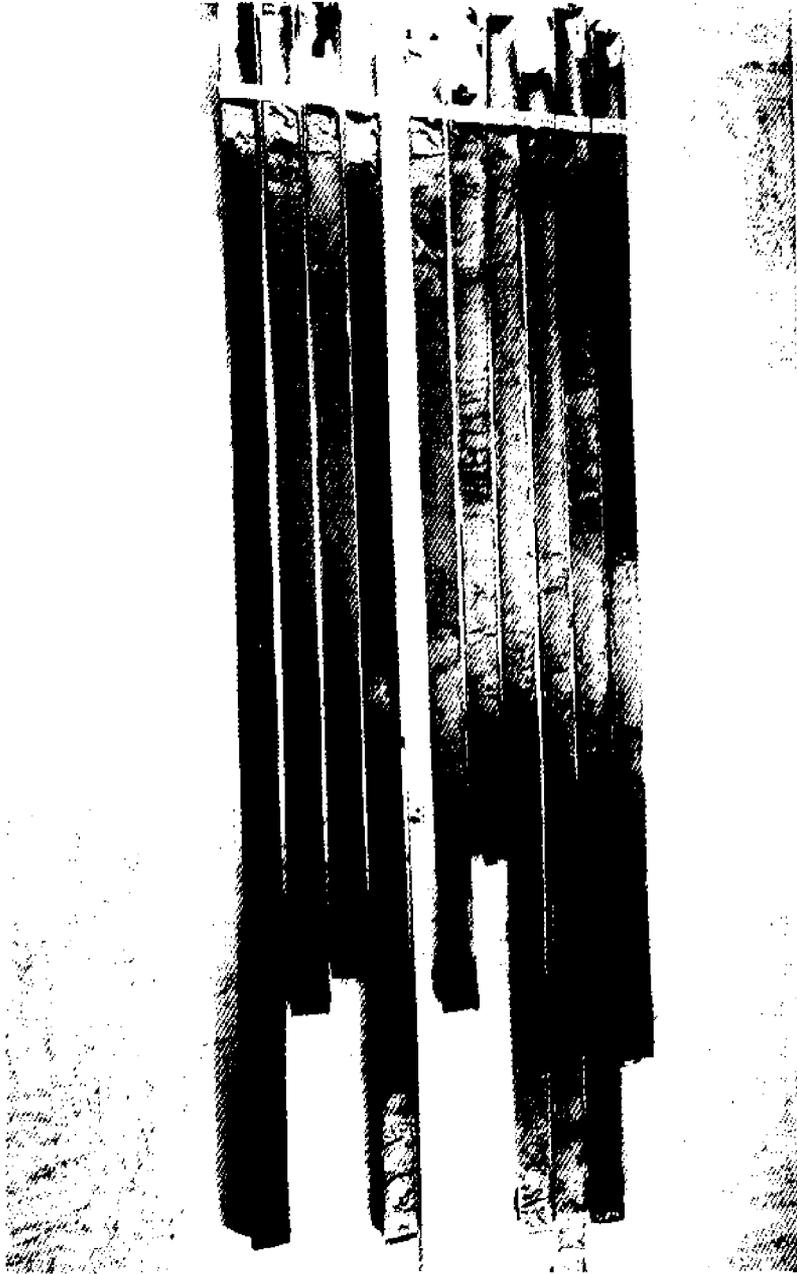


Figure 1.30 Photograph of cores retrieved in Port Valdez aboard the *R/V Acona*, 11-14 May 1972.

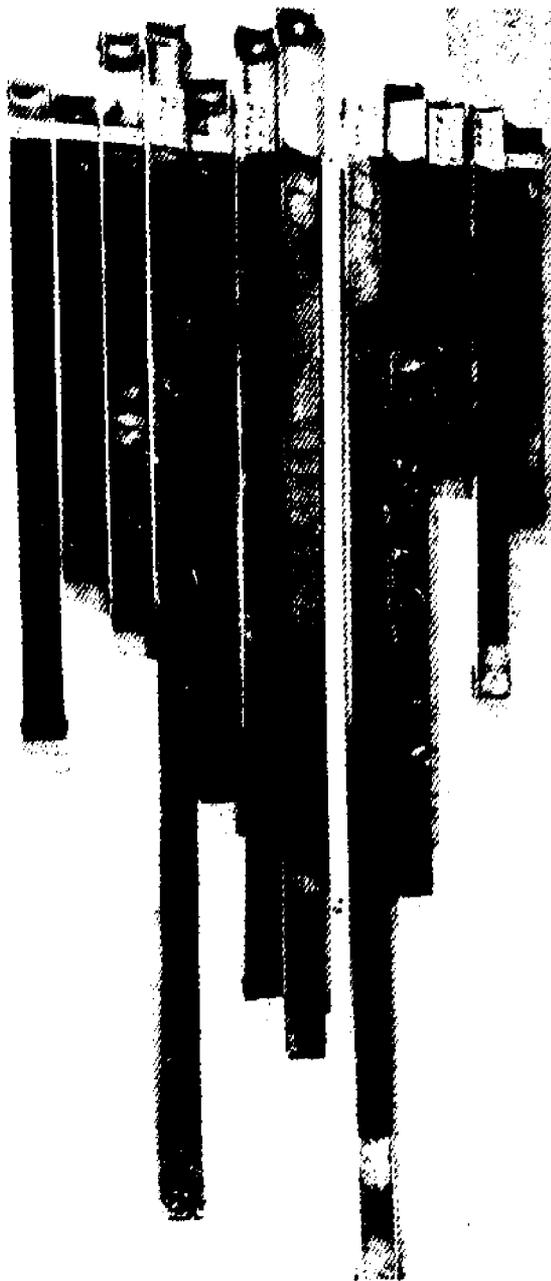


Figure 1.31 East-west core profile across Valdez Fans I and II.



**Figure 1.32** Close-up photograph of cores showing cyclic sedimentation.

Subsurface studies revealed that the coarser fraction of sediments originating at the head of the inlet during the 1964 slump was deposited at the mouth of Valdez Channel, thus forming Valdez Fan II; however, the sand, silt and clay portion was distributed throughout the Port. Additional sediments were supplied apparently by concurrent slumping in the vicinity of Cliff Mine. The sediments transported in the turbid suspension resulting from the 1964 earthquake were confined within Port Valdez, as was inferred by the presence of sediment grading in cores within Port Valdez and the absence of sediment grading in cores from Valdez Arm. The texture of the sediment grab samples from Cliff Mine Fan and from the topographic high south of Shoup Bay indicated that the origin of these features was similar to that of Valdez Fan II. It is believed that Valdez Fan I was formed during an earlier (possibly 1911) earthquake. Submarine cable breaks as an aftermath of past earthquakes have been reported in these areas, further suggesting that severe earthquakes can cause sliding and slumping of deposits that are rapidly built, steep, and unconsolidated. Such slumping results in rapid headward erosion of submarine valleys and formation of submarine fans, and the large-scale turbidity currents generated during slumping are capable of transporting sediments over long distances.

#### 1.4.6 Eh and pH (of subsurface sediments)

Measurements of Eh and pH were obtained on board from cores (Data Vol. I: Table 1.9) which were split longitudinally upon their retrieval. The Eh and pH were measured in different lithologic units at various depths, and these parameters were measured also in sediments retained in the core catcher. The Eh was always positive and varied irregularly over a wide range, although pH varied with a small range.

#### 1.4.7 Organic carbon (in subsurface sediments)

From determinations of organic carbon in sediments from two cores (Data Vol. I: Table 1.5), the weight percent organic carbon in the sediments decreased with depth within the core.

#### 1.4.8 Clay mineralogy (of subsurface sediments)

X-ray diffractograms of sediments at various depths from several cores (Data Vol. I: Table 1.6) indicated no significant variation in clay mineralogy due to depth of burial. Clay mineral ratios also appeared to be similar to those observed in surface sediments. Distinct color differences found between the top layer and underlying sediments were evidently due to the oxidizing state of some minerals and not due to differences in the clay mineralogy.

### *Sediments in suspension*

#### 1.4.9 General remarks

Suspended matter in seawater generally represents an early step in the formation of marine sediments that is closely related to the physical-morphological regime and to the chemical, hydrological and biological characteristics of the seawater. Suspended matter that was measured and described here includes terrigenous particles brought into the inlet by rivers and wind, material resuspended by tides, organic matter (living and dead), and material formed from inorganic chemical processes. The distribution and composition of suspended matter vary with such factors as distance from shore, bottom topography, season, prevailing wind pattern and biological productivity. The dominant form of suspended matter observed in Port Valdez was terrigenous particles and is therefore referred to as the *suspended sediment load*.

Suspended sediments in coastal waters have significant effects on the physical and chemical properties of seawater. The particles in suspension affect the transparency of seawater and the scattering of light and sound waves. The concentration of nutrients in the water column is also partially controlled by suspended particles. Many pelagic and benthonic organisms are filter feeders and depend on suspended matter as their food.

The distribution and seasonal variation in the concentration of suspended matter in Port Valdez waters during September 1971-November 1972 were recorded, together with measurements of salinity, temperature and light transmissibility. The combined collection of these related data was considered pertinent in elucidating the spatial distribution of suspended matter in Port Valdez and characterizing its movement. The results of this study will contribute towards the understanding of tidal, geostrophic and other current movements and mixing of waters in the inlet.

#### 1.4.10 River input of suspended sediments

The major fresh waters draining into Port Valdez are the Lowe River and Valdez Glacier Stream at the head of the Port and Mineral Creek and Shoup Glacier Stream to the north. Suspended sediment load, estimated water flow rates and total suspended sediment discharge rates for these major and a few minor rivers and streams are listed in Table 1.11 of Data Vol. I. The many smaller streams are relatively insignificant in terms of suspended sediment load and water flow rate compared to those rivers and streams classified here as major.

The water flow rates and suspended sediment loads for the Lowe River, Mineral Creek and Shoup Glacier Stream during summer and early fall are shown in Figure 1.33. The suspended sediment loads of the major rivers and streams draining into Port Valdez tended to follow the same general pattern as the water flow rate of the specific river or stream. Many short-term variations can be expected due to such factors as precipitation; however, the same general discharge patterns can usually be anticipated.

The total amount of suspended sediment discharged from each of the major rivers and streams measured during 1972 (Data Vol. I: Table 1.11) was approximately  $9.66 \times 10^{11}$  gm from the Lowe River,  $6.48 \times 10^{11}$  gm from Mineral Creek and  $3.69 \times 10^{11}$  gm from Shoup Glacier Stream. According to the available data the discharge from Valdez Glacier Stream was approximately the same as that from Mineral Creek. Most of the suspended sediment load discharged by Shoup Glacier Stream appeared to be deposited within Shoup Bay; thus the Lowe River, Mineral Creek and Valdez Glacier Stream were the major contributors of suspended sediment to Port Valdez.

#### 1.4.11 Water sediment load, light transmission, temperature and salinity

Suspended sediments derived from the major rivers and streams draining into Port Valdez were carried into the Port in a surface layer (plume) of relatively low-salinity water overlying higher-salinity water of greater density. This surface layer was typically about 2-10 m thick. The suspended sediment load in the surface layer normally decreased rapidly with increase in depth in the surface layer.

Several factors affect the maintenance of the surface suspended sediment layer. The strong halocline exerts a pronounced effect. Surface turbulence due to wind and waves tends to keep the sediments in suspension at the surface, but at the same time wind and wave action increases the thickness of the surface layer and thus causes a decrease in the sediment concentration. In addition to these processes, flocculation of the suspended sediments exerts an important influence. The sediments suspended in the fresh-water surface layer remain in a highly dispersed condition; when brought into contact with salt water by mixing with the underlying more saline water, however, the suspended sediments (mostly

clay particles) rapidly flocculate. These flocculated aggregates of clay particles have a greatly increased settling velocity. Were it not for this flocculation process, the finer clay particles would stay in suspension for a considerably longer period. The thermocline, although highly variable, can also be highly effective in maintaining sediments in suspension because the reduced temperature also increases the viscosity of seawater, causing a decrease in the particle settling velocity. Sand and silt size particles are affected only slightly by the change in viscosity; however, the residence time of clay minerals and other clay-size particles in seawater is prolonged. Choppy seas (0.5-1 m waves) in Port Valdez have been observed to considerably disperse heavy, well-defined plumes of suspended sediment. This condition was attributed to the several factors mentioned previously: destruction of the halocline and thermocline, flocculation of the finer sediments, and an increase in the thickness of the surface suspended sediment layer.

The spatial distribution of the surface suspended sediment load is a function of several variables such as river input; tidal, geostrophic and wind-induced circulation; and mixing. In general, the surface suspended sediment load increased in proportion to the increase in water flow of the major rivers and streams discharging into Port Valdez (Figure 1.33). Suspended sediments were sampled at various times during 1971 and 1972 to provide a seasonal distribution pattern for the suspended sediment load. Data obtained in September 1971 and April 1972 (Figures 1.34-1.38) aboard the *R/V Acona* were collected over periods of several days and provide a reasonable assessment of the distribution of suspended sediments for these periods, particularly since the detrital suspended sediment input was minimal and concentrations were quite low. The rapid method of sampling employed during June 1972 revealed, however, that the distribution of surface suspended sediments during heavy river discharge was highly variable over short periods, particularly in relation to the tidal cycle (Figure 1.40); the remaining summer sampling was therefore rapidly conducted within 3 to 4-hr periods over the entire Port to measure an essentially *instantaneous* distribution of surface suspended sediment load. Suspended sediment sampling during the summer of 1972 was supplemented by measurements of light transmissibility (10-cm pathlength), salinity and water temperature (Figures 1.41-1.56; also Data Vol. I: Tables 1.13-1.16). Station numbers and locations of suspended sediment sampling for the period of June to November 1972 are shown in Figure 1.39 and Data Vol. I: Table 1.12, respectively. The correlation of light transmissibility with the measured surface suspended sediment load is shown in Figure 1.57.

The usual distribution of surface suspended sediment, as observed throughout the summer of 1972, consisted of a relatively heavy and well-defined plume originating from the Lowe River and Valdez Glacier Stream at the head of the Port. Along the southern shore this plume extended westward to Fort Liscum (located midway between Jackson Point and Solomon Gulch), whereas along the northern shore it extended farther west and finally merged with the suspended sediment plume from Mineral Creek. The combined plume then continued west from Mineral Creek, terminating at a point 1-2 km west of Gold Creek. A small, narrow and elongated surface suspended sediment plume originating in Shoup Bay entered the northwest corner of the Port and usually stayed close to the western coastline as it passed on out the Narrows.

The surface suspended sediment plumes were characterized also by relatively low values of light transmissibility, temperature, and salinity.

A wedge of relatively clear, warm and higher-salinity water was characteristically observed in the eastern half of the Narrows and extended east along the southern half of the Port as far as Sawmill Creek.

#### 1.4.12 Suspended sediment distribution in the water column

As discussed in section 1.4.11, the concentration of suspended sediment in summer and early fall usually decreased rapidly with increase in depth within the 10-m surface layer

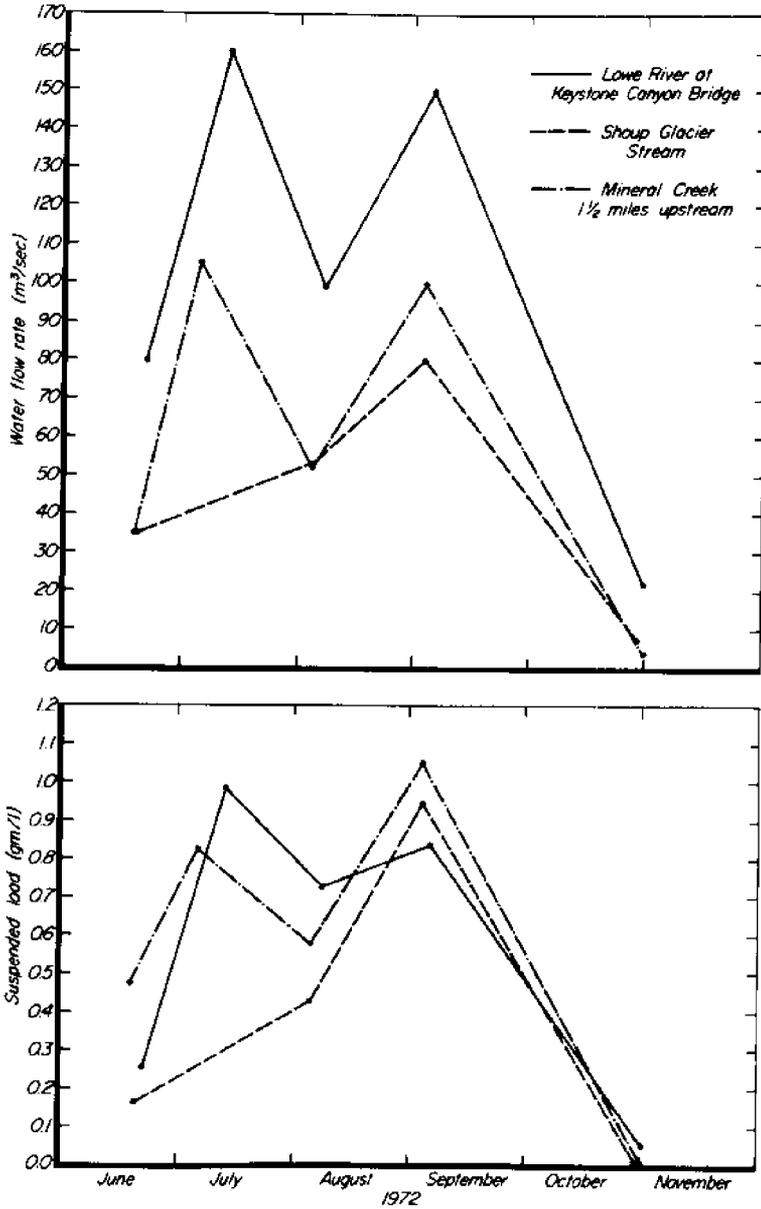


Figure 1.33 Water flow-rate and suspended sediment load of three major rivers draining into Port Valdez.

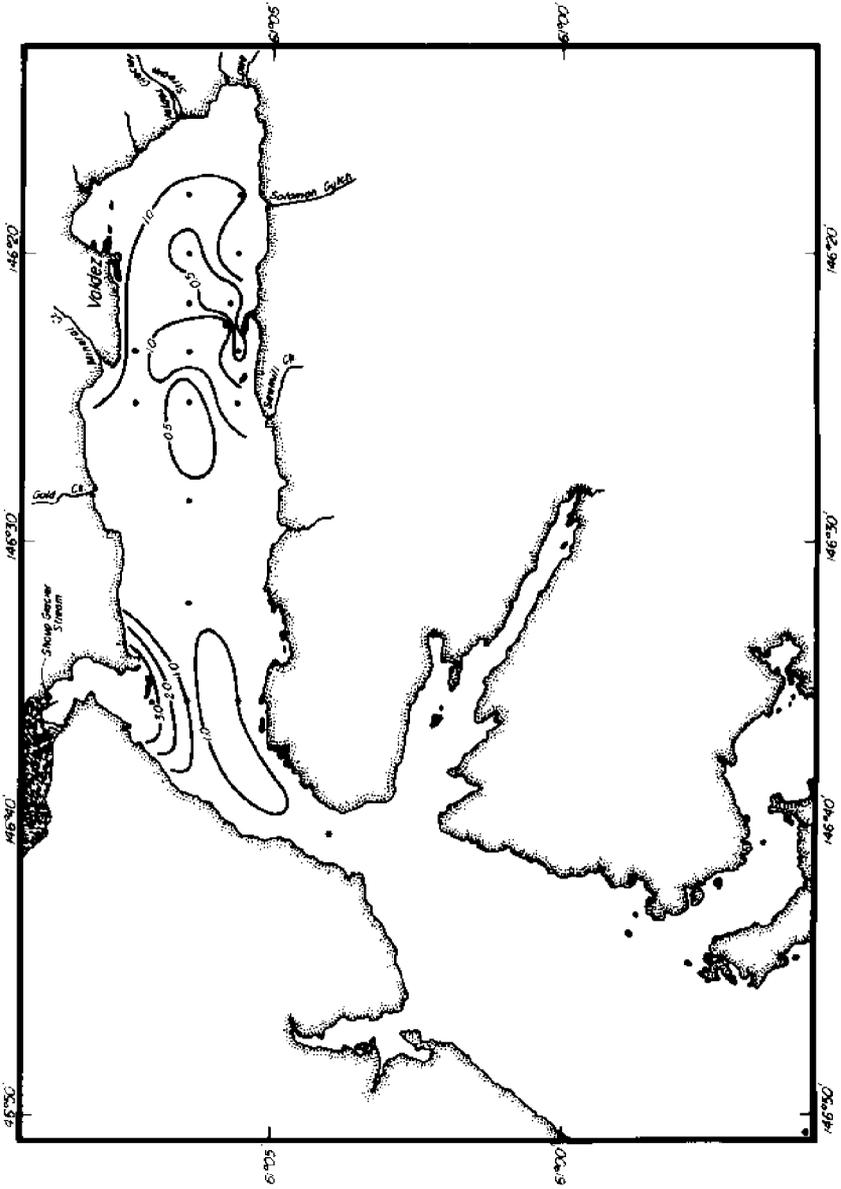


Figure 1.34 Suspended sediment distribution (mg/liter) in surface waters of Port Valdez, 20-30 September 1971.

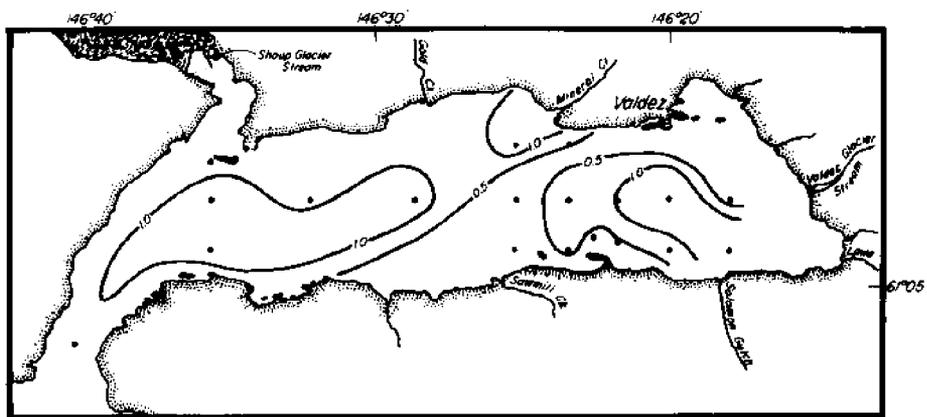


Figure 1.35 Suspended sediment distribution (mg/liter) at 50 m depth in Port Valdez, 20-30 September 1971.

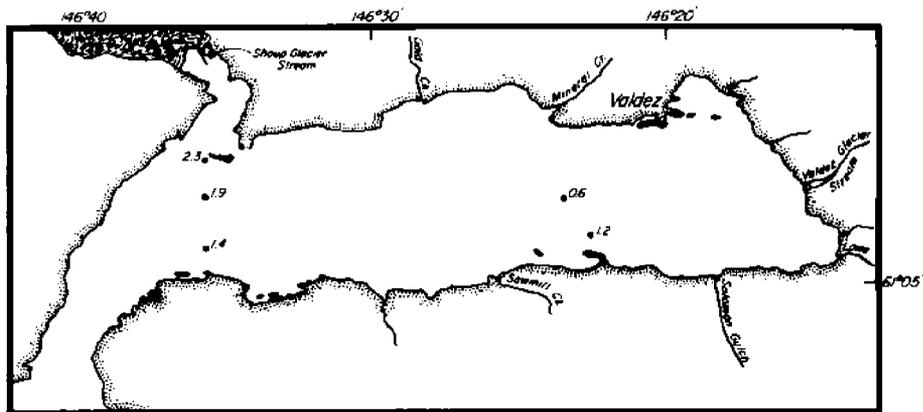


Figure 1.36 Suspended sediment measurements (mg/liter) at 100 m depth in Port Valdez, 20-30 September 1971.

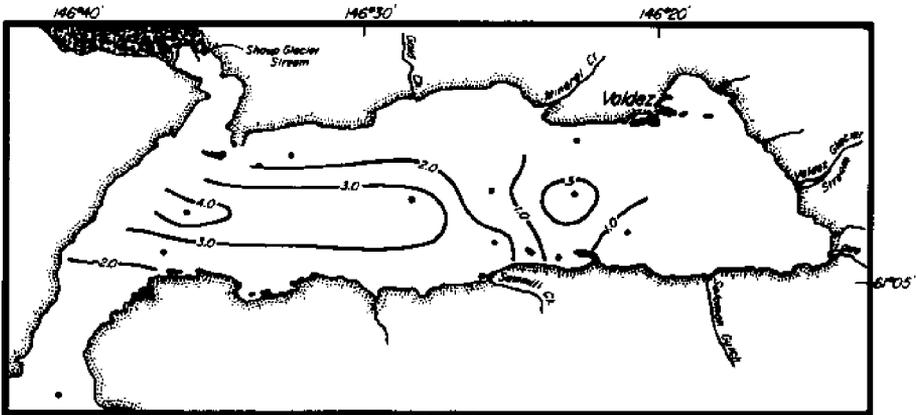


Figure 1.37 Suspended sediment distribution (mg/liter) in surface waters of Port Valdez, 12-18 April 1972.

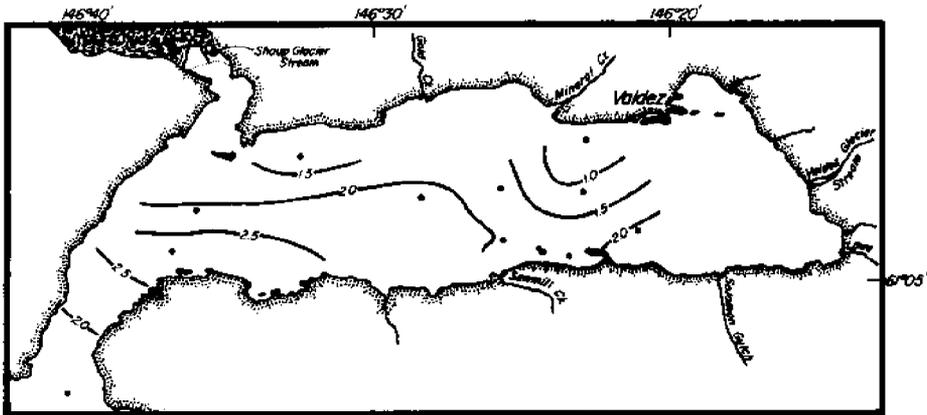


Figure 1.38 Suspended sediment distribution (mg/liter) at 50 m depth in Port Valdez, 12-18 April 1972.

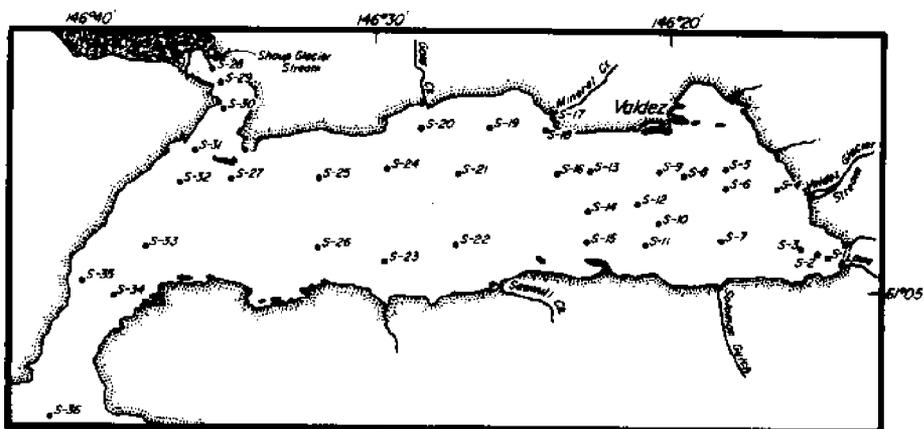


Figure 1.39 Station grid for suspended sediment sampling during June-November 1972.

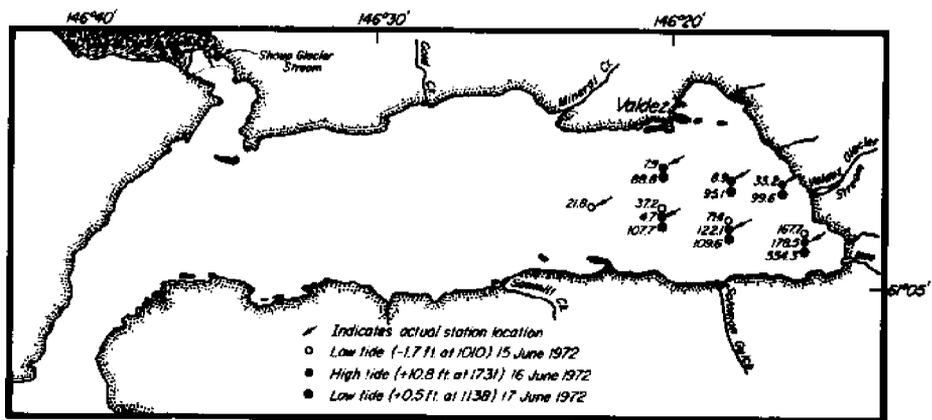


Figure 1.40 Variations of the surface suspended sediment load (mg/liter) at high and low tide, 15-17 June 1972.

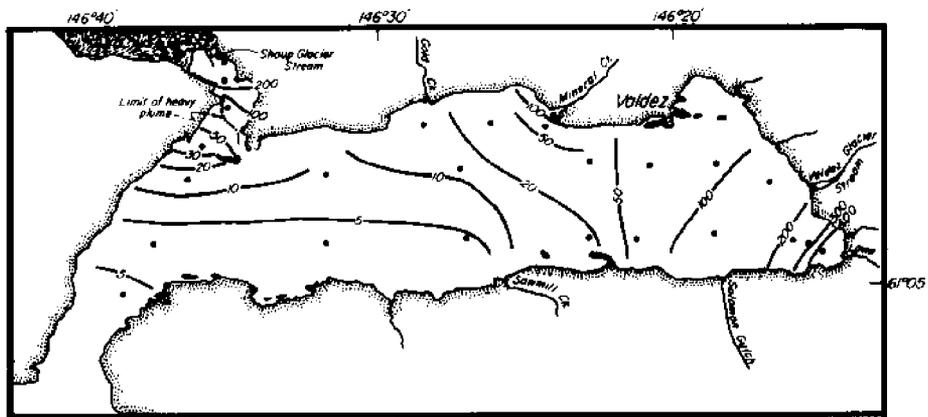


Figure 1.41 Distribution of the surface suspended sediment load (mg/liter) in Port Valdez on 2 August 1972 (1153 ADST) at low tide of 0.9 m (3.1 ft).

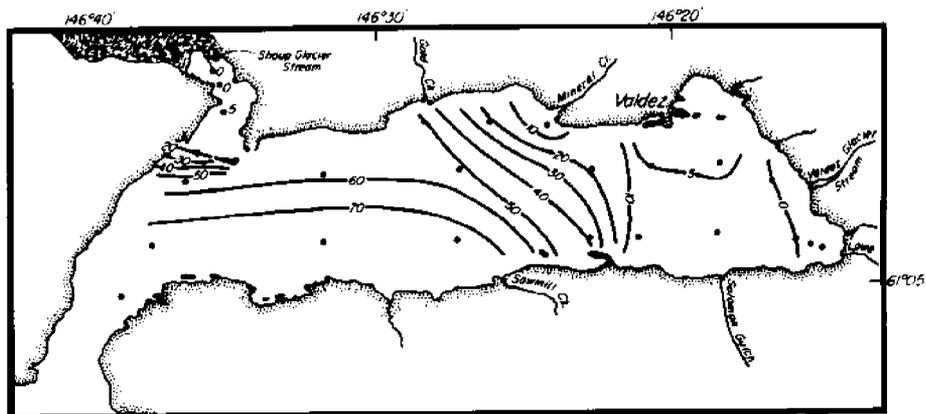


Figure 1.42 Variation of light transmissibility (%) in surface waters of Port Valdez on 2 August 1972 (1153 ADST) at low tide of 0.9 m (3.1 ft).

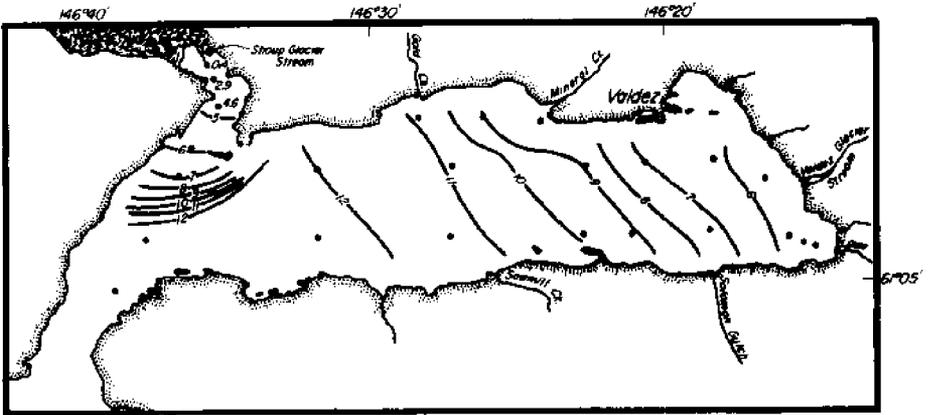


Figure 1.43 Surface water isotherms ( $^{\circ}\text{C}$ ) in Port Valdez on 2 August 1972 (1153 ADST) at low tide of 0.9 m (3.1 ft).

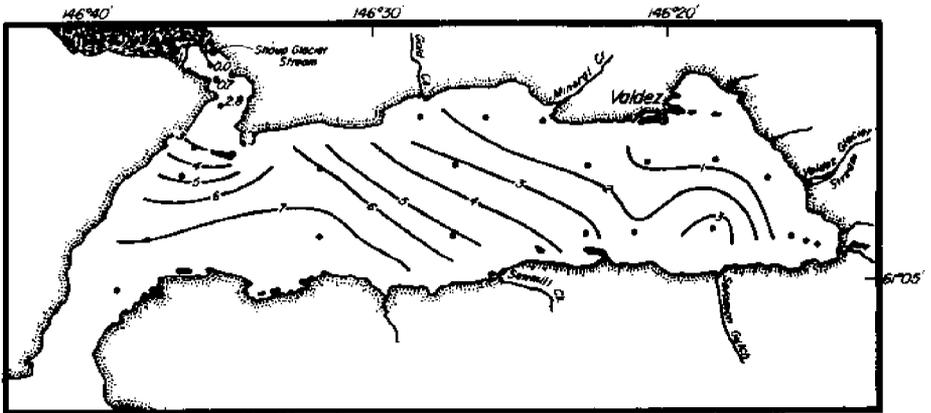


Figure 1.44 Surface water isohalines ( $\text{‰}$ ) in Port Valdez on 2 August 1972 (1153 ADST) at low tide of 0.9 m (3.1 ft).

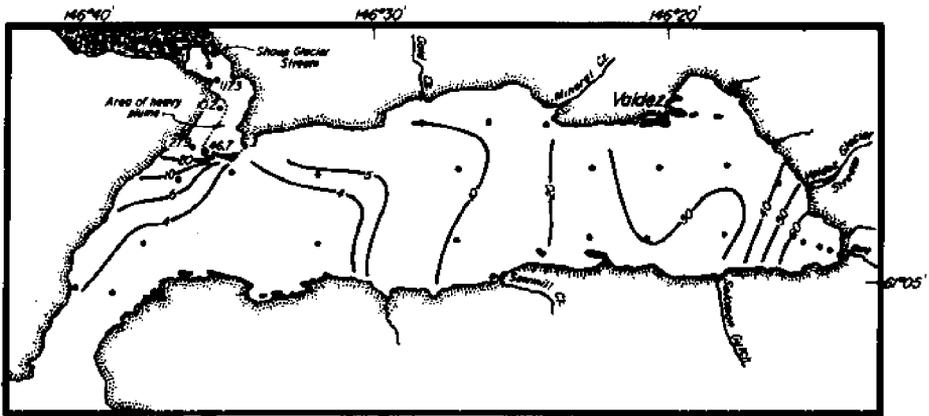


Figure 1.45 Distribution of the surface suspended sediment load (mg/liter) in Port Valdez on 31 August 1972 during flood tide: low tide 1.2 m (4.1 ft) at 1134 ADST, high tide 3.6 m (11.7 ft) at 1737.

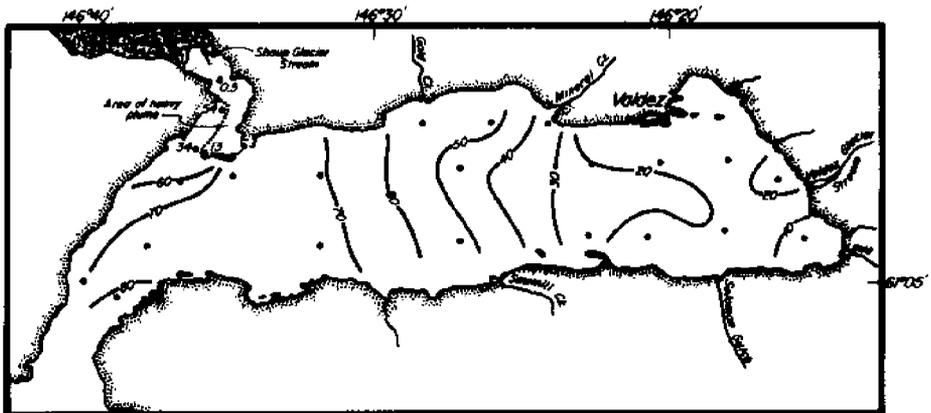


Figure 1.46 Variation of light transmissibility (%) in surface waters of Port Valdez on 31 August 1972 during flood tide: low tide 1.2 m (4.1 ft) at 1134 ADST, high tide 3.6 m (11.7 ft) at 1737.



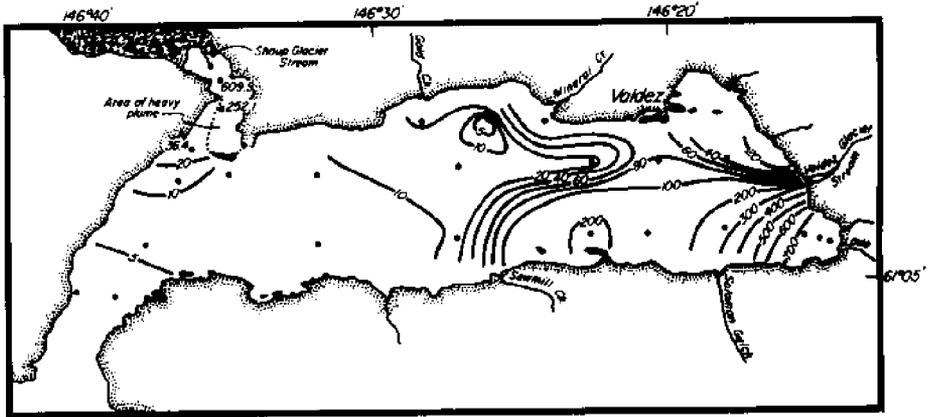


Figure 1.49 Distribution of the surface suspended sediment load (mg/liter) in Port Valdez on 4 September 1972 during flood tide: low tide 1.1 m (3.5 ft) at 1647 ADST, high tide 3.7 m (12.0 ft) at 2056.

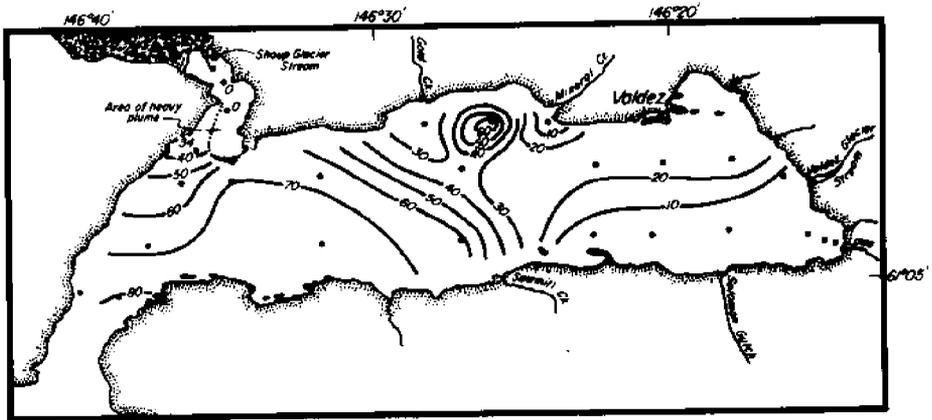


Figure 1.50 Variation of light transmissibility (%) in surface waters of Port Valdez on 4 September 1972 during flood tide: low tide 1.1 m (3.5 ft) at 1647 ADST, high tide 3.7 m (12.0 ft) at 2056.

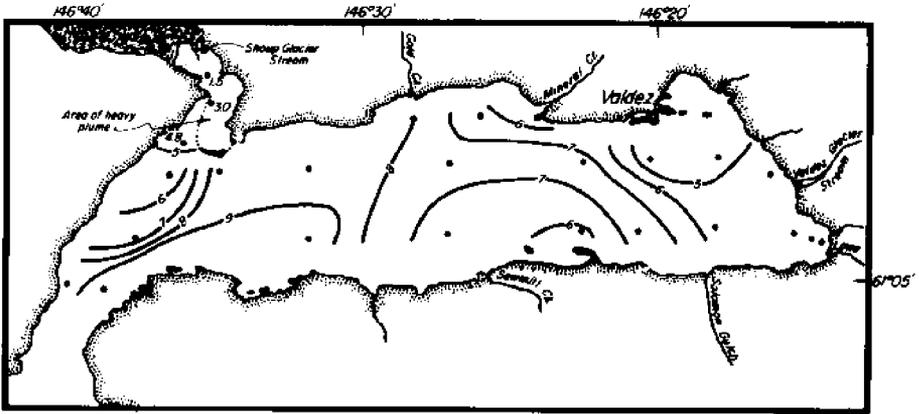


Figure 1.51 Surface water isotherms ( $^{\circ}\text{C}$ ) in Port Valdez on 4 September 1972 during flood tide: low tide 1.1 m (3.5 ft) at 1647 at 1647 ADST, high tide 3.7 m (12.0 ft) at 2056.

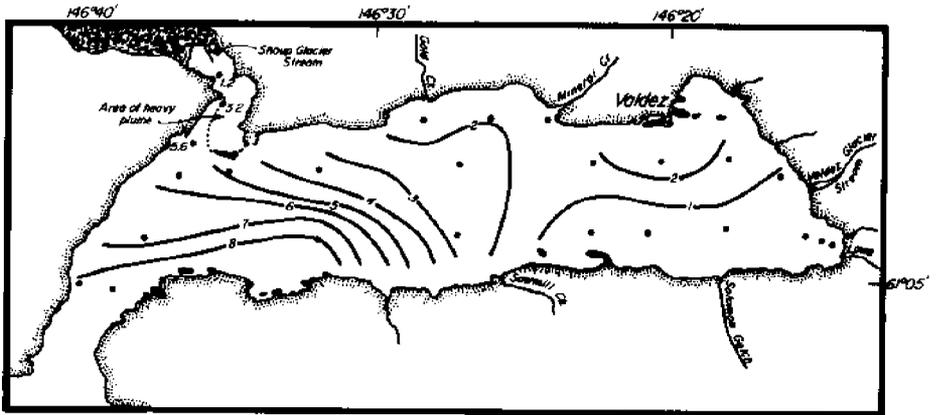


Figure 1.52 Surface water isohalines ( $\text{‰}$ ) in Port Valdez on 4 September 1972 during flood tide: low tide 1.1 m (3.5 ft) at 1647 ADST, high tide 3.7 m (12.0 ft) at 2056.

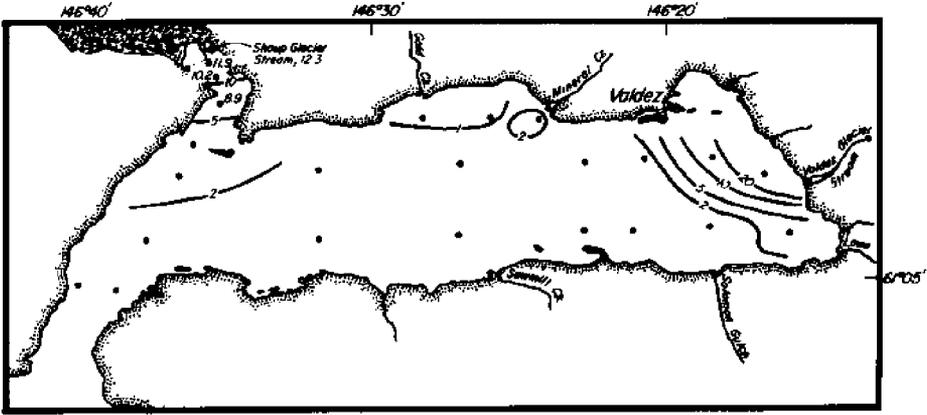


Figure 1.53 Distribution of the surface suspended sediment load (mg/liter) in Port Valdez on 28 October 1972 during flood tide: low tide 1.5 m (4.9 ft) at 1123 ADST, high tide 3.4 m (11.2 ft) at 1710.

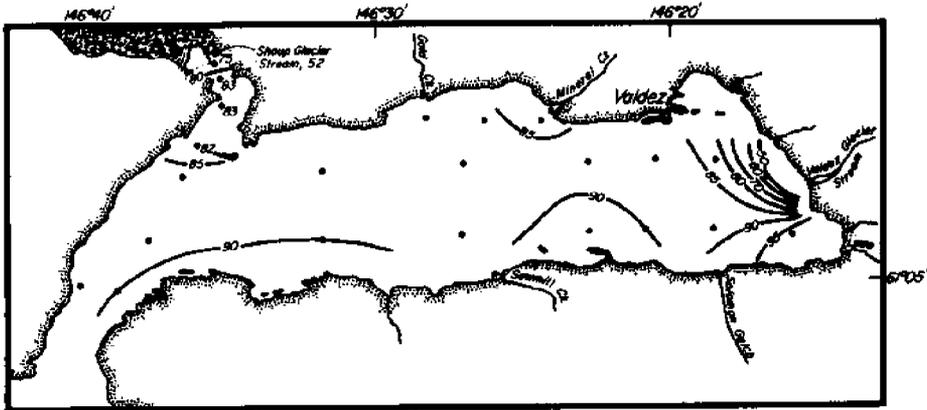


Figure 1.54 Variation of light transmissibility (%) in surface waters of Port Valdez on 28 October 1972 during flood tide: low tide 1.5 m (4.9 ft) at 1123 ADST, high tide 3.4 m (11.2 ft) at 1710.

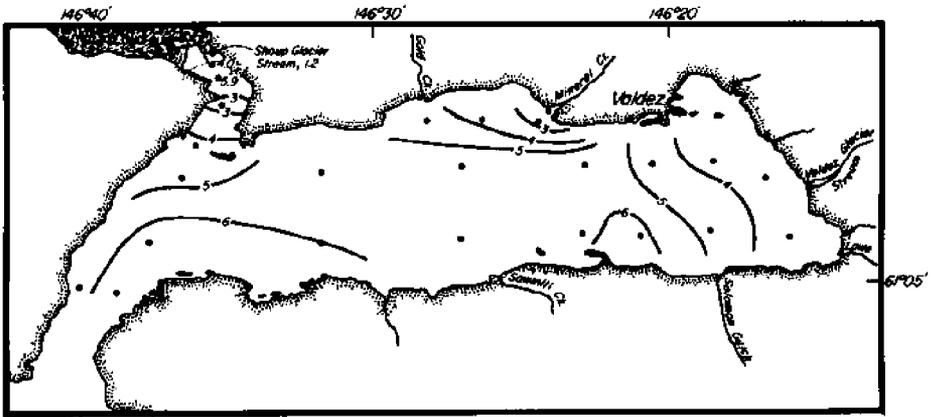


Figure 1.55 Surface water isotherms ( $^{\circ}\text{C}$ ) in Port Valdez on 28 October 1972 during flood tide: low tide 1.5 m (4.9 ft) at 1123 ADST, high tide 3.4 m (11.2 ft) at 1710.

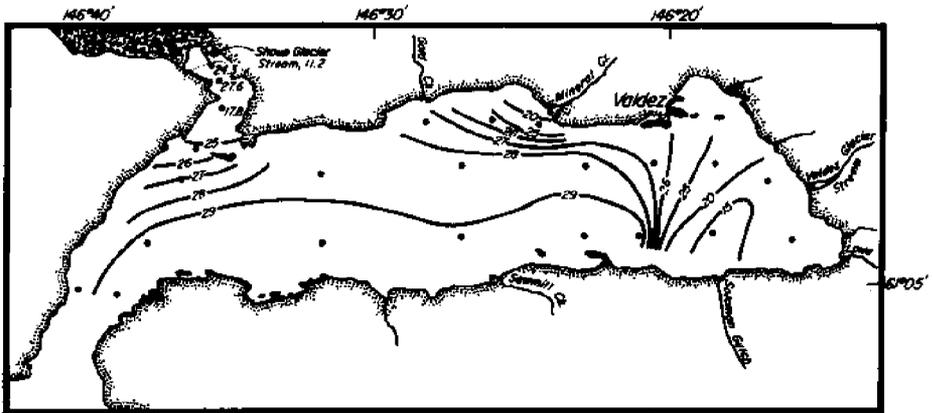


Figure 1.56 Surface water isohalines ( $\text{‰}$ ) in Port Valdez on 28 October 1972 during flood tide: low tide 1.5 m (4.9 ft) at 1123 ADST, high tide 3.4 m (11.2 ft) at 1710.

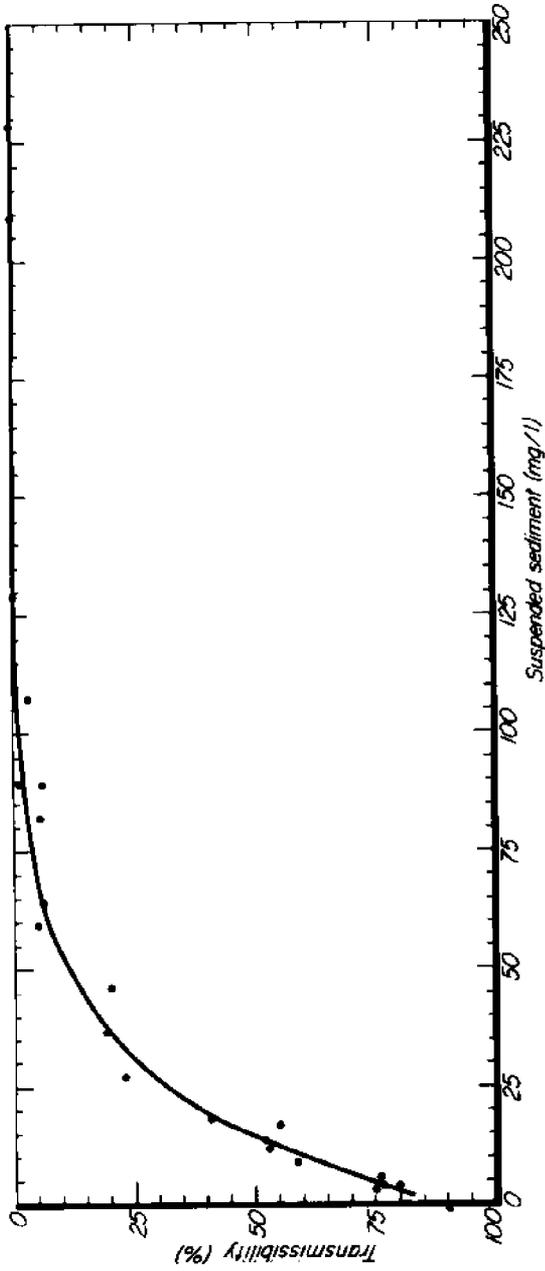


Figure 1.57 Light transmissibility as a function of suspended sediment load for Port Valdez surface waters, 2 August 1972.

(Figures 1.58-1.71), accompanied by a rapid increase in salinity. The nature of the thermocline in the surface layer is highly variable and may increase or decrease.

Below 10 m the suspended sediment load was relatively uniform down to the generally maximum sampling depth of 100 m, ranging from about 2-5 mg/liter (Figures 1.58-1.71). Occasional samples below 100 m were suggestive that the relatively low suspended sediment load persisted to the bottom (Figures 1.63 and 1.69). A subsurface maximum or increase in the suspended sediment load was frequently found in the upper 10 m and sometimes at greater depths. Deeper subsurface maxima in the suspended sediment load have been observed in the Narrows at about 20 m (Figures 1.61 and 1.69). The subsurface maxima do not appear to be confined to any particular area in the Port. The existence of nepheloid layers (Figures 1.58, 1.62, 1.65, 1.71) below the surface layer suggests subaqueous transport in the inlet. Microscopic examination of the suspended sediments from station S-7 (Figure 1.58) at about 100 m depth revealed that the material in these layers consisted of well-sorted silt. The size and extent of these layers remain unknown. Turbid layer transport in southern Alaskan fjords is considered significant and has been discussed by Wright (1971).

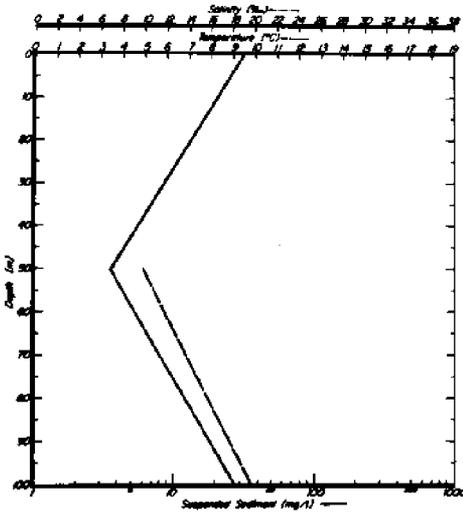
#### 1.4.13 Suspended sediment transport

The relatively high concentrations of suspended sediment found below the 10-m surface layer indicated that suspended sediment transport in subsurface layers might be an important mode of sediment transport in Port Valdez. To evaluate the net sediment movement in Port Valdez, it was essential to measure the suspended sediment load throughout the water column and throughout the Port during at least one tidal cycle. Suspended sediments were sampled from 0-100 m at 10 evenly spaced stations (Figure 1.72), beginning at the west end of the Port just after high tide and proceeding such that all 10 stations were sampled during a single ebb tide. Following this the stations were again sampled, this time from east to west, on the following flood tide. The distribution of suspended sediment load and temperature with depth at each station is given in Figures 1.64-1.68 (31 July data); vertical cross-sections along transects A-B and C-D of Figure 1.72 are presented in Figures 1.73-1.76.

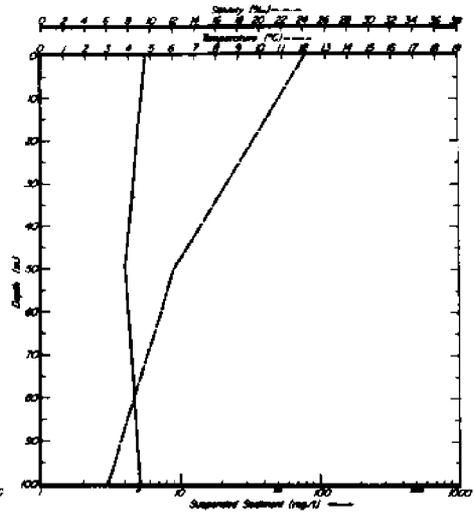
The water movements in Port Valdez, as interpreted from the limited measurements of suspended sediment load, temperature and salinity during summer 1972, can be described at best only qualitatively. The primary objective of this study was to delineate the sediment movement; however, measurements of the conservative properties (temperature and salinity) of seawater were conducted to aid in the thorough interpretation of suspended sediment data and allow the investigators to propose a general circulation pattern for Port Valdez (Figure 1.77).

The surface water circulation pattern in Port Valdez is a result of water discharge from various rivers, tides, winds and the Coriolis Effect. These factors set up a relatively stable, counterclockwise circulation cell (Figures 1.41, 1.43-1.44, 1.47, 1.55-1.56), which consists of several smaller eddies throughout the Port. Aerial photographs of Port Valdez taken from aboard NASA aircraft (Mission 209, Site 314, Flights 3 and 4 on 17-18 July 1972) confirmed the surface circulation pattern described here. The surface layer in the northern and eastern parts of the Port was comprised predominantly of water discharged by rivers, whereas the surface layer in the southern and western parts was dominated by incoming seawater. It appeared that the area north and east of Sawmill Creek was a zone of mixing between incoming seawater and fresh water brought in by the Lowe River and Valdez Glacier Stream.

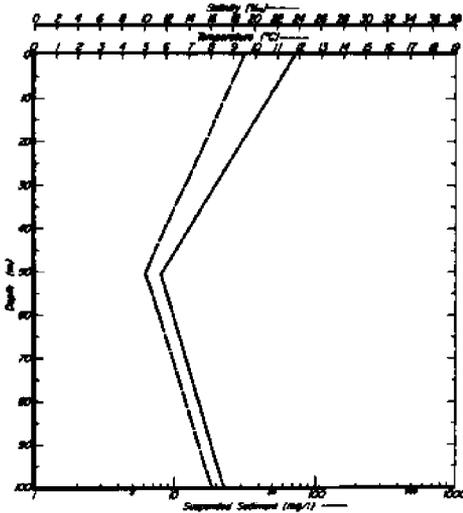
Subsurface measurements of various parameters and the representative transects of suspended sediment load and temperature variations made during a full tidal cycle on 31 July 1972 (Figures 1.73-1.76) indicated significant subsurface water movement in Port



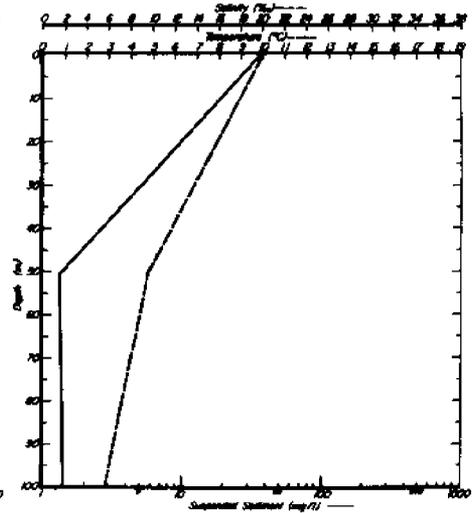
Station: S-7  
 Date: 14 June 1972  
 Time: 0430 ADST  
 Tide: Low (-2.7 ft at 0500)



Station: S-10  
 Date: 14 June 1972  
 Time: 0430 ADST  
 Tide: Low (-2.7 ft at 0500)

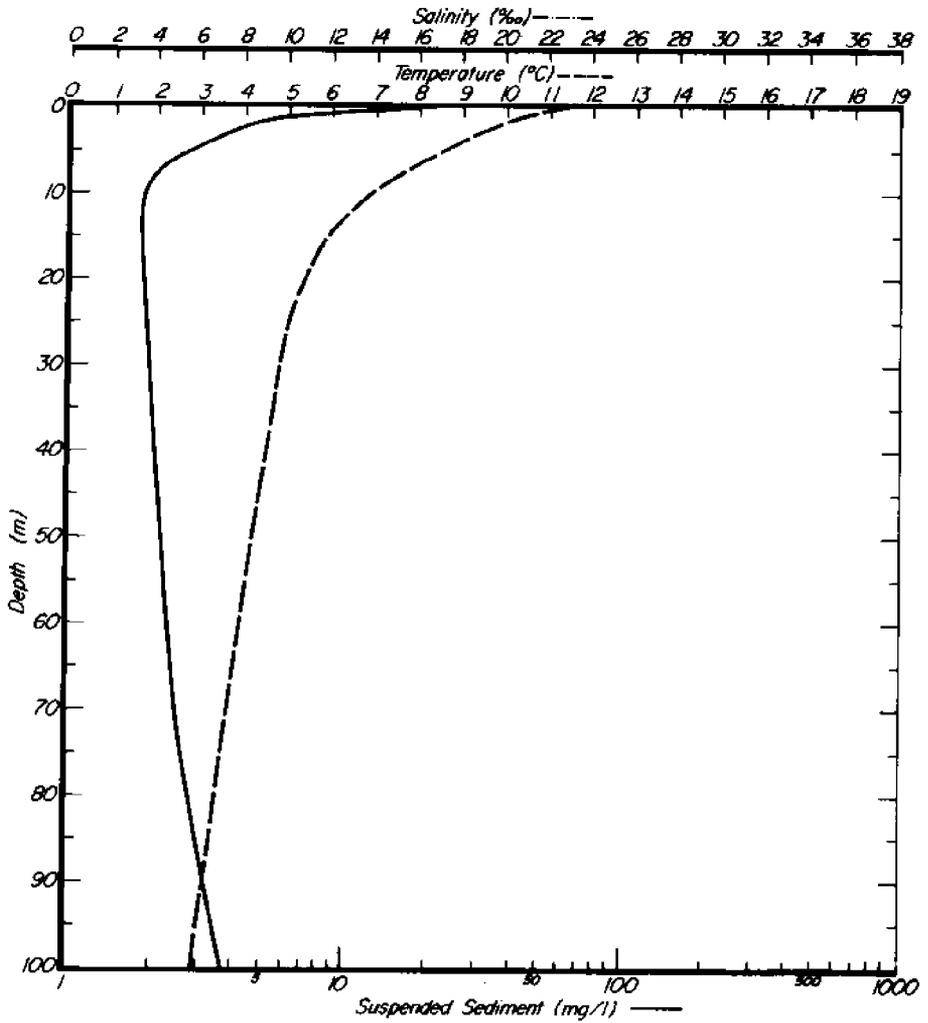


Station: S-7  
 Date: 15 June 1972  
 Time: 0430 ADST  
 Tide: Low (-1.7 ft at 0400)



Station: S-10  
 Date: 15 June 1972  
 Time: 0430 ADST  
 Tide: Low (-1.7 ft at 0400)

Figure 1.58 Depth profiles of suspended sediment load and temperature in Port Valdez, 14-15 June 1972.



Station: S-14  
 Date: 15 June 1972  
 Time: 1135 ADST  
 Tide: Low (-1.7 ft at 1010)

Figure 1.59 Depth profiles of suspended sediment load and temperature in Port Valdez, 15 June 1972.

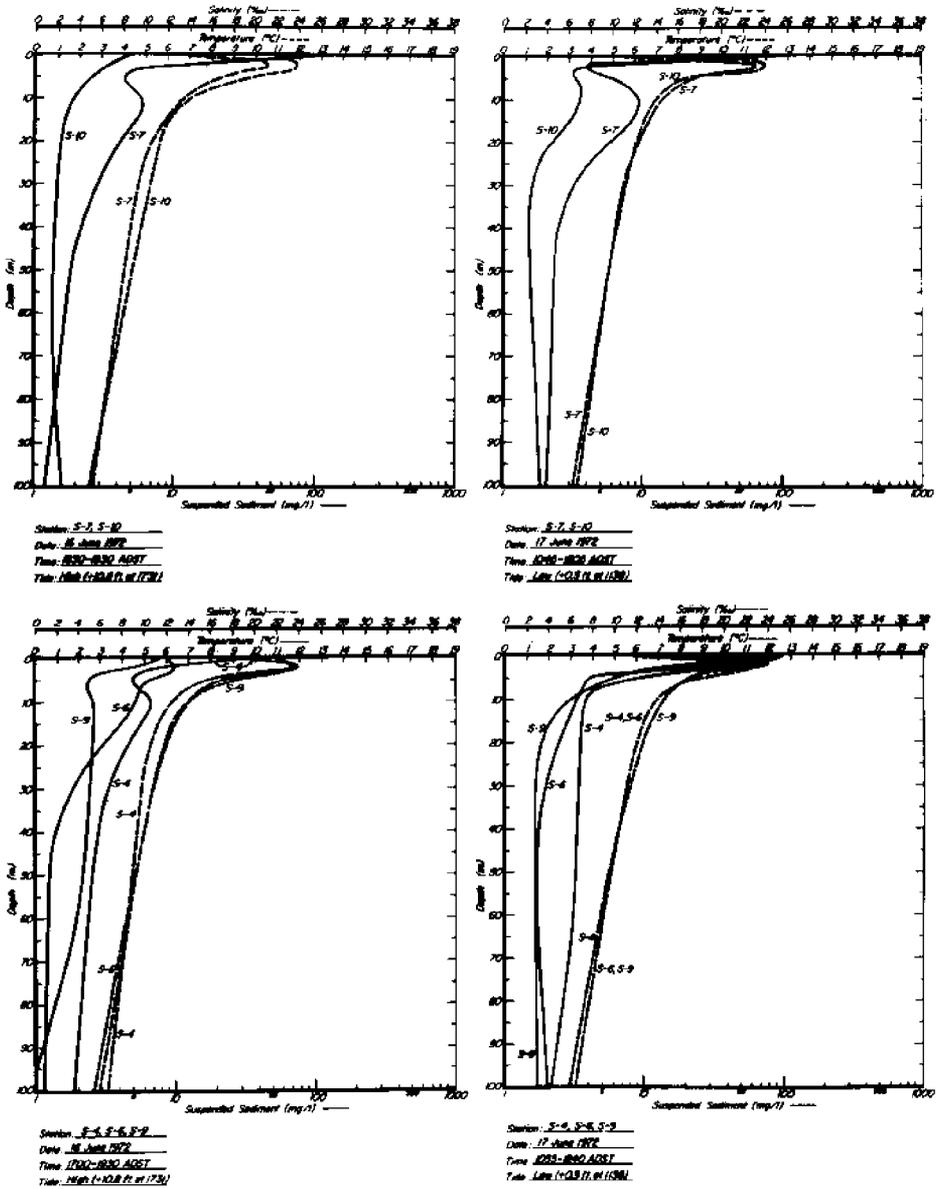


Figure 1.60 Depth profiles of suspended sediment load and temperature in Port Valdez, 16-17 June 1972.

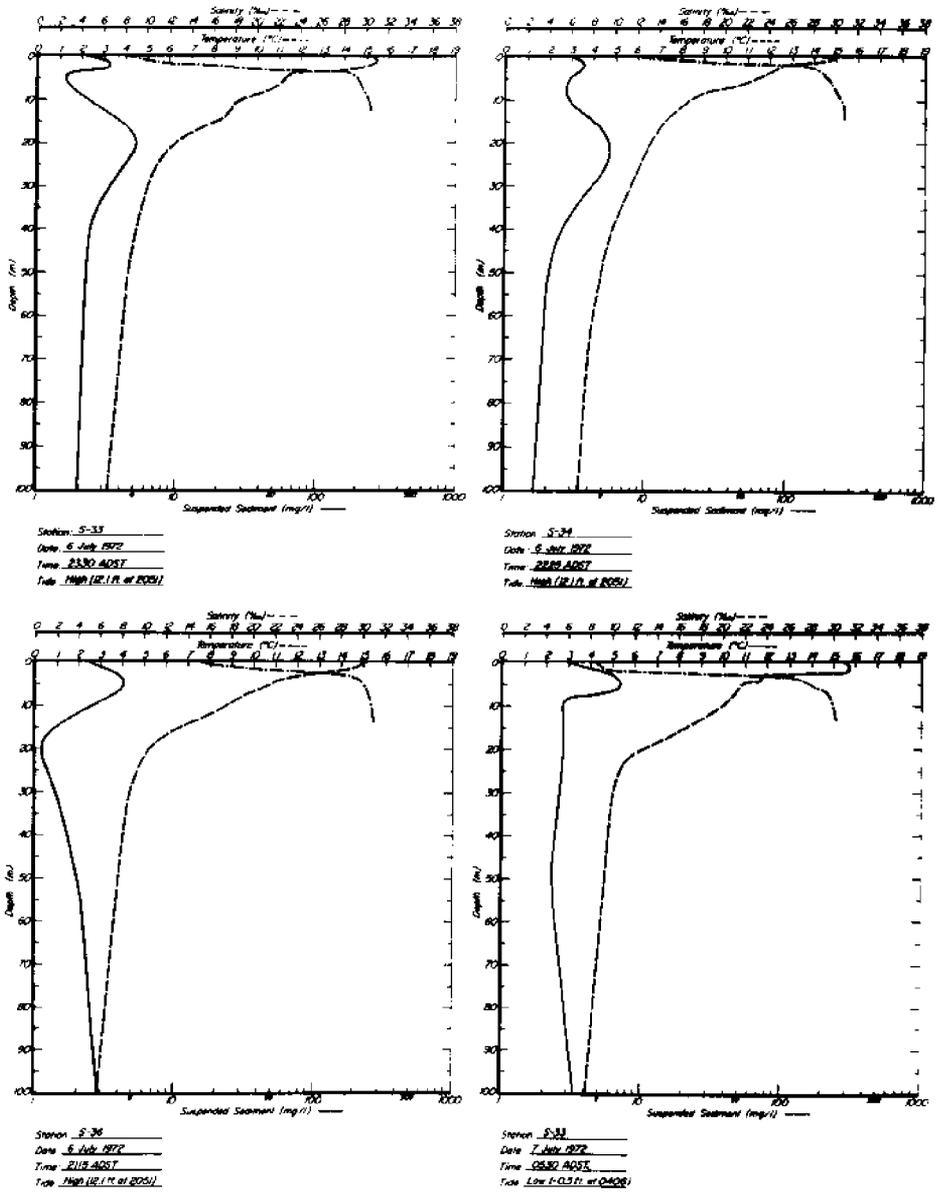


Figure 1.61 Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 6-7 July 1972.

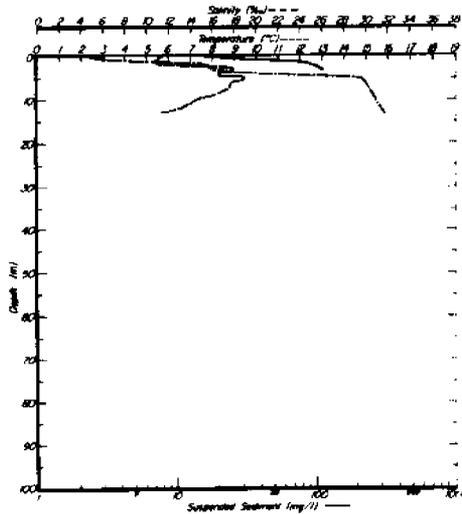
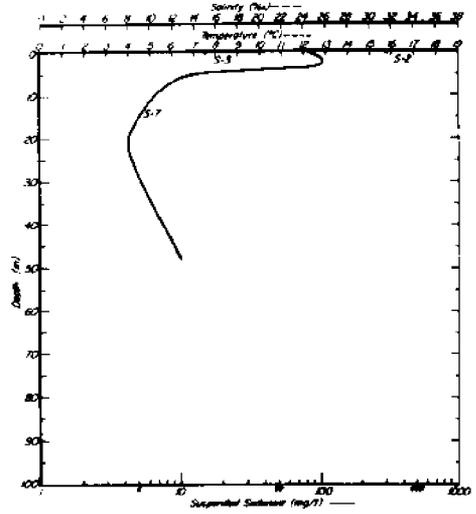
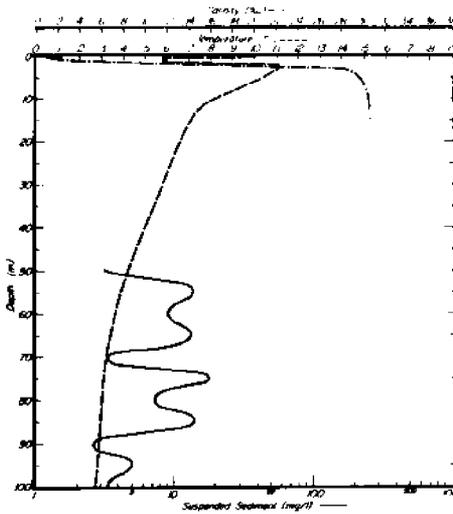


Figure 1.62 Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 6-10 July 1972.

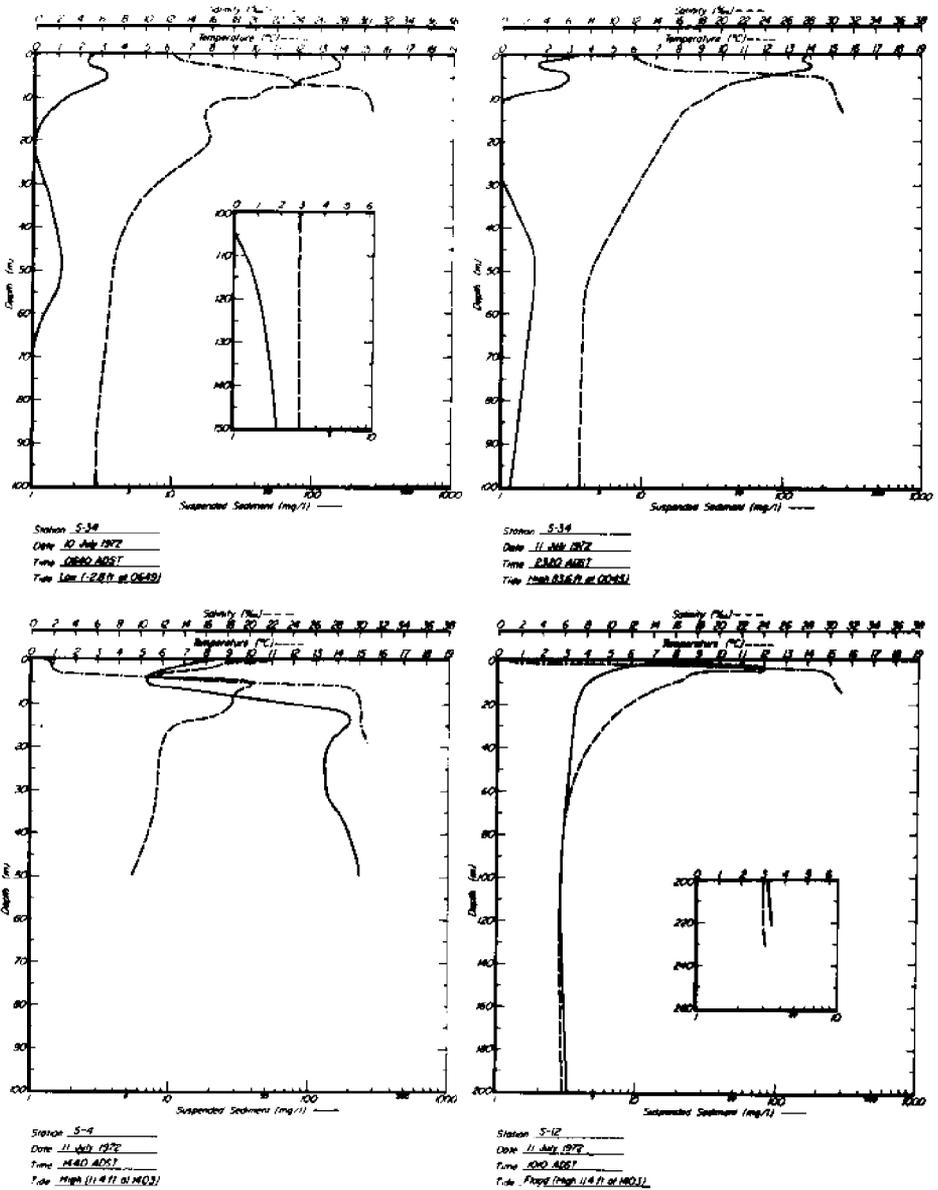


Figure 1.63 Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 10-11 July 1972.

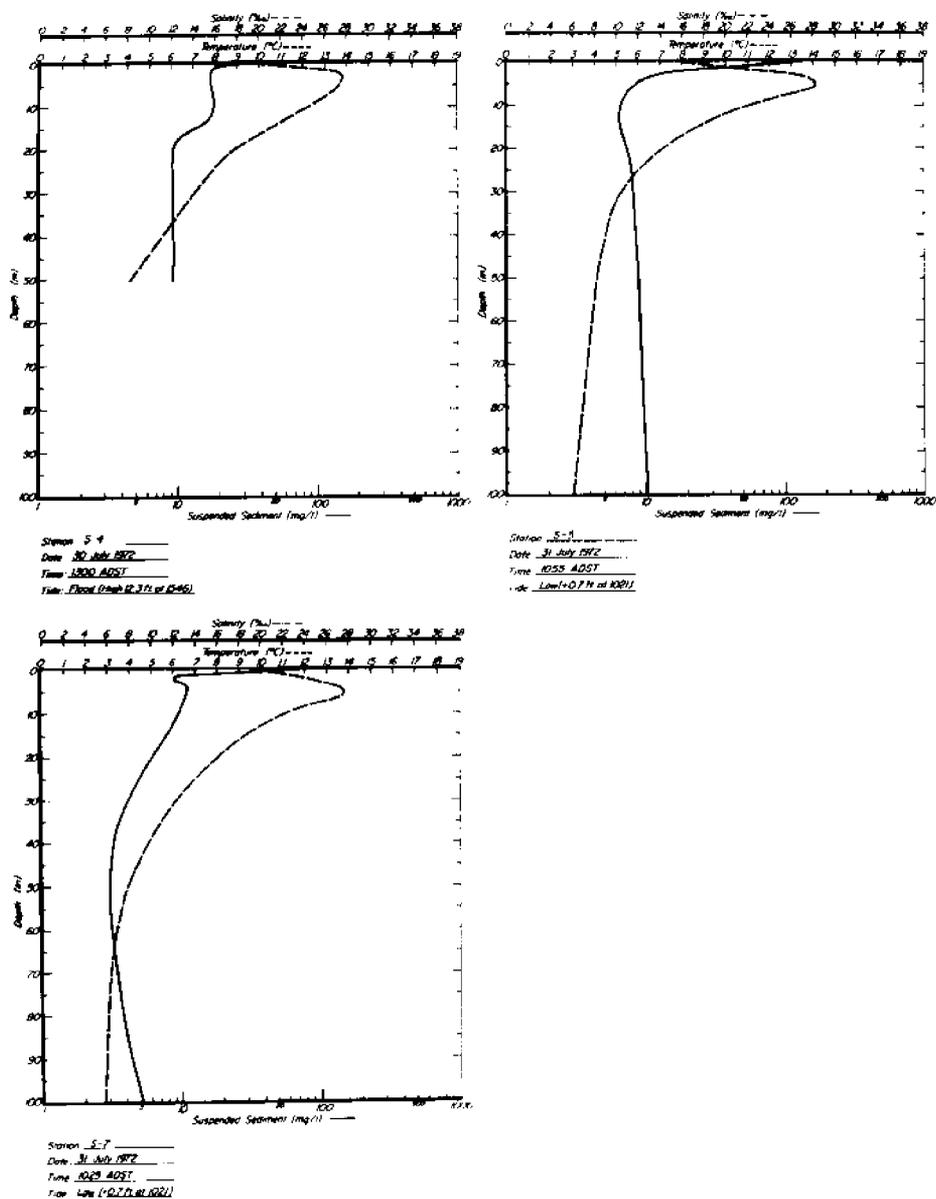


Figure 1.64 Depth profiles of suspended sediment load and temperature in Port Valdez, 30-31 July 1972.

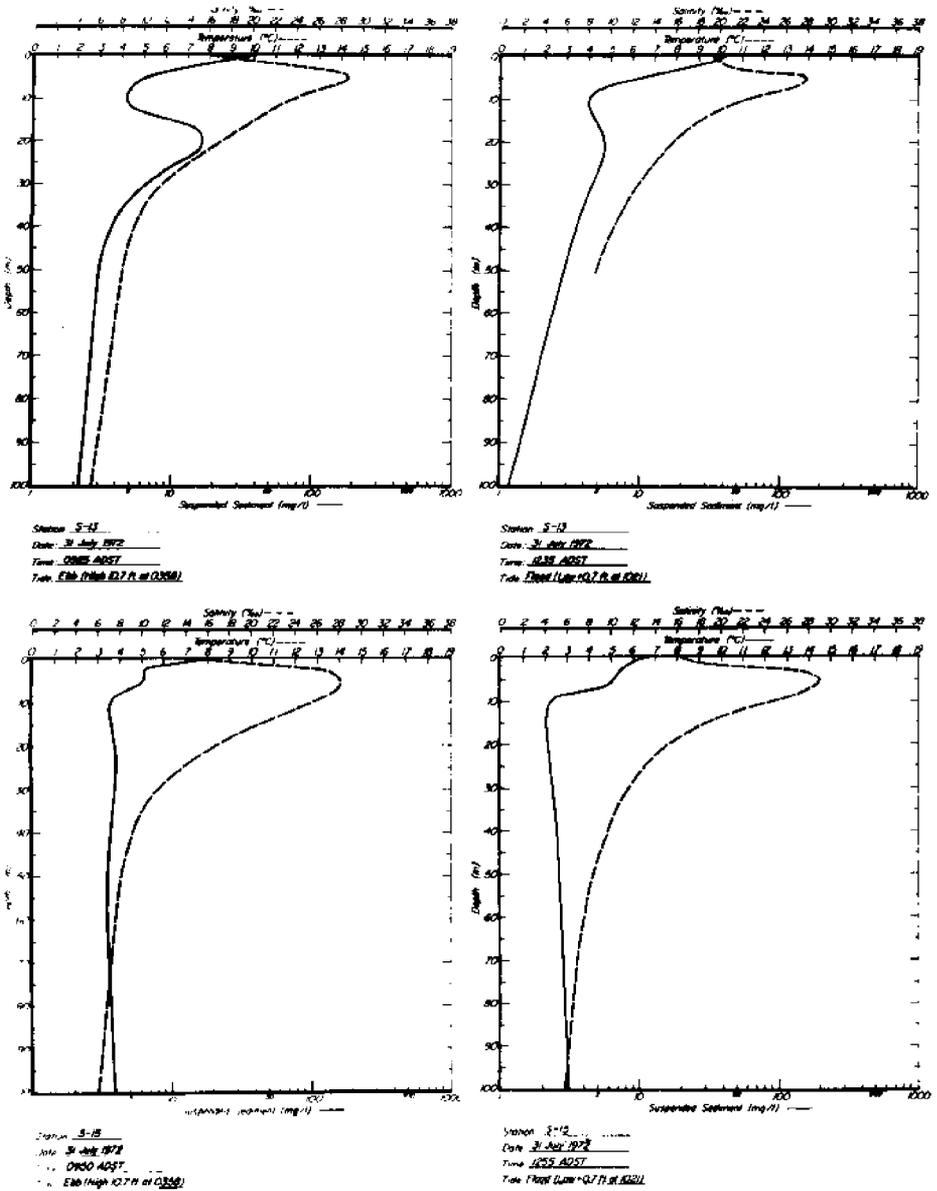


Figure 1.65 Depth profiles of suspended sediment load and temperature in Port Valdez, 31 July 1972, stations S-13 and S-15.

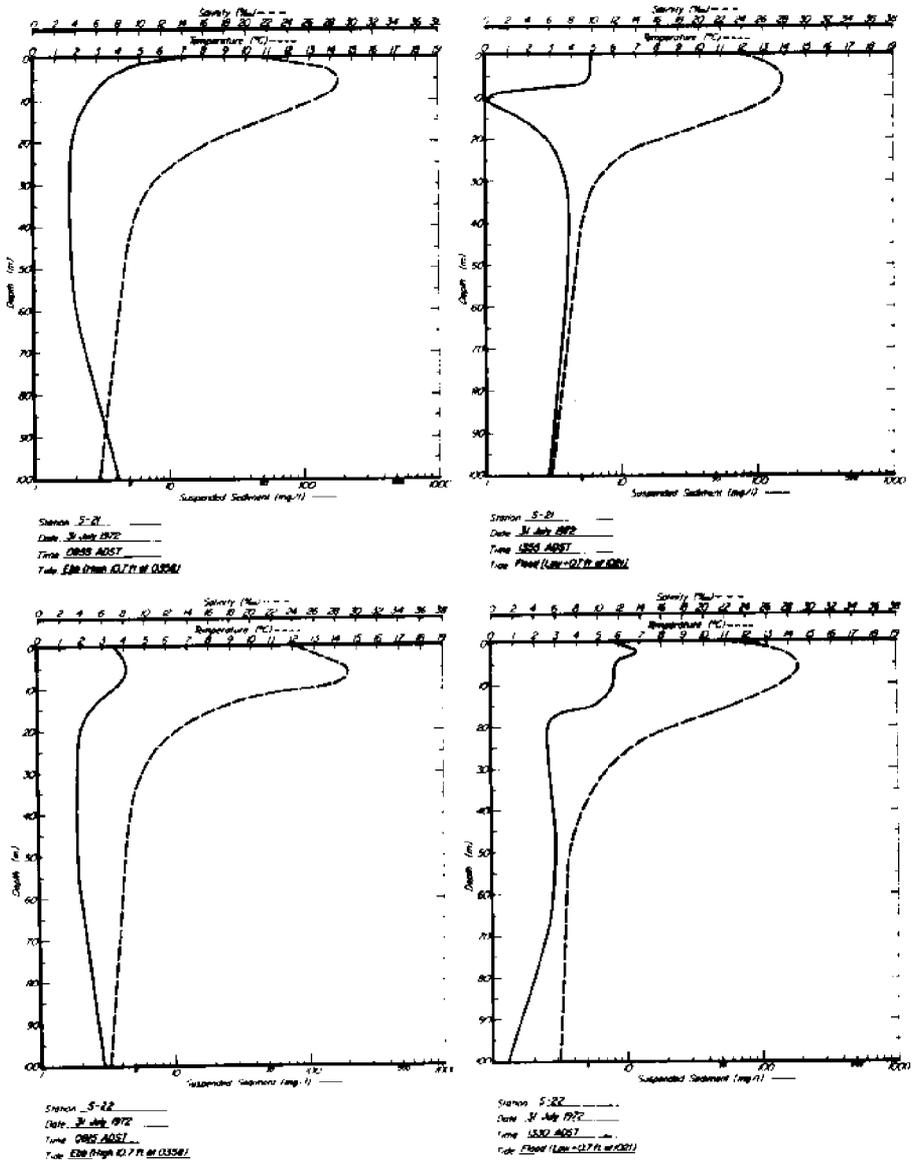


Figure 1.66 Depth profiles of suspended sediment load and temperature in Port Valdez, 31 July 1972, stations S-21 and S-22.

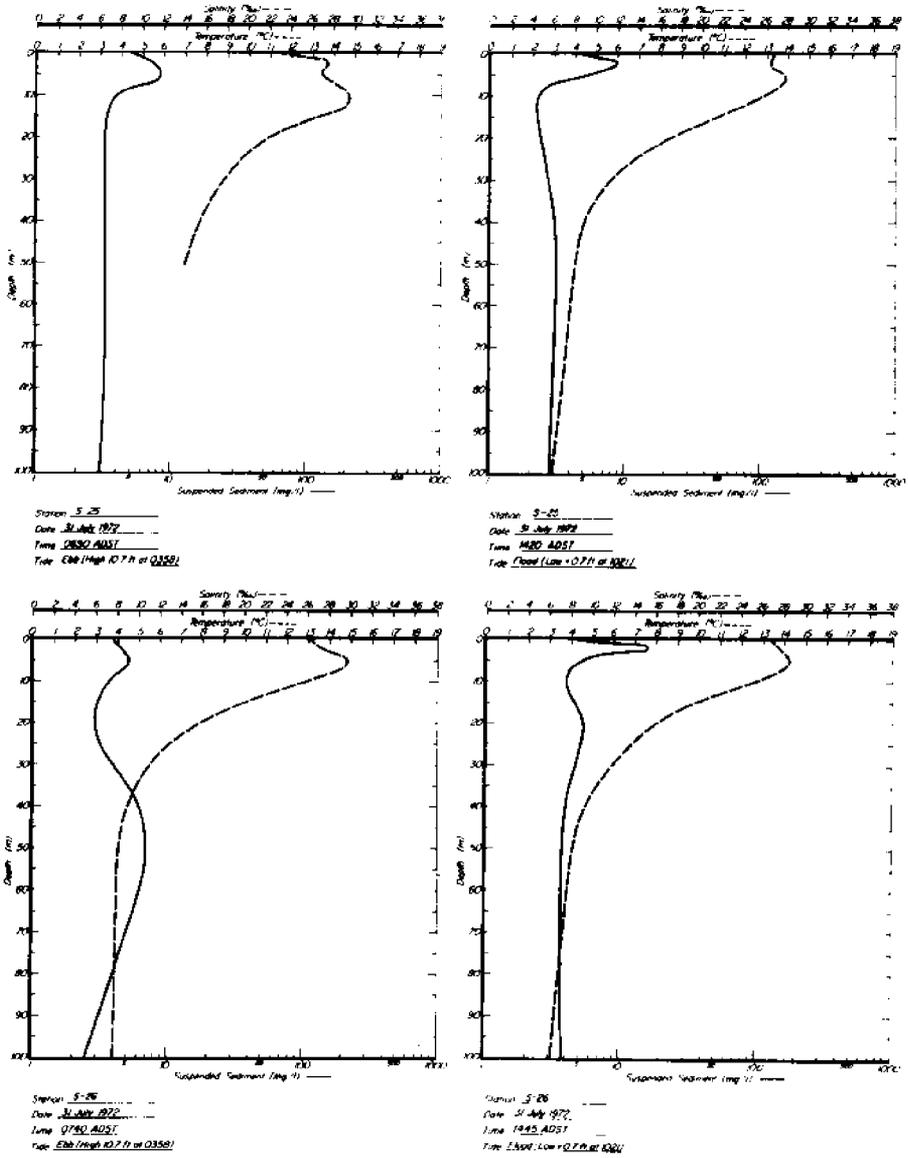


Figure 1.67 Depth profiles of suspended sediment load and temperature in Port Valdez, 31 July 1972, stations S-25 and S-26.

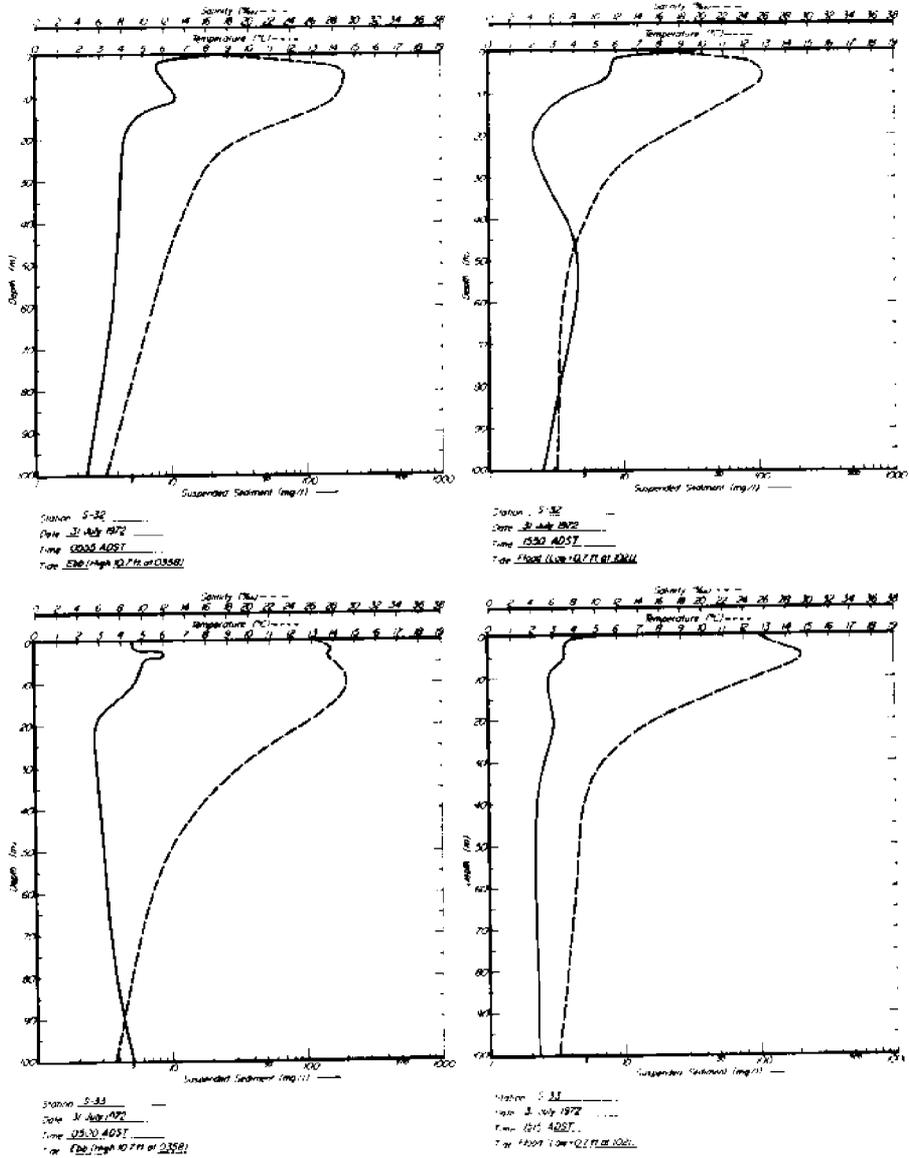


Figure 1.68 Depth profiles of suspended sediment load and temperature in Port Valdez, 31 July 1972, stations S-32 and S-33.

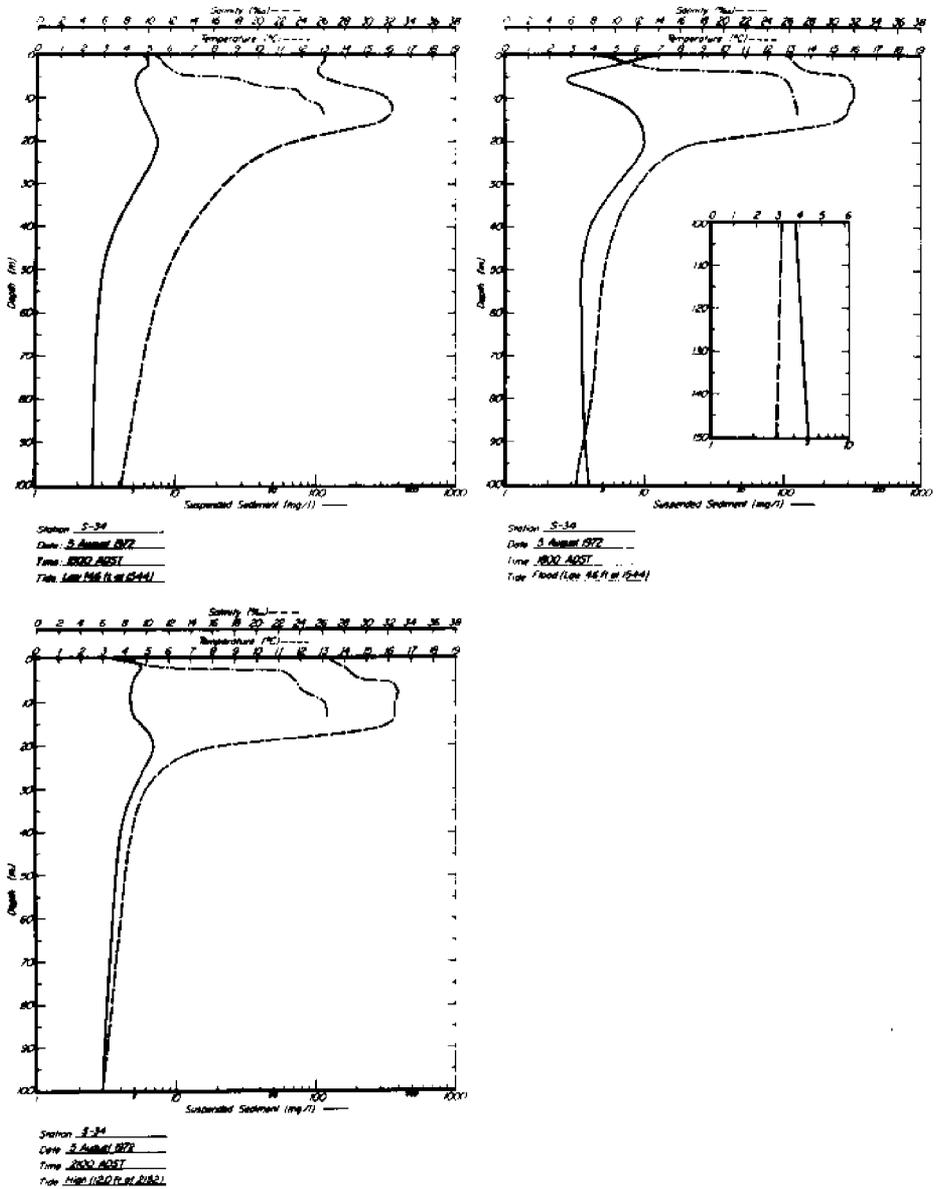


Figure 1.69 Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 5 August 1972, station S-34.

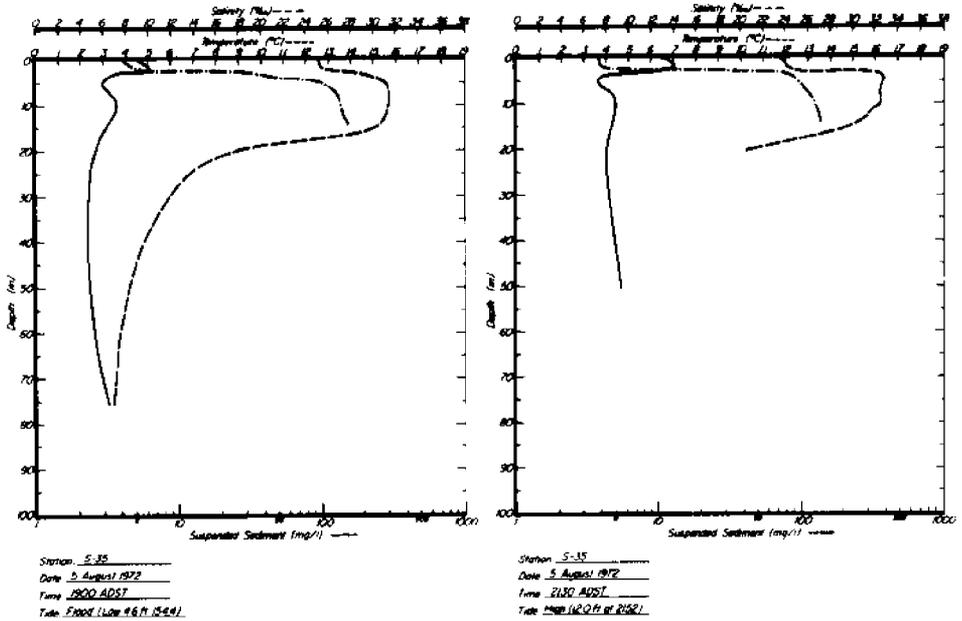
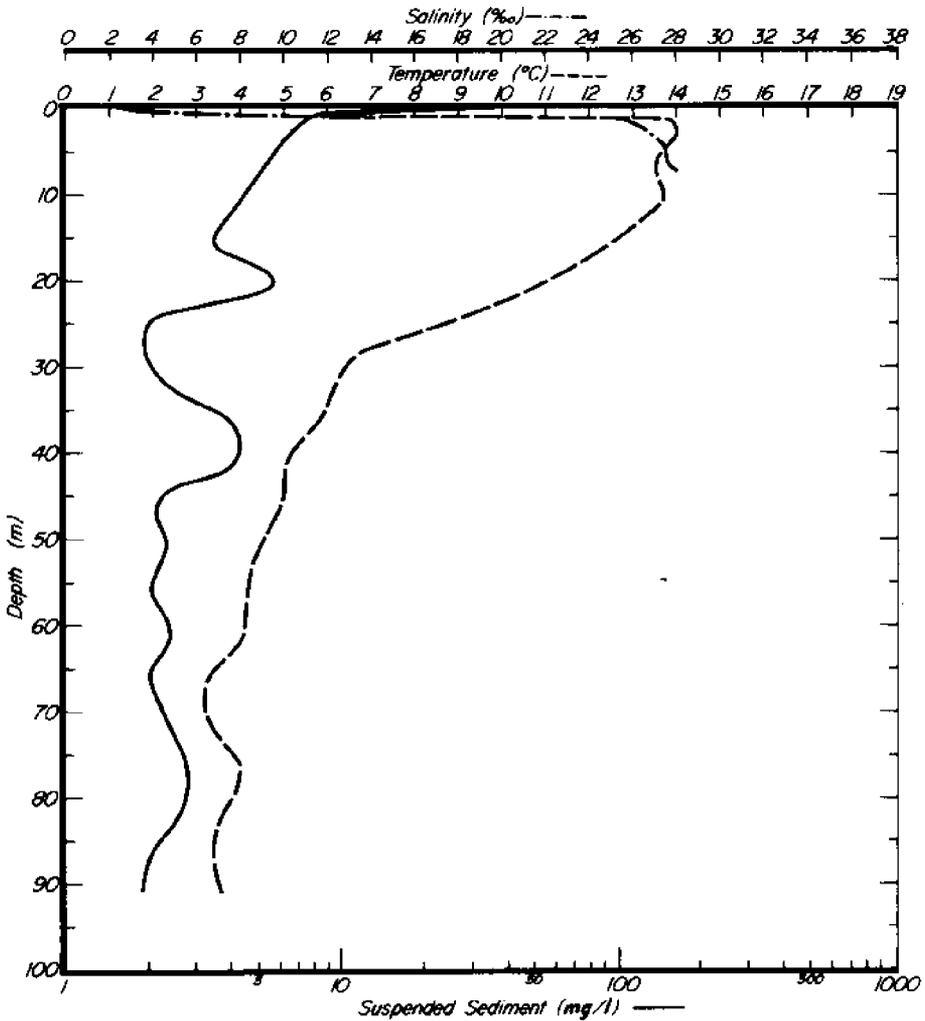


Figure 1.70 Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 5 August 1972, station S-35.



Station: S-12  
 Date: 4 September 1972  
 Time: 1215 ADST  
 Tide: Ebb (High 10.3 ft. at 1122)

**Figure 1.71** Depth profiles of suspended sediment load, temperature, and salinity in Port Valdez, 4 September 1972.

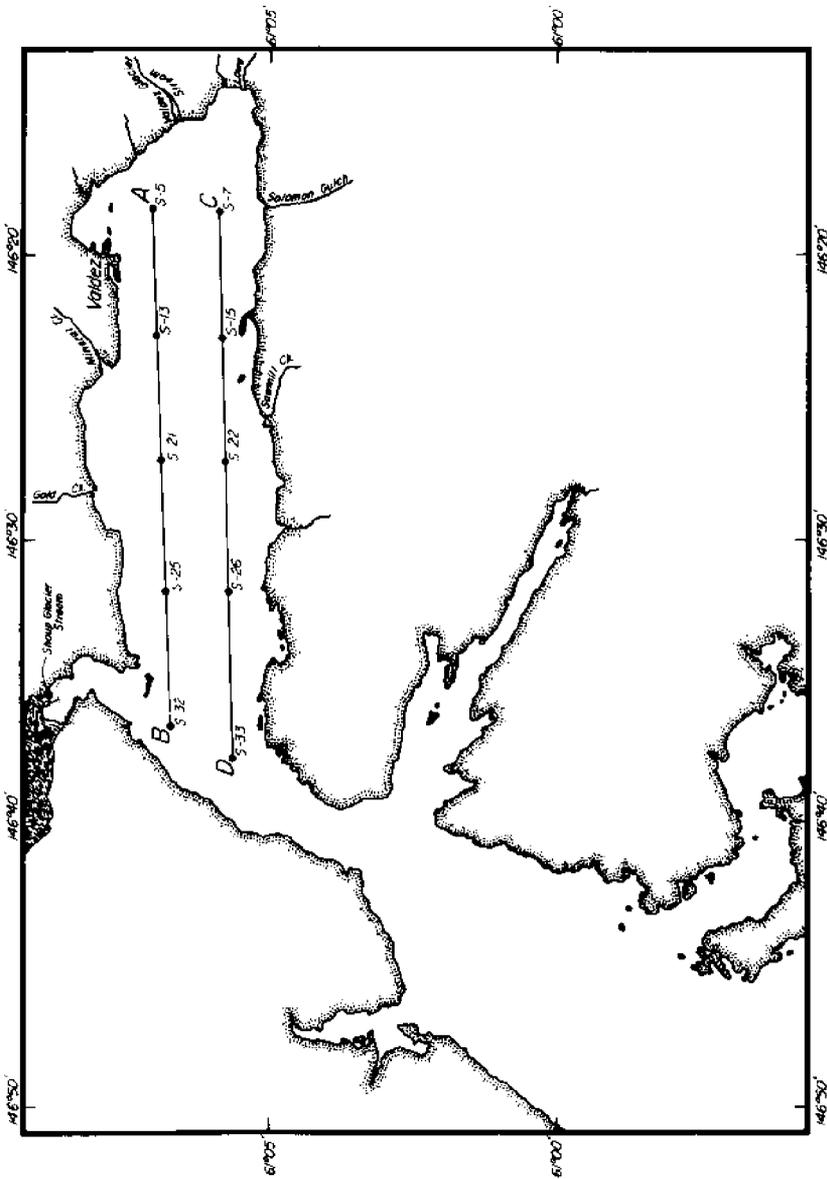


Figure 1.72 Locations of northern and southern east-west transects occupied on 31 July 1972 to determine the distribution of suspended sediment load and temperature in Port Valdez during one tidal cycle.

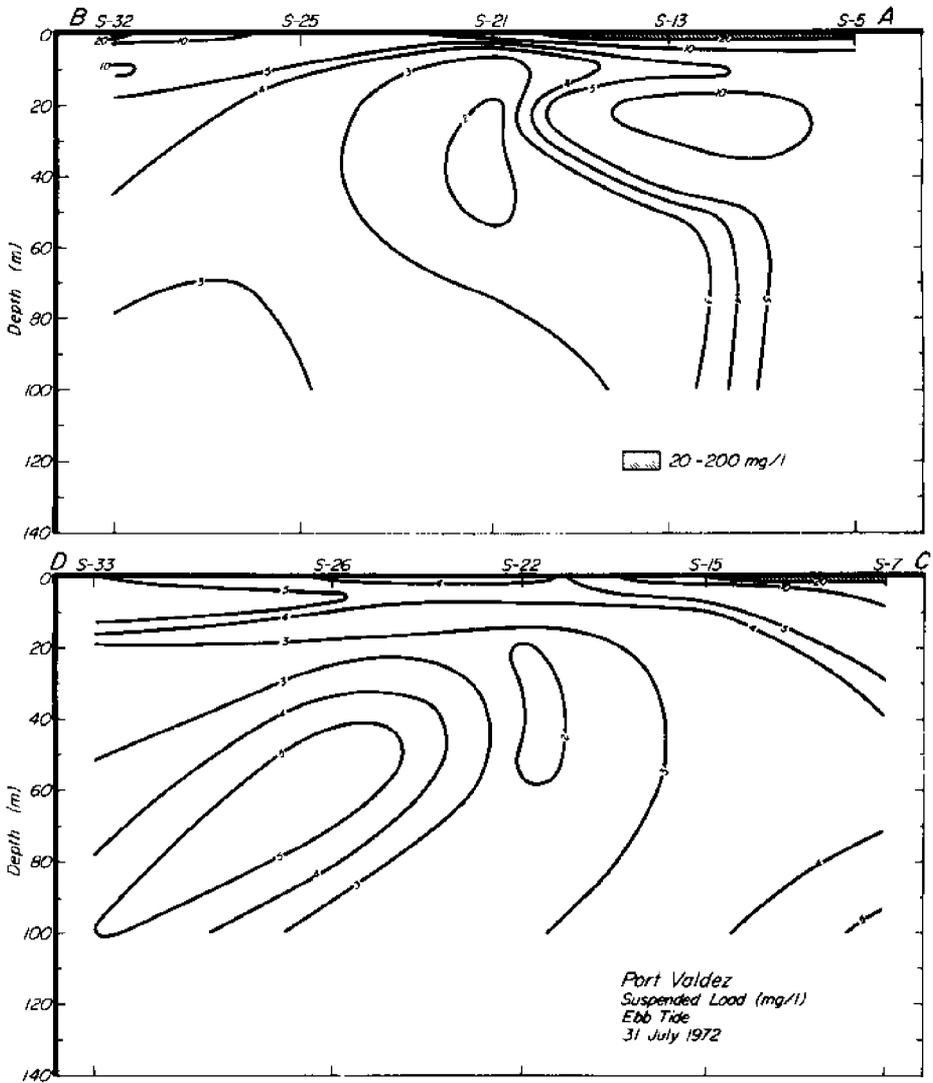


Figure 1.73 Northern and southern transects of the suspended sediment load distribution during ebb tide.

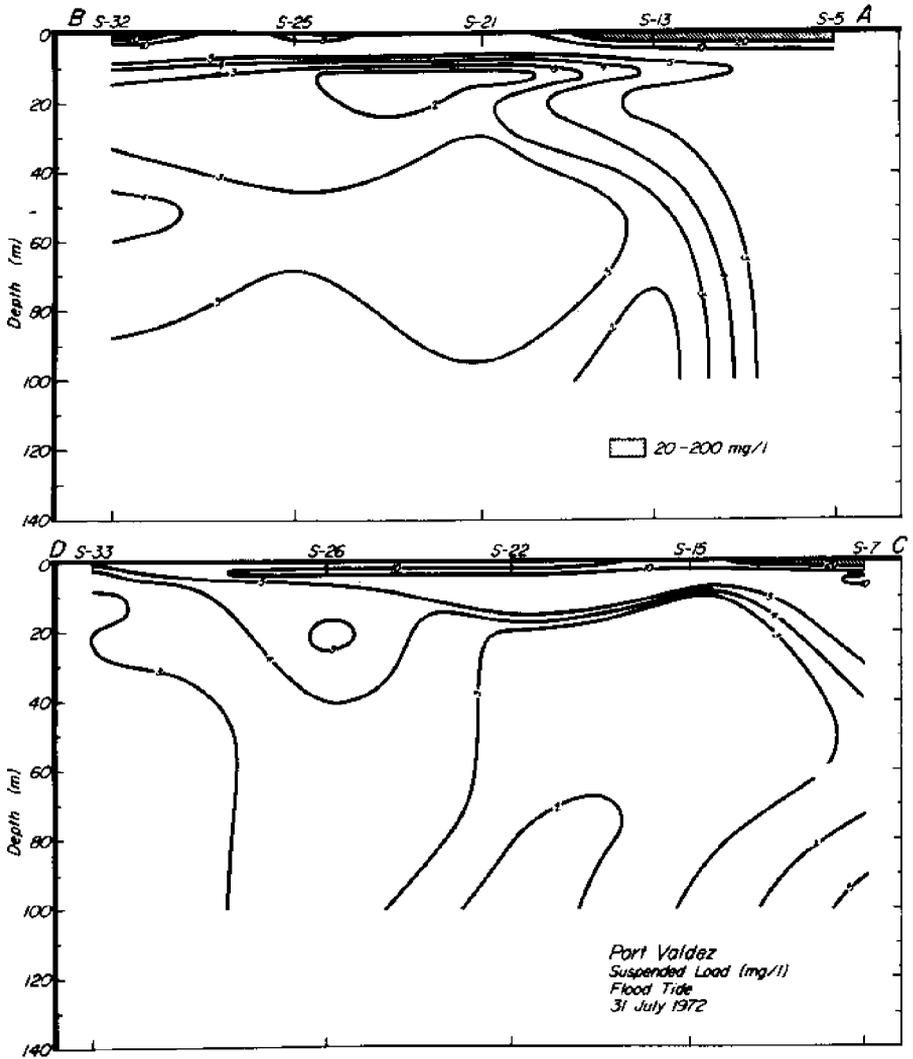


Figure 1.74 Northern and southern transects of the suspended sediment load distribution during flood tide.

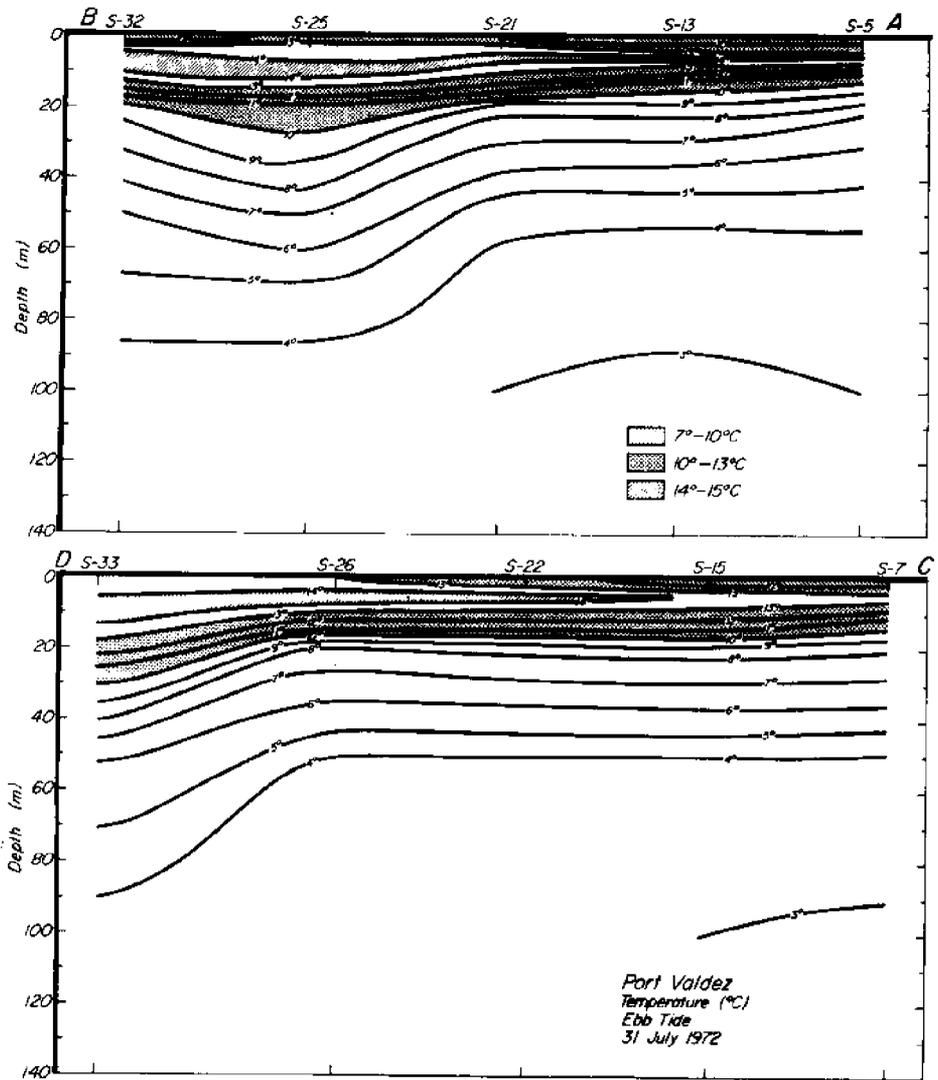


Figure 1.75 Northern and southern transects of isotherms during ebb tide.

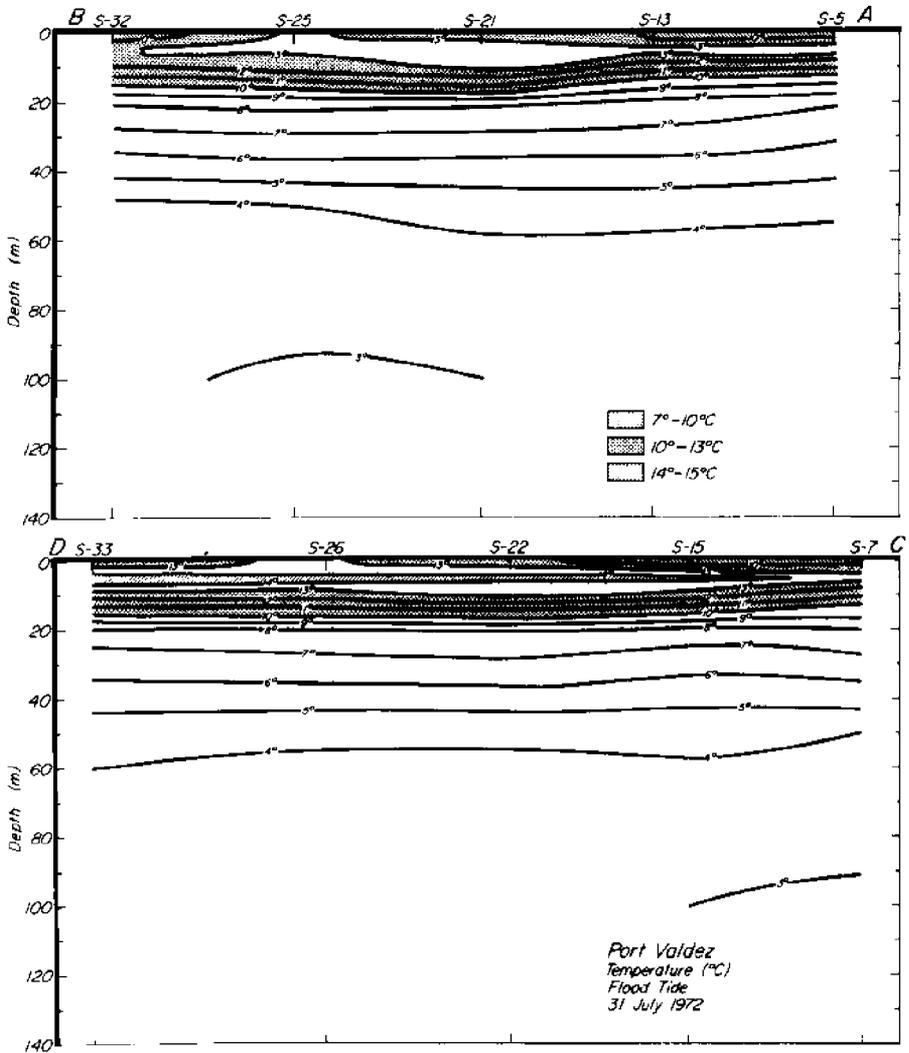


Figure 1.76 Northern and southern transects of isotherms during flood tide.



Figure 1.77 Schematic diagram of water movements in Port Valdez. Interpretation is based on the suspended sediment load and temperature distribution during summer 1972.



piston corer



sediment texture analysis

## SEDIMENTATION STUDIES

Shipek and van Veen grab samplers were used to obtain surficial bottom sediments. Free-fall modified Ewing piston and gravity corer with liner were utilized to retrieve sediment at depth. These cores displayed annual sediment layers and a distinct coarse-grained turbidite sediment layer deposited during 1964 Great Alaskan Earthquake.

Valdez (Figure 1.77). The isotherm configurations (Figures 1.75 and 1.76) during ebb and flood tides suggest that there was significant lateral as well as vertical water movement at intermediate and shallow depths. During ebb tide, concurrent with the outward surface flow, there was an inflow of seawater at the sill level. This condition was further evidenced by the presence of a 5 mg/liter suspended sediment contour in the southern transect of Figure 1.73. Since the eastward and upward movement of the intruding water is based on a nonconservative property (the suspended sediment load), it is thus a matter of considerable interpretation and speculation. This same pattern has been noted, however, in the recent model study by Harleman and Ippen (1967). It is apparent that the maximum diurnal and seasonal variations occur in the upper portion of the water column. The information gathered during summer 1972 suggests that a complex and dynamic exchange of water occurred at the sill level. Data for depths below 100 m are insufficient to allow an accurate interpretation of water movement and mixing in deep water. The presence of sediment varves near Valdez Fan II and in sediments elsewhere indicate, however, that the bottom environment was relatively still in comparison to movement in the upper portion of the water column.

In summary, it appears that the water in the surface layer moved outward in a counterclockwise gyre, while water in the intermediate layers oscillated with a net inward and upward movement. It was apparent also that some influx in the bottom water occurred, due perhaps to upward entrainment in response to outflow at the head of the Port. The presence of oxidized sediments covering western Port Valdez further suggests movement of well-oxygenated water at deeper depths.

## 1.5 Discussion

### 1.5.1 Sediment source

The source for sediments in Port Valdez lies in glacial and glacio-lacustrine deposits. The major river and streams that carry the glacially eroded material to Port Valdez and estimates of their suspended sediment load during 1972 are (1) the Lowe River,  $9.66 \times 10^{11}$  gm, (2) Mineral Creek,  $6.48 \times 10^{11}$  gm and (3) Valdez Glacier Stream,  $6.48 \times 10^{11}$  gm. Although these three sources contributed the bulk of suspended sediments during 1972 ( $2.26 \times 10^6$  metric tons), additional suspended sediments were brought into Port Valdez by various other streams: notably by Shoup Glacier Stream (most of whose suspended sediment load was deposited within Shoup Bay), and by Gold and Sawmill creeks. Bedloads were not included in the above amounts. Generally the bedload of streams and rivers near the continental margin is estimated to be 10-50 percent of the total load, depending upon the geologic and hydrologic conditions. Measurements of sediments deposited between 1935 and 1945 in Lake Mead, however, were found to be equal to suspended load measurements (Gould 1960; Howard 1960). The steep slopes, high seasonal runoff, glacier-fed streams and high rate of erosion suggest that the bedload in the Port Valdez region is probably equal to the suspended load.

The question of whether marine suspended sediments are contributed from Prince William Sound remains unanswered. Profiles of the distribution of suspended sediment load with depth in the Narrows during ebb and flood tides indicate that a small net movement of sediments into Port Valdez occurred during flood tide; however, it is not clear whether these sediments were marine or whether the suspended material was Shoup Bay detritus which had been transported out the Narrows at the surface, settled and was then carried back into Port Valdez at depth. More extensive mineralogical analyses would be required to delineate and estimate the marine sediment contribution to Port Valdez.

Results of X-ray diffraction analyses of the  $<4\mu$  fraction of bottom surficial sediments have further delineated the major sources for sediments (Figures 1.23-1.25). The sediments brought in by the rivers become relatively enriched in chlorite and illite but deficient in quartz with increasing distance from river mouths. It also appears that relatively more illite than chlorite settled out close to the source.

### 1.5.2 Sediment transport

The lateral and vertical size distributions noted in sediments of Port Valdez indicate that a complex sediment transport system prevails. Sediment dispersal in the Port can be explained in terms of *typical* and *atypical* geological processes.

Under *typical* circumstances most rivers, due to gradient reduction and decreased transport energy, deposit coarse sediment (including the bedload and coarser suspended sediments) at their mouths and build deltas. The bulk of the suspended sediments is carried out into the Port in a surface layer, where it flocculates and settles out within a few kilometers of the river mouths. Some suspended sediment may be carried in subsurface turbid (nepheloid) layers; however, their extent and importance is obscure. Material deposited on the beaches and tidal flats becomes resuspended and redeposited during each tidal cycle. This *typical* mode of sediment transport occurs primarily during the summer months when the sediment discharge from the rivers is high. Detritus input is negligible during late fall, winter and early spring.

The *atypical* processes of sediment transport are characterized by submarine slides and subsequent turbidity currents generally set in motion by regional or local tectonic activities. Recurrent reports of slumping in the Old Valdez dock area, submarine cable breaks, burying of submarine cables, tsunamis and the data presented in this report (such as the sedimentology of the topographic highs and cores with multiple grading) all confirm that severe earthquakes are generally followed by one or more submarine slides in Port Valdez. Evidence for three subaqueous slides in Port Valdez as an aftermath of the 1964 Great Alaskan Earthquake is given by USGS geologists (Plafker and Mayo 1965).

Submarine slides in Port Valdez have occurred generally on the steep slopes of unconsolidated sediments which form the submerged river deltas or glacial terminal moraines. The coarser material (gravel and coarse sand) carried with the submarine slide has been deposited close to the base of the slope, although the finer sand, silt and clay fractions have been generally carried much farther in suspension. The turbulence generated by a submarine slide is often sufficient to erode sediments in the path of the slide and redeposit the clayey fragments with the settling suspension. The extent and degree of transport is dependent on the magnitude of the submarine slide.

### 1.5.3 Sediment deposition

The sediments studied in Port Valdez consisted of gravel, sand, silt and clay. Nearshore sediments were mostly polymodal and coarse-grained with some silt and clay, whereas basin sediments were predominantly unimodal and fine-grained silt and clay. The variation in textural characteristics of surficial sediments from inshore to offshore was typical of particle size differentiation due to settling.

The rate of sedimentation near the river mouths and on the slopes of the river deltas was higher than in the basin. Within the basin itself, there also were significant differences in the rates of sedimentation. Annual varves in cores from the eastern part of the harbor suggested that the rate of sedimentation was high in this region. The presence of brown, oxidized surficial sediments, prevalent in the western region of Port Valdez, were indicative of a relatively slow rate of sedimentation.

Based on the suspended sediment load entering Port Valdez, the rate of sedimentation in Port Valdez was estimated. It is first assumed that the bedloads of the rivers are deposited on or very near the river deltas and are not distributed throughout the Port except in cases of *atypical* sediment transport such as that which follows major submarine slides. Furthermore, it is assumed that most of the suspended sediment load from Shoup Glacier Stream is trapped within Shoup Bay and that all suspended sediment introduced into Port Valdez is deposited within the Port. Under these conditions, then, an estimated total 1972 suspended sediment load of  $2.26 \times 10^6$  metric tons was carried into a  $105 \text{ km}^2$  area of Port Valdez. Using a grain density of  $2.70 \text{ g/cm}^3$  and 50-percent porosity, a sedimentation rate of  $1.67 \text{ cm/yr}$  is obtained. This result is based on the assumption, of course, that the suspended sediments are distributed evenly throughout the Port.

In order to provide some quantification of the variability of *typical* sedimentation rates in Port Valdez, estimates were made on the basis of varves in a few well-preserved gravity cores and on the basis of total thickness of sediments overlying the 1964 Great Alaskan Earthquake unconformity. Although these estimates are approximations only, they provide the only quantitative information available on the variability of the sedimentation rate within the Port. In the gravity cores obtained during the 11-14 May 1972 cruise, varves found in three of the cores showed the following approximate depositional rates:  $13.5 \text{ cm/yr}$  in core B-3A collected 3 km from the mouth of the Lowe River (4 annual varves in a length of 54 cm);  $4.3 \text{ cm/yr}$  in core B-2C taken about 3.5 km from the mouth of the Lowe River (8 annual varves in a length of 34 cm); and  $1.9 \text{ cm/yr}$  in core B-8A retrieved on Valdez Fan II (15.5 cm covering the 1964 Great Alaskan Earthquake unconformity).

In the western portion of the Port, grab samples from the tops of the topographic highs south of Shoup Bay contained total surficial mud thicknesses ranging from 0-6 cm over coarse gravel (the unconformity marking the 1964 earthquake), suggesting a rate of sedimentation of  $<1 \text{ cm/yr}$  in the region. This compares well with the estimated sedimentation rate as derived from the Port Valdez suspended sediment input.

#### 1.5.4 Sedimentary environments and associated benthic fauna

Generally known factors which affect both sedimentation and the benthic habitat in a region are the bathymetry, water dynamics, rates of deposition and bottom agitation. These factors comprise a common denominator which tends to relate sediments with benthic fauna. Secondary selective influence on benthos is exerted by such properties of the substrate as sediment grain size, compaction, coherence and stability. The significance of the relationship of sedimentation to the biogenic assemblage was observed over a century ago (Forbes 1844). There is evidently a close relation between the composition of an animal population and the sediment in which it lives, and in some cases it appears to be the nature of substrate that attracts a species or a number of species capable of living together on it.

The different topographic features of the Port Valdez region are steep slopes and a smooth flat bottom. Few samples were obtained from the slope, and therefore it is difficult to relate its sediments to the benthos. The sedimentation on the smooth bottom regime is grossly controlled by sediment source and hydrodynamics in Port Valdez, giving rise to two distinct clastic sedimentary environments. The area east of Jackson Point consists of bedload and suspended sediments introduced by rivers and is characterized by a relatively higher rate of sedimentation. The western half of Port Valdez is covered by a thin oxidized, yellowish-brown clayey sediments.

The taxonomic groups represented by distinct variable density and abundance in the Port are the Crustacea and the Polychaeta. Nonselective detritus-feeder polychaetes are more abundant in the eastern half, and crustaceans are found in greater number in the western half of the Port. These zonal variations of taxonomic groups are clearly not related

to water depth but rather to sedimentation and hydrodynamics in the region. The high rate of sedimentation, limited light penetration in the water column and relatively less phytoplankton productivity in the eastern half of the Port provide an environment suitable for polychaetes. The relatively clear, sediment-free and well oxygenated water in the western half is well suited for crustaceans.

### 1.6 Summary

Port Valdez is a relatively deep, narrow, east-west oriented glaciated re-entrant or fjord indented in the high, rugged Chugach Mountains in Southcentral Alaska. The fjord is a typical U-shaped valley with steep, rocky shores and a remarkably flat bottom varying between 230-250 m in depth. The head of Port Valdez is fed by the Lowe and Robe rivers and Valdez Glacier Stream which form an extensive outwash delta. At the mouth of the inlet there is a narrow constriction with two sills.

The source for sediments in Port Valdez lies in glacial and glacio-lacustrine deposits, which are supplied by the major rivers and streams both in suspension and as bedload. The sediments observed in the Port consisted of gravel, sand, silt and clay. Nearshore sediments were mostly polymodal and coarse-grained with some silt and clay, whereas basin sediments were predominately unimodal and fine-grained silt and clay.

Distribution of sediments is largely controlled by the water circulation in Port Valdez. Most sediments brought by rivers entering the Port at the head are deposited in the eastern half. The rate of sedimentation in the eastern half of the Port is significantly higher than in the western half. Large-scale sediment transport and deposition occur as a result of submarine landslides caused by orogenic movements in the Valdez region.

## 1.7 References

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# *Chapter 2*

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## PHYSICAL OCEANOGRAPHY





## 2. PHYSICAL OCEANOGRAPHY

by

R. D. Muench and D. L. Nebert

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### 2.1 Introduction

The physical oceanographic aspects of estuarine circulation and hydrography have been well documented in an abundant range of literature extending from that of primarily descriptive content (Pickard 1956, 1967), through a mixture of descriptive and theoretical material (Pritchard 1954, 1956, 1958), to distinctly theoretical approaches (Hansen and Rattray 1965, 1966). An adequate summary of composite perspectives on this subject has been compiled by Lauff (1967).

Despite the substantial volume of research devoted to estuaries in general, little work has been directed to subarctic systems. Typically fjordal in nature, estuaries such as those situated in Alaska are subject to uniquely harsh and widely varying conditions throughout the year. An essentially total lack of year-round hydrographic data and current measurements has precluded comprehensive quantitative research in these subarctic estuaries, although recent work has qualitatively clarified hydrographic and circulatory features in isolated cases (Quinlan 1970; Nebert 1972). Thus the work in Port Valdez was undertaken with only minimal knowledge of the prevailing circulation and hydrography.

Objectives of the physical oceanographic program in Port Valdez were to determine the following conditions:

- Spatial and temporal variations in temperature and salinity
- Circulation patterns
- Mixing and flushing processes as derived from the above factors

Six oceanographic cruises were conducted in the Port Valdez region over a period of approximately 1 year at selected intervals to allow detection of seasonal variations in temperature, salinity and circulation. Observations were made of temperature and salinity distributions during each cruises; circulation was studied by use of drogues and current meters. The research methods and results are discussed in detail in the following text.

## 2.2 Field Program

Physical oceanographic field work in the Port Valdez region was conducted during six separate cruises to the study area aboard the *R/V Acona*, research vessel of the Institute of Marine Science, University of Alaska. Dates of these cruises were scheduled so as to allow collection of information from the region during periods of maximum runoff (summer and fall), of maximum cooling and wind mixing (late fall and winter) and of maximum warming (early spring and summer).

The oceanographic stations were geographically located to yield maximum data density in the areas of fresh-water input at the head and mouth of Port Valdez, in Valdez Narrows and in the Jackson Point region — site of the proposed ballast water outfall (Figure 2.1). Stations 101-153 were occupied on all six cruises, and additional stations in their surrounding areas were occupied as necessary to provide sufficiently detailed information. Six stations were occupied also in eastern Prince William Sound during each cruise (Figure 2.2) to obtain data on seasonal temperature and salinity variations in that region, which is the source of marine water for the Port Valdez system.

The individual cruises varied in length from 9-12 days and averaged 10.5 days' duration (Table 2.1). Variations in cruise duration were due primarily to weather conditions as they affected implementation of the research program aboard ship. The longer cruises generally corresponded to stormy weather conditions during the winter period. It was determined that about three days were sufficient for occupation of the physical oceanographic stations, although these stations were not always occupied during three consecutive days due to weather and other factors. The remainder of the time on each cruise was fully utilized in carrying out chemical and biological oceanographic investigations, mooring and retrieving current meters, tracking drogues and conducting dye studies.

**Table 2.1 Oceanographic cruises to the Port Valdez region**

<i>Acona</i> cruise no.	Cruise date	Cruise duration (days)
113	18-26 May 1971	9
117	27 July-4 August 1971	9
122	4-13 October 1971	10
125	29 November-9 December 1971	11
128	9-20 March 1972	12
131	19-30 April 1972	12
	Total number of cruise days	63

### 2.2.1 Collection of hydrographic data

Temperature and salinity data were obtained at all stations on cruises 113, 125, 128 and 131 with a Bissett-Berman Model 9040 salinity-temperature-depth measuring unit (STD). These data were augmented by temperature and salinity data from discrete Nansen bottle samples collected during at least every sixth station as a check on the STD calibration. On cruises 117 and 122 the STD was nonfunctional, and all temperature and salinity data were obtained from Nansen casts. Surface-water temperatures were measured with a bucket thermometer at all stations on every cruise.

Data from the STD were obtained in the form of charts showing continuous analog traces of temperature and salinity versus depth. This information was simultaneously recorded in digital form on magnetic tape at 0.2-sec intervals. The on-station analog traces served also to detect possible malfunctioning of the STD. Digital data were forwarded to the Institute of Marine Science in Fairbanks for post-cruise processing and calibration using the Nansen data.

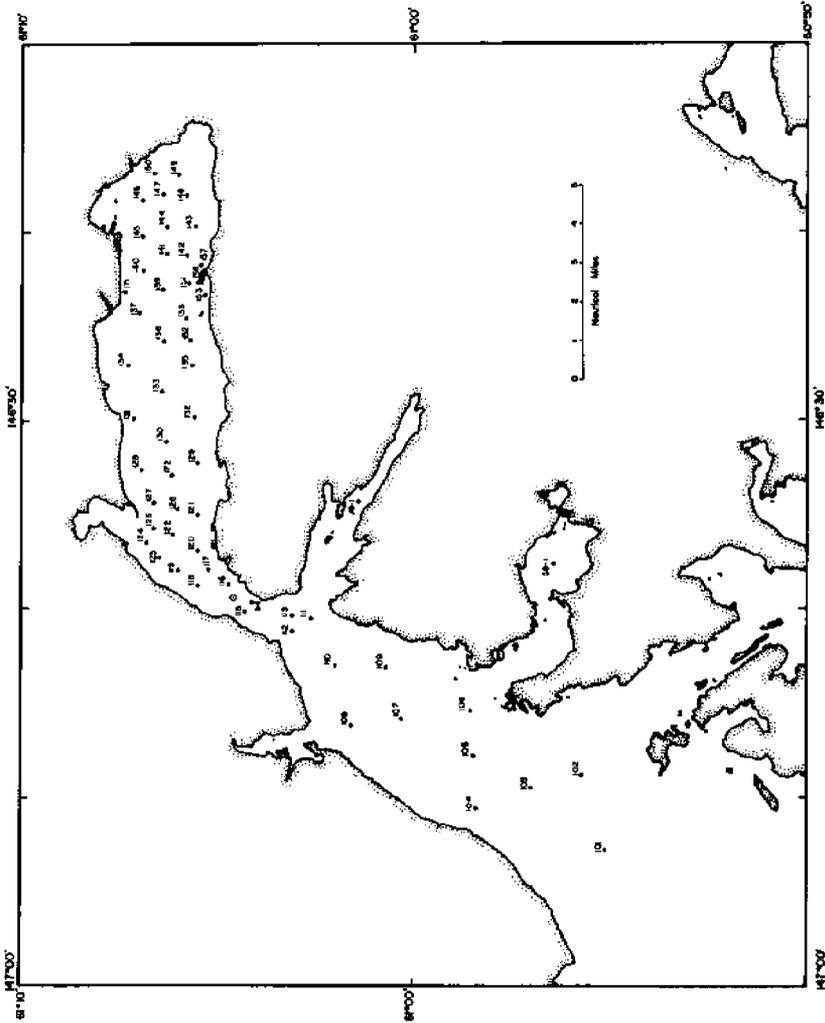


Figure 2.1 Geographical locations of oceanographic stations in the Port Valdez region and location of current meter moorings (open circles) in Valdez Narrows.

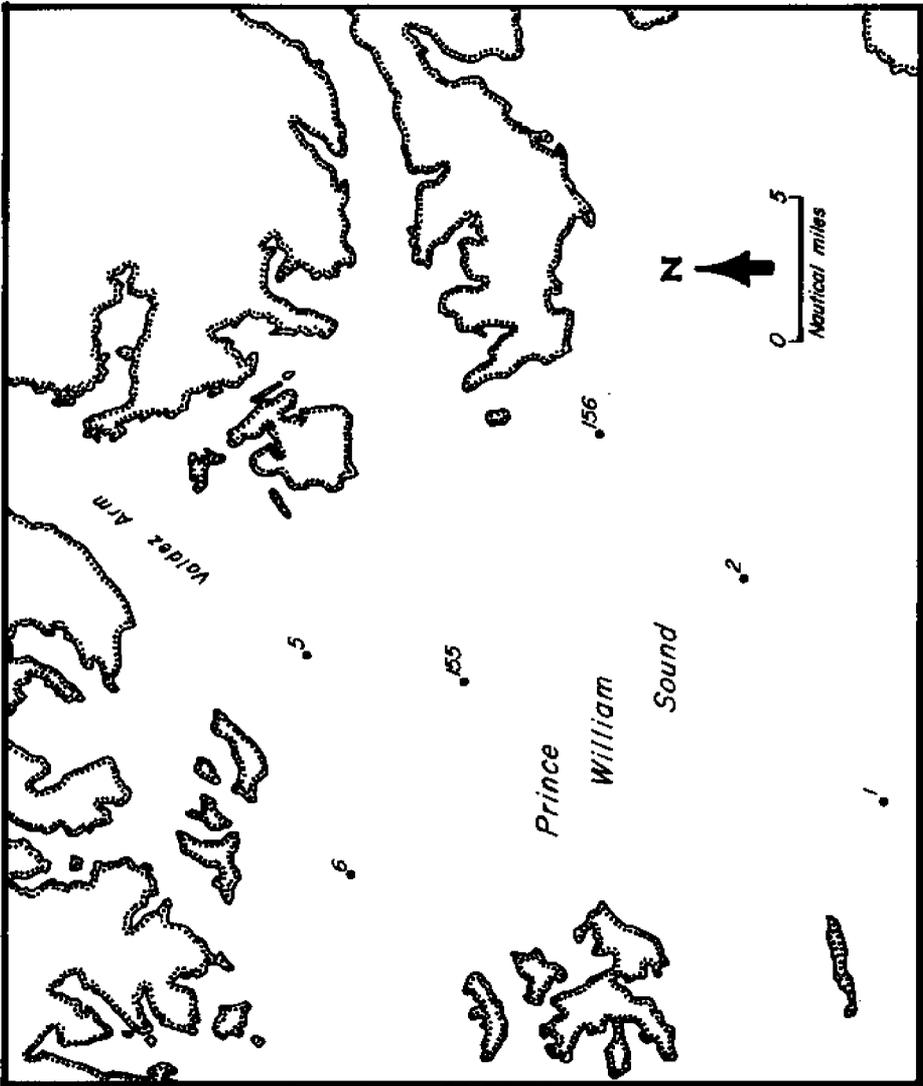


Figure 2.2 Geographical locations of oceanographic stations in eastern Prince William Sound.

Temperatures were obtained from the Nansen casts by a pair of protected deep-sea reversing thermometers at each sample depth. The salinity of samples decanted from the Nansen bottles was determined on a Bissett-Berman Model 6220 or 6230 Laboratory Salinometer. Depths of samples obtained from below 200 m were computed from unprotected reversing thermometer readings as a check on the depth calculated from the length of hydrowire released from the winch during station operations.

Allowing for errors of drift and other factors, the accuracy of temperature and salinity data obtained by use of the STD was estimated to be within  $\pm 0.05^{\circ}\text{C}$  and  $\pm 0.05$  ‰ respectively, as compared to a precision of about  $\pm 0.03$  units each for values obtained from the Nansen casts. In the discussion which follows (2.3), the STD accuracy is applied to the overall data; the precision of the temperature and salinity measurements made during cruises 117 and 122 may have been slightly higher, however, as the STD was not used during those cruises. Surface temperatures obtained with the bucket thermometer were accurate only to  $\pm 0.1^{\circ}\text{C}$  and were useful merely as a crude check against surface temperatures recorded by the STD or from Nansen casts.

The unprocessed temperature and salinity data from the Nansen casts appear in Data Volume I of this report. Data from STD stations were too voluminous for inclusion but are available from the National Oceanographic Data Center, Washington, D.C.

### 2.2.2 Circulation studies

A vertical string of recording current meters was moored in Valdez Narrows for the duration of cruises 125 and 128. Four meters were in the string on the earlier cruise and five were used during the later period. The taught-wire mooring (Figure 2.3) included a suspension float about 6 m (20 ft) below the water surface to minimize the effects of anticipated wave action on the near-surface current meters. A timed-release mechanism at the bottom of the moored array released the assemblage from the anchor at a pre-set time to allow retrieval of the current meters.

Braincon Model 318 Histogram Current Meters were used to record mean currents at 20-min intervals, which were averaged over the preceding 20-min period. The instrument precision according to the manufacturer's specifications was  $\pm 3$  percent of the full scale for speed and  $\pm 1$  percent of the full scale for direction (relative to magnetic N) or  $\pm 3.6^{\circ}$ . The lower-speed threshold of the meters was assumed as stated to be 0.05 knots (2.6 cm/sec). The current meters were loaned by the National Marine Fisheries Service Laboratory in Auke Bay, Alaska, where the data was returned for processing to yield a print-out of north and east current components (relative to magnetic north) for the period the meters had been in use.

In addition to the current meters, parachute drogues were used to study the circulation within Port Valdez. The drogues consisted of standard personnel parachutes connected with polypropylene lines to marked surface floats (Figure 2.4). Actions of wind and current on the surface floats and connecting lines were assumed negligible in comparison to the drag of currents on the opened parachute; therefore, motion of the entire drogue was considered to represent motion of water parcels at the parachute level. Opening of the parachute was ensured at launch by exerting strain on the line until the chute was observed to be open. As a final check, the extent of drag on the line during retrieval indicated whether the chute had opened properly; no failure was observed. At least twice a day (weather permitting), the drogues were positioned either by fixing the surface float directly with radar or by obtaining a radar fix on a skiff lying just off the surface float. Foul weather, particularly during cruises 125 and 129, greatly reduced the number of drogue positions obtainable.

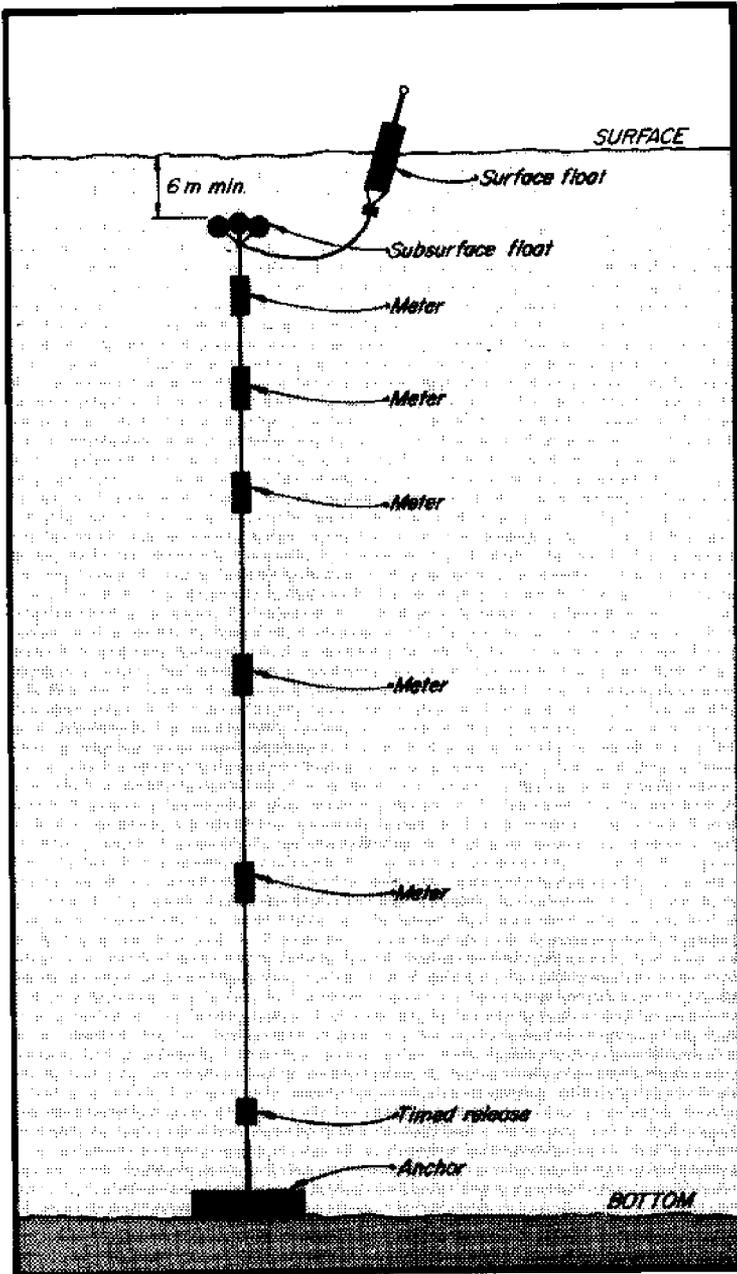


Figure 2.3 Configuration of mooring used to suspend recording current meters in Valdez Narrows during December 1971 and March 1972.

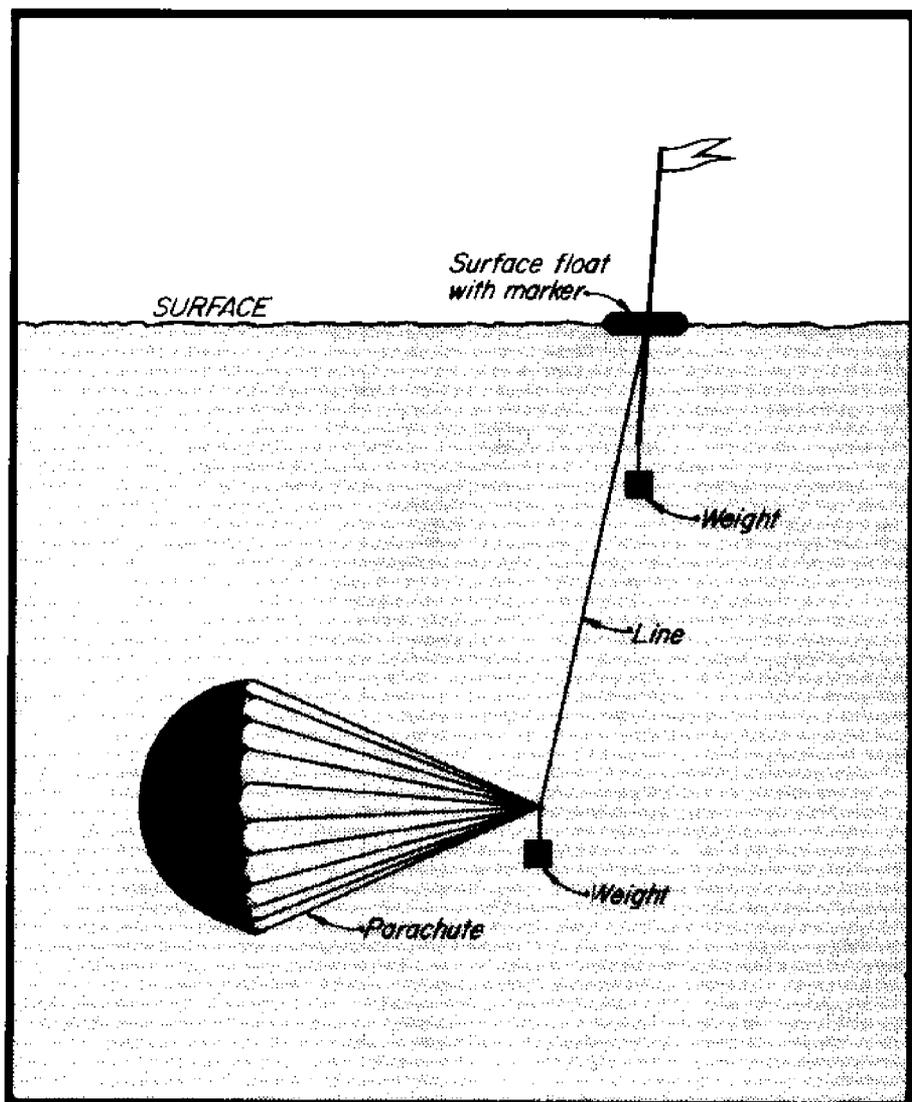


Figure 2.4 Configuration of parachute drogues used to study circulation within Port Valdez.

### 2.2.3 Meteorological observations

In addition to the oceanographic parameters measured, observations were made from aboard the vessel of dry- and wet-bulb temperature, atmospheric pressure, cloud cover, overall weather conditions, and wind speed and direction at each station.

## 2.3 Discussion

### 2.3.1 Temperature and salinity structure

The distributions of temperature and salinity in the Port Valdez region during each of the six oceanographic cruises are indicated in Figures 2.5-2.16. Station 130 data are considered representative of the detailed vertical distribution of temperature, salinity and  $\sigma_t$  (density) throughout Port Valdez, since the cross-sections (Figures 2.5-2.16, lower portion) indicate very little cross-channel variation in temperature or salinity within the Port. In fact, during all cruises except 113, the variations closely coincided with the estimated error in the temperature and salinity determinations. These negligible cross-channel variations exhibited no detectable pattern and are not discussed further herein; the longitudinal sections (Figures 2.5-2.16, upper portions) are assumed to adequately represent the distributions of temperature and salinity in Port Valdez during the period of study.

Water temperatures observed in the Port Valdez region ranged from winter minima of  $<2.5^\circ\text{C}$  (Figure 2.13) to summer maxima of  $>11^\circ\text{C}$ . Below about 75 m, most temperatures measured were in the 3 to  $6^\circ\text{C}$  range, although greater seasonal variations occurred above this depth.

Salinities below the upper 20 m of the water column varied generally from about 28 to  $>32.5\text{‰}$ . Salinity was always observed to increase in downward direction. In the upper 20 m, extremely low salinities ( $<1.0\text{‰}$ ) were observed during the summer (Figure 2.8), and higher values ( $>32.0\text{‰}$ ) occurred during the winter (Figure 2.14). The overall seasonal variation in salinity was more pronounced in the upper 20-m layer than in the deeper water.

Neither temperature nor salinity exhibited regular horizontal variations above the 140-m Valdez Narrows sill on any of the cruises. Below this depth, both temperature and salinity tended to be higher in Valdez Arm than in Port Valdez, which suggests that the sill was impeding the exchange of water through the Narrows below 140 m.

A seasonal variation was observed in the distribution of temperature and salinity. Vertical stratification of both was observed to be most pronounced during the summer with a maximum during July-August 1971 (Figures 2.7-2.8, 2.17b). By October 1971 (Figures 2.9-2.10, 2.17c) the stratification had lessened and was weakened yet further by December 1971 (Figures 2.11-2.12, 2.17d). In March 1972 the water showed near-vertical uniformity within Port Valdez (Figures 2.13-2.14, 2.17e). The vertical  $\sigma_t$  profile (Figure 2.17e) shows, in fact, that the water was of uniform density to the bottom in March. This was reflected also in the high bottom-oxygen concentrations observed in March; vertical mixing, necessary for creation of the uniform layer, appears to have supplied the bottom waters with oxygen from the overlying oxygen-richer water. By April 1972 the water had begun to exhibit temperature and salinity stratification near the surface (Figures 2.15-2.16, 2.17f). During May 1971 the salinities below about 75 m showed less vertical variation than was noted two months later (Figures 2.6-2.8, 2.17a,b). This vertically near-uniform layer may have represented the remnant of a convective layer formed during the preceding winter (1970-71). Although the data are insufficient for a significant conclusion, the mixing processes which have observed in a climate known to be severe do suggest that vertical mixing to the bottom reaches may be a regular occurrence in Port Valdez.

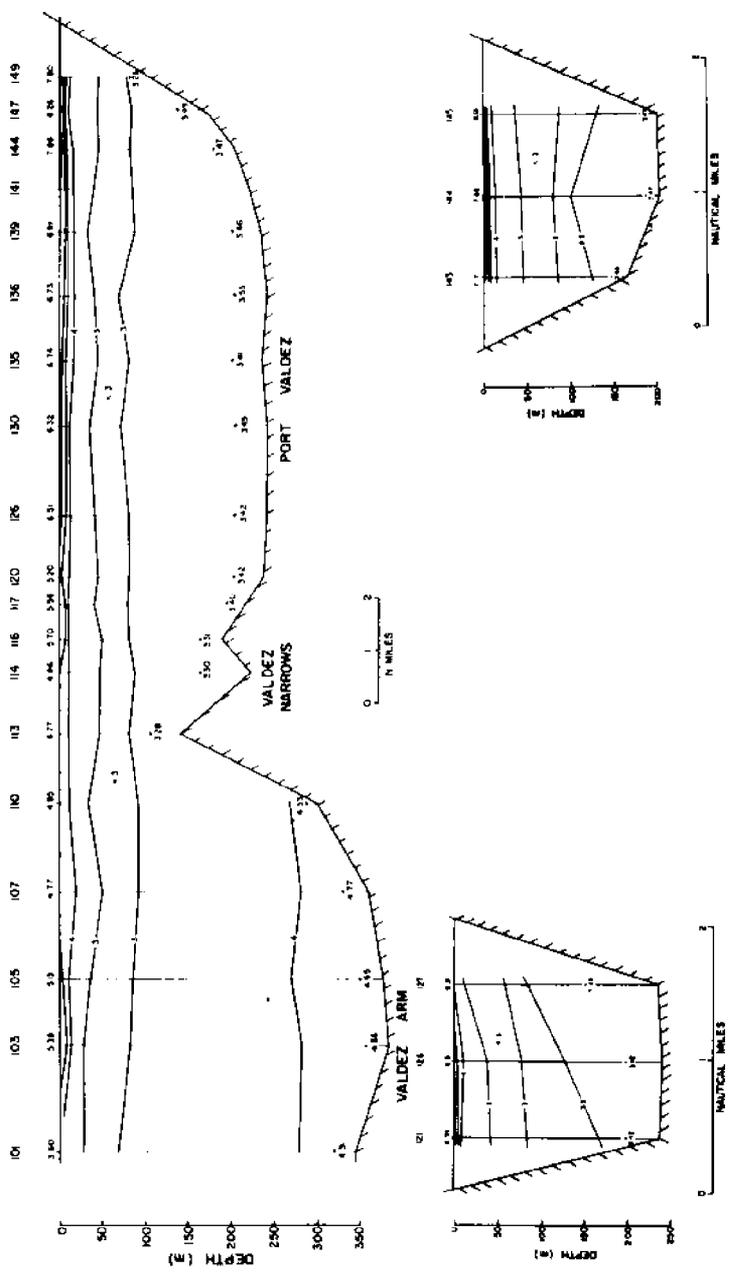


Figure 2.5 Vertical distribution of temperature in the Port Valdez region during late May 1971.

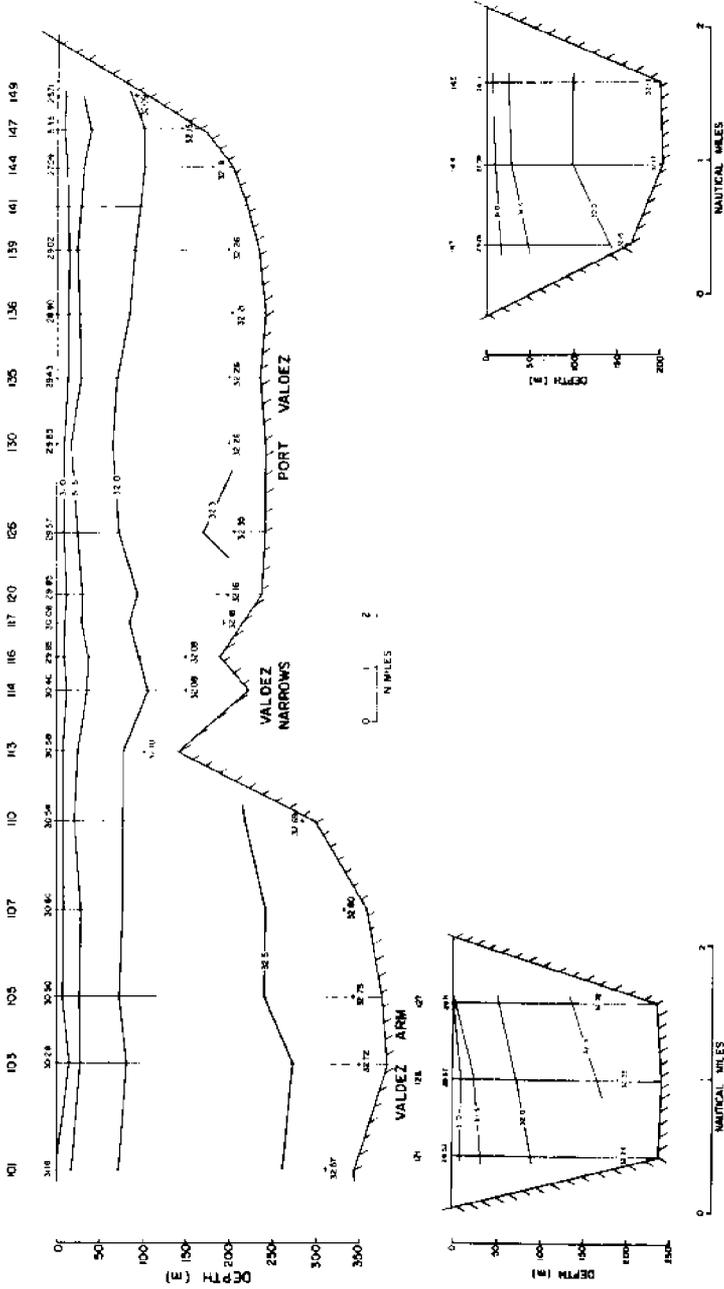


Figure 2.6 Vertical distribution of salinity in the Port Valdez region during late May 1971.

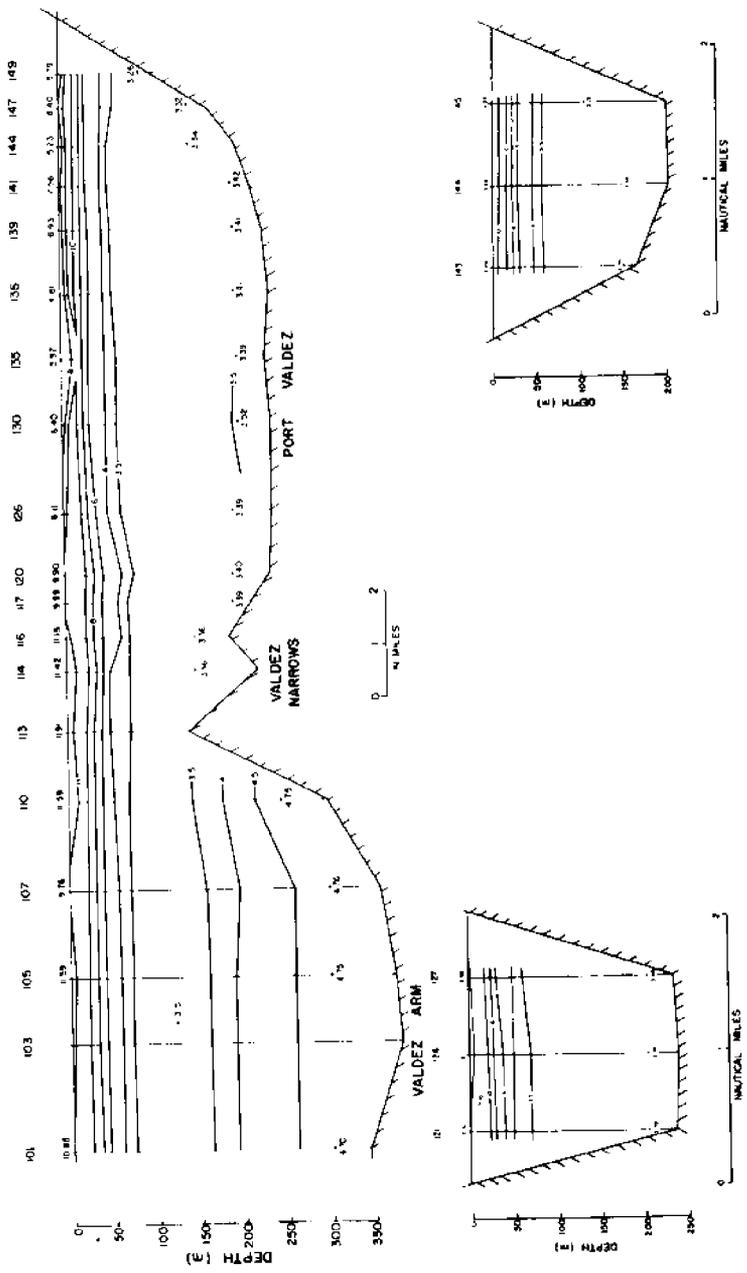


Figure 2.7 Vertical distribution of temperature in the Port Valdez region during late July-early August 1971.

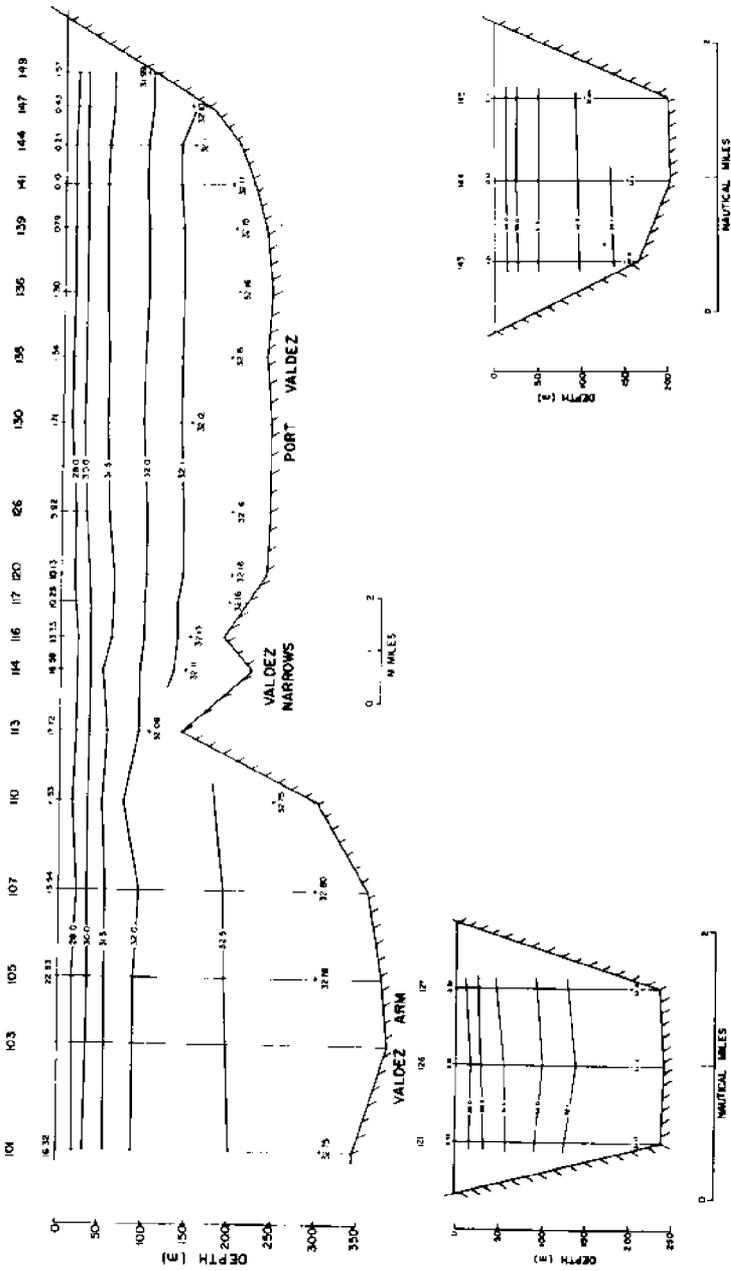


Figure 2.8 Vertical distribution of salinity in the Port Valdez region during late July-early August 1971.

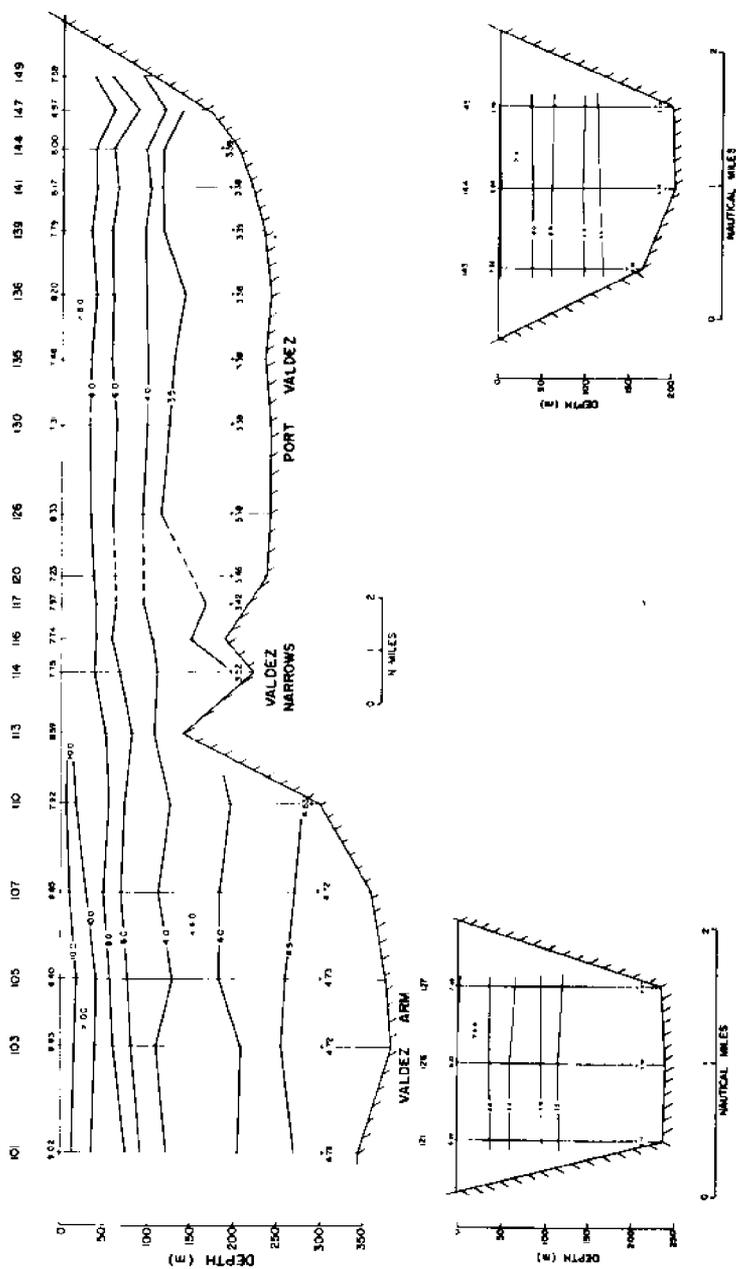


Figure 2.9 Vertical distribution of temperature in the Port Valdez region during early October 1971.

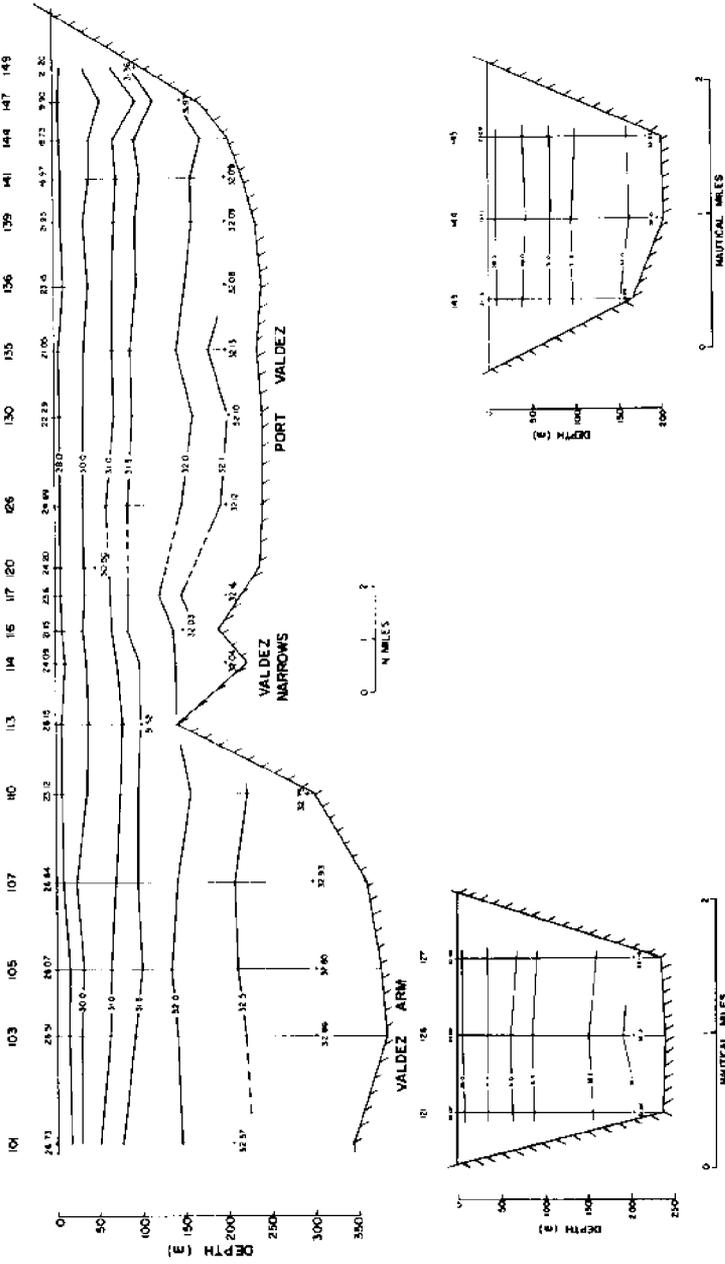


Figure 2.10 Vertical distribution of salinity in the Port Valdez region during early October 1971.

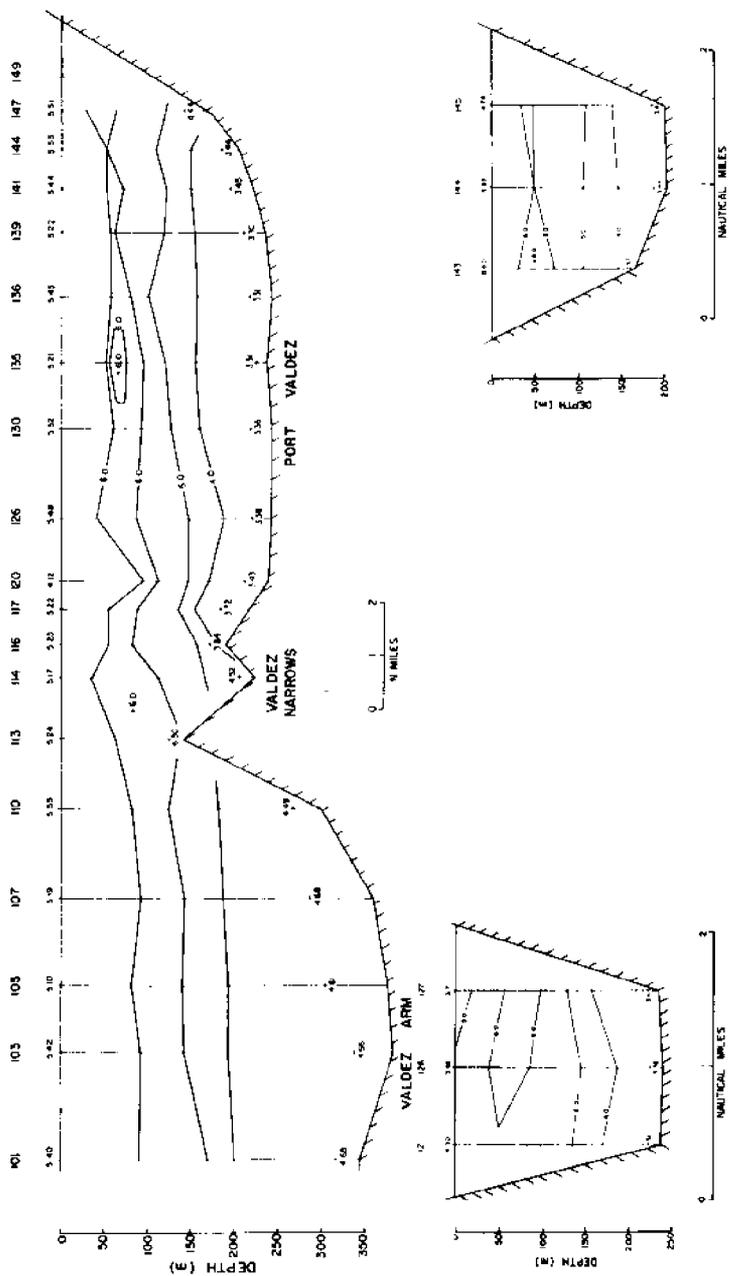


Figure 2.11 Vertical distribution of temperature in the Port Valdez region during early December 1971.

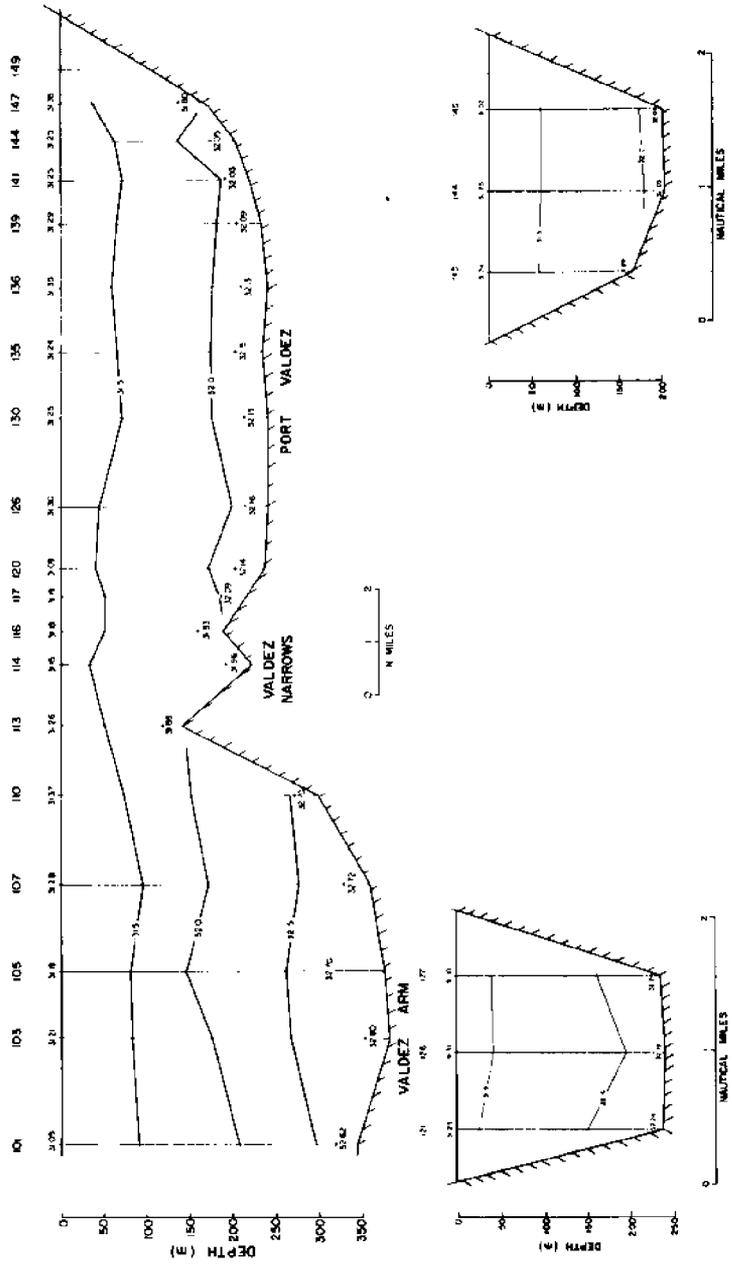


Figure 2.12 Vertical distribution of salinity in the Port Valdez region during early December 1971.



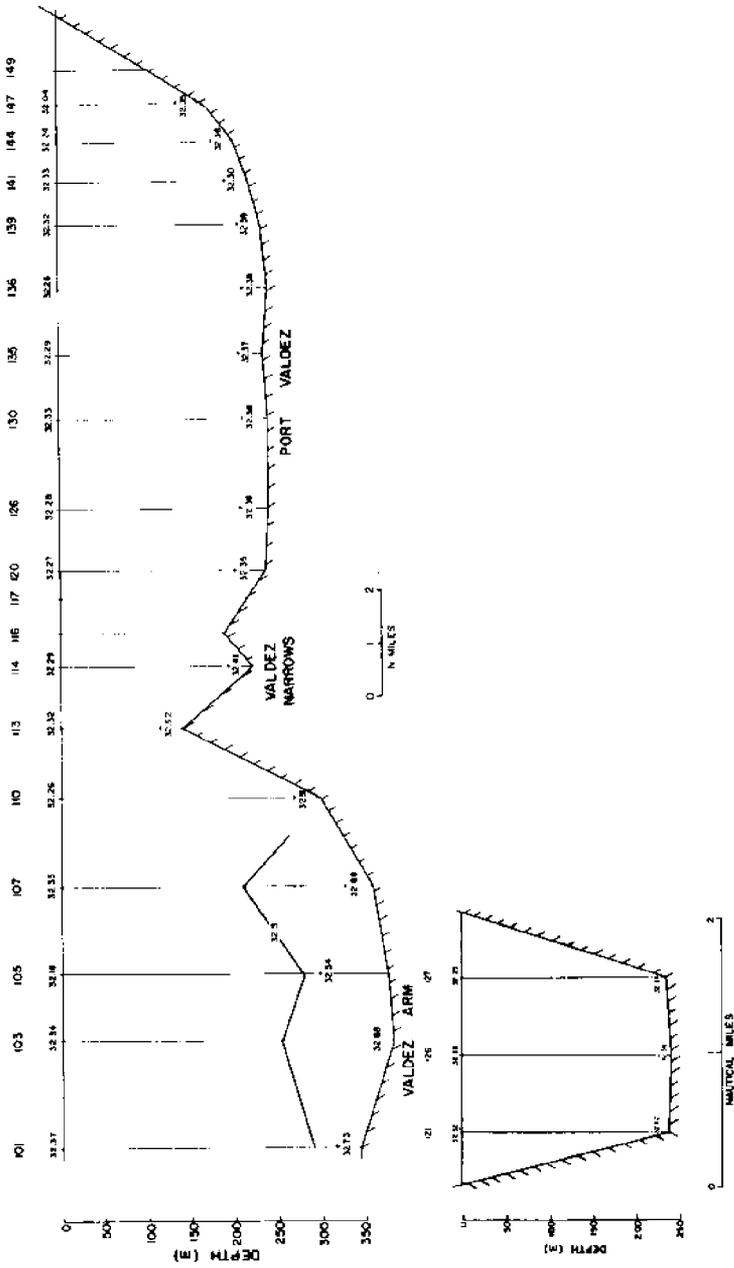


Figure 2.14 Vertical distribution of salinity in the Port Valdez region during early March 1972.

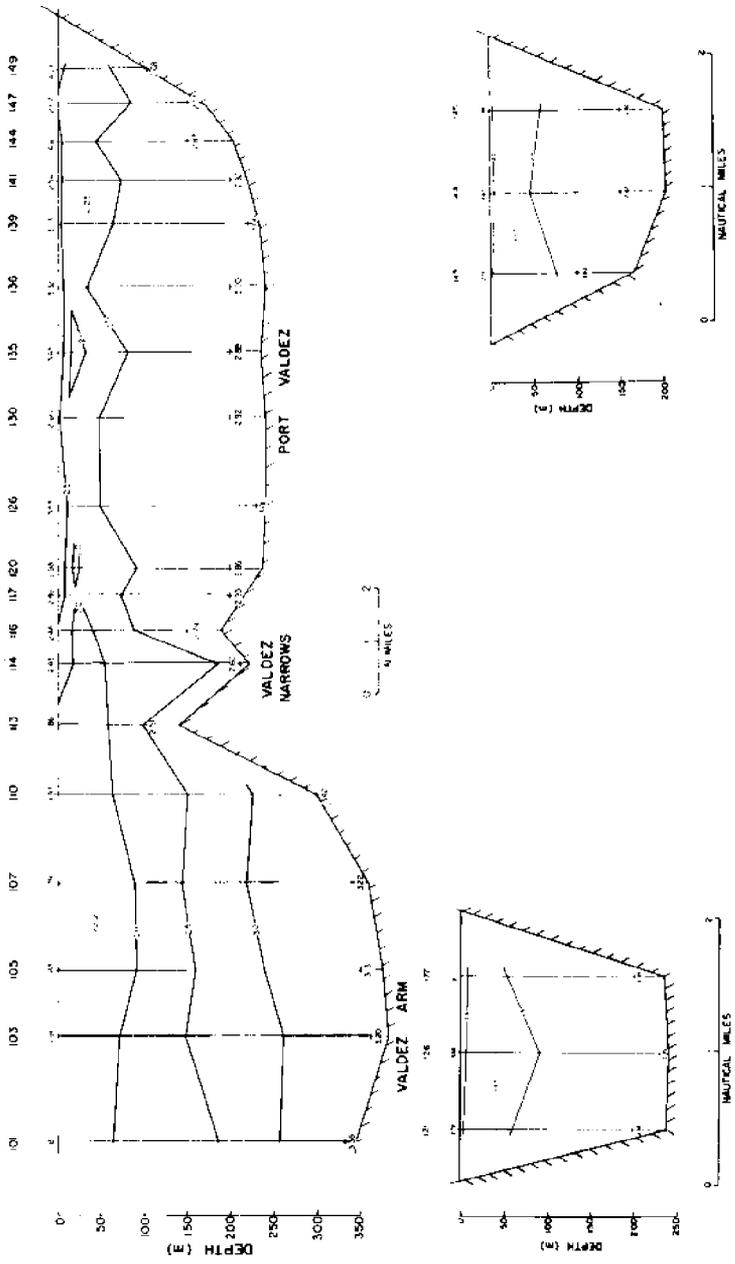
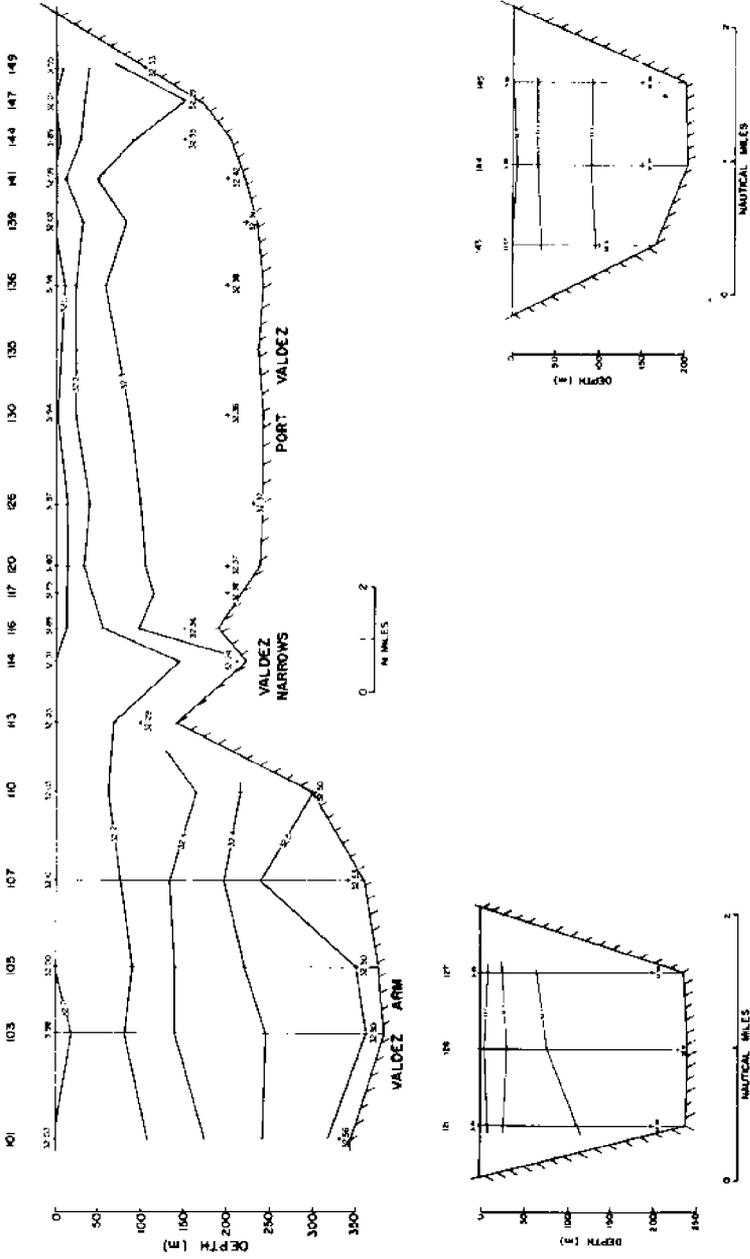


Figure 2.15 Vertical distribution of temperature in the Port Valdez region during late April 1972.



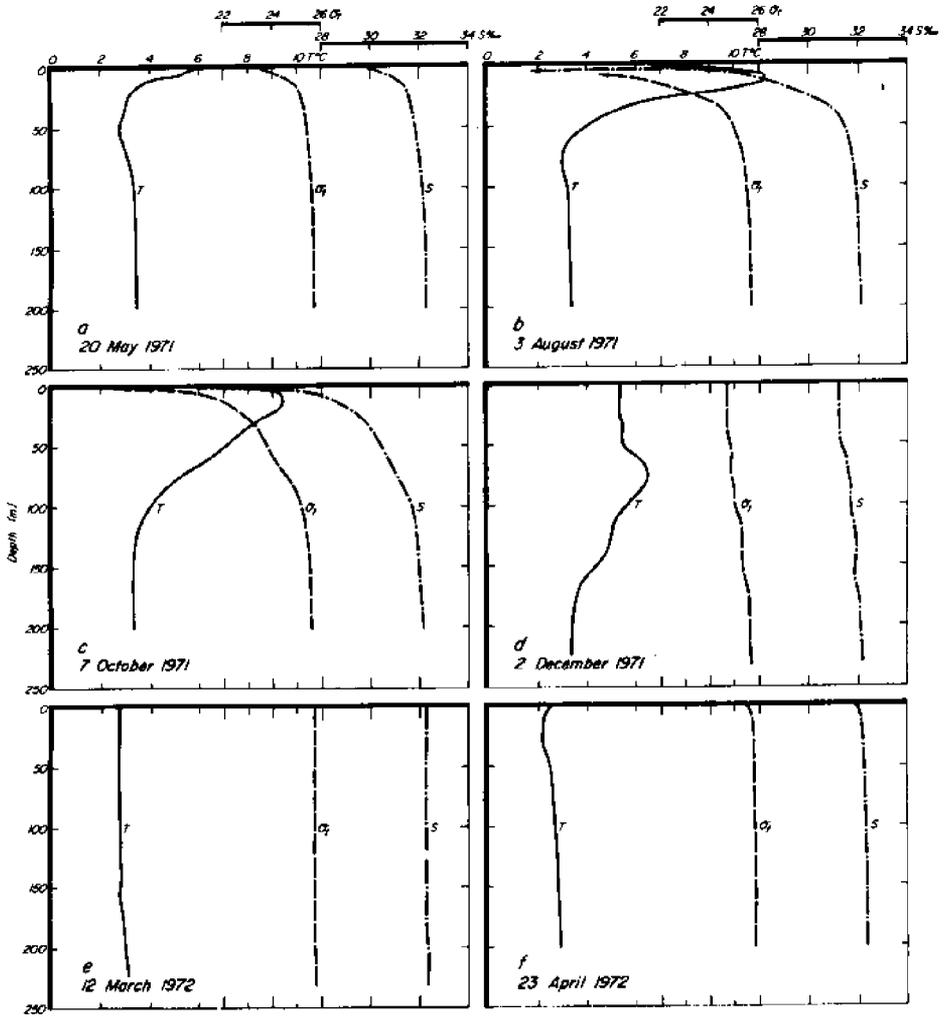


Figure 2.17 Vertical profiles of temperature, salinity and  $\sigma_t$  (density) at station 130 in Port Valdez for six different times during the period May 1971-April 1972.

The observed seasonal temperature and salinity variations in the Port Valdez region may be explained qualitatively in terms of meteorological and hydrological effects. The summer vertical stratification is established by solar warming and addition of fresh water at the surface from both precipitation and terrestrial runoff. According to Carlson et al. (1969), maximum runoff occurs typically during July and August, which is when the maximum vertical salinity stratification was observed (Figures 2.8 and 2.17b). Maximum solar warming would be expected during June and July, and this would therefore account for the maximum near-surface temperatures and consequent vertical temperature stratification observed during July-August 1971 (Figures 2.7 and 2.17b). Appreciable solar warming had in fact commenced by May 1971, as evidenced by higher temperatures at the surface than in the underlying cold ( $<3^{\circ}\text{C}$ ) core at 50 m (Figures 2.5 and 2.17a). Presence of lower surface temperatures in July-August 1971 than those directly below the surface appeared to be due to the low temperature of the fresh-water input, which was constrained to the surface due to its low density relative to seawater. By October 1971 the low surface temperatures, relative to those 20-30 m below, may have been due partly to the addition of cold fresh water at the surface but must also have shown the effect of surface cooling consequent to the 5 to  $6^{\circ}\text{C}$  atmospheric temperatures observed throughout the cruise (Figures 2.9 and 2.17c).

By December 1971 surface cooling and consequent vertical convection had begun, as suggested by the decreased stratification near the surface (Figures 2.11-2.12, 2.17d). The decrease in salinity stratification must have been due in part also to a cessation of fresh-water addition at the surface. Surface air temperatures observed during the December cruise were at or below  $0^{\circ}\text{C}$ , and winds of 20-25 knots were frequently encountered. By March 1972 vertical mixing had reached the bottom. It is suspected that minimum atmospheric temperatures and maximum winds occurred during January and February 1972, as these were the mid-winter months; these conditions, however, were not directly observed. In March the ambient temperature was about  $-2$  to  $-3^{\circ}\text{C}$ , and winds of 20 knots with gusts to 80 knots were noted.

Oceanographic data acquired from Prince William Sound were insufficient in coverage to allow more than a general corroboration of the above observations. Since Valdez Arm connects freely with Prince William, the conditions described above are considered representative of those in the adjacent Sound during the study.

Salinity data obtained from the Port Valdez region were sufficient for estimating the nature of the circulation there. In a classical estuarine circulation, fresh water is added at the head and flows seaward, being constrained by its relatively low density to remain near the surface. As it flows seaward, it entrains saline water from below. To satisfy continuity, there is a net inflow of water within the saline, subsurface layer to replace that entrained into the upper layer. The near-surface layer of lower-salinity water increases in salinity as it passes from the head to the mouth of estuary, due to the continual upward entrainment of saline water from the underlying layers.

The Port Valdez region was divided into cross-sections along its length (Figure 2.18). By use of the hydrographic data, mean salinities throughout the water column were determined for each of these sections. In order to better determine the effects of the 110 to 128-m Valdez Narrows sill, the mean salinities were determined separately for the 0 to 110-m (above sill depth) depth interval and for the 125-200 m (below sill depth) depth interval (Tables 2.2 and 2.3, respectively).

During the May 1971 cruise, longitudinal salinity variations above 125 m within Port Valdez approximated the error in the salinity determinations, although there was some tendency for salinity to increase toward the Narrows. There was no difference between salinities inside and outside Valdez Narrows; apparently random variations were confined close to a mean value of  $31.69 \text{‰}$ . In July-August 1971 there was a slight, poorly defined



Nansen bottle being removed from hydrowire (left) was formerly used as the only method for measuring salinity, temperature and depth — now used for calibration of automated STD system (below).

HYDROGRAPHIC ASSEMBLY  
FOR MEASURING PARAMETERS OF  
SALINITY, TEMPERATURE AND DEPTH (STD)  
IN SEAWATER



Signals from electronic 80-lb. stainless steel STD sensor "fish" unit on bottom of line are transmitted through hydrowire from STD winch (left) and recorded on magnetic tape and strip chart (above) located aboard ship.



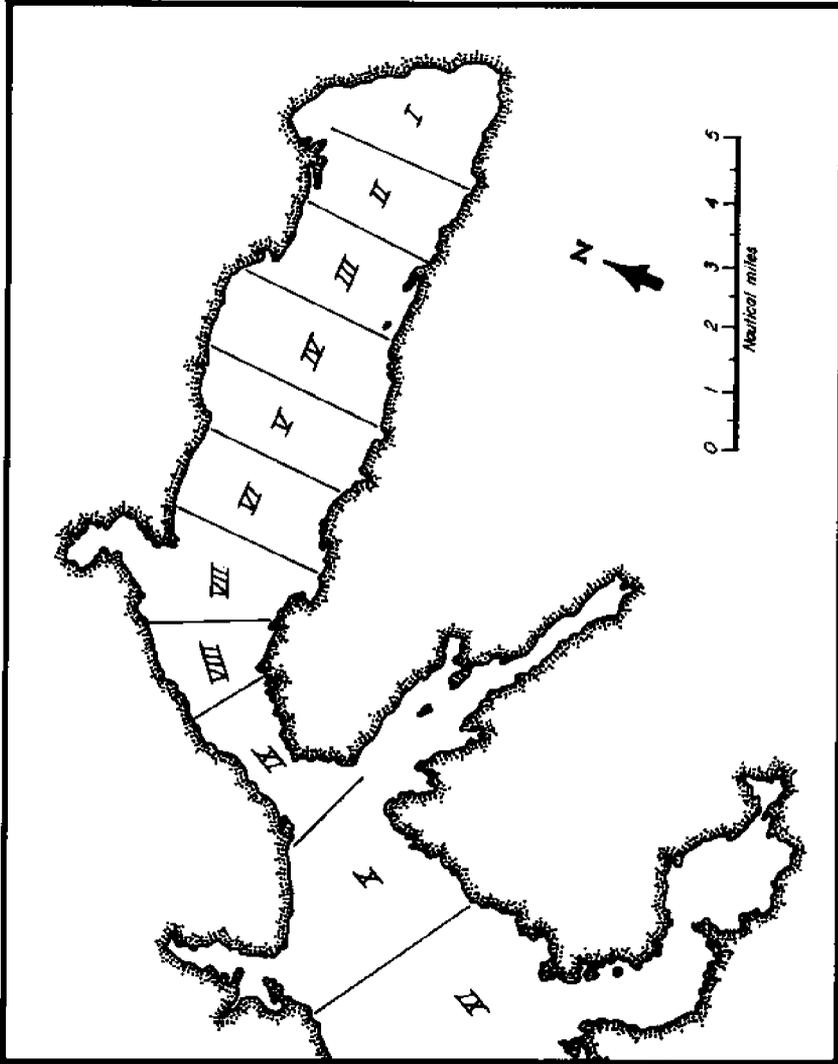


Figure 2.18 Geographical regions used in computing mean salinity distribution throughout the Port Valdez system.

**Table 2.2** Variation of mean 0-125 m salinities in the Port Valdez region

Date	Location (see Figure 2.18)											Mean
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
May	31.63	31.63	31.71	31.67	31.69	31.68	31.79	31.67	31.66	31.73	31.71	31.69
July-August	30.67	30.58	30.57	30.54	30.57	30.55	30.50	30.38	30.49	30.61	30.61	30.55
October	30.08	30.20	30.30	30.29	30.39	30.40	30.46	30.44	30.34	30.46	30.40	30.34
November-December	31.57	31.47	31.47		31.53	31.52	31.61	31.52	31.62	31.52	31.45	31.53
March	32.33	32.31			32.31	32.31	32.31		32.35	32.35	32.33	32.33
April	32.22	32.24	32.23	32.19	32.22	32.24	32.22	32.21	32.14	32.15	32.14	32.20

**Table 2.3** Variation of mean 125-200 m salinities in the Port Valdez region

Date	Location (see Figure 2.18)											Mean
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
May		32.17	32.20	32.19	32.23	32.18	32.24	32.13		32.28	32.23	32.21
July-August		32.15	32.13	32.13	32.12	32.13	32.13	32.13		32.43	32.36	32.19
October		32.01	32.01	31.97	32.02	32.02	32.03	32.10		32.16	32.22	32.06
November-December		31.92	31.82		31.95	31.97	32.04	31.97	32.01	32.03	32.04	31.97
March		32.34			32.35	32.34	32.34		32.42	32.41	32.40	32.37
April		32.36	32.36	32.34	32.32	32.36	32.35	32.34	32.22	32.32	32.33	32.33

salinity decrease from the head towards the Narrows, contrary to what would be expected if classical entrainment flow were occurring. Salinities attained minimum values in the Narrows and, as in May, there was little difference between the salinities inside and outside the Narrows. By October this pattern had reversed; there was now first evidence of a clear-cut salinity increase from the head to the Narrows within Port Valdez, and maximum salinities occurred in the Narrows. During the remaining months there was no detectable pattern in the variation of the mean salinities. These variations closely coincided, moreover, with the accuracy of the salinity determination.

Salinities below 125 m within Port Valdez showed no detectable pattern of variation during the study. During the period May 1971-March 1972, salinities below 125 m outside the Narrows in Valdez Arm were as much as  $0.4 \text{ ‰}$  higher than those in the Port. In April 1972 salinities in Valdez Arm differed from those in Port Valdez by only a small amount ( $0.02\text{-}0.03 \text{ ‰}$ ).

The mean salinities indicate that a seasonal variation was present throughout the water column, with maximum salinities having been observed during March 1972 ( $32.38 \text{ ‰}$ ) below 125 m. Minimum salinities were observed during November-December 1971 for the 125-200 m interval and during October 1971 for depths above 125 m. This variation is probably due partially to annual salinity fluctuations in the Gulf of Alaska, which have been observed but are poorly documented (T. C. Royer, personal communication). Varying fresh-water input to the Prince William Sound system would also be expected to play a role. The observed winter salinity increase in the Gulf of Alaska, coupled with the addition of fresh water in summer, would contribute to the observed variation in Port Valdez. Data from Prince William Sound were too widely spaced geographically to allow more than a general observation of agreement with variations in Valdez Narrows as would be expected.

In the absence of fresh-water influence during the winter months, when runoff was observed to be essentially nil (see also Carlson et al. 1969), there was an expected lack of longitudinal salinity variation in the Port Valdez region. Instead of conforming to conditions of classically estuarine circulation, the waters there were now behaving apparently more as a basin driven primarily by forces of a wind-generated or tidal nature.

During May, July-August and October 1971, when runoff was appreciable, based on historical records (Carlson et al. 1969) and visual observation of rivers at the time, it was expected that estuarine circulation would be evident. Except during October, the salinities gave no indication that an estuarine mode of circulation was present. Examination of the longitudinal salinity sections representing those periods suggests, moreover, that the mean salinity variations were reflections primarily of variations in the upper 10-20 m of the water column, since below that depth the isohalines showed little longitudinal variation (Figures 2.6, 2.8, 2.10). It is concluded that estuarine circulation within Port Valdez was confined, even during periods of maximum runoff, to the upper 20 m or less of the water column. Motion of the water below that depth must therefore have been a response primarily to wind and tidal currents.

The lack of appreciable estuarine circulation within Port Valdez may have been due to one or both of two factors. Firstly, runoff into the Port even during maximum runoff season is small (about 5 percent of the tidal prism) and so might provide insufficient energy to drive an appreciable estuarine circulation. Secondly, this runoff is supplied both at the head (by the Lowe and Valdez rivers) and at the mouth (by the Shoup River) of the estuary. There would thus have been a tendency for the fresh-water layer to spread out and form a uniform layer throughout Port Valdez without attaining appreciable seaward velocities necessary for entrainment. The tendency for fresh water to spread as a uniform layer over Port Valdez was best seen in October 1971, when appreciable river runoff was still entering the system (Figure 2.19). Low-salinity regions at the head and near the mouth were evident, and they clearly correlated with the indicated major fresh-water inputs. Entrainment due to shear flow was not evident in the Narrows.

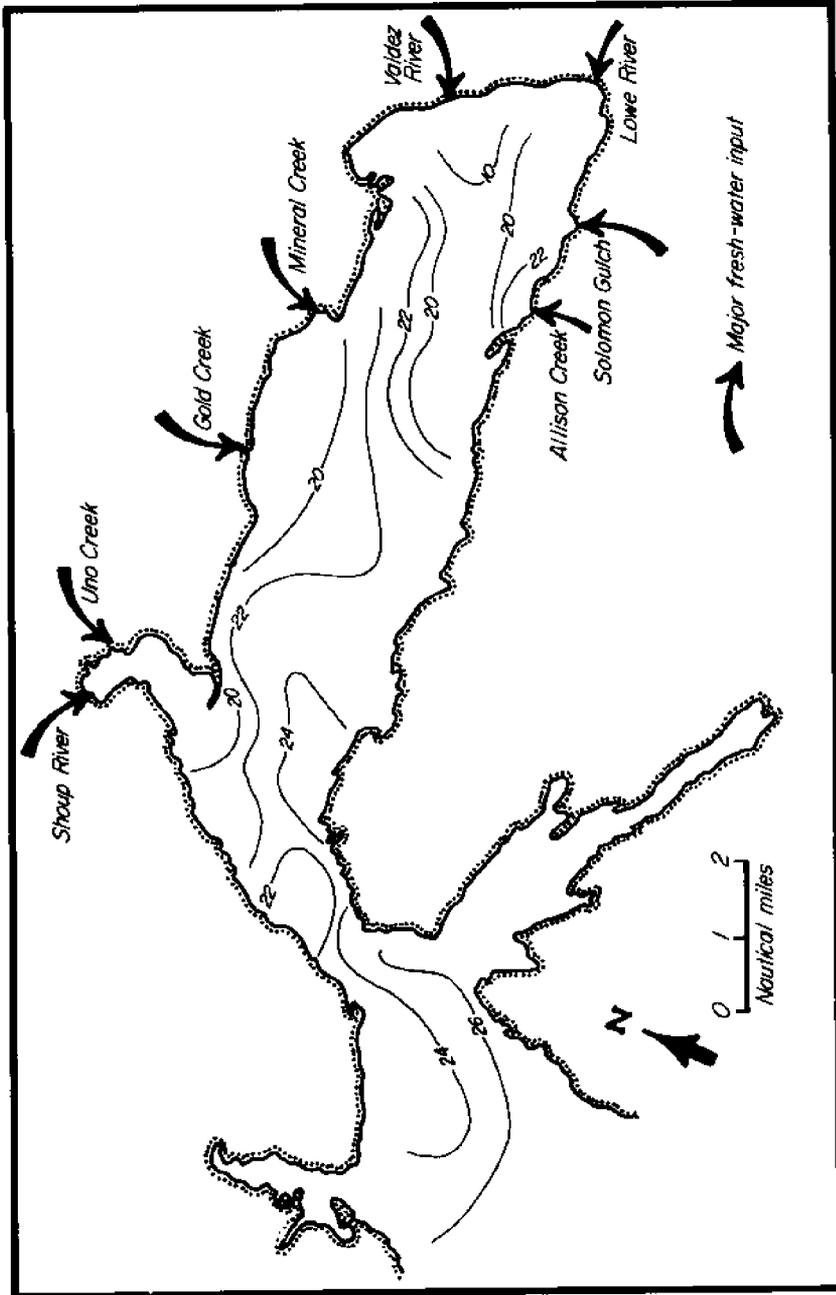


Figure 2.19 Distribution of salinity at the surface of Port Valdez during early October 1971.

Apparently the increase in salinity stratification below 10-20 m which was observed during the summer was due primarily to an increase in stratification of the water in Prince William Sound as reflected in Valdez Narrows. This water was then advected into Port Valdez. This mechanism would have allowed for a seasonal variation in salinity stratification within Port Valdez without the longitudinal salinity variation which would have been evident had the variation been due to the local fresh-water input within Port Valdez. Data from Prince William Sound were too geographically scattered for verification by determination of seasonal effects there, however.

### 2.3.2 Observed circulation

Water circulation within Port Valdez and in Valdez Narrows was observed directly on several occasions using recording current meters and parachute drogues. Details of the field measurement programs have been discussed above (2.2.2).

The drogue studies were intended to allow a general estimation of the large-scale circulation within Port Valdez. In late May 1971, two 30-m (100-ft) deep drogues were launched and tracked over a 2-day period (Figure 2.20). The tracking period was too short to allow estimation of large-scale circulation features. The drogue tracks did suggest, however, a net motion from the Jackson Point region toward the head of Port Valdez. A tendency for the drogues to progress most rapidly during the daytime may have been due to diurnally varying westerly winds which reached maximum speeds during the afternoons.

A single surface drogue launched west of Jackson Point in May 1971 (track not shown) drifted eastward directly onto the beach, apparently in response to westerly winds. No further attempts were made to track surface drogues, since it was recognized that they would be heavily influenced by winds, an effect which would tend to mask other circulation features. All of the subsequent drogues were launched 15 m (50 ft) deep for study of circulation at the anticipated depth of the planned ballast water outfall.

In July-August 1971, seven drogues were launched in Port Valdez and tracked for the duration of the cruise (Figures 2.21 and 2.22). With the exception of drogues 1, 2 and 5, the net movements were only about 2-3 n. miles over a 6-day period. Drogues 1, 2 and 5 moved in a westerly-northwesterly direction from Jackson Point, with drogue 5 exhibiting the greatest net displacement. Irregularities in the tracks may have been a reflection of tidal motions.

Six drogues were launched in October 1971 and tracked for an 8-day period (Figures 2.23-2.25). These drogues exhibited greater motion than was observed during the earlier cruises. Three of the six drogues travelled throughout the entire length of Port Valdez during the 8-day study period. One escaped from the system through Valdez Narrows, while another moved from the Narrows nearly to the head of Port Valdez in less than a day at a net speed of approximately 1 knot during that period. The tracks showed no detectable pattern but appeared considerably irregular.

In November-December 1971, six drogues were tracked over a 9-day period (Figure 2.26). Due to foul weather during the December cruise, positioning of the drogues was less frequent than during previous cruises. Each of the drogues travelled westward; the maximum excursion was indicated by drogue 3, which drifted about 8 n. miles during a 4-day period. The westerly drift appears to have been a response to easterly winds which prevailed throughout the cruise. The westerly drogue motion in the region of Valdez Narrows was in qualitative agreement with a westerly near-surface current which was recorded by the current meters.

Five drogues were tracked during March 1972. As in December, foul weather prevented frequent positioning of the drogues (Figure 2.27). The drogues all moved in a westerly direction, in qualitative agreement with a probable westerly surface current due to prevailing easterly winds during the cruise. This agreed qualitatively, as in December, with current



preparation of current meter array on deck

### CURRENT METER STUDIES OF WATER MOVEMENT



To predict flushing rates of Port Valdez, the velocity and direction of water circulation are photographically recorded at 20-minute intervals on 16-mm coded film exposed by radiation.



Orbital vane component of Braincon current meter. Typically, 5 such recording instruments are spaced on vertical string throughout the water column at depths from 10-130 m and secured by timed-release anchor.

Surface buoy to mark location of current meters submerged in Valdez Narrows. A flashing xenon light atop the assembly is visible up to a mile.

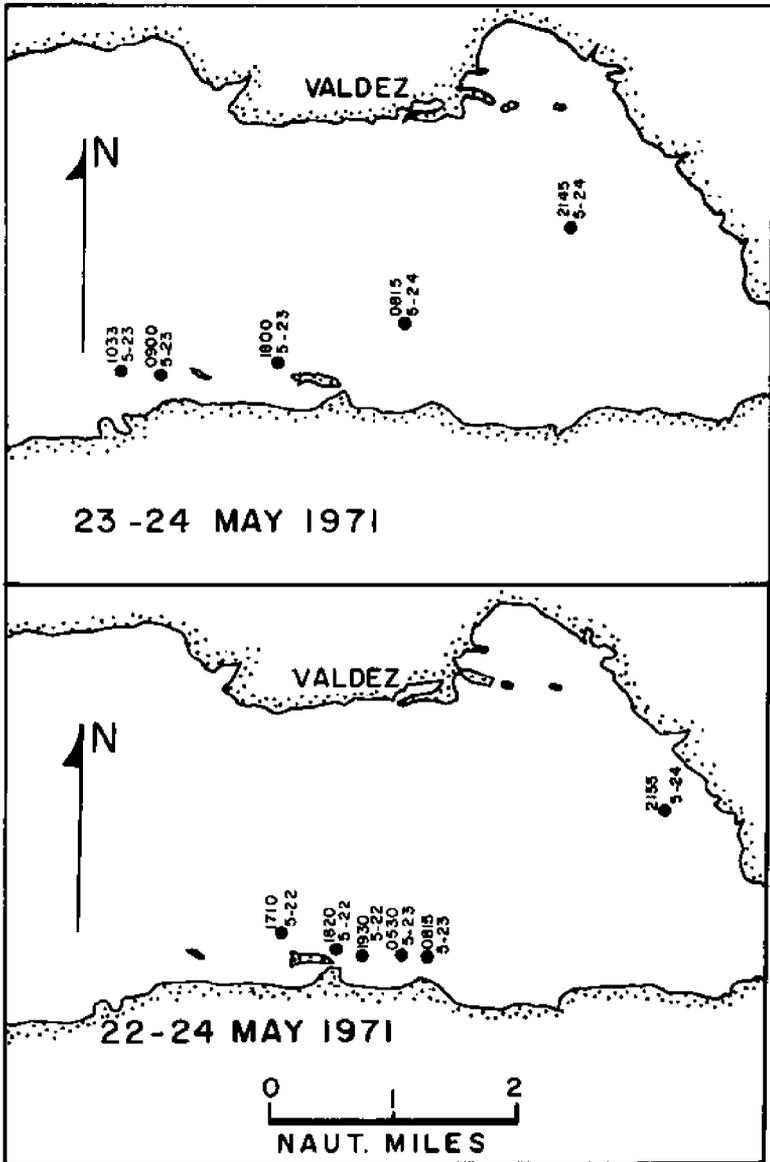


Figure 2.20 Positions of 30-m (100-ft) deep drogues tracked during 22-24 May 1971.

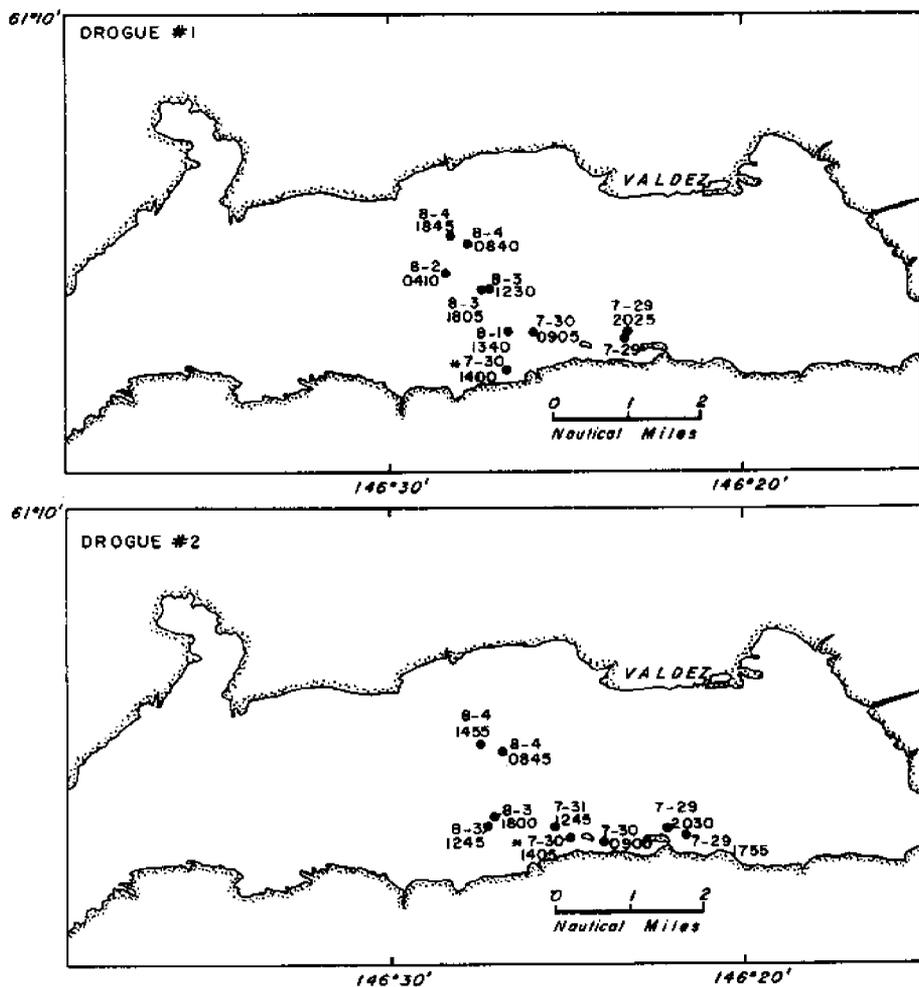


Figure 2.21 Positions of two 15-m (50-ft) deep drogues tracked during 29 July - 4 August 1971.

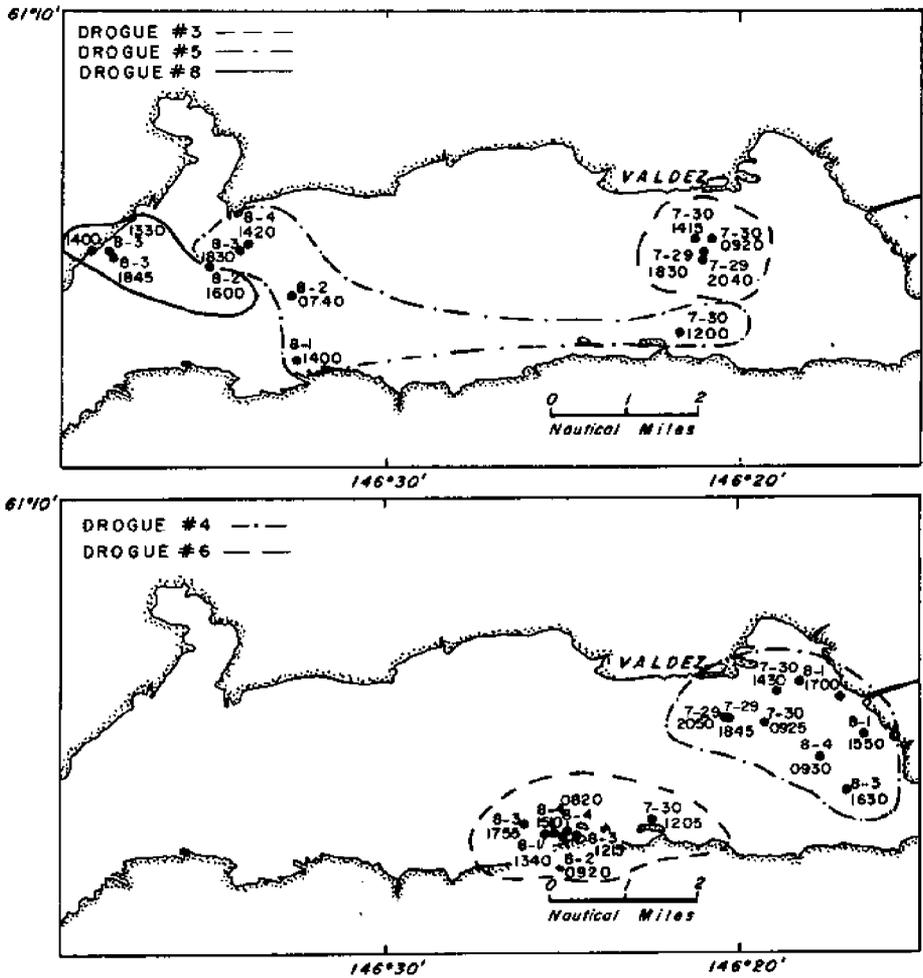


Figure 2.22 Positions of five 15-m (50-ft) deep drogues tracked during 29 July - 4 August 1971.

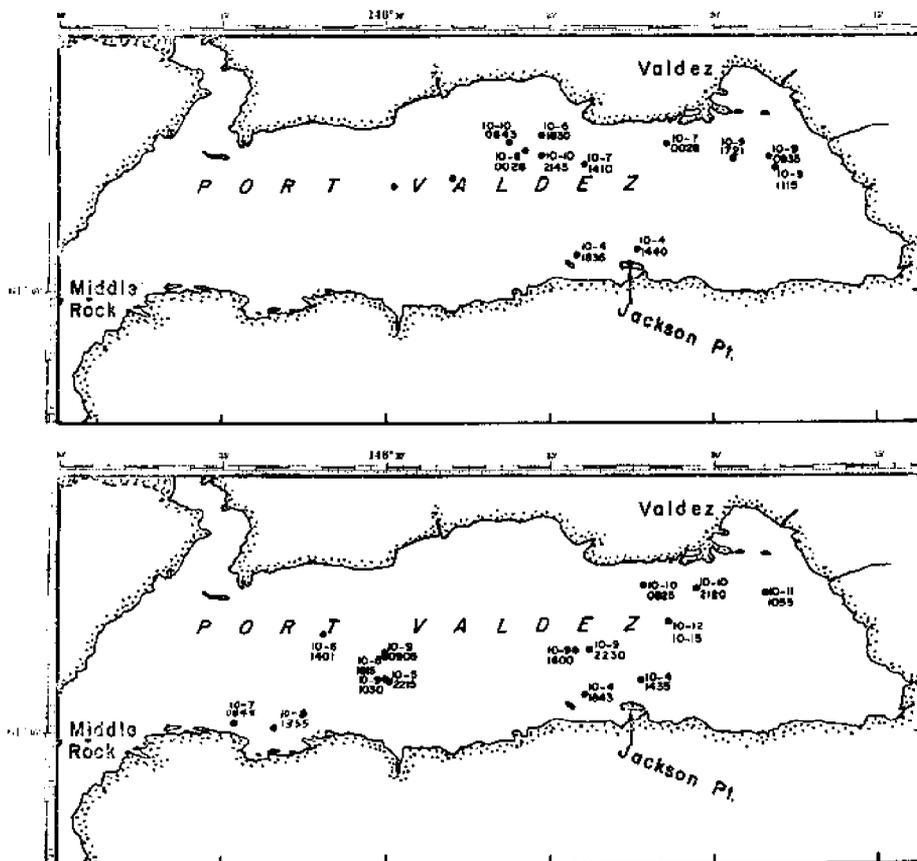


Figure 2.23 Positions of two 15-m (50-ft) deep drogues tracked during 4-11 October 1971.

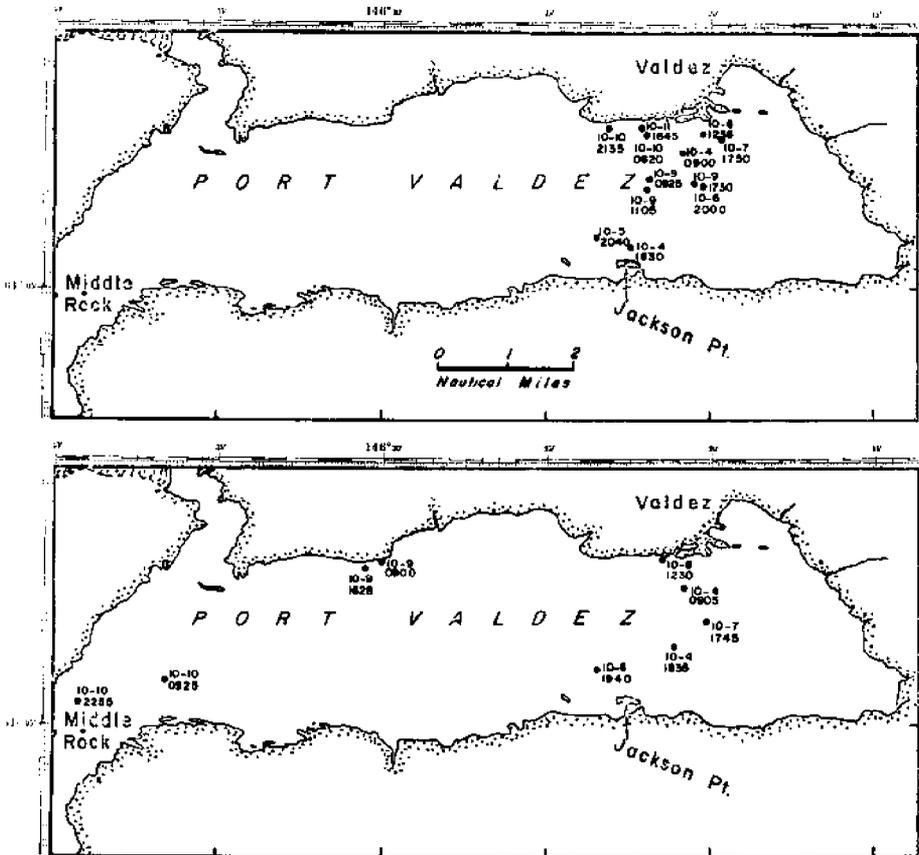


Figure 2.24 Positions of two 15-m (50-ft) deep drogues tracked during 4-11 October 1971 (continued on Figure 2.25).

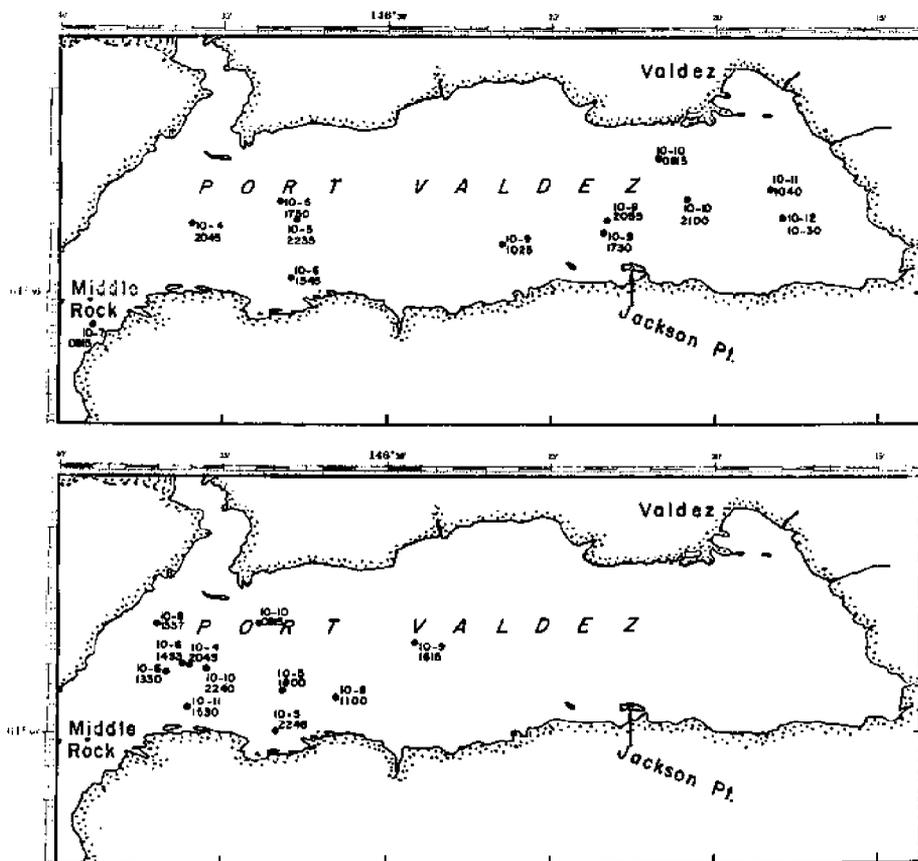


Figure 2.25 Positions of two 15-m (50-ft) deep drogues tracked during 4-11 October 1971 (continued from Figure 2.24).

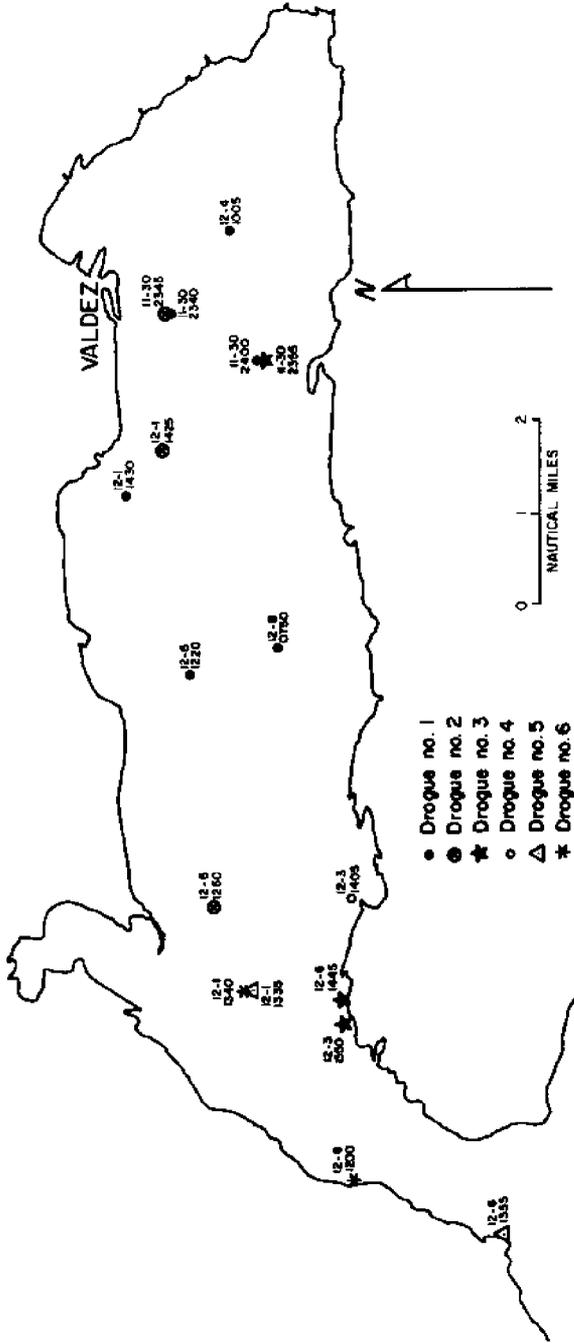


Figure 2.26 Positions of six 15-m (50-ft) deep drogues tracked during 30 November 8 - December 1971.

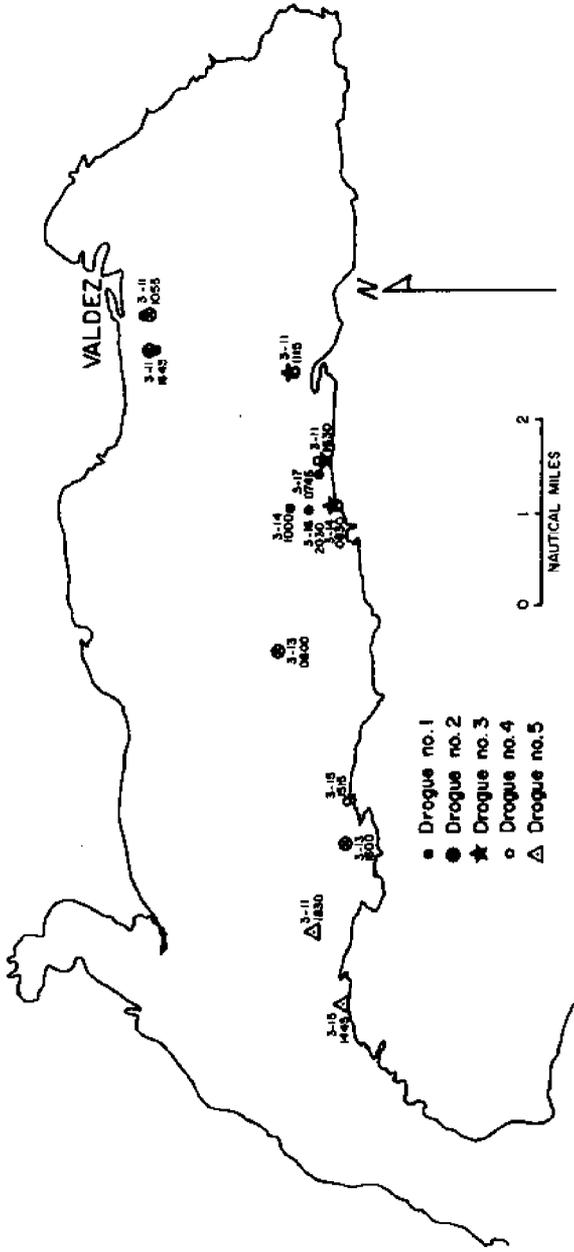


Figure 2.27 Positions of five 15-m (50-ft) deep drogues tracked during 11-17 March 1972.

measurements. All drogues had become grounded by the end of the study on the southern shore of Port Valdez.

The final drogue studies were carried out in April 1972, when six drogues were tracked over a 7-day period (Figures 2.28-2.29). As during earlier studies, the predominant feature of the tracks was their irregularity. Since wind action was negligible in April, the drogue motions were interpreted as currents attributable to other influences. Because there is normally little river runoff in April (Carlson et al. 1969) and only negligible fresh-water input was evident, tidal currents are suspected to have played a significant role in the observed drogue drifts.

Although the drogue studies were successful in that tracks were obtained during different seasons of the year, the tracks did not define any constant circulation pattern within Port Valdez. The circulation appeared to be irregular when no wind was blowing. During the winter, easterly winds appear to have forced a regular westward movement of water at 15 m, as reflected in the drogue tracks. Since easterly winds are common in Port Valdez during the winter (Searby 1969), it is suggested that westerly surface currents down to at least 15 m are common during the winter. During the summer the circulation at 15 m appeared to have been due primarily to tidal and transient wind-driven influences. This agrees with the above conclusions, based on hydrographic data, that the circulation created by river runoff was restricted to the upper 10-15 m of the water column and would therefore probably not have affected the drogue motion. Large excursions exhibited by some of the drogues indicated that currents as great as 1 knot occurred within Port Valdez at 15-m depths but that these currents appeared to be random in direction. The data were insufficient for determination of the causes of these currents.

Supplementary current meter studies were conducted in Valdez Narrows to gain information concerning the exchange of water between Port Valdez and Prince William Sound.

From 3-9 December 1971, recording current meters were moored in a vertical string in Valdez Narrows at depths of 10, 20, 80 and 130 m (Figure 2.31). Configuration of the mooring has been discussed above. The processed data from these meters were supplied in the form of northerly and easterly components relative to magnetic north. Magnetic north approximately parallels the axis of the channel in Valdez Narrows, so the northerly component represents the long-channel current component there. This long-channel current is plotted as a function of time for each of the four meters (Figure 2.31). The nature of the tidal currents is clearly seen to be mixed, mainly semidiurnal. Maximum tidal currents observed were about 20 cm/sec. There was no detectable variation with depth in the magnitudes of the tidal currents. There was, however, a phase lag of 1-2 hours between peak tidal current speeds at the surface (10 m) and the bottom (130 m).

In order to estimate the mean currents over the sampling period, all current measurements were averaged over 10 semidiurnal tidal cycles in an attempt to cancel out tidal motions (Figure 2.32a). Although this method is cruder than filtering out the tidal components numerically, it was sufficient for the short records available. The Narrows were assumed to be homogeneous in cross-section, based on the hydrographic structure measured at stations 114 and 115 (Figure 2.1), producing an identical current pattern across the channel. The smooth curve was drawn using the constraint that volume continuity within Port Valdez had to be preserved; i.e., the same volume of water must flow out that is flowing in if no change in sea level within is assumed. The profile also assumes that current velocities reach zero at the bottom due to frictional effects. The curve was left incomplete at the upper surface due to a lack of knowledge concerning probable wind-driven effects on that area.

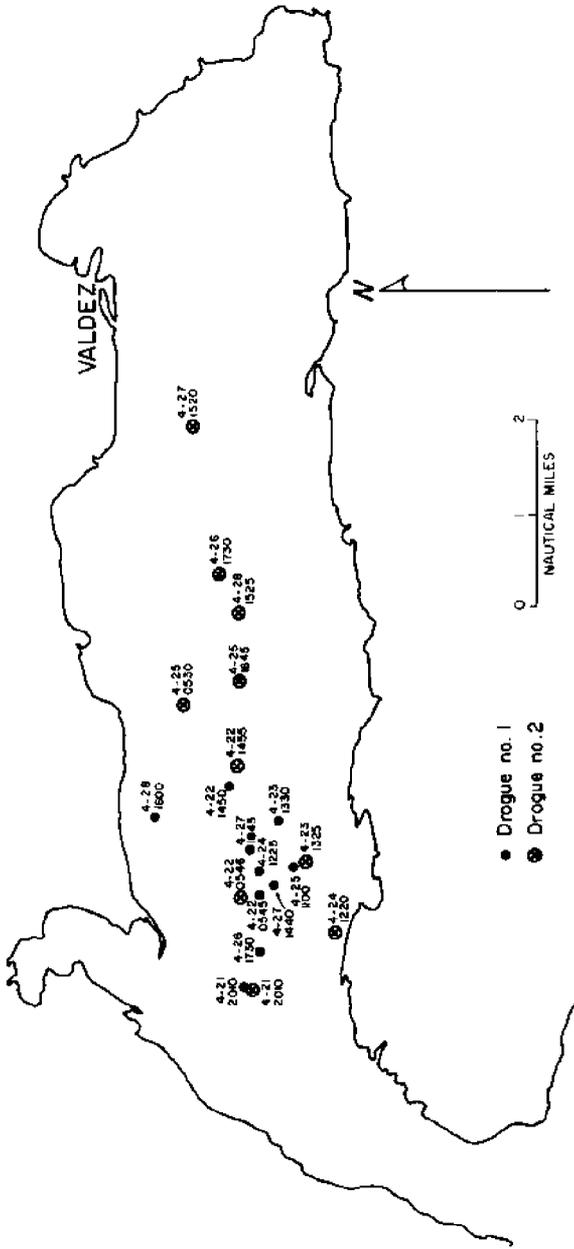


Figure 2.28 Positions of two drogues (#1 and #2) launched at 15-m (50-ft) depth near Valdez Narrows and tracked during 21-28 April 1972.

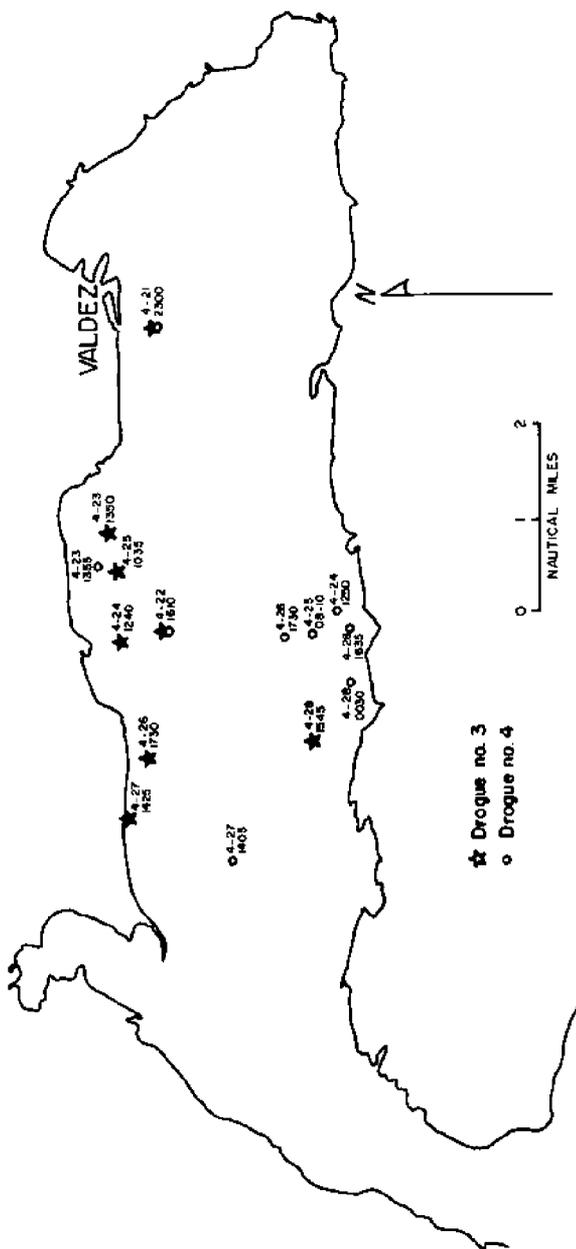


Figure 2.29 Positions of two drogues (#3 and #4) launched at 1.5-m (50-ft) depth off Valdez and tracked during 21-28 April 1972.

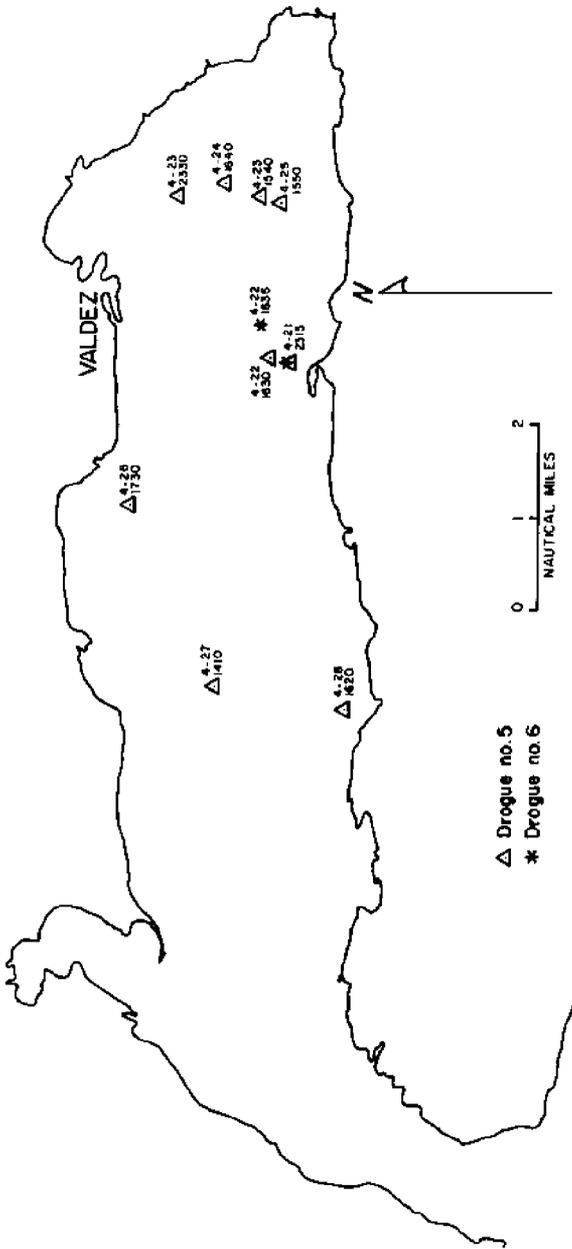
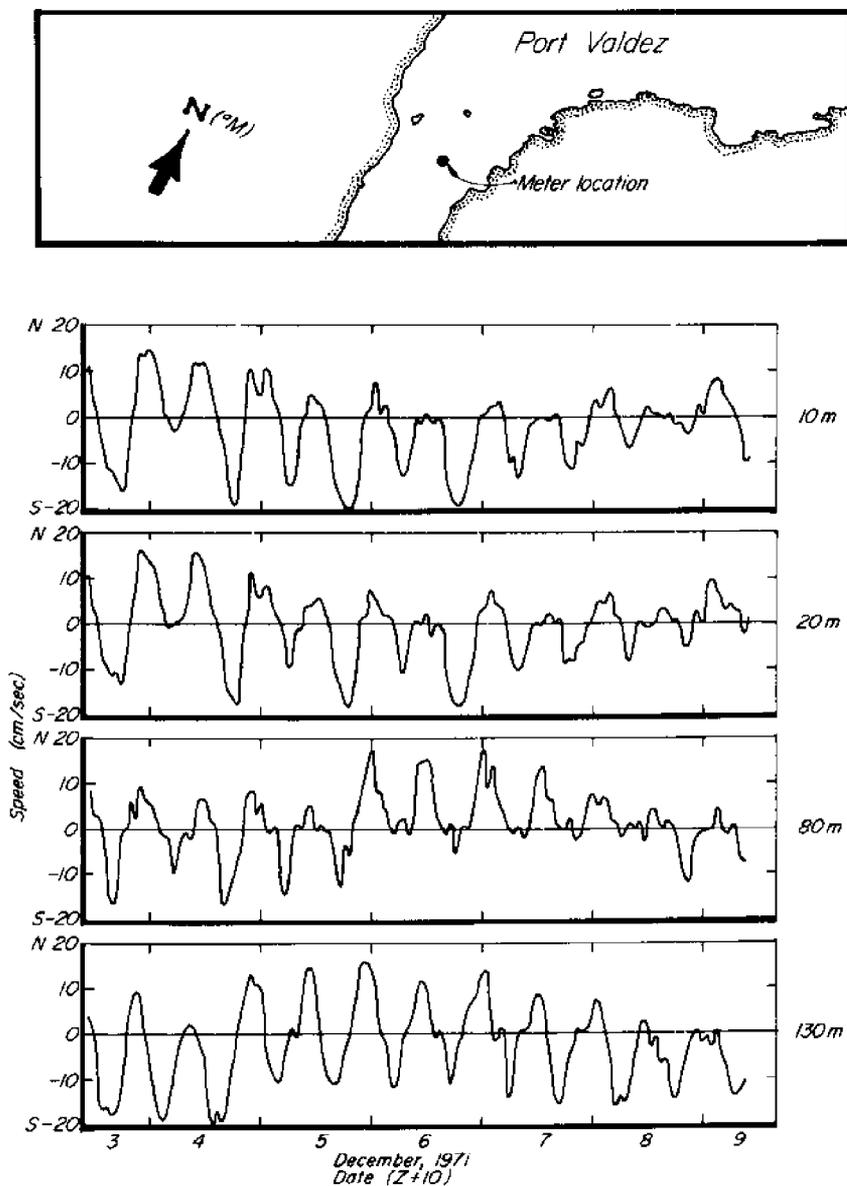


Figure 2.30 Positions of two drogues (#5 and #6) launched at 15-m (50-ft) depth off Jackson Point and tracked during 21-28 April 1972.



**Figure 2.31** North and south ( $^{\circ}$ M) current speeds through Valdez Narrows during 3-9 December 1971, showing meter location and relation of channel orientation to magnetic north.

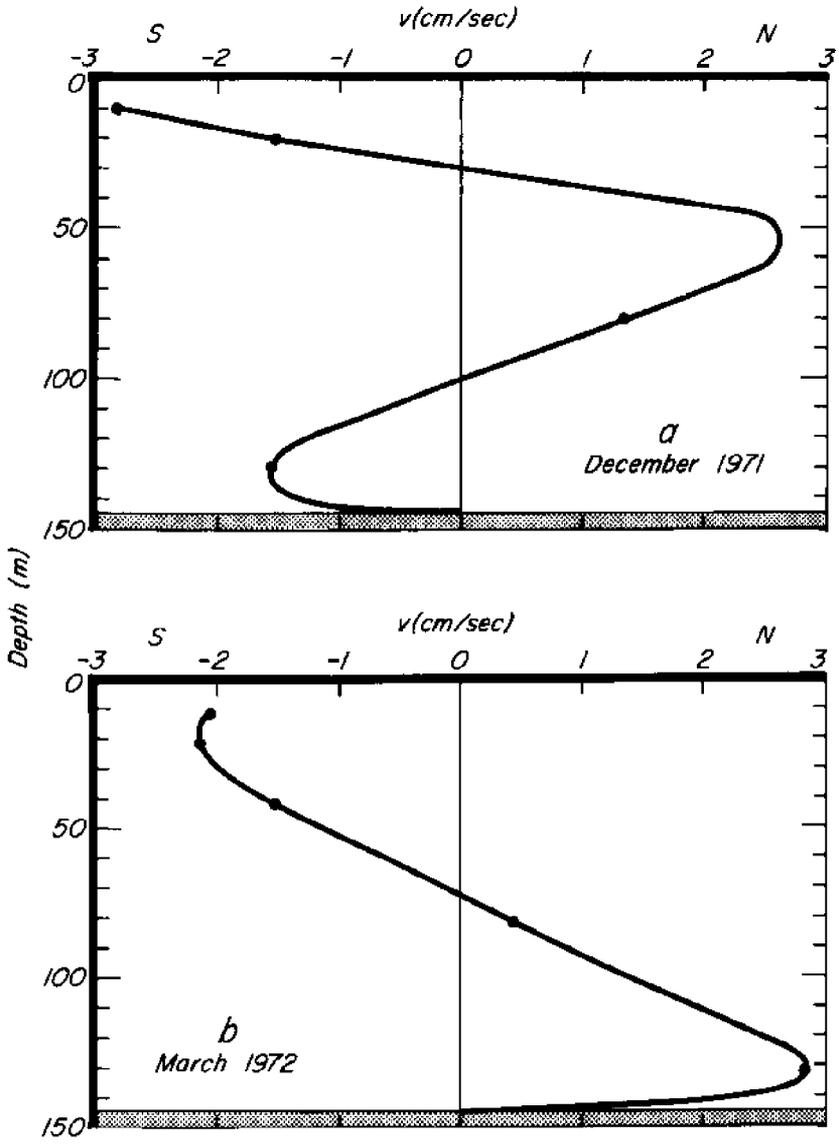


Figure 2.32 Mean current speeds (N and S °M) through Valdez Narrows during 3-9 December 1971 (a) and 13-19 March 1972 (b).

The mean flow consisted of near-surface and deep outflows and a mid-depth inflow, with current speeds about 2-3 cm/sec for both inflows and outflows. The mid-depth inflow correlated with the warm ( $>6^{\circ}\text{C}$ ) layer observed while the meters were recording, which suggests that presence of the warm layer was due to its inward advection from Prince William Sound (Figure 2.11). This would agree with the above conclusions that flow through Valdez Narrows entails a continual horizontal interchange of water.

From 3-9 March 1971, recording current meters were moored in Valdez Narrows, at the same location as those moored during December, at depths of 10, 20, 40, 80 and 130 m. As in the case of the December data, long-channel components of the measured currents show a mixed, mainly semidiurnal tide (Figure 2.33). Maximum observed current speeds were about 20 cm/sec. The mean currents over 10 semidiurnal tidal cycles show a different vertical pattern than that observed in December (Figure 2.32b). A net surface outflow was occurring, but there was inflow at depth as opposed to the deep outflow noted earlier. Maximum mean currents were about 2-3 cm/sec.

It is probable that the observed surface outflows through Valdez Narrows were due primarily to wind stress consequent to observed strong easterly winds. This surface outflow would then have required a deep inflow to satisfy volume continuity. The cause of the deep outflow observed during December was not known.

It is possible, using the mean currents from December 1971 to March 1972 and assuming cross-channel homogeneity, to estimate a residence time for the waters within Port Valdez. The residence time under these conditions is found to be about 40 days for both observed current patterns. This would be valid only if the observed circulation persisted for as long as 40 days. It should also be pointed out that this residence time is computed independently of any tidal flushing action that might occur and which would tend to reduce the residence time. No attempt was made to compute tidal flushing, since nothing is known of the fraction of water from the preceding outgoing tide which would re-enter Port Valdez on the next incoming tide. Although tidal current models are now feasible, tidal flushing models (Ketchum 1951) for fjord estuaries are at a preliminary stage of development and not practical to consider in this study based on data available.

#### 2.4 Summary

The hydrography and circulation within Port Valdez are controlled by a variety of external influences such as tides, precipitation and fresh-water runoff, winds, surface air temperatures, and the character of marine source-water available from Prince William Sound.

During May-October 1971, when runoff was at its annual maximum, the waters within Port Valdez were stratified in both temperature and salinity. The maximum stratification was observed during July 1971. Estuarine circulation, due to addition of fresh water at the surface, appeared to be confined to the upper 15 m of the water column. Lack of temperature and salinity differences below that depth between Valdez Arm and Port Valdez suggests that horizontal exchange was occurring continually between these two water bodies throughout the water column above the sill. It is probable that tides played a significant role in the exchange. The data were insufficient, however, to allow an estimate of exchange rate during the summer.

From December 1971-April 1972, when runoff was at a minimum and surface cooling and wind mixing were maximal, the waters of Port Valdez became vertically mixed (completely to the bottom by March 1972). This vertical mixing may be explained qualitatively by cooling, together with cessation of fresh-water addition, at the surface. Based on climatic records, it is probable that this mixing is a common winter occurrence in Port Valdez. By April 1972 stratification had begun to appear in the upper 20 m of the water column, subsequent to the onset of spring warming and fresh-water addition at the

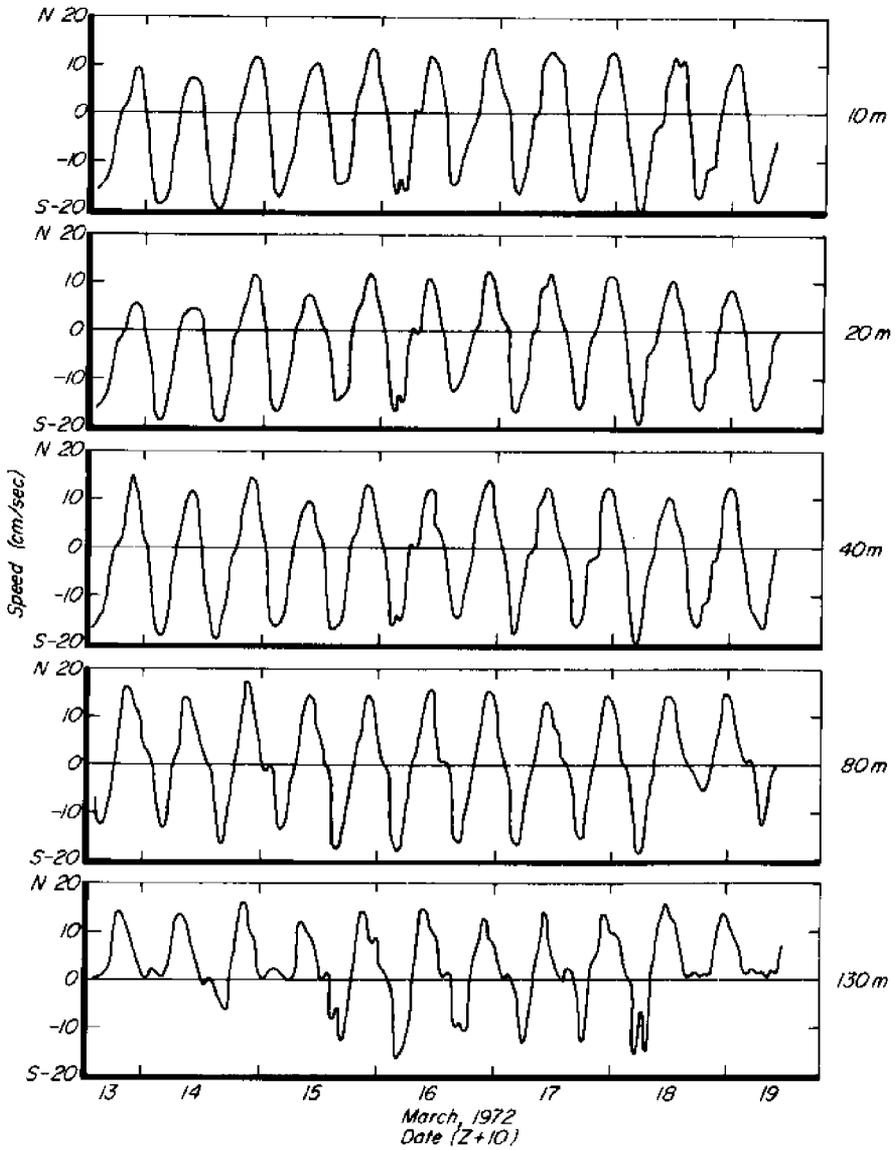


Figure 2.33 North and south ( $^{\circ}$ M) current speeds through Valdez Narrows during 13-19 March 1972.

surface. A winter salinity increase throughout the system coincided with a poorly documented salinity increase in the Gulf of Alaska, which supplies marine source water for the Prince William Sound and Port Valdez systems.

Current measurements in Valdez Narrows during December 1971 and March 1972 allowed estimation of tidal and non-tidal currents there. Maximum tidal current speeds were about 20 cm/sec, while mean non-tidal currents were about 2-3 cm/sec. Assuming cross-channel homogeneity, the mean currents observed at this time would have caused a renewal of the waters within Port Valdez in approximately 40 days (provided that the observed currents persisted for that long a period). The effects of tidal currents would have shortened this renewal period. Data were insufficient, however, to attempt estimation of tidal flushing.

Studies carried out with parachute drogues indicated that there was little detectable pattern or seasonal variation in the circulation at 15-m depths other than an ill-defined westerly motion consequent to easterly winter winds. The drogues indicated an irregular motion at all times and would not have been expected to reflect the small mean currents necessary for renewal of the waters in Port Valdez. During December 1971 and March 1972 a westward-tending drogue motion, not evident at other times, could be explained qualitatively in terms of the prevailing easterly winter winds. Based on historical weather records which indicate common winter occurrence of easterly winds, it is probable that westerly near-surface motion in Port Valdez is common during the winter.

Data obtained from Prince William Sound were sufficient only to substantiate that variations in the temperature and salinity structure there in the Sound approximately paralleled those in the Port Valdez system.

## 2.5 References

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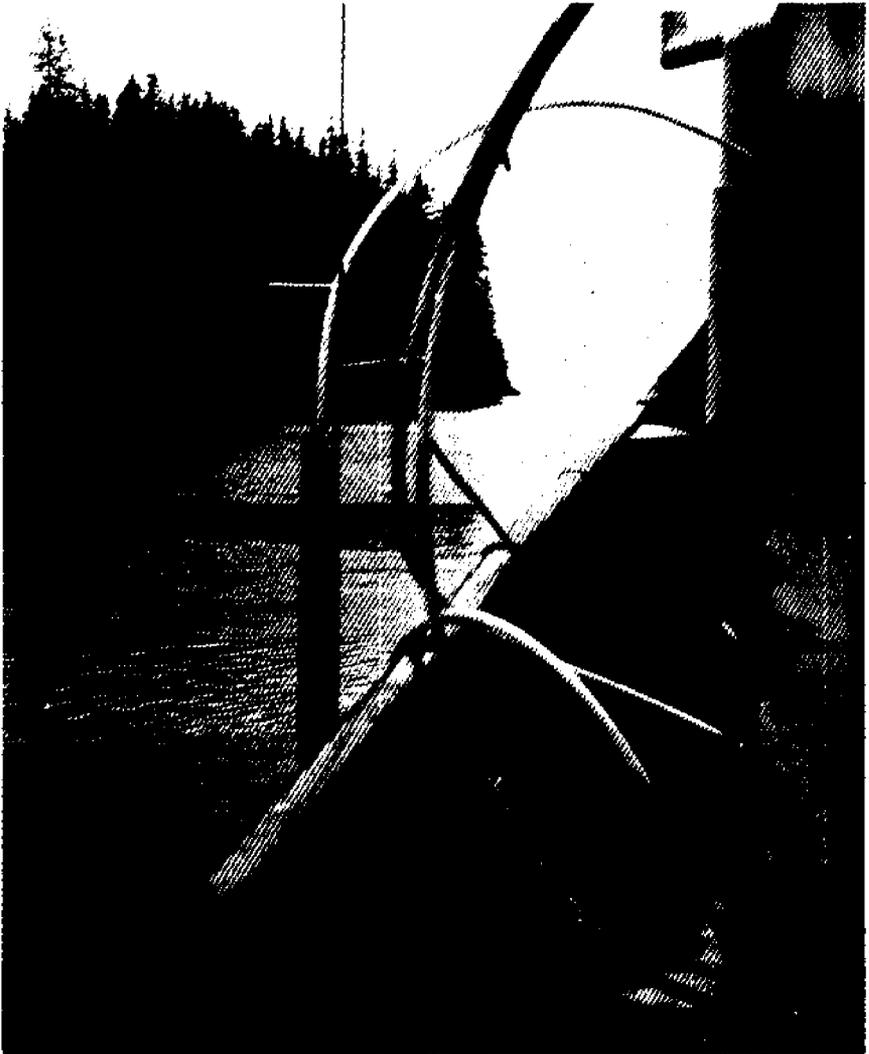


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# *Chapter 3*

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## DYE DISPERSION STUDIES





### 3. DYE DISPERSION STUDIES

by

D. L. Nebert, R. D. Muench and D. W. Hood

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#### 3.1 Introduction

When a tracer such as rhodamine-B dye is introduced continuously into a motionless homogenous fluid from a stationary point source, it forms a spherical pattern within which dye concentration decreases with distance from the source. If the fluid has a stable vertical density stratification, which is frequently observed in marine waters and was the case in Port Valdez during all months observed except December and March, the tracer will disperse more as a horizontally flattened disc within which concentration decreases with distance from the source; the stratification impedes vertical mixing, hence vertical extent, of the tracer.

In an estuary, distribution of the tracer is complicated by the presence of oscillating tidal currents, and the disc assumes the form of a horizontally oriented cigar-shaped plume with its long axis parallel to the tidal currents and trending from the source toward the prevailing direction of these currents. A build-up of tracer may occur about the source during periods of slack tide, only to stream away as a plume during the next ebb or flood tide. The presence of medium-scale turbulence within the water column may further distort the plume by breaking it up so that it no longer has a clearly defined shape. Such turbulence is commonly generated by the interaction between currents and boundaries such as shorelines; all dye plumes generated within Port Valdez exhibited the broken, irregular appearance indicative of medium-scale turbulence.

Whatever the final disposition of the plume, its form and dimensions are a useful indication of the magnitude and nature of the dispersive processes which affect contaminants introduced into natural systems. Dye introduced in surface waters have been photographed from the air and sampled by surface ship to experimentally establish a horizontal diffusion coefficient (Isayeva and Isayev 1963a; Reinert 1965). Vertical diffusion has been directly measured by Isayeva and Isayev (1963b), who used fluorescent dyes introduced within the water column a known distance beneath a submerged fluorometer. Wilson (1970) describes a series of experiments in Baltimore Harbor, which furnished input for a numerical model of mixing in the northwest branch of Baltimore Harbor.

The work by Wilson (1970) was directed to a similar problem as that which prompted the Valdez study, in that water quality of an embayment was possibly threatened by the introduction of contaminants. Since it was necessary to predict how rapidly pollutants would be dispersed in the Jackson Point area of Port Valdez, an experiment was designed to simulate the introduction of a contaminant (rhodamine-B dye) at a specified depth. The dye was then located by means of shipboard fluorimeters to which water was pumped by a hose system. Such dye dispersion studies were conducted at three locations near Jackson Point, Port Valdez, on six occasions: May 1971; July-August 1971; October 1971; December 1971; March 1972; and April 1972. The locations of the studies coincide with those proposed for treated ballast water outfalls. Locations 1, 2 and 3 correspond respectively to stations 153, 158 and 157 (Figure 2.1).

Results from dye studies were presented in the following manner. Concentration of rhodamine-B dye in ppb was plotted on a logarithmic scale against distance in nautical miles from the point of injection (e.g., Figure 3.1). For certain plots it was possible to construct a "worst possible case," i.e. a straight line chosen as representative of the maximum dye concentration observed at a given distance from the source. This approach yields more meaningful results than a curve representing an average concentration, since the points corresponding to lower concentrations at a given distance may not have represented the major part of the dye plume. A tenfold dilution distance has been determined from the worst case plots, as presented in Table 3.1 below:

**Table 3.1 Tenfold dilution distances (K) of rhodamine-B dye**

Location no. (Figure 2.1)	Date	Depth (ft) (m)	Phase of tide	Distance K required for tenfold dilution (n. mi)
1	1 Aug 1971	8 (2.5)	flood	0.35
	1 Aug 1971	8	ebb	0.40
	1 Aug 1971	50 (15.0)	flood	0.36
	1 Aug 1971	50	ebb	-
	8 Oct 1971	8	flood/ebb	0.76
	8 Oct 1971	50	flood/ebb	0.20
	4 Dec 1971	50	ebb/flood/ebb	-
	5 Dec 1971	75 (23.0)	flood/ebb	0.17
	14 Mar 1972	75	ebb/flood/ebb/flood	0.24
	25 Apr 1972	50	ebb/flood/ebb	-
	26 Apr 1972	75	flood/ebb	0.11
2	31 Jul 1971	8	ebb	1.16
	31 Jul 1971	8	flood	0.50
	31 Jul 1971	50	ebb	0.79
	31 Jul 1971	50	flood	-
	9 Oct 1971	8	flood/ebb	0.60
	9 Oct 1971	50	flood/ebb	0.59
3	30 Jul 1971	8	ebb	-
	30 Jul 1971	8	flood	0.12
	30 Jul 1971	50	ebb	-
	30 Jul 1971	50	flood	-
	10 Oct 1971	8	flood/ebb	0.58
	10 Oct 1971	50	flood/ebb	0.40

Location No. 3, July 30, 1971

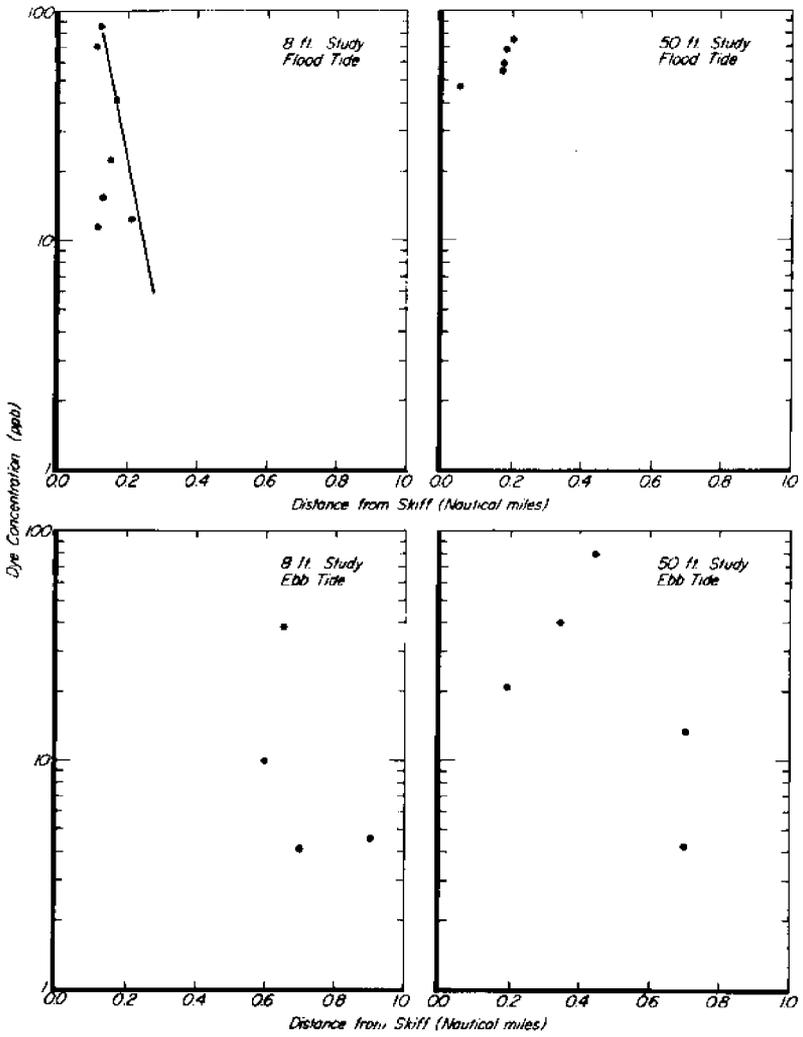
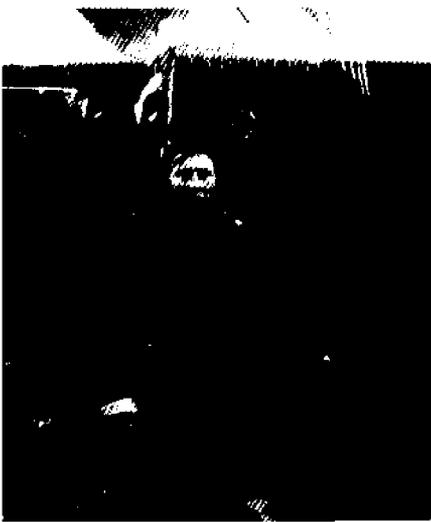


Figure 3.1 Dye concentration (ppb) versus distance (n. miles) for location 3 on 30 July 1971.



hydrographic winch operation

Dye diffusion studies to aid in prediction of treated ballast water discharge at three prospective pipeline outfall locations with different shore features



In series of two-day runs, fluorescent magenta rhodamine-B dye was dispersed from skiff (below) at selected depths of 50, 75 and 100 m and traced by shipboard fluorometers to which seawater is returned by submersible pump and plastic tubing system. Dye pumps are raised and lowered until trimmed to maximum fluorometer response to current. The resulting plume indicates at what depth and locations the horizontal and vertical dispersion rates are most favorable.



To compute the distance required for the concentration  $C_1$  (at the source) to become diluted to concentration  $C_2$ , the following relation may be used:

$$d = K \log C_1 / C_2$$

where  $d$  is the distance to be determined and  $K$  is the tenfold dilution distance (a constant for each case). A brief discussion of each set of experiments is presented, because each is regarded as a unique study.

### 3.2 Methods

The mechanics of the dye study included introduction of dye into the water, sampling for the dye, and reduction of the data. Dye was introduced from an anchored skiff which contained a gasoline-powered generator to drive the pumps. Water was pumped up from the selected depth, and a metered quantity of dye was injected. The water-dye mixture was then returned to the depth from which it was taken. Dye was initially introduced at a rate of 15 ml/min, but this was increased to a rate of 25 ml/min for the October and subsequent studies.

Hoses (2.0 cm i.d. polypropylene) were suspended over the rail of the *R/V Acona* to the selected depth of dye injection, and water was pumped aboard for analysis. Two methods were employed to accomplish the pumping. The first employed stainless steel submersible pumps to lift the water; the second used deck-mounted pumps. The submersible pumps moved a greater volume of water, thus reducing the response time, but they proved less reliable than the deck pumps. (Response time was about 0.5 min for the submersible pumps and about 1 min for the deck pumps). A portion of the water pumped aboard was diverted from each hose and routed through a Turner continuous-flow fluorometer, where dye concentration was measured and plotted on a strip chart recorder. As many as three separate channels were employed, each including a separate pump, tubing and fluorometer. The fluorometers were calibrated at the start of each experiment by pumping rhodamine-B dye solutions of known concentration through each instrument.

In order to initially locate the dye, the pump intakes were lowered to the approximate depth of dye injection and towed around the skiff while the pumps were trimmed vertically to obtain a maximum response on the fluorometers. Once the direction of the dye flow was determined, the vessel repeatedly crossed perpendicular to that flow in order to further define the dye plume. Locations of the dye were determined by use of radar fixes.

Dye concentrations were computed from the strip chart records using the fluorometer calibration data. The locations where dye was found were correlated with the computed concentrations, allowing plots of concentrations versus distance to be prepared. Dilution rates were then estimated from these plots.

### 3.3 Results of Individual Dye Studies

#### 3.3.1 May 1971 dispersion study

Dye dispersion studies were first conducted on 21 May 1971 at location 1, west of Jackson Point (station 153, Figure 2.1). The object of this study was to develop techniques for subsequent dispersion studies in Port Valdez. As a result of the exploratory nature of this first study, insufficient data were collected for satisfactory determinations of dispersion or plume development.

### 3.3.2 July-August 1971 dispersion study

During this study (30 July-1 August) experiments were conducted at all three dye-study locations (Figure 2.1) at depths of 2.5 and 15 m (8 and 50 ft). Dye injection and sampling were done at both depths simultaneously. Concentration versus distance plots and plume configurations for this study (Figures 3.1-3.9) indicated that:

1. Shallow (2.5-m) tenfold dilution distances varied from 0.12 n. miles at location 3 on a flood tide, to 1.16 n. miles at location 2 on an ebb tide. The average tenfold dilution at 2.5 m was 0.5 n. miles.

2. Deep-water dilution distances were calculable for only two (out of six) of the 15-m studies. A distance of 0.36 n. miles was determined for the flood at location 1, and a distance of 0.79 n. miles was found for location 2 on the ebb tide.

3. Dye was detected farthest from the point of injection at location 2 for both depths. The smallest radius of dye excursion was found at location 3, which suggests superficially that dilution was greatest near this location. The concentration, however, did not drop appreciably within this radius: surface (2.5-m) concentrations of 40 ppb were found at a distance of  $>0.6$  n. miles, and deep dye concentrations (15-m) were over 10 ppb at 0.7 n. miles from the source. Therefore, this condition may have been indicative rather of low dilution rates near location 3, coupled with an accumulation or pooling of dye at the point of injection.

4. The asymmetry of the dye plume with reference to flood and ebb tides was least at location 1 and greatest at location 3. The asymmetry at location 3 is noteworthy because the flood and ebb tides during the study there were of about the same magnitude, although during the study at location 1 they were considerably different (Figures 3.4-3.5, 3.8-3.9). It is possible that the dye was "pooling" on the flood tide and streaming out in the ebb tide at location 3.

Current measurements were obtained throughout the water column at locations 1 and 3 using a deck readout current meter with a claimed accuracy of about  $\pm 3$  percent full scale. These measurements were taken between dye studies (Figure 3.10). Current meter readings were not obtained at location 2 because the steep bottom slope there precluded anchoring. Since turbulence (which is primarily responsible for diffusive processes in the marine environment) is related to the current speed, such measurements are considered an integral portion of the dispersion studies. Results of the July-August current measurements are presented in hodograph form (Figures 3.11-3.13).

Currents were maximum at the surface at both locations. Current speeds decreased rapidly with increasing depth down to 5 m, with little change in magnitude observed below this depth. A large current shear in the upper 1-2 m layer was observed qualitatively on several occasions during servicing of the dye injection pumps. This was in agreement with the apparent shallow nature of the outflowing surface layer within Port Valdez during high fresh-water input conditions (see Chapter 2).

The currents at 15 m at location 1 were small and westerly during the measurement period (Figure 3.13). Currents at 15 m at location 3 were smaller and more variable, being negligible during the flood tide. This was in qualitative agreement with the suspected pooling of the dye around the source, at location 3, during the flood tide.

Fluctuations of 2-3 seconds duration in both speed and direction were noted on the direct readout meters, which suggested that subsequent current measurements should be of a more continuous nature in order to delineate such variations.

Location No. 2, July 31, 1971

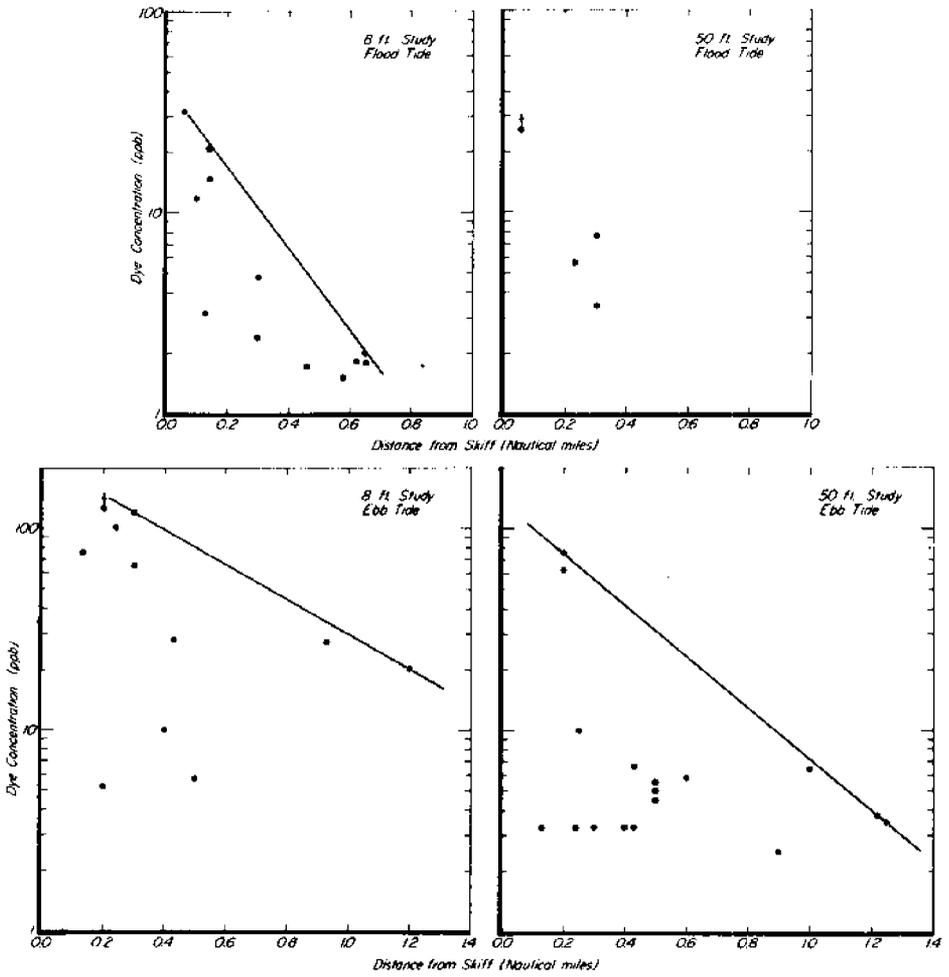
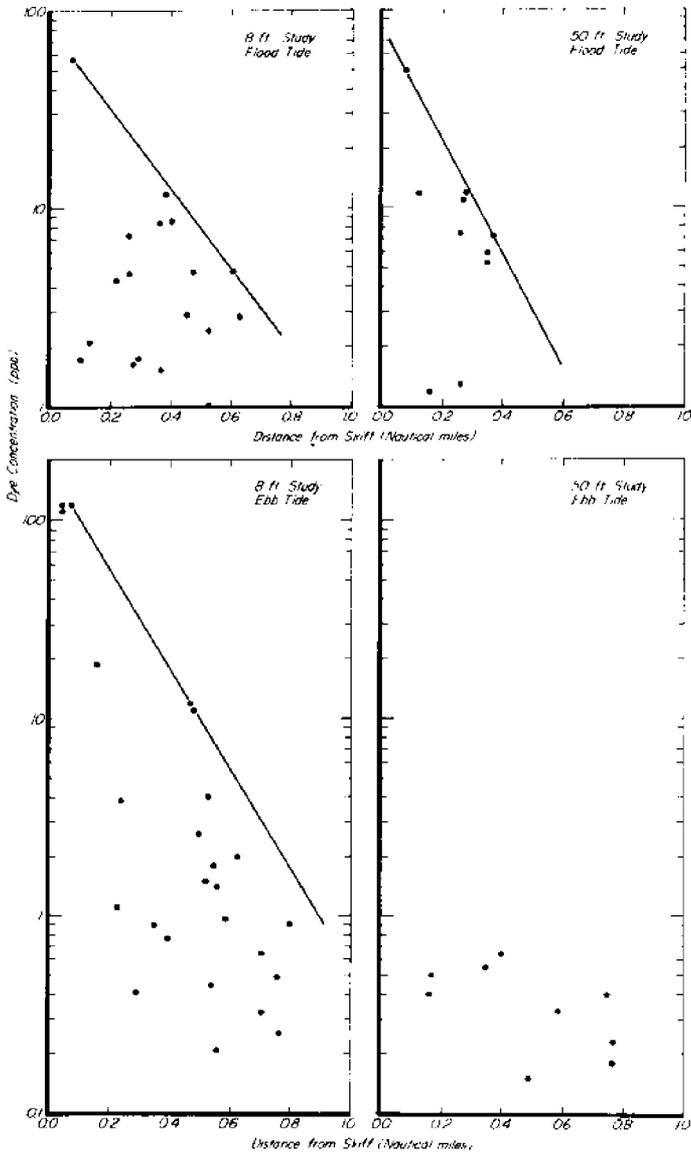
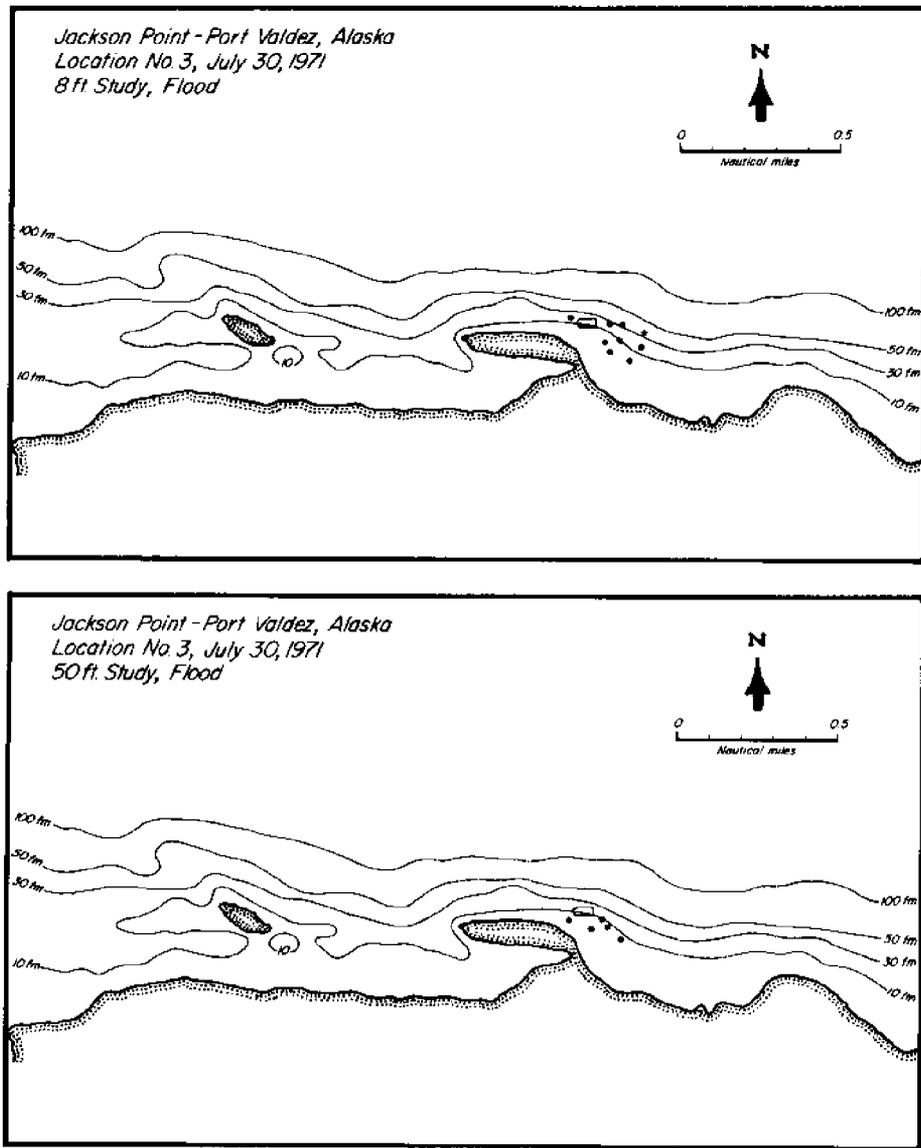


Figure 3.2 Dye concentration (ppb) versus distance (n. miles) for location 2 on 31 July 1971.

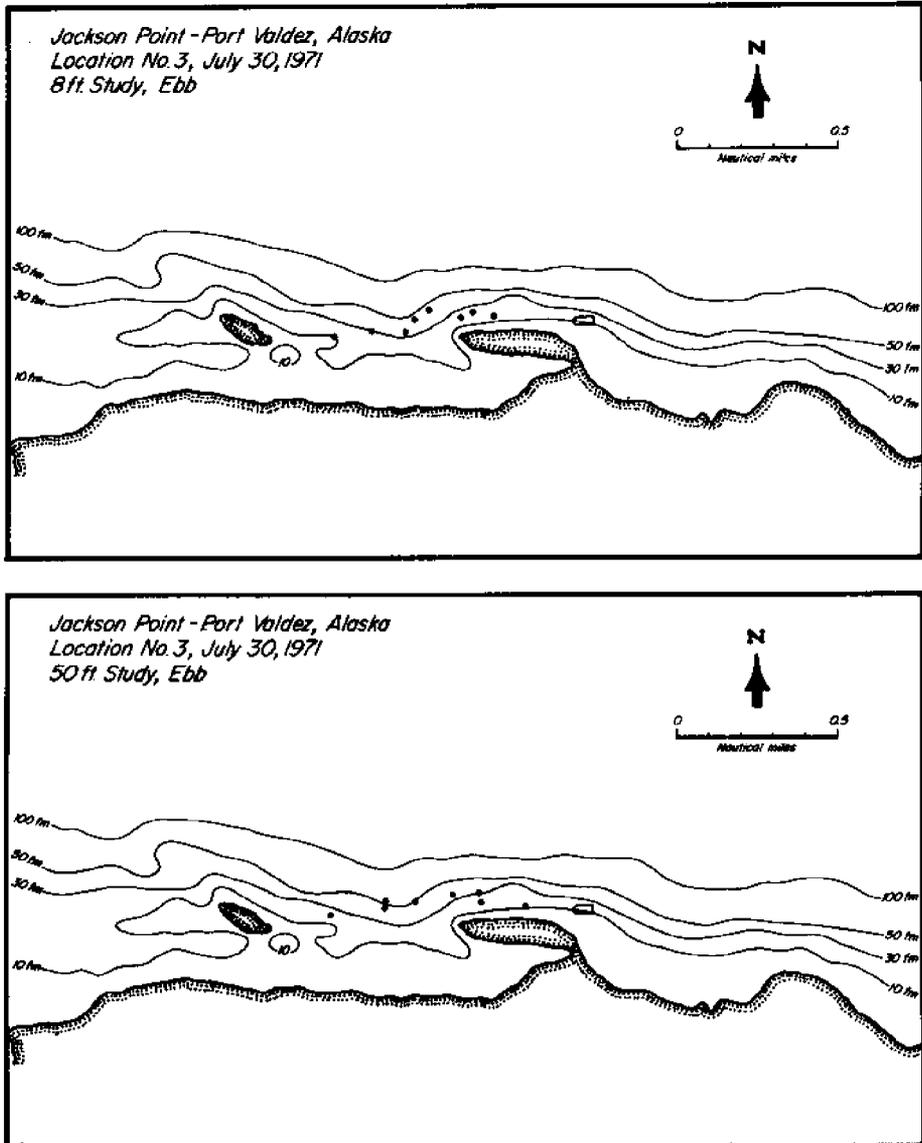
Location No 1, August 1, 1971



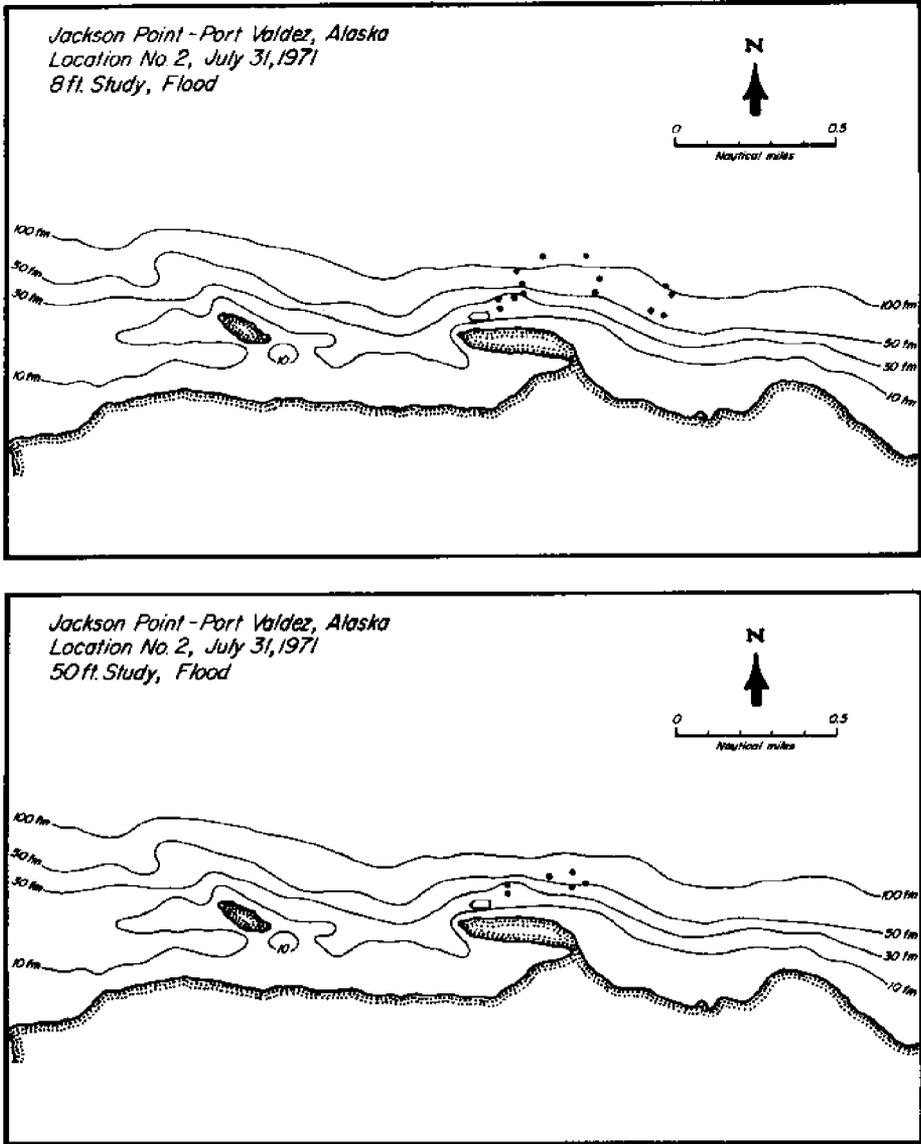
**Figure 3.3** Dye concentration (ppb) versus distance (n. miles) for location 1 on 1 August 1971.



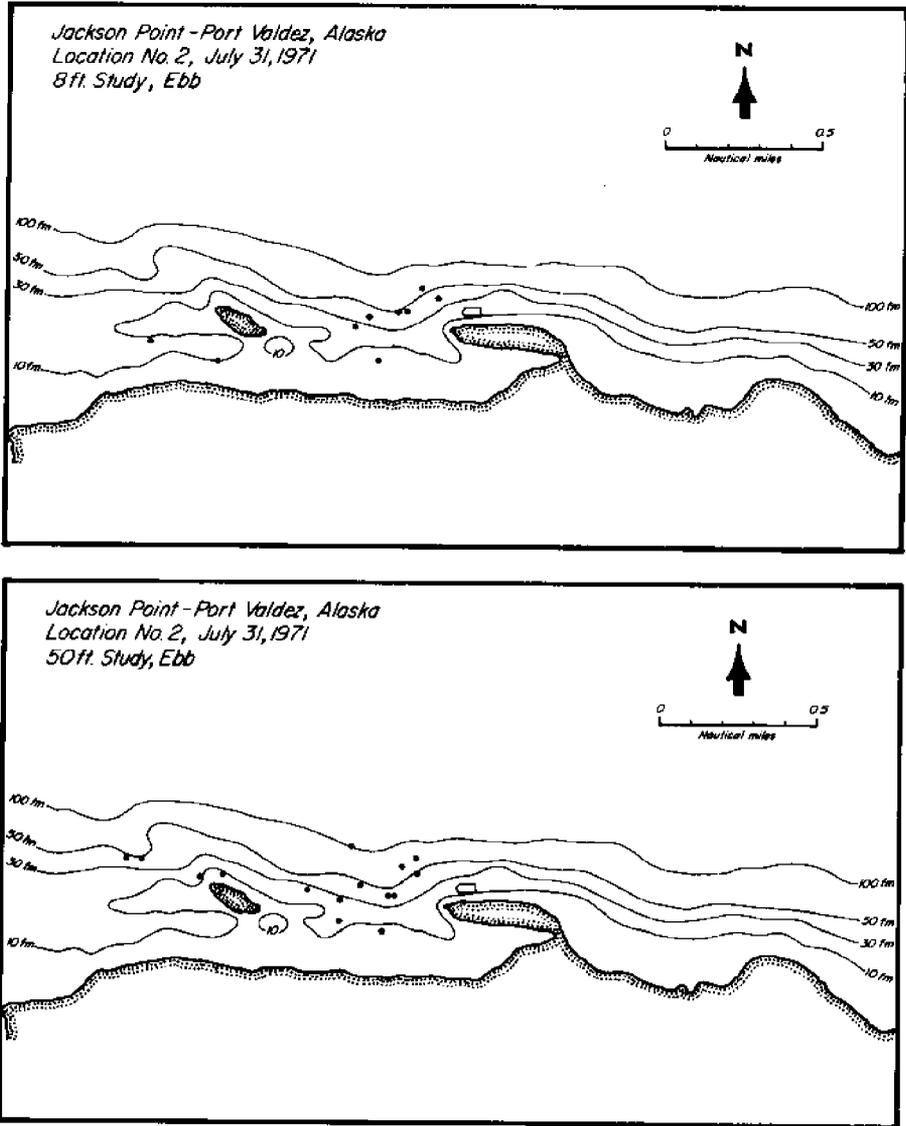
**Figure 3.4** Positions where dye was found at location 3 on a flood tide, 30 July 1971, at depths of 2.5 m (upper) and 15 m (lower).



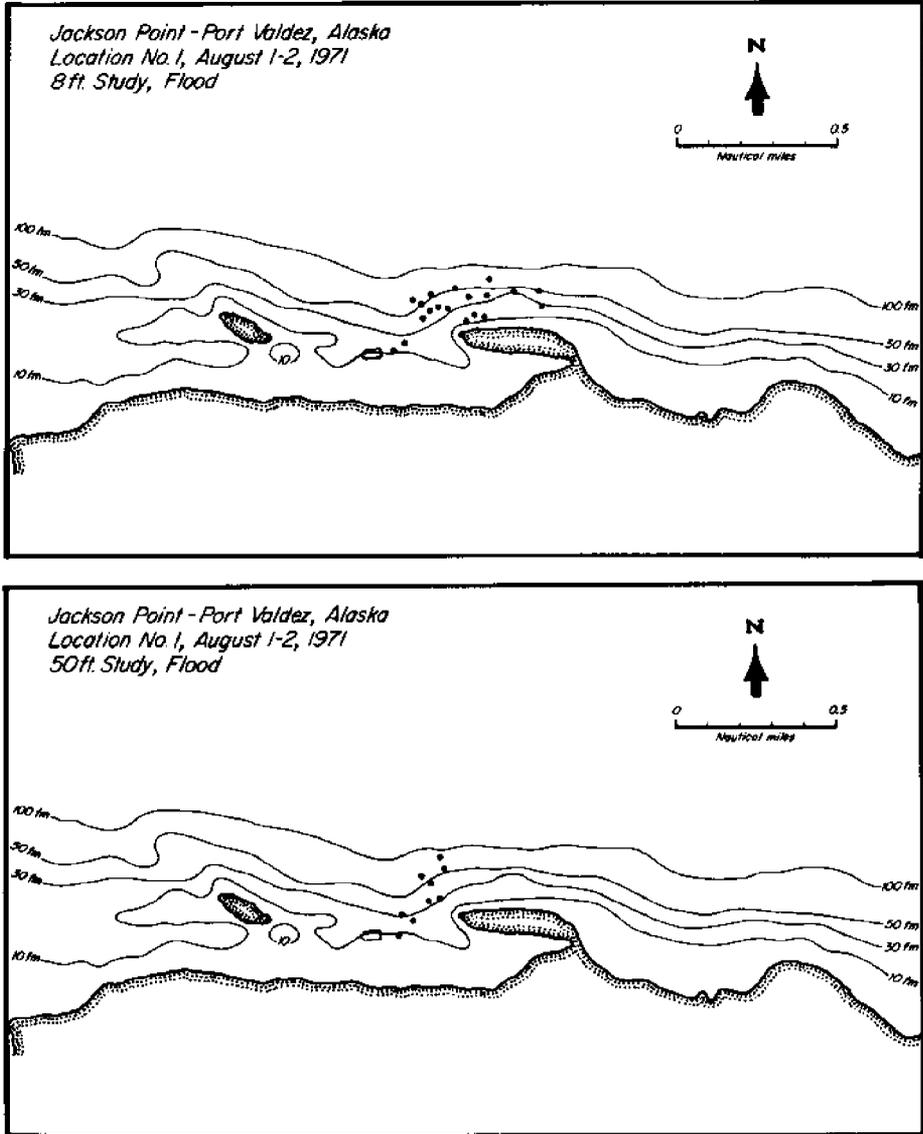
**Figure 3.5** Positions where dye was found at location 3 on an ebb tide, 30 July 1971, at depths of 2.5 m (upper) and 15 m (lower).



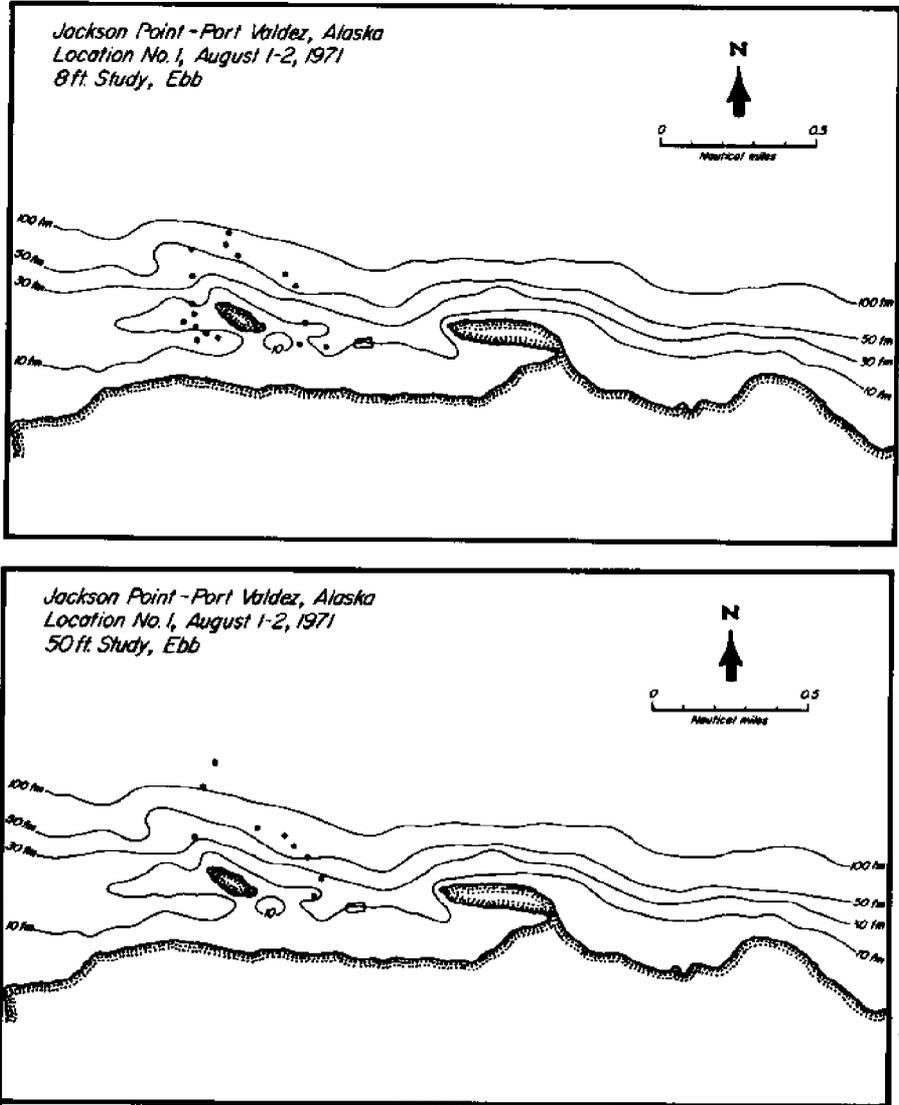
**Figure 3.6** Positions where dye was found at location 2 on a flood tide, 31 July 1971, at depths of 2.5 m (upper) and 15 m (lower).



**Figure 3.7** Positions where dye was found at location 2 on an ebb tide, 31 July 1971, at depths of 2.5 m (upper) and 15 m (lower).



**Figure 3.8** Positions where dye was found at location 1 on a flood tide, 1-2 August 1971, at depths of 2.5 m (upper) and 15 m (lower).



**Figure 3.9** Positions where dye was found at location 1 on an ebb tide, 1-2 August 1971, at depths of 2.5 m (upper) and 15 m (lower).

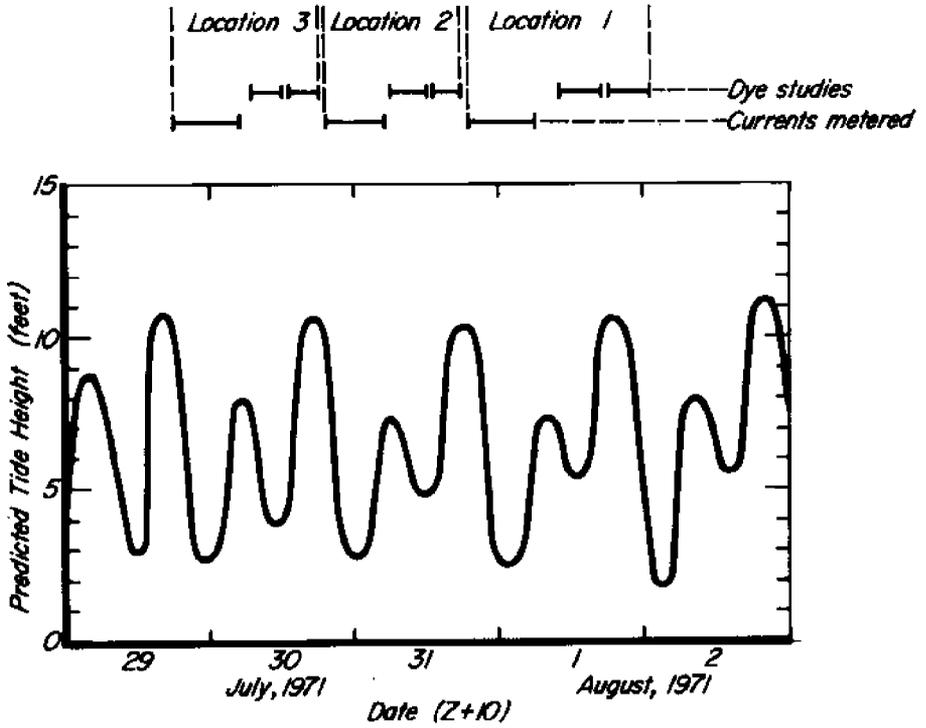


Figure 3.10 Predicted tidal height (ft) at town of Valdez during 29 July-2 August 1971.

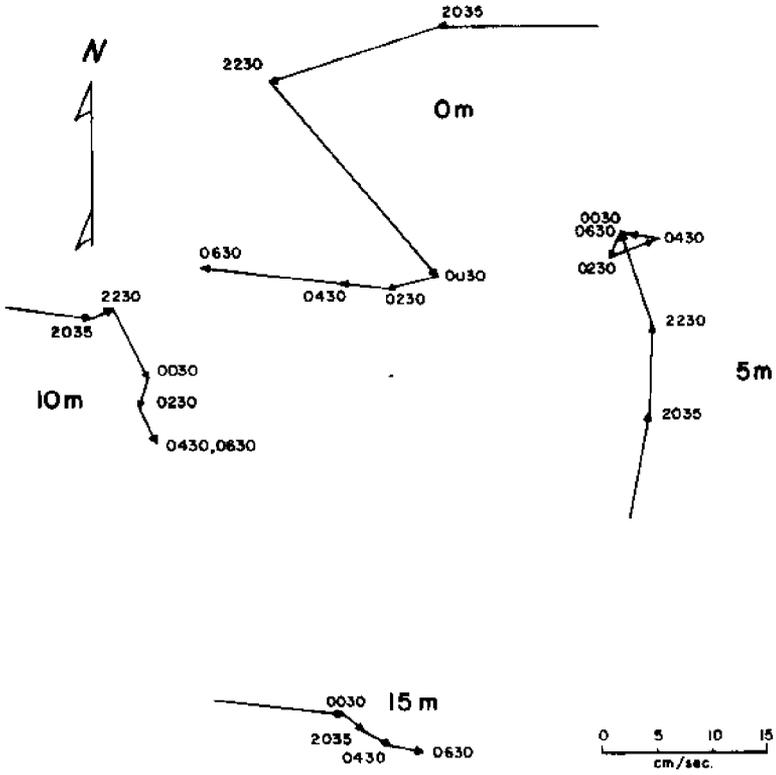


Figure 3.11 Current vectors at location 3 on 29-30 July 1971.

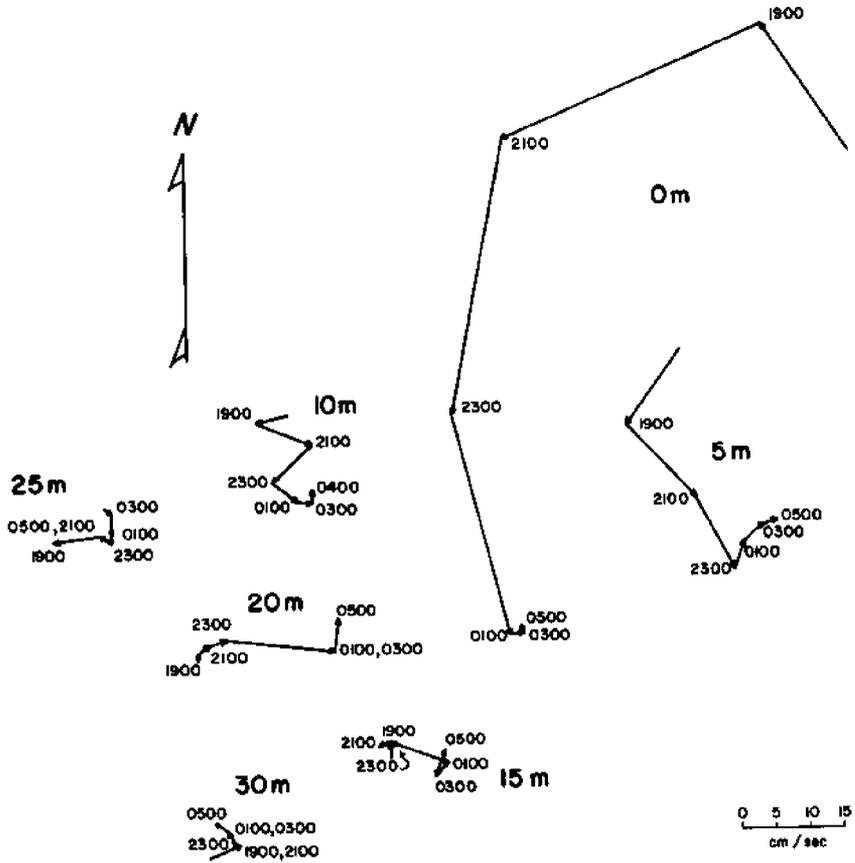


Figure 3.12 Current vectors at locations 3 on 29-30 July 1971.



### 3.3.3 October 1971 dispersion study

Experiments were conducted at the same three locations on 8-10 October 1971 as during the July-August study. Dye was found at the locations shown in Figures 3.17-3.19, and concentration versus distance plots are shown in Figures 3.14-3.16. The experiment was not divided into separate flood and ebb tide studies but was treated as one continuous investigation more representative of a steady state. The dispersion data indicated that:

1. Tenfold dilution distances varied from 0.58-0.76 n. miles at the 2.5-m level, with an average value of 0.65 n. miles.

2. In the deep 15-m studies, the tenfold dilution distances ranged from 0.20-0.59 n. miles, with an average value of 0.40 n. miles.

3. Asymmetries were apparent in the dye plumes during this study. At location 1 the dye plume at both depths was found between the skiff and Jackson Point. At location 2 the dye at both depths appeared to pool up to the east of the skiff on the flood tide and to stream westward on the ebb tide. At location 3 the deep dye moved only to the northwest, while the shallow dye moved more symmetrically with respect to the tide. The dye at location 3 (both depths) did not appear to dilute appreciably with distance (Figure 3.16).

A recording current meter was placed at the dye source and the currents at 15 m were measured during the studies (Figure 3.20). The indicated current directions were of debatable validity and are not presented, but the current speed record appeared valid (Figures 3.21 and 3.22).

At location 1 the predominant speed was 5.0-7.4 cm/sec with a peak speed of 37.5-39.9 cm/sec. The speed at location 2 was predominantly  $<2.4$  cm/sec, with a minor peak at 12.5-14.9 cm/sec and a maximum observed speed of 15.0-17.4 cm/sec. At location 3, the predominant speed was 2.5-4.9 cm/sec with a maximum speed of 10.0-12.4 cm/sec. The current data suggest that location 1 should have exhibited the most rapid dispersion. This agrees qualitatively with results shown in Table 3.1.

### 3.3.4 December 1971 dispersion study

During 4-5 December 1971, dye was injected at depths of 15 and 23 m (50 and 75 ft) as two separate experiments at location 1. The study was continuous in that no break was made between ebb and flood tides. The water column was less vertically stratified during December 1971 than during previous cruises (see Chapter 2). The dye dispersion data provided the following results (Figures 3.23 and 3.24):

1. During the 15-m study the maximum dye concentrations were found at depths varying from approximately 15 m to as shallow as  $<8$  m (25 ft). This vertical scatter was due probably to active vertical mixing as a result of surface cooling and wind stress.

2. At 15 m the dye did not dilute appreciably with distance, although the dilution at 23 m appeared to be more rapid, with a tenfold dilution distance of only 0.17 n. miles.

Currents at 15 m were measured during the period 3-8 December 1971 at location 1 with a self-contained current meter having a threshold velocity of  $<3$  cm/sec and an estimated accuracy of  $\pm 3$  percent full scale (Figures 3.25). The semidiurnal tidal nature of

Location No. 1, October 8, 1971

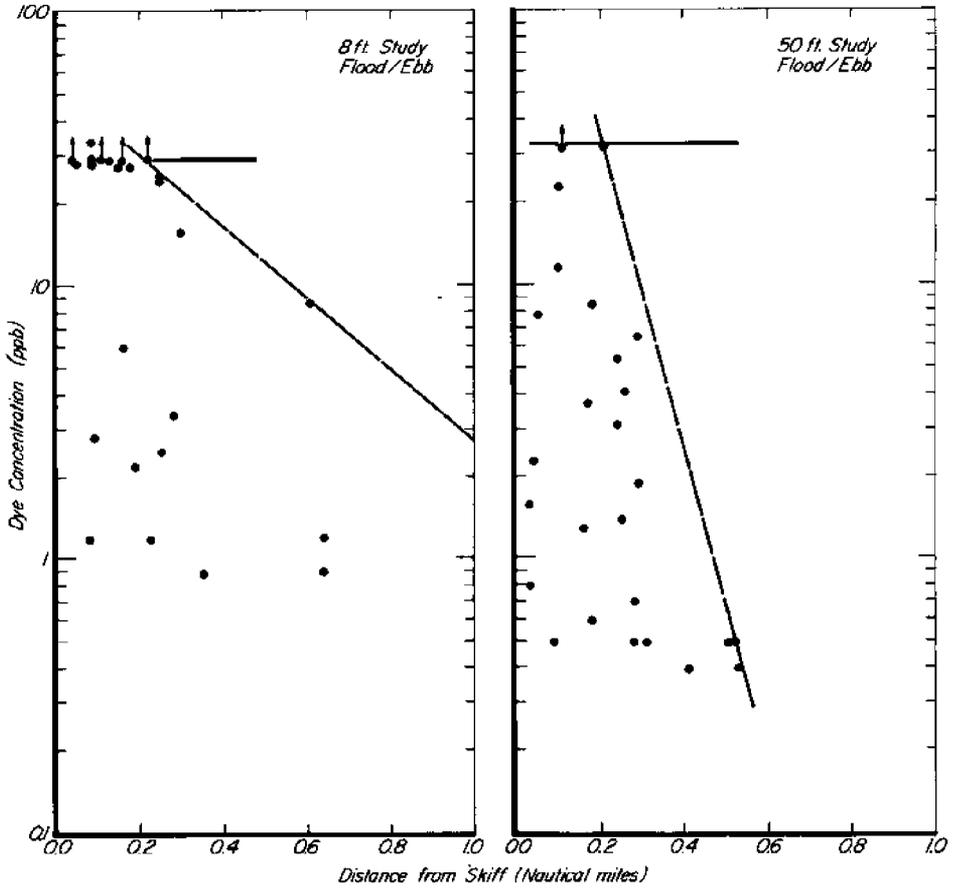


Figure 3.14 Dye concentration (ppb) versus distance (n. miles) near location 1 on 8 October 1971.

Location No. 2, October 9, 1971

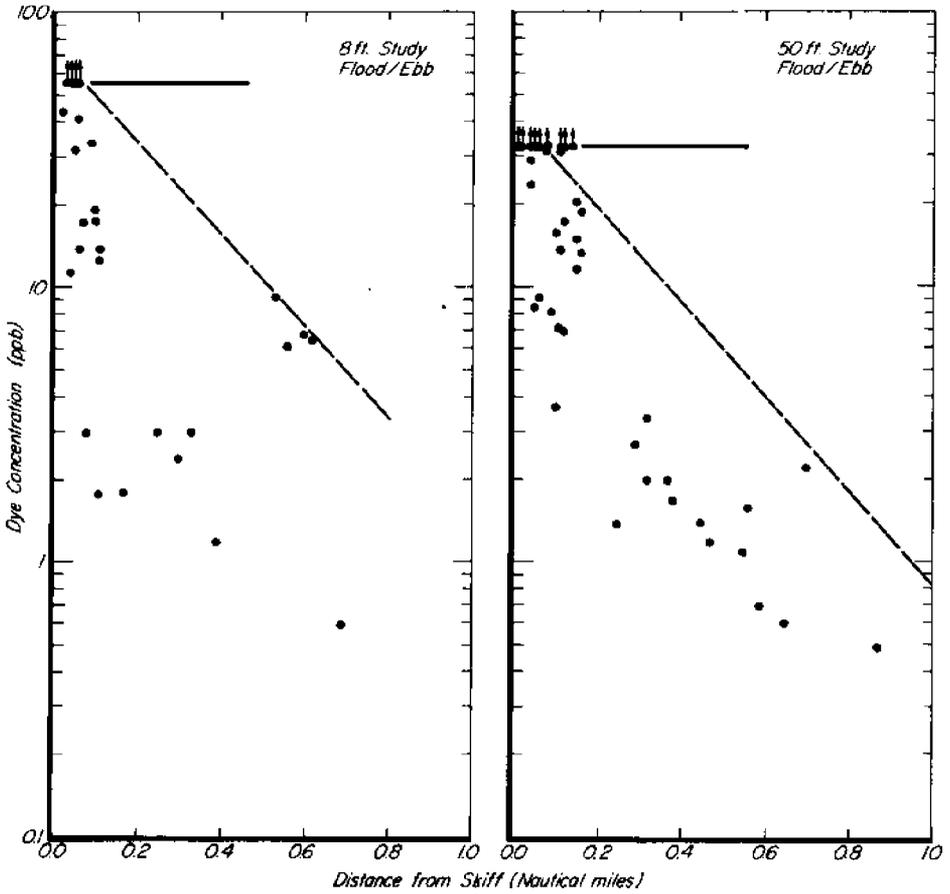


Figure 3.15 Dye concentration (ppb) versus distance (n. miles) near location 2 on 9 October 1971.

Location No. 3, October 10, 1971

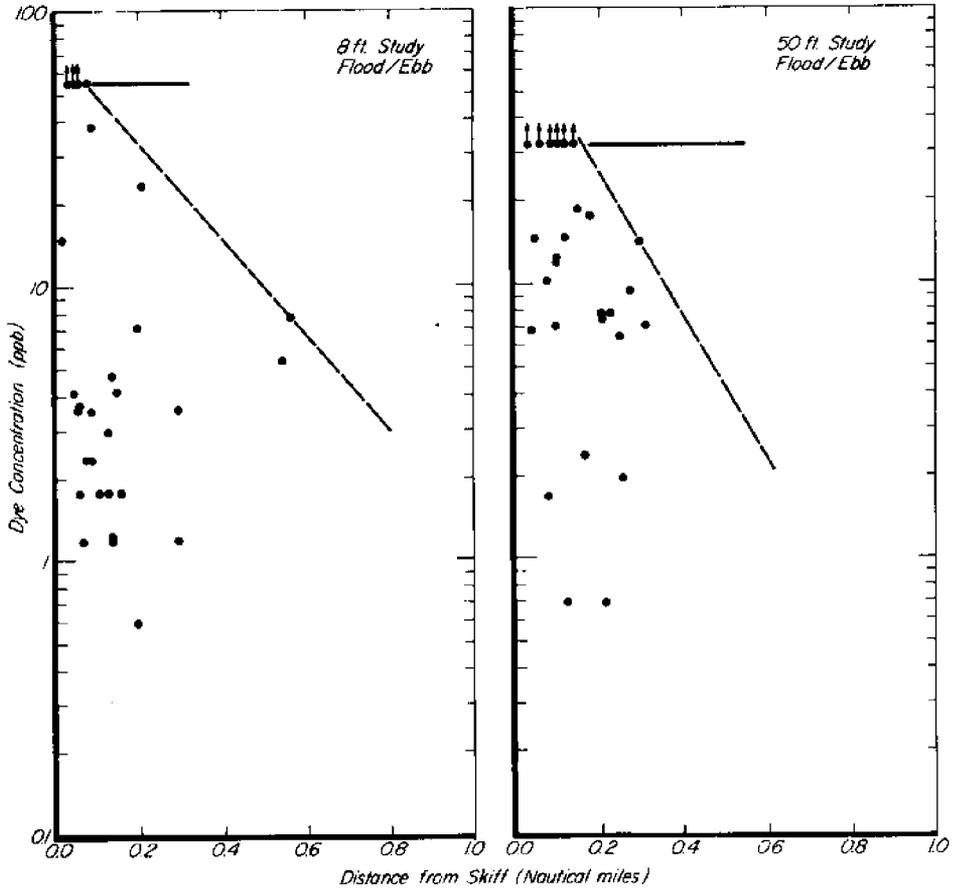


Figure 3.16 Dye concentration (ppb) versus distance (n. miles) near location 3 on 10 October 1971.

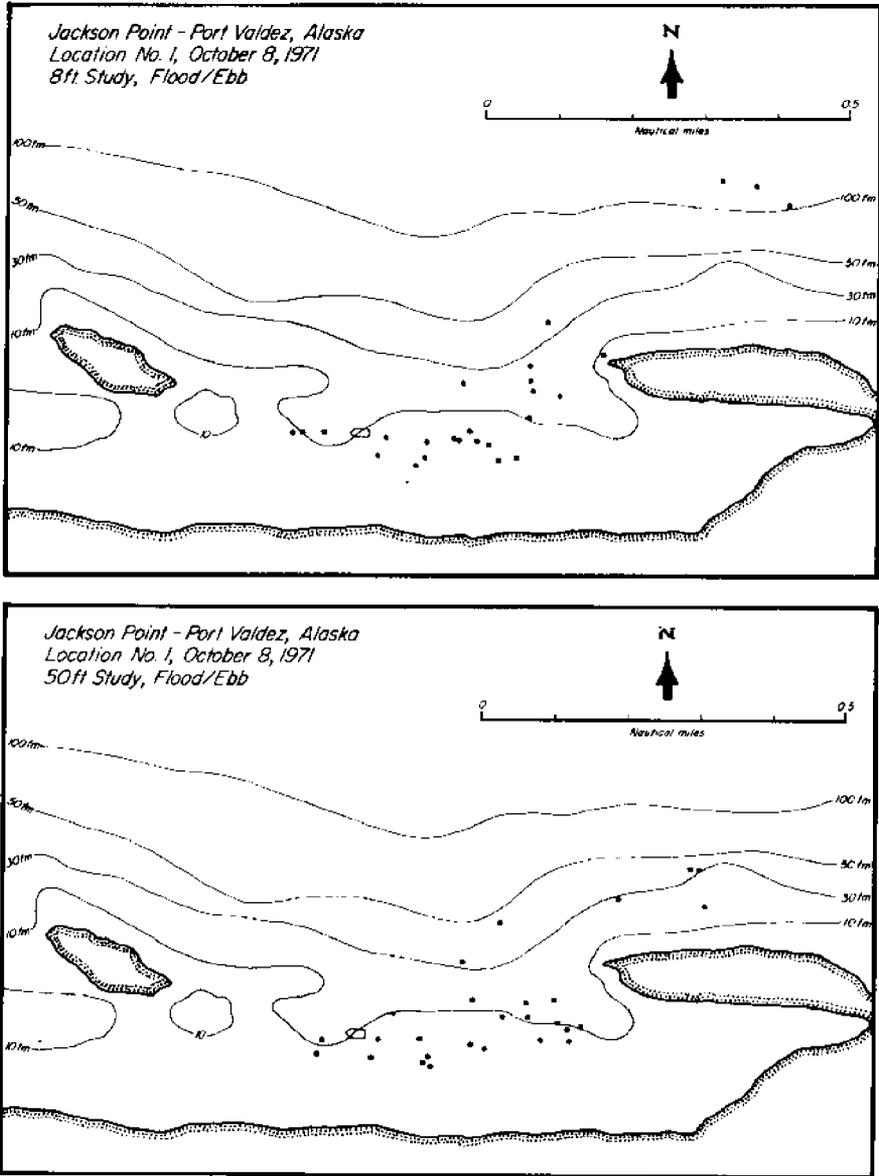
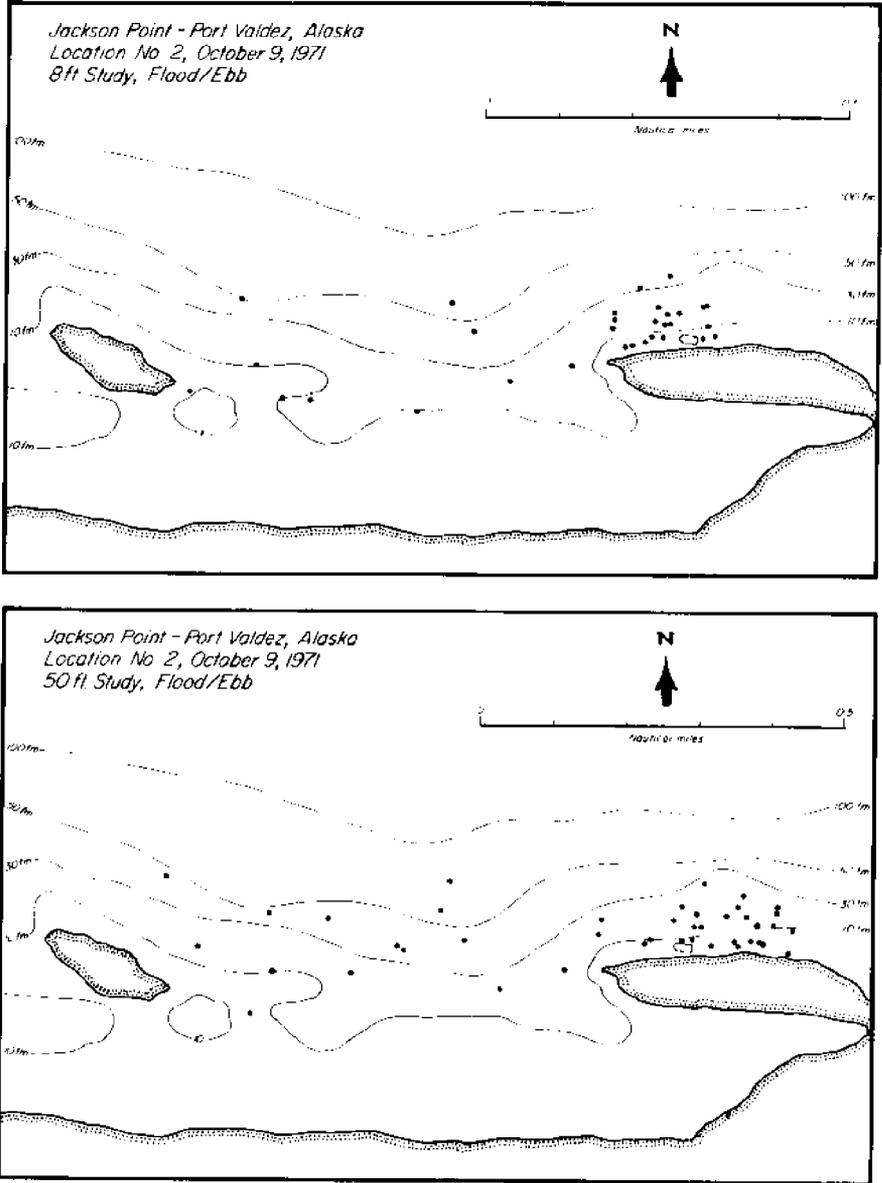


Figure 3.17 Positions where dye was found at location 1 on 8 October 1971.



**Figure 3.18** Positions where dye was found at location 2 on 9 October 1971.

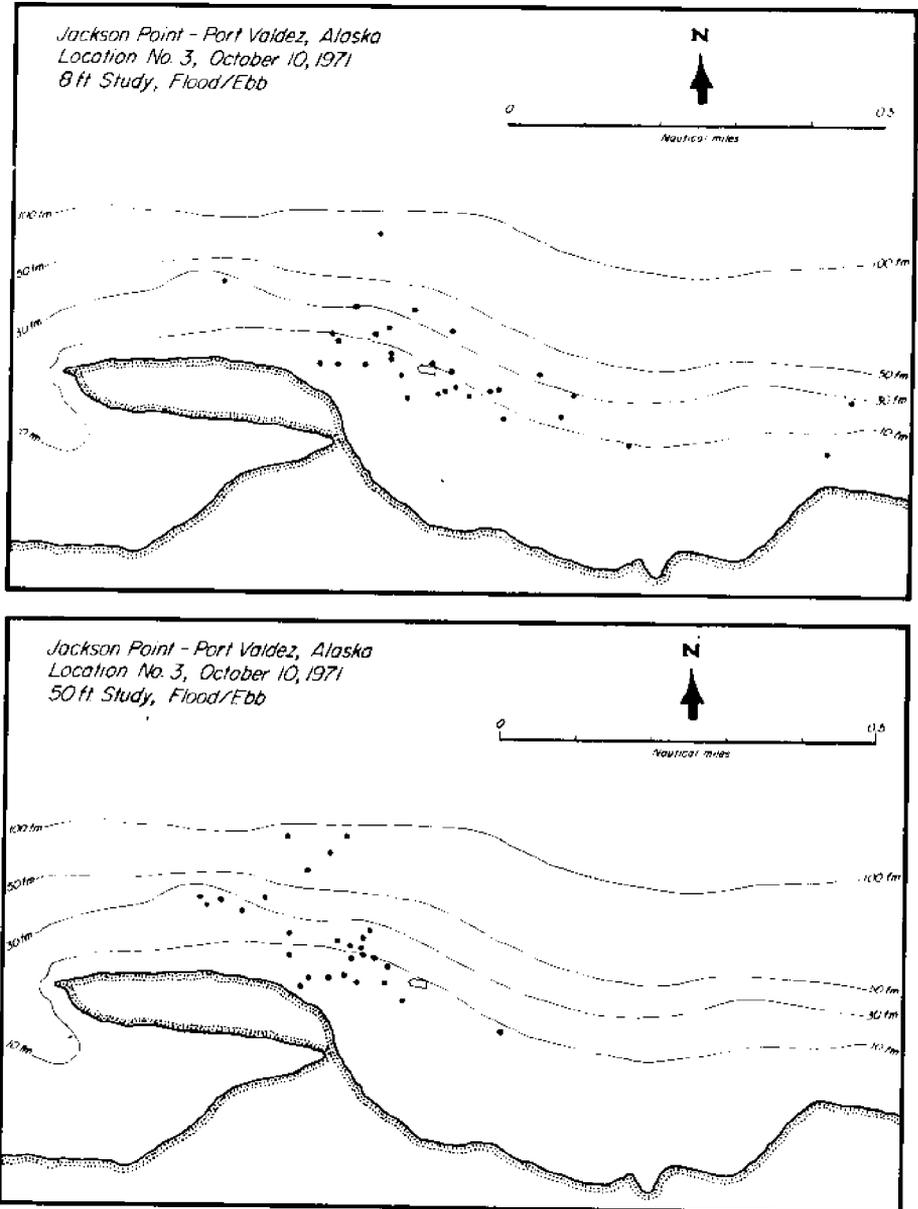


Figure 3.19 Positions where dye was found at location 3 on 10 October 1971.

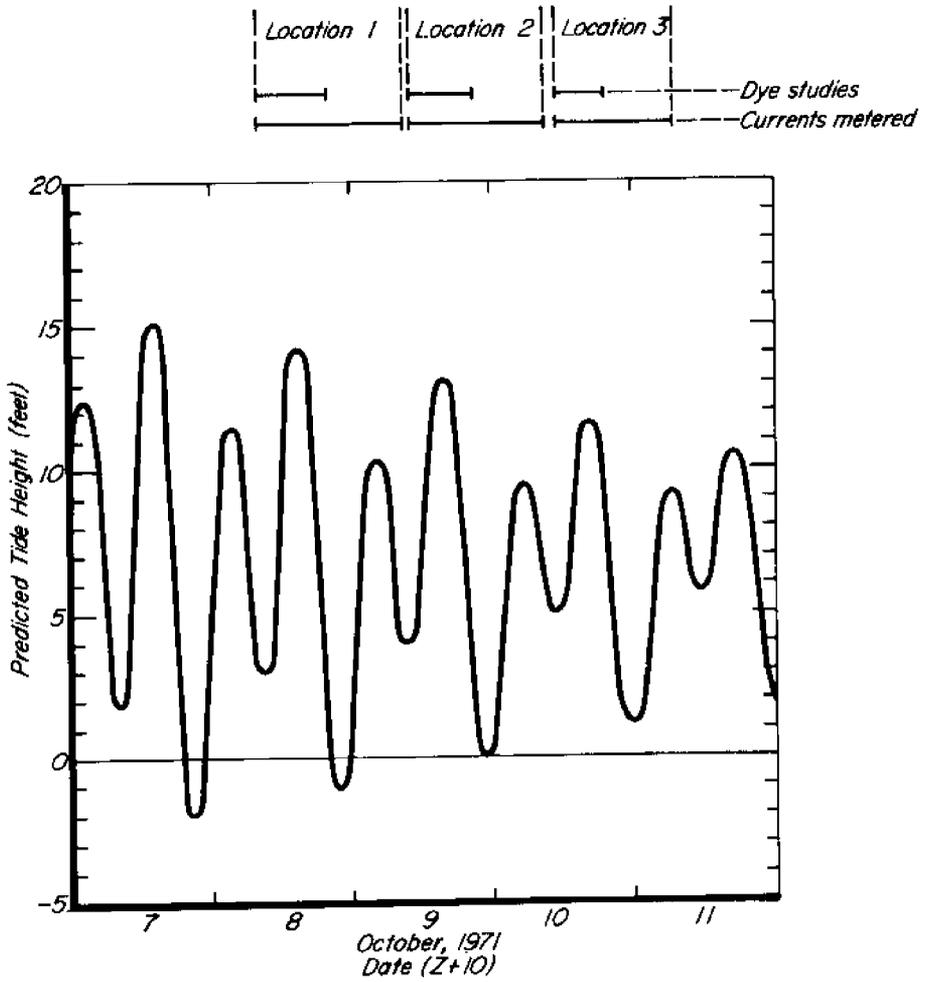


Figure 3.20 Predicted tidal height (ft) at town of Valdez during 7-11 October 1971.

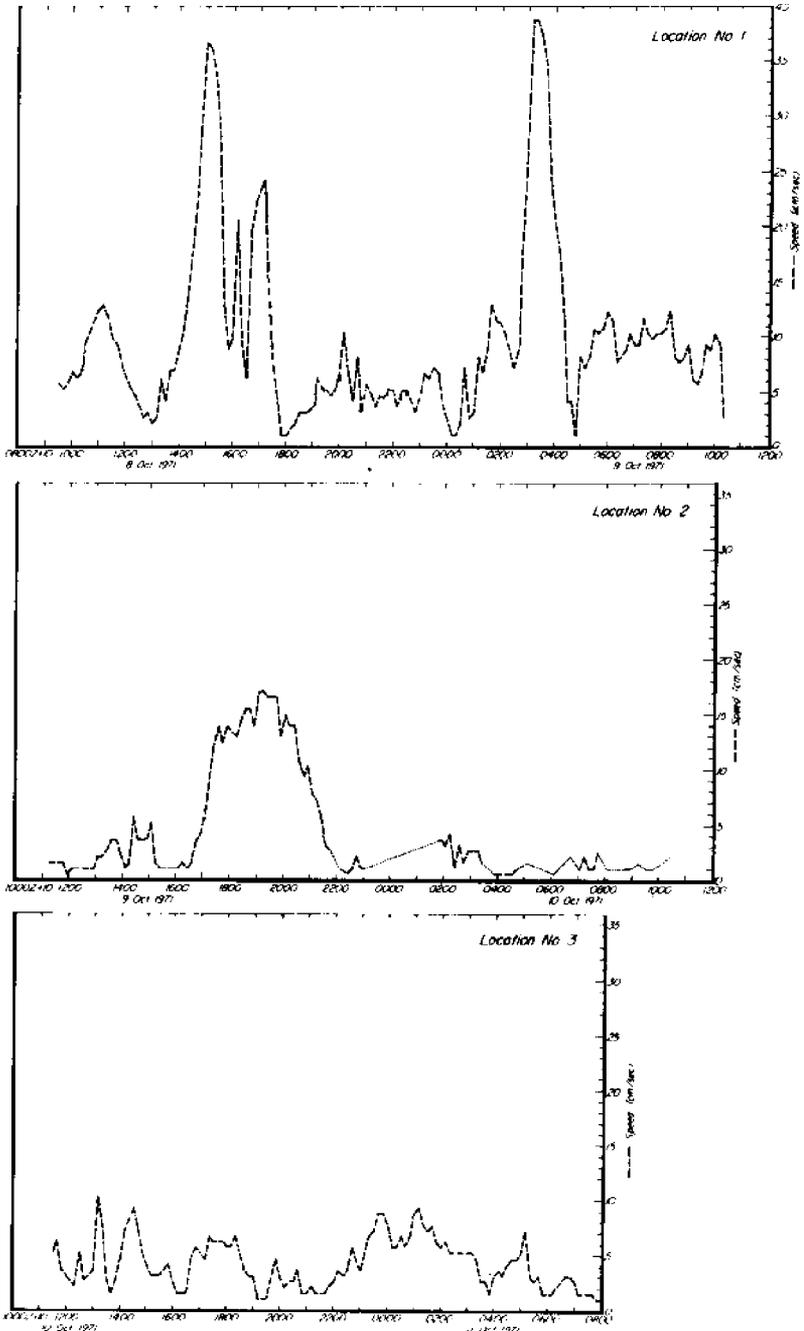


Figure 3.21 Current speed at 15 m (50-ft) at three locations near Jackson Point during October 1971.

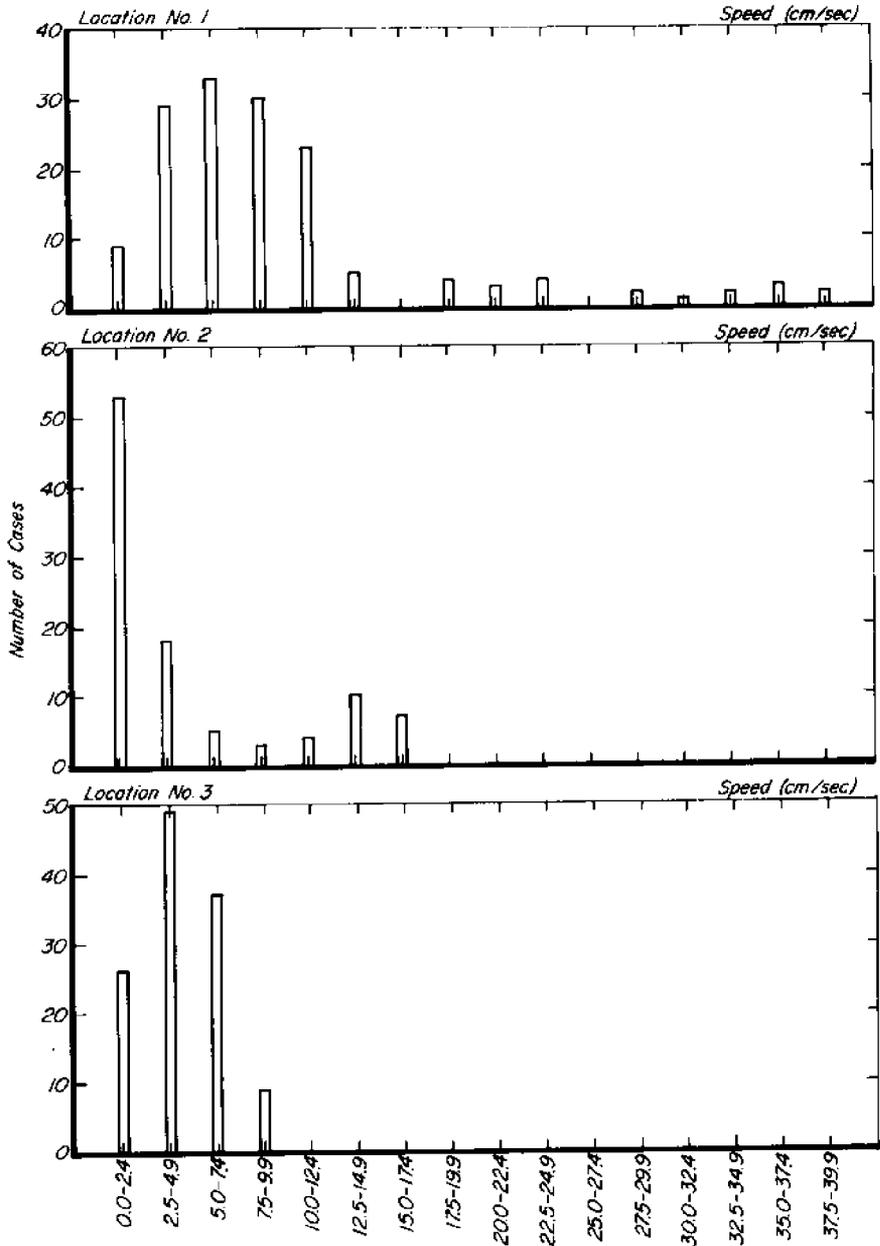


Figure 3.22 Histograms of current speed for three locations near Jackson Point during October 1971 (from Figure 3.21).

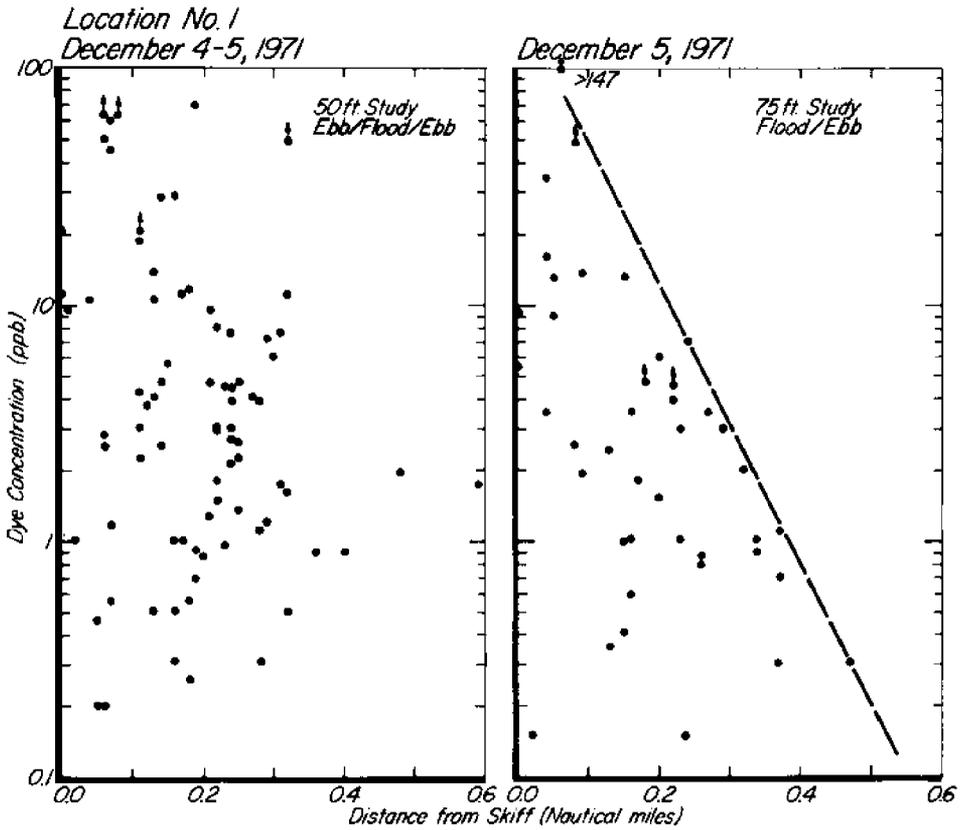
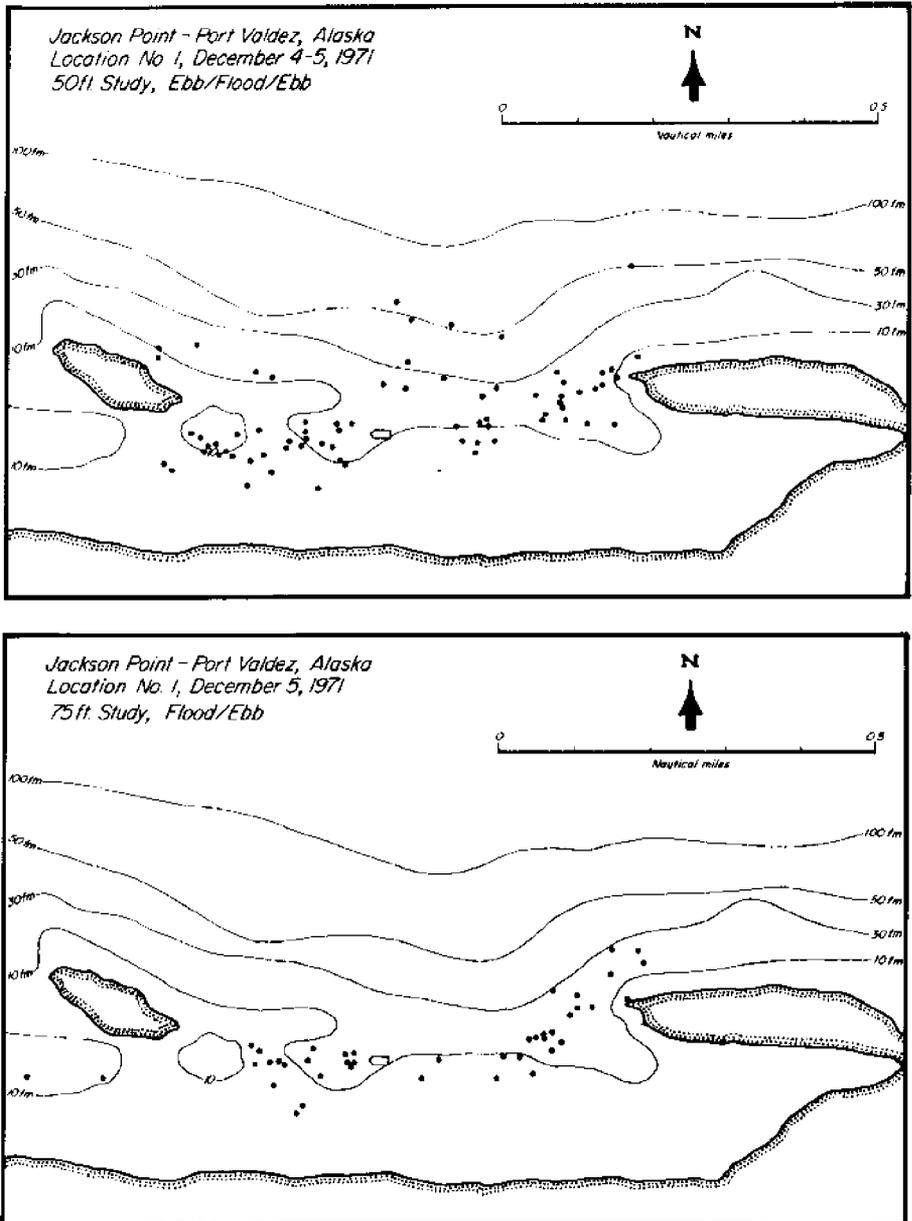


Figure 3.23 Dye concentration (ppb) versus distance (n. miles) for location 1 on 4-5 December 1971.



**Figure 3.24** Positions where dye was found near location 1 on 4-5 December 1971 at depths of 15 m (upper) and 23 m (lower).

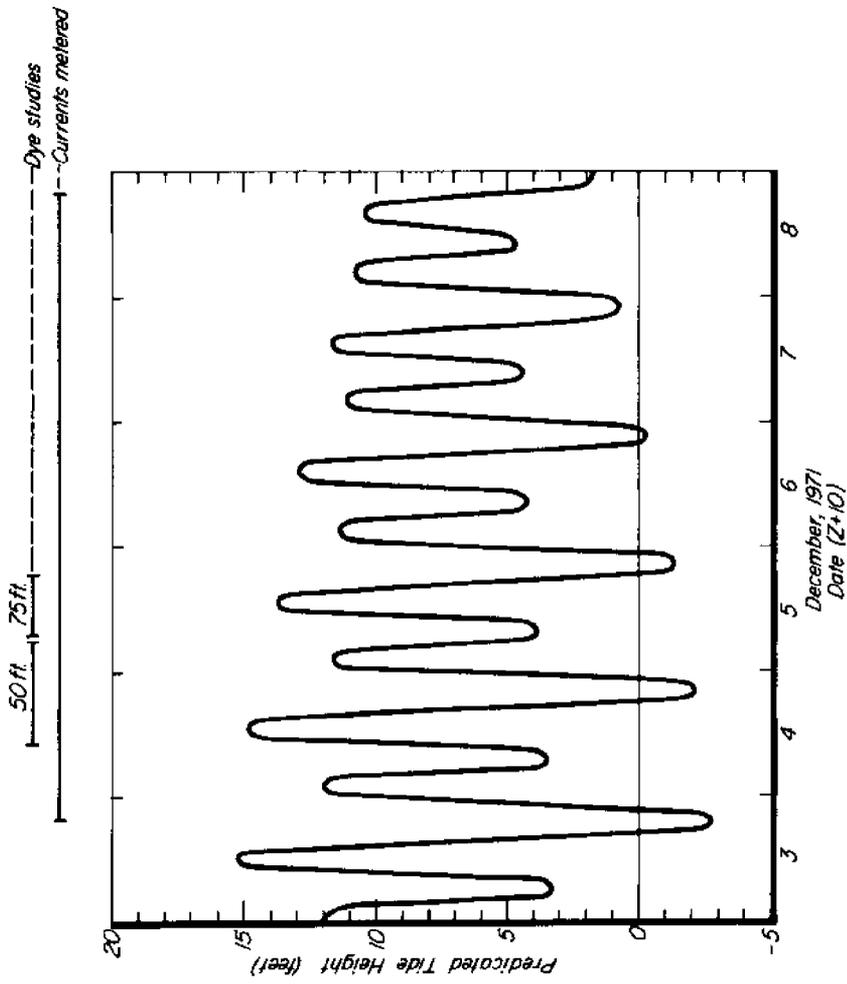


Figure 3.25 Predicted tidal height (ft) at town of Valdez during 3-8 December 1971.

the currents was clearly detected (Figure 3.26). The current direction was bimodal, with preferred directions of  $81-100^{\circ}\text{T}$  and  $241-260^{\circ}\text{T}$  (Figure 3.27). The preferred speed was 6.0-7.9 cm/sec with a secondary peak at 16.0-17.9 cm/sec. Maximum currents were in the range of 22.0-23.9 cm/sec.

The current direction record was found to be out of phase with the tide; i.e., if the tide was flooding, the current at location 1 appeared to be moving toward the west (compare Figures 3.25 and 3.26). This was confirmed by the direction of dye movement. The reason for this is uncertain, although it is possible that location 1 falls in a large eddy system connected with Jackson Point and Saw Island.

### 3.3.5 March 1972 diffusion study

During this study from 13-14 March 1972, the water column was well mixed from top to bottom (see Chapter 2). It was therefore assumed that a study with dye injected at 23 m would be representative also of one in which dye was injected at 15 m, a supposition that was verified during the study conducted at location 1. The pumping arrangement used for the detectors during this investigation was different from that used previously. Two separate pumping systems sampled water at depths 2 m apart. The dispersion data showed the following conditions (Figure 3.28 and 3.29):

1. Dye moved only eastward from the source, even though it was followed for about 24 hours or over two full semidiurnal tidal cycles (Figures 3.29 and 3.30).
2. The tenfold dilution distance was about 0.24 n. miles.
3. Dye was often detected from both intake depths centered at 15 m, indicating a vertical extent greater than that separating the two intakes (2 m), and with concentrations of dye varying greatly between the two intakes. Attempts to trim the pumps vertically to maximize detector response were seldom successful, due probably to patchy distribution of the dispersed dye as opposed to a well-defined plume.

A self-contained current meter was again suspended at location 1 at 15 m and operated from 14-19 March 1972. The current direction was found to be highly variable with little relationship to the predicted tides (Figures 3.31), in contrast to the December current records (Figure 3.26). During the dye study period (13-14 March 1972) the record shows that a predominantly eastward flow was occurring, which supports the fact that dye was found only to the east of the source. Over the complete current recording period there was a slight bimodal preference in direction at  $81-100^{\circ}$  and  $241-260^{\circ}$  (Figure 3.32). Current speed was variable with maxima up to 40.0-41.9 cm/sec. There appeared to be no speed preference, but the March 1972 record revealed the highest overall speeds observed at any time during the study.

### 3.3.6 April 1972 dispersion study

Dye studies were conducted at depths of 15 and 23 m (two separate experiments) at location 1 on 25-27 April 1972 (Figures 3.33-3.35). The water column showed more near-surface structure than during the March 1972 cruise but was still well mixed just below this zone (see Chapter 2). The dispersion data showed the following conditions:

1. The preferred direction of the dye plume at the 15-m depth was east and north, even though the study period included two ebb tides (Figures 3.34 and 3.35). The dye did not dilute sufficiently with distance at the 15-m depth, to enable estimation of a tenfold dilution distance.

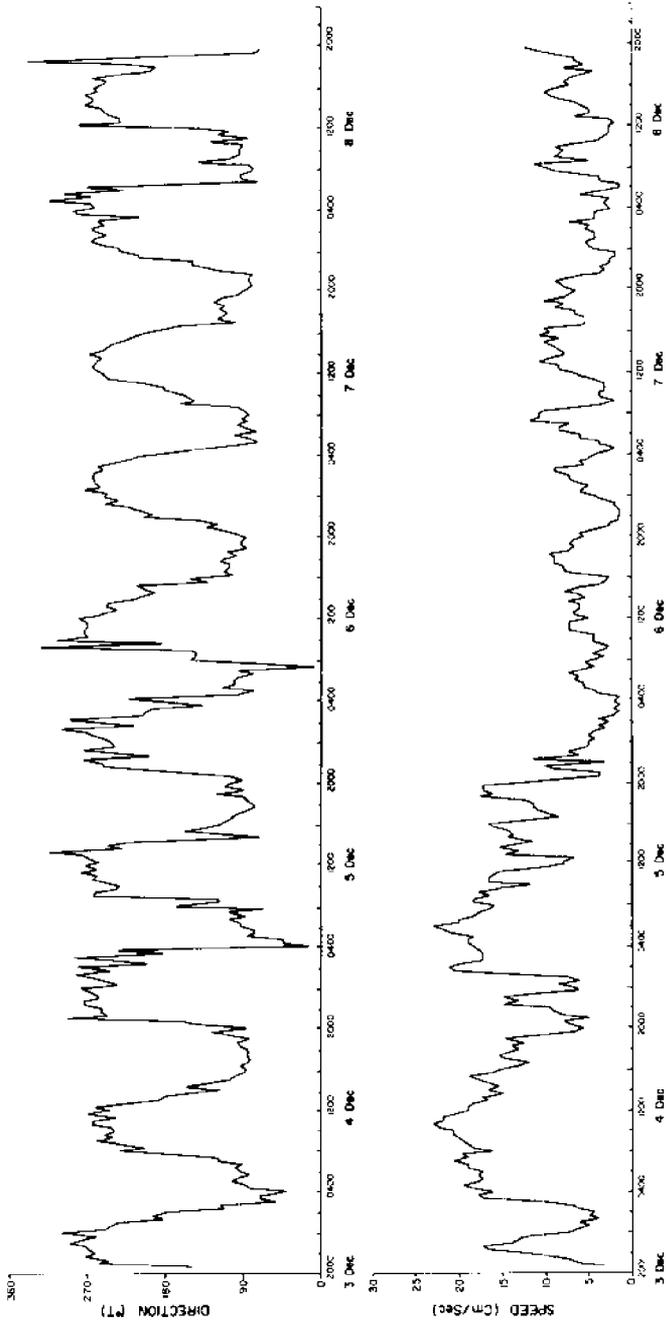


Figure 3.26 Current speed and direction at 15 m (50 ft) at location 1 during 3-8 December 1971.

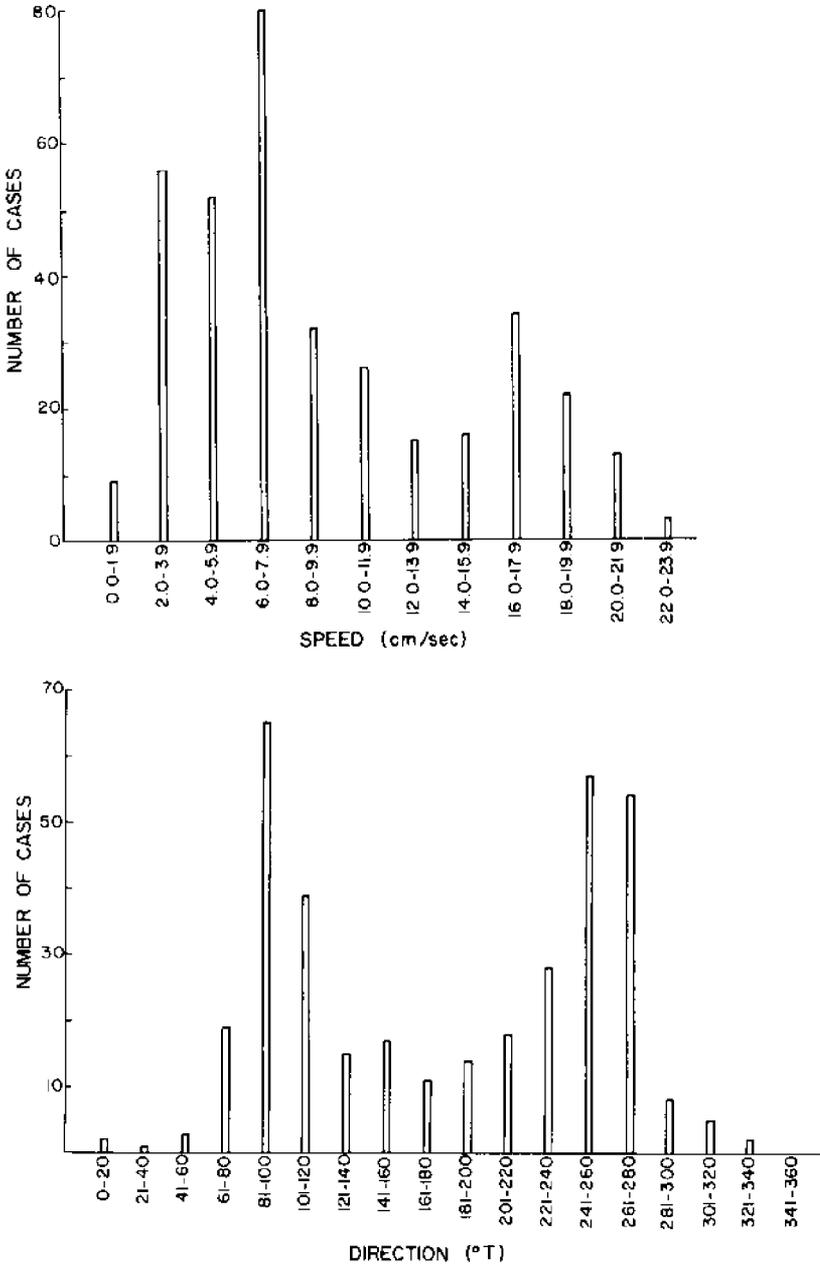
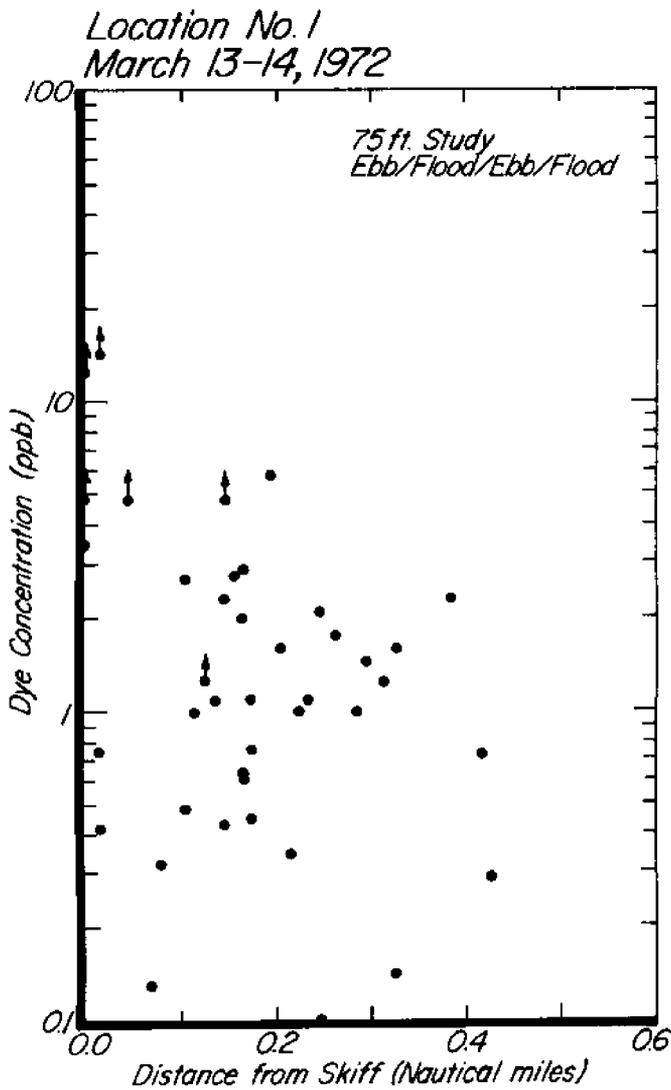


Figure 3.27 Histograms of current speed and direction at 15 m (50 ft) at location 1 during December 1971 (from Figure 3.26).



**Figure 3.28** Dye concentration (ppb) versus distance (n. miles) near location 1 during 13-14 March 1972.

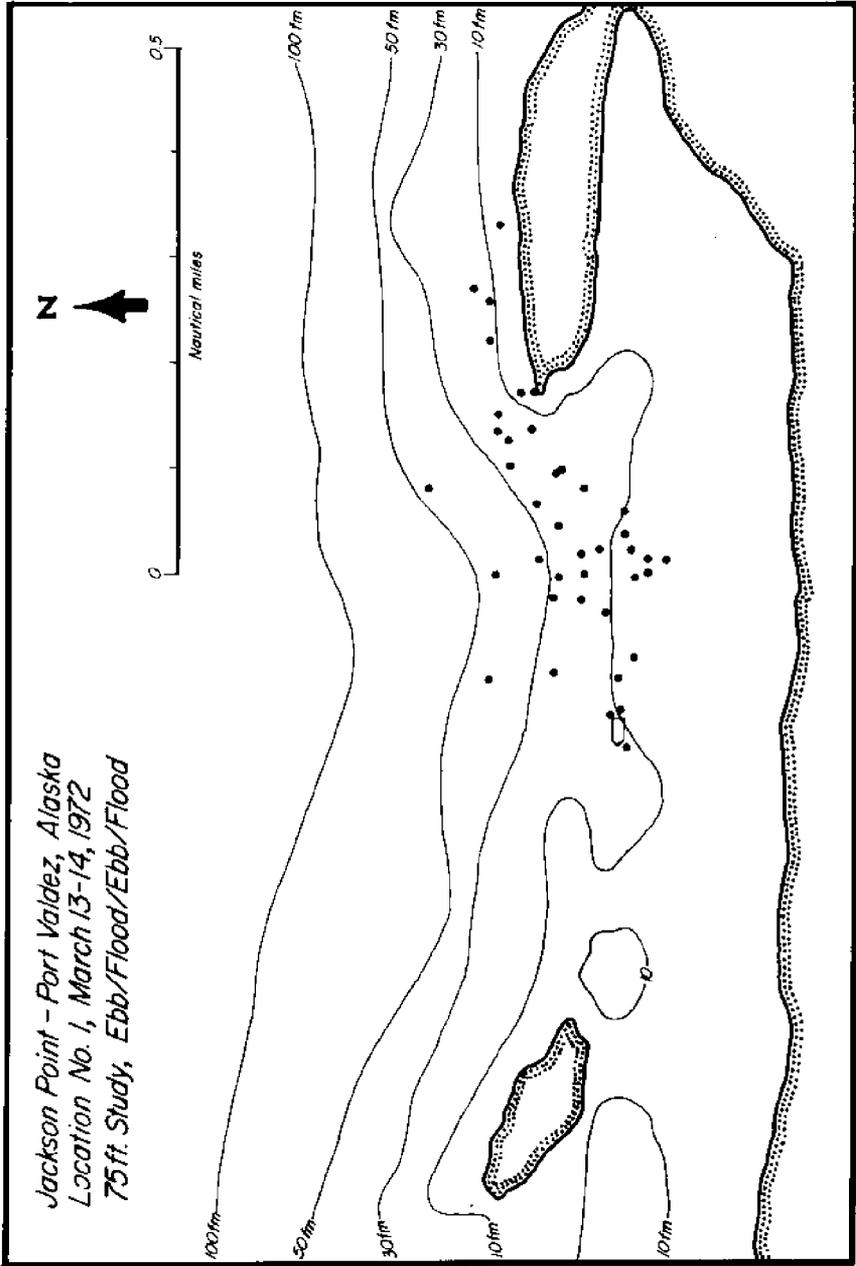


Figure 3.29 Positions where dye was found near location 1 on 13-14 March 1972 at 23-m depth.

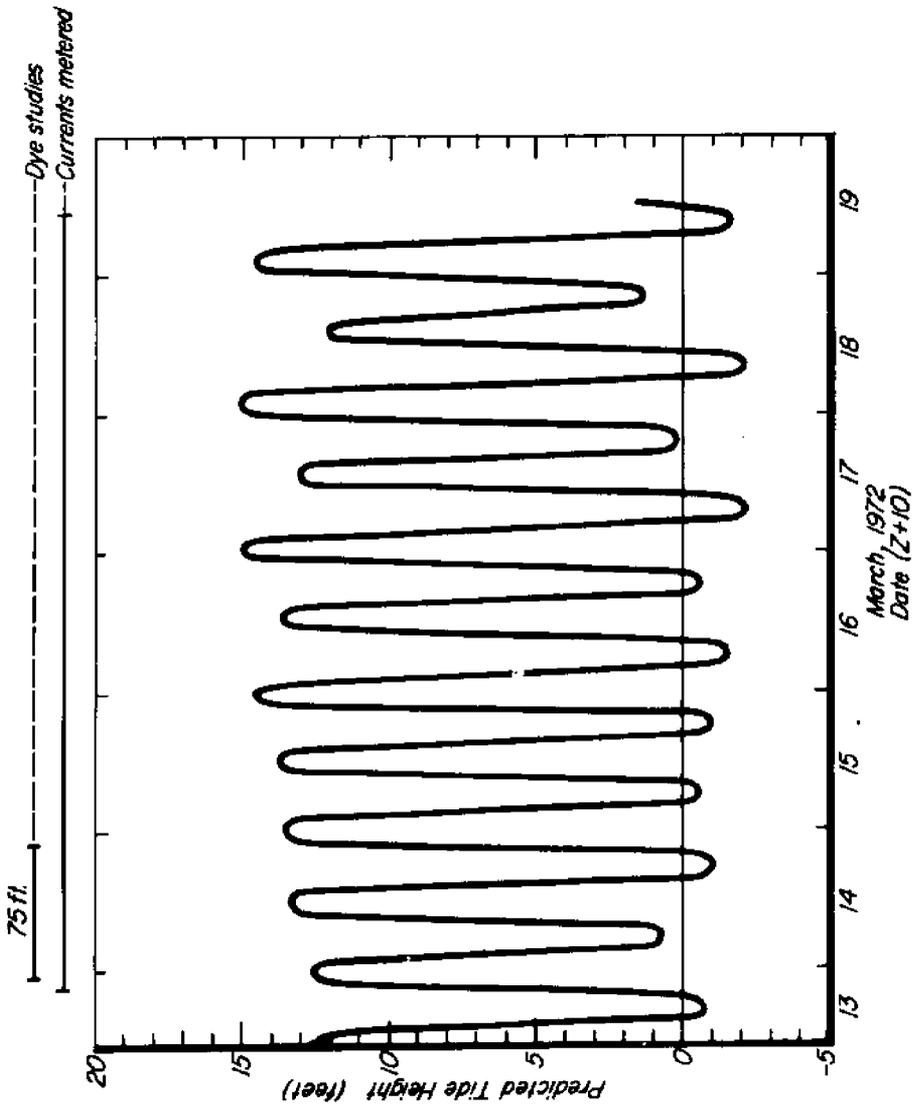


Figure 3.30 Predicted tidal height (ft) at town of Valdez during 13-19 March 1972.

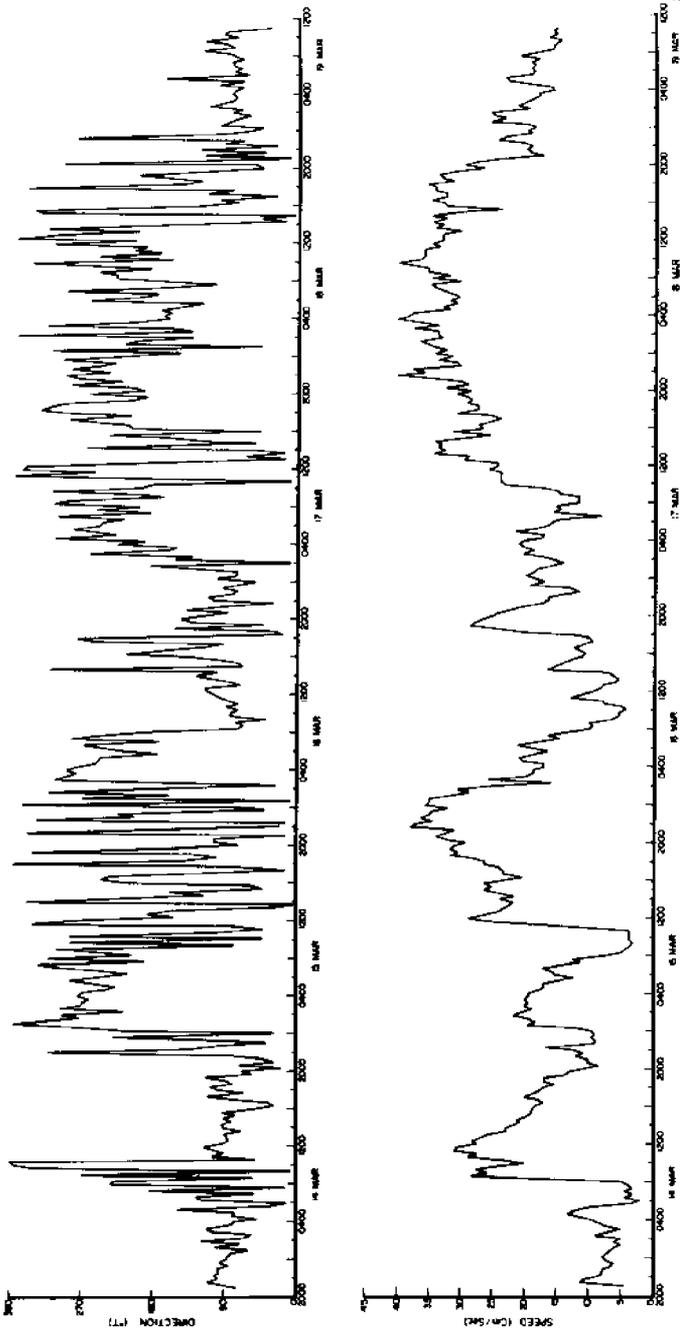
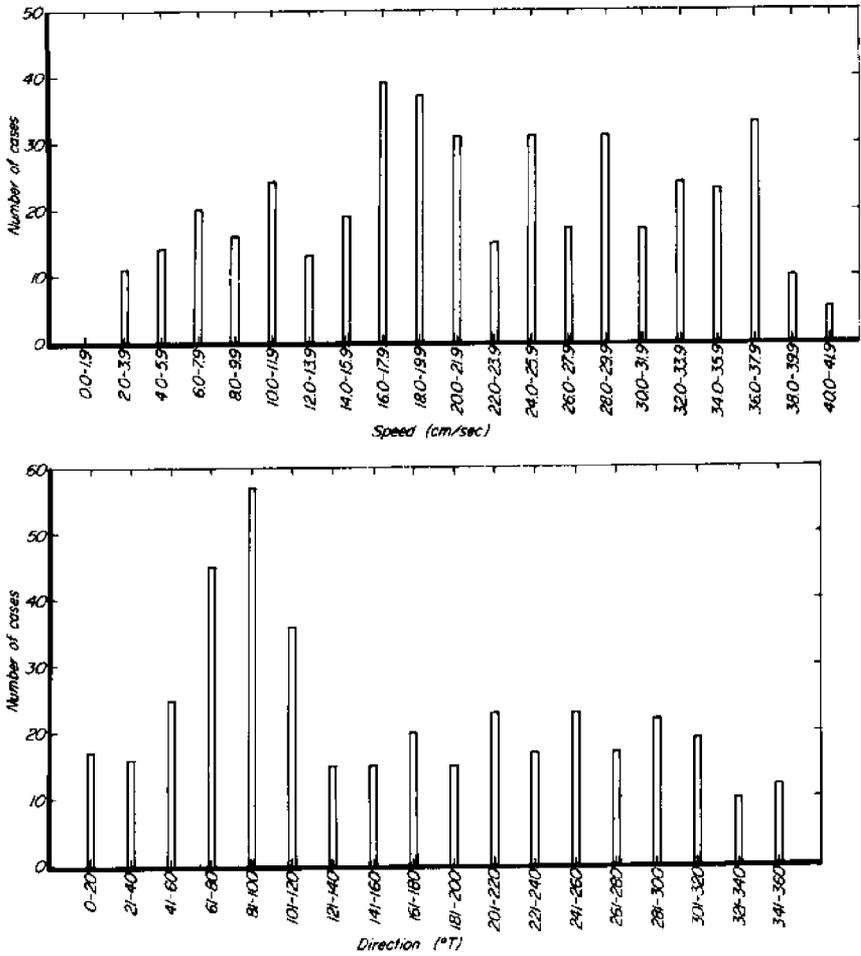


Figure 3.31 Current speed and direction at 15 m (50 ft) at location 1 during 13-19 March 1972.



**Figure 3.32** Histograms of current speed and direction at 15 m (50 ft) at location 1 during March 1972 (from Figure 3.31)

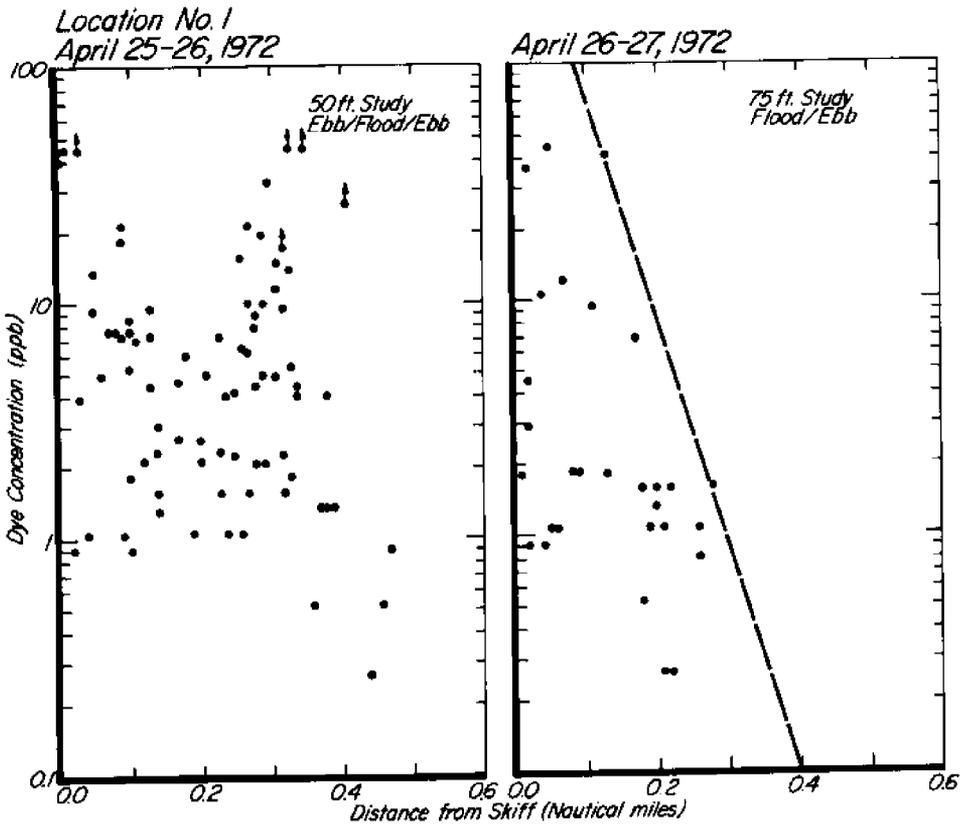
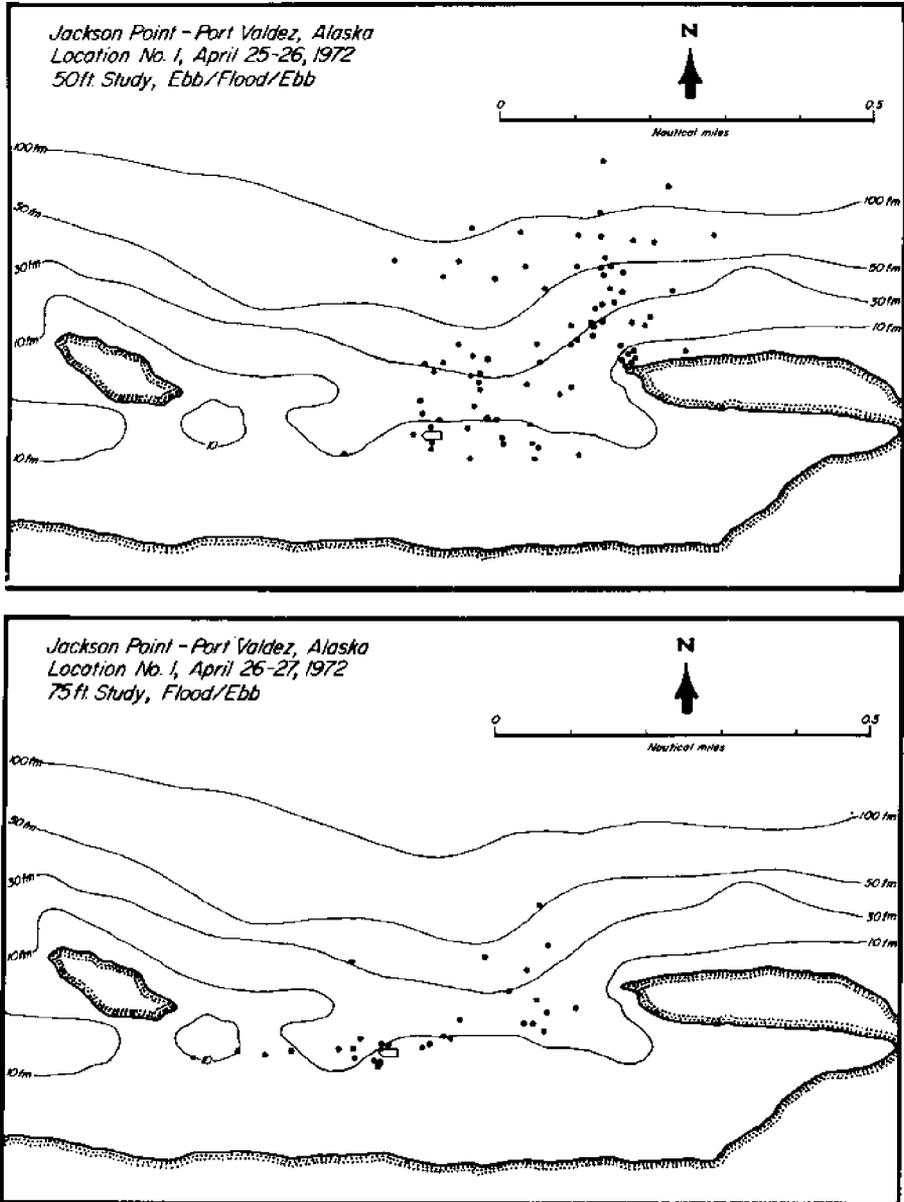


Figure 3.33 Dye concentrations (ppb) versus distance (n. miles) near location 1 during 25-27 April 1972.



**Figure 3.34** Positions where dye was found near location 1 on 25-27 April 1972 at depths of 15 m (upper) and 23 m (lower).

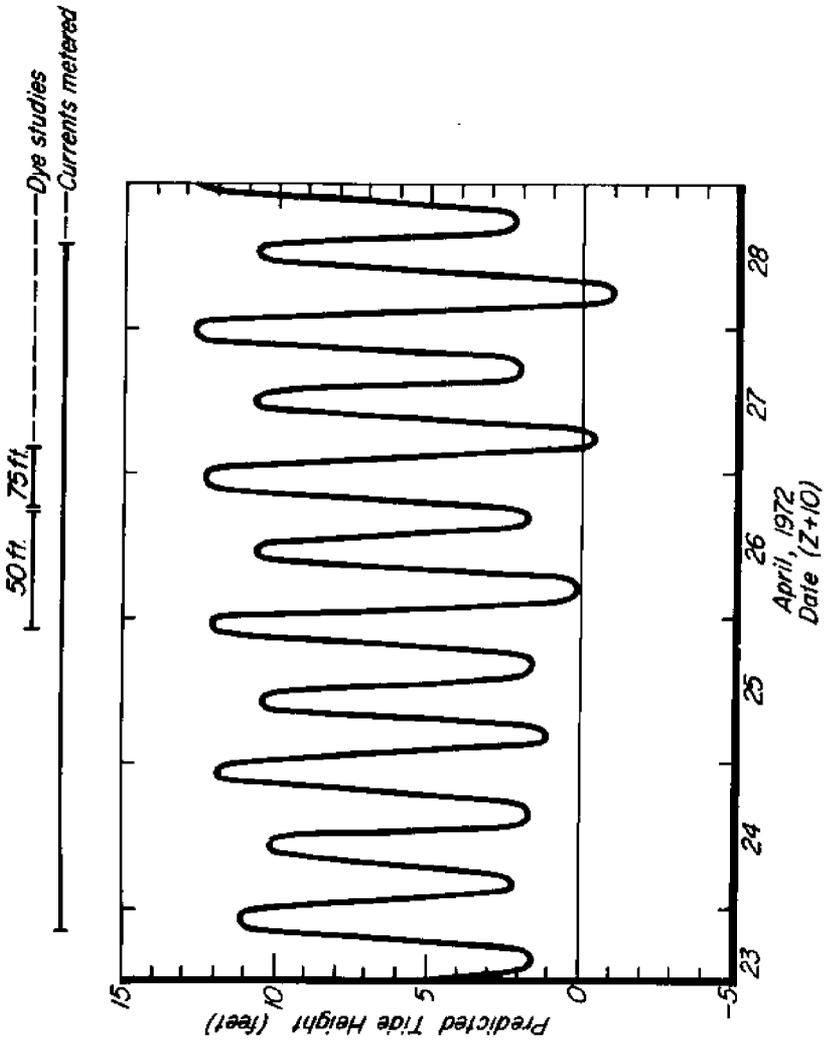


Figure 3.35 Predicted tidal height (ft) at town of Valdez during 23-28 April 1972.

2. At 23 m the dye plume developed both toward the east and west and exhibited a tenfold dilution distance of 0.11 n. miles (Figure 3.34).

The surface readout (and recording) current meter used during the October 1971 study was employed again at 15 m from 23-28 April 1972. Malfunctioning of the meter during part of this period may have biased the directional record (Figure 3.36). The preferred direction at 15 m appeared to be 81-100°T with a lesser peak at 221-240°T (Figure 3.37). The direction appeared to fluctuate more than indicated on most previous records, but it was not as variable as noted during March 1972 studies. The preferred speed centered around 6.1-8.1 cm/sec with a maximum speed of 24.6-26.5 cm/sec.

### 3.4 Summary

The dye studies were conducted six times, under varying hydrographic conditions. The average tenfold dilution distance in all cases for which it was calculable was 0.46 n. miles. The average tenfold dilution distances for shallow (2.5-m) and deep (15- and 23-m) studies were 0.56 and 0.36 n. miles respectively, suggesting that the deep dye was diluted more rapidly than the shallow dye. These figures are biased, however, by the fact that shallow dispersion studies were not conducted in December, March or April, when the fjord waters were observed to be relatively homogeneous. More vertical mixing and a shorter tenfold dilution distance would be expected with vertically homogeneous water provided there were a constant tidal energy input together with surface cooling and winds. When it was possible to determine tenfold dilution distances for both shallow and deep studies, however, the deep dilution distances tended to be as small or less than the shallow values.

When summer and winter conditions are compared, dilution rates were more rapid during winter than in summer. This appears reasonable in view of the seasonal differences in water structure discussed above. Only three dilution rates were obtained during the winter, however, as compared to 13 values during the summer. There are therefore insufficient data to draw a statistically significant conclusion concerning these apparent seasonal variations.

The most rapid dispersion of dye was observed at location 1, even after excluding the winter (December and March) values that would tend to bias these dispersion figures towards lower values. Although the data were insufficient to allow a statistically significant conclusion to this effect, it is noteworthy that more rapid dispersion at location 1 agreed qualitatively with the fact that higher current speeds were generally observed at location 1 than at locations 2 or 3.

It should be noted that in the analysis of all of the dye data, the maximum concentrations found at each station were determined through use of continuously recording fluorescent meters - a technique which emphasizes the *worst possible case* for the dispersion. Had average values been chosen, i.e., a best-fit curve for the data as determined by the least-squares method, the time required to reach tenfold dilution would have been consistently less than that reported. Justification for this kind of data treatment rests in the fact that wastes tend to disperse in a patchy manner; the primary concern under this condition is the maximum concentrations to which organisms will be exposed, rather than a description of the dispersion field.

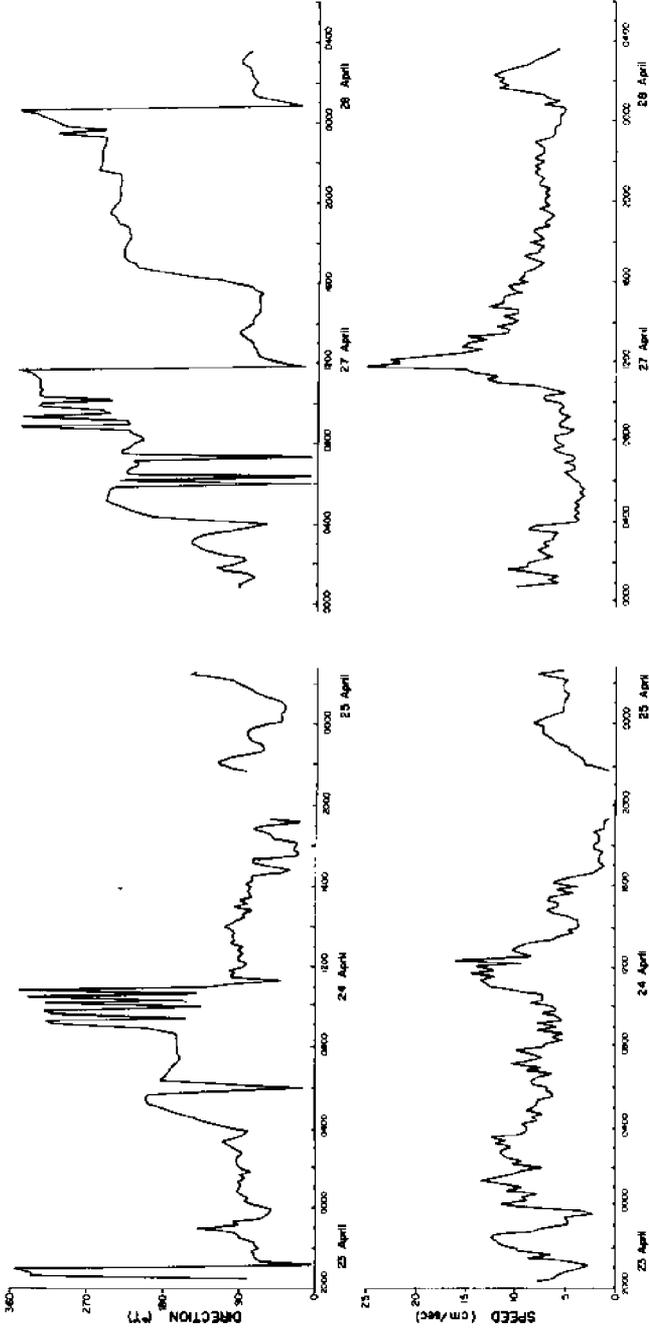


Figure 3.36 Current speed and direction (1.5-m depth) at location 1 during 23-28 April 1972.

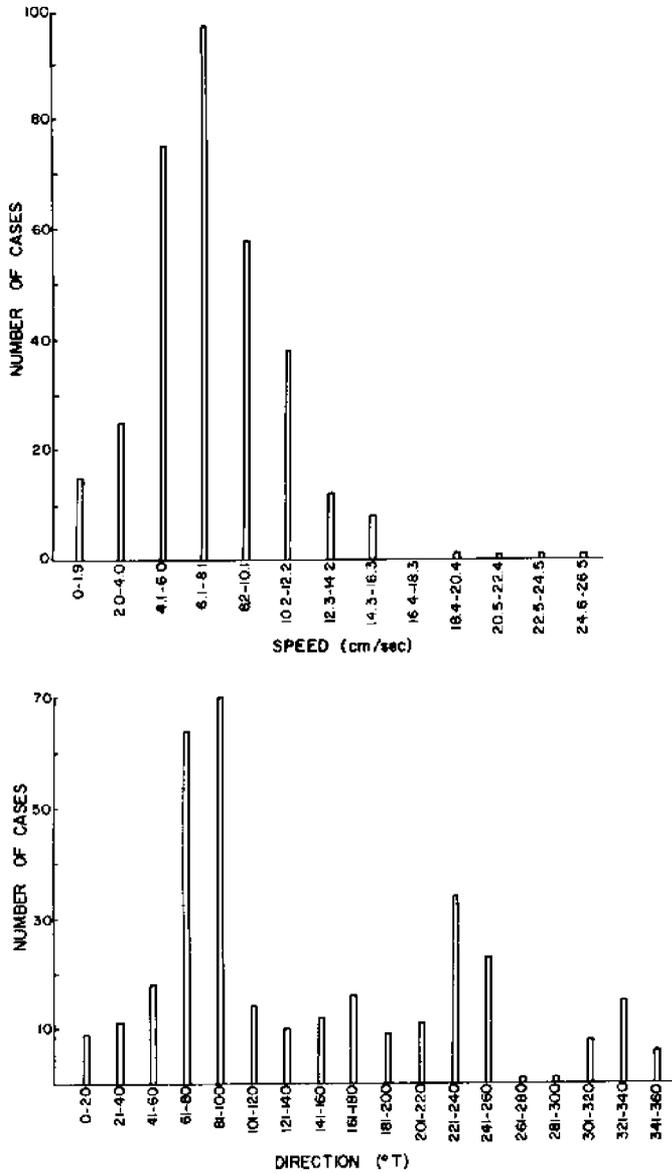


Figure 3.37 Histograms of current speed and direction at 15 m (50 ft) at location 1 during April 1972 (from Figure 3.36).

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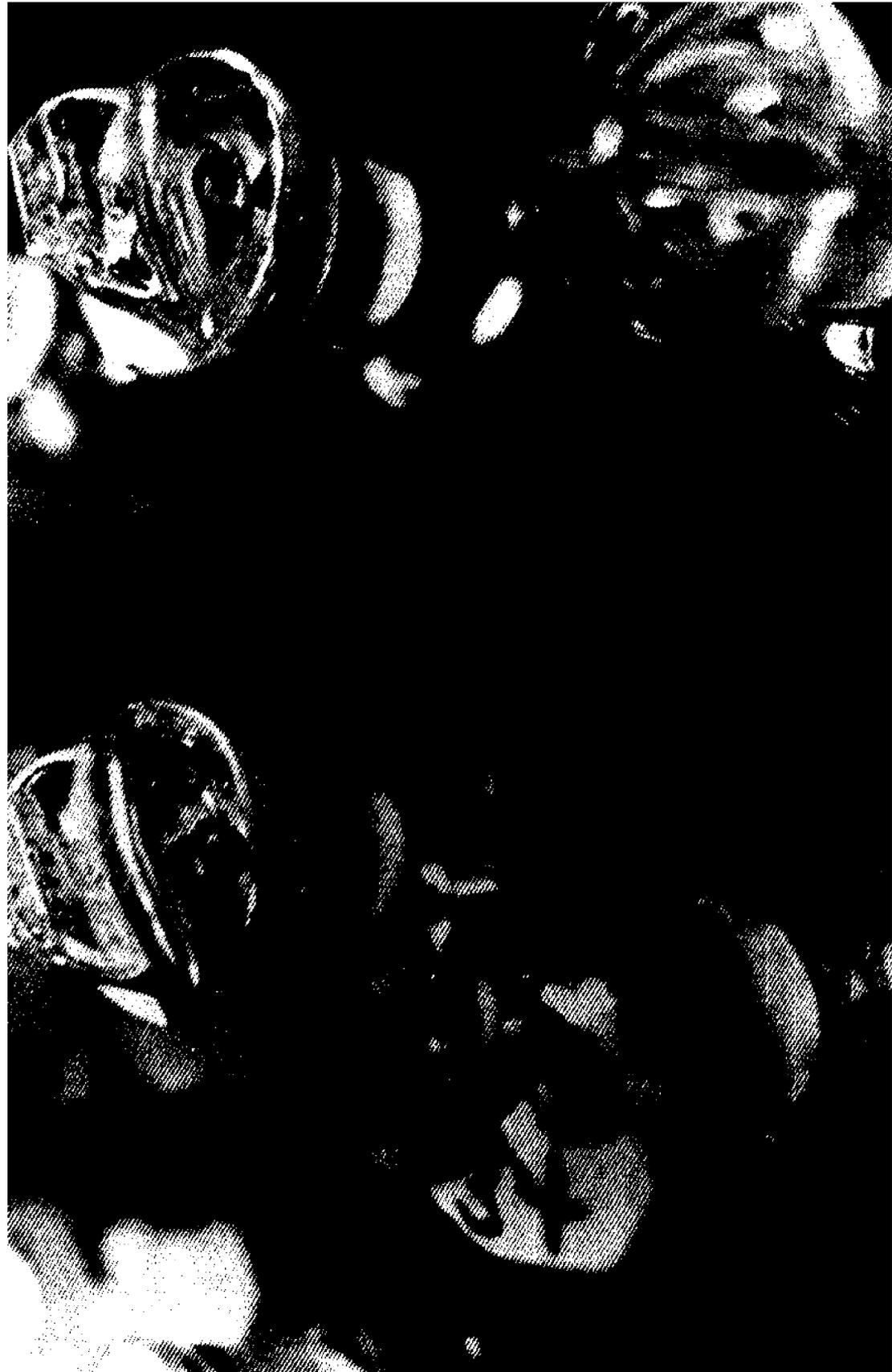
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# *Chapter 4*

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## CHEMICAL OCEANOGRAPHY





## 4. CHEMICAL OCEANOGRAPHY

by

D. W. Hood and C. J. Patton

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### 4.1 Introduction: Significance of Measurements

The several topics of pH, alkalinity, total carbon dioxide and oxygen are presented as a unit in this chapter because of the unique interrelation of these factors in the composite baseline marine chemistry of the Port Valdez environment.

#### 4.1.1 pH

The pH in seawater is affected by temperature, salinity, photosynthesis, respiration, deposition of ions of the buffer system, and exchange with the atmosphere. The measurement of pH values (the negative log of hydronium ion concentrations) in seawater is usually made routinely at sea as a parameter needed in computations of the concentration of certain ionic and molecular species present. The ratio of bicarbonate, carbonate and borate ion concentrations present and the partial pressure of molecular carbon dioxide in the water are indicated by the pH. The concentrations of each of these components of the carbon dioxide system can be estimated by using pH and alkalinity data and known equilibrium constants for carbonic acid in seawater. The complexation of trace metals with both organic and inorganic components of the ocean is heavily dependent upon pH. Although the significance of this phenomenon is not well understood with respect to availability of required trace metals for growth of organisms or the toxicity of certain heavy metals to organisms, it is clear that complexation is important to the chemical behavior of these elements in the sea. Intensive studies are proceeding on this subject at the present time.

Excursions of pH in the marine environment can be extreme under conditions of high productivity. In Redfish Bay, Texas, a diurnal shift was observed in pH between 7.8 and 8.4 in December and 8.2 and 8.9 in July of 1957 (Park et al. 1958). J. J. Kelley and C. P. McRoy (pers. comm.) have found pH values in summer as high as 9.7 over an eelgrass (*Zostera*) bed in Izembek Lagoon (near Cold Bay, Alaska) and winter values as low as 7.1 under the

ice in Safety Lagoon (near Nome, Alaska). The shift of several orders of magnitude in the  $\text{H}_3\text{O}^+$  concentration found in shallow bays does not occur naturally in deeper water. The values found in surface waters of Port Valdez and Valdez Arm during this survey ranged from 8.1 in December 1971 to 8.8 in July 1971. These low and high values correlate with the minimum and maximum biological productivity data (Chapter 6), respectively.

The effect of pH variation on the metabolism of organisms has not been well established and is too complex to review here. In general, however, organisms that live in an ecosystem characterized by natural fluctuations of pH have wide tolerance for change. Likewise, in a natural environment that is subject to only minor pH shifts, a greater sensitivity to change would be expected in the indigenous organisms.

The fluctuations of pH in the environment are greatest in surface waters of shallow bays, near coasts, and in highly productive areas of the open sea. The pH in seawater below the 200-m depth is typically confined to a range of 7.2 to 7.6.

The buffer capacity of seawater against pH changes is quite high, as discussed below, and small additions of low or high pH effluents to seawater affect the pH of the environment in a minor way.

#### 4.1.2 Alkalinity

The International Association of Physical Oceanography in 1939 defined alkalinity as the number of milliequivalents of hydrogen ion neutralized by 1 liter of seawater at 20C. The major influence is from the bicarbonate ion, although carbonate, borate, silicate, phosphate and arsenate play a minor role. Alkalinity and carbonate alkalinity along with pH are important measurable factors in the total carbon dioxide system of seawater. All components of the  $\text{CO}_2$  system may be determined by solving the following equations:

$$A = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + \text{H}_2\text{BO}_3^-$$

$$\Sigma\text{CO}_2 = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3]$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

where A,  $\text{CO}_2$ ,  $\text{H}^+$  and  $\text{H}_2\text{BO}_3^-$  are measurable. Such calculations are necessary to measure primary production, as discussed in Chapter 6.

There is a general linear relationship between alkalinity and the total salt content of ocean water. Salt content bears the following relationship to chlorosity in seawater (chlorosity is defined as halogen equivalents in gm/liter seawater at 20C):

$$\text{Specific alkalinity} = \frac{\text{alkalinity} \times 10^3}{\text{chlorosity}} = 0.123$$

Coastal water deviates widely from this relationship; if an error of 10-15 percent cannot be accepted, the alkalinity must be measured directly in near-shore areas.

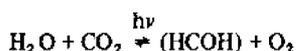
Alkalinity is not affected by pH, photosynthesis or respiration, but it can be changed by precipitation of carbonate species or by addition of mineral acid or base to the system.

#### 4.1.3 Total carbon dioxide

The total carbon dioxide in seawater is that amount which can be derived from the bicarbonate and carbonate ions in seawater and from the molecular carbon dioxide present. Its concentration is affected by photosynthesis, respiration, precipitation of carbonate species, or through exchange of  $\text{CO}_2$  with the atmosphere.

#### 4.1.4 Oxygen

Oxygen concentration varies widely in the marine environment, originating both in the atmosphere and as a product of photosynthesis:



where  $h\nu$  is energy provided from sunlight. Dissolved oxygen is lost to the system by respiration and chemical utilization. Exchange with the atmosphere, however, causes a net effect of seawater saturation in dissolved oxygen with respect to the air according to Henry's Law:

$$M = C_s P$$

where  $M$  is the concentration of oxygen in the water,  $C_s$  is the solubility of  $\text{O}_2$  in seawater of a given temperature and salinity under an atmosphere of pure oxygen, and  $P$  is the partial pressure of oxygen in the atmosphere. Waters may become supersaturated with oxygen to as much as 130 percent at the surface because of photosynthesis, or they may become anoxic at depth due to respiration and isolation from the atmosphere under conditions of slow vertical circulation. Low-oxygen or anoxic waters are more common in low and mid-latitude areas of the oceans. In uncontaminated Alaskan waters, oxygen is rarely found to be deficient. Minimum values dip to about 5 mg/liter at the bottom of some fjords during the summer months. All fjord systems investigated so far undergo thorough bottom-water renewal and thus replenish oxygen content at least once per year (Matthews 1972).

#### 4.1.5 Water quality standards pertaining to pH and dissolved oxygen

The Water Quality Standards for Interstate Water within the State of Alaska, 1967, state that Port Valdez and Prince William Sound are classified for water use of growth and propagation of fish and other aquatic life. Enforcement will be based on samples essentially representative of the receiving waters and not upon samples taken immediately adjacent to an outfall. Water quality standards for pH and oxygen are specified as follows:

*pH.* The natural conditions outside the range of 7.5 and 8.5 shall be maintained without change. Within the range, an induced change of 0.5 pH units/hour is maximum.

*Oxygen.* Dissolved oxygen shall be maintained at concentrations greater than 6 ml/liter.

## 4.2 Methods

Samples were collected and analyzed on the same cruises at the same stations as those occupied for physical oceanography (Figures 2.1 and 2.2; also Data Vol. I: Tables 2.1-2.6) during the period May 1971-May 1972.

### 4.2.1 pH analysis

Measurement of pH in seawater has been discussed in detail by Smith and Hood (1964), who established a secondary buffer based on an organic base called *Trizma*, composed of tris (hydroxymethyl) amino-methane, which is compatible with seawater. The ordinary phosphate and borate buffers commonly used as pH standards for fresh-water systems must be made up in distilled water. Standardizing of the glass electrode with these buffers and then switching to the high ionic strength of seawater causes slow and sometimes uncertain electrode response. *Trizma* buffers used as pH standards in the Valdez studies were obtained from the Sigma Chemical Company, St. Louis, Missouri.

Measurements of pH were made with a model 37A Coleman pH Meter using a Sargent-Welch Model S-30070-10 miniature combination glass-calomel electrode. Seawater samples were collected in 125-ml polyethylene bottles promptly upon retrieval of Niskin bottles from a hydrographic cast. Air-free techniques were used as in collection of samples for oxygen analysis. The samples for the entire cast were then placed in a water bath maintained at surface-seawater temperature by continuous flushing with surface seawater obtained by pumping from a sea chest at the 2-m level in the hull of the ship. After temperatures had equalized to surface-water temperatures, the pH meter was standardized with *Trizma* buffers of pH 8.00 controlled to the same temperature as the samples. Each sample bottle in turn was then uncapped, the electrode tip was inserted to near the bottom, and the pH was read. As shown in Table 4.1 below, the time after collection before pH was measured is not critical with this system. Biological activity would tend to change the pH, however, and all samples were therefore analyzed within 1 hour after collection. The pH values are thought to be accurate to  $\pm 0.02$  pH units.

Table 4.1 Effect of standing on pH values measured at surface seawater temperature (7C) on 21 May 1971 at station 152 (*Acona* cruise 113)

Depth (m)	Time After Sampling		$\Delta$
	1 hour	5 hours	
0	8.530	8.510	0.020
2	8.545	8.540	0.005
5	8.556	8.550	0.006
10	8.490	8.485	0.005
20	8.290	8.340	0.050
30	8.313	8.325	-0.012
50	8.205	8.190	0.015
75	8.102	8.110	-0.008
100	8.085	8.078	0.007
195	8.090	8.100	0.010

#### 4.2.2 Alkalinity determination

A 100-ml seawater sample was pipetted into a 250-ml flask containing 10 ml of standard 0.04 N hydrochloric acid. Three drops of bromocresol green-methyl red mixed indicator solution was added, and the mixture was swirled. The liberated  $\text{CO}_2$  was stripped by purging for 2-3 min with nitrogen gas dispensed through a fritted glass sparger. The excess acid was back-titrated with standard 0.02 N NaOH to an endpoint indicated by a permanent pale green color. Samples were run in duplicate and the results calculated by the following formula:

$$\begin{aligned} &(\text{volume of acid} \times \text{normality}) - (\text{volume of base} \times \text{normality}) \\ &\times 10 = \text{alkalinity in milliequivalents/liter} \end{aligned}$$

#### 4.2.3 $\Sigma\text{CO}_2$ calculation

Total carbon dioxide was calculated for productivity stations from pH, salinity and alkalinity data by use of Tables 7-10 in Strickland and Parsons (1968).

#### 4.2.4 Dissolved oxygen determination

Analysis of dissolved oxygen has been described by Wallen and Hood (1968); a brief description of the method follows. Samples to be analyzed for dissolved oxygen content were drawn first from the sampling container, using glass tubes coupled with Tygon hoses. Care was taken that no bubbles were present in either the hose or bottle. The sample bottles were of either standard BOD type or calibrated "125-ml" glass-stoppered reagent bottles. (Most of the reagent bottles commercially available contain around 128 ml). If the volume in all the bottles varied less than 2 ml (127-129 ml), the bottles could be used and the calibrated volume was considered to be 128 ml.

After sampling into a twice-rinsed bottle was completed, the stopper was replaced without trapping any air bubbles. The stopper was then suddenly removed and 1 ml of manganous chloride solution ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) added, followed by 1 ml of sodium hydroxide-potassium iodide solution. The stopper was again replaced without trapping air bubbles, the solution was well shaken and the resulting precipitate was allowed to settle. The sample was shaken again and after the precipitate had settled the second time, 1 ml of 10 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was added. The sample was thoroughly shaken until the precipitate was dissolved.

Fifty milliliters of the treated sample were pipetted into a cleaned and drained 125-ml Erlenmeyer flask and titrated against the 0.01 N thiosulfate solution until the color was light yellow, at which point 0.25 ml of starch solution was added. Finally, the sample was titrated (reproducible to within 0.02 ml) to the starch endpoint marked by the disappearance of blue starch-iodine complex.

Calculations of oxygen content were made from the above data with use of the following equation:

$$\text{DO} = \frac{(R - R_{\text{blk}}) V_{\text{IO}_3} \cdot N_{\text{IO}_3} \cdot E \cdot V_b}{(R_{\text{std}} - R_{\text{blk}}) \cdot (V_b - V_{\text{reg}}) \cdot V_a} - \text{DO}_{\text{reg}}$$

where

R = sample titration burette reading

$R_{\text{std}}$  = standard burette reading

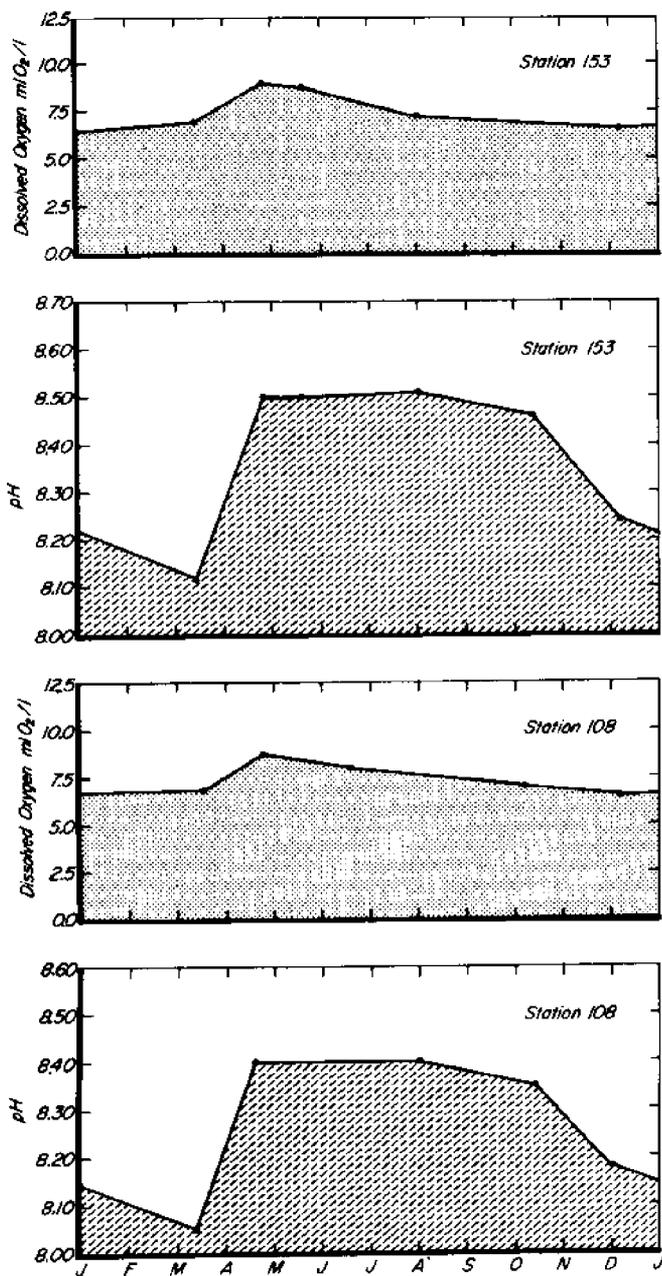


Figure 4.1 Seasonal variations in pH and O<sub>2</sub> at the 50 percent light level at stations 108 in Valdez Arm and 153 in Port Valdez, Alaska.

$R_{\text{blk}}$  = blank value

$V_{\text{IO}_3}$  = volume of primary standard solution

$V_{\text{reg}}$  = volume of sample displaced by reagents

$N_{\text{IO}_3}$  = normality of standard solution

$E$  = 5598 ml  $\text{O}_2$ /equivalent

$V_{\text{b}}$  = volume of sample bottle

$V_{\text{a}}$  = volume of titrated aliquot

$\text{DO}_{\text{reg}}$  = dissolved oxygen contained in reagents

$\text{DO}_{\text{reg}}$  should amount to about 0.018 ml/liter when 125-ml reagent bottles are used and 1 ml of each reagent is added.

### 4.3 Results

#### 4.3.1 pH data

pH measurements of the surface waters were made at all productivity stations occupied during the study period. The measurements were made at light depths corresponding to 100, 50, 25, 10 and 1 percent of surface incident solar radiation (Data Vol. I: section 4).

Figure 4.1 shows the change of pH at the 50 percent light level with time of year for stations 108 and 153. The shift in pH with time of year closely correlated with the oxygen level and also with productivity (Chapter 6). The pH at this light level decreased from August until the middle of March, when it reached values near 8.2, then rose rapidly to 8.5 in mid-April and remained at about that level until August.

Detailed pH data for all depths of Port Valdez were obtained during December 1971 on *Acona* cruise 125 (Figure 4.2; Table 4.2); as is typical in ocean waters, the pH decreased with depth in a nearly linear fashion at this time of year. Decrease in pH is caused by carbon dioxide produced by the biodegradation of organic matter. Minimum values of about pH 8.0 were found in the bottom waters (Table 4.2). The pH data for other seasons of the year (Data Vol. I: section 4) indicate that the deep-water pH values did not undergo significant seasonal fluctuations.

#### 4.3.2 Alkalinity data

Alkalinity was determined at all stations in Port Valdez where primary productivity was measured (Data Vol. I: section 4). Specific alkalinity values were estimated for selected stations on cruise 113 (May 1971) and 125 (December 1971); these data are tabulated in Table 4.3. Computations were difficult because of the need to extrapolate for the salinity values at biological sampling depths between the values at standard hydrographic depths. Surface alkalinity is not easily evaluated because changes in salinity can be abrupt, particularly during heavy fresh-water runoff in summer, and extrapolation must assume linearity in concentration changes. Because of this problem, errors can be expected at the shallow depths where brackish surface water exists.





## MARINE CHEMISTRY

Winkler colorimetric titration (above) for determination of dissolved oxygen content in seawater samples collected in Nansen bottles (in rack below). Determinations were made also of salinity, pH and alkalinity.



Table 4.2 Measurements of pH in Port Valdez during *Acona* cruise 125 (4-13 December 1971)

Station	Depth (m)	pH	Station	Depth (m)	pH	Station	Depth (m)	pH
101	0	8.20	110	0	8.18	115	0	8.20
	2	8.18		2	8.16		2	8.20
	5	8.19		5	8.16		5	8.17
	10	8.21		10	8.16		10	8.17
	20	8.18		20	8.14		20	8.17
	30	8.20		30	8.13		30	8.16
	50	8.18		50	8.11		50	8.12
	75	8.18		75	8.06		75	8.07
	100	8.17		100	8.04		100	8.05
	150	8.12		150	8.01		150	8.20
	200	8.06		200	7.96			
	250	8.00		250	7.96			
	300	7.99						
105	0	8.25	112	0	8.22	120	0	8.19
	2	8.19		2	8.24		2	8.20
	5	8.21		5	8.24		5	8.18
	10	8.19		10	8.22		10	8.18
	20	8.20		20	8.23		20	8.18
	30	8.23		30	8.23		30	8.15
	50	8.21		75	8.17		50	8.14
	75	8.23					75	8.15
	100	8.20					100	8.15
	150	8.14					150	8.10
	200	8.08					200	8.04
	300	-						
	106	0		8.17	113		0	8.16
2		8.17	2	8.15		2	8.20	
5		8.16	5	8.15		5	8.19	
10		8.15	10	8.17		10	8.17	
20		8.17	20	8.18		20	8.11	
30		8.16	30	8.17		30	8.17	
50		8.16	50	8.16		50	8.17	
75		8.12	75	8.12		75	8.16	
100		8.14	100	8.11		100	8.14	
150		8.07	150	8.10		150	8.13	
200		8.02	200	8.04		200	8.00	

Table 4.2 (continued)

Station	Depth (m)	pH	Station	Depth (m)	pH	Station	Depth (m)	pH
122	0	8.21	130	0	8.14	142	0	8.20
	2	8.19		2	8.11		2	8.24
	5	8.19		5	8.12		5	8.22
	10	8.19		10	8.12		10	8.21
	20	8.18		20	8.12		20	8.17
	30	8.16		30	8.12		30	8.19
	50	8.13		50	8.13		50	8.17
	75	8.10		75	8.12		75	8.14
	100	8.10		100	8.10		100	8.14
	150	8.02		150	8.06		150	8.08
200	8.00	200	8.00					
124	0	8.18	131	0	8.14	146	0	8.18
	2	8.16		2	8.18		2	8.19
	5	8.19		5	8.14		5	8.20
	10	8.21		10	8.16		10	8.16
	20	8.20		20	8.15		20	8.17
	30	8.16		30	8.15		30	8.16
	50	8.17		50	8.13		50	8.16
	75	8.14		75	8.13		75	8.16
	100	8.16		100	8.11		100	8.13
	150	8.09		150	8.08			
200	8.03	200	8.00					
128	0	8.16	132	0	8.15	148	0	8.16
	2	8.18		2	8.16		2	8.17
	5	8.17		5	8.13		5	8.17
	10	8.18		10	8.14		10	8.17
	20	8.18		20	8.14		20	8.17
	30	8.15		30	8.15		30	8.18
	50	8.15		50	8.13		50	8.15
	75	8.12		75	8.11		75	8.14
	100	8.15		100	8.11		100	8.12
	150	8.13		150	8.07			
200	8.03	200	8.02					

Table 4.2 (continued)

Station	Depth (m)	pH	Station	Depth (m)	pH	Station	Depth (m)	pH
150	0	8.16	164	232	7.98			
	2	8.17						
	5	8.14	165	232	7.99			
	10	8.18						
	20	8.12	166	232	7.99			
	30	8.15						
	50	8.16	167	236	8.02			
	75	8.11						
100	8.12	168	234	8.01				
152	0	8.19	169	232	8.02			
	2	8.18						
	5	8.14	170	243	8.03			
	10	8.14						
	20	8.15	171	0	8.17			
	30	8.16		2	8.18			
	50	8.15		5	8.12			
	75	-		10	8.19			
	100	8.09		20	8.16			
	150	8.07		30	8.16			
	200	8.00		50	8.16			
		75	8.13					
		100	8.12					
153	0	8.22						
	2	8.24						
	5	8.24						
	10	8.23						
	20	8.23						
	30	8.22						
	50	8.20						
160	178	8.04						
161	198	8.00						
162	213	7.99						
163	226	8.01						

Table 4.3 Alkalinity data for selected stations in Port Valdez during *Acona* cruise 113 (May 1971) and cruise 125 (December 1971)

Cruise 113 (May 1971)						
Station No.	Depth (m)	Salinity	Sigma T	Chlorosity	Alkalinity	Specific alkalinity
128	0	29.079	22.83	16.42	2.01	0.122
	2.4	29.522	23.23	16.67	2.05	0.122
	4.8	29.965	23.64	16.92	2.02	0.119
	7.9	30.537	24.16	17.25	2.08	0.120
	16.4	31.144	24.72	17.59	2.08	0.118
150	0	24.142	18.91	13.63	1.95	0.142
	1	26.610	19.49	15.03	2.02	0.134
	3.5	29.891	21.45	16.88	2.00	0.118
	6.5	30.830	22.69	17.41	1.95	0.112
	12.0	31.188	24.79	17.61	2.16	0.122
151	0	29.064	22.75	16.42	2.02	0.123
	2.3	29.521	23.18	16.67	2.05	0.122
	4.5	29.958	23.60	16.92	2.10	0.124
	7.3	30.515	24.12	17.23	2.13	0.123
	14.4	31.252	24.83	17.65	2.15	0.121
152	0	28.909	22.68	16.33	2.00	0.122
	2.2	29.386	23.12	16.60	2.01	0.121
	4.2	29.820	23.51	16.84	2.06	0.122
	6.8	30.381	24.03	17.16	2.10	0.122
	13.0	31.165	24.74	17.60	2.15	0.122
153	0	29.550	23.21	16.69	2.00	0.119
	2.5	29.942	23.58	16.91	1.93	0.114
	5.1	30.351	23.97	17.14	2.04	0.119
	8.3	30.853	24.45	17.42	2.03	0.116
	16.7	31.194	24.77	17.62	2.04	0.115
GB-1	0	28.943	22.52	16.35	1.69	0.103
	6.3	30.318	23.89	17.12	1.98	0.115
	12.6	31.158	24.73	17.60	1.95	0.110
	21.0	31.259	24.84	17.65	2.01	0.113
	42.0	31.437	25.00	17.76	2.07	0.116

Table 4.3 (continued)

## Cruise 125 (December 1971)

Station	Depth (m)	Salinity	Sigma T	Chlorosity	Alkalinity	Specific alkalinity
108	0	31.346	24.73	17.70	2.28	0.128
	2.75	31.348	24.73	17.70	2.28	0.128
	8.0	31.352	24.73	17.71	2.28	0.128
	16.0	31.384	24.75	17.72	2.27	0.128
	34.0	31.399	24.77	17.73	2.26	0.127
113	0	31.277	24.73	17.66	2.23	0.126
	19.0	31.331	24.75	17.70	2.24	0.133
	29.0	31.344	24.75	17.70	2.24	0.126
	47.0	31.444	24.79	17.76	2.25	0.127
	94.0	31.803	24.99	17.96	2.24	0.124
120	0	31.102	24.69	17.57	2.23	0.126
	4.0	31.188	24.73	17.61	2.22	0.126
	10.0	31.318	24.78	17.69	2.22	0.125
	18.0	31.360	24.80	17.71	2.28	0.128
	25.0	31.413	24.82	17.74	2.26	0.127
128	0	30.797	24.55	17.39	2.20	0.126
	3.5	30.989	24.65	17.50	2.21	0.126
	10.5	31.343	24.84	17.70	2.23	0.125
	22.0	31.300	24.74	17.68	2.25	0.127
	45.0	31.518	24.84	17.80	2.26	0.126
142	0	31.006	24.63	17.51	2.27	0.129
	4.5	31.124	24.67	17.58	2.26	0.128
	9.25	31.249	24.72	17.65	2.28	0.129
	15.5	31.307	24.75	17.68	2.28	0.128
	31.0	31.335	24.75	17.70	2.26	0.127
150	0	29.850	23.85	16.86	2.22	0.124
	4.0	30.476	24.23	17.21	2.23	0.129
	10.0	31.414	24.79	17.74	2.23	0.125
	19.0	31.355	24.75	17.71	2.24	0.126
	33.0	31.390	24.80	17.73	2.26	0.127
152	0	31.260	24.74	17.66	2.22	0.125
	5.0	31.260	24.72	17.66	2.24	0.126
	11.0	31.264	24.71	17.66	2.23	0.126
	18.0	31.293	24.73	17.67	2.24	0.126
	35.0	31.470	24.77	17.77	2.24	0.126

Table 4.3 (continued)

Cruise 125 (December 1971)

Station	Depth (m)	Salinity	Sigma T	Chlorosity	Alkalinity	Specific alkalinity
153	0	31.305	24.76	17.68	2.22	0.125
	3.0	31.297	24.75	17.68	2.23	0.126
	8.5	31.283	24.74	17.67	2.22	0.125
	16.0	31.298	24.75	17.68	2.22	0.126
	32.0	31.316	24.75	17.68	2.22	0.126
171	0	-	-	-	2.16	-
	2.5	-	-	-	2.24	-
	6.5	-	-	-	2.25	-
	14.5	31.262	24.73	17.66	2.22	0.125
	29.0	31.358	24.77	17.71	2.22	0.125
GB-1	0	30.720	24.30	17.35	2.20	0.126
	3.0	30.871	24.38	17.44	2.27	0.130
	9.25	31.184	24.54	17.61	2.26	0.128
	18.75	31.257	24.56	17.65	2.23	0.126
	37.5	31.465	24.64	17.77	2.28	0.128
JB-1	0	31.292	24.71	17.67	2.28	0.129
	17.0	31.443	24.80	17.76	2.28	0.128
	29.0	31.585	24.82	17.84	2.28	0.127
	47.0	31.875	25.30	18.00	2.27	0.126
	94.0	31.753	25.50	17.93	2.28	0.127

Alkalinity of the waters in Port Valdez during May varied widely with location and depth and were generally less alkaline than open seawater. In December 1971 the alkalinity was quite uniform and tended to be slightly higher than the open sea.

#### 4.3.3 $\Sigma\text{CO}_2$ data

Total- $\text{CO}_2$  values in Port Valdez waters were calculated (according to Strickland and Parsons 1968) at all stations where productivity was measured (Data Vol. I: section 4). For comparison, direct measurements of total carbon dioxide were made by an IR method developed in this laboratory (Table 4.4) and values were usually lower than those calculated. The maximum deviation was 14 percent, but most values were less than 10 percent. The direct measured values are thought to be more reliable than those computed from tables, although much more time is required for analysis. Since the total carbon dioxide values in this study were considered mainly in connection with productivity measurements that are subject to even greater error, the computation method was adequate for the purpose.

Total- $\text{CO}_2$  values in Port Valdez appear to be characteristic of coastal areas which have similar productivity, salinity and alkalinity regimes. Vertical profiles of total carbon dioxide and dissolved oxygen are shown in Data Volume I (Figures 4.1-4.12) for 12 stations in Port Valdez and adjacent waters. The total- $\text{CO}_2$  is affected by photosynthesis, as in the form of the carbon dioxide component in the water. The concentration of dissolved carbon dioxide gas rarely reaches equilibrium values of about 320 ppm (by volume) in highly productive areas due to the stress of photosynthesis, respiration, temperature and salinity.

Understanding the carbon dioxide system in an ocean situation where the stress of pollution may occur is of importance because this system is fundamental to vital life processes as well as to many physical-chemical interactions in the ocean. The complexity of the system and the incomplete knowledge of many details of the system, however, lead one to consider other parameters such as primary productivity, direct toxicity measurements, species diversity, direct analysis of the polluting contaminants, and pH and  $\text{O}_2$  measurements in assessing environmental quality and possible changes in the ecosystem due to the stress of contaminants. As our knowledge of carbon dioxide kinetics advances, the determination of ecosystem welfare will one day be greatly enhanced by detailed evaluation of the dynamics of the  $\text{CO}_2$  system.

#### 4.3.4 Oxygen data

Oxygen data were taken on selected hydrographic stations occupied in the Port Valdez study. These complete data are presented in sections 2 and 4 of Data Volume I. Isopleths of dissolved oxygen distribution in a longitudinal section of Port Valdez are presented in Figure 4.3, representing conditions during winter (*Acona* cruise 125) and spring (*Acona* cruise 131). Figure 4.4 shows values for oxygen 1 m from the bottom that were obtained on cruises 117 (August), 122 (October), 125 (December), 128 (March) and 131 (April). No values below 5.0 ml/liter were observed at any time during the survey period. Vertical profiles of dissolved oxygen are plotted along with total carbon dioxide for 12 selected stations in Port Valdez and adjacent waters (Data Vol. I: Figures 4.1-4.12).

It is apparent from these data that the Port Valdez basin was replenished with oxygen between December 1971 and March 1972. These results agree with those obtained in Chapter 2 based on temperature and salinity data. Replenishment of oxygen occurs probably throughout the year; otherwise, more conspicuous seasonal depletion would be expected. Since high oxygen values were maintained throughout the year at all depths of Port Valdez, there appears to be little danger of anoxic conditions forming in this Port

Table 4.4 Comparison of results of  $\Sigma\text{CO}_2$  measurement by infrared analysis to those obtained by Strickland and Parsons technique (1968) during *Acona* cruise 131

Station	Light transmissibility (%)	$\Sigma\text{CO}_2$ measurement (mmole $\text{CO}_2$ /liter)		
		Strickland and Parsons	IR analysis	$\Delta$
108	100	1.99	1.87	0.12
	50	1.99	1.94	0.05
	25	1.97	1.88	0.09
	10	1.98	1.84	0.14
	1	1.99	1.95	0.04
113	100	1.99	1.88	0.11
	50	2.00	1.83	0.17
	25	1.96	1.92	0.04
	10	1.96	1.92	0.04
	1	1.93	1.94	-0.01
120	100	1.86	1.70	0.16
	50	1.91	1.72	0.19
	25	1.91	1.70	0.21
	10	1.90	1.76	0.14
	1	1.97	1.85	0.12
128	100	1.87	1.68	0.19
	50	1.83	1.64	0.19
	25	1.78	1.66	0.12
	10	1.81	1.76	0.05
	1	1.85	1.78	0.07
152	100	1.92	1.84	0.08
	50	1.90	1.68	0.22
	25	1.97	1.96	0.01
	10	1.95	1.96	-0.01
	1	1.98	2.06	-0.08
153	100	2.03	1.86	0.17
	50	1.99	1.71	0.28
	25	1.98	1.76	0.22
	10	1.92	1.89	0.03
	1	1.88	1.68	0.20
JB-1	100	1.98	1.85	0.13
	50	1.97	1.75	0.22
	25	1.92	1.83	0.09
	10	1.92	1.88	0.04
	1	1.93	1.89	0.04

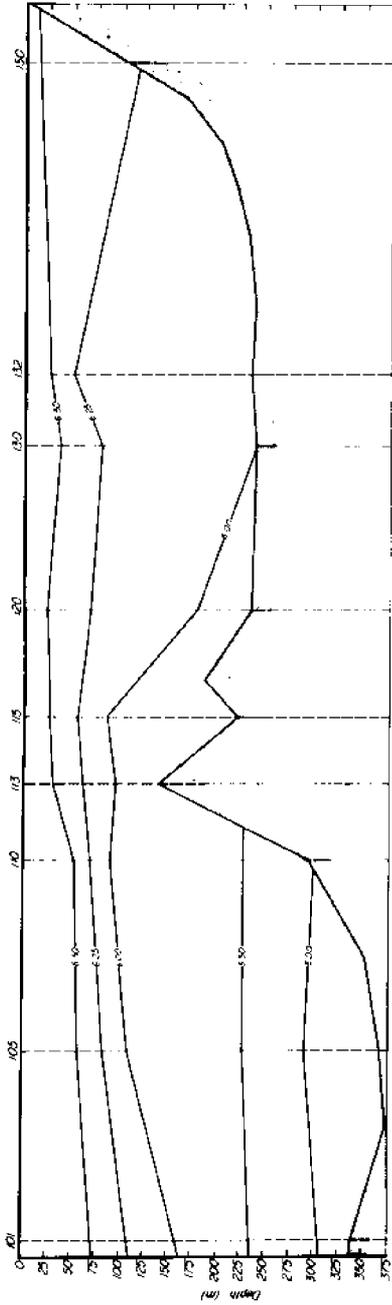


Figure 4.3a Oxygen isopleths in longitudinal section of Port Valdez during December 1971 (Aconia cruise 125).

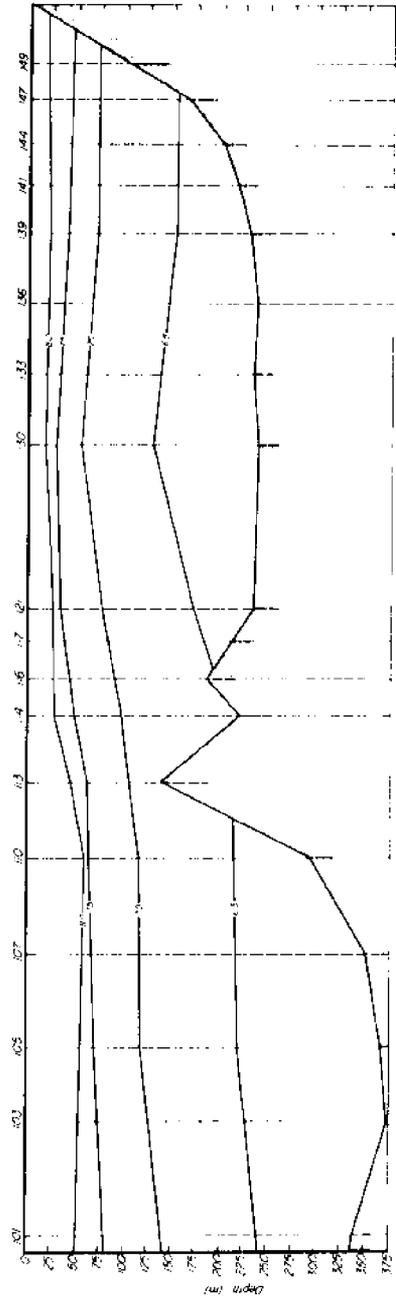
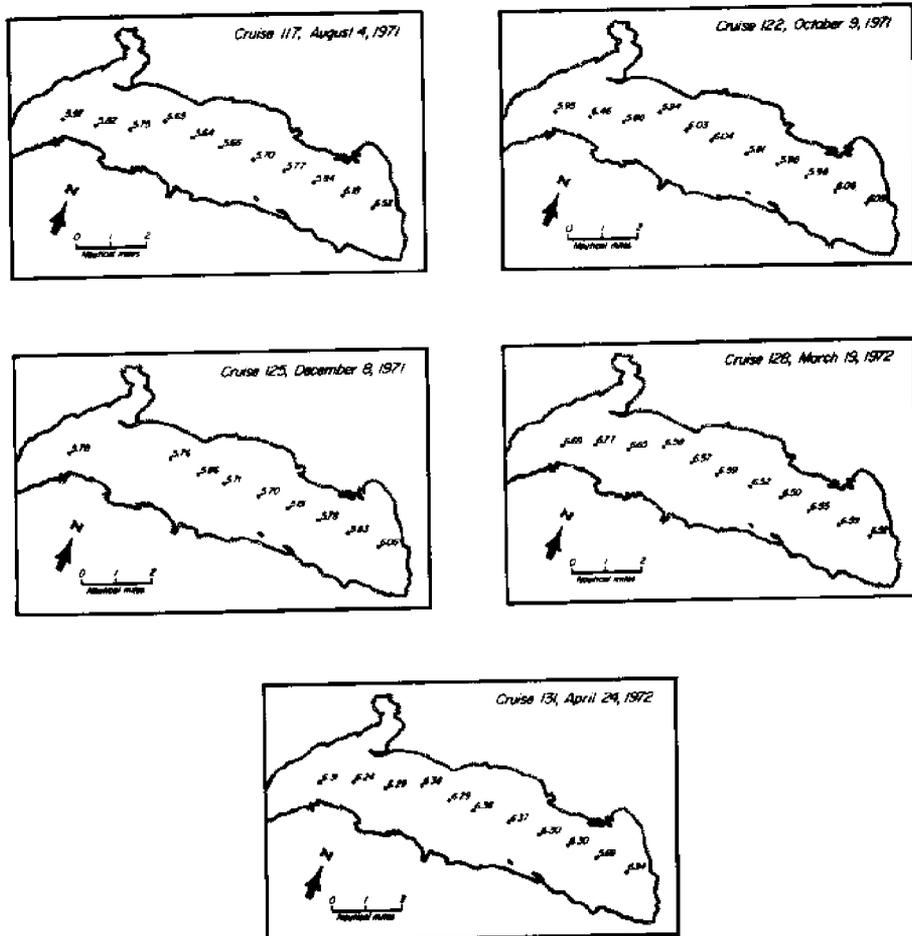


Figure 4.3b Oxygen isopleths in longitudinal section of Port Valdez during April 1972 (Aconia cruise 131).



**Figure 4.4** Oxygen values at 1 m above the bottom in Port Valdez during five cruises of the R/V Acona from August 1971 to April 1972.

unless very high loads of organic wastes of high biological oxygen demand are added through man's activities. In general, about 4 g of oxygen are required to oxidize 1 g of hydrocarbon to carbon dioxide and water. Using this ratio, each cubic meter of bottom water in Port Valdez could oxidize about 1.5 g of hydrocarbon without replenishment before becoming anoxic. Since replenishment rates are not known at this time, depletion of bottom-water oxygen values should be carefully monitored during additions of hydrocarbon or other organic matter to the system.

#### 4.4 Summary

The pH of Port Valdez and Valdez Arm surface water during this survey reached a maximum of 8.86 in July and a minimum of 8.10 in December 1971. These values correlate closely with the primary productivity observed in the system.

The alkalinity of surface waters varied widely during summer months. The Port waters were less alkaline than ocean water in summer, but in winter the alkalinity was more uniform and a little higher than in the open ocean.

Total carbon dioxide varied between 1.62-2.04 mmole/liter in surface water during May 1971 to 2.03-2.28 mmole/liter in December 1971. The high variability in the spring was apparently associated with a high rate of photosynthesis. Even lower values were observed during the summer (minimum of 0.72 mmole/liter), associated with high fresh-water input to the Port during this period. The more uniform high values found in the winter resulted probably from vertical mixing, minimum photosynthesis and low fresh-water input.

Oxygen values were uniformly high in the surface waters throughout the year. During the period of high productivity, the dissolved oxygen content was as high as 8 ml/liter; in winter, the surface values dropped to 6.5 ml/liter. In deep water, the minimum values occurred in winter, and values of less than 5 ml/liter were not found anywhere in the system. The minimum oxygen value observed in Port Valdez was 5.50 ml/liter. These data indicate complete replenishment of Port Valdez water at least in the winter, and no evidence exists for oxygen deficiency at any time of the year.

#### 4.5 References

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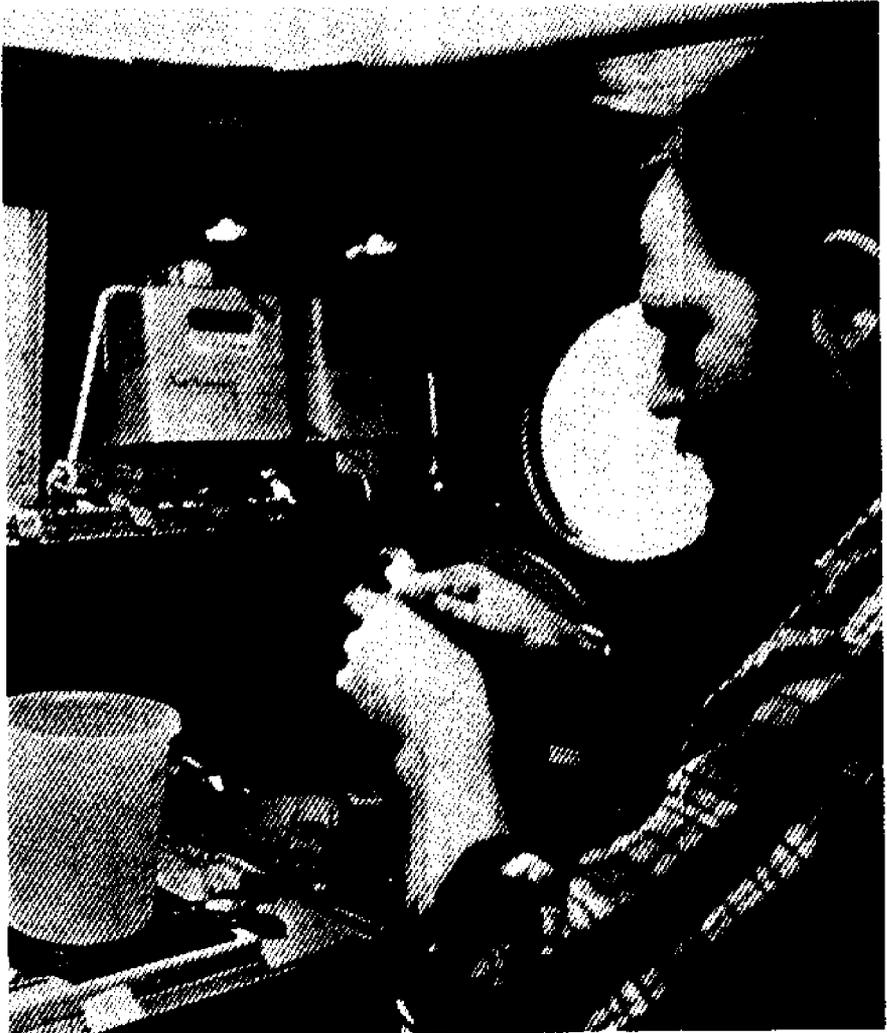


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# *Chapter 5*

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## NUTRIENT CYCLES





## 5. NUTRIENT CYCLES

by

J. J. Goering, C. J. Patton and W. E. Shiels

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### 5.1 Introduction

Seawater contains relatively high concentrations of certain inorganic nutrients such as sulfur, magnesium, potassium and sodium that are essential for growth of marine phytoplankton and macrophytes. Other essential elements (including nitrogen, phosphorus, silicon, cobalt and iron) are present only in minute amounts; however, they are apparently adequate to sustain marine phytoplankton growth. The remarkable growth of marine phytoplankton under such dilute nutrient conditions, as compared to the growth of terrestrial plants, is explained partly by the minute size of phytoplankton cells that provides a vastly higher surface-to-volume ratio for maximal absorption of nutrients. For example, the presence of trace amounts of nitrate ( $\text{NO}_3^-$ ), phosphate ( $\text{PO}_4^{3-}$ ) and silicic acid ( $\text{Si}(\text{OH})_4$ ) in seawater, as compared with the relatively large proportion of ionic potassium sulfate, magnesium and sodium, is indicative that those nutrient constituents which exist in minor proportion may become limiting both in space and in time.

The cycling of inorganic nitrogen (in the form of nitrate, nitrite and ammonia), dissolved inorganic phosphate and soluble silica was studied in Valdez Arm and Port Valdez for one year from May 1971 to April 1972. The locations of sampling stations are shown in Figures 2.1 and 2.2. Nutrient concentrations were plotted versus depth for numerous stations (Data Vol. I: Figures 5.1-5.12), and seasonal isopleths of the various nutrients are presented in Figures 5.1-5.5 of this text.

The data indicate that inorganic nutrients have regular seasonal cycles in this coastal Alaska marine system (Figures 5.6 and 5.7). Maximum surface concentrations were present during the winter, and marked reductions were observed during the early spring in association with accelerated phytoplankton growth which occurred at this time. The upper water layers in certain areas were nearly depleted in nutrients during the summer, but sufficient amounts were normally present to support limited phytoplankton growth. In general, nutrient concentration values tended to remain low throughout the summer, except for certain fluctuations in areas receiving large inputs of glacial river water; during the fall, there was typically a rise until winter maximum values were re-established. Cycling of these individual nutrients is discussed in detail in the following text.

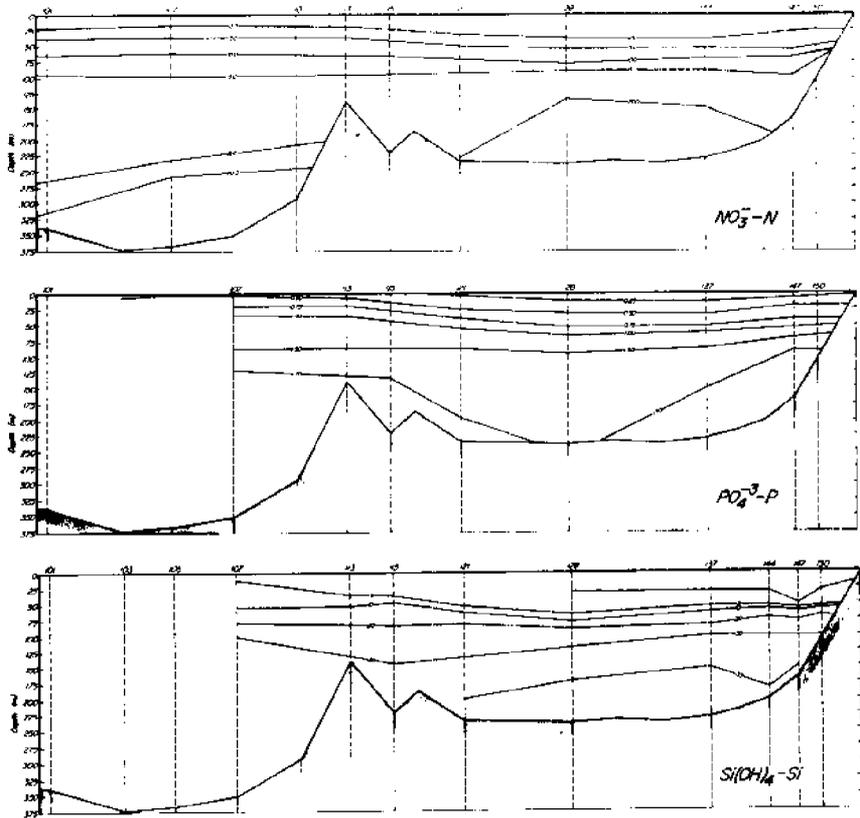


Figure 5.1 Isopleths of  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  concentrations in Port Valdez and Valdez Arm, Alaska, on 15 May 1971 (*R/V Acona* cruise 113).

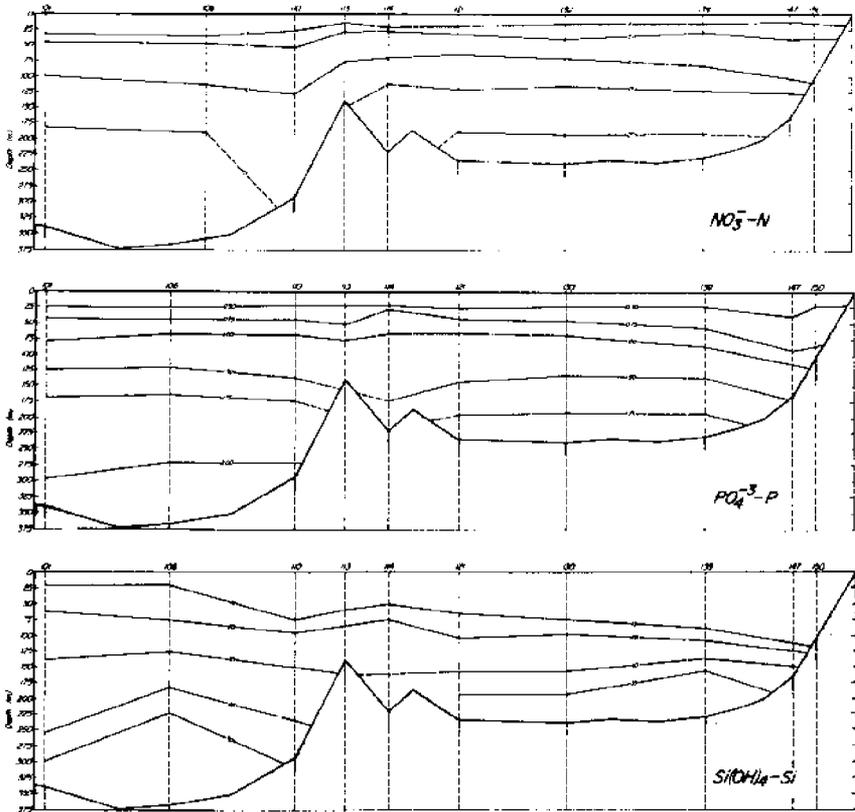


Figure 5.2 Isopleths of  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  concentrations in Port Valdez and Valdez Arm, Alaska, on 5 October 1971 (*R/V Acona* cruise 122).

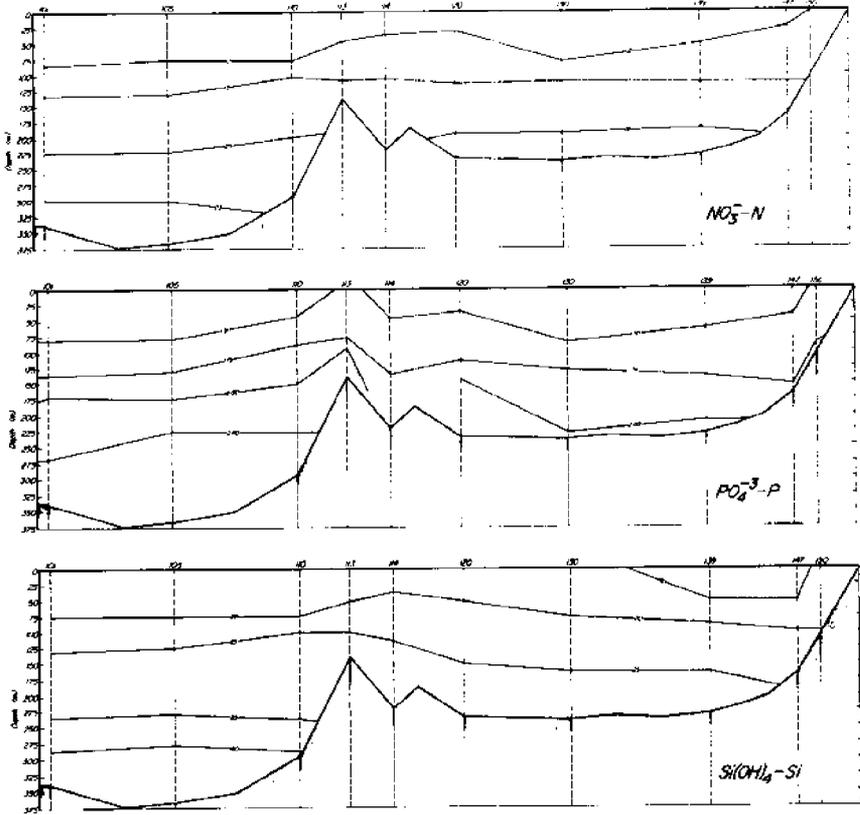


Figure 5.3 Isopleths of  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  concentration in Port Valdez and Valdez Arm, Alaska, on 9 December 1971 (R/V *Acona* cruise 125).

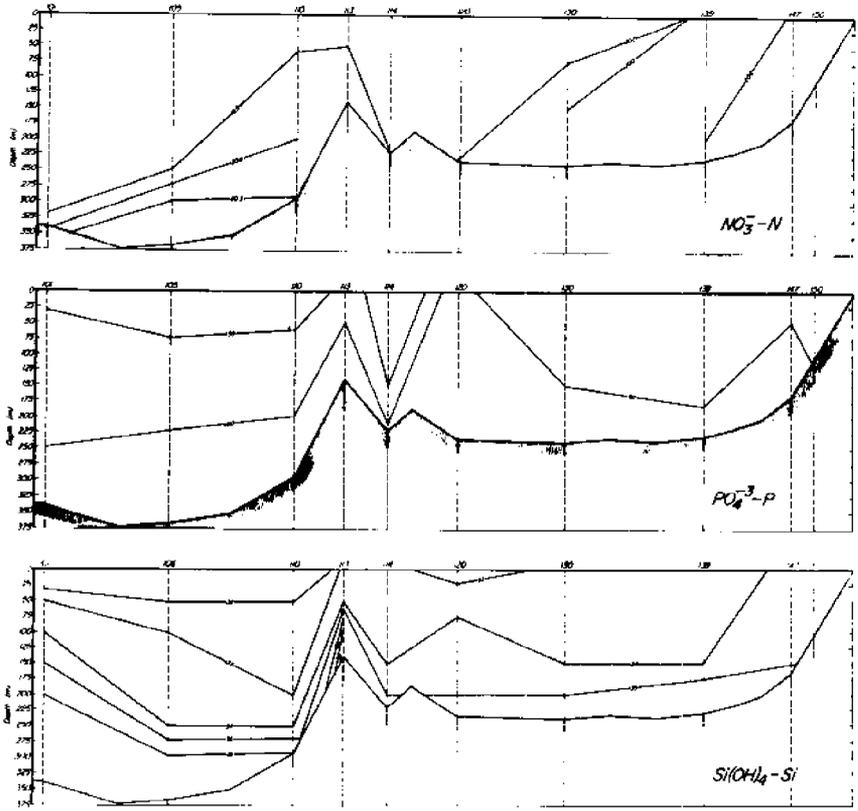


Figure 5.4 Isopleths of  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  concentrations in Port Valdez and Valdez Arm, Alaska, on 16 March 1972 (R/V *Acona* cruise 128).

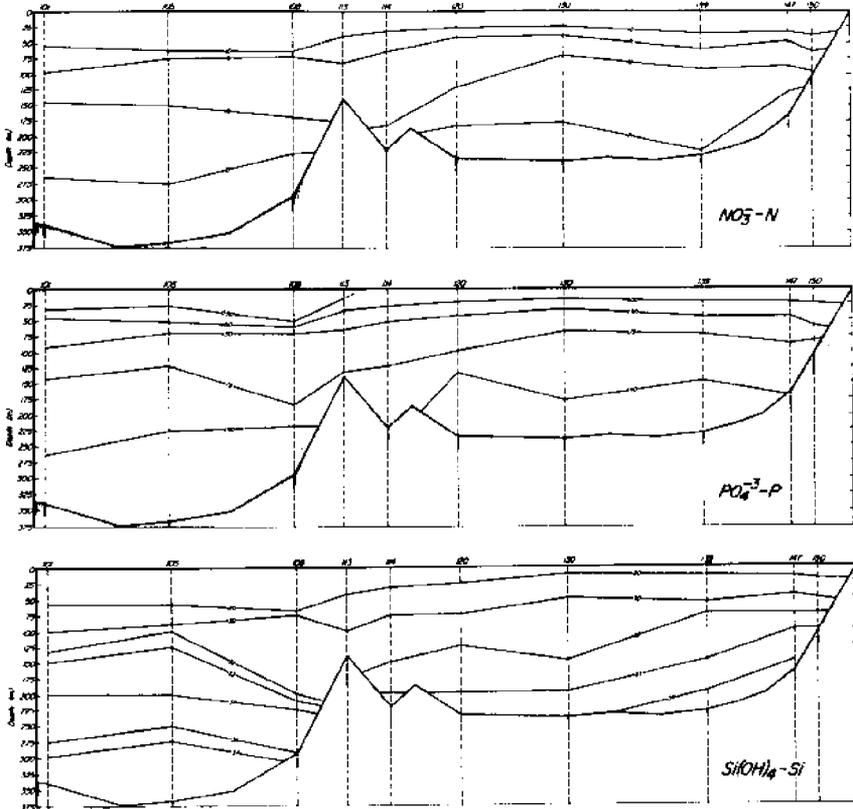
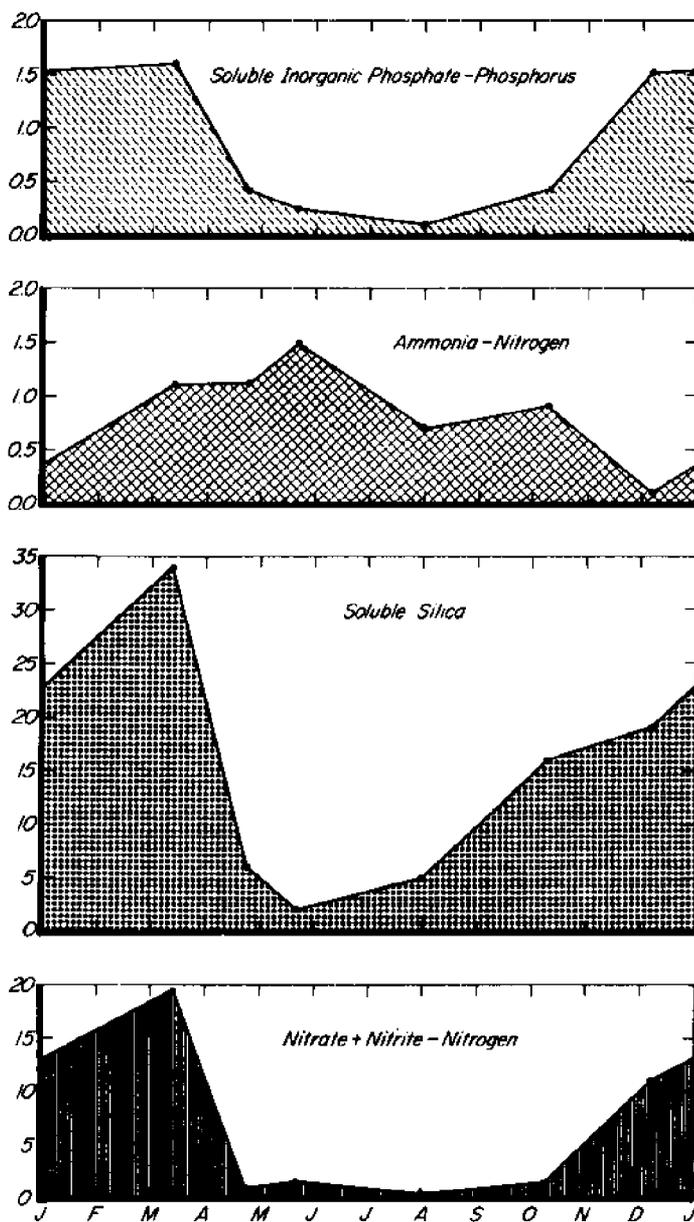


Figure 5.5 Isopleths of  $\text{NO}_3^-$ ,  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  concentrations in Port Valdez and Valdez Arm, Alaska, on 22 April 1972 (R/V *Acona* cruise 131).



**Figure 5.6** Seasonal variations in the distribution of nutrients at the 50-percent light depth at station 108 in Valdez Arm.

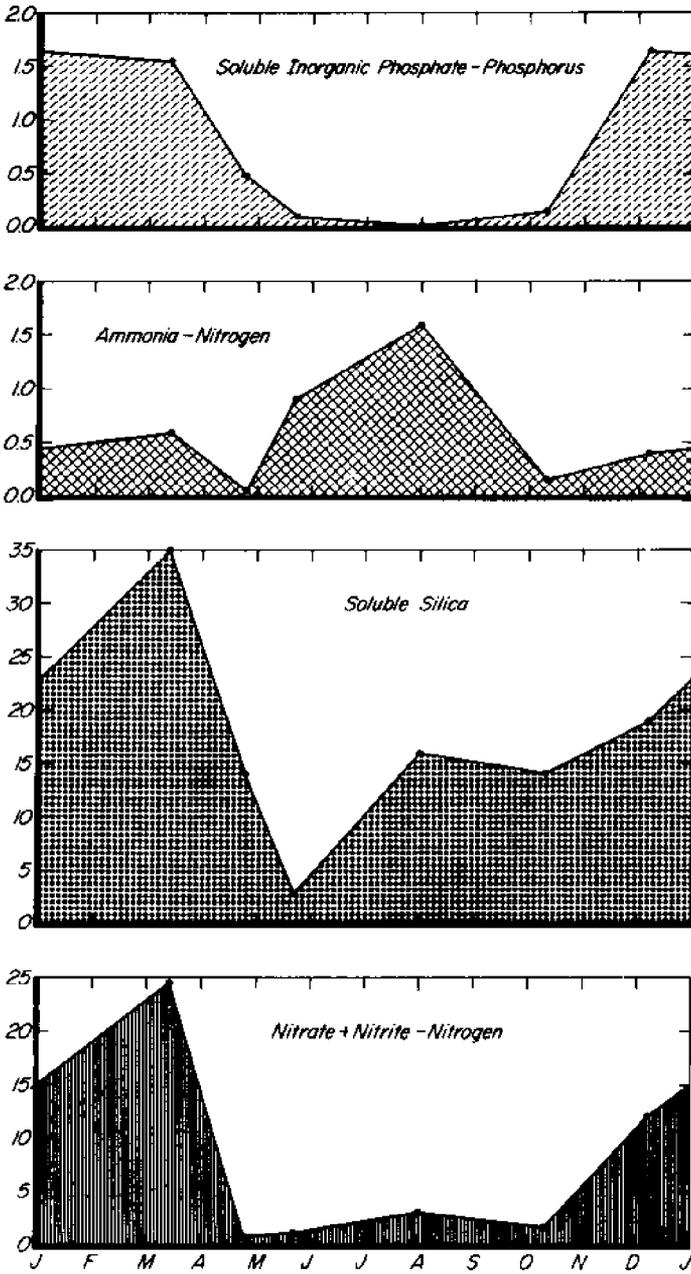


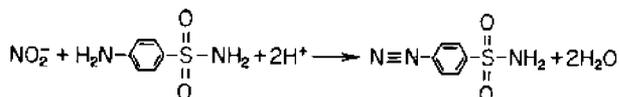
Figure 5.7 Seasonal variations in the distribution of nutrients at the 50-percent light depth at station 142 in Port Valdez.

## 5.2 Nutrient Methods

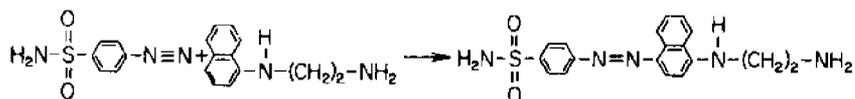
Five nutrient parameters were routinely assayed on board the *R/V Acona*: nitrate nitrogen ( $\text{NO}_3^-$ -N), nitrite nitrogen ( $\text{NO}_2^-$ -N), ammonia nitrogen ( $\text{NH}_3$ -N), soluble inorganic phosphate phosphorus ( $\text{PO}_4^{3-}$ -P), and soluble silica as orthosilicic acid [ $\text{Si}(\text{OH})_4$ -Si]. Automated analytical procedures incorporating the use of the Technicon AutoAnalyzer® were used for all nutrient determinations except ammonia, in which case the technique of Solórzano (1969) was followed, (text 5.2.3; also Data Vol. I).

### 5.2.1 Nitrite

Nitrite at  $\text{pH} \sim 1$  was diazotized with sulfanilamide for nitrogen determination by the method of Bendschneider and Robinson (1952):



The product of this reaction was subsequently coupled with N-(1-naphthyl)ethylenediamine to yield a highly colored diazo dye.



The linear function of nitrite concentration to the optical density of this dye was measured at 530 nm for 0.01-3.0  $\mu\text{M}$  concentrations of nitrite within a precision range of about 10 percent.

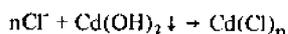
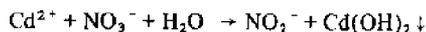
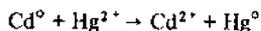
The following reagents were used in the automated procedure of Strickland and Parsons (1968):

Sulfanilamide: 10 g in 1 liter of 10% v/v HCl

N-(1-naphthyl)ethylenediamine dihydrochloride: 1 g in 1 liter distilled water

### 5.2.2 Nitrate

Nitrate was reduced to nitrite with cadmium-mercury amalgam and determined by means of the nitrite procedure. A wash of 10% w/v ammonium chloride was used to prevent buildup of reduction-inhibiting cadmium hydroxide on the surfaces of the amalgam.



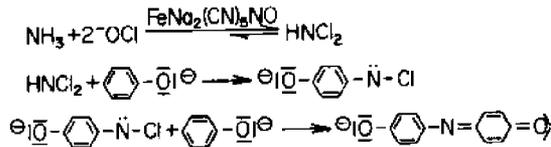
The sample was diluted on the manifold to provide linear detection of nitrate in the 0.1 to 20- $\mu$ M range.

The reduction was carried out in a 0.8 X 15-cm glass column containing mercury-cadmium amalgam, prepared by treating 40 to 60-mesh cadmium filings with 2% w/v mercuric chloride at a reduction efficiency of about 95 percent.

The automated method used in this study, developed at the Institute of Marine Science (Fairbanks) by D. M. Schell in 1967, has a precision of about 10 percent.

### 5.2.3 Ammonia

Ammonia was determined by a reaction with hypochlorite and phenol to form an indophenol blue indicator. The reaction was catalyzed by sodium nitroferrocyanide, which drives the initial N-chlorination to the right:



The following reagents were used in the Solórzano procedure (1969) for ammonia determination:

Phenol: 10 g phenol in 100 ml 95% ethanol

Sodium nitroferrocyanide: 1 g nitroferrocyanide in 200 ml of distilled water

Alkaline citrate: 100 g trisodium citrate and 5 g sodium hydroxide in 500 ml distilled water

Oxidizing solution: 100 ml alkaline citrate solution and 20 ml Clorox®

Duplicate 50-ml samples in 125-ml Erlenmeyer flasks were treated successively with 2 ml phenol solution, 2 ml sodium nitroferrocyanide solution and 5 ml oxidizing solution. The flasks were capped with aluminum foil, and the color was allowed to develop for 1 hour. The optical density at 640 nm was then read against distilled water on a Beckman D.U. Spectrophotometer using 10-cm cells. Response is linear for ammonia concentrations from 0.1-10  $\mu$ M, although precision is poor in the concentration range of 0.1-0.5  $\mu$ M. Blanks were run on distilled water used for preparing reagents and standards, and particular care was taken to prevent contamination. Only freshly deionized distilled water was used, and all glassware was rinsed copiously with 10% hydrochloric acid and distilled water just prior to use.

### 5.2.4 Phosphate

Phosphate was determined by its reaction with ammonium paramolybdate under strongly acidic conditions to form a phospho-molybdate complex, which was reduced by ascorbic acid to a *heteropoly-blue*. Small quantities of potassium antimonyl-tartrate were added to enhance color development.



Concentrations of dissolved inorganic plant nutrients (nitrogen, phosphate and silica compounds) are routinely measured onboard ship, utilizing both manual methods (left) and autoanalyzer (below) equipped for continuous monitoring while ship is underway.

#### COLORIMETRIC METHODS OF NUTRIENT ANALYSIS



This automated procedure, taken from Strickland and Parsons (1968), is an adaptation of the Murphy and Riley manual method (1962). The following reagents were used:

34 g ammonium paramolybdate and 0.25 g potassium antimonyl tartrate in 4 liters 10% v/v  $H_2SO_4$

4 g ascorbic acid in 100 ml acetone and 100 ml distilled water

A working ascorbic acid solution consisting of 20 ml of the above solution in 100 ml distilled water (prepared daily)

Maximum absorbance of the heteropoly-blue complex was at 880 nm and linear response for phosphate ranging in concentration from 0.1 to 10  $\mu M$  was obtained at this wave length by use of silicon photo-cells at a precision of about 10 percent.

### 5.2.5 Soluble silica

Soluble silica, like phosphate, was determined as a colored molybdate complex formed in acidic media from the reaction of orthosilicic acid and ammonium paramolybdate. This complex was reduced by stannous chloride to the *heteropoly-blue* form, with tartaric acid used to inhibit phosphate and arsenate interference. The following reagents were used in this automated procedure (Strickland and Parsons 1968):

Stock molybdate: 200 g ammonium paramolybdate in 4 liters distilled water

Working molybdate: 80 ml stock molybdate in 120 ml 10% v/v hydrochloric acid

Tartaric acid: 400 g tartaric acid in 3.8 liters distilled water

Stock reductant: 40 g stannous chloride dissolved in 50 ml 50% v/v hydrochloric acid

Working reductant: 2.5 ml stock reductant in 100 ml 10% v/v hydrochloric acid (prepared daily)

Linear response was obtained from the silico-molybdate complex at 700 nm, although this was not the region of maximum response. Samples were diluted with distilled water on the manifold to give linear response for soluble silica concentrations from 1-120  $\mu M$  at a precision of about 10 percent.

## 5.3 Results

### 5.3.1 Inorganic nitrogen

#### *General remarks*

The universal presence of nitrogen in all living matter is indicative of the fundamental association of this element with biological systems. The biological transformations of nitrogen in aquatic ecosystems appear to be qualitatively similar in most respects to those occurring in the better-known soil ecosystems. The various *kinds* of transformations are thus well understood, but a thorough understanding of the rates and mechanisms controlling these reactions in marine ecosystems is lacking.

The fixed nitrogen in aquatic environments is readily oxidized and reduced by biologically catalyzed reactions, and nitrogen can exist in nine different oxidation states (-3 to +5). The most abundant form of nitrogen in unpolluted aquatic systems is molecular nitrogen with an oxidation state of zero, and its general incidence is about 20 times that of other forms of nitrogen. The most plentiful forms of reduced nitrogen are generally ammonia (-3) or ammonium ion and organic nitrogen as  $\text{NH}_2$  (-2) or  $\text{NH}$  (-1) in dissolved and particulate matter. Although nitrate (+5) is normally the most abundant form of oxidized nitrogen, nitrite (+3) is also present at times.

The cycling of inorganic nitrogen (i.e.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_3$ ) was studied in Valdez Arm and Port Valdez for the year from May 1971 to April 1972, with major emphasis on the circulation of nitrogen in the euphotic zone (Figure 5.8). Ammonia, nitrate, and nitrite are available for plant growth in marine ecosystems, together with smaller amounts of other nitrogenous compounds such as urea, uric acid and amino acids produced largely by the excretion of animals. These organic sources of nitrogen can be particularly important for growth in areas that have become depleted in nitrate or other inorganic nitrogen. Also, organic compounds are converted rapidly to ammonia, which is the nitrogen compound preferred by marine phytoplankton and macrophytes.

#### *Seasonal and spatial distribution*

The locations of sampling stations occupied during the study year are given in Figures 2.1 and 2.2. Distributions of inorganic nitrogen compounds were tabulated (Data Vol. 1), and the nutrient concentrations were plotted versus depth (Data Vol. 1: Figures 5.1-5.12). Isoleths of  $\text{NO}_3^-$  for cruises 113, 122, 125, 128 and 131 were identified (Figures 5.1-5.5), and contours were mapped of the nitrate distribution at 2.5 m in Port Valdez and Valdez Arm during May and October 1971 (Figures 5.9 and 5.10). Seasonal variations were noted in the distribution of ammonia and nitrate at the 50-percent light depth in Port Valdez and Valdez Arm (Figures 5.6 and 5.7).

#### *Ammonia*

The concentrations of  $\text{NH}_3$  within the euphotic zone in Valdez Arm and Port Valdez appear to be similar to those reported for other marine coastal systems, ranging from  $<0.1$ - $2.5 \mu\text{g-atoms NH}_3\text{-N/liter}$ . Although only limited data were obtained, the concentrations of  $\text{NH}_3$  below the euphotic zone were found to vary with depth depending on station location, presumably as a result of decomposing organic matter. The near-depletion of  $\text{NH}_3$  within the euphotic zone occurred probably from its use as a nitrogen source for phytoplankton growth, since it is the preferred source of nitrogen for most marine plants. The distribution of  $\text{NH}_3$  in the euphotic zone appeared to exhibit a regular seasonal pattern (Figures 5.6 and 5.7). In general, concentrations were maximum during late spring and then declined throughout the summer to minimum values in the fall and winter. Concentrations tended to remain low even during periods of maximum vertical mixing in winter, which may infer that the maximum spring concentrations are attributable to zooplankton excretion.  $\text{NH}_3$  is the major excretory product of zooplankton, which were extremely abundant in the Arm and Port during the spring phytoplankton bloom.

The content of  $\text{NH}_3$  in the fresh water discharged into Port Valdez appears to be similar to that contained in seawater, since no elevated concentrations are evident in surface water near river inputs. In contrast, nitrate and soluble silica are abundant in river water.

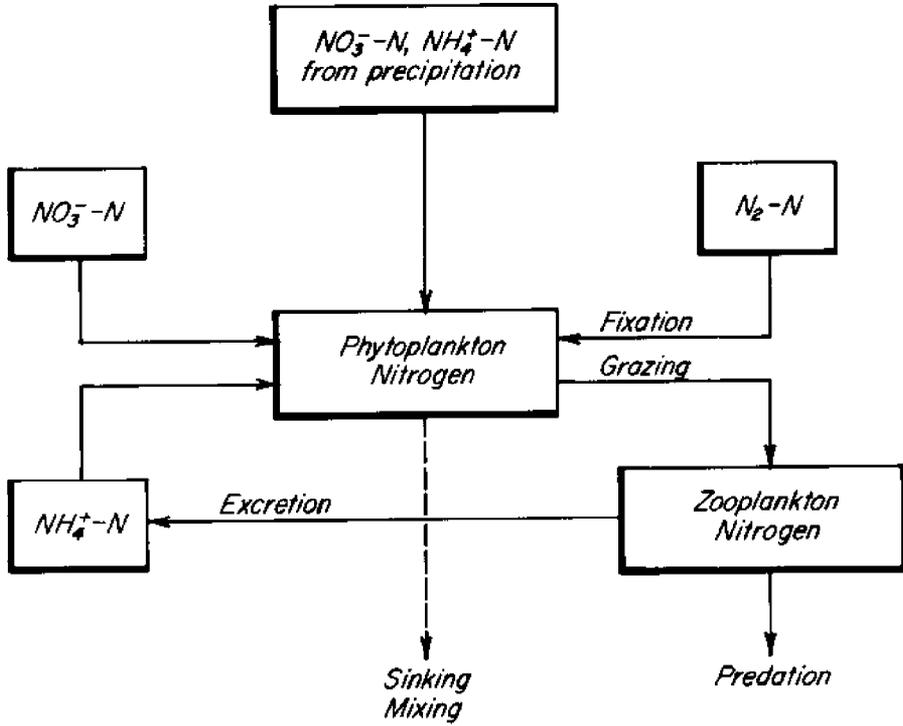


Figure 5.8 Circulation of nitrogen in the euphotic zone.

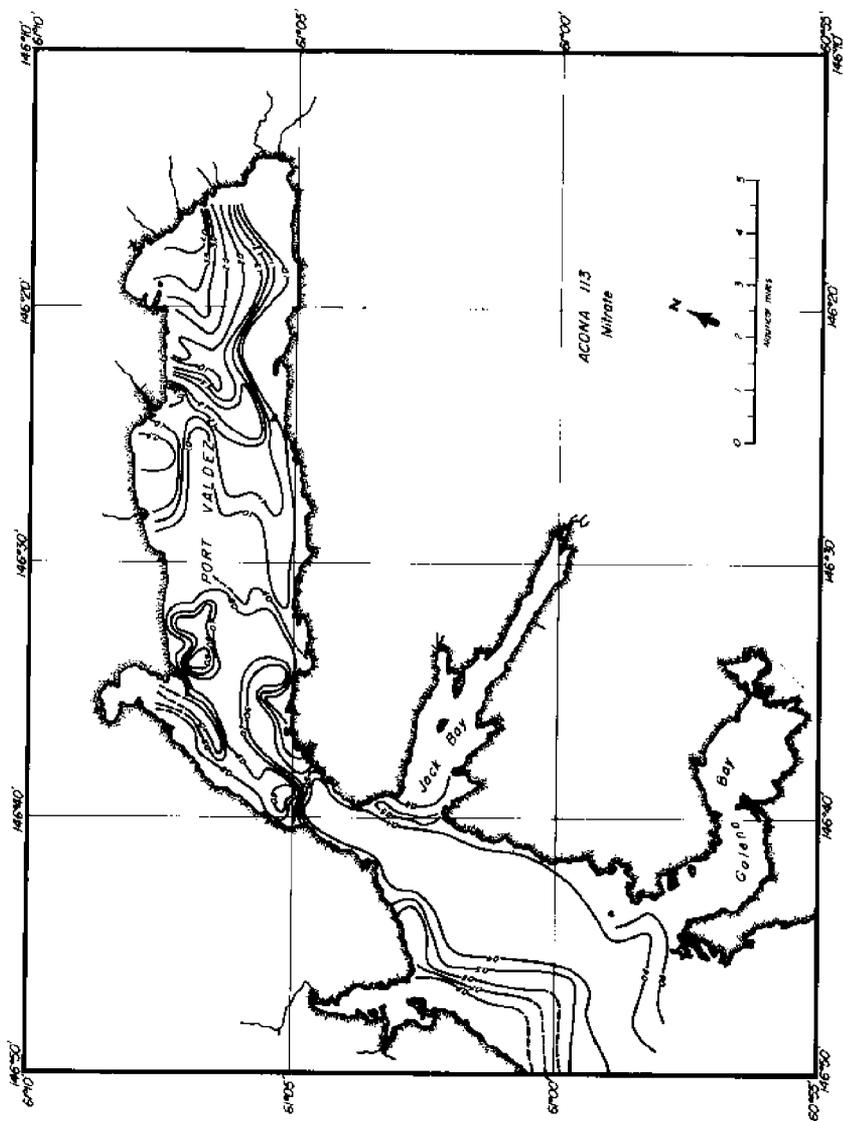


Figure 5.9 Contour map showing the distribution of  $\text{NO}_3^-$  in the near surface waters (2.5 m) of Port Valdez and Valdez Arm, Alaska, in May 1971 (R/V *Acona* cruise 113).

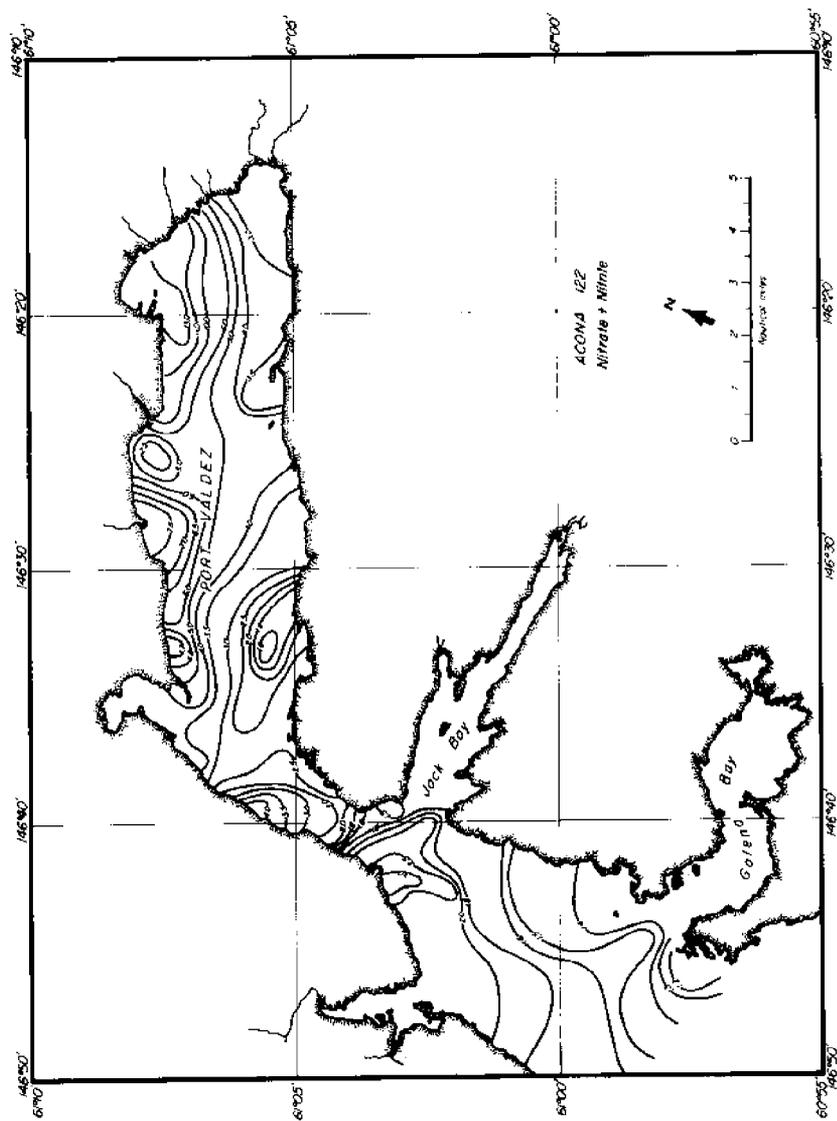


Figure 5.10 Contour map showing the distribution of  $\text{NO}_2^- + \text{NO}_3^-$  in the near surface waters (2.5 m) of Port Valdez and Valdez Arm, Alaska in October, 1971 (R/V *Acona* cruise 122).

### *Nitrate*

The concentrations of  $\text{NO}_3^-$  in Valdez Arm and Port Valdez are typical of those reported for other coastal marine systems, with nitrate levels ranging from  $<0.2$ - $20 \mu\text{g-atoms NO}_3^- \text{-N/liter}$  in the euphotic zone depending upon season and location. Concentrations below the euphotic zone increased with depth, reaching maximum concentrations of about  $23 \mu\text{g-atoms NO}_3^- \text{-N/liter}$  near the bottom.

The  $\text{NO}_3^-$  in the euphotic zone varied seasonally and with location between Valdez Arm and Port Valdez. During late spring (April; Figure 5.5),  $\text{NO}_3^-$  levels were lower in Valdez Arm than in Port Valdez, a condition brought about by the spring phytoplankton bloom (Chapter 6.3.2) which typically begins earlier in Valdez Arm than in Port Valdez. By early summer (May), the  $\text{NO}_3^-$  content had been severely depleted ( $<0.2 \mu\text{g-atoms N/liter}$ ), in both waters, although more so in Port Valdez than in Valdez Arm (Figure 5.1). Vertical mixing of the water is presumably more vigorous in the Arm at this time of year, thereby increasing the deep water transport of  $\text{NO}_3^-$  and  $\text{Si(OH)}_4$  (Data Vol. I: Figure 5.7). In winter, the concentration of  $\text{NO}_3^-$  in surface waters of the Arm and Port was again replenished by deep vertical mixing which occurs during this time of year.

Nitrate appeared to be produced in the water near the bottom of Port Valdez, as evidence by its higher concentration there than in Valdez Arm (Figure 5.2). Other nutrients such as  $\text{Si(OH)}_4$  and  $\text{PO}_4^{3-}$  did not show this distribution. The  $\text{NO}_3^-$  production resulted presumably from bacterial oxidation of  $\text{NH}_3$  to  $\text{NO}_3^-$  (nitrification). Nitrifying bacteria are known to exist in water and sediments containing sufficient levels of oxygen, which is present at high concentrations in water near the bottom of Port Valdez during all seasons (Chapter 4).

#### 5.3.2 Silica

##### *General remarks*

The concentration of silica in marine coastal systems is affected both by geological and biological processes. Silicon is present in seawater as dissolved silica, or it may be found in either biogenic or non-biogenic suspension as respectively diatomaceous or clay-particulate silica. Dissolved silica exists exclusively as monomeric  $\text{Si(OH)}_4$  at pH values commonly encountered in marine systems (Sillén 1961) and is therefore the species of silicon utilized by diatoms to construct their frustules. Because diatoms are of primary significance in marine productivity and have an absolute requirement for silicon, the cycling of silicon is of ecological importance to the marine system.

The cycling of dissolved silica ( $\text{Si(OH)}_4$ ) was studied in Valdez Arm and Port Valdez for the year from May 1971 to April 1972, with emphasis on its circulation in the euphotic zone (Figure 5.11). Silicic acid is normally present in sufficient amounts in marine coastal systems to support diatom growth, especially in association with fresh-water contributions of this required nutrient.

##### *Seasonal and spatial distribution of soluble silica*

The distribution of  $\text{Si(OH)}_4$  was recorded at sampling stations occupied during the study year (Figure 2.1) and is plotted versus depth in Data Vol. I (Figures 5.1-5.12). Isoleths of  $\text{Si(OH)}_4$  for cruises 113, 122, 125, 128 and 131 were delineated in Port Valdez and Valdez Arm, and 2.5-m contour maps were constructed for May and October 1971 (Figures 5.1-5.5, 5.12-5.13). Seasonal variations were noted in the distribution of  $\text{Si(OH)}_4$  at the 50-percent light depth in both areas (Figures 5.6 and 5.7).

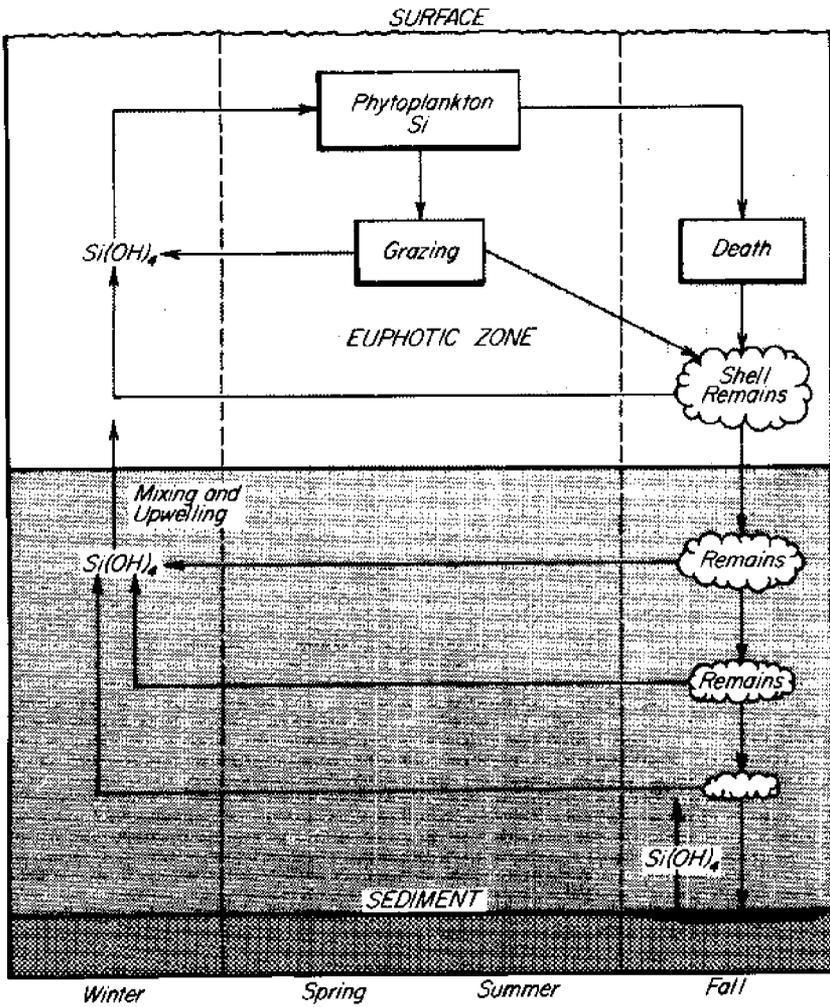


Figure 5.11 Circulation of silicon in the sea.

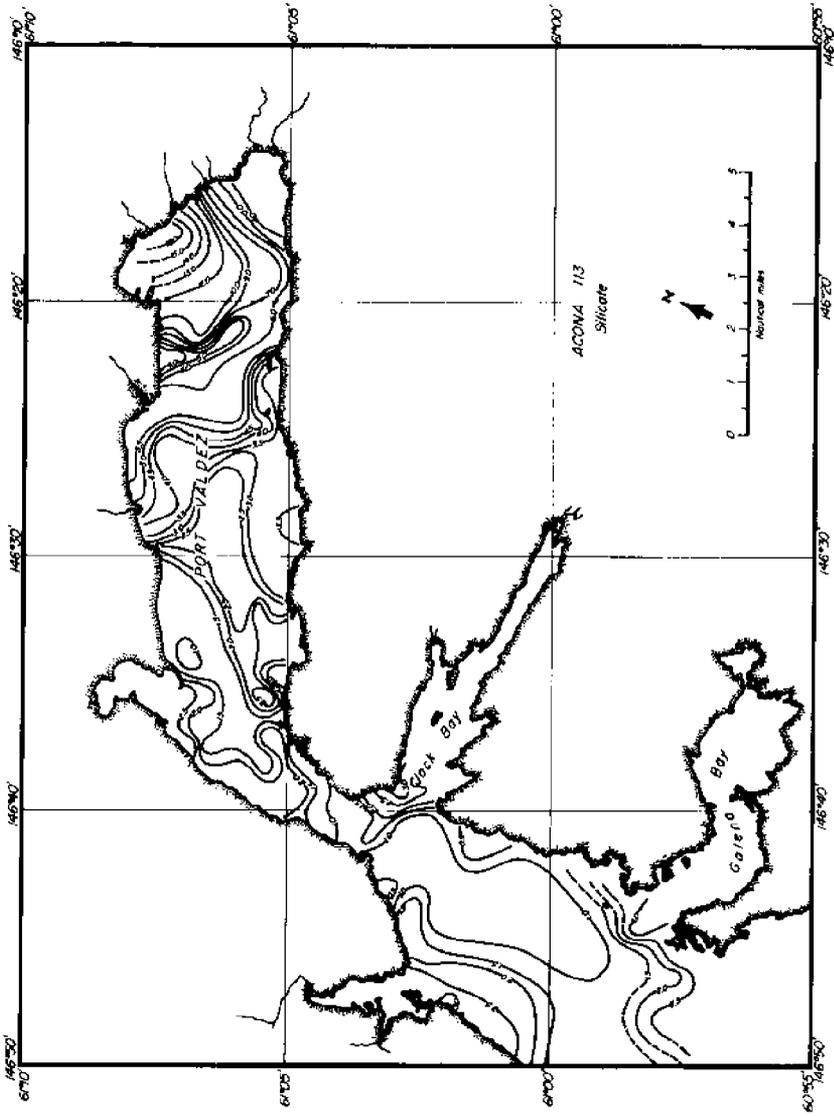


Figure 5.12 Contour map showing the distribution of  $\text{Si(OH)}_4$  in the near surface waters (2.5 m) of Port Valdez and Valdez Arm, Alaska, in May 1971 (R/V *Acona* cruise 113).

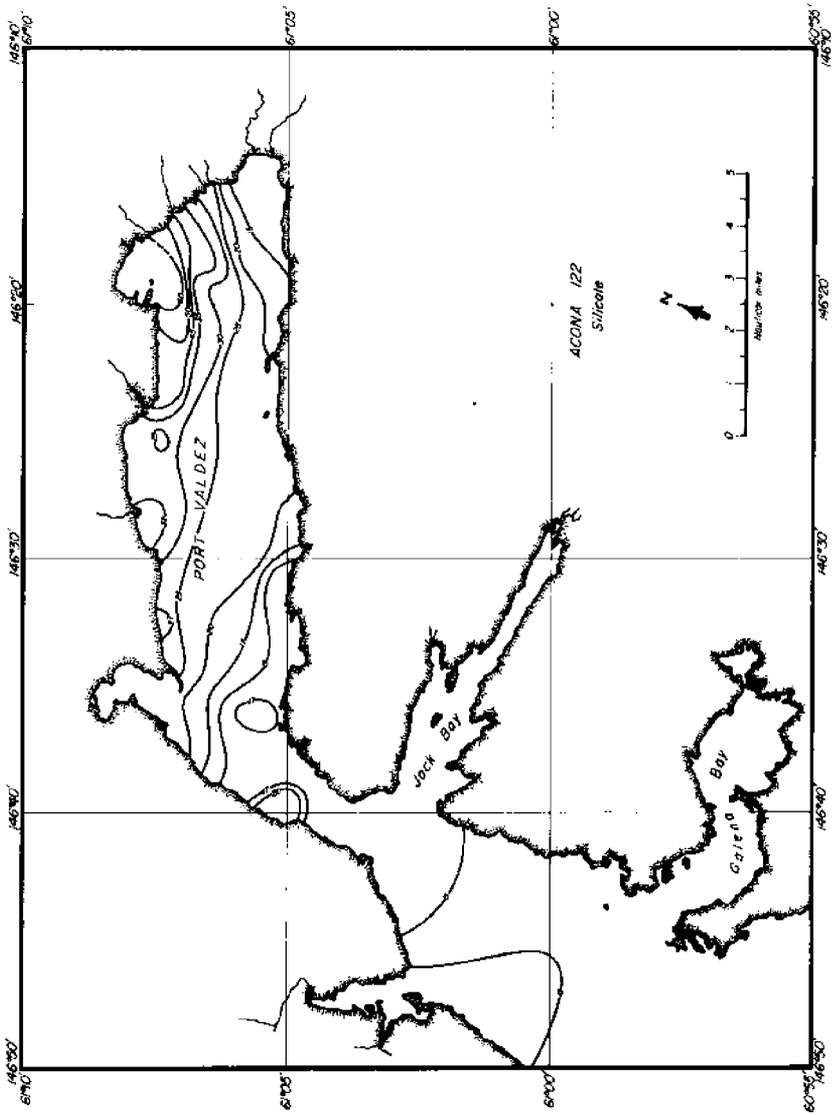


Figure 5.13 Contour map showing the distribution of  $\text{Si(OH)}_4$  in the near surface waters (2.5 m) of Port Valdez and Valdez Arm, Alaska in October, 1971 (R/V Acona cruise 122).

The concentration of  $\text{Si(OH)}_4$  in Valdez Arm and Port Valdez are typical of those reported for other Pacific coastal ecosystems, ranging from  $<1\text{-}50 \mu\text{g-atoms Si(OH)}_4\text{-Si/liter}$  in the euphotic zone depending upon season and location. The highest concentrations occurred in areas receiving river input. In general, concentrations below the euphotic zone increased with depth, reaching maximum values of about  $36 \mu\text{g-atoms/liter}$  near the bottom.

The seasonal cycle of  $\text{Si(OH)}_4$  in Valdez Arm and Port Valdez is similar to that of  $\text{NO}_3^-$  (Figures 5.6 and 5.7). During late spring (April; Figure 5.5),  $\text{Si(OH)}_4$  levels were lower in Valdez Arm than in Port Valdez; this was attributed to the spring diatom bloom which begins in Valdez Arm and then spreads into Port Valdez as the primary source of silica for diatom growth. By early summer (May; Figure 5.1) the  $\text{Si(OH)}_4$  concentration was reduced to  $<1 \mu\text{g-atoms Si(OH)}_4\text{-Si/liter}$  in some areas, especially in the subsurface waters of the Port. Surface waters at the head of Port Valdez remained enriched with  $\text{Si(OH)}_4$ , presumably as a result of low but significant fresh-water input. Concentrations were particularly elevated in summer ( $50 \mu\text{g-atoms Si(OH)}_4\text{-Si/liter}$ ) in the upper meter of water near major river inputs (Table 5.1 and Data Vol. I: Figure 5.7. River water entering Port Valdez contained large amounts of suspended and soluble silica. During the fall  $\text{Si(OH)}_4$  levels began to increase in the euphotic zone of both the Arm (Figure 5.2) and Port. In the winter the deep vertical mixing markedly increased the  $\text{Si(OH)}_4$  content of the euphotic zone until early spring (March; Figure 5.4), when the concentrations were nearly uniform throughout the entire water column. Lack of significant river discharge during the spring period resulted in similar horizontal concentrations of  $\text{Si(OH)}_4$  throughout the Arm and Port.

### 5.3.3 Inorganic phosphorus

#### *General remarks*

Phosphorus is an element required by all living matter. In seawater it exists in many forms such as dissolved organic phosphorus compounds, dissolved inorganic phosphate, insoluble and adsorbed inorganic phosphates in suspension, and organically combined phosphorus in suspension. Unlike nitrogen, which is present in several inorganic forms, inorganic phosphorus occurs nearly exclusively as dissolved phosphate present in seawater as the  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$  ion, with only negligible amounts of ionic orthophosphate ( $\text{PO}_4^{3-}$ ) or free phosphoric acid (Cooper 1948). Organically combined phosphorus is usually present in smaller amounts than inorganic phosphate, which is therefore utilized by phytoplankton as their primary source of nutrient phosphorus. The cycle of phosphorus in the sea is shown in Figure 5.14.

The cycling of dissolved inorganic  $\text{PO}_4^{3-}$  was studied in Valdez Arm and Port Valdez for the year from May 1971 to April 1972, with emphasis on its circulation in the euphotic zone. Inorganic phosphate is in intermittent short supply during intense phytoplankton blooms and can therefore become the major limiting factor in phytoplankton growth.

#### *Seasonal and spatial distribution of dissolved inorganic phosphate*

Distributions of nutrient phosphate were recorded at locations shown in Figure 2.1 and are plotted versus depth in Data Vol. I (Figures 5.1-5.12). Isoleths of  $\text{PO}_4^{3-}$  for cruises 113, 122, 125, 128 and 131 were determined (Figures 5.1-5.5), and seasonal distribution variations at the 50-percent light depth were noted in Port Valdez and Valdez Arm (Figures 5.6 and 5.7).

The measured concentrations of phosphate in Valdez Arm and Port Valdez were typical for those observed in other Pacific coastal areas, ranging from  $0.03\text{-}2.0 \mu\text{g-atoms PO}_4^{3-}\text{-P/liter}$ . Phosphate concentrations below the euphotic zone increased with depth and reached maximum levels near the bottom. Unlike the case of  $\text{Si(OH)}_4$  and  $\text{NO}_3^-$ , the river water entering the Port was depleted in  $\text{PO}_4^{3-}$ .

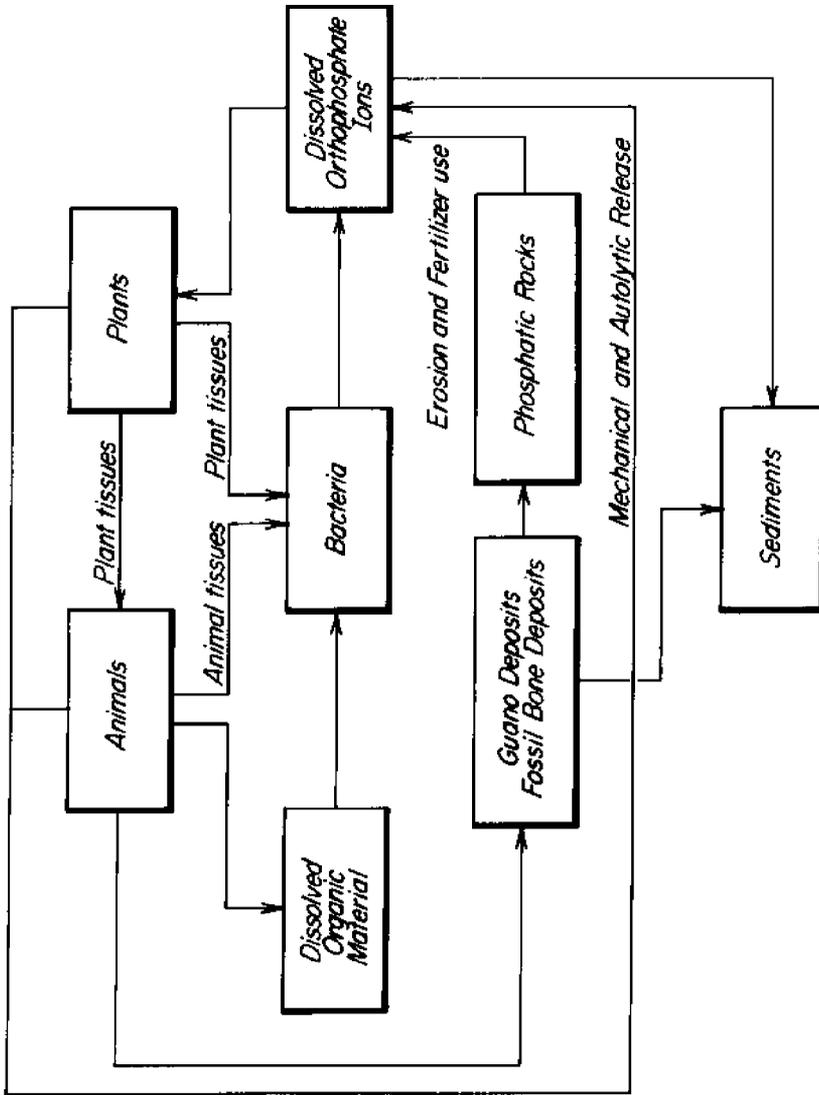


Figure 5.14 Circulation of phosphorus in the sea.

As expected, the seasonal cycle of  $\text{PO}_4^{3-}$  in Valdez Arm and Port Valdez was similar to that of  $\text{NO}_3^-$  and  $\text{Si(OH)}_4$ . This suggests that phytoplankton growth is responsible for the major concentration alternations of these nutrients. The content of  $\text{PO}_4^{3-}$  in the euphotic zone varied seasonally. As with the  $\text{NO}_3^-$  and  $\text{Si(OH)}_4$  patterns, the late spring phosphate levels were lower in Valdez Arm than in Port Valdez (Figure 5.5). By early summer (May),  $\text{PO}_4^{3-}$  had become nearly depleted ( $<0.1 \mu\text{g-atoms PO}_4^{3-}\text{-P/liter}$ , more severely so in Port Valdez than in Valdez Arm). During the summer and fall,  $\text{PO}_4^{3-}$  levels remained low and approached values that are limiting to phytoplankton growth (Figure 5.1). In the winter,  $\text{PO}_4^{3-}$  in the surface waters of the Arm and Port was again replenished by the deep vertical mixing that typically occurs during this time of year. River water entering Port Valdez was devoid of  $\text{PO}_4^{3-}$  in comparison to deep-sea water (Table 5.1), although  $\text{Si(OH)}_4$  and  $\text{NO}_3^-$  were present in large amounts.

**Table 5.1** Concentrations of nitrate, silicic acid, and phosphate (in  $\mu\text{g-atoms/liter}$ ) at two stations in Port Valdez, October 1971

	Station 150 (surface, near river input)	Station 130 (200 m, near center of Port)
$\text{NO}_3^-$	15.0	20.3
$\text{PO}_4^{3-}$	0.02	1.78
$\text{Si(OH)}_4$	51	18

#### 5.4 Summary

A seasonal study of the cycling of inorganic nitrogen (ammonia and nitrate), dissolved inorganic phosphate, and silicic acid in Valdez Arm and Port Valdez was completed for the period May 1971 to April 1972. Emphasis was directed to the circulation of these nutrients in the euphotic zone of the Valdez coastal system. These nutrients were selected for study because all are required for the production of organic matter by marine plants.

This nutrient study revealed a regular seasonal cyclicality of these important biological constituents (Figures 5.6 and 5.7), similar to that occurring in other coastal marine systems. Inorganic nitrogen, phosphate and silicic acid displayed generally the same cycles. Maximum concentrations of these nutrients occurred in the euphotic zone during the winter, a period of vigorous vertical mixing in the water column. Marked reductions occurred in the spring due to the major phytoplankton bloom at this time (Figures 5.6-5.7, 6.2). Although euphotic zone waters underwent nearly total nutrient depletion during the summer, sufficient amounts were normally present to support limited phytoplankton growth. Throughout the summer, nutrient values tended to remain low, although there were certain fluctuations particularly in areas receiving fresh-water river discharge (river water is especially rich in silicic acid and nitrate); during the fall, there was a rise in content until the large winter values were re-established through deep vertical mixing with water characteristically high in concentrations of these nutrients.

## 5.7 References

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# PART II

## THE LIVING BASELINE

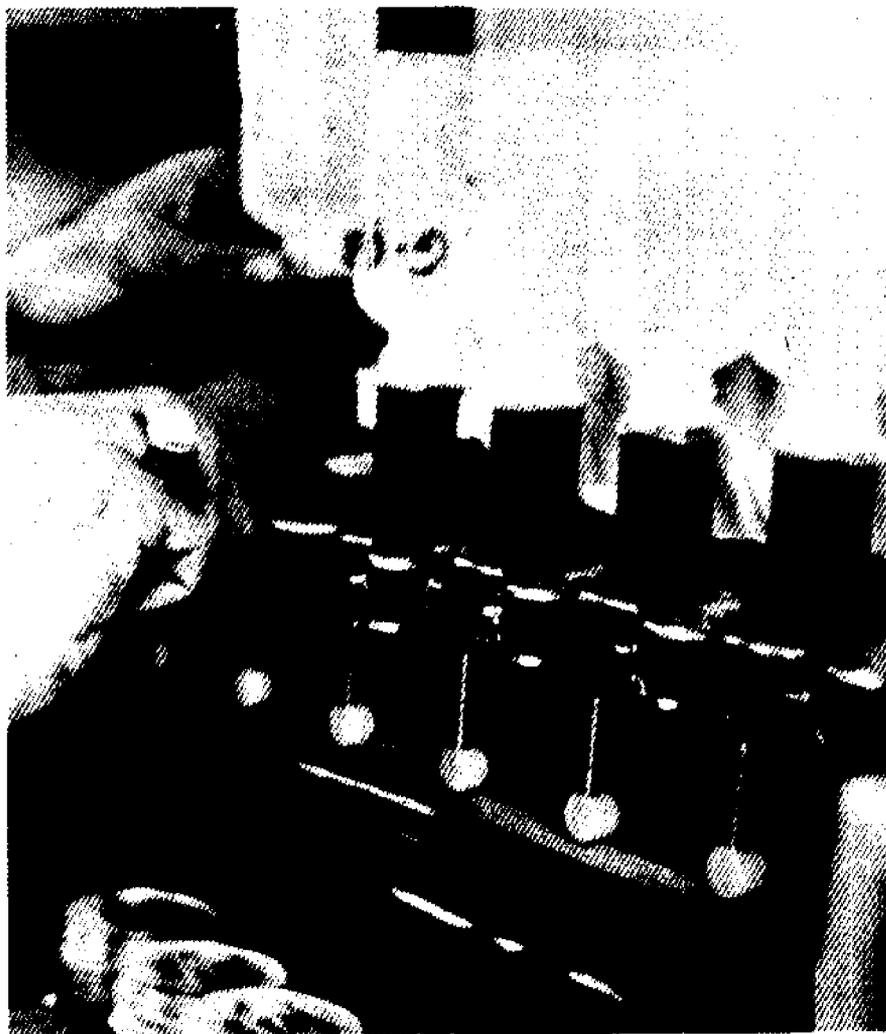


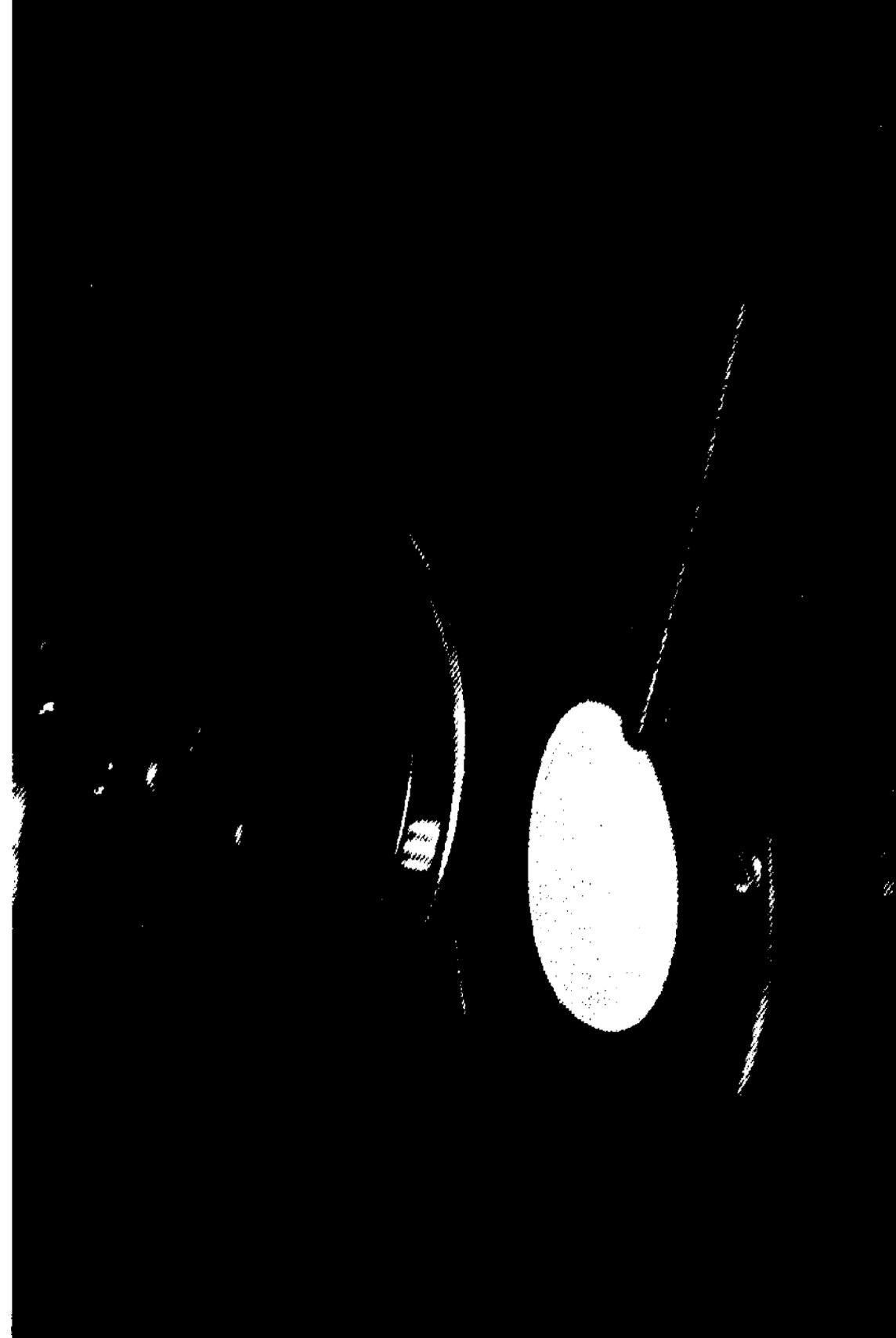
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# *Chapter 6*

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## PRIMARY PRODUCTION





## 6. PRIMARY PRODUCTION

by

J. J. Goering, W. E. Shiels, and C. J. Patton

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### 6.1 Introduction

The sun is the ultimate source of energy that drives all biological systems. Plants, whether terrestrial or marine, utilize solar radiation, carbon dioxide and inorganic nutrients to build organic matter in the process of what is termed *primary production*. All green plants obtain the energy required for their life functions through respiratory processes in which synthesized organic substances are broken down to simpler chemical forms. The net productivity of any plant depends therefore on the excess of its synthetic activities over respiration; the exact proportion will vary with the age of the plant, the season of the year and the time of day. The excess organic material thus produced may become available as food for growth of animals (Figure 6.1).

The production of organic matter by plants in the sea is of utmost importance because it initiates the entire marine food chain that terminates in larger fishes and mammals. Although production by large bottom dwelling aquatic plants (benthic macrophytes) is vital to the ecology of certain shallow areas, by far the greatest amount of aquatic photosynthesis (and probably of total photosynthesis on our planet) is carried out by microscopic plants known collectively as phytoplankton.

Marine primary productivity can be measured directly by several techniques; the  $^{14}\text{C}$  method of Steemann Nielsen (1952) is perhaps the most preferred method due to its high sensitivity. Conventional measurements of primary production alone, however, do not reveal the capacity of a region to support production at higher levels in the food chain. The  $^{15}\text{N}$  technique of measuring productivity (Dugdale and Goering 1967) makes it possible to separate the fractions of primary productivity corresponding to *new* nitrogen (nitrogen advected in as nitrate and molecular nitrogen) and *regenerated* nitrogen (ammonia) in the euphotic zone, thereby indicating the nutrient source responsible for phytoplankton growth.

In the sea it is important to distinguish clearly between the relative importance of ammonia and nitrate as sources of nitrogen for the cell and for the population. Ammonia generally results from short-term regeneration of organic nitrogen; only new sources such as nitrate from deep water or nitrogen fixation allow an increase in population size or a production shift to higher trophic levels. Under quasi-steady-state conditions ammonia can

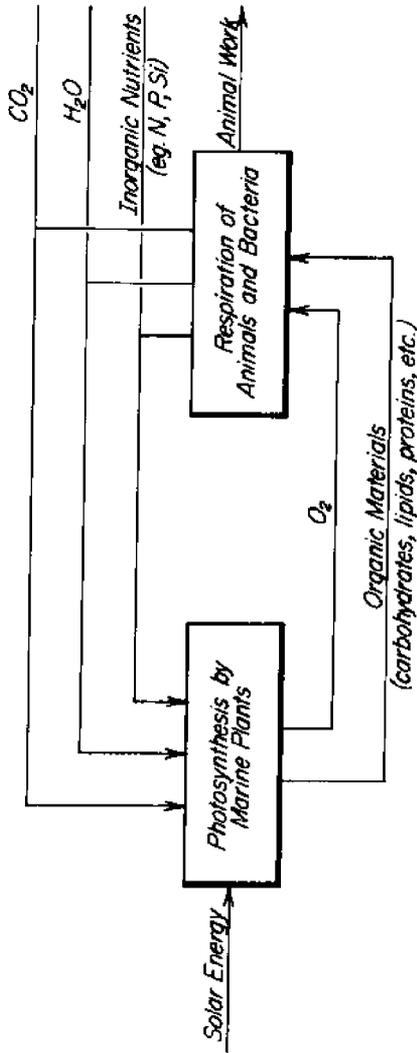


Figure 6.1 Simplified organic cycle in a community of plants and animals.

circulate indefinitely if the phytoplankton population incurs no losses. In the actual primary production system losses are incurred, however, primarily through sinking and mixing processes and by zooplankton grazing. The amount of these losses must be balanced by nitrate uptake, by nitrogen fixation, or by the assimilation of non-regenerated nitrogen from other sources such as precipitation on the sea surface and land runoff. In the sea, ammonia is therefore an important nitrogen source that maintains the cell in a healthy state and provides much of the nitrogen used in reproduction when nitrate levels are low. Assimilation of dissolved nitrate and nitrogen fixation, on the other hand, are the most important factors in nitrogen limitation of primary productivity. There appears to be only minimal nitrogen fixation in the sea (Goering et al. 1966), indicating that nitrate transport from the deep water into the euphotic zone, precipitation on the sea surface and runoff from land are the primary mechanisms controlling nitrogen limitation. In Port Valdez, runoff from land is a major contributor of nitrate during the growing season (see Chapter 5).

A study of the seasonal cycle of primary productivity in Valdez Arm and Port Valdez was conducted from May 1971 to April 1972. Locations of sampling stations are shown in Figures 2.1 and 2.2. A diagrammatic representation of the seasonal cycles appears as Figure 6.2, and productivity values are tabulated in Data Vol. I (Tables 6.1-6.6).

## 6.2 Methods

The objective of primary productivity studies is to evaluate the capacity of an ecosystem to build up, at the expense of external energy (both radiant and chemical), primary organic compounds of high energy potential for further transformation and flow to higher system levels. Earlier primary production studies in aquatic environments were generally concentrated on the flow of carbon. Dugdale and Goering (1967), however, later suggested that the flow of nitrogen through aquatic systems may reveal the capacity of a water parcel to support production at higher levels in the food chain, a property not indicated by the conventional  $^{14}\text{C}$  method.

Both the  $^{14}\text{C}$  and  $^{15}\text{N}$  techniques were used in this study to measure rates of primary production. Chlorophyll studies were also conducted to determine phytoplankton standing stocks.

### 6.2.1 Measurements of chlorophyll and phaeo-pigments

Seawater samples were collected with a 30-liter PVC Niskin bottle (General Oceanics, Inc., Model 1010) from light depths corresponding to various levels of surface incident solar radiation (100, 50, 25, 10 and 1 percent) and were transferred into 4-liter polyethylene sample bottles. One milliliter of a  $\text{MgCO}_3$  suspension was added to each bottle, and the contents were then filtered through a fine glass fiber filter (Gelman Type A). The filter containing the particulate matter was folded in half, inserted into a glassine envelope and kept frozen in the dark until extraction could be carried out.

In the laboratory the filters were added to 7 ml of spectrophotometric-grade acetone and vigorously agitated with a microspatula attached to an electric motor until the filters were completely pulverized. The tubes were next placed in a refrigerator for 20 hours, removed and allowed to come to room temperature, then centrifuged at 3000 rpm for 15 min. The clear supernatant liquid was pipetted into a 10-cm spectrophotometric cell and analyzed in a Perkin-Elmer Model 202 scanning spectrophotometer. Absorbance was recorded for each sample over the wavelength range 350-750 nm, after which the cell was removed and 1 drop of 50% HCl added. After the sample was mixed and allowed to stand for 1 minute, the sample was read a second time over the same range in order to correct the chlorophyll *a* value for phaeo-pigment.

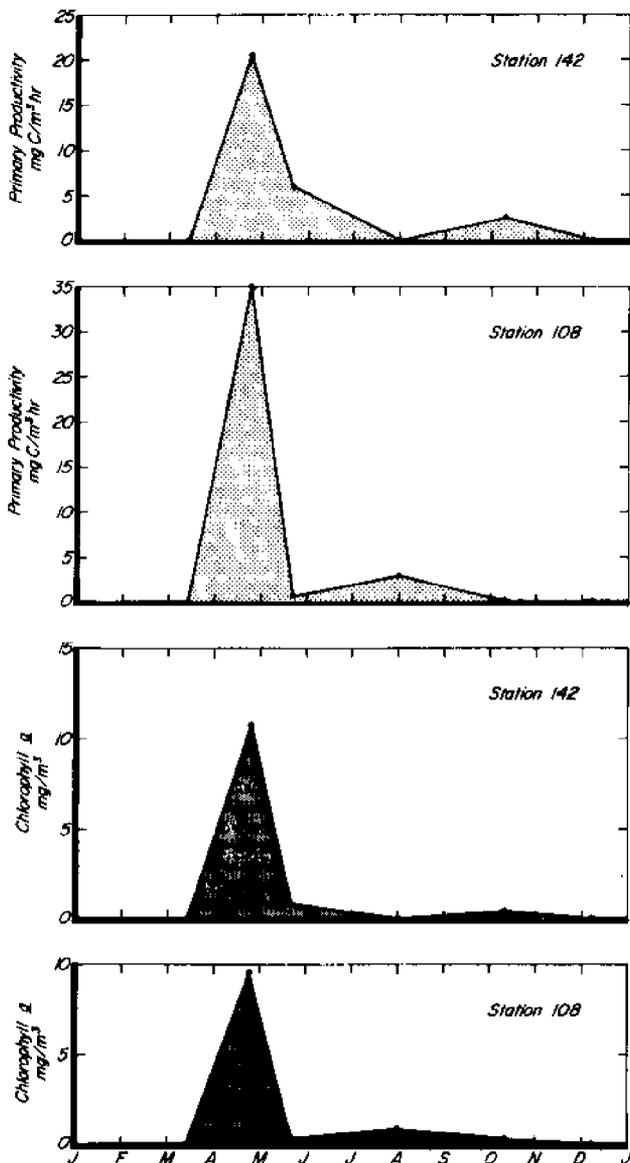


Figure 6.2 Seasonal cycles of surface carbon-14 uptake and chlorophyll *a* concentration at station 142 in Port Valdez and station 108 in Valdez Arm, Alaska.

Chlorophyll *a* and phaeo-pigment values were calculated by the method of Strickland and Parsons (1968) using the following formulas:

$$\text{mg chlorophyll } a/\text{m}^3 = \frac{26.7 (665_{\text{O}} - 665_{\text{A}}) \times v}{V \times l}$$

$$\text{mg phaeo-pigments}/\text{m}^3 = \frac{26.7 [1.7(665_{\text{A}}) - 665_{\text{O}}] \times v}{V \times l}$$

where

$665_{\text{O}}$  = extinction at 665 nm minus extinction at 750 nm before acidification

$665_{\text{A}}$  = extinction of 665 nm minus extinction at 750 nm after acidification

$v$  = volume of acetone used for extraction (ml)

$l$  = path length of spectrophotometric cell (cm)

$V$  = volume of seawater filtered (liters)

The computation of integrated values for chlorophyll *a* and phaeo-pigments in the euphotic zone was based on the summation of trapezoids, opposed to the subjective approach of drawing a curve. Points representing concentrations of chlorophyll *a* or phaeo-pigments were plotted against depth and the points connected from surface (100 percent light) to depth (1 percent light). The points were connected also to corresponding depths on the Z axis, and the areas of the four resulting trapezoids were summed. This method of integration was used also to compute particulate nitrogen values and carbon-14 and nitrogen-15 uptake rates in the euphotic zone.

#### 6.2.2 Measurements of primary production by the $^{14}\text{C}$ method

Five each of light and dark 125-ml reagent bottles were filled with seawater from the five selected light depths (100, 50, 25, 10 and 1 percent). Two milliliters of seawater were removed from each bottle, and 1 ml of a  $^{14}\text{C}\text{-HCO}_3^-$  solution (5  $\mu\text{c}$ ) was added. The 10 reagent bottles from each station were incubated for 4 hours in a deck incubator in neutral-density, light-screened pyrex glass tubes which approximated the light intensities at the depths samples. Seawater flowed continuously through the deck incubator, keeping samples at approximate sea surface temperatures.

After incubation the samples were filtered through 25-mm, 0.45 $\mu$  Millipore membrane filters (Type HA). After being rinsed with 5 ml of 0.005 N HCl solution made up with filtered seawater, the filters were placed in perforated plastic petri dishes, stored over a desiccant and returned to the laboratory for counting. There the filters were mounted on aluminum planchettes and counted on a Picker low-background  $\beta$ -counter for 10 min or  $10^5$  counts.

The rate of carbon uptake (primary productivity) was calculated according to Strickland and Parsons (1968):

$$\text{mg C}/\text{m}^3\text{-hr} = \frac{(R_{\text{S}} - R_{\text{D}}) \times W \times 1.05}{R \times N}$$

where

$R_s$  = normalized counting rate of sample planchette

$R_b$  = normalized counting rate of blank

$R$  = normalized counting rate of  $^{14}\text{C-HCO}_3^-$  solution added (ampoule contents)

$N$  = number of hours the sample was exposed to light

$W = 12,000 \times A \times F_T$

$A$  = total carbonate alkalinity

$F_T$  = factor which converts carbonate alkalinity to total carbon dioxide

The primary productivity beneath a square meter of sea surface was computed by the same method as described for chlorophyll *a*.

#### *Alkalinity and pH*

The pH values were determined as soon as possible after collection of the water samples with a Coleman Model 37A Portable pH Meter equipped with a Sargent-Welch miniature pH electrode.

Alkalinity determinations were made by the method of Strickland and Parsons (1968; pH measurement after acid addition) during the first three cruises and by back-titration for the remaining cruises as described in Chapter 4.2.

#### 6.2.3 Measurement of $^{15}\text{N}$ uptake by phytoplankton

The  $^{15}\text{N}$  method of measuring uptake of inorganic forms of nitrogen has been described by Neess et al. (1962). This procedure includes several steps: addition of  $^{15}\text{N}$ -labelled nitrogen compounds to seawater; incubation under conditions chosen for the experiment; filtration of the water through glass fiber filters (Gelman Type A) to capture the particulate matter; conversion of nitrogen compounds in the particulate matter to gaseous nitrogen by a Dumas method (Barsdate and Dugdale 1965); and determination of the nitrogen isotope ratio of the gas with a mass spectrometer and comparison of the ratio with standards to determine if any  $^{15}\text{N}$  has been incorporated into the particulate fraction during incubation.

#### *Field measurements of $^{15}\text{N}$ uptake*

Four-liter pyrex bottles, covered with neutral density light screens to simulate *in situ* light conditions, were filled with seawater from the selected light depths (100, 50, 25, 10 and 1 percent), and  $^{15}\text{N}$  labelled  $\text{NH}_4^+$  or  $\text{NO}_3^-$  ions were added as nutrient salts. The bottles were incubated for 24 hours in deck incubators under natural light and at surface seawater temperatures.

After incubation the contents of each bottle were filtered through glass fiber filters (Gelman Type A), dried, and stored over a desiccant until mass spectrometric analysis could be made.

In the laboratory the filters were combusted in a Coleman nitrogen analyzer. Combustion gases were passed through a liquid nitrogen trap to remove  $\text{CO}_2$  and water vapor, and the  $\text{N}_2$  gas was then pumped into a mass spectrometer for determination of the nitrogen isotope ratios. Uptake velocities were calculated as described below.

*Calculation of  $^{15}\text{N}$  uptake*

Sample conversion and mass spectrometry were carried out in the laboratory using a Bendix Time-of-Flight Model 17-210 or an AEI MS-20 Mass Spectrometer. The precision of the mass spectrometer is about 0.01 atom percent for replicate samples containing the natural abundance of  $^{15}\text{N}$  (0.370 atom percent).

Following mass spectrometry, the variables  $V_{\text{NO}_3^-}$  and  $V_{\text{NH}_4^+}$  were obtained directly from the following computations according to the notation suggested by Sheppard (1962):

$$V_{\text{NO}_3^-} = \frac{\rho_{1,4}}{N_1} = \frac{da_1/dt}{a_4 - a_1} \quad (1)$$

where  $\rho_{1,4}$  = the rate of transport of  $^{15}\text{N}$  nitrate from seawater into the initially  $^{15}\text{N}$  unenriched phytoplankton;  $N_1$  = the concentration of nitrogen in the phytoplankton;  $a_4$  = the atom percent  $^{15}\text{N}$  in the dissolved nitrate; and  $a_1$  = the atom percent  $^{15}\text{N}$  in the phytoplankton.  $V_{\text{NO}_3^-}$  is essentially a growth rate in terms of nitrogen and has units of  $\text{time}^{-1}$ .

Rearranging equation (1):

$$\rho_{1,4} = V_{\text{NO}_3^-} \times N_1 \quad (2)$$

The computations for  $V_{\text{NH}_4^+}$  follow in similar fashion.

The measurement of inorganic nitrogen uptake is influenced by the varying amount of nitrogen detritus which dilutes the living fraction of particulate nitrogen and thus produces an underestimate of  $V$  in the following manner:

$$V_{\text{cells}} = V_{\text{measured}} \times \frac{N_{1 \text{ cells}} + N_{1 \text{ detritus}}}{N_{1 \text{ cells}}} \quad (3)$$

$$= V_{\text{measured}} \times \frac{N_{1 \text{ total}}}{N_{1 \text{ cells}}} \quad (4)$$

$$\frac{V_{\text{NO}_3^- \text{ cells}}}{V_{\text{NH}_4^+ \text{ cells}}} = \frac{V_{\text{NO}_3^- \text{ measured}} \times \frac{N_{1 \text{ total}}}{N_{1 \text{ cells}}}}{V_{\text{NH}_4^+ \text{ measured}} \times \frac{N_{1 \text{ total}}}{N_{1 \text{ cells}}}} \quad (5)$$

Since all V determinations from a particular water sample are in error by the same factor, the effect of detritus disappears when V ratios are obtained:

$$\frac{V_{\text{NO}_3^- \text{ cells}}}{V_{\text{NH}_4^+ \text{ cells}}} = \frac{V_{\text{NO}_3^- \text{ measured}}}{V_{\text{NH}_4^+ \text{ measured}}} \quad (6)$$

The effect of detritus also cancels when the transport rates are computed:

$$p_{14 \text{ cells}} = V_{\text{NO}_3^- \text{ cells}} \times N_{1 \text{ cells}} \quad (7)$$

$$= V_{\text{NO}_3^- \text{ measured}} \times \frac{N_{1 \text{ total}}}{N_{1 \text{ cells}}} \times N_{1 \text{ cells}} \quad (8)$$

$$= V_{\text{NO}_3^- \text{ measured}} \times N_{1 \text{ total}} \quad (9)$$

The addition of tracer nitrate and ammonia to raw seawater results in increased rates of nitrogen uptake from those sources unless the pre-existing levels are already high. Addition of the labelled compound was therefore limited to 10 percent of that already present in the water, or the labelled compound was added in large enough amounts to induce maximum rates of uptake.

#### *Particulate nitrogen*

Seawater samples for particulate nitrogen determination were collected and filtered in the same manner as for chlorophyll *a*; but eliminating the addition of  $\text{MgCO}_3$ . After filtration the filters were dried and stored over desiccant until laboratory analyses could be performed.

In the laboratory the filters were combusted in a Coleman nitrogen analyzer, and the volume of  $\text{N}_2$  gas evolved was measured. After making corrections for temperature and pressure, the amount of nitrogen in the form of particulate organic matter could be calculated for a known volume of seawater. Calculation were made as follows:

$$\mu\text{g N/liter} = \frac{P_c \times V_c}{T} \times \frac{0.449}{V}$$

where

$P_c$  = corrected barometric pressure (mm Hg)

T = temperature ( $^{\circ}$ K)

$V_c$  = corrected nitrogen volume ( $\mu$  liter)

V = volume of seawater filtered (liters)

## 6.3 Results

### 6.3.1 Introduction

The seasonal variations in the production of organic matter in Valdez Arm and Port Valdez were studied for one year (May 1971-April 1972). The  $^{14}$ C and  $^{15}$ N methods of measuring primary production were employed in this study. An example of the precision attainable with the  $^{14}$ C method is given in Table 6.1. Spatial and temporal distributions of productivity and standing concentrations of chlorophyll *a* were emphasized.

**Table 6.1** Mean, range, standard deviation, and standard error of 10 replicate seawater samples incubated with carbon-14 for 4 hours under artificial light during December 1971 (*Acona* cruise 125)

Sample No.	1	2	3	4	5	6	7	8	9	10
Sample (less background) cts/min	45.4	51.6	50.7	40.6	52.9	39.5	50.0	54.8	63.7	79.0
Precision: Mean 52.82, range 39.5 standard deviation 11.56, standard error $\pm$ 3.66										

The seasonal primary productivity regime of Valdez Arm and Port Valdez appeared to be typical of other marine systems of high northern latitudes. In general, a large spring bloom of phytoplankton occurred in April, which resulted in maximum levels of chlorophyll and primary productivity (Figures 6.2 and 6.3). The phytoplankton outburst at this time of year consisted mainly of diatoms (see Chapter 7). Following the spring peak, the rates of productivity and crops of phytoplankton tended to remain fairly low throughout summer and fall, although the standing stock varied in amount and kind with month and place. In winter the phytoplankton growth virtually ceased, and only low productivity and few phytoplankton cells were observed in the marine system under study.

### 6.3.2 Seasonal trends in $^{14}$ C primary production and chlorophyll *a*

The distribution of primary productivity and chlorophyll *a* for station 108 in Valdez Arm and for station 142 in Port Valdez are given in Figures 6.2 and 6.3. Both exhibit generally the same seasonal pattern.

A typical flowering of phytoplankton in spring resulted in maximum rates of primary production and chlorophyll *a* concentrations that coincided with the increase in daylight (see Figures 6.2 and 6.4). The temperature of the surface water also increased slightly at this time. Nutrient nitrate, silicate and phosphate were at maximal concentrations prior to



## STUDIES OF BIOLOGICAL PRODUCTION

Plankton net is prepared (above) for tow to collect particulate organic matter for productivity measurements by radioactive tracer method.



Seawater samples are drawn from 5-liter Niskin bottles in study of nitrogen utilization dynamics.

recovery of zooplankton net



PRIMARY PRODUCTION

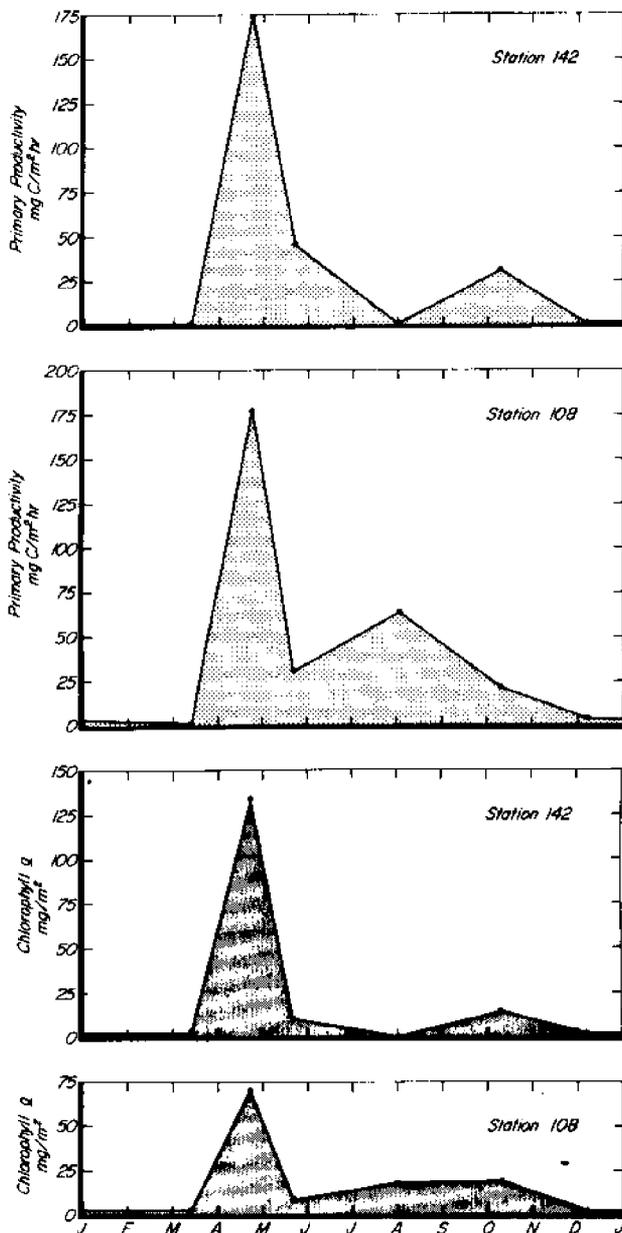


Figure 6.3 Seasonal cycles of carbon-14 uptake and chlorophyll a concentration throughout the euphotic zone for station 142 in Port Valdez and station 108 in Valdez Arm, Alaska.

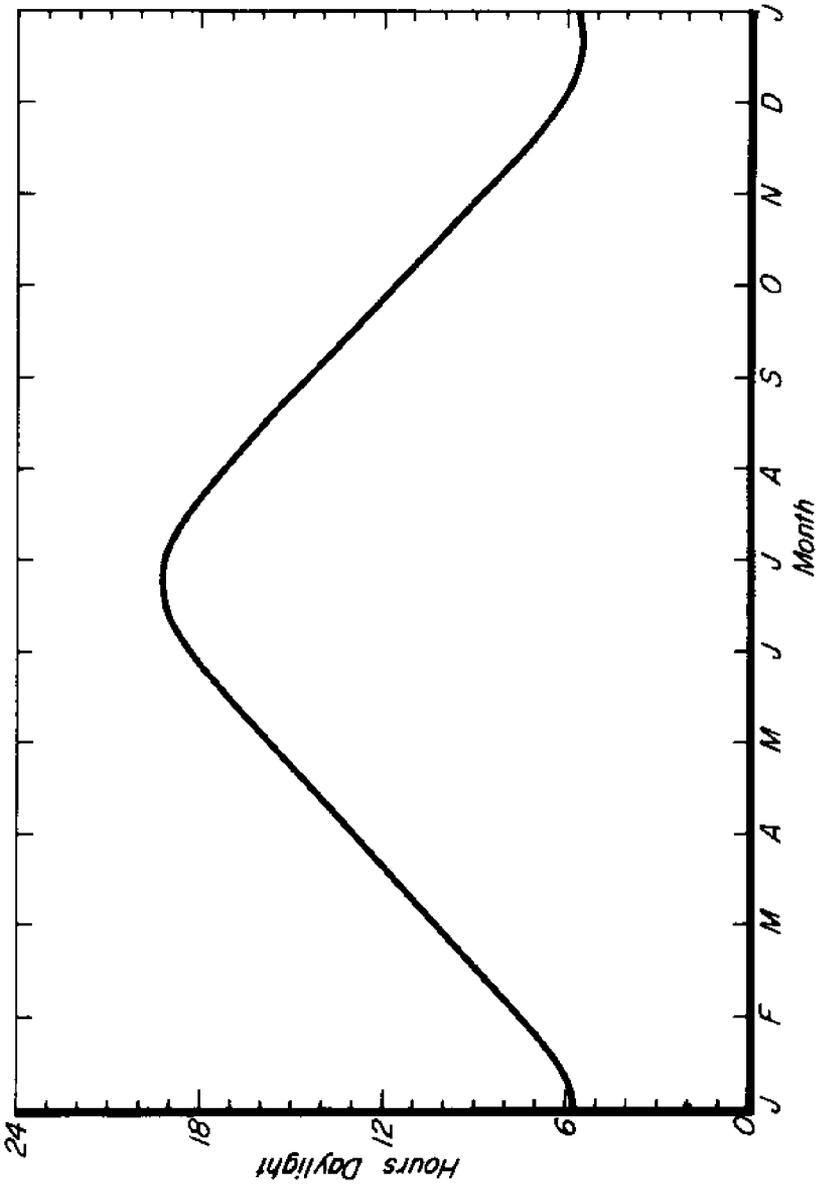


Figure 6.4 Seasonal changes in hours of sunlight for a latitude of 61°N (Port Valdez). Taken from Johnson and Hartman, 1969.

initiation of the bloom (Figure 5.6). The rapid diatom growth in the spring was probably a result of the increasing daylight and abundant nutrient supply. The extensive growth of diatoms and other phytoplankton soon depleted the nutrients in the upper layers of Valdez Arm and Port Valdez, however. Despite the favorable summer light conditions in Valdez Arm, the amount of phytoplankton growth became limited by the lack of nutrients and the establishment of a thermocline which restricted transport of nutrients to the surface from the richer waters below. In Port Valdez, particularly near major river mouths, light was a severely limiting growth factor during periods of high fresh-water discharge. The heavy sediment load reduced light penetration at the head end of the Port to such an extent that only about the upper first meter contained adequate light for phytoplankton growth (Figure 6.3). In October and November, the cooling of the surface water and increased winds broke up the thermocline and allowed mixing. A supply of nutrients therefore became available again in the upper layers, but the burst of phytoplankton growth that sometimes occurs in coastal ecosystems during late fall was not pronounced in the Valdez Arm and Port Valdez region, due probably to the absence of adequate light at this time of year. During the winter, phytoplankton growth virtually ceased, although concentrations of nitrate, silicate and phosphate built up to late winter maxima.

### 6.3.3 Surface distribution of primary production

The seasonal variation in the distribution of primary production and plant pigments within Port Valdez was more pronounced than in Valdez Arm (Figures 6.3, 6.5-6.7; also Data Vol. I). Such large variations suggest that fresh water and suspended sediments were significantly inhibiting organic production, particularly in the head of the Port during the summer period of maximum fresh-water input; Valdez Arm received comparably little direct fresh-water influx. Data presented in Figure 6.3 clearly demonstrate the seasonal difference in total water column productivity within Port Valdez. The primary productivity at station 142 near the head of the Port showed about a 20-fold reduction from the late spring to summer values, but near the Narrows productivity remained about the same during these two periods (Figure 6.5). The summer productivity measured just outside of Valdez Narrows was higher than that recorded in late spring. This summer increase in productivity was brought about probably by low but significant additions of nutrients in the surface water leaving the Port, which receives large amounts of nutrients from summer river input.

The marked reduction of phytoplankton growth and hence primary productivity in Port Valdez during summer probably resulted from light limitation imposed by the influx in silt-laden river water. Euphotic zone depths at the head of the Port were reduced to <1 m. The salinity of the water was also reduced to <1 ‰ (see Figure 2.17), which probably likewise inhibited the growth of most marine species of phytoplankton. Therefore, a light and salinity environments adequate for marine phytoplankton growth did not exist in much of the Port during the summer.

### 6.3.4 $^{15}\text{N}$ uptake

The uptake of phytoplankton of  $^{15}\text{N}$ -labelled ammonia and nitrate was measured at selected stations in Port Valdez and Valdez Arm to assess primary production and nitrogen uptake kinetics. The  $^{15}\text{N}$  technique served also to separate the fractions of euphotic-zone primary productivity corresponding to *new* nitrogen (nitrate and molecular nitrogen) and *regenerated* nitrogen (ammonia), thereby indicating the nutrient source responsible for phytoplankton growth and the amount of primary production that is available for consumption at higher trophic levels.

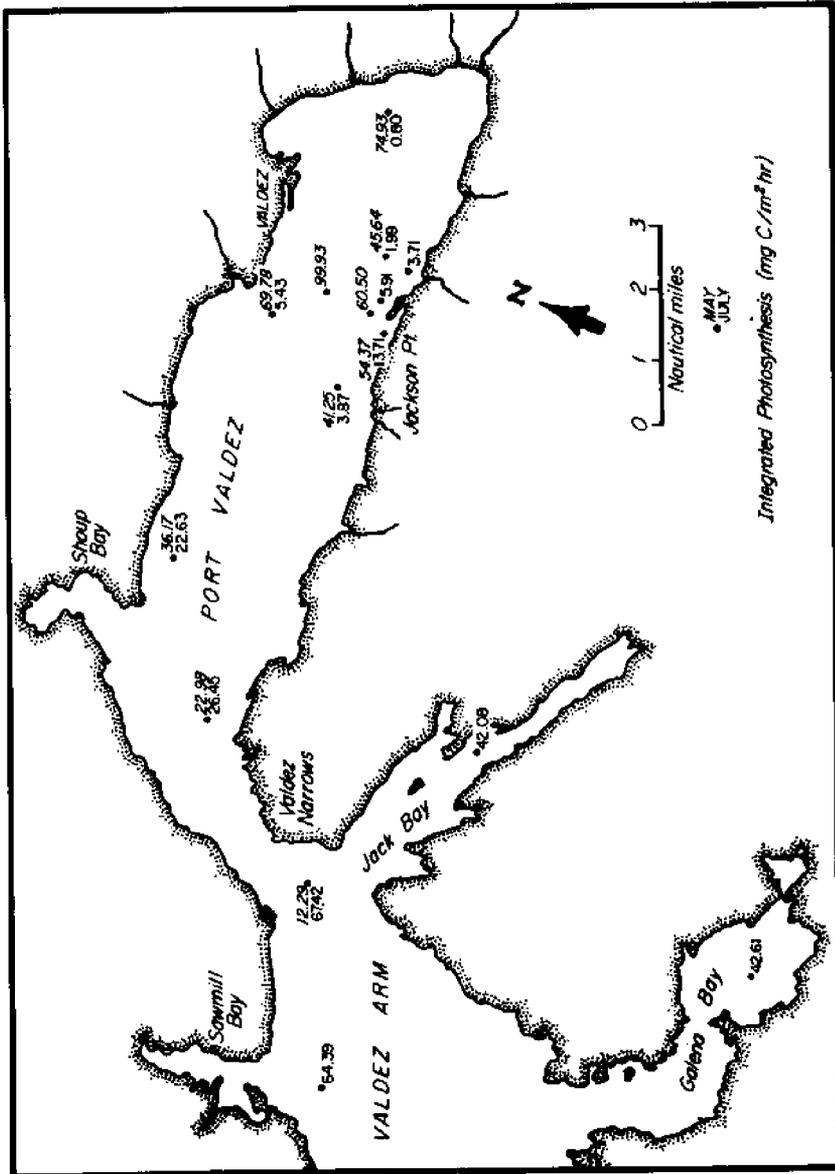


Figure 6.5 Map of integrated phytoplankton primary production in Valdez, Alaska, region in late spring (R/V. Aconaz cruise 117).

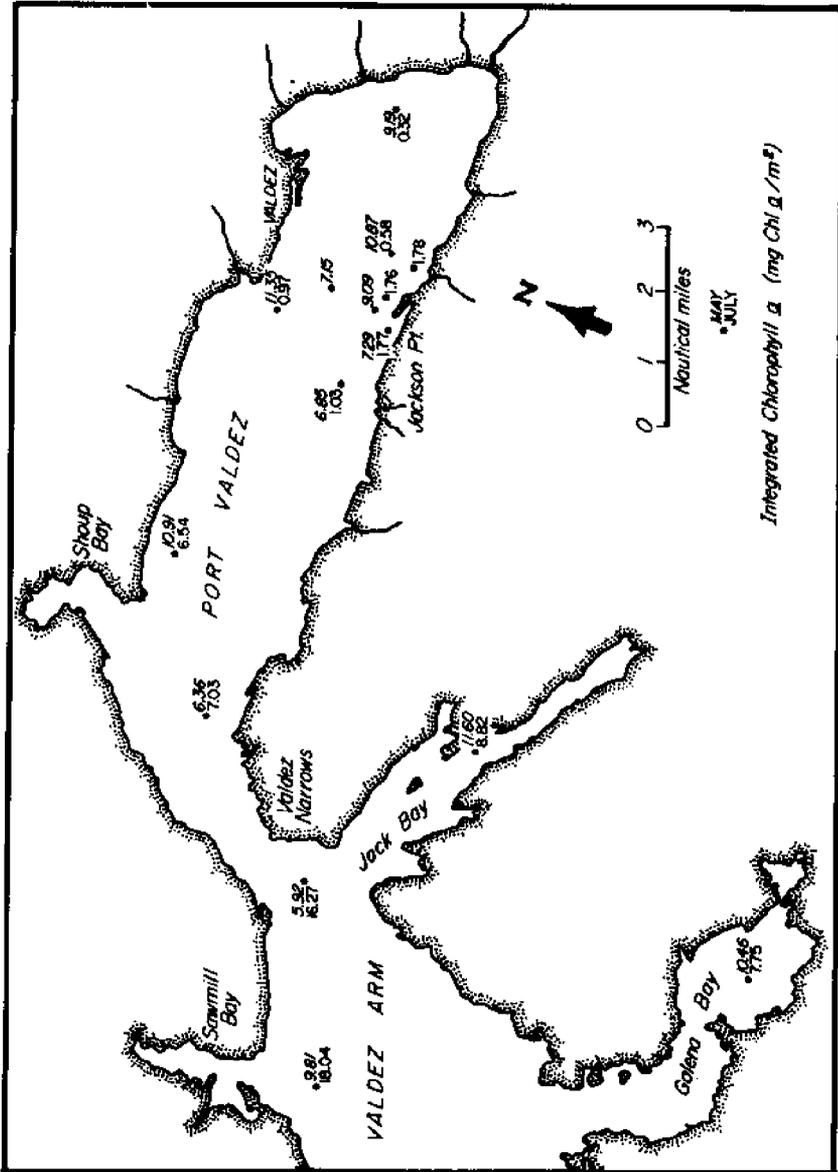


Figure 6.6 Map of integrated chlorophyll *a* values in the Valdez, Alaska, region in late spring (R/V Acona cruise 113) and summer (R/V Acona cruise 117).

*Kinetics of nitrate and ammonia uptake by phytoplankton*

The uptake of nitrate and ammonia by pure cultures of phytoplankton is known to obey the Michaelis-Menten kinetics equation (Dugdale 1967; Eppley et al. 1969), an expression that has been shown to hold for heterogeneous populations of marine phytoplankton (MacIsaac and Dugdale 1969). The equation for catalyzed nitrate uptake is expressed:

$$V_{\text{NO}_3^-} = V_{(\text{NO}_3^-)\text{max}} \frac{N}{N + K_T(\text{NO}_3^-)}$$

where

$V_{\text{NO}_3^-}$  = fractional uptake of nitrate by algae

$V_{(\text{NO}_3^-)\text{max}}$  = maximum fractional uptake rate

$N$  = ambient concentration of nitrate

$K_T(\text{NO}_3^-)$  = half-saturation transport constant (i.e., the concentration of nitrate at which  $V_{\text{NO}_3^-} = \frac{1}{2}V_{(\text{NO}_3^-)\text{max}}$ )

The Michaelis-Menten expression for ammonia uptake is similar. When  $V_{\text{NO}_3^-}$  for natural populations of marine algae was plotted against ambient nitrate concentrations, a resulting rectangular hyperbola confirmed that Michaelis-Menten kinetics were obeyed.

It would be valuable in ecological studies to be able to predict which species will result from various ambient nitrate and ammonia concentrations. One important aspect of nutrient limitation theory is its potential application to predicting phytoplankton succession that results from competition for limiting nutrients; the half-saturation transport constant appears to be useful in these predictions. There is also evidence that these constants for marine phytoplankton are species-specific and temperature-dependent, but they are not influenced by irradiance or other external factors which influence growth rate (Eppley and Thomas 1969).

The kinetics for ammonia and nitrate uptake by natural populations of phytoplankton residing in Port Valdez (station 157, Figure 2.1) were determined in July 1971. The population of phytoplankton within the Port at this time of year was dominated by the dinoflagellate *Ceratium longipes* (Table 6.2). Half-saturation constants for ammonia uptake of 0.15  $\mu\text{g-atoms NH}_3\text{-N/liter}$  and for nitrate uptake of 1.20  $\mu\text{g-atoms NO}_3\text{-N/liter}$  were obtained. These values are similar to those reported for other natural near-shore phytoplankton populations (Goering 1972).

According to the theory of nutrient limitation advanced by Dugdale (1967), the kinetics data presented here may be used to indicate the presence or absence of nitrogen limitation on growth of phytoplankton. When ambient ammonia or nitrate is taken up at a rate that lies at a point along the plateau of the hyperbola (Figure 6.7), that nutrient can be assumed *non-limiting*. When the uptake rate of ambient ammonia or nitrate intersects the slope of the hyperbola, the concentration can be considered *limiting* to phytoplankton growth.

Table 6.2 Nitrogen-15 and carbon-14 uptake rates by phytoplankton during spring and summer at Jackson Point, Port Valdez

Depth (m)	NO <sub>3</sub> <sup>-</sup> uptake (μg-atoms NO <sub>3</sub> <sup>-</sup> -N/liter-hr)	NH <sub>3</sub> uptake (μg-atoms NH <sub>3</sub> -N/liter-hr)	Percent NO <sub>3</sub> <sup>-</sup> * uptake	Carbon uptake (μg-atoms HCO <sub>3</sub> <sup>-</sup> -C/liter-hr)	Ratio C uptake to N uptake
31 July 1971					
0	0.0003	0.0091	2.8	0.0508	5.4
5.0	0.0006	0.0397	1.5	0.0350	0.9
10.0	0.0002	0.0230	0.9	0.0250	1.1
15.0	0.0001	0.0108	0.9	0.0100	0.9
20.0	0.0001	0.0025	2.0	0.0058	2.3
25 April 1972					
0	0.0184	0.0019	90.6	0.8525	42.0
2.0	0.0038	0.0023	62.8	1.5775	258.6
3.5	0.0102	0.0022	81.9	1.6917	136.5
5.0	0.0103	0.0026	79.6	1.3858	107.4
10.5	0.0009	0.0057	13.3	0.1467	22.4

\* % NO<sub>3</sub><sup>-</sup> uptake =  $\frac{\text{NO}_3^- \text{ uptake}}{\text{NO}_3^- \text{ uptake} + \text{NH}_3 \text{ uptake}} \times 100$

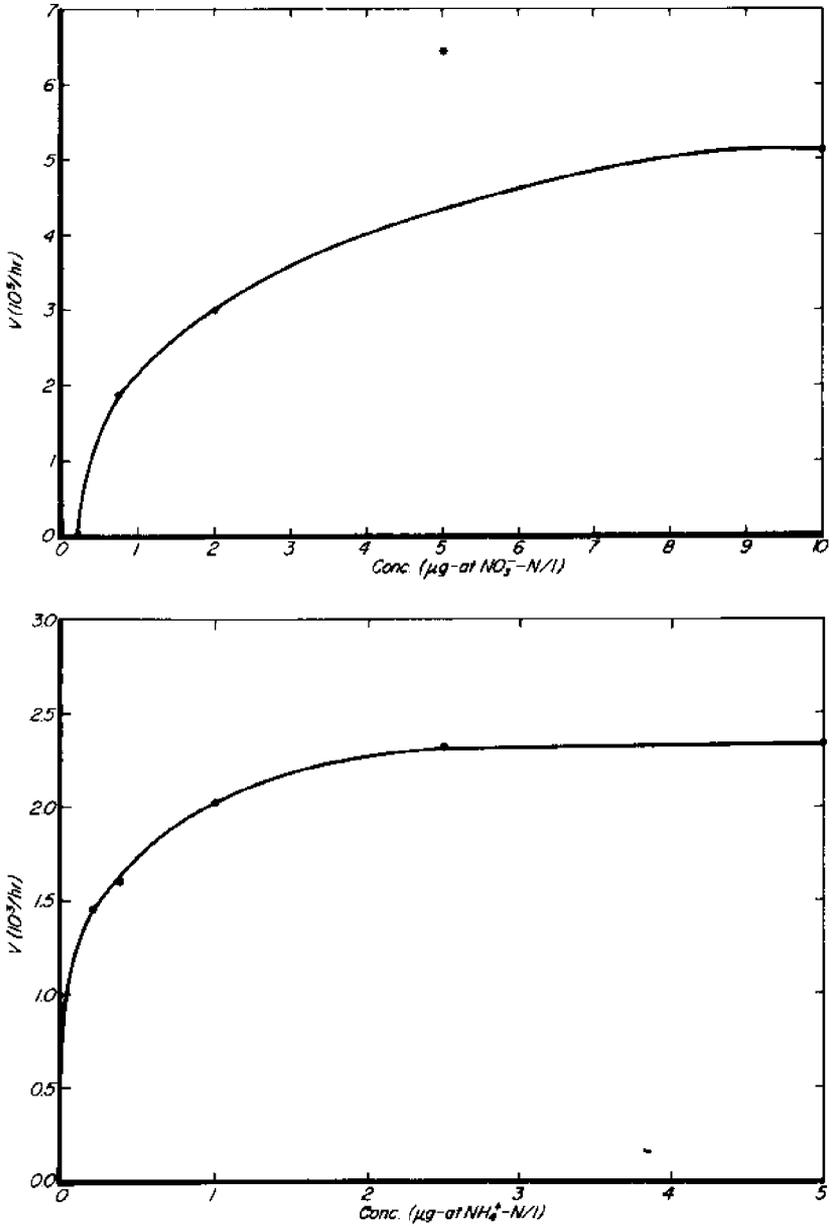


Figure 6.7  $V_{NH_3}$  and  $V_{NO_3^-}$  as a function of ammonia and nitrate concentrations at station 157 in Port Valdez, Alaska.

### <sup>15</sup>N productivity

As described above, the <sup>15</sup>N technique of measuring productivity allows separation of the fractions of primary productivity corresponding to new nitrogen and regenerated nitrogen in the euphotic zone, thereby indicating the nutrient source responsible for phytoplankton growth. The uptake of <sup>15</sup>N labelled ammonia and nitrate was measured in spring and summer at selected stations in Port Valdez near Jackson Point (Table 6.2). The percentage of nitrate uptake in the spring ranged from 79.6 to 90.6 percent at the 10-percent light depth and above. This high percentage of uptake signifies that nitrate was the major inorganic source of nitrogen for phytoplankton growth. Consequently, new production associated with nitrate at this time of year is important, and the fraction of primary production available for consumption at higher trophic levels is high. The population of phytoplankton within the Port at this time was dominated by *Phaeocystis pouchetti*, a brown-colored flagellate (Table 6.3).

In summer the population of phytoplankton residing in Port Valdez apparently had to rely on regenerated nutrients, as evidenced by the high percentage of ammonia uptake (Table 6.2). Most of the primary production is thus used to sustain the phytoplankton population, and only little is available for consumption at higher trophic levels. The phytoplankton population at this time of year was dominated by the dinoflagellate *Ceratium longipes* (Table 6.3).

The ratios of <sup>14</sup>C to <sup>15</sup>N uptake obtained in the summer (Table 6.2) were somewhat lower than the expected value of about 7 to 1 (Fleming 1940). The reason for the enhanced uptake of nitrogen relative to carbon in summer remains obscure. The explanation may entail a condition of nitrogen-starved phytoplankton; a significant level of heterotrophically associated nitrogen uptake; or release of photosynthetic products to the water sufficient to result in an underestimate of carbon fixation.

The ratios of <sup>14</sup>C to <sup>15</sup>N uptake obtained in the late spring were much higher than expected (Table 6.2). Possibly compounds of unlabelled dissolved organic nitrogen (such as amino acids and urea) were important sources of nitrogen for late-spring phytoplankton growth.

#### 6.3.5 Seasonal relationship between phytoplankton, productivity and nutrients

In temperate regions phytoplankton tend to vary both in total number and in species composition, depending on changes in water temperature, nutrient content and irradiance (Sverdrup et al. 1942). Generally only a few species are markedly abundant at one time, and the dominant species change with time. Even though the dominant form does vary to some extent from one year to another in this species succession, the pattern is often clear and constant.

The colonial alga *Phaeocystis pouchetti* has been reported not to be significantly grazed upon by zooplankton (Harvey 1966). In spite of the great abundance of zooplankton in Port Valdez during April, a large standing stock of *Phaeocystis* was also noted (Table 6.3), perhaps as a result of this phenomenon.

The seasonal succession of phytoplankton has been studied in Valdez Arm and Port Valdez for one year (May 1971-April 1972). It is necessary to study the composition of the phytoplankton over several years to gain a clear idea of the succession of species, but some preliminary statements concerning the seasonal composition of the phytoplankton in Galena Bay and Port Valdez are given. Seasonal net phytoplankton (i.e., those retained by a No. 25 mesh net) cell counts of major species in Galena Bay and Port Valdez are given in Table 6.3. Some differences in the species composition between the two stations were noted.



The species composition observed along a transect through Valdez Arm and Port Valdez dramatically illustrates the species non-homogeneity of these two regions (Figure 6.8). During the early winter (December) when standing stocks are low, the phytoplankton population in Port Valdez was dominated by species of the diatom *Chaetoceros* (Table 6.3), whereas in Galena Bay the diatom *Skeletonema costatum* and dinoflagellate *Peridinium pallidum* were the most abundant. In late winter (March) the diatom *Melosira moniliformis* was most abundant in Port Valdez, while the diatom *Biddulphia aurita* was dominant in Galena Bay. The spring (April) burst of phytoplankton in Port Valdez was characterized largely by the flagellate *Phaeocystis pouchetii*; in contrast, species of *Chaetoceros* appeared to dominate in Galena Bay. In the Port during early summer (May), the dinoflagellate *Ceratium longipes* was extremely abundant; later in the year (October) another dinoflagellate, *Ceratium fusus* occurred in large numbers along with *Chaetoceros convolutus*. In Galena Bay *S. costatum* appeared to dominate during this latter period.

The seasonal succession of net phytoplankton genera noted in Galena Bay is similar to successions observed in other temperate waters such as the Irish Sea (Raymont 1963). The succession of net plankton in Port Valdez, however, appeared to be somewhat atypical.

The concurrent heavy incidence of both the colonial phytoplankton *P. pouchetii* and zooplankton observed during the period (April) was of particular interest. Harvey (1966) has reported that zooplankton do not graze significantly on this colonial alga, which may explain this phenomenon noted in Port Valdez.

#### *Relationship between productivity and nutrients*

The seasonal cycling of productivity and nitrate are depicted in Figure 6.9. The decline in nitrate was attributed to an increase in plant production and standing crop (as exemplified by chlorophyll *a*), which was likewise responsible for the seasonal reduction in other nutrients such as phosphate and silicate that have similar euphotic zone seasonal cycling patterns.

#### 6.3.6 Annual primary production

The production of organic matter in Port Valdez and Valdez Arm was studied from May 1971 to April 1972 (Figure 6.10) at stations located in Valdez Arm and contiguous bays (GB-1, 108, 113 and JB-1), and at stations 120 to 150 in the Port (Figure 2.1). The productivity data reported here are expressed on an areal basis as grams of carbon fixed beneath a square meter of sea surface per day and year. The  $^{14}\text{C}$  technique was employed in these studies. The conversion from hourly to daily rates of primary production was made by assuming that the rates measured were the same for the entire sunlight period of that day (Figure 6.4). The average rate of yearly production in Port Valdez ( $\sim 150 \text{ g C/m}^2\text{-year}$ , with a range from  $116 \text{ g C/m}^2\text{-year}$  to  $213 \text{ g C/m}^2\text{-year}$ ) was somewhat lower than that in Valdez Arm and its contiguous bays ( $\sim 220 \text{ g C/m}^2\text{-year}$ , ranging from  $189 \text{ g C/m}^2\text{-year}$  to  $243 \text{ g C/m}^2\text{-year}$ ). The major difference in production in these two systems occurred in summer, at which time production was significantly lower in the Port than in the Arm. This resulted primarily from light limitation in the Port caused by the summer influx of large amounts of silt-laden fresh water.

The annual net primary production in these Alaskan waters ( $\sim 185 \text{ g C/m}^2$ ) is somewhat higher than production reported for inshore waters similar latitudes. Average values of  $75 \text{ g C/m}^2$  have been recorded for Danish inshore waters and  $180 \text{ g C/m}^2$  in the more southerly coastal environment of Long Island Sound, New York (Ryther 1963).

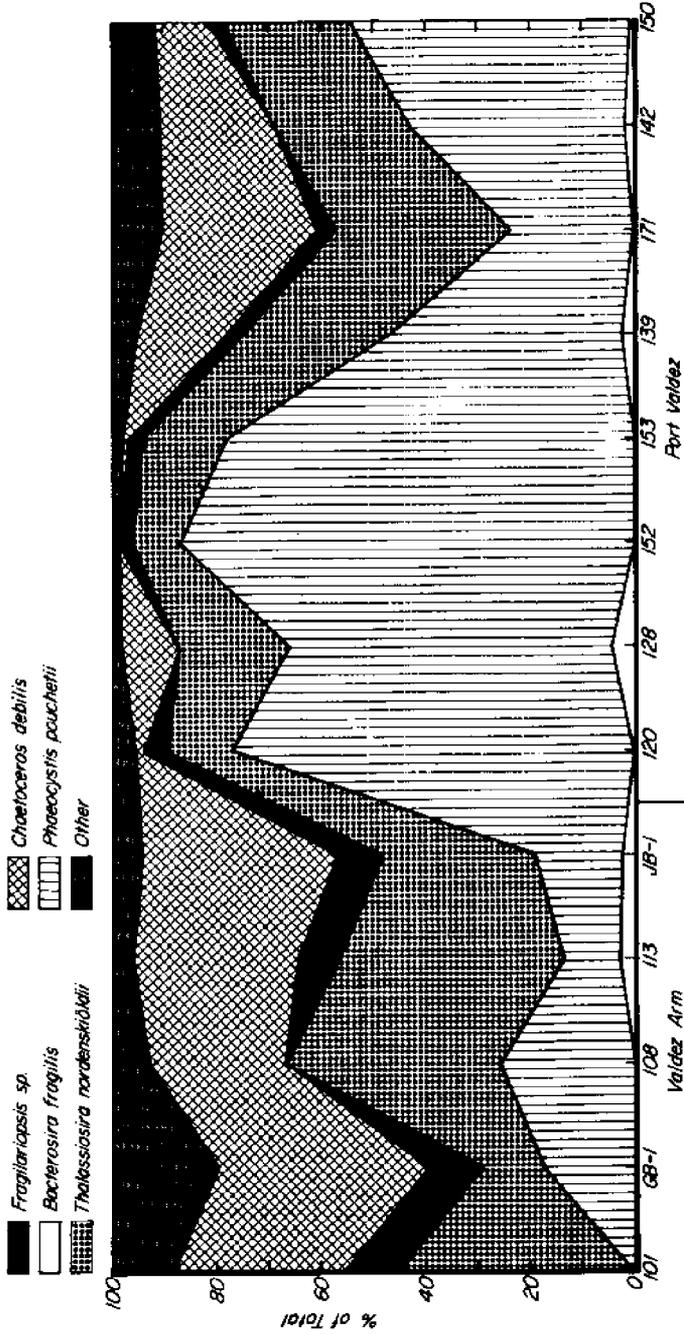


Figure 6.8 Cell counts of major net phytoplankton species (given as percentage of total) collected in vertical tow samples from the Valdez region (see Figure 1.1 for station locations).

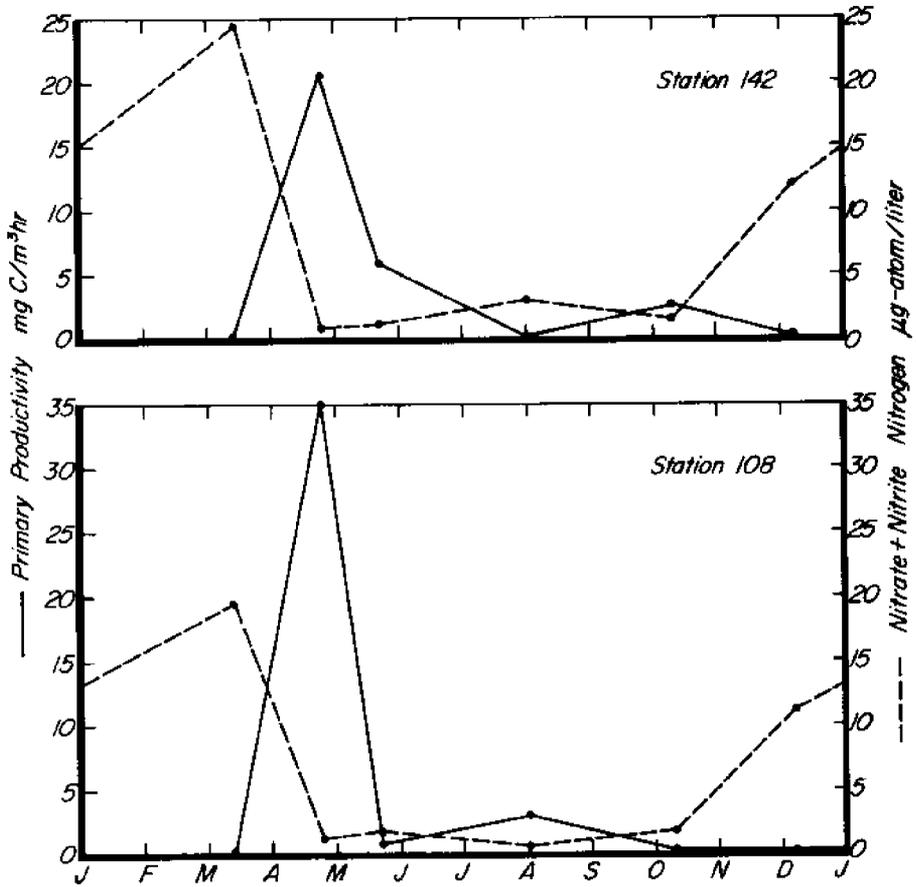
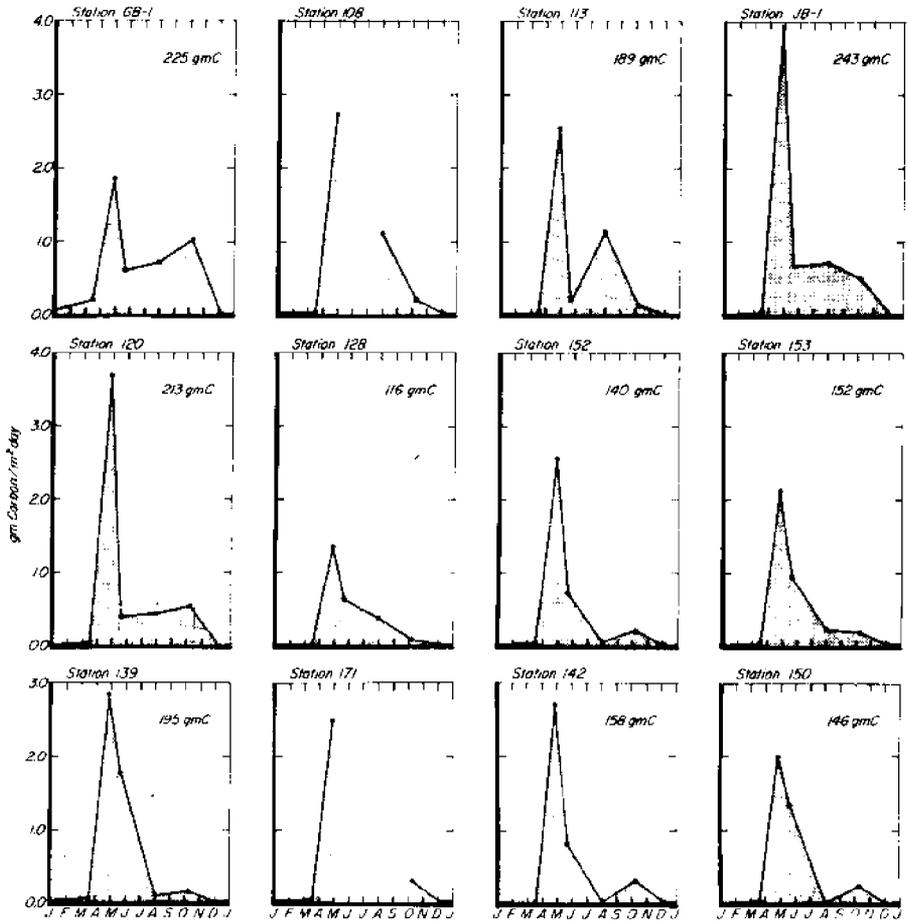


Figure 6.9 Seasonal cycles of primary production and nitrate at the 50-percent light depth for station 142 in Port Valdez and station 108 in Valdez Arm, Alaska.



**Figure 6.10** Daily and annual rates of primary production in Port Valdez and Valdez Arm, Alaska, and contiguous bays.

The daily primary production rates are impressive in these systems during the spring bloom period, when the majority of annual production occurs. One value as high as  $4 \text{ g C/m}^2\text{-day}$  was obtained in Jack Bay (Figure 6.10) and magnitudes near  $2 \text{ g C/m}^2\text{-day}$  were common at all stations during the bloom. These values approach those observed in the coastal upwelled waters off Peru, claiming one of the world's most productive open-ocean ecosystems, where a range in production rates from 3.14 to  $11.74 \text{ g C/m}^2\text{-day}$  has been reported (Ryther et al. 1966).

#### 6.4 Summary

The seasonal cycle of primary productivity in Valdez Arm and Port Valdez appears to resemble other marine systems of similar latitudes. In general, a large bloom of phytoplankton occurred in spring and produced maximum amounts of organic matter. Following the spring peak, the rates of productivity and standing crop of phytoplankton tended to remain low through summer and fall, although varying with month and place. In Port Valdez, particularly near major river inputs, productivity in summer and fall was low because of severe light limitation caused by the large sediment load in the entering river water. During the winter, phytoplankton growth and the standing crop were minimal.

The annual net primary productivity reported in Valdez Arm ( $\sim 200 \text{ g C/m}^2\text{-year}$ ) and Port Valdez ( $\sim 150 \text{ g C/m}^2\text{-year}$ ) appears to be somewhat higher than production reported for inshore waters of similar latitudes. Daily rates during the spring bloom (up to  $4 \text{ g C/m}^2\text{-day}$ ) approached those reported for the most productive marine phytoplankton crops known.

The introduction of large amounts of silt-laden fresh water into Port Valdez during summer limited the vertical zone of water than can support phytoplankton growth. The heavy sediment load in some regions of the Port reduced light penetration to such an extent that only about the first upper meter contained adequate light for phytoplankton growth. The salinity of the near-surface water was also dramatically reduced. Much of the Port in summer is therefore an inadequate environment for marine phytoplankton growth except for a very narrow horizon.

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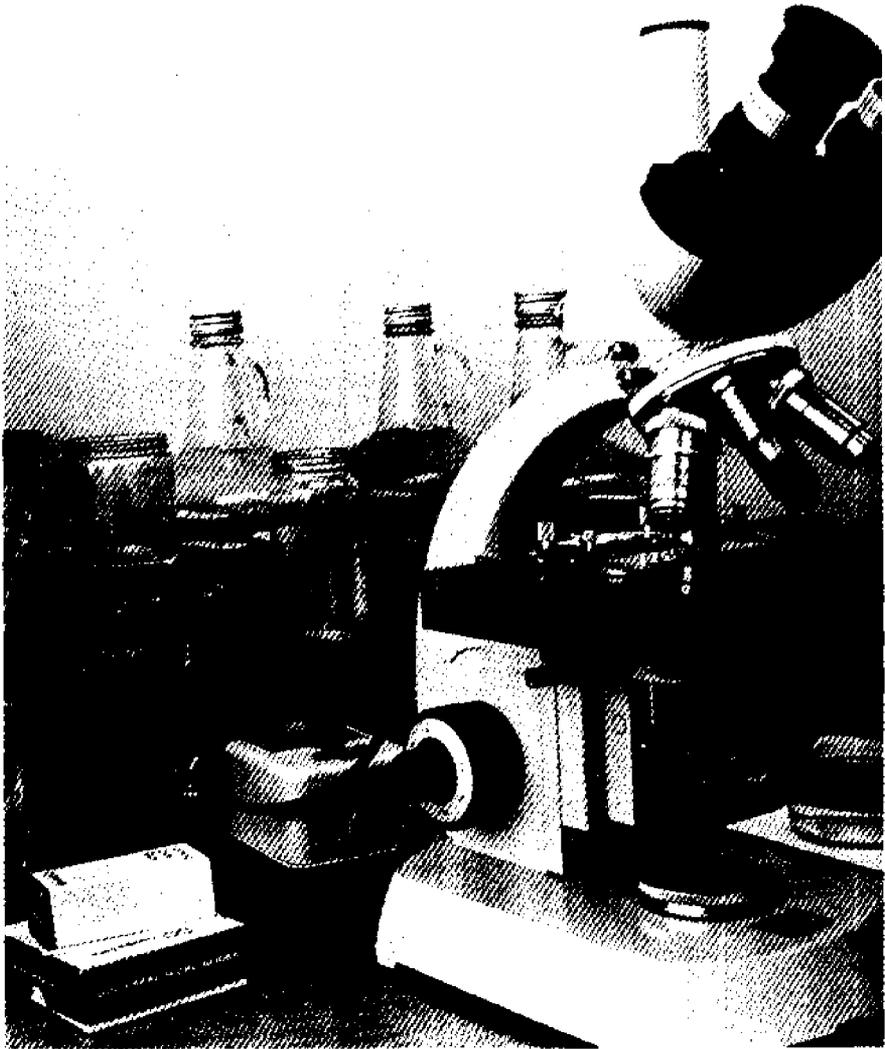


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# *Chapter 7*

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## PHYTOPLANKTON STUDIES





## 7. PHYTOPLANKTON STUDIES

by

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### 7.1 Introduction

The principal objective of this portion of the study was to survey the seasonal and spatial distribution of phytoplankton in the Valdez area. Sampling during this investigation was conducted at stations in Port Valdez, Valdez Arm, Jack Bay and Galena Bay during the 1-year period from May 1971 to April 1972 (see Figures 2.1 and 2.2 for station locations). Oceanographic observations were made in these regions during six cruises of the *R/V Acona*: cruise 113 (early summer, 16-26 May), cruise 117 (late summer, 27 July-4 August), cruise 122 (fall, 4-13 October), cruise 125 (early winter, 29 November-8 December), cruise 128 (early spring, 9-20 March), and cruise 131 (late spring, 21-30 April). As far as is known, the only other quantitative study of phytoplankton distribution conducted in the Valdez area is that reported by Alexander and Nauman (1969). The latter study was conducted during an 8-day cruise in September 1969, at which time dinoflagellates were found as the dominant organisms in Port Valdez. These were primarily species of *Ceratium*, *Peridinium* and *Gonyaulax*. In Jack Bay, *Gonyaulax* sp. was dominant, while in Galena Bay the diatoms *Skeletonema costatum* and *Chaetoceros* sp. were the most abundant forms.

### 7.2 Methods

Phytoplankton for standing stock determinations were collected in 30-liter polyvinylchloride Niskin bottles (General Oceanics Inc.). Subsamples were drained into 8-oz sample jars, and 5-10 ml of 4% formalin neutralized with sodium acetate were added to each sample.

The Utermöhl inverted microscope technique (Utermöhl 1931) was used to determine phytoplankton standing stock. A Zeiss phase-contact inverted microscope and Zeiss counting chambers were used to count these samples. A detailed outline of this technique is included in Data Vol. 1, section 7.1. The major taxonomic literature is listed in the reference section (Apstein 1908; Cupp 1943; Gemeinhardt 1930; Gran 1908; Hustedt 1930 and 1959; Lebour 1925; Lemmermann 1908; Paulsen 1908; and Schiller 1933).

Because of the amount of time needed to count phytoplankton standing stock samples, only four stations were thoroughly counted: GB-1, 113, 153, 171 (see Figures 2.1 and 2.2 for station locations). Station GB-1, located in Galena Bay, is considered a control station because of its environmental similarity to Valdez but is sufficiently separated to prevent being affected in case of contamination. Station 113 is important because of its position in Valdez Narrows; station 153 is inshore and at the site of the proposed pipeline terminus. Station 171 is across Port Valdez and is influenced by the city of Valdez. All four of these stations were sampled on the last four cruises only. Samples from other stations are available and could be analyzed on request.

Vertical tows were taken with a 0.5-m net (mesh size of 48  $\mu\text{m}$ ), which was lowered to the bottom of the euphotic zone and then towed to the surface at a rate of 13 m/min. Neutralized formalin was added to each sample; the amount of preservative added varied with the concentration of the sample but was usually 20-25 ml per 8-oz jar.

To determine the species present in the tow samples, an approximate 1-ml sample was taken from the bottom of the sample jar, placed on a microscope slide and examined with a Zeiss phase-contrast compound microscope. More than one slide per sample was usually examined in compiling the species list. These lists do not always agree with tabulations from the counted samples because of the methods used to collect the samples and mesh size of the net. Some species are present in very small numbers and do not appear in the unconcentrated water sample collected with the Niskin bottle, although they are present in the concentrated net samples. Small organisms (<50  $\mu\text{m}$ ) are likely to be missed in the net samples, because they are smaller than the pore size of the net, unless the net becomes clogged and the filtering efficiency decreased.

### 7.3 Results

A summary of the phytoplankton collected by vertical tow sampling in the Valdez area during the period of study is given by station and cruise in Table 7.1 (also Data Vol. I: section 7.3). To determine the concentrations of the most important species, the number of cells per milliliter was counted in samples collected from the top (100-percent light depth) and bottom (1-percent light depth) of the euphotic zone at selected stations (text 7.2) during each cruise (Tables 7.2-7.5). A summary of the phytoplankton standing stock is presented in section 7.2 of Data Vol. I.

#### *Cruise 113*

Only the Galena Bay station was sampled for phytoplankton standing stock during this cruise. In the surface water small flagellates and a few cells of the diatom *Nitzschia closterium* were present. In the deep water of Jack Bay at the 10-percent light level, a small yeast-like organism occurred in concentrations as high as  $1.67 \times 10^8$  cells/liter. Since there was no live material to culture, positive identification of the organism was not possible. The same organism has been found also in samples from stations 108 (cruise 113) and 153 (cruises 117 and 128), suggesting that it may be widely distributed throughout the area during much of the year.

Vertical tow samples from station 153 and other stations in Port Valdez and Jack Bay contained a few diatoms and dinoflagellates.

#### *Cruise 117*

Very few diatoms and dinoflagellates were found in the unconcentrated water samples collected at station 153, although *Chaetoceros decipiens*, *Melosira* sp., *Ceratium fusus*, *C. llineatum*, and *C. tripos* were found in the vertical tow.

The yeast-like organism described above was abundant in the water bottle samples at station 153; nearly 9500 cells were seen in a single transect of the bottom of the 5-ml counting chamber, which represents only about 1/25 of the sample.

Vertical tows taken at other stations during this cruise showed a summer phytoplankton community with only a few species.

#### Cruise 122

Small flagellates were numerically dominant in Galena Bay; few diatoms were present, although one genus, *Melosira moniliformis* cf., was relatively abundant. The cell walls of this diatom were weakly silicified, however, and identification was difficult.

At Jackson Point (station 153), the small flagellates were also dominant, but more diatoms were present at all light levels. The most abundant species were *Nitzschia closterium*, *Skeletonema costatum*, *Leptocylindrus danicus*, and *Thalassiosira gravida*.

A few diatom and dinoflagellate species were present in the vertical tow samples. Both Jack Bay and Galena Bay contained a more diverse community than was observed in Port Valdez.

#### Cruise 125

Standing stock samples contained very few cells. At all stations the small flagellates remained dominant, and the major diatoms present were *Nitzschia closterium*, *Skeletonema costatum*, and *Rhizosolenia stolterfothii*.

A greater number of species was present in the net tows from this cruise. Among the common forms were four species of *Ceratium*: *C. fusus*, *C. lineatum*, *C. longipes*, and *C. tripos*.

#### Cruise 128

The spring phytoplankton increase was beginning in Galena Bay as evidenced by the appearance of *Fragilariopsis* sp., which is not found in the unconcentrated water samples during other times of the year and seems to be indicative of spring blooms in other cold water areas of the world such as Scoresby Sound off East Greenland (Raymont 1963).

In Port Valdez and Valdez Narrows, *Nitzschia closterium* was still the dominant diatom species, although the small flagellates were the most abundant organisms. *Fragilariopsis* sp. had not appeared in the water bottle samples but was present in the concentrated net samples, indicating its occurrence in small numbers.

#### Cruise 131

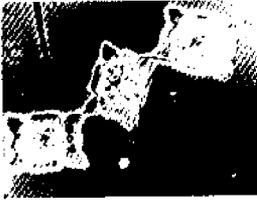
In Galena Bay the spring bloom was already declining, as seen by the low numbers of *Phaeocystis pouchetii* at all depths except the 1-percent light level. Also *Chaetoceros debilis* and *Thalassiosira nordenskioldii* had replaced *Fragilariopsis* sp. as the most abundant diatoms.

At station 113 in Valdez Narrows, *P. pouchetii* was also on the decline except at 1-percent light depth; other flagellates, with the exception of the choanoflagellate *Monosiga marina*, were nearly absent. Diatoms were more numerous by cell count but not in terms of species diversity.

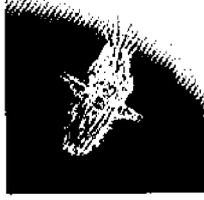
In Port Valdez, *P. pouchetii* persisted in high numbers at all light levels; unidentifiable flagellates were nearly absent; *M. marina* occurred in large numbers, but diatom concentrations had probably not yet reached a peak. *Fragilariopsis* sp., *T. nordenskioldii*, and *C. debilis* were all present in about equal numbers.







*Biddulphia aurita*



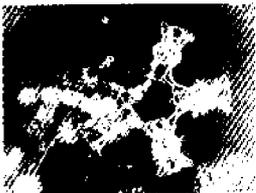
Nauplius Larva



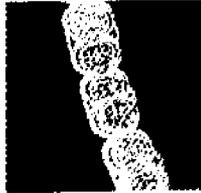
*Chaetoceros convolutus*



*Chaetoceros decipiens*



*Biddulphia aurita*



*Melosira maniliformis*



Nauplii Larvae

Table 7.2 Phytoplankton counts (cells/ml) of samples collected at Galena Bay (station GB-1), from 100-percent and 1-percent light depths.

Species	Cruise					
	113	(117) not sampled this cruise	122	125	128	131
100-percent light depth						
Small flagellates	108.8		249.6	18.4	36.0	8.8
<i>Chaetoceros brevis</i>						8.0
<i>Chaetoceros debilis</i>						305.0
<i>Chaetoceros decipiens</i>						16.8
<i>Fragilariopsis</i> sp.					12.8	3.2
<i>Melosira moniliformis</i> cf.			80.0			
<i>Nitzschia closterium</i>	0.8				2.4	1.6
<i>Skeletonema costatum</i>			1.6		3.2	2.4
<i>Thalassiosira decipiens</i>						27.2
<i>Thalassiosira nordenskioldii</i>						61.6
<i>Monosiga marina</i>						80.8
<i>Phaeocystis pouchetti</i>						2.4
Total	109.6		331.2	18.4	54.4	517.8
1-percent light depth						
Small flagellates			6.4	40.0	24.8	29.6
<i>Chaetoceros debilis</i>						356.0
<i>Coscinosira polychorda</i>						26.4
<i>Fragilariopsis</i> sp.					1.6	79.2
<i>Nitzschia closterium</i>				0.4	4.0	3.2
<i>Skeletonema costatum</i>				2.4		12.8
<i>Thalassiosira decipiens</i>						39.2
<i>Thalassiosira graviora</i>						13.6
<i>Thalassiosira nordenskioldii</i>						288.8
<i>Monosiga marina</i>						186.4
<i>Phaeocystis pouchetti</i>						1148.0
Yeast (?)	65219.2					
Total	65219.2		6.4	42.8	30.4	2183.2

Table 7.3 Phytoplankton counts (cells/ml) of samples collected at Valdez Narrows (station 113) from 100-percent and 1-percent light depths

Species	Cruise					
	(113 not sampled these cruises)	117	122)	125	128	131
100-percent light depth						
Small flagellates				50.0	19.6	
<i>Bacterosira fragilis</i>						6.4
<i>Chaetoceros debilis</i>						261.6
<i>Chaetoceros decipiens</i>						2.4
<i>Fragilariopsis</i> sp.						2.4
<i>Nitzschia closterium</i>					2.4	4.8
<i>Skeletonema costatum</i>				0.8		
<i>Thalassiosira decipiens</i>						54.4
<i>Thalassiosira gravida</i>						18.4
<i>Thalassiosira nordenskioldii</i>						431.2
<i>Phaeocystis pouchetii</i>						1063.2
Total				50.8	22.0	1844.8
1-percent light depth						
Small flagellates				14.8	35.2	
<i>Chaetoceros debilis</i>						307.2
<i>Chaetoceros decipiens</i>						2.4
<i>Fragilariopsis</i> sp.						96.0
<i>Nitzschia closterium</i>				0.4	2.0	7.2
<i>Thalassiosira decipiens</i>						13.6
<i>Thalassiosira gravida</i>						9.6
<i>Thalassiosira nordenskioldii</i>						592.0
<i>Monosiga marina</i>						153.6
<i>Phaeocystis pouchetii</i>						1009.6
Total				15.2	37.2	2191.2

**Table 7.4** Phytoplankton counts (cells/ml) of samples collected at Jackson Point (station 153) from 100-percent and 1-percent light depths.

Species	(113) not sampled this cruise	Cruise				
		117	122	125	128	131
100-percent light depth						
Small flagellates			125.6	12.0	6.4	6.4
<i>Bacterosira fragilis</i>						49.6
<i>Chaetoceros brevis</i>						5.6
<i>Chaetoceros debilis</i>						105.6
<i>Fragilariopsis</i> sp.						24.8
<i>Leptocylindrus danicus</i>			0.4			
<i>Nitzschia closterium</i>			25.2	0.4	1.6	9.6
<i>Skeletonema costatum</i>			4.8			16.8
<i>Thalassiosira decipiens</i>						48.0
<i>Thalassiosira gravida</i>			3.2			16.8
<i>Thalassiosira nordenskioldii</i>						184.0
<i>Monosiga marina</i>			0.4			828.8
<i>Phaeocystis pouchetii</i>						2791.2
Yeast (?)		245.0				
Total		245.0	159.6	12.4	8.0	4087.2
1-percent light depth						
Small flagellates		0.4	15.6	18.0	371.2	
<i>Bacterosira fragilis</i>						23.2
<i>Chaetoceros debilis</i>						128.8
<i>Fragilariopsis</i> sp.						180.0
<i>Leptocylindrus danicus</i>			4.4			
<i>Nitzschia closterium</i>			1.6	0.8		10.4
<i>Skeletonema costatum</i>				1.6		
<i>Thalassiosira decipiens</i>						36.6
<i>Thalassiosira gravida</i>				0.4		52.8
<i>Thalassiosira nordenskioldii</i>			3.2			92.8
<i>Monosiga marina</i>			0.4			448.0
<i>Phaeocystis pouchetii</i>						1488.8
Total		0.4	24.8	20.8	317.2	2461.4

Table 7.5 Phytoplankton counts (cells/ml) of samples collected at Valdez (station 171) from 100-percent and 1-percent light depths.

Species	Cruise					
	(113 not sampled these cruises)	117	122)	125	128	131
100-percent light depth						
Small flagellates				23.2	27.6	28.0
<i>Bacterosira fragilis</i>						15.6
<i>Chaetoceros brevis</i>						2.8
<i>Chaetoceros debilis</i>						144.8
<i>Fragilariopsis</i> sp.						21.2
<i>Nitzschia closterium</i>				1.2	2.8	6.4
<i>Skeletonema costatum</i>						16.4
<i>Thalassiosira decipiens</i>						23.6
<i>Thalassiosira gravida</i>						13.6
<i>Thalassiosira nordenskioldii</i>						190.8
<i>Monosiga marina</i>						588.4
<i>Phaeocystis pouchetii</i>						1741.2
Total				24.4	30.4	2792.8
1-percent light depth						
Small flagellates				229.6	32.8	8.8
<i>Chaetoceros debilis</i>						108.0
<i>Fragilariopsis</i> sp.						84.8
<i>Nitzschia closterium</i>				0.4	5.6	8.0
<i>Skeletonema costatum</i>						10.4
<i>Thalassiosira decipiens</i>						24.0
<i>Thalassiosira gravida</i>						10.4
<i>Thalassiosira nordenskioldii</i>						152.8
<i>Monosiga marina</i>						512.8
<i>Phaeocystis pouchetii</i>						1382.2
Total				230.0	38.4	2302.2

#### 7.4 Summary

The phytoplankton bloom and species succession in Galena Bay, Valdez Narrows and Port Valdez followed a pattern typical for the north temperate zone. A spring diatom bloom in March-April was followed by a summer population composed primarily of small flagellates, whereas the number of diatom species and the total number of diatoms were low. The only indication of a fall maximum of phytoplankton was an abundance of small flagellates in October recorded at Galena Bay and Jackson Point. It is possible that a more pronounced fall maximum was not seen because of the timing of the cruises. In winter, phytoplankton cell counts were low; during this time of year the dinoflagellate species were relatively abundant but did not occur in large numbers in the unconcentrated water samples.

The species that occurred were the same ones found in other areas at similar latitudes and included *Phaeocystis pouchetii*, *Fragilariopsis* sp., *Thalassiosira* spp., and *Skeletonema costatum* in the spring and the dinoflagellates *Peridinium* spp. and *Ceratium* spp. later in the fall.

The occurrence of the choanoflagellate *Monosiga marina* in large numbers is probably not unusual. Choanoflagellates are small, delicate and easily overlooked in standing stock samples.

The presence of the yeast-like organism in several samples was unexpected. A thorough examination of the occurrence and metabolism of this organism should be undertaken.

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# *Chapter 8*

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## ZOOPLANKTON STUDIES





## 8. ZOOPLANKTON STUDIES

by

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### 8.1 Introduction

Animals in the 0.6 to 20.0-mm size range that live between the seabed and the surface were examined by season for species composition at several locations within the study areas of Port Valdez and Valdez Arm. A total of 111 samples was taken from 21 station locations (Figures 2.1 and 2.2) in Port Valdez, Valdez Arm and contiguous bays during six cruises of the *R/V Acona* from May 1971 to April 1972. Results described herein are based on partial synthesis of data obtained; the identification and enumeration of organisms formed the basis of a graduate-level marine ecology course (W.F. 694; Coastal and Oceanic Zooplankton of Alaska) offered on the Fairbanks campus of the University of Alaska during the Spring Semester 1972. Although this study was not part of the original investigation, the opportunity was taken to obtain a limited amount of data that would be useful in making further studies of the entire ecosystem of Port Valdez.

### 8.2 Materials and Methods

Single vertical hauls were taken at selected stations on each cruise by fishing a 0.5 or 1.0-m net (0.571-mm Nitex) from near the bottom to the surface, retrieving the net at about 20 m/min. Catches were preserved immediately in buffered 10% formalin and returned to the University for storage and processing.

Since most samples contained thousands of organisms, subsamples were removed for identification and counting. A reference collection was developed and exchanged with taxonomists at the University of Washington for verification of species identifications.

The numerically dominant organisms from stations at Jackson Point (station 153), the middle of Port Valdez (station 133), northern Valdez Arm (station 108) and Galena Bay (station GB-1) were chosen for demonstration and study programs because of differing hydrographic regimes and depths. The remaining samples have been stored for future reference.

### 8.3 Results

Forty categories of large zooplankters, including 30 genera, were removed from the net samples (Table 8.1). The most diverse communities were found in the relatively isolated waters of Galena Bay, while a zooplankton assemblage of lower diversity was representative of the deeper waters of central Port Valdez. Calanoid copepods comprised the largest number of species within any single taxonomic group.

Since the sampling design was one based more on opportunity than strict scheduling, no attempt was made to obtain statistical information to evaluate seasonal differences; however, the temporal succession of dominant zooplankters in the four areas of interest was studied (Table 8.2). Although no clear seasonal pattern was common to all stations or even to adjacent locations, it appeared that copepods of the genus *Calanus* (*C. plumchrus*; *C. sp. n.*) are numerically dominant in the early spring and that the genus *Metridia* (*M. lucens*; *M. okhotskensis*) and the chaetognath *Sagitta elegans* are more conspicuous during the fall and winter months. The euphausiid *Thysanoessa raschii* was abundant only in the summer, in Galena Bay and central Port Valdez. With the exception of *S. elegans*, no single organism dominated the fall community at any location.

### 8.4 Discussion

A portion of the zooplankton community in northeastern Prince William Sound was described in this study; most of the species found are representative of plankton communities in southeastern Alaska as well (Wing and Reid 1972). This listing of species cannot be considered inclusive due to gear limitations, the relatively small number of samples collected, and subsampling selectivity for numerically dominant animals. The information does indicate, however, that the areas examined support a typical boreal zooplankton assemblage. Seasonal shifts in dominance undoubtedly reflect responses to differing environmental factors such as temperature, salinity and ambient light, and this suggests that any future sampling program must include *temporal* as well as *spatial* components in order to be representative. Apparent differences between the complexity of the community found inside Port Valdez, as opposed to locations south of the Narrows, may be related to the general salinity gradient through the area, although this contention cannot be thoroughly substantiated with the observations now at hand.

### 8.5 Summary

Forty categories of large zooplankton, including representatives of 30 genera, were described for locations in Port Valdez and Valdez Arm. Calanoid copepods dominated the community with few exceptions during most of the year. Changes in numerical dominance indicate temporal responses to fluctuating environmental conditions. The assemblage of zooplankton found in Valdez Arm and Galena Bay was slightly more complex than that in Port Valdez.

### 8.6 Reference

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Table 8.1 Large zooplankton collected from May 1971 to March 1972 in northeastern Prince William Sound (GB = Galena Bay; VA = Valdez Arm; CPV = Central Port Valdez; JP = Jackson Point)

Taxa	Location			
	GB	VA	CPV	JP
<b>Annelida</b>				
Polychaeta				
<i>Tomopteris</i> sp.	X		X	
Polychaeta sp.	X			
Bipinnaria	X	X	X	X
<b>Arthropoda</b>				
Crustacea				
Amphipoda				
<i>Cyphocaris challengeri</i>	X	X	X	X
Gammarid amphipod sp.	X	X	X	X
Hyperiid amphipod sp.	X			
Cirripedia				
<i>Balanus</i> sp.				
Nauplii	X	X		
Cyprids		X		
Copepoda				
<i>Acartia longiremis</i>	X			X
<i>Acartia tumida</i>	X			
<i>Acartia</i> sp.		X		
<i>Calanus plumchrus</i>	X	X	X	X
<i>Calanus</i> sp. n.	X	X	X	X
<i>Candacia columbiae</i>		X		
<i>Centropages abdominalis</i>	X			
<i>Chiridiella</i> sp.	X	X		
<i>Chiridius</i> sp.		X		
<i>Eucalanus bungii</i>	X	X	X	X
<i>Euchaeta elongata</i>	X	X	X	
<i>Gaetanus</i> sp.		X		
<i>Metridia longa</i>	X		X	X
<i>Metridia lucens</i>	X	X	X	X
<i>Metridia okhotensis</i>	X	X	X	X
<i>Pseudocalanus elongatus</i>	X	X	X	X
<i>Tortanus discaudatus</i>	X			
Decapoda				
Zoea	X		X	X
Shrimp larvae	X	X	X	X
Euphausiacea				
<i>Thysanoessa raschii</i>	X	X	X	X
Ostracoda				
<i>Conchoecia</i> sp.	X	X	X	X

Table 8.1 (continued)

(GB = Galena Bay; VA = Valdez Arm; CPV = Central Port Valdez; JP = Jackson Point)

Taxa	Location			
	GB	VA	CPV	JP
<b>Chaetognatha</b>				
<i>Sagitta elegans</i>	X	X	X	X
<i>Eukrohnia hamata</i>	X	X	X	X
<b>Coelenterata</b>				
Hydrozoa				
<i>Aglantha digitale</i>	X		X	X
Other medusae	X	X	X	X
<b>Chordata</b>				
Larvacea				
<i>Oikopleura</i> sp.	X	X	X	X
Osteichthyes				
Fish eggs	X	X		
Fish larvae	X	X		
<b>Ctenophora</b>				
<i>Mertensia</i> sp.				X
<b>Mollusca</b>				
Gastropoda				
<i>Clione limacina</i>	X	X	X	X
<i>Limacina helicina</i>	X	X		X
Totals	33	29	22	23

Table 8.2 Numerically dominant large zooplankton by season and location May 1971 to March 1972

Season	Location			
	Galena Bay	Valdez Arm	Port Valdez	Jackson Point
Late Spring (May 1971)	<i>Calanus plumchrus</i> <i>Calanus</i> sp. n. <i>Sagitta elegans</i>	<i>Calanus plumchrus</i> <i>Metridia okhotensis</i> <i>Sagitta elegans</i>	No Sample	No Sample
Summer (July 1971)	<i>Calanus</i> sp. n. <i>Thysanoessa raschii</i>	<i>Metridia okhotensis</i>	<i>Metridia lucens</i> <i>Metridia okhotensis</i> <i>Thysanoessa raschii</i>	<i>Calanus</i> sp. n.
Fall (October 1971)	<i>Sagitta elegans</i>	No dominants	No dominants	No dominants
Winter (December 1971)	<i>Metridia lucens</i>	<i>Metridia okhotensis</i>	No dominants	<i>Metridia lucens</i>
Early Spring (March 1972)	No dominants	<i>Metridia okhotensis</i>	<i>Metridia lucens</i> <i>Metridia okhotensis</i> <i>Sagitta elegans</i>	No dominants

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# *Chapter 9*

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## PRELIMINARY BENTHOS SURVEY





## 9. PRELIMINARY BENTHOS SURVEY

by

H. M. Feder, G. J. Mueller, M. H. Dick and D. B. Hawkins

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### 9.1 Introduction

Marine food webs are complex and incompletely understood (Hunt 1925; Hedgpeth 1957; Green 1968; Friedrich 1969; Steele 1970; Thorson 1971), although portions of food webs are known from many parts of the world (Thorson 1957, 1966; Sander 1960; Zenkevitch 1963; Semenov 1964, 1965), and knowledge of the interrelationships between different trophic levels, especially in terms of energy exchange, is increasing (see Steele 1970 for review).

Little information is available on the basic biology or the trophic interactions of Alaskan marine organisms. The only intensive biological studies which have been completed on marine organisms of Alaska are management-oriented investigations of the pink salmon *Oncorhynchus gorbuscha* (Helle et al. 1964), descriptive ecological studies by the National Research Council (1971) following the Great Alaskan Earthquake of 1964, and fisheries-oriented research in Prince William Sound on *Protothaca staminea* (Feder and Paul 1973). Certain shellfish studies are in progress by the Alaska Department of Fish and Game (razor clam *Siliqua patula*: R. Nickerson, unpublished manuscript; the king crab *Paralithodes camtschatica*: Rothschild et al. 1970), the National Marine Fisheries Service (scallops, primarily *Pactinopecten caurinus*: Haynes 1970; shrimp *Pandalus* spp.: Barr 1970; E. Haynes, personal communication), and the University of Alaska (littleneck clam *P. staminea*: H. M. Feder and A. J. Paul, unpublished data; Paul and Feder 1973).

Preliminary biological information from Port Valdez is available on planktonic, intertidal, and benthic organisms. Two studies are providing quantitative intertidal information: the National Marine Fisheries Service is monitoring two macrofaunal species (*Macoma inconspicua* and *Mytilus edulis*) (L. R. Myron, personal communication), and the Institute of Marine Science of the University of Alaska is examining sediment microflora and meiofauna in Port Valdez and Galena Bay, Alaska (H. M. Feder, unpublished data). A

brief investigation by Smith et al. (1969) did not generate quantitative data nor consider intertidal or benthic infauna. No intensive benthic surveys by other agencies are in progress in Port Valdez at present.

Benthic organisms have long been recognized as an important and integral part of marine ecosystems (Petersen and Jensen 1911; Molander 1928; Thorson 1957; Zenkevitch 1963; Longhurst 1964), and recent work on the benthos has resulted in a large number of published studies on the basic biology of infaunal benthic communities (Jones, N. 1950; Sanders 1956, 1958; Lie 1968; Pamatmat 1968; Ellis 1969; Jones, G. 1969; Pearson 1970; Hughes and Thomas 1971; Young and Rhoads 1971; Gage 1972 a,b). Examination of the benthic biota as an indicator of change in an enclosed body of water following industrial activity has been assessed in various parts of the world (Reish 1955, 1959; Hynes 1963; Beyer 1968; Bagge 1969; McNulty 1970; Pearson 1970). For reviews on the effects of oil on marine life, see Olson and Burgess 1967; Carthy and Arthur 1968; Smith 1968; Cowell 1971; Straughan 1971, Waddington, 1971.

Jaegersten (1940) demonstrated that the distribution of bottom invertebrates is influenced by subtle differences in the grain-size distribution of the sediments; these relationships are discussed further by N. Jones (1950). Lie (1968) established that the nature of the substrate was the most important factor governing the benthic infaunal assemblages in Puget Sound, Washington, and Sanders (1956, 1958) was able to relate fauna to sediment type in Long Island Sound, New York, and Buzzards Bay, Massachusetts. Rhoads and Young (1970, 1971; Young and Rhoads 1971) have described animal-sediment relationships in Cape Cod Bay, Massachusetts, and have considered the influence of deposit-feeding organisms on sediment stability and community trophic structure. Sediment analysis is therefore essential to a benthic ecological investigation (Buchanan and Kain 1971) and is discussed in detail by Sharma and Burbank in Chapter 1 of this volume.

## 9.2 Objectives

The primary purpose of this investigation was to provide a framework for future monitoring of the benthic infauna, in order to determine the quantitative effect of the addition of petroleum fractions to waters of Port Valdez and restricted portions of the adjacent Valdez Arm. Benthic infauna as defined here consists of those organisms that were quantitatively collected by the bottom sampler used in this study and includes a few species of relatively slow-moving epifauna. The study was one year in duration, preliminary, and designed to contribute to the following goals:

1. Identification and location of the major infaunal associations of the benthos of Port Valdez and adjacent waters
2. Examination of the population density and biomass of selected species in relation to various biological and physical parameters, specifically adjacent biological associations and sediment properties

## 9.3 Methods and Materials

Benthic fauna was collected by means of a van Veen bottom grab on four cruises of the *R/V Acona* in September, December, March, and April, 1971-1972. To satisfy the objectives of the project, stations were selected on the following basis for optimal data comparability:

1. Five major transects were established at similar depths from the head of Port Valdez to the Valdez Narrows along uniform bottom contours.
2. Fifty stations were located equidistant along the five major transects to allow uniform coverage of Port Valdez.
3. Sampling intensity was increased by the addition of 11 stations in the vicinity of the proposed pipeline terminus and the City of Valdez.
4. To further aid the development of a future monitoring program, five additional stations outside of Port Valdez were examined (Valdez Arm see Figure 9.1).

Individual stations were located by selecting a minimum of two shore targets positioned approximately 90° apart and determining the position by Precision Decca Radar. Shore targets were either established visually during nearshore ship position or taken from U. S. Coast and Geodetic Survey Chart No. 8519. Depth was measured by a precision sonic recorder.

Samples were taken with a 0.1-m<sup>2</sup> van Veen grab with bottom-penetration facilitated by the addition of 70 pounds of lead weight. Two 1.0-mm mesh screen doors on the top of the grab permitted removal of undisturbed sediment samples. Three replicate grabs were routinely collected per station. On two occasions, additional replicates were taken for statistical assessment of the sampling program. Material from each grab was washed on a 1.0-mm screen and preserved in 10% formalin buffered with hexamine.

Limited trawling was included only in the April sampling program. Drags were made for approximately five minutes with a small otter trawl, and the material was treated as above.

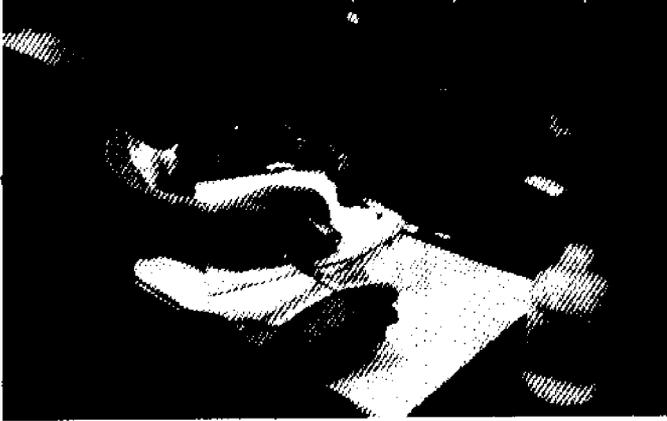
In the laboratory (Invertebrate and Marine Collections Section, University of Alaska Museum) all samples to be examined in detail were rinsed to remove the last traces of sediment, spread on a gridded tray, covered with water, and rough-sorted by hand. The sorted material was then transferred to fresh preservative (buffered 10% formalin), and identifications were made. All organisms were counted and wet-weighted after excess moisture was removed with absorbent towel.

## 9.4 Results

The basic plan of operation presented in the initial proposal was carried to fruition with little alteration. Unanticipated allocation of three full days of ship time to the grab-sampling program on the first cruise (September) of the *R/V Acona* made it possible to sample 55 stations during this period (Figure 9.1; Table 9.1) instead of the 20 stations stipulated in the original proposal. Such broad coverage on the first cruise allowed detection of major species distributions throughout Port Valdez and vicinity at the very inception of the investigation. During the subsequent three cruises in December, March, and April (Table 9.1), 32, 26 and 11 stations were sampled, respectively. Specific allotment of vessel time within the scope of the composite program limited the benthic study to an eight-month period which precluded sampling during the summer season. For the extent of the investigation, however, every station on the grid pattern was sampled at least once, and all samples from September and April were examined in detail. The December and March samples selected for study were from stations not occupied on the other cruises.

### 9.4.1 Grab samples

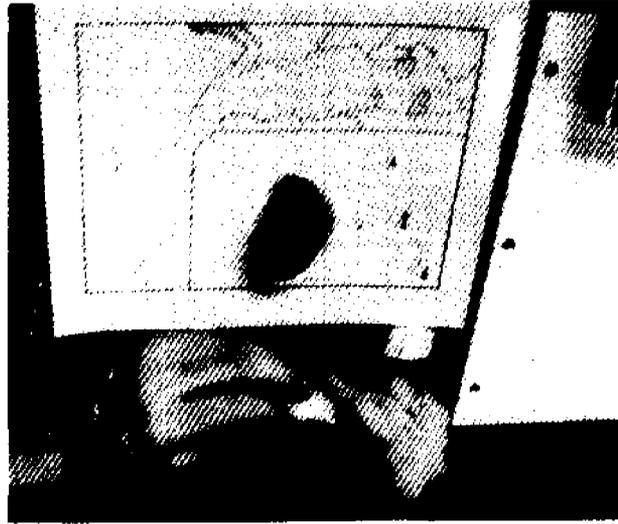
The van Veen grab functioned effectively and delivered sample volumes of 16 to 20 liters except in the case of five stations. Problems of limited volume samples (min. 5 liters)



specimen identification and cataloging

Maps of sampling grids show distribution of individual species (such as the clam *Yoldia thraciaeformis* illustrated below) by stations corresponding to inset histograms representing relative abundance and biomass.

## BENTHOS SURVEY



*Lithodes aequispinus* taken by trawl at station 19



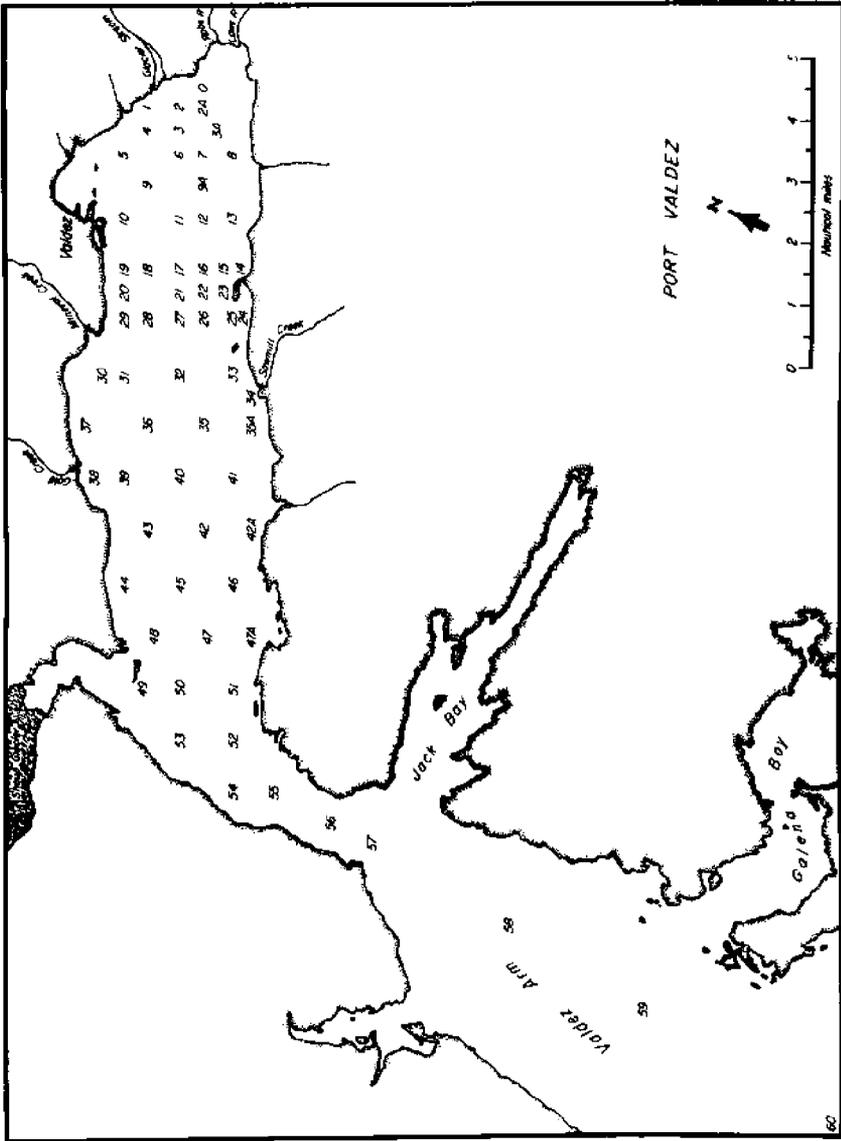


Figure 9.1 Station grid used in the biological sampling program.

Table 9.1 Stations sampled during four cruises in Port Valdez 1971-1972

								X = sample analyzed	
								Δ = sample collected but not analyzed	
Station	Latitude N	Longitude W	Depth (m)	Sept.	Dec.	March	April		
0	61° 05.0'	146° 15.7'	13	X					
1	61° 06.7'	146° 16.4'	55	X					
2A	61° 06.05'	146° 16.4'	59	X	Δ	Δ			
3	61° 06.37'	146° 17.2'	165	X					
3A	61° 06.0'	146° 17.1'	98		X				
4	61° 06.8'	146° 17.16'	141	X	Δ				
5	61° 07.2'	146° 17.9'	113	X		Δ			
6	61° 06.35'	146° 17.9'	187	X	Δ				
7	61° 06.0'	146° 17.9'	150	X					
8	61° 05.5'	146° 17.8'	40	X	X				X
9	61° 06.9'	146° 18.9'	176		X				trawl
9A	61° 06.05'	146° 18.9'	173		X				
10	61° 07.2'	146° 20.0'	147	X	Δ	Δ		X	
11	61° 06.35'	146° 20.0'	200			X			
12	61° 05.9'	146° 20.0'	205	X					trawl
13	61° 05.5'	146° 20.0'	198	X	Δ				X
14	61° 05.4'	146° 21.8'	15	X	Δ	Δ			
15	61° 05.63'	146° 21.8'	219			X			trawl
16	61° 05.9'	146° 21.8'	232	X		Δ			
17	61° 06.35'	146° 21.8'	232	X	Δ				
18	61° 06.8'	146° 21.8'	232	X	Δ	Δ		X	
19	61° 07.2'	146° 21.8'	217	X	Δ				trawl
20	61° 07.2'	146° 22.53'	223	X	X				
21	61° 06.35'	146° 22.5'	234	X					trawl
22	61° 05.9'	146° 22.53'	235	X	Δ				
23	61° 05.68'	146° 22.53'	235	X	Δ				
24	61° 05.35'	146° 23.4'	18	X					
25	61° 05.5'	146° 23.4'	234		X				
26	61° 05.9'	146° 23.4'	234		X				
27	61° 06.35'	146° 23.4'	235	X					
28	61° 06.8'	146° 23.4'	235	X	Δ				trawl
29	61° 07.2'	146° 23.4'	227	X	Δ				
30	61° 07.55'	146° 25.3'	40	X	Δ			X	
31	61° 07.2'	146° 25.3'	231			X			
32	61° 06.35'	146° 25.3'	237	X	Δ	Δ			
33	61° 05.5'	146° 25.3'	60	X	Δ				X
34	61° 05.3'	146° 26.1'	20	X	Δ	Δ			X
35	61° 05.9'	146° 27.0'	237	X					
35A	61° 05.5'	146° 27.0'	82		Δ				X
36	61° 06.8'	146° 27.0'	47	X					trawl

Table 9.1 (continued)

Station	Latitude N	Longitude W	Depth (m)	X = sample analyzed Δ = sample collected but not analyzed			
				Sept.	Dec.	March	April
37	61° 07.8'	146° 27.0'	45	X	Δ		trawl
38	61° 06.7'	146° 28.7'	116	X		Δ	
39	61° 07.2'	146° 23.7'	139	X		Δ	
40	61° 06.35'	146° 28.7'	235	X		Δ	trawl
41	61° 05.5'	146° 28.7'	235	X		Δ	
42	61° 05.9'	146° 30.5'	238	X			trawl
42A	61° 05.5'	146° 34.0'	48				X
43	61° 06.08'	146° 30.5'	245	X			trawl
44	61° 07.2'	146° 32.2'	244	X		Δ	
45	61° 06.35'	146° 36.2'	244	X	Δ		trawl
46	61° 05.5'	146° 32.2'	244	X		Δ	
47	61° 05.85'	146° 34.0'	245	X			
47A	61° 05.1'	146° 34.0'	217			X	
48	61° 05.7'	146° 34.0'	245	X	Δ	Δ	
49	61° 06.9'	146° 35.7'	224	X	Δ	Δ	
50	61° 06.35'	146° 35.7'	248	X		Δ	
51	61° 05.5'	146° 35.7'	246	X		Δ	
52	61° 05.5'	146° 37.4'	248	X	Δ		
53	61° 06.35'	146° 32.4'	245	X	Δ	Δ	
54	61° 05.5'	146° 39.2'	247	X	Δ	Δ	
55	61° 04.8'	146° 39.2'	150	X		Δ	
56	61° 03.9'	146° 40.3'	239	X		Δ	
57	61° 03.2'	146° 40.9'	219	X		Δ	
58	61° 01.1'	146° 43.7'	342	X			
59	60° 58.9'	146° 46.6'	385	X			
60	60° 55.52'	146° 50.6'	382	X			

encountered at stations 0, 14, 55, 56 and 57 were related to rocky or cobbly substrate or to steep slopes not readily sampled by a quantitative sampler. The surface of all samples, examined through the top doors of the grab, was undisturbed as evidenced by the smooth detrital cover. (See addendum text 9.9 for a review on use of the van Veen grab for benthic investigations). Development of a washing system based on a series of shower heads resulted in enhanced efficiency in washing and screening the sample material on board ship.

#### *Determination of Biologically Important Species*

Isolation of 210 species was made from the various grab samples (Table 9.2; also Data Vol. II). Criteria were developed to recognize those organisms which could be considered *Biologically Important Species* (BIS) in Port Valdez. By use of these criteria, a species was considered independently (items 1 and 2 below) as well as in combination with other benthic species (items 3 and 4, adopted from Ellis 1969). Each species classified as BIS in this study met at least one of four conditions:

1. It was distributed in 50 percent or more of the total stations sampled.
2. It comprised over 10 percent of either the composite population density or biomass collected at any one station.
3. Its population density was significant at any given station. This significance was determined by the following test:
  - a. A percentage was calculated for each taxon with the sum of the population density of all taxa equalling 100 percent.
  - b. These percentages were then ranked in descending order.
  - c. The percentages of the taxa were summed in descending order until a cut-off point of 50 percent was reached. The BIS were those taxa whose percentages were used to reach the 50 percent cut-off point. When the cut-off point of 50 percent was exceeded by the percentage of the last taxon added, this taxon was also included.
4. Its biomass was significant at any given station. This significance was determined by the following test:
  - a. A percentage was calculated for each taxon with the sum of the biomass of all taxa equalling 100 percent.
  - b. These percentages were then ranked in descending order.
  - c. The percentages of the taxa were summed in descending order until a cut-off point of 50 percent was reached. The BIS were those taxa whose percentages were used to reach the 50 percent cut-off point. When the cut-off point of 50 percent was exceeded by the percentage of the last taxon added, this taxon was also included.

A list of Biologically Important Species is presented in Table 9.3. The distribution and abundance of these species are shown in Figures 9.2-9.41.

#### *Methods of statistical data analysis*

1. Gleason's Index of Diversity was calculated for the Biologically Important Species (Table 9.5; also see Lie 1968).
2. An analysis of variance of grab-sample data (population density and biomass) was carried out (Data Vol. II; also see McIntyre 1971).
3. A computer program was designed to simulate multiple grab-sampling (Figures 9.43 and 9.44; also Data Vol. II).
4. A cluster analysis was performed to examine certain Biologically Important Species for associative trends (Figures 9.45-9.48; also Data Vol. II).

#### 9.4.2 Trawl samples

Thirteen trawl stations were occupied in April (see Table 9.1; also Data Vol. I), adding an additional 32 species not collected in any of the grabs (Table 9.4). Included in this collection were 346 specimens of snow crab, *Chthonocetes Bairdi*, which were measured and sexed; size frequencies by sex are presented in Figure 9.42. Crabs ranging from 0.5-14.5 cm in carapace width were collected; no females over 9.0 cm were taken.

### 9.5 Discussion

#### 9.5.1 Grab-sampling simulation program

A program entitled GRAB was written specifically to simulate multiple grab-sampling of the bottom-dwelling organisms of Port Valdez. (Computer format for this program is included in Data Vol. I). The purpose of the program was to obtain an estimate of the cumulative percentage of species that could be collected at each step in a cumulative sequence of one to eight grabs, based on 100 percent obtained in eight grabs. The percentage of recruits in the new species added at each subsequent grab was estimated; in this case, the fraction of recruits is the number of individuals per new species added per grab divided by the sum over all eight grabs of the number of individuals per new species added per grab. The cumulative number of individuals, cumulative percentage of individuals, and the cumulative number of species were calculated (Data Vol. II). Input data to this program consisted of the number of organisms collected in each of eight grabs at stations 2 and 20; the two stations were analyzed separately.

The program formed a new eight-grab sequence by randomly selecting grabs *with replacement* from the original data matrix. The cumulative number of individuals, cumulative percentage of individuals, cumulative number of species, cumulative percentage of species, and the percentage of recruits for this eight-grab sequence were calculated and stored. The process was repeated and groups of simulations averaged until unchanging values were obtained, which occurred at 200 simulations. Standard deviations were then calculated (Data Vol. II).

A difference matrix was constructed to represent the increments in the number of individuals, percentage of individuals, number of species, and percentage of species in each grab (Data Vol. II).

From the data shown in Figures 9.43 and 9.44 (also Data Vol. II), it is seen that 68-72 percent of the species present in eight grabs were collected in the first three grabs, and about 75-80 percent of the recruit individuals were obtained in these first three grabs.

It has been suggested that a cumulative species analysis, resulting in percentage values such as those cited above and presented in Figures 9.43 and 9.44, is not a reliable means for determining the minimal number of samples needed per station (Longhurst 1959; Holme 1964; Lie 1968). A more meaningful method indicated by this study as well as the investigations of others is an examination of the numbers of recruit individuals collected at each grab. The latter method shows that the most abundant species are adequately sampled in the first two or three samples taken by a 0.1-m<sup>2</sup> grab, and that recruitment of numbers of individuals in the subsequent samples represents only the less abundant species.

#### 9.5.2 Species composition

The distribution of infaunal species throughout Port Valdez and five areas in adjacent Valdez Arm is now well documented (Table 9.2; Figures 9.2-9.41) with only 25 additional

species, 12 percent, recruited in the fourth sampling period, April (Table 9.6). Standard deviations have been computed for population densities and biomass of each species per grab at each station sampled (Data Vol. II).

Members of most marine phyla were collected in this investigation (Table 9.2). The polychaetous annelids represented by far the most important group in Port Valdez. They were not only the most diverse, with 103 species, but various members were widely distributed and often comprised a relatively large percentage of the organisms at any station in both population density and biomass (e.g., see stations 1, 4, 38 and 54 in September). Mollusks were next in importance with approximately 60 species; occasionally they represented high-density and biomass components at a station (e.g., see station 2A in September and 42A in April). Echinoderms were third in significance, and all other groups were less important.

Of the many species in Port Valdez, only nine were considered ubiquitous: *Lumbrineris similabris*, *Nephtys ciliata*, *Heteromastus filiformis*, *Prionospio malmgreni*, *Axinopsida serricata*, *Eudorella emarginata*, *Tharyx monilaris*, *Chaetoderma robusta*, and *Cylichna attonsa*. Only five species, *N. ciliata*, *H. filiformis*, *A. serricata*, *C. robusta*, and *C. attonsa*, fit all four of the criteria used in this study for definition of Biologically Important Species (see 9.4.1).

Other species such as *Ophiura sarsi* (Figure 9.8) and *Cossura longicirrata* (Figure 9.31) were restricted in distribution, but occasionally they were of importance in terms of population density and biomass. Such restricted distributions probably reflect local differences in environmental parameters such as rate of silt deposition, substrate, or other physical and chemical factors, but they may be the result of biological influences in the area as well (Friedrich 1969; Jones, G. 1969).

As suggested by Lie (1968), "Most animal communities are so complex and rich in species that it is necessary to make a choice of the species that supposedly are most important to the communities and subject them to detailed analysis." Such species have been variously termed "characterizing species" (Thorson 1957), "numerically dominant species" (Lie 1968), "prevalent species" (Jones, G. 1969), and "ecologically significant species" (Ellis 1969). The criteria used for selection of such species vary; criteria used in this study for distinguishing species of biological importance in Port Valdez are listed in section 9.4.1.

Species of importance were determined for two reasons: (1) One of the goals of this study was to identify the individual species and determine their associations in Port Valdez. This could best be accomplished by mapping the Biologically Important Species, and determining if they were parts of assemblages making up statistical or biological groupings. (2) Species of obvious ecological importance might be of value in the development of a monitoring program. Those Biologically Important Species with limited distribution (e.g., *O. sarsi* and *C. longicirrata*) are nevertheless successful in their particular living areas at the present time and under existing conditions. Such species, with their localized distributions and sizable numbers, biomass, or both, are important candidates for consideration in a monitoring program.

Widely distributed and abundant species that make up the major portion of the biomass are generally the ones with the greatest influence on the biology of the area. Other species, though not fitting the criteria for biological importance, may have more importance than is immediately obvious. For example, species in low abundance may represent important prey organisms, and their low density might only be the result of continuous cropping by predators. (See Thorson 1966 for review of factors influencing the establishment of marine benthic associations; Friedrich 1969 for a general discussion on predator-prey relationships of the benthos; and Christensen 1970 for comments on the relationship of the predatory sea star *Astropecten irregularis* and its prey *Spisula subtruncata*).

Table 9.2 List of all species collected by van Veen grab and trawl

Species I.D. Code No.	Classification	Species I.D. Code No.	Classification
	<b>Cnidaria</b>		<b>Crustacea (cont'd)</b>
1	<i>Acanthoptilum ptile</i>	20	Amphipoda type 5
2	Ceriantharia species A	21	Amphipoda type 6
3	Ceriantharia species B	22	Amphipoda type 7
4	<i>Stegopoma plicatile</i>	23	Amphipoda type 8
5	<i>Verticillina verticillata</i>	24	Amphipoda type 9
219	<i>Obelia</i> sp.	25	Amphipoda type 10
225	Actiniaria species A	213	Amphipoda type 11
226	Actiniaria species B	214	Amphipoda type 12
		218	<i>Gnathia elongata</i>
		26	<i>Balanus crenatus</i>
	<b>Porifera</b>	27	<i>Balanus evermanni</i>
		28	<i>Chionoecetes bairdi</i>
6	Porifera species A	29	<i>Crangon communis</i>
224	Porifera species B	30	<i>Diasyllis</i> sp. A
		31	<i>Diasyllis</i> sp. B
		32	<i>Eudorella emarginata</i>
	<b>Nematoda</b>	33	<i>Leucon</i> sp. A
		195	<i>Leucon</i> sp. B
7	Nematoda species A	34	Leptostraca species A
		35	Ostracoda species A
		36	<i>Pagurus</i> sp.
	<b>Sipunculida</b>	37	<i>Pinnixa schmitti</i>
		38	<i>Pugettia gracilis</i>
8	<i>Golfingia margaritacea</i>	231	<i>Pandalus borealis</i>
9	<i>Golfingia</i> sp. A	232	<i>Pandalus hypsinotus</i>
		233	<i>Pandalopsis dispar</i>
		234	<i>Argis</i> lar
	<b>Nemertinea</b>	235	<i>Hyas lyrata</i>
		236	<i>Cancer magister</i>
10	Nemertinea (several unidentified species)	237	<i>Lithodes aequispina</i>
		238	<i>Pagurus splendescens</i>
	<b>Brachiopoda</b>		<b>Echiuroidea</b>
11	<i>Laqueus californicus</i>	39	<i>Echiurus echiurus</i>
12	<i>Terebratulina unguicula</i>		
	<b>Bryozoa</b>		<b>Echinodermata</b>
		40	<i>Amphiodia craterodmeta</i>
13	Bryozoa (several unidentified species)	41	<i>Brisaster townsendi</i>
		42	<i>Ctenodiscus crispatus</i>
		43	<i>Cucumaria</i> sp.
	<b>Crustacea</b>	44	<i>Molpadia intermedia</i>
		45	<i>Ophiura quadrispina</i>
16	Amphipoda type 1	46	<i>Ophiura sarsi</i>
17	Amphipoda type 2	47	<i>Ophiura</i> sp. A
18	Amphipoda type 3	48	<i>Pentamera</i> sp.
19	Amphipoda type 4	49	<i>Strongylocentrotus drobachiensis</i>
		228	Porcellanasteridae species A

Table 9.2 (continued)

Species I.D. Code No.	Classification	Species I.D. Code No.	Classification
	<b>Mollusca</b>		<b>Pelecypoda (cont'd)</b>
	<b>Gastropoda</b>	86	<i>Macoma carlottensis</i>
		87	<i>Macoma inconspicua</i>
50	<i>Acmaea</i> sp.	88	<i>Macoma moesta</i>
51	Aeolidiidae species A	212	<i>Macoma balthica</i>
239	Ophisthobranchia species A	89	<i>Modiolus modiolus</i>
52	<i>Boreotrophon</i> sp.	90	<i>Mya priapus</i>
53	<i>Cylichna attonsa</i>	91	<b>Pelecypoda species A</b>
54	<i>Dendronotus subramosus</i>	92	<i>Nucula tenuis</i>
55	<i>Fustritron oregonensis</i>	93	<i>Nuculana minuta</i>
56	<i>Lora</i> sp. A	94	<i>Nuculana pernula</i>
57	<i>Lora</i> sp. B	223	<i>Nuculana fossa</i>
207	<i>Amphissa reticulata</i>	95	<i>Psephidia lordi</i>
58	<i>Margarites</i> sp. A	96	<i>Pseudopithina compressa</i>
208	<i>Margarites</i> sp. B	97	<i>Serripes groenlandicus</i>
59	<i>Mitrella gouldi</i>	98	<i>Thracia adamsi</i>
60	<i>Nassarius mendicus</i>	209	<i>Thracia trapezoides</i>
61	<i>Natica clausa</i>	99	<i>Thyasira flexuosa</i>
62	<i>Odostomia</i> sp.	100	<i>Yoldia arctica</i>
63	<i>Puncturella galeata</i>	101	<i>Yoldia thraciaeformis</i>
64	<i>Puncturella noachina</i>	194	<i>Pandora forresterensis</i>
65	Gastropoda species A	206	<i>Hiatella arctica</i>
66	Gastropoda species B	240	<i>Bankia setacea</i>
67	<i>Trichotropis borealis</i>	241	<i>Pecten randolphii</i>
200	<i>Trichotropis cancellata</i>		
68	<i>Turbonilla</i> sp. A		<b>Amphineura</b>
69	<i>Turbonilla</i> sp. B	102	<i>Chaetoderma robusta</i>
	<b>Scaphopoda</b>		
70	<i>Cadulus aberrans</i>		<b>Annelida</b>
71	<i>Cadulus</i> sp.		
72	<i>Dentalium pretiosum</i>		<b>Hirudinea</b>
73	<i>Dentalium</i> sp.		
	<b>Pelecypoda</b>	226	<b>Hirudinea species A</b>
74	<i>Astarte esquimalti</i>		<b>Polychaeta</b>
75	<i>Astarte alaskensis</i>		
76	<i>Axinopsida serricata</i>		<b>Polynoidae</b>
77	<i>Aximula ferruginosa</i>	103	<i>Antinoella</i> sp.
78	<i>Cardiomya pectinata</i>	104	<i>Antinoe macrolepida</i>
79	<i>Chlamys rubida</i>	105	<i>Enipo canadensis</i>
80	<i>Clinocardium californiense</i>	106	<i>Lagisca rarispina</i>
81	<i>Clinocardium ciliatum</i>	107	<i>Gattyana brunnea</i>
82	<i>Cyclopecten</i> sp.	108	<i>Gattyana cirrosa</i>
83	<i>Dacridium pacificum</i>	109	<i>Gattyana treadwelli</i>
84	<i>Lyonsia norvegi</i>	110	<i>Harmothoe imbricata</i>
85	<i>Macoma calcarea</i>	111	<i>Lepidonotus caelorus</i>

Table 9.2 (continued)

Species I.D. Code No.	Classification	Species I.D. Code No.	Classification
	Sigalionidae		Goniadidae
112	<i>Phloe minuta</i>	131	<i>Goniada annulata</i>
	Acoetidae	132	<i>Goniada maculata</i>
		133	<i>Glycinde picta</i>
113	<i>Peisidice aspera</i>		Onuphidae
	Phyllodocidae	187	<i>Onuphis conchylega</i>
114	<i>Eteone barbata</i>	134	<i>Onuphis geofiliformis</i>
115	<i>Eteone longa</i>	135	<i>Onuphis iridescens</i>
116	<i>Phyllodoce maculata</i>		Lumbrinereidae
201	<i>Phyllodoce</i> sp. A		
204	<i>Phyllodoce groenlandica</i>	136	<i>Lumbrinereis similabris</i>
	Hesionidae		Dorvilleidae
117	<i>Podarke pugettensis</i>	138	<i>Dorvillea pseudorubrovittata?</i>
	Pilargidae		Orbiniidae
118	<i>Ancistrosyllis hamata</i>	139	<i>Haptoscoloplos panamensis</i>
	Syllidae		Paraonidae
120	<i>Eusyllis blomstrandii</i>	141	<i>Aedicira antennata</i>
121	<i>Pionosyllis magnifica</i>	142	<i>Aricidea suecica</i>
202	<i>Syllis sclerolaema</i>	143	<i>Paraonis gracilis</i>
210	<i>Exogone?</i> sp.		Spionidae
122	<i>Syllis alternata</i>	144	<i>Laonice cirrata</i>
123	<i>Syllis armillaris</i>	145	<i>Prionospio malmgreni</i>
	Nereidae	146	<i>Spio filicornis</i>
124	<i>Nereis procera</i>	193	<i>Polydora</i> sp. A
125	<i>Nereis</i> sp. A		Magelonidae
126	<i>Platynereis agassizi</i>		
199	<i>Nereis paucidentata</i>	147	<i>Magelona japonica</i>
	Nephtydididae		Cirratulidae
127	<i>Nephtys caeca</i>	148	<i>Chaetozone setosa</i>
128	<i>Nephtys ciliata</i>	149	<i>Cossura longicirrata</i>
129	<i>Nephtys cornuta</i>	150	<i>Tharyx monilaris</i>
	Glyceridae	151	<i>Tharyx multifidus</i>
130	<i>Glycera nana</i>	152	<i>Tharyx parvus</i>
			Flabelligeridae
		153	<i>Flabelligera infundibularis</i>
		154	<i>Stylarioides papillata</i>

Table 9.2 (continued)

Species I.D. Code No.	Classification	Species I.D. Code No.	Classification
	Scalibregmidae		Ampharetidae (cont'd)
155	<i>Scalibregma inflatum</i>	172	<i>Lysippe labiata</i>
	Opheliidae	173	<i>Melinna cristata</i>
		190	<i>Melinna</i> sp. A
156	<i>Ammotrypane aulogaster</i>		Terebellidae
196	<i>Armandia?</i> sp.		
216	<i>Ophelia limacina</i>	174	<i>Amphitrite cirrata</i>
	Sternaspidae	175	<i>Pista cristata</i>
		176	<i>Pista fasciata</i>
		177	<i>Terebellides stroemi</i>
157	<i>Sternaspis scutata</i>	178	<i>Trichobranchus glacialis</i>
	Capitellidae	191	<i>Artacama coniferi</i>
		217	<i>Polycirrus medusa</i>
158	<i>Capitella capitata</i>	221	<i>Artacamella hancocki</i>
159	<i>Heteromastus filiformis</i>		Sabellidae
183	<i>Mediomastus?</i> sp.		
211	<i>Notomastus tenuis</i>	179	<i>Chone gracilis</i>
	Maldanidae	180	<i>Euchone analls</i>
		189	<i>Euchone</i> sp. A
160	<i>Axiothella rubrocincta</i>	181	<i>Fabricia</i> sp.
161	<i>Maldane glebifex</i>	182	<i>Fabrisabella</i> sp.
162	<i>Praxillella gracilis</i>	183	<i>Pseudopotamilla reniformis</i>
163	<i>Rhodine bitorquata</i>	184	<i>Myxicola infundibulum</i>
192	<i>Leiochone columbiana</i>		Serpulidae
197	<i>Asychis similis</i>		
215	<i>Notoproctus pacificus</i>	186	<i>Spirorbis</i> sp.
	Oweniidae	188	<i>Crucigera zygophora</i>
		198	<i>Crucigera irregularis</i>
164	<i>Myriochele heeri</i>	220	<i>Chitonopoma groenlandica</i>
	Sabellariidae		Chordata
165	<i>Idanthyrus armatus</i>		Ascidacea
	Pectinariidae	242	<i>Ascidia prunum</i>
166	<i>Pectinaria auricola</i>		Vertebrata
203	<i>Pectinaria brevicoma</i>	243	<i>Atheresthes stomias</i>
	Ampharetidae	244	<i>Hippoglossoides elassodon</i>
		245	<i>Parophrys vetulus</i>
		246	<i>Glyptocephalus zachirus</i>
167	<i>Amage perfecta</i>	247	<i>Lycodes brevipes</i>
168	<i>Amage?</i> sp.	248	<i>Lumpenella longirostris</i>
169	<i>Ampharete arctica</i>	249	<i>Radulinus asprellus</i>
170	<i>Amphicteis scaphobranchiata</i>	250	<i>Malacocottus kincaidi</i>
171	<i>Anobothrus gracilis</i>	251	<i>Theragra chalcogramma</i>

Table 9.3 List of Biologically Important Species (BIS) as determined by criteria discussed in text section 9.4.1

Species	Distribution shown in Figure No.:
<i>Acanthoptilum ptille</i>	9.2
Cerianthid A	9.3
<i>Eudorella emarginata</i>	9.4
<i>Pinnixa schmitti</i>	9.5
<i>Amphiodia craterodmeta</i>	9.6
<i>Ctenodiscus crispatus</i>	9.7
<i>Ophiura sarsi</i>	9.8
<i>Cylichna attonsa</i>	9.9
<i>Odostomia</i> sp.	9.10
<i>Dentalium</i> sp.	9.11
<i>Axinopsida serricata</i>	9.12
<i>Clinocardium ciliatum</i>	9.13
<i>Macoma calcaria</i>	9.14
<i>Macoma inconspicua</i>	9.15
<i>Nuculara minuta</i>	9.16
<i>Yoldia arctica</i>	9.17
<i>Yoldia thraciaeformis</i>	9.18
<i>Chaetoderma robusta</i>	9.19
<i>Eteone barbata</i>	9.20
<i>Phyllodoce maculata</i>	9.21
<i>Podarke pugettensis</i>	9.22
<i>Nephtys ciliata</i>	9.23
<i>Glycera nana</i>	9.24
<i>Goniada annulata</i>	9.25
<i>Lumbrineris similabris</i>	9.26
<i>Haploscoloplos panamensis</i>	9.27
<i>Aricidea suecica</i>	9.28
<i>Prionospio malmgreni</i>	9.29
<i>Chaetozone setosa</i>	9.30
<i>Cossura longicirrata</i>	9.31
<i>Tharyx monilaris</i>	9.32
<i>Tharyx parvus?</i>	9.33
<i>Sternaspis scutata</i>	9.34
<i>Heteromastus filiformis</i>	9.35
<i>Praxillella gracilis</i>	9.36
<i>Amphicteis scaphobranchiata</i>	9.37
<i>Lysippe labiata</i>	9.38
<i>Melinna cristata</i>	9.39
<i>Pista cristata</i>	9.40
<i>Myxicola infundibulum</i>	9.41

Table 9.4 Species collected only by trawl

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Sponge B	<i>Lithodes aequispinus</i>
Anemone A	<i>Pagurus splendescens</i>
Anemone B	Opisthobranch A
Cerianthid B	<i>Pandora forresterensis</i>
Porcellanasterid	<i>Bankia setacea</i>
Leech	<i>Pecten randolphii</i>
<i>Antinoe macroleptida</i>	<i>Ascidia prunum</i>
<i>Lagisca rarispina</i>	<i>Atheresthes stomias</i>
<i>Nereis</i> A	<i>Hippoglossoides elassodon</i>
Amphipod 11	<i>Parophrys vetulus</i>
<i>Pandalus borealis</i>	<i>Glyptocephalus zachirus</i>
<i>Pandalopsis dispar</i>	<i>Lycodes brevipes</i>
<i>Argis</i> lar	<i>Lumpenella longirostris</i>
<i>Pandalus hypsinotus</i>	<i>Radulinus asprellus</i>
<i>Hyas lyrata</i>	<i>Malacocottus kincaidi</i>
<i>Cancer magister</i>	<i>Theragra chalcogramma</i>

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Table 9.5 Gleason's Index of Diversity calculated by station and grab

(Symbol: S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab)

Station	Grab	September	December	March	April
0A	S	1.0			
	1	1.0			
	2	1.4			
	3	0.9			
1	S	1.7			
	1	1.3			
	2	2.0			
	3	1.4			
2A	S	4.8	3.7		
	1	3.7	3.3		
	2	4.1	2.6		
	3	2.6	3.1		
3	S	0.0			
	1	0.0			
	2	0.0			
	3	0.0			
3A	S		5.2		
	1		4.6		
	2		2.3		
	3		3.9		
4	S	3.8			
	1	2.4			
	2	2.7			
	3	3.0			
5	S	3.7			
	1	2.9			
	2	2.4			
	3	3.2			
6	S	3.4			
	1	2.0			
	2	2.2			
	3	2.7			
7	S	4.7			
	1	3.2			
	2	3.5			
	3	2.5			

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab					
Station	Grab	September	December	March	April
8	S	5.0			5.1
	1	3.6			3.8
	2	3.3			4.5
	3	3.4			2.9
9	S	3.2			
	1	2.3			
	2	2.6			
	3	2.1			
10	S	4.8			
	1	3.6			
	2	3.3			
	3	4.6			
11	S			4.0	
	1			2.3	
	2			2.4	
	3			3.8	
12	S	5.2			
	1	4.6			
	2	3.0			
	3	3.3			
13	S	4.2			3.3
	1	3.5			2.8
	2	3.3			1.8
	3	3.2			3.5
14	S	5.7			
	1	2.0			
	2	3.8			
	3	4.1			
15	S			4.0	
	1			1.7	
	2			2.8	
	3			3.7	
16	S	4.6			
	1	3.6			
	2	3.5			
	3	4.8			
17	S	4.1			
	1	3.3			
	2	4.3			
	3	4.0			

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab					
Station	Grab	September	December	March	April
18	S	4.6			4.8
	1	2.1			2.4
	2	2.3			2.5
	3	3.0			3.6
19	S	4.4			
	1	3.6			
	2	2.5			
	3	4.7			
20	S	4.6			
	1	3.3			
	2	3.1			
	3	3.2			
21	S	5.9			
	1	2.8			
	2	3.9			
	3	3.9			
22	S	4.8			
	1	3.3			
	2	3.5			
	3	3.9			
23	S	4.8			
	1	4.5			
	2	3.6			
	3	4.1			
24	S	8.3			
	1	6.4			
	2	6.0			
	3	5.9			
25	S		6.1		
	1		5.2		
	2		3.2		
	3		3.5		
26	S		3.7		
	1		3.5		
	2		3.8		
	3		2.0		
27	S	4.9		4.5	
	1	3.2		2.7	
	2	3.7		3.8	
	3	3.1		2.2	

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab					
Station	Grab	September	December	March	April
28	S	4.2			
	1	3.6			
	2	3.2			
	3	4.1			
29	S	5.0			
	1	3.7			
	2	2.5			
	3	4.7			
30	S	6.1			7.6
	1	5.4			5.4
	2	2.1			3.8
	3	3.6			3.8
31	S			4.4	
	1			3.3	
	2			3.1	
	3			3.7	
32	S	5.2			
	1	3.1			
	2	3.8			
	3	4.0			
33	S	6.9			9.2
	1	4.4			6.3
	2	5.4			7.0
	3	4.0			6.2
34	S	11.6			12.1
	1	9.0			9.1
	2	4.9			3.3
	3	9.4			8.5
35	S	5.0			
	1	3.2			
	2	3.8			
	3	4.5			
35A	S	8.9			
	1	5.5			
	2	5.7			
	3	6.9			

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab

Station	Grab	September	December	March	April
36	S	5.7			
	1	3.8			
	2	4.2			
	3	5.4			
37	S	7.6			
	1	3.8			
	2	5.4			
	3	10.7			
38	S	5.0			
	1	4.7			
	2	3.4			
	3	4.7			
39	S	3.9			
	1	3.2			
	2	3.1			
	3	2.5			
40	S	4.8			5.7
	1	3.6			3.4
	2	3.5			4.7
	3	4.1			4.5
41	S	4.4			
	1	2.8			
	2	2.8			
	3	2.8			
42	S	3.5			
	1	2.2			
	2	4.0			
	3	2.2			
42A	S				6.6
	1				3.6
	2				5.1
	3				3.5
43	S	3.6			
	1	2.5			
	2	2.7			
	3	3.6			
44	S	4.1			
	1	3.0			
	2	3.3			
	3	3.1			

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab					
Station	Grab	September	December	March	April
45	S	4.2			
	1	2.8			
	2	3.1			
	3	2.3			
46	S	4.1			
	1	2.6			
	2	2.1			
	3	3.2			
47	S	2.8			
	1	3.0			
	2	1.7			
	3	2.2			
47A	S			4.4	
	1			3.0	
	2			2.0	
	3			4.9	
48	S	4.1			
	1	3.2			
	2	1.9			
	3	3.2			
49	S	5.1			
	1	2.8			
	2	4.6			
	3	3.1			
50	S	4.2			
	1	2.1			
	2	2.8			
	3	3.8			
51	S	4.6			
	1	3.2			
	2	4.1			
	3	1.8			
52	S	5.3			
	1	3.4			
	2	4.4			
	3	4.3			
53	S	4.4			
	1	4.3			
	2	4.0			
	3	2.8			

Table 9.5 (continued)

S = pooled data per station; 1 = first grab; 2 = second grab; 3 = third grab

Station	Grab	September	December	March	April
54	S	3.8			
	1	3.0			
	2	3.3			
	3	3.6			
55	S	7.3			
	1	3.9			
	2	5.9			
	3	5.7			
56	S	6.8			
	1	4.8			
	2	4.3			
	3	4.5			
57	S	8.7			
	1	7.8			
	2	7.1			
	3	5.3			
58	S	4.0			
	1	2.7			
	2	3.4			
	3	1.7			
59	S	5.6			
	1	3.2			
	2	4.1			
	3	3.7			
60	S	5.1			
	1	2.5			
	2	3.6			
	3	5.8			

Table 9.6 Species collected only in the April grab-sampling program

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<i>Melinna</i> A	<i>Phyllodoce groenlandica</i>
<i>Arctacama conferti</i>	<i>Amphisca reticulata</i>
<i>Leiochone columbiana</i>	<i>Margarites</i> B
<i>Polydora</i> sp.	<i>Exogone?</i> sp.
<i>Pandora forresterensis</i>	<i>Notomastus tenuis</i>
<i>Leucon</i> B	<i>Notoproctus pacificus</i>
<i>Armania?</i> sp.	<i>Ophelia limacina</i>
<i>Asychis similis</i>	<i>Pseudopotamilla reniformis</i>
<i>Crucigera irregularis</i>	<i>Grathia elongata</i>
<i>Nereis paucidentata</i>	<i>Obelia</i> sp.
<i>Trichotropis cancellata</i>	<i>Chintonopoma groenlandica</i>
<i>Syllis sclerotaema</i>	<i>Artacamella hancocki</i>
<i>Pectinaria brevicoma</i>	

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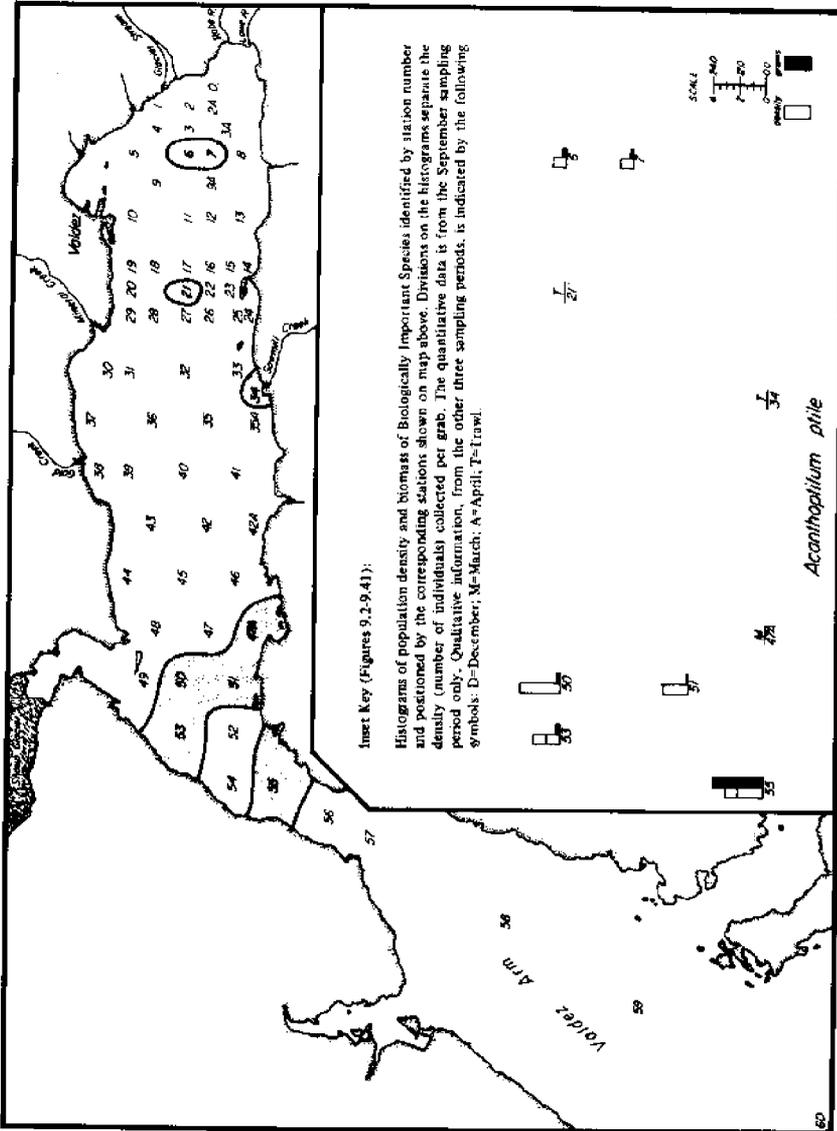


Figure 9.2 Map of sampling grid with the stippled area indicating the distribution of *Acanthopeltium ptille*.

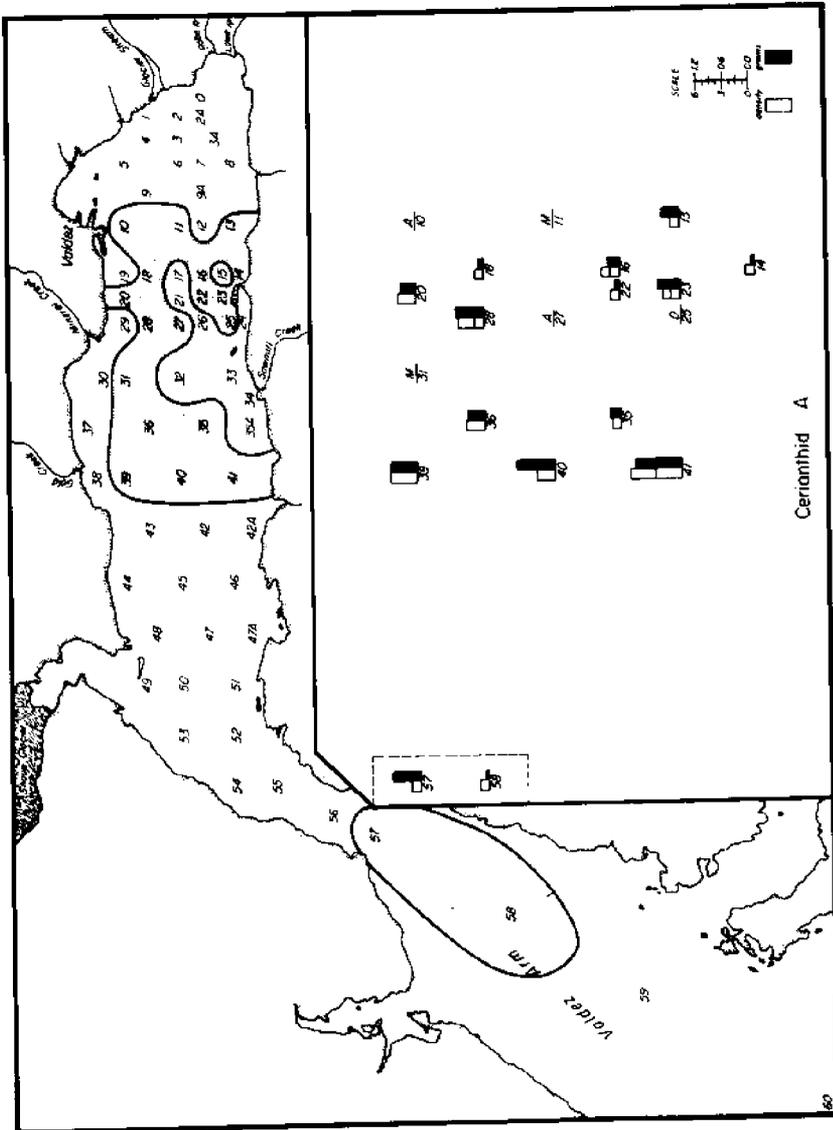


Figure 9.3 Map of sampling grid with the stippled area indicating the distribution of Cerianthid A. (See Figure 9.2 for inset key to histograms).

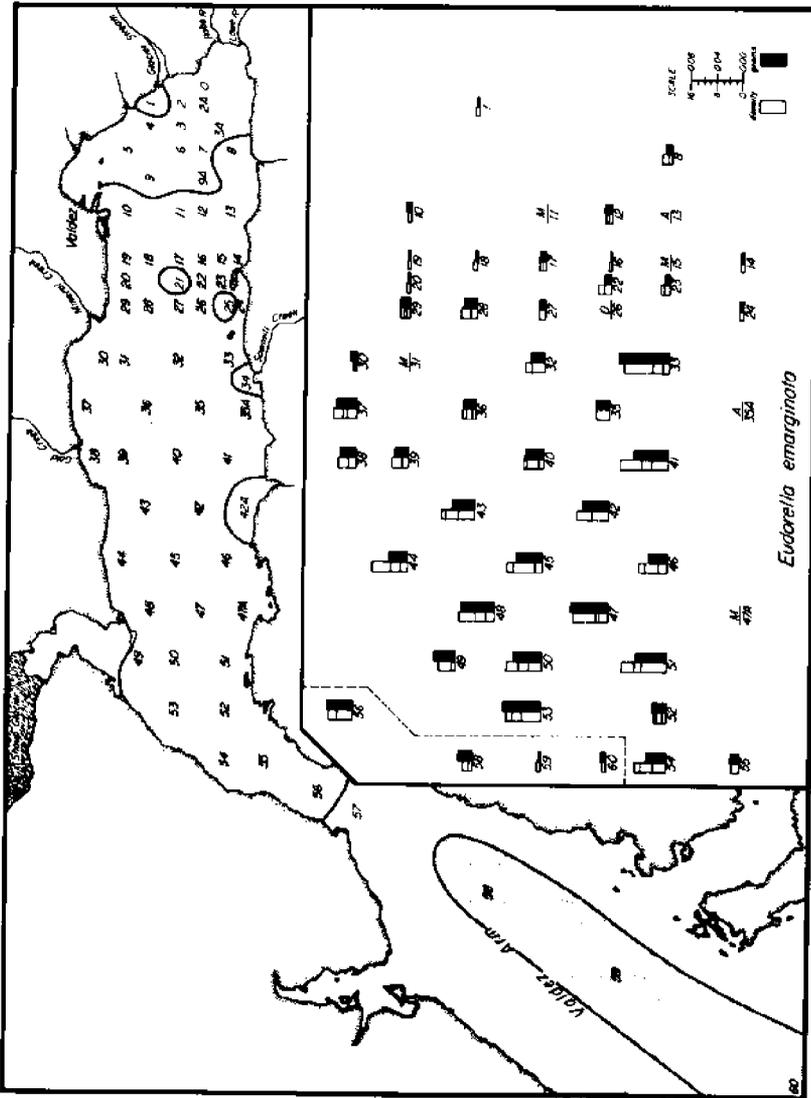


Figure 9.4 Map of sampling grid with the stippled area indicating the distribution of *Eudorella emarginata*. (See Figure 9.2 for inset key to histograms).

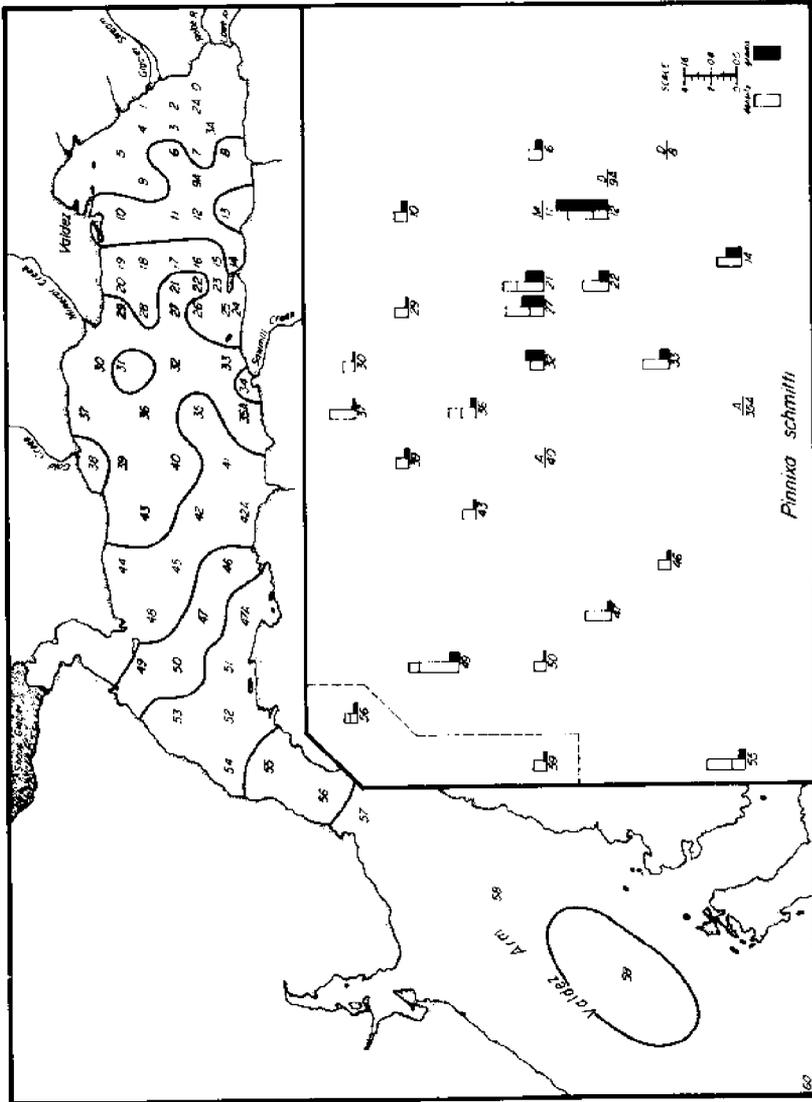


Figure 9.5 Map of sampling grid with the stippled area indicating the distribution of *Pinnixa schmitti*. (See Figure 9.2 for inset key to histograms).

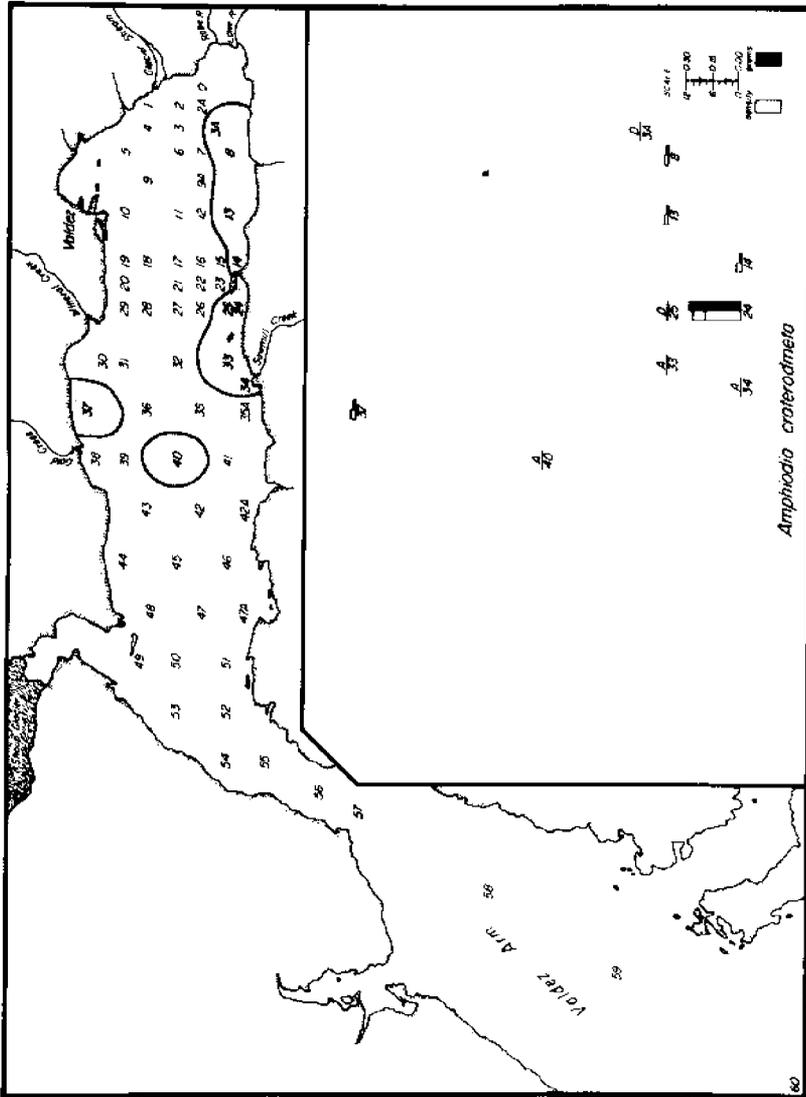


Figure 9.6 Map of sampling grid with the stippled area indicating the distribution of *Amphiodia crateradmetra*. (See Figure 9.2 for inset key to histograms).

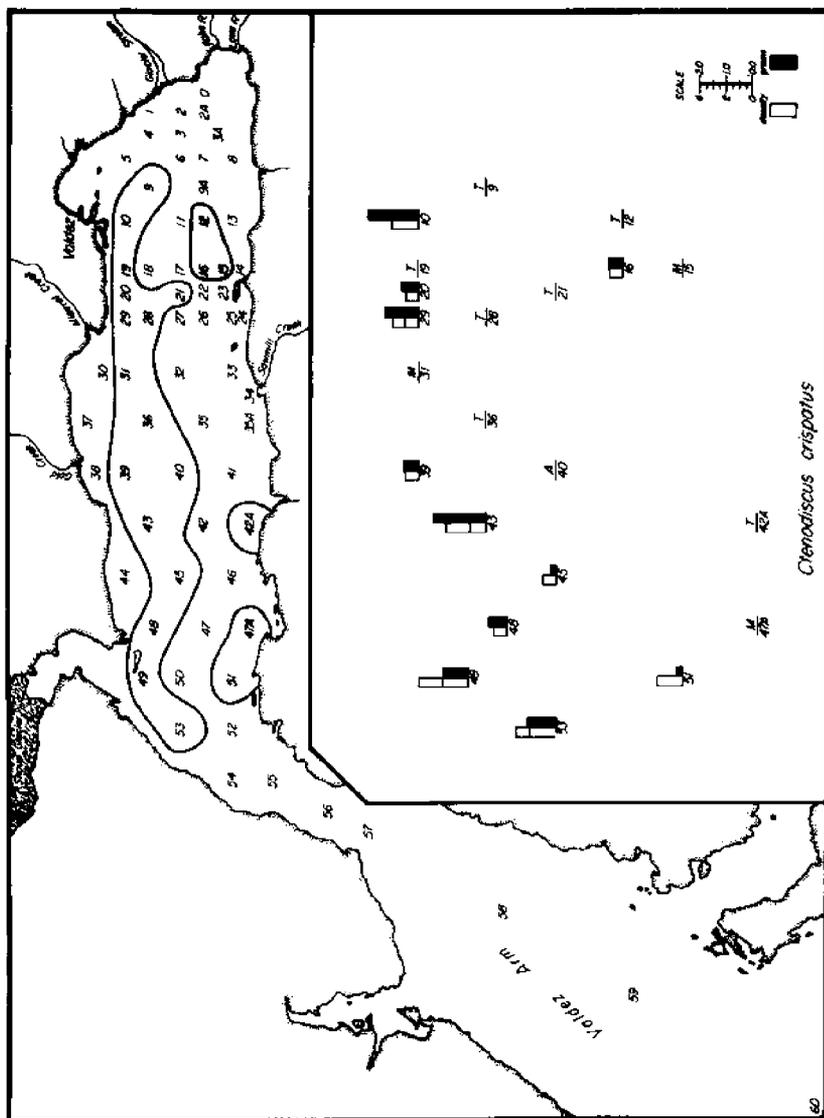


Figure 9.7 Map of sampling grid with the stippled area indicating the distribution of *Ctenodiscus crispatus*. (See Figure 9.2 inset key to histograms).

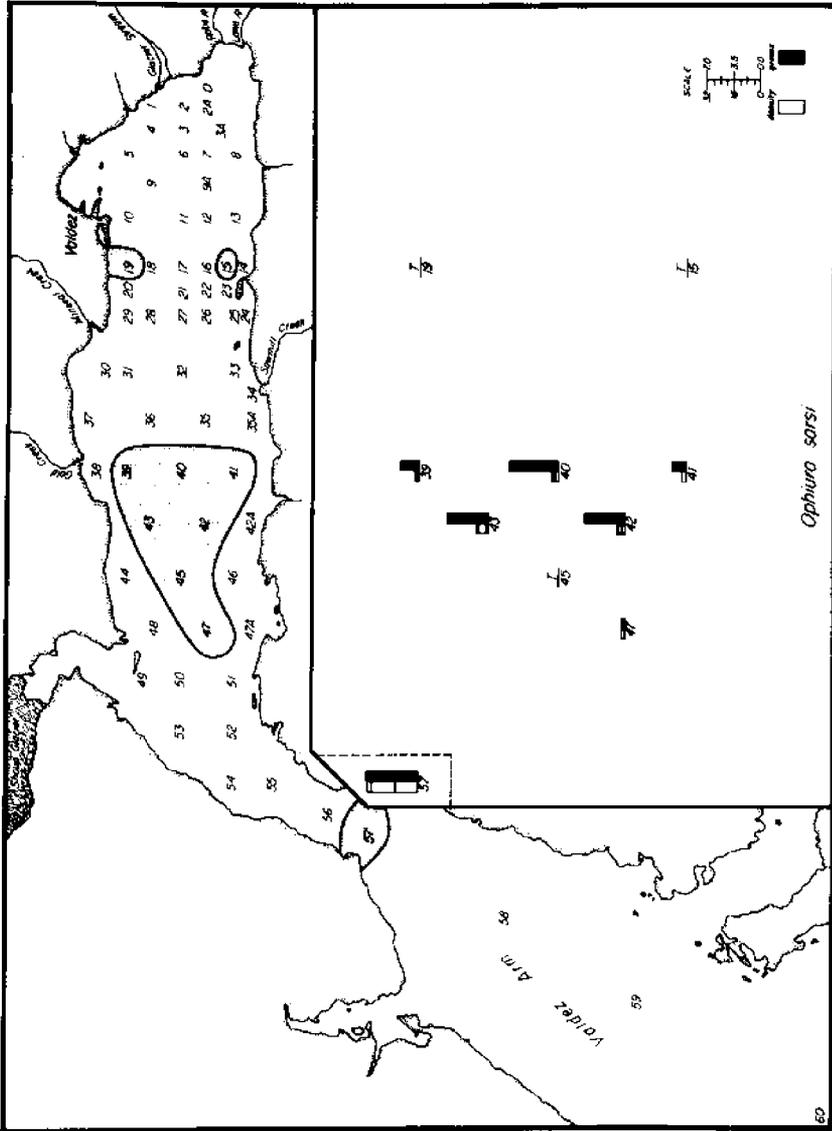


Figure 9.8 Map of sampling grid with the stippled area indicating the distribution of *Ophiura sarsi*. (See Figure 9.2 for inset key to histograms).

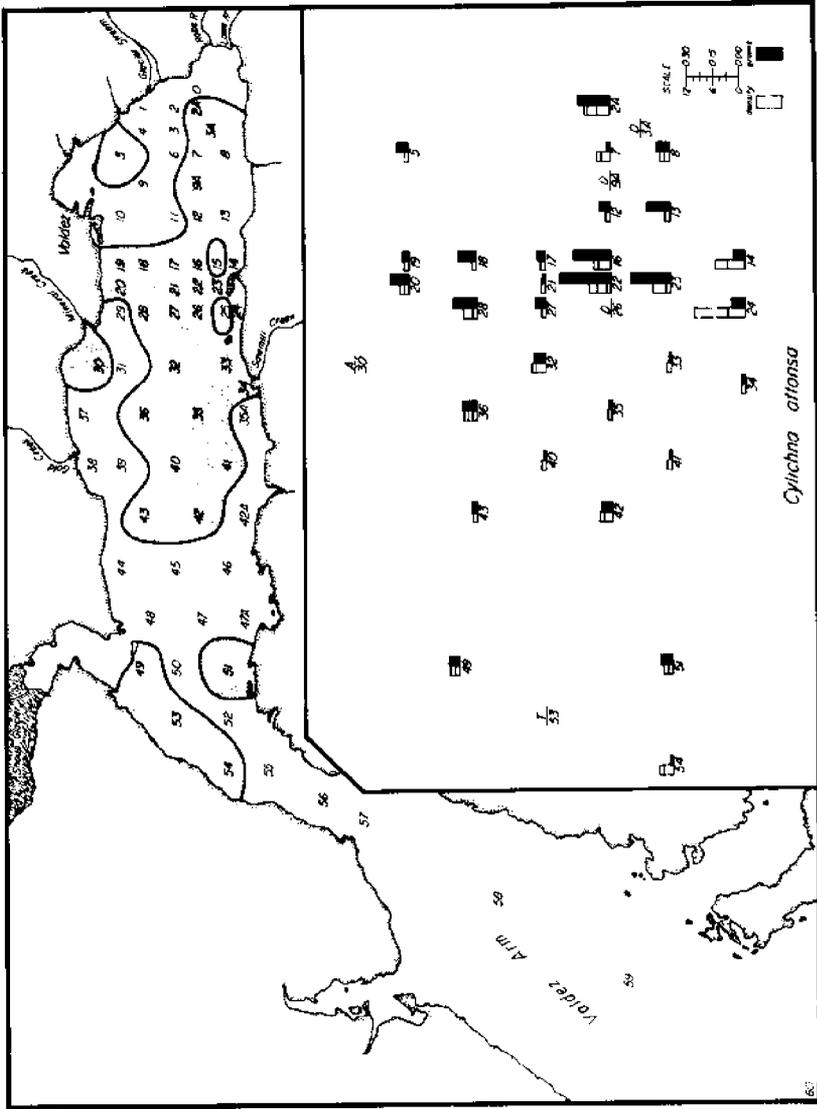


Figure 9.9 Map of sampling grid with the stippled area indicating the distribution of *Cyllichna atronasa*. (See Figure 9.2 for inset key to histograms).

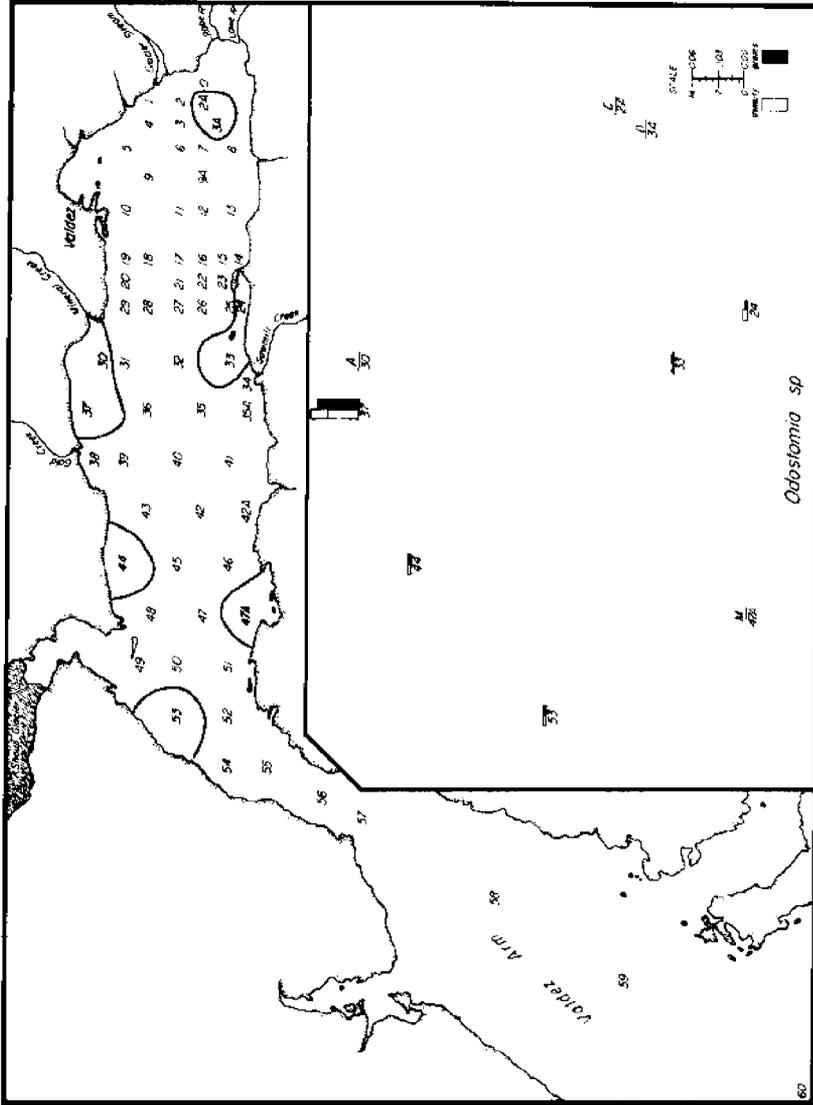


Figure 9.10 Map of sampling grid with the stippled area indicating the distribution of *Odostomia* sp. (See Figure 9.2 for inset key to histograms).

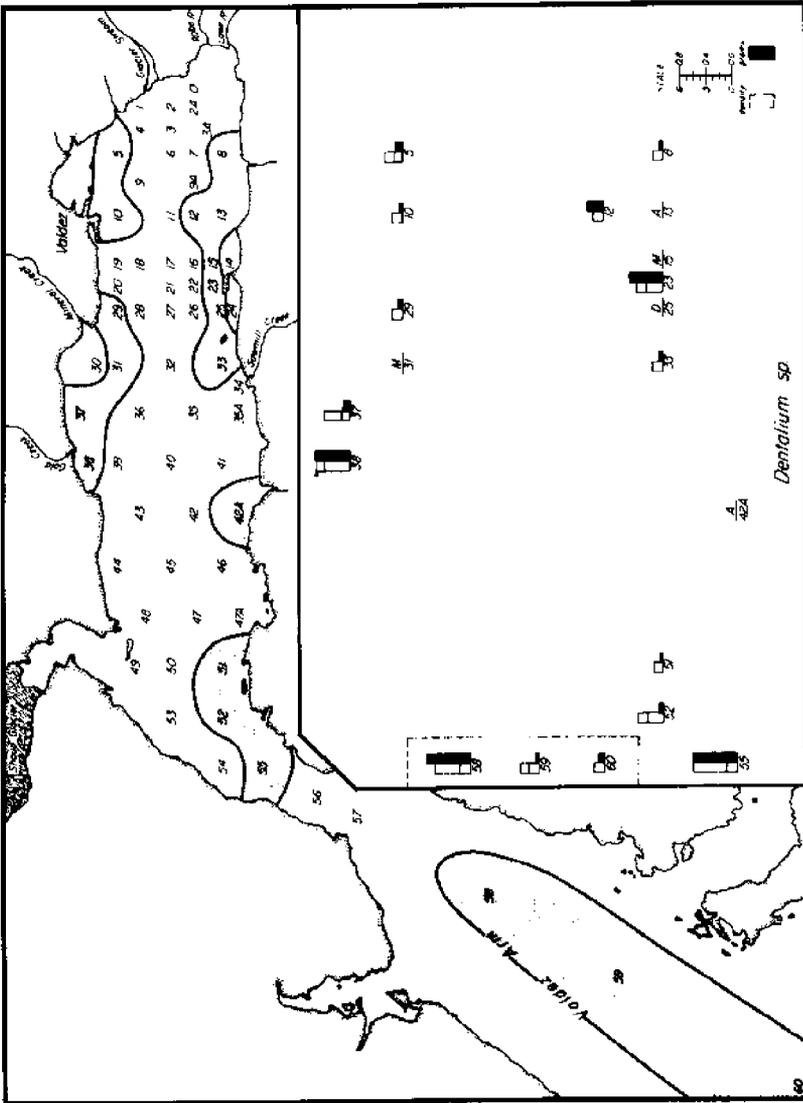


Figure 9.11 Map of sampling grid with the stippled area indicating the distribution of *Dentalium* sp. (See Figure 9.2 for inset key to histograms).

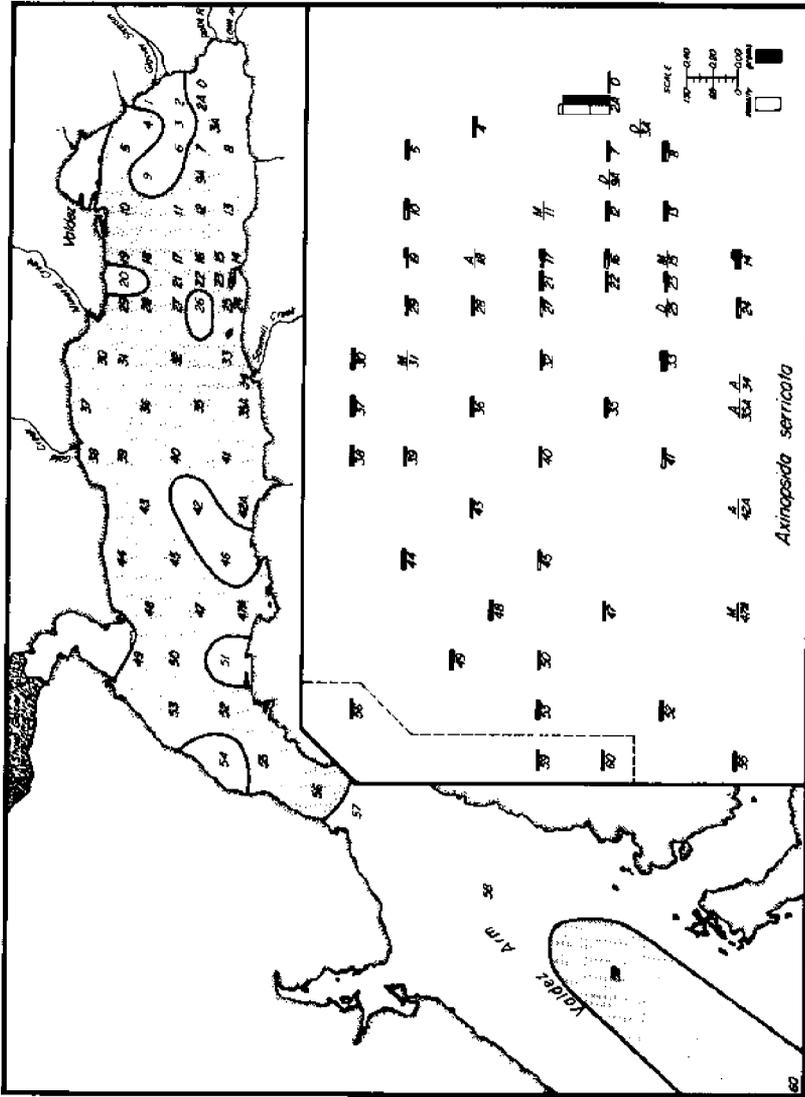


Figure 9.12 Map of sampling grid with the stippled area indicating the distribution of *Axiopsisida serricata*. (See Figure 9.2 for inset key to histograms).

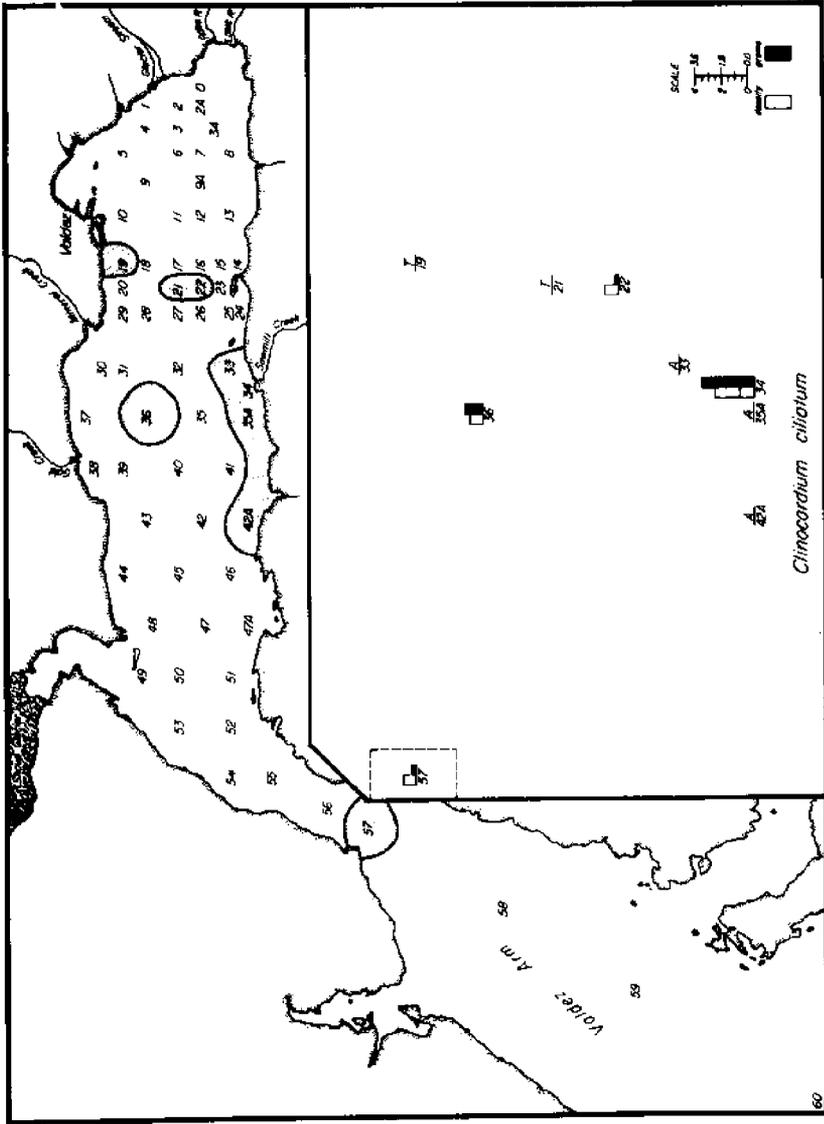


Figure 9.13 Map of sampling grid with the stippled area indicating the distribution of *Clinocardium ciliatum*. (See Figure 9.2 for inset key to histograms).

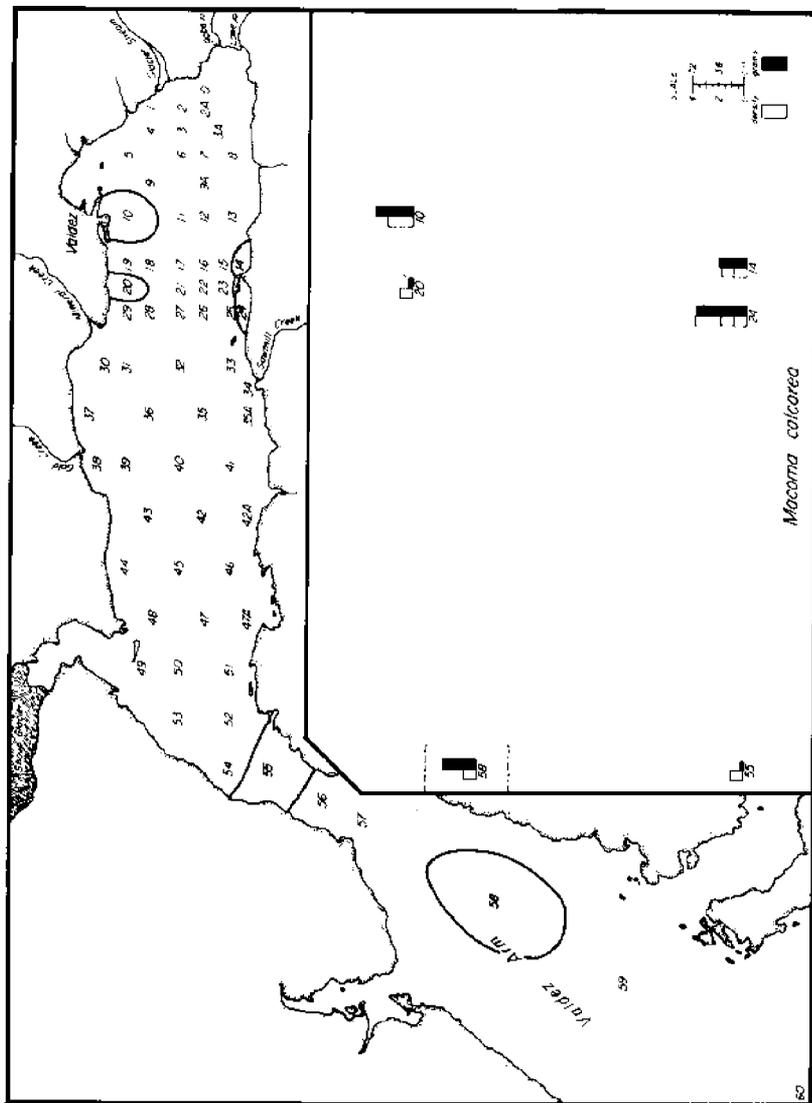


Figure 9.14 Map of sampling grid with the stippled area indicating the distribution of *Macoma calcareo*. (See Figure 9.2 for inset key to histograms).

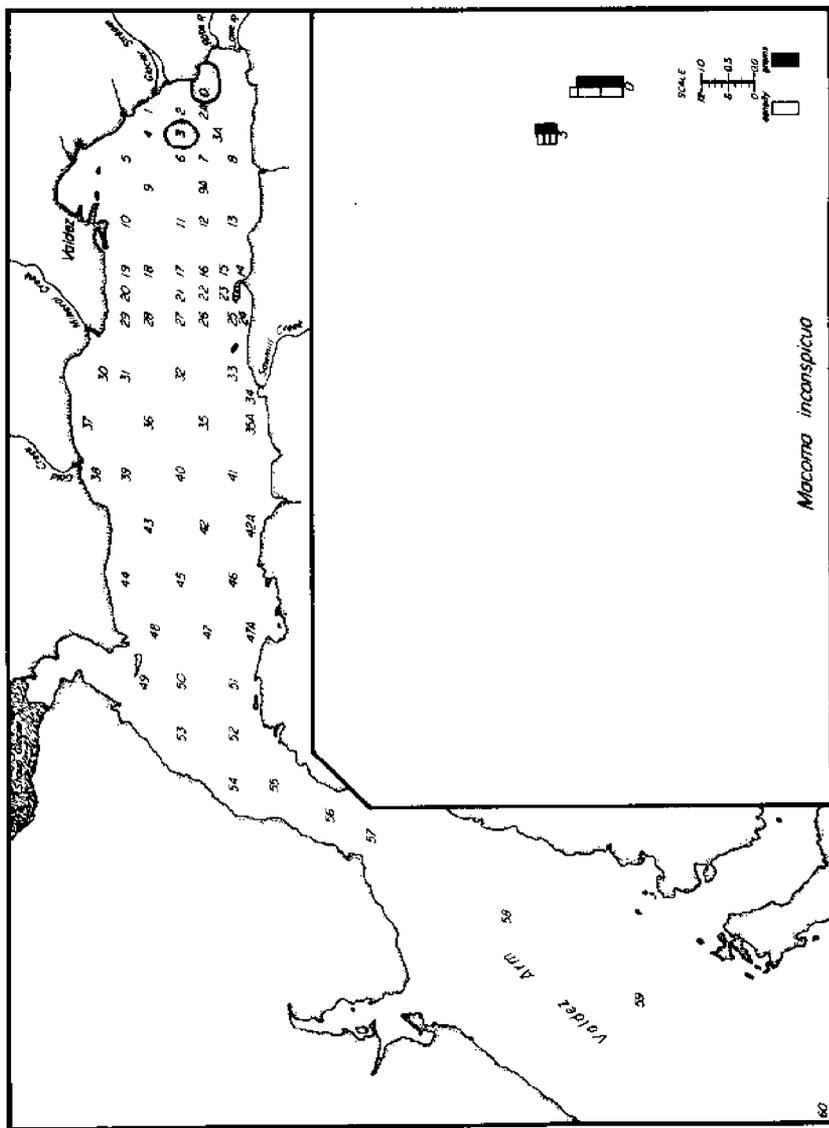


Figure 9.15 Map of sampling grid with the stippled area indicating the distribution of *Macoma inconspicua*. (See Figure 9.2 for inset key to histograms).

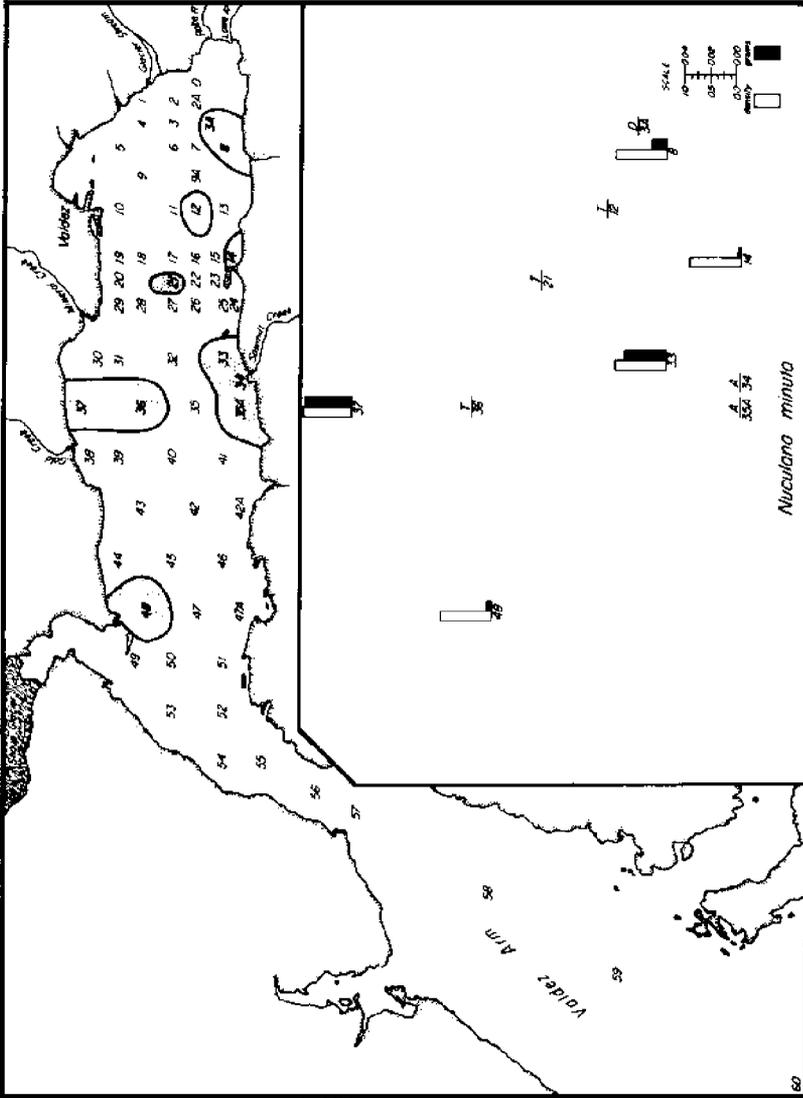


Figure 9.16 Map of sampling grid with the stippled area indicating the distribution of *Nuculana minuta*. (See Figure 9.2 for inset key to histograms).

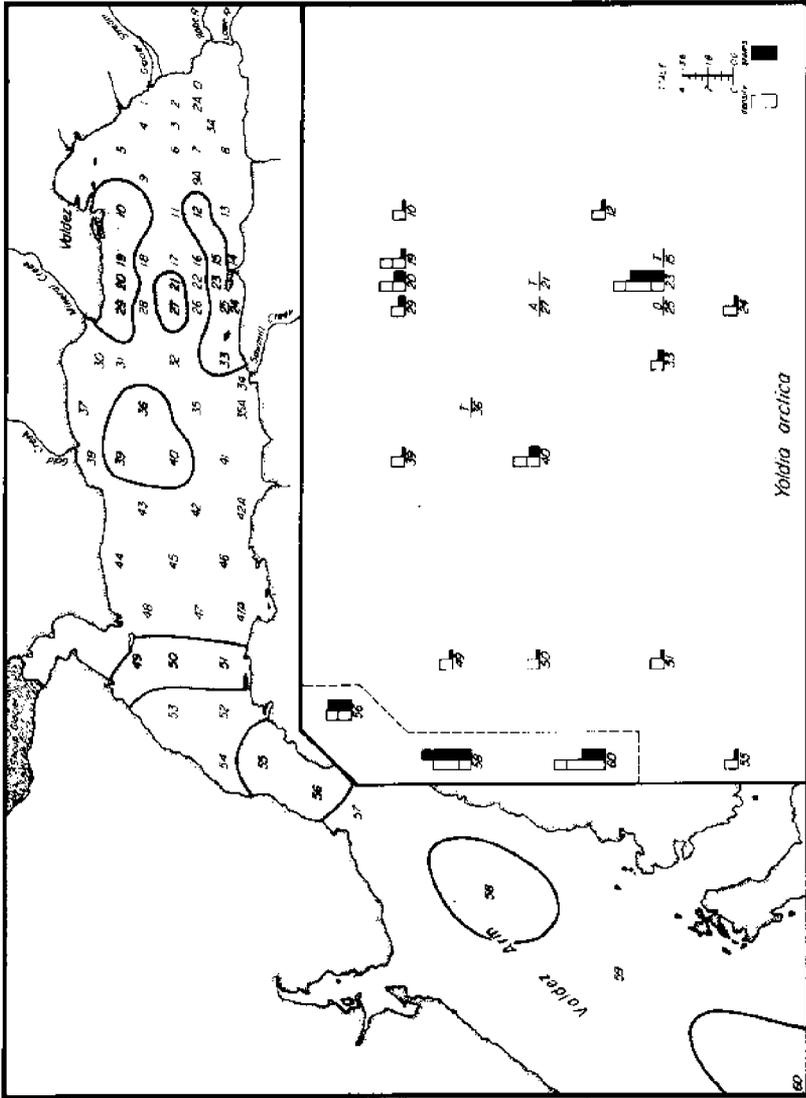


Figure 9.17 Map of sampling grid with the stippled area indicating the distribution of *Yoldia arctica*. (See Figure 9.2 for inset key to histograms).

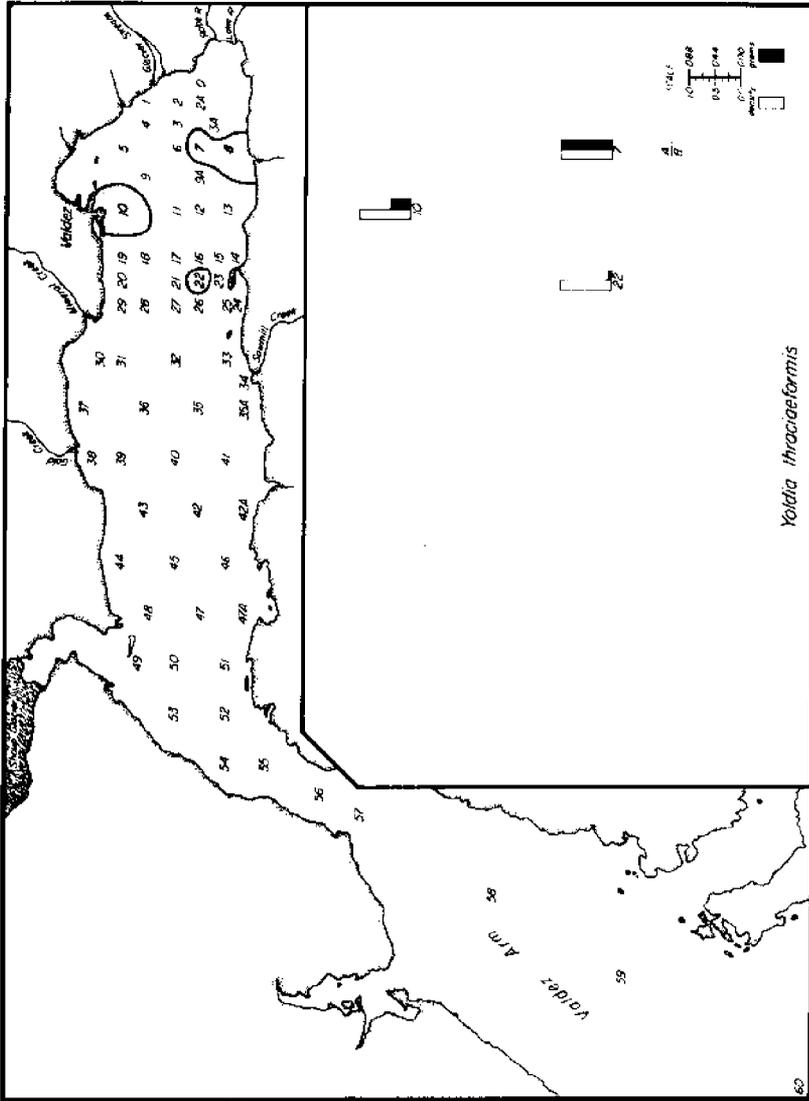


Figure 9.18 Map of sampling grid with the stippled area indicating the distribution of *Yoldia thraciaeformis*. (See Figure 9.2 for inset key to histograms).

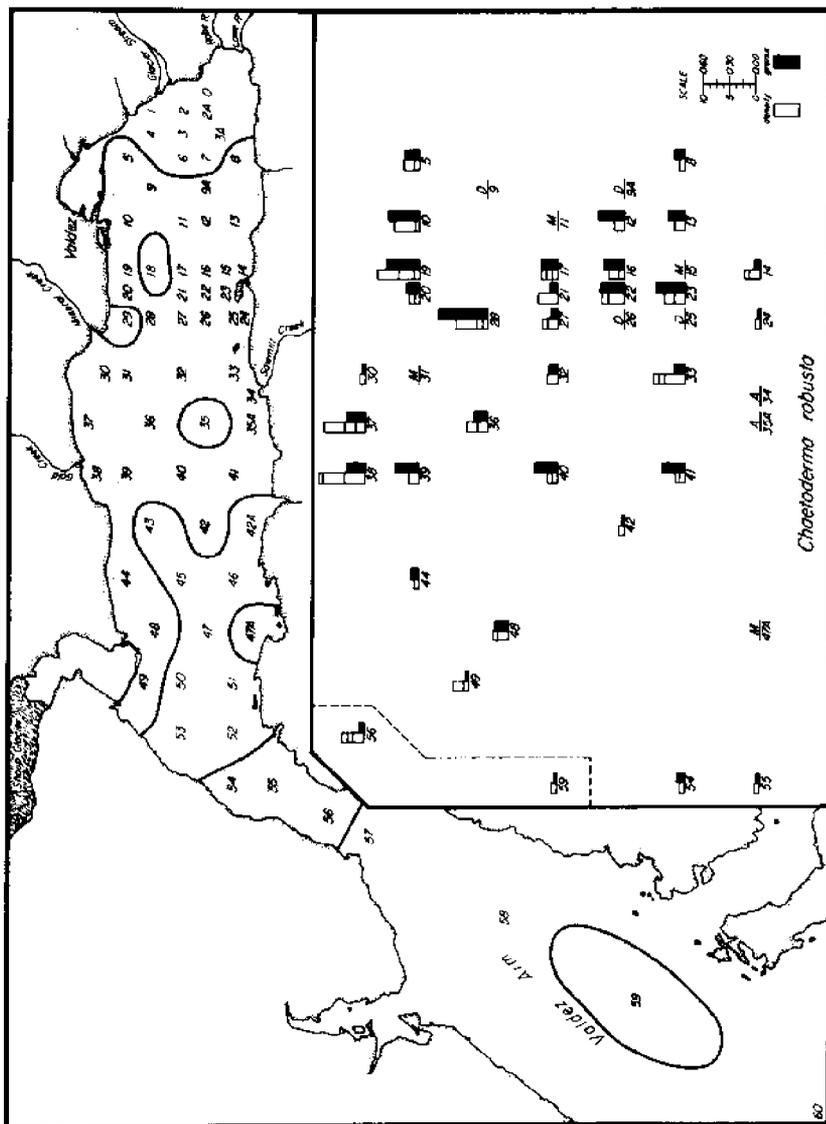


Figure 9.19 Map of sampling grid with the stippled area indicating the distribution of *Chaetoderma robusta*. (See Figure 9.2 for inset key to histograms).

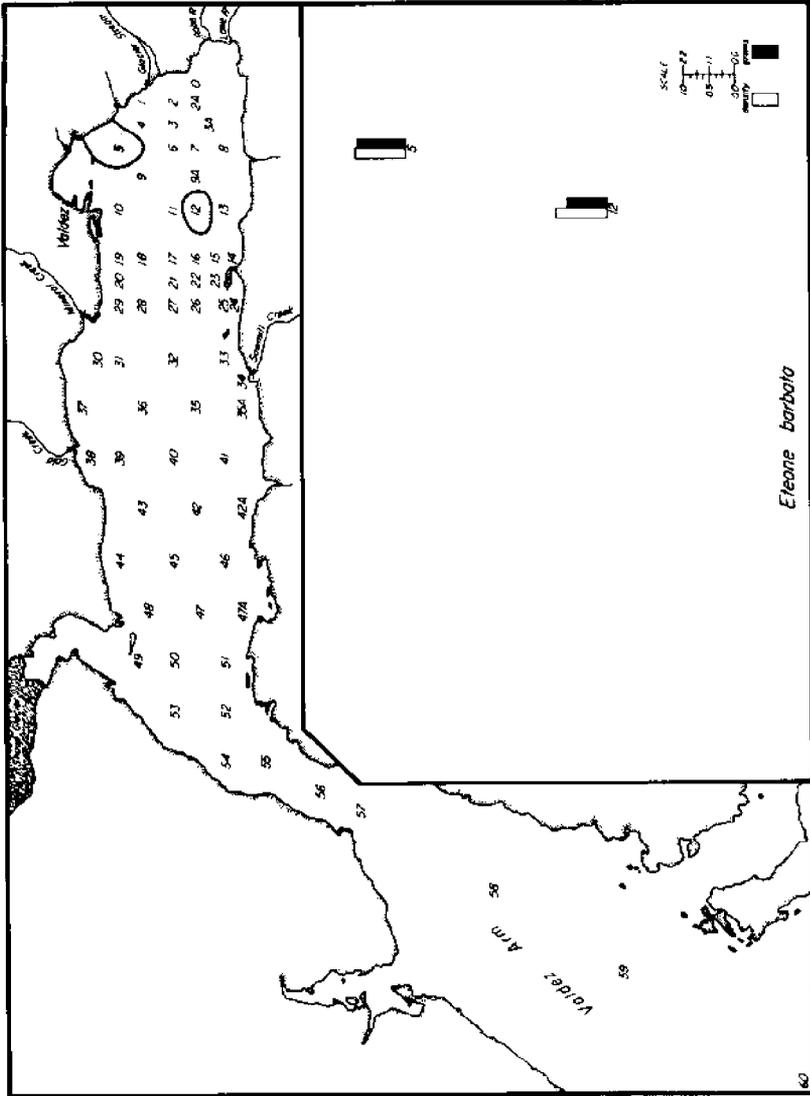


Figure 9 20 Map of sampling grid with the stippled area indicating the distribution of *Eteone barbata*. (See Figure 9.2 for inset key to histograms).

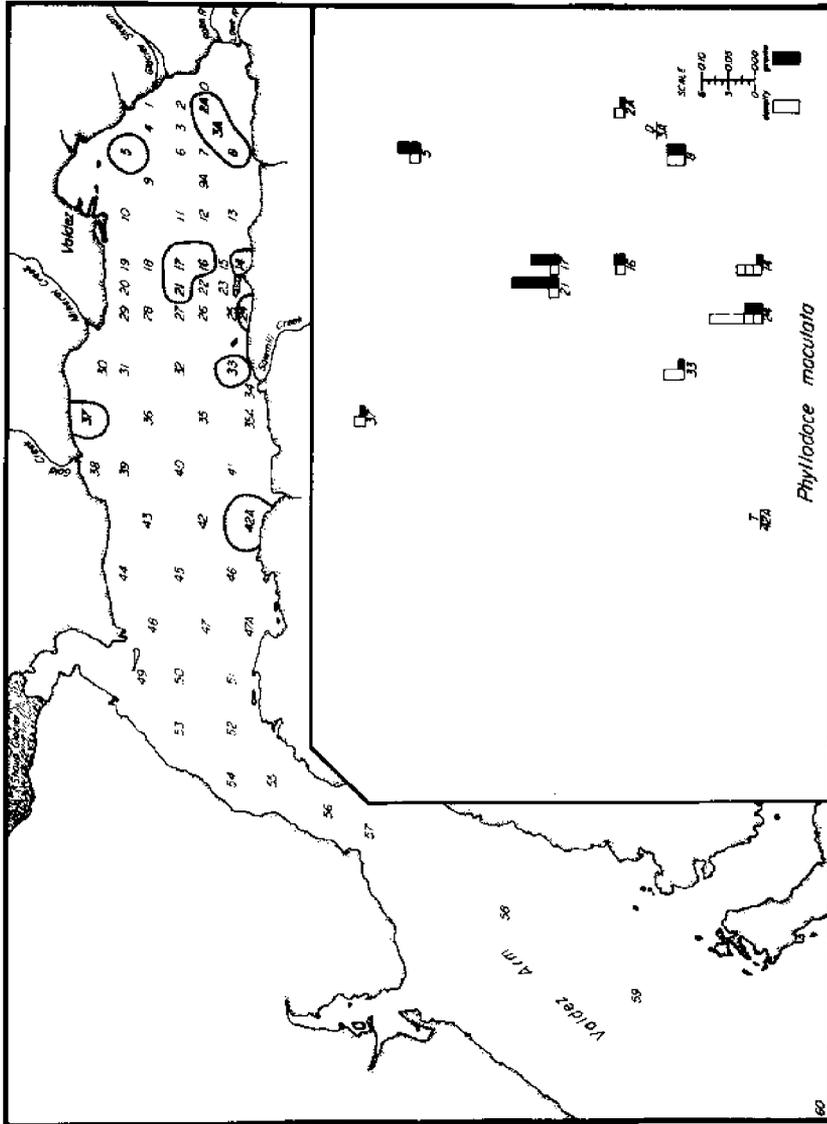


Figure 9.21 Map of sampling grid with the stippled area indicating the distribution of *Phyllocladus maculata*. (See Figure 9.2 for inset key to histograms).

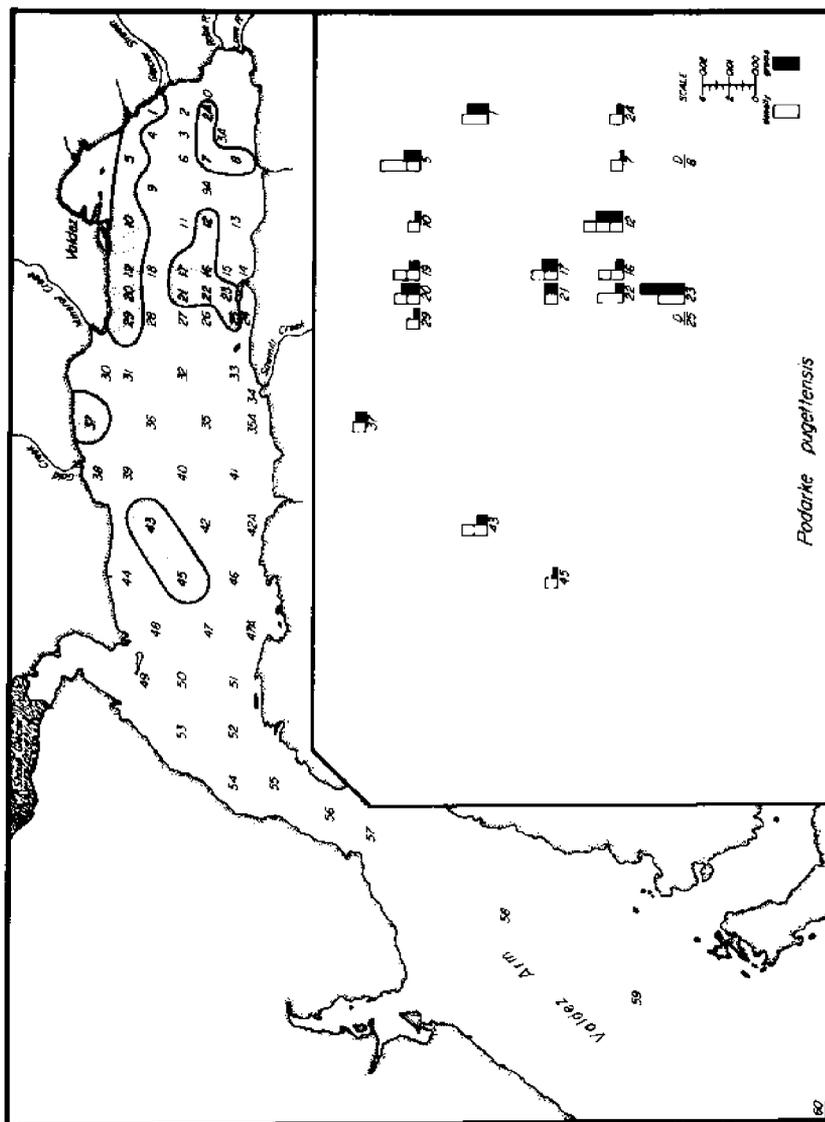


Figure 9.22 Map of sampling grid with the stippled area indicating the distribution of *Podarke pugetensis*. (See Figure 9.2 for inset key to histograms).

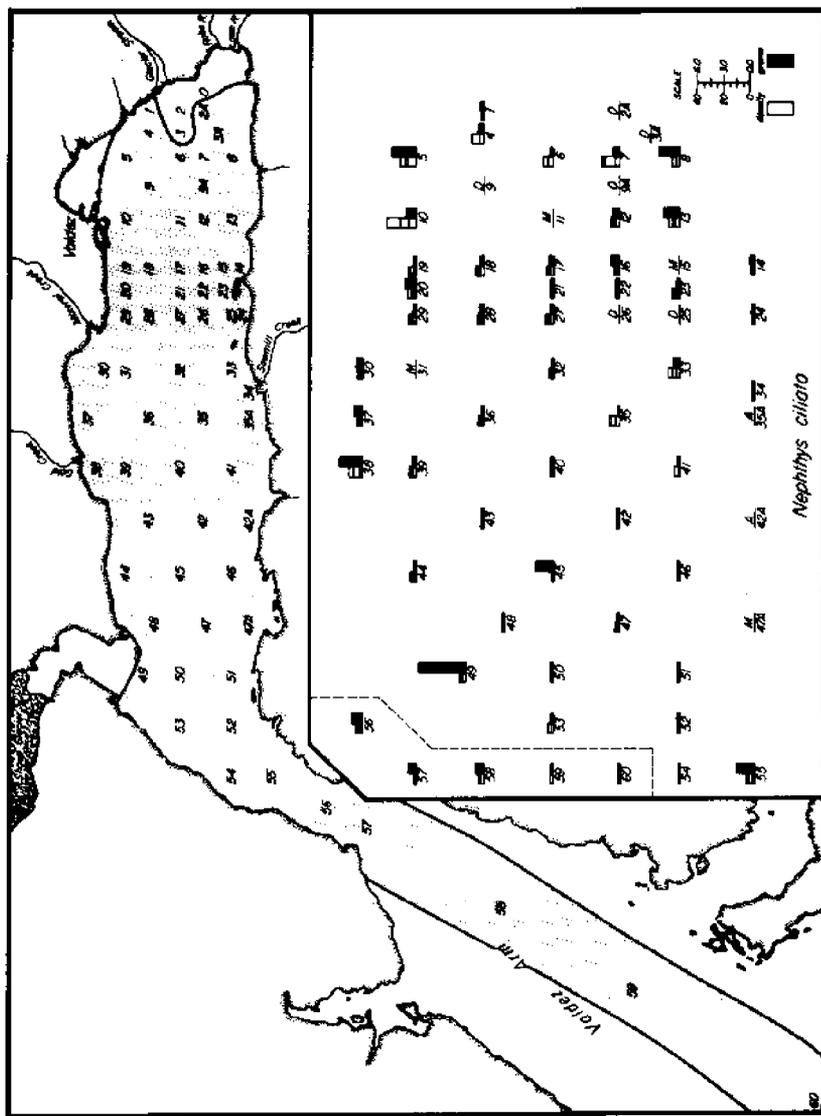


Figure 9.23 Map of sampling grid with the stippled area indicating the distribution of *Nephthys ciliata*. (See Figure 9.2 for inset key to histograms).

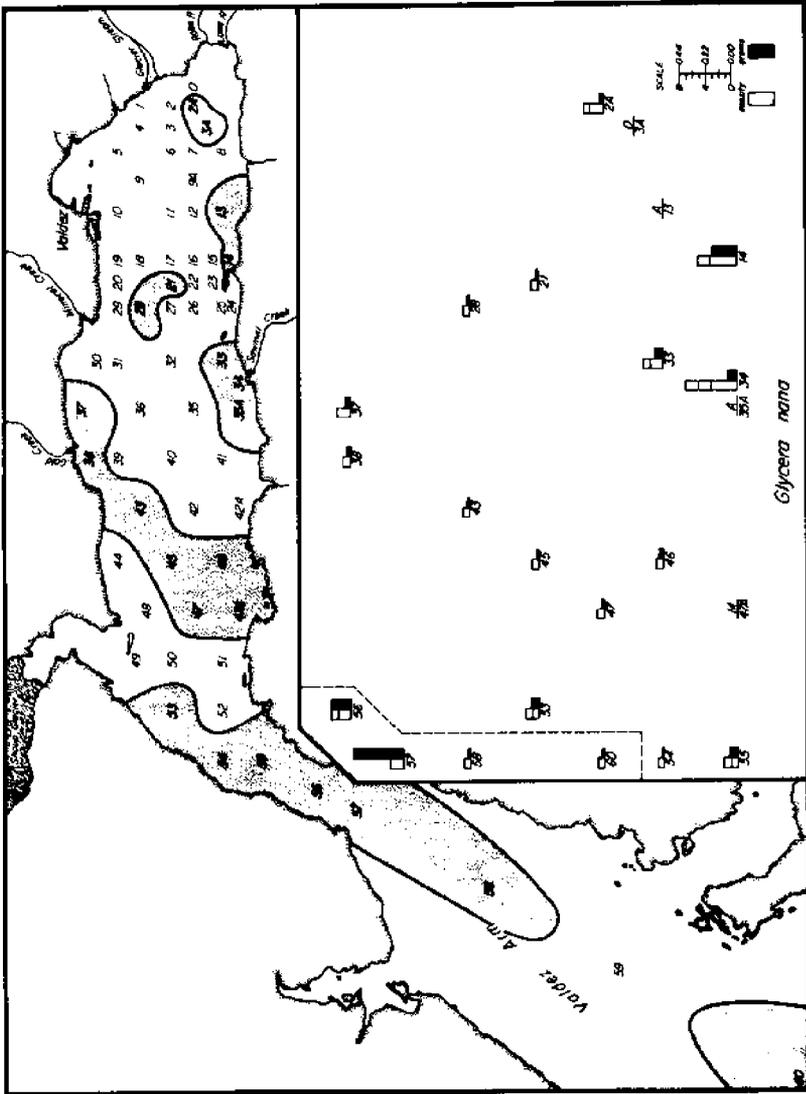


Figure 9.24 Map of sampling grid with the stippled area indicating the distribution of *Glycyca nana*. (See Figure 9.2 for insert key to histograms).

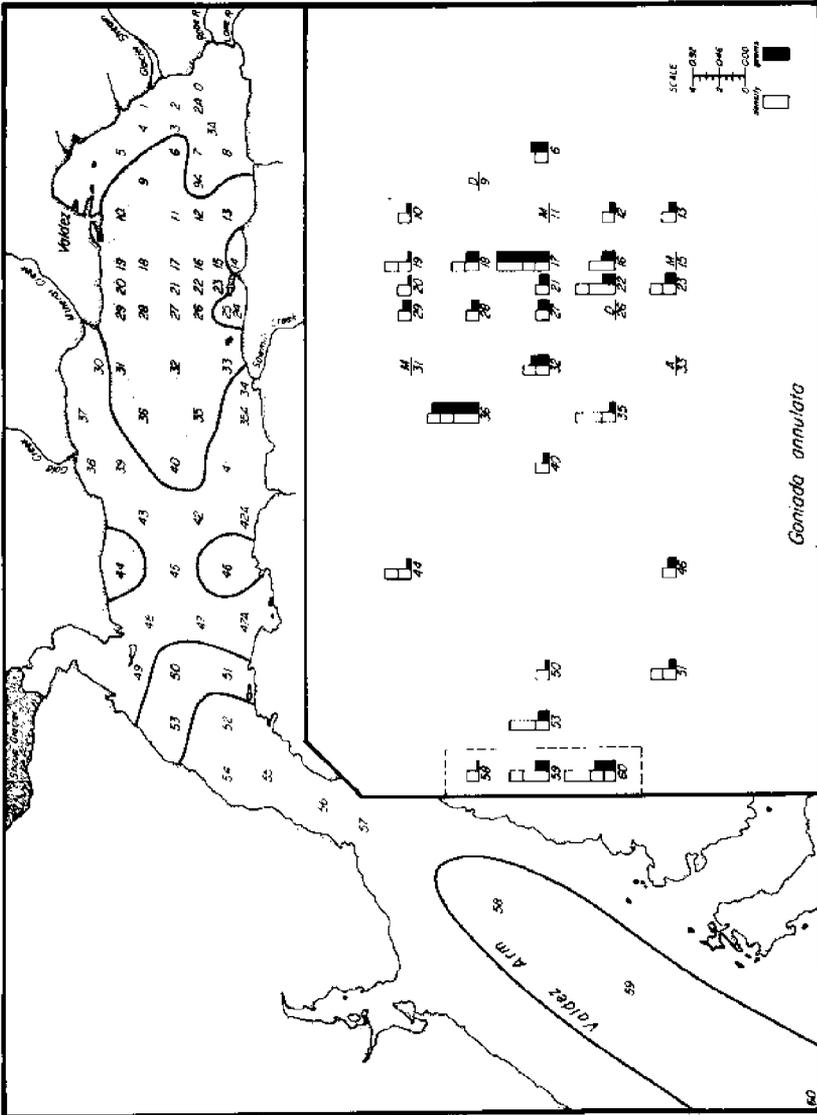


Figure 9.25 Map of sampling grid with the stippled area indicating the distribution of *Gonioda annulata*. (See Figure 9.2 for inset key to histograms).

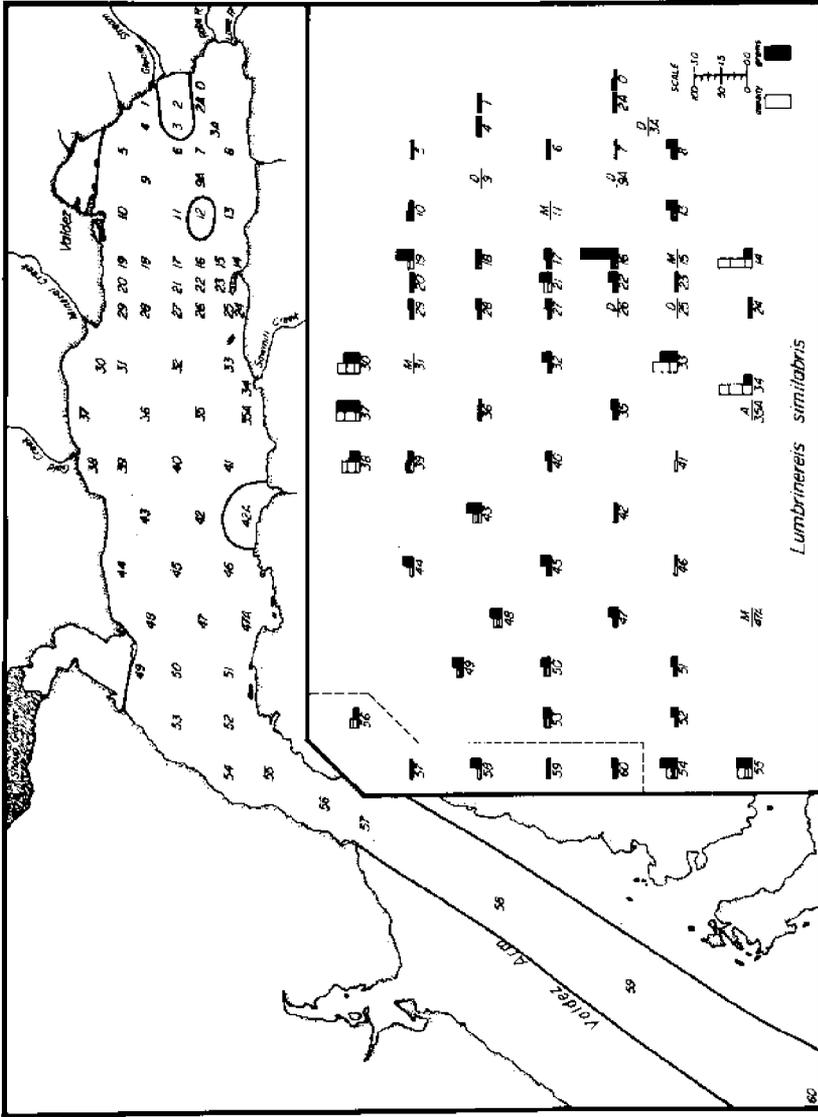


Figure 9.26 Map of sampling grid with the stippled area indicating the distribution of *Lumbrineris similabris*. (See Figure 9.2 for inset key to histograms).

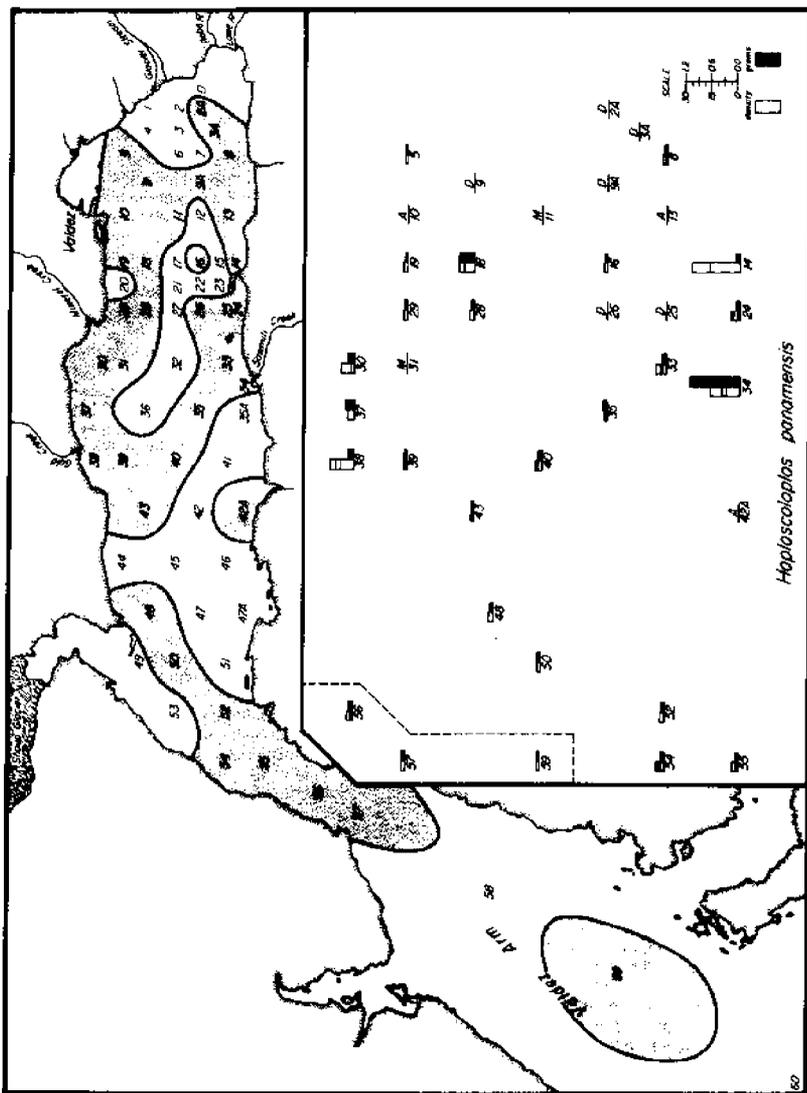


Figure 9.27 Map of sampling grid with the stippled area indicating the distribution of *Haploscoloplos panamensis*. (See Figure 9.2 for insect key to histograms).

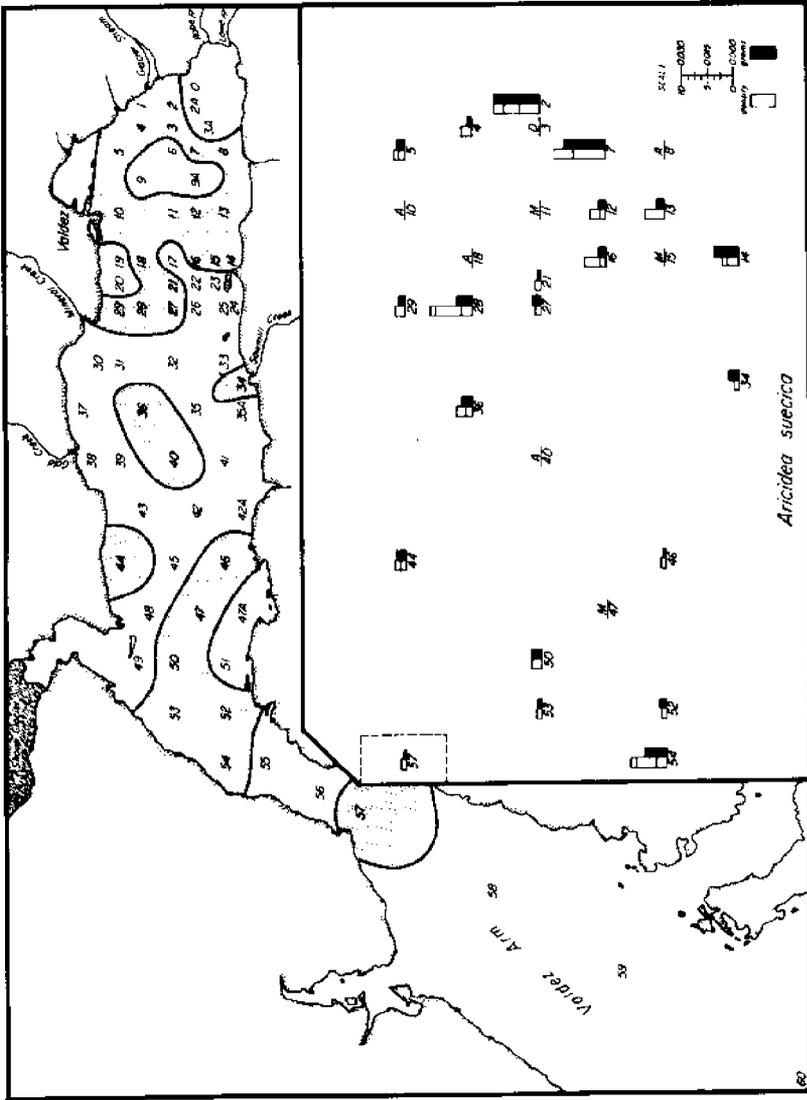


Figure 9.28 Map of sampling grid with the stippled area indicating the distribution of *Aricidea suecica*. (See Figure 9.2 for inset key to histograms).

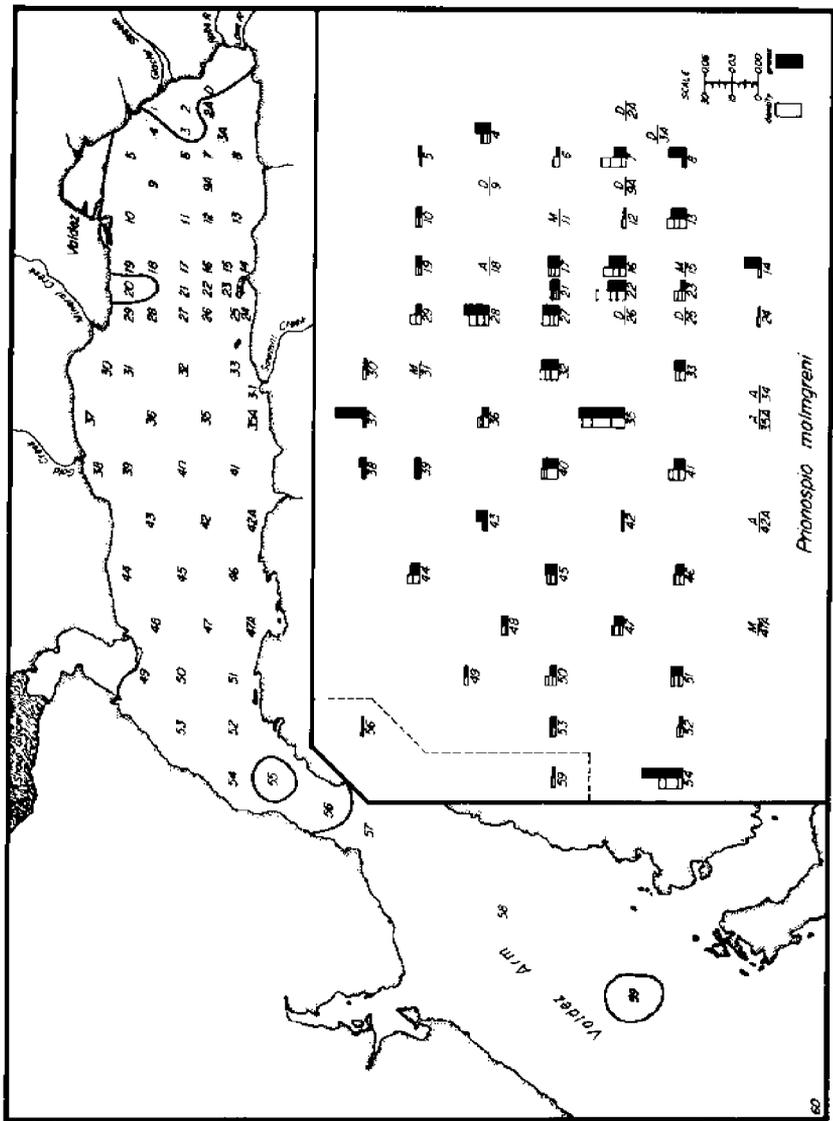


Figure 9.29 Map of sampling grid with the stippled area indicating the distribution of *Prionospio malmgreni*. (See Figure 9.2 for inset key to histograms).

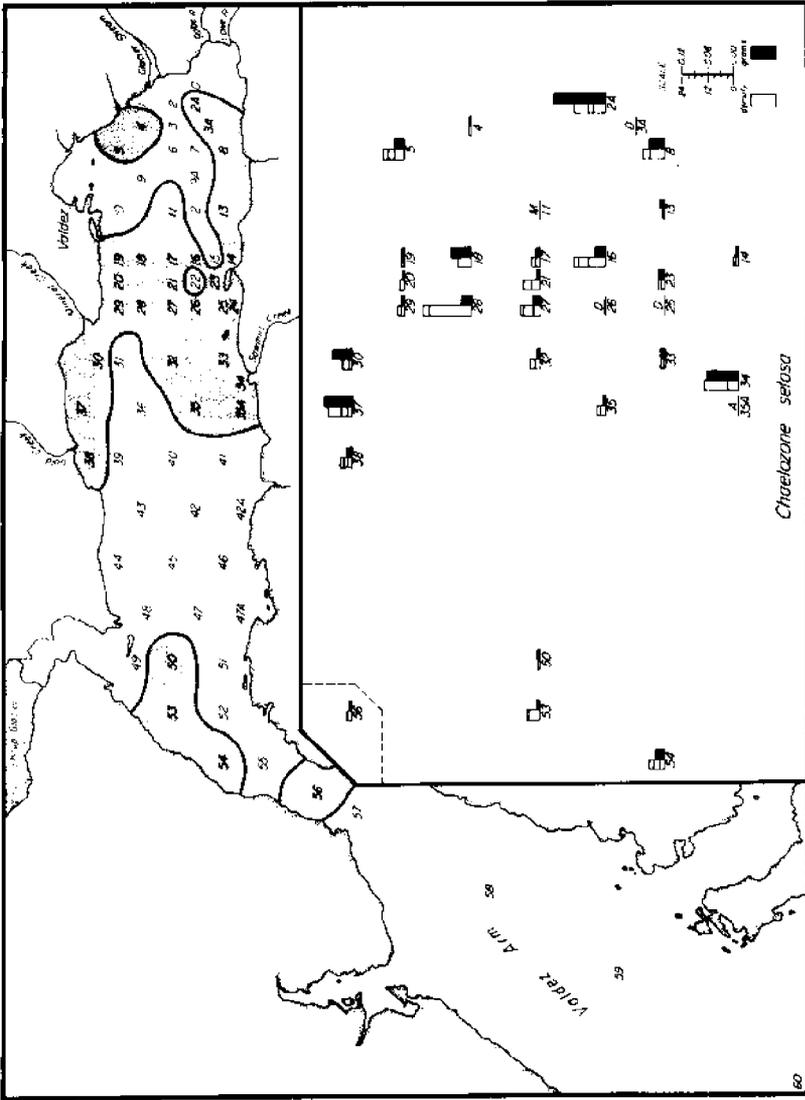


Figure 9.30 Map of sampling grid with the stippled area indicating the distribution of *Chaetozone setosa*. (See Figure 9.2 for inset key to histograms).

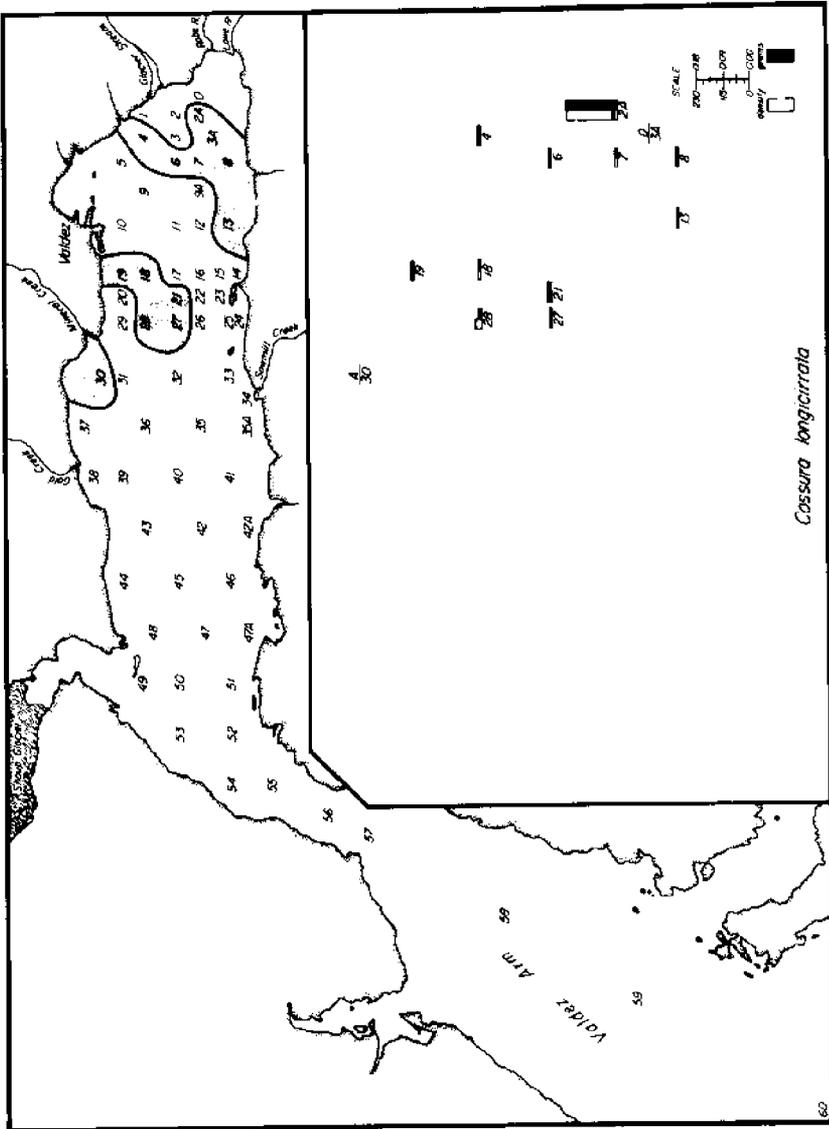


Figure 9.31 Map of sampling grid with the stippled area indicating the distribution of *Cassura longicirrata*. (See Figure 9.2 for inset key to histograms).



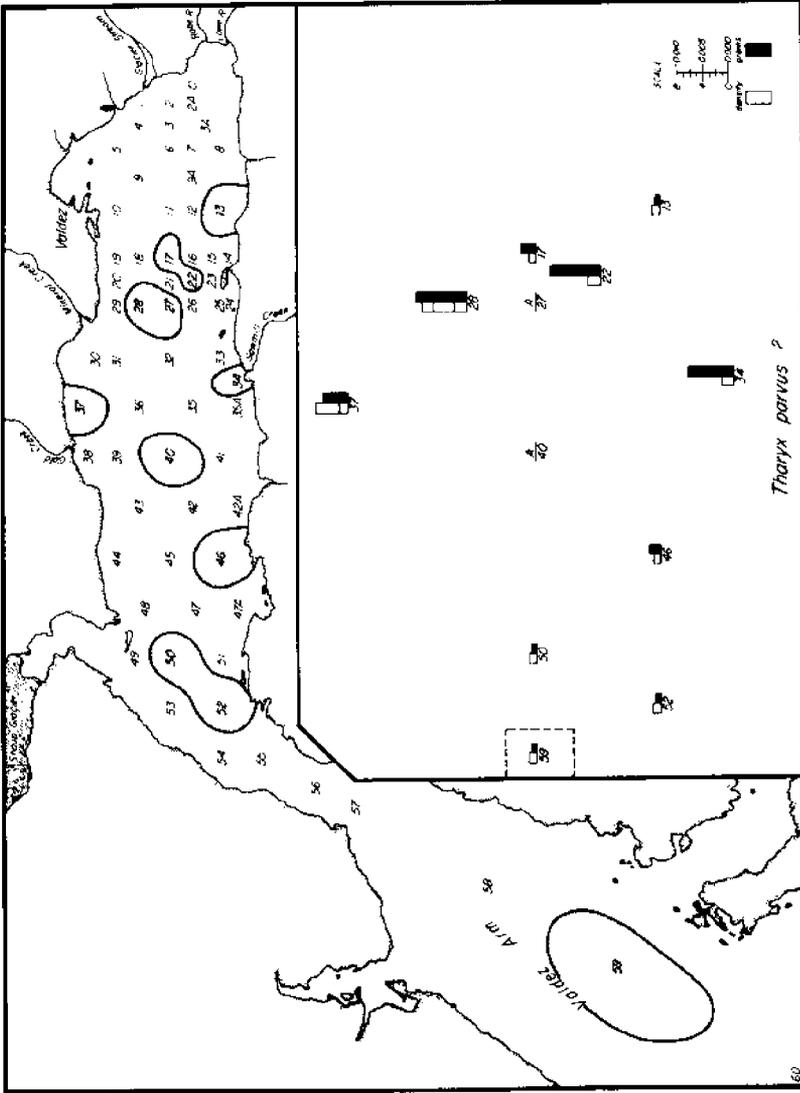


Figure 9.33 Map of sampling grid with the stippled area indicating the distribution of *Thiaryx parvus*. (See Figure 9.2 for inset key to histograms).

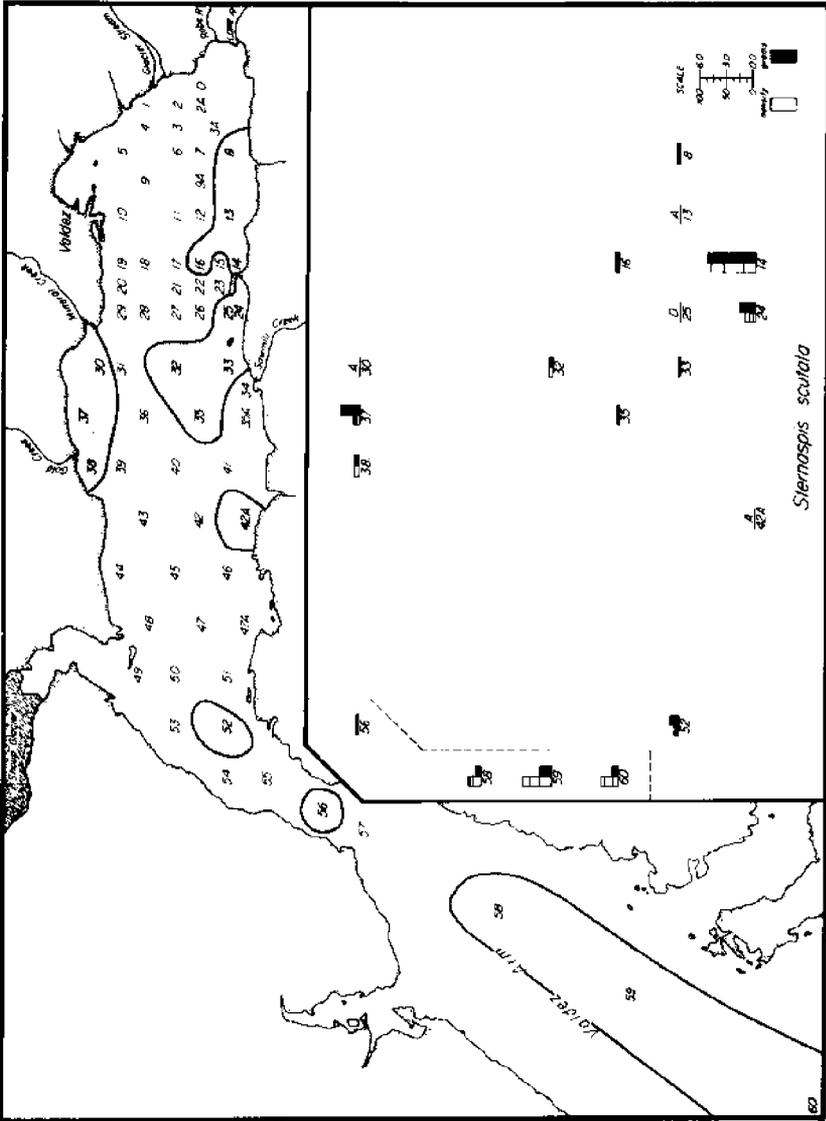


Figure 9.34 Map of sampling grid with the stippled area indicating the distribution of *Sternaspis scutata*. (See Figure 9.2 for inset key to histograms).

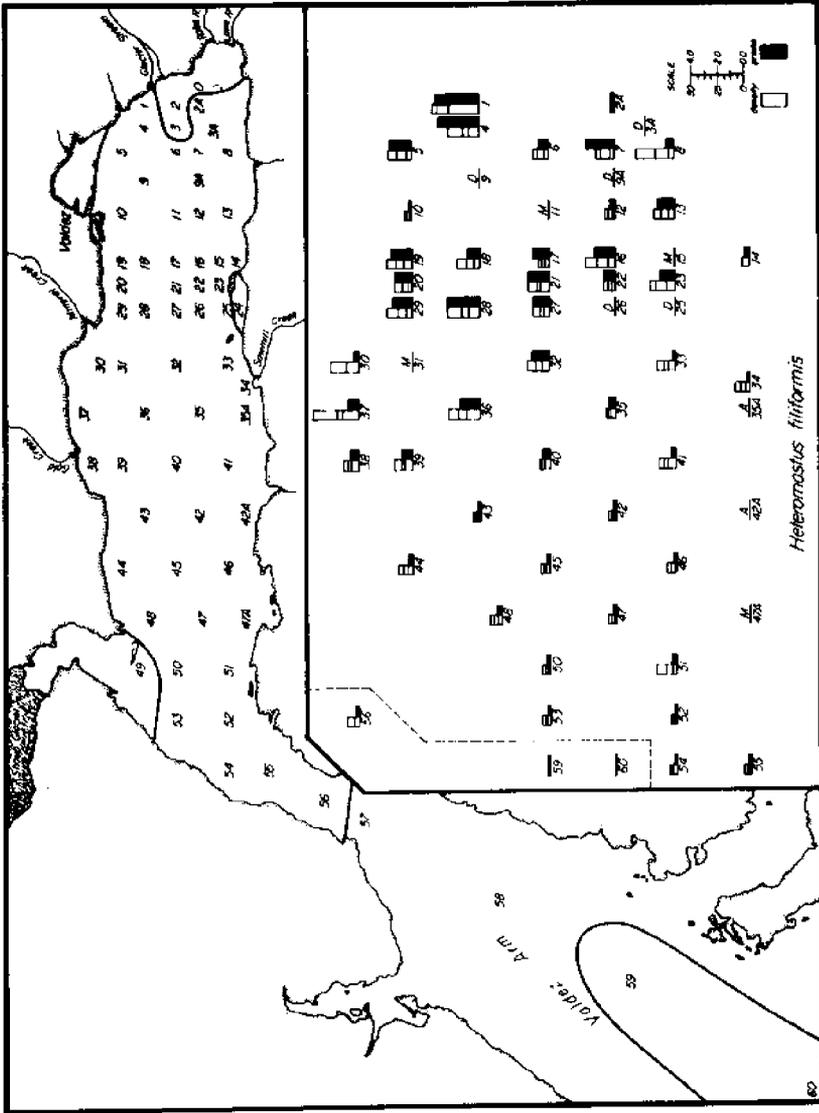
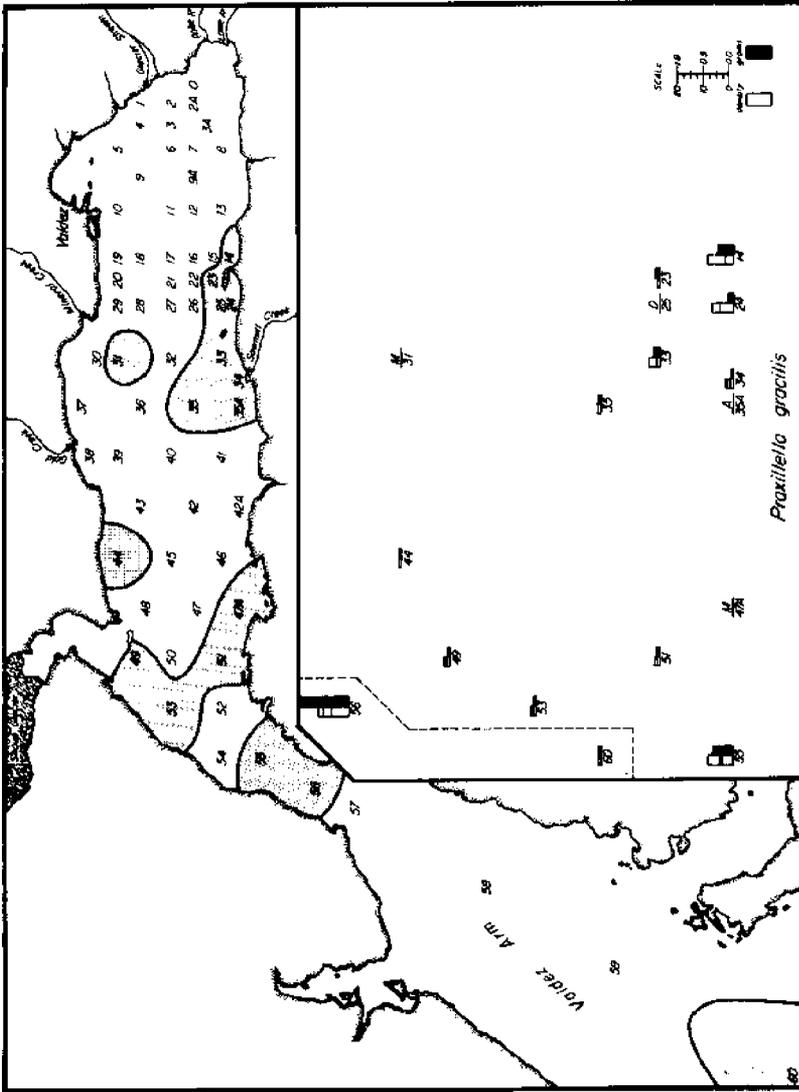


Figure 9.35 Map of sampling grid with the stippled area indicating the distribution of *Heteromastus filiformis*. (See Figure 9.2 for inset key to histograms).



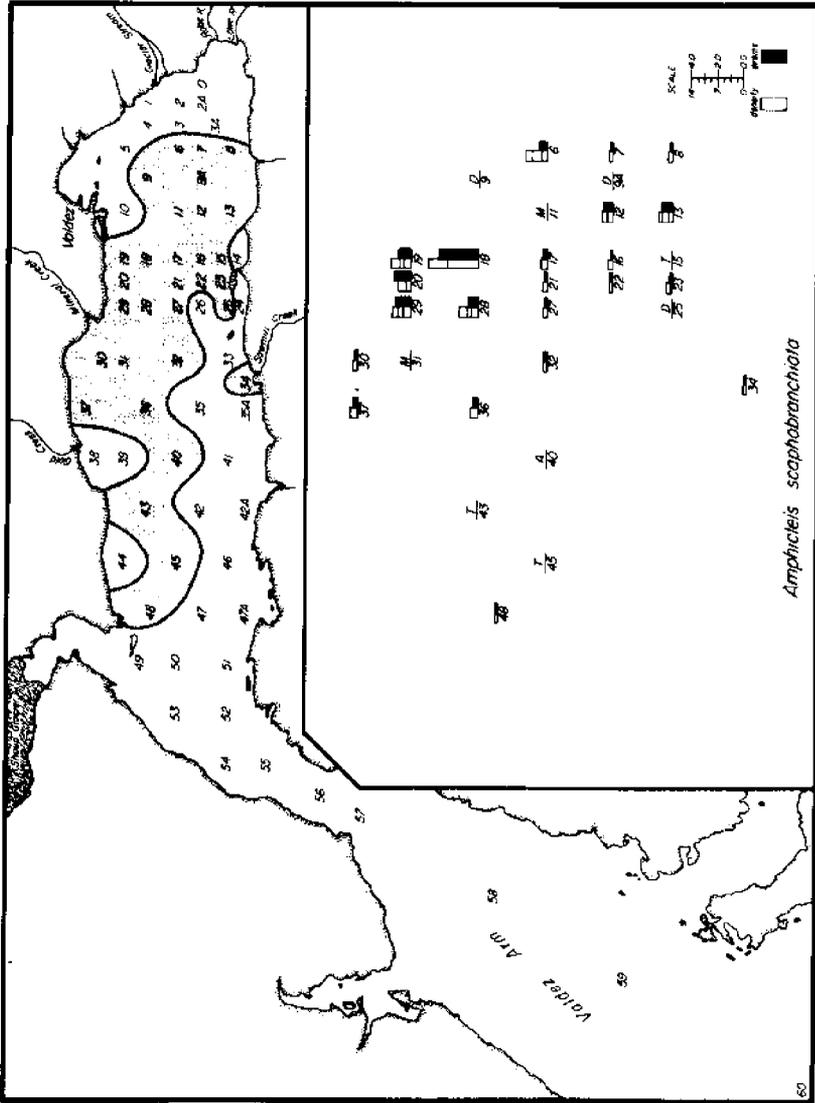


Figure 9.37 Map of sampling grid with the stippled area indicating the distribution of *Amphicleis scaphobranchiata*. (See Figure 9.2 for inset key to histograms).

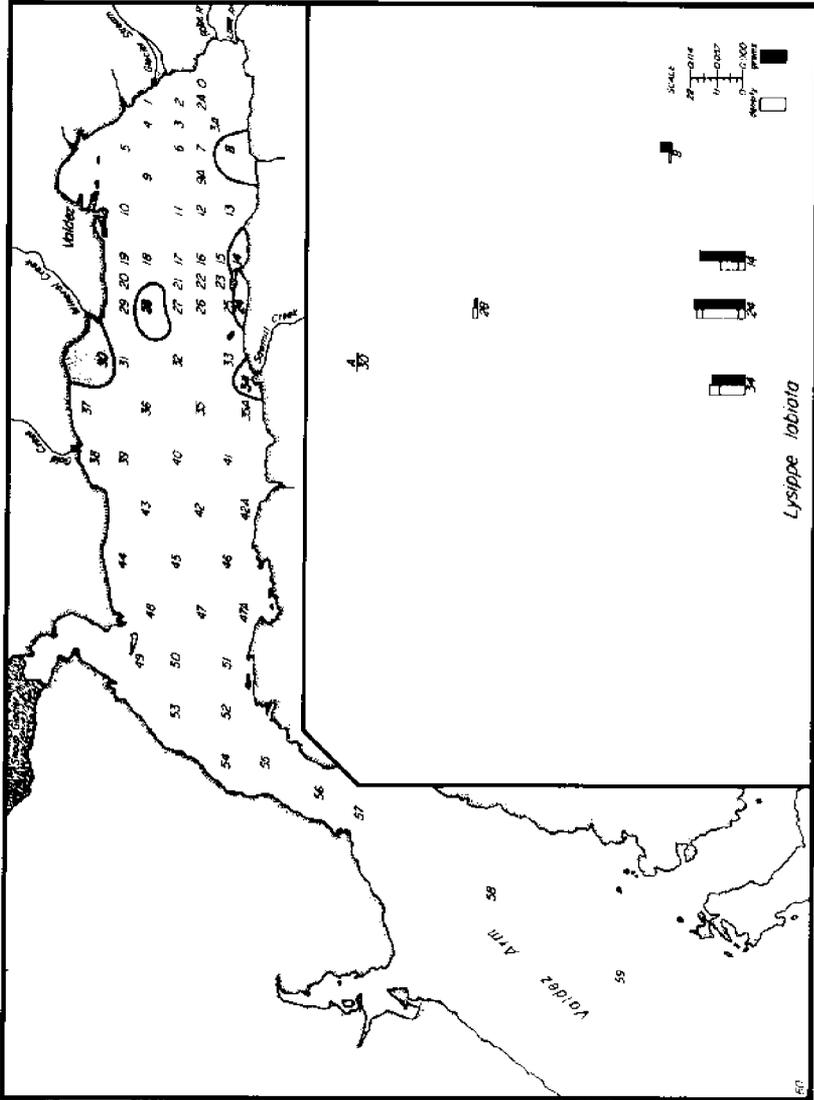


Figure 9.38 Map of sampling grid with the stippled area indicating the distribution of *Lysippe labiata*. (See Figure 9.2 for inset key to histograms).

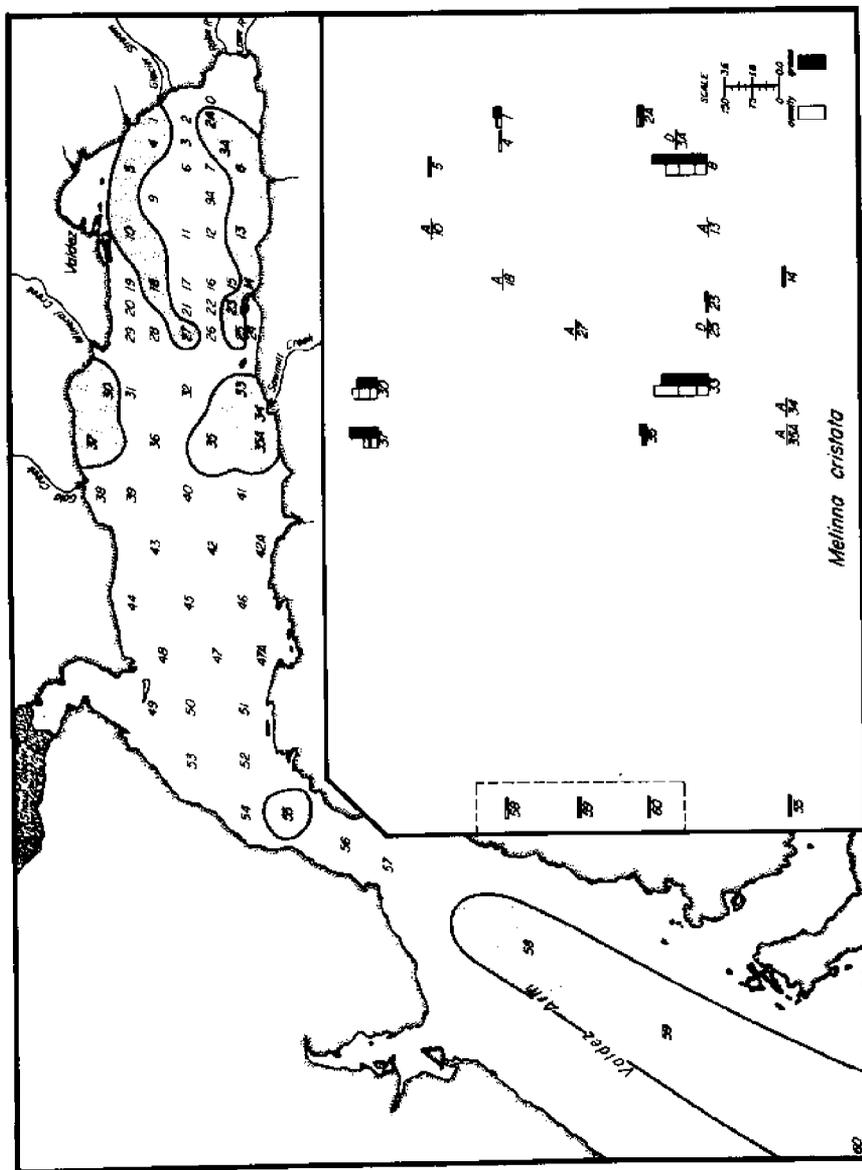


Figure 9.39 Map of sampling grid with the stippled area indicating the distribution of *Melinna cristata*. (See Figure 9.2 for inset key to histograms).

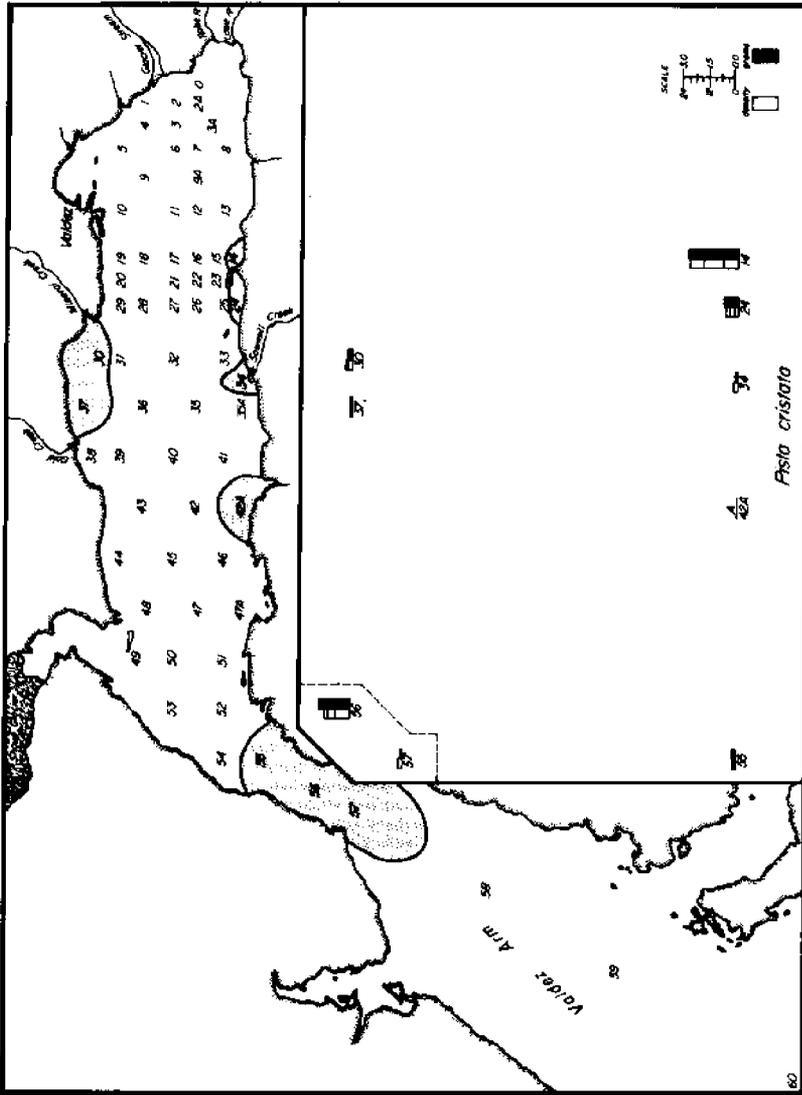


Figure 9.40 Map of sampling grid with the stippled area indicating the distribution of *Pista cristata*. (See Figure 9.2 for inset key to histograms).

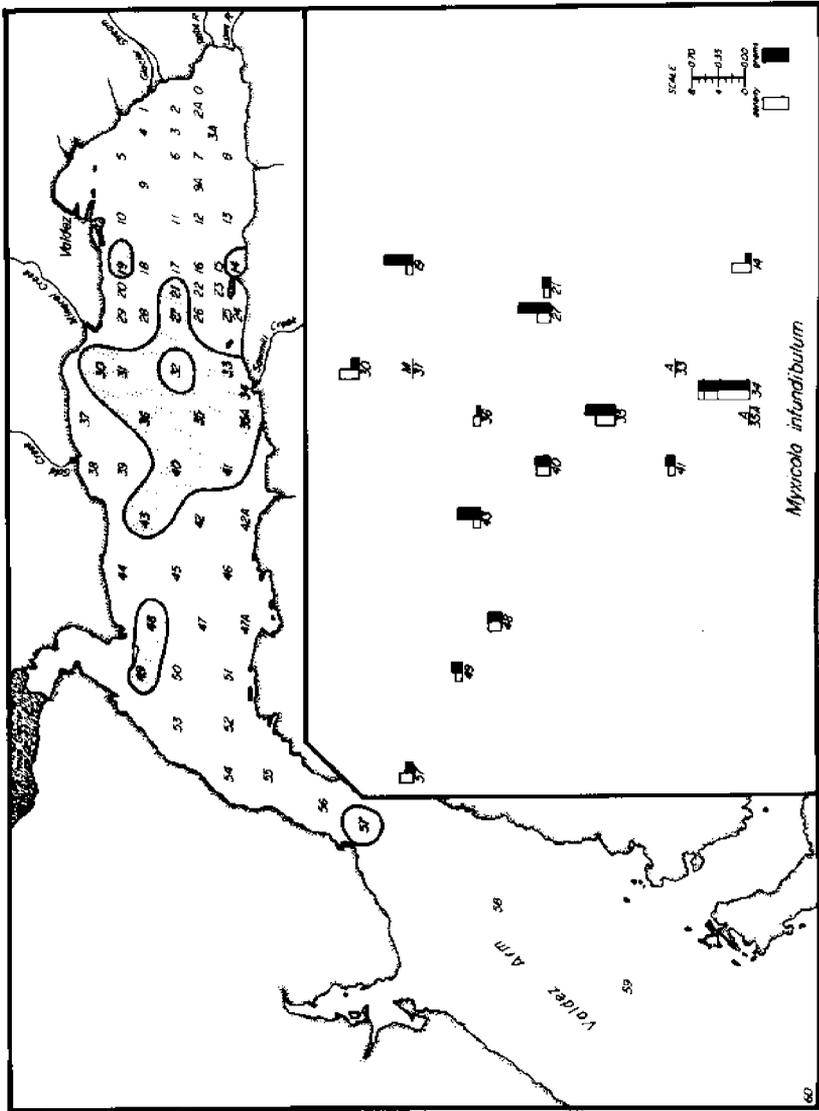


Figure 9.41 Map of sampling grid with the stippled area indicating the distribution of *Myxicola infundibulum*. (See Figure 9.2 for inset key to histograms).

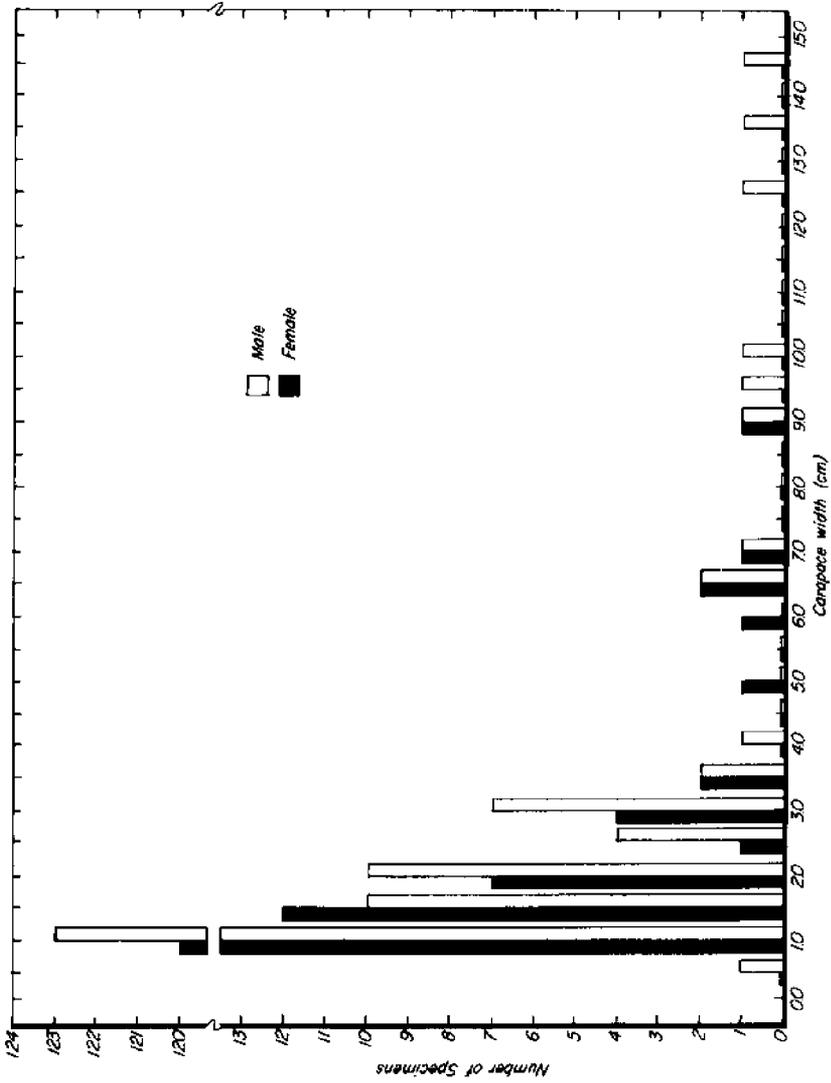


Figure 9.42 Size frequency data by sex for the snow crab *Chionoecetes bairdi* from April trawl samples.

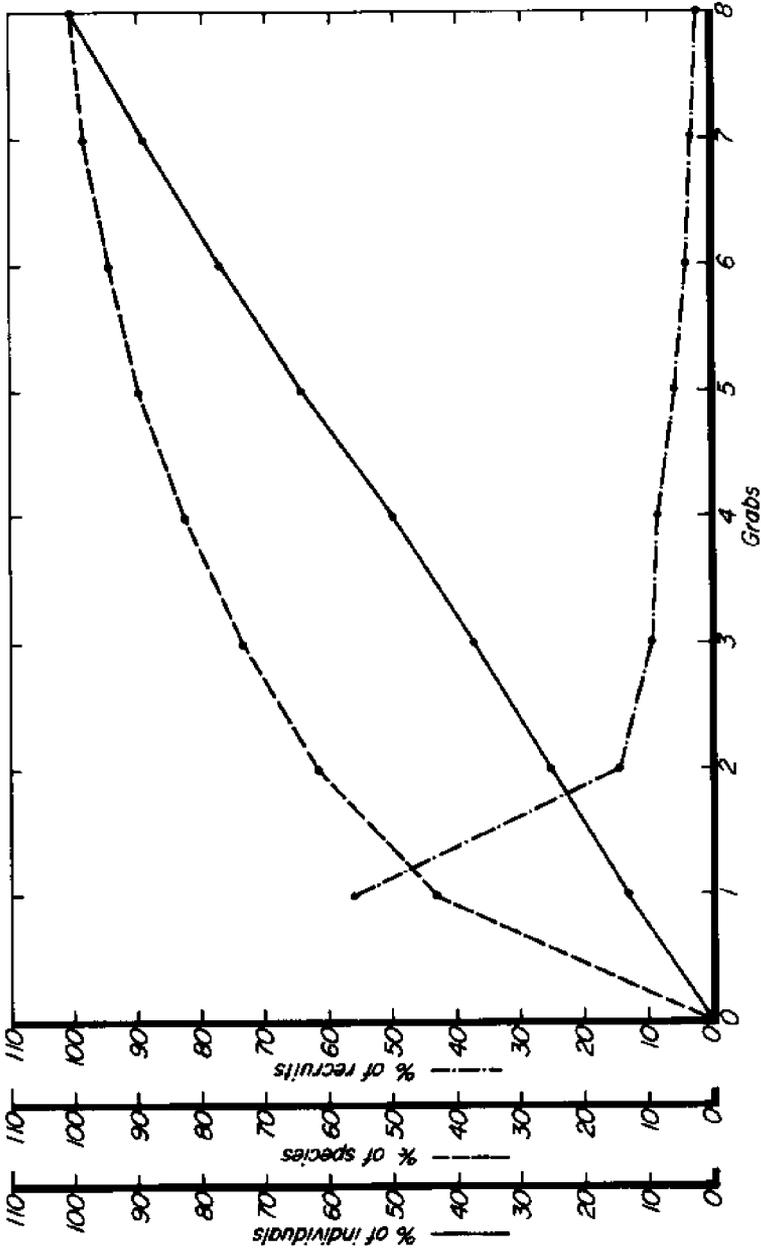


Figure 9.43 Plots of cumulative percentage of individuals and species added at each subsequent grab for station 2; plot of percentage number of recruits of the new species added at each subsequent grab for station 2. The total number of individuals and total number of individuals and total number of species collected in eight grabs equals 100 percent.

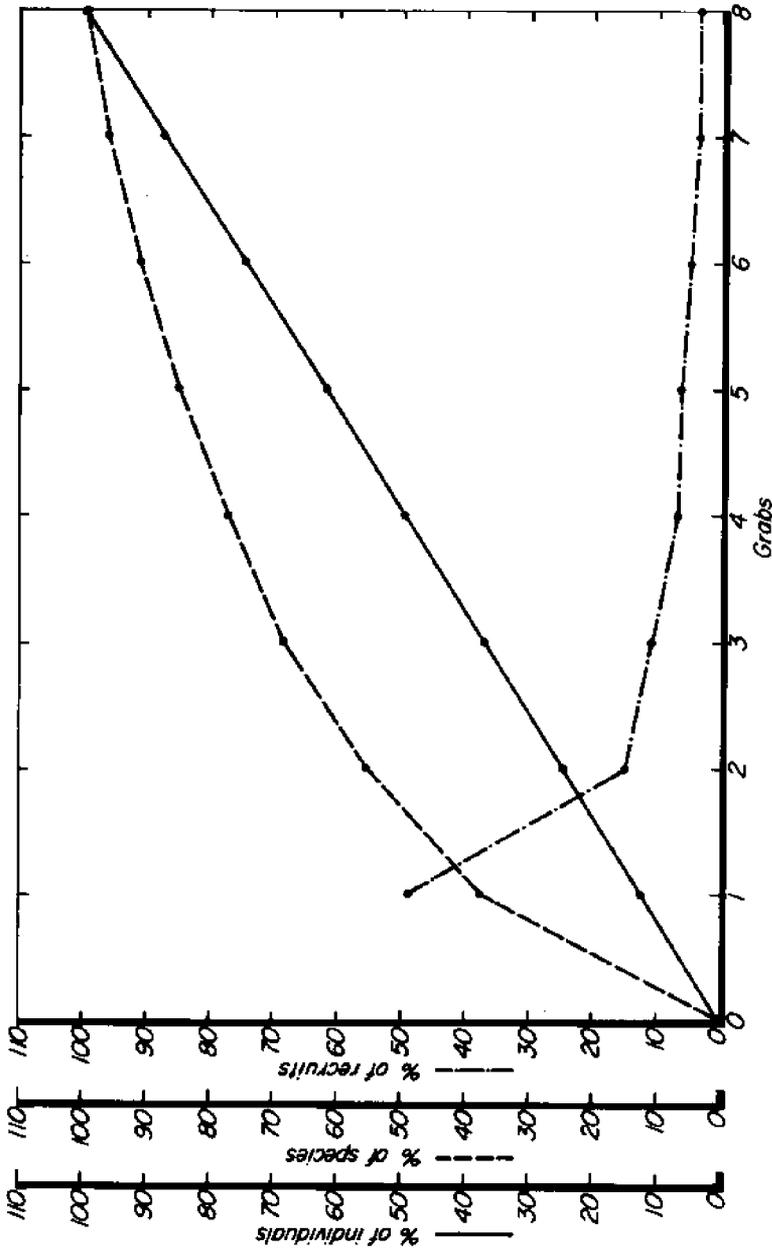


Figure 9.44 Plots of cumulative percentage of individuals and species added at each subsequent grab for station 20; plot of percentage number of recruits of the new species added at each subsequent grab for station 20. The total number of individuals and total number of species collected in eight grab equals to 100 percent.

As indicated by Lie (1968), "Many aspects of the dynamics of communities will have to be explained through detailed studies of the component species . . ." (also see Friedrich 1969 and Jones, G. 1969 for reviews). Not enough is yet known about the biology of organisms in Port Valdez to completely understand the subtleties of the biological interactions there.

### 9.5.3 Diversity index

It is generally accepted that an altered environment will result in changes in numbers of species and their population densities (Pearson et al. 1967). Thus, examination of species diversity can serve as a basis for comparison in the future. In order to avoid subjective appraisal, a *quantitative* measure of diversity must be used. Such a measure should typically consider the *number* of species present as well as the *density* of each species. Various diversity indices are available, and at least two different types should be used to give the greatest insight into the faunal conditions present (Lloyd et al. 1968). The theory and applications of diversity indices to ecological problems have been widely discussed (MacArthur 1965; Stein and Denison 1967; Lie 1968; Sanders 1968; Fager 1972; Gage 1972b; Loya 1972).

Lie (1968) successfully used Gleason's Index,  $d = (S - 1)/1_n N$ , in which S = the number of species and N = the number of individuals at each station. This index is easily computed but is sensitive primarily to changes in *numbers of species*. It is generally not suitable for a description of changes in *numbers of individuals* of each species. (Lie 1968 discusses an example of such a problem). Benthic data from the Port Valdez study of 1971-1972 can be readily adapted for calculation of diversity indices (Data Vols. I and II). Gleason's Index was calculated as a basis for comparison of stations using species currently present (Table 9.5). The Shannon-Wiener Function is another index that has been applied successfully (Lie 1968; Sanders 1968) and appears readily applicable to the Port Valdez data. The Rarefaction Method of Sanders (1968), a technique that is independent of sample size, has been tested by several workers recently (Day et al. 1971; Fager 1972; Gage 1972b). This technique has been used to examine species diversity in Scottish lochs (Gage 1972b), and it is applicable to the similar semi-enclosed inshore waters of Port Valdez.

### 9.5.4 Statistical treatment of data

The statistical analysis carried out in this work relied mainly on Dixon's (1971) *BMD Biomedical Computer Programs*. A cluster analysis program from the Kansas Geological Survey (Parks 1970) and a program written specifically to simulate multiple-grab sampling in Port Valdez constituted the remaining statistical programs used.

*Data Description:* The Biomedical Program BMD01D was used to obtain a statistical description of the biological data (Dixon 1971). The mean standard deviation, standard error of the mean, range, maximum value, and minimum value of population density and biomass of each of the 210 grab samples were calculated by station (Data Vol. II).

*Analysis of Variance:* A one-way analysis of variance of the grab-sample data was carried out using the BMD01V program. The density of individuals of seven species widely distributed throughout Port Valdez were selected as variables. The details of this calculation

are presented by Dixon (1971); see Peng (1967, Chapter 9) for a discussion of the requirements for a variance analysis. The distribution of organisms in Port Valdez, as determined from the station data, approximated a Poisson distribution; therefore, the data were transformed to the square roots of the variables to give a distribution more appropriate to an analysis of variance (Data Vol. II). The results showed ( $P < 0.05$ ) that the *between-station* variance was significantly greater than the *within-station* variance.

*Cluster Analysis:* Cluster analyses have been used elsewhere to demonstrate the presence of aggregations of species in the benthos (Barnard 1970; Hughes and Thomas 1971). In this study the cluster approach was applied to only those nine species included in the first category of Biologically Important Species, which were present at 50 percent or more of the stations.

In the particular cluster analysis used in this case (Parks 1970), grouping was based solely on the minimization of within-group and maximization of between-group variances. This procedure began with an R-mode principal components analysis, using a correlation coefficient as a measure of similarity between variables. In R-mode analysis, the original variables were transformed into an uncorrelated orthogonal set of variables. Factor scores were then calculated for these orthogonal variables, and a Q-mode cluster analysis was performed on the R-mode factor scores by use of a simple distance function as the measure of similarity. After the distance functions for all the samples were calculated, the samples having like distances were clustered together and the resultant clustering was printed in dendrogram form (Figures 9.45 and 9.47; also Data Vol. II).

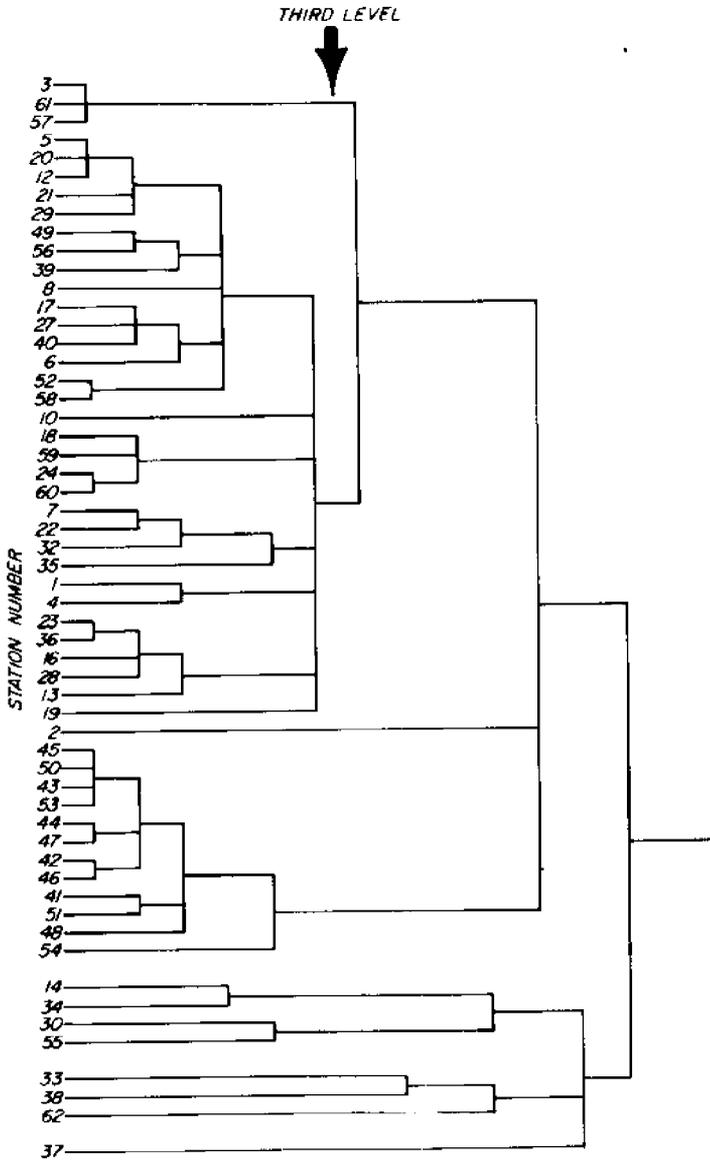
The analysis delineated four or five major groups (Figures 9.46 and 9.48), which were determined at the third level of the printed dendrograms (Data Vol. II). These groups, in general, reflect trends observable in the distribution maps for most of the nine selected Biologically Important Species (Figures 9.4, 9.9, 9.12, 9.19, 9.23, 9.26, 9.29, 9.32 and 9.35). This was a preliminary analysis and should be applied to all Biologically Important Species.

#### 9.5.5 Suggested approach for monitoring program in Port Valdez

An undisturbed marine environment is characterized by stable assemblages of organisms that often exhibit a high diversity of species (Olson and Burgess 1967). When changes in the environment occur, the distribution of some species may be changed and marginal species may be eliminated. Certain species, those able to do well under the new conditions, may become dominant, and new species from adjacent areas can become established. The essence of any monitoring program is to document such changes. Some possible ways to accomplish this documentation have been discussed elsewhere in this report; also see Ketchum (1972) for review of coastal zone problems and monitoring recommendations.

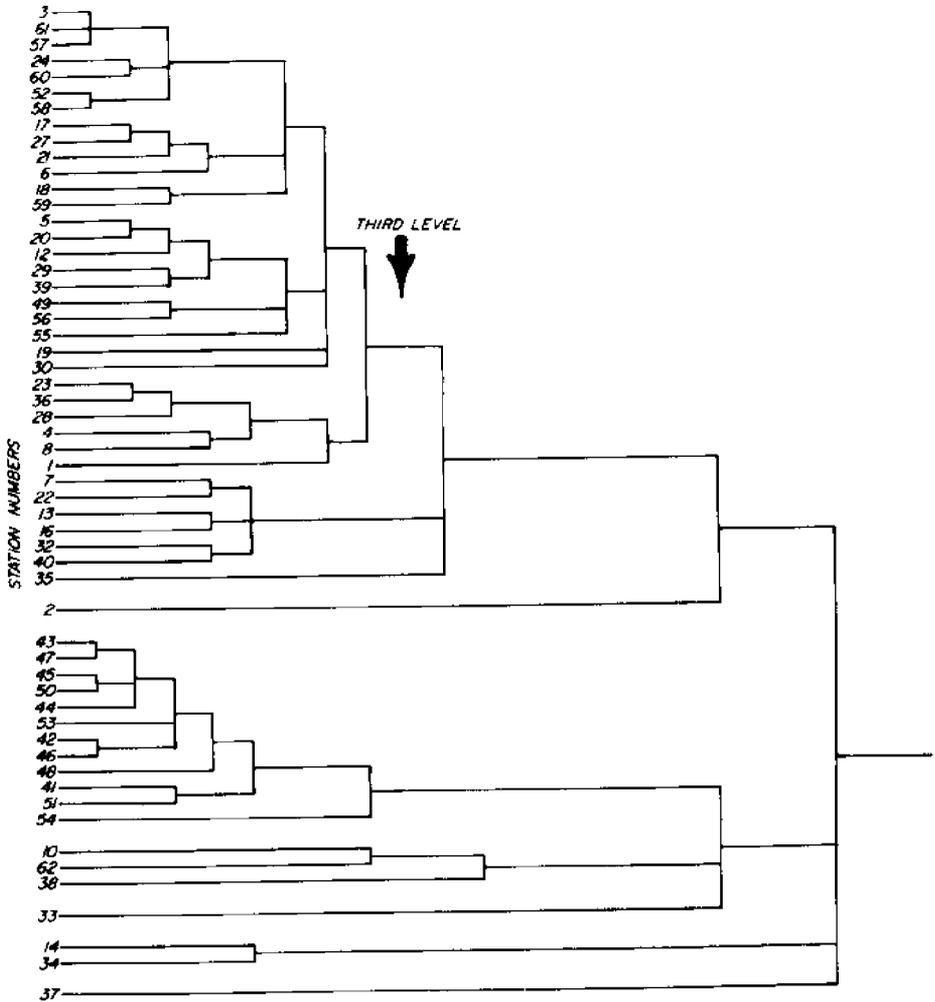
#### 9.6 Concluding Remarks

The classical community concept of the distribution of benthic fauna as originated by Petersen (see Thorson 1957 for discussion) has formed the basis for many subsequent analyses of animal relationships in the benthos, and recent investigators (Lie 1968; Jones, G. 1969; Pearson 1970; Gage 1972b) have generally attempted to compare their results with those communities described by Thorson (1957); however, G. Jones (1969) has pointed out



**Figure 9.45** Dendrogram resulting from a *weighted* cluster analysis of benthic station data (Data Vol. II). All calculations were based on population densities of nine ubiquitously distributed Biologically Important Species (see text 9.4.1 and 9.5.2). Groupings delineated in Figure 9.46 were interpreted at the third level of the dendrogram.





**Figure 9.47** Dendrogram resulting from an *unweighted* cluster analysis of benthic station data (Data Vol. II). All calculations were based on population densities of nine ubiquitously distributed Biologically Important Species (see text 9.4.1 and 9.5.2). Groupings delineated in Figure 9.48 were interpreted at the third level of the dendrogram.

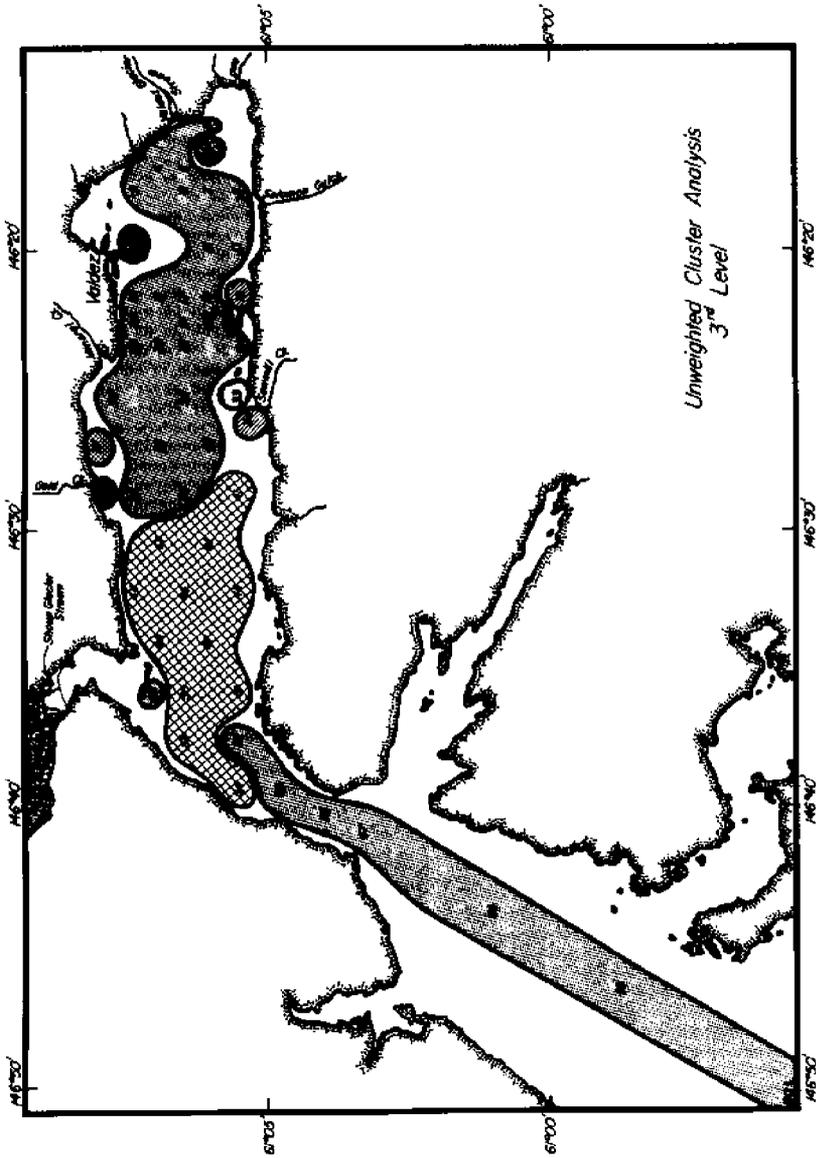


Figure 9.48 Map showing clustering of stations based on population densities of the ubiquitously distributed Biologically Important Species. The groups were determined by means of an unweighted cluster analysis interpreted at the third level of the printed dendrogram (see Figure 9.47).

serious deficiencies in both the Petersen-Thorson concept of the benthic "community" and in the environmentally determined association described by N. Jones (1950); see Lindroth (1962) for further discussion.

G. Jones (1969) points out that the Petersen-Thorson system emphasizes dominant species and excludes both ubiquitous and predatory species, thereby eliminating an important part of the trophic structure of a marine community. This system also accents dissimilarities and suppresses similarities between associations by emphasizing the mollusks and the echinoderms and by excluding the crustaceans as well as the polychaetes - the dominant organisms in Port Valdez. G. Jones (1969) has indicated further that a purely environmental approach to the determination of associations of organisms is no improvement over the biological approach since "... the limits of variables used to define categories are either purely arbitrary ... or are subjective and difficult to define." Fager (1963) and Longhurst (1964) have commented on the obvious importance of both physical and biological factors as determiners of faunal composition, and they strongly recommend that a combination approach be employed.

Most recent investigations of the benthos utilize statistical grouping techniques for defining, identifying, and classifying fauna (Sanders 1960; Lie 1968; Ellis 1969; Jones, G. 1969; Barnard 1970; Nichols 1970; Hughes and Thomas 1971; Gage 1972a). In the opinion of G. Jones (1969), such methods provide a degree of objectivity and reproducibility lacking in older, descriptive methods. Investigations in semi-enclosed marine areas have pointed out the apparent lack of distinctive Petersen-Thorson communities (see Pearson 1970 for review; Gage 1972a,b). In his recent survey of a loch system in Scotland, Pearson (1970) concluded that although the faunal groupings he observed corresponded largely to the major boreal benthic communities described from grounds of similar sediment types elsewhere, there was a high degree of intermingling between the various groups. He found it "... difficult to draw definite demarcation lines between any proposed communities." (Also see Gage 1972a). In the initial attempts to delineate communities or definite animal assemblages in the Valdez study, the problem of overlapping species from one region to another was also encountered.

A combination approach of BIS quantitative distribution maps, a cluster analysis, and one diversity index has been used to examine Valdez benthic data for associative trends. The organisms selected as the basis for these analyses were (as suggested by G. Jones 1969) all widespread Biologically Important Species. Feeding methods used by the BIS were tabulated as well (Table 9.7). Assessment of the infauna of Port Valdez in terms of the classic *bottom community* concept indicates only a limited conformity to published descriptions of such communities (Thorson 1957; H. M. Feder and G. J. Mueller, unpublished data).

The intensive sampling effort in Port Valdez and the preliminary analyses of resulting biological data have given background information that will aid in the development of a monitoring program.

Table 9.7 Feeding methods used by the (BIS) Biologically Important Species at the generic level (X) or as inferred from related types (Δ)

Species	Deposit feeders		Suspension feeder	Scavenger	Ectoparasite	Data source <sup>a</sup>
	Selective	Non-selective				
<i>Acanthopfilum ptille</i>			X			3
Cerianthid A			X			8
<i>Eudorella emarginata</i>	X			Δ		
<i>Pinnixa schmitti</i>				X		
<i>Amphiodia craterodonta</i>	Δ			Δ		5, 10, 16
<i>Ctenodiscus crispatus</i>		X				5, 16
<i>Ophiura sarsi</i>	Δ			X		5, 10, 16
<i>Cylichna attonsa</i>				X		11, 15, 17
<i>Odostomia</i> sp.					X	1, 2, 11, 13
<i>Dentalium</i> sp.	X			X		12, 13
<i>Axiropsida serricata</i>			Δ			8
<i>Clinocardium ciliatum</i>			X			8, 16
<i>Macoma calcarea</i>	X					14, 15, 16, 17
<i>Macoma inconspicua</i>	X					15, 17
<i>Nuculana minuta</i>	X					12, 15, 16, 17
<i>Serripes groenlandicus</i>			X			16
<i>Yoldia arctica</i>	X					12, 15, 16, 17
<i>Yoldia thraciaformis</i>	X					12, 15, 16, 17
<i>Chetoderma robusta</i>	X			X		3, 11, 13
<i>Eteone barbata</i>				Δ		3, 17
<i>Phyllodoce maculata</i>	Δ			Δ		12
<i>Podarke pugettensis</i>						
<i>Nepithys ciliata</i>				Δ		4, 6, 8, 9, 15, 17
<i>Glycera nana</i>				X		4, 7, 17

<sup>a</sup>Data source (citation omissions above represent unpublished observations of H. M. Feder and colleagues):

- Abbott 1954
- Baer 1951
- Bagge 1969
- Banse and Hobson 1968
- Beolootian 1966
- Clark 1962
- Hartman 1950
- Hunt 1925
- Lie 1968
- MacGinitie and MacGinitie 1949
- Morton 1958
- Newell 1970
- Purchon 1968
- Reid and Reid 1969
- Sanders 1960
- Semenov 1965
- Young and Rhoads 1971

Table 9.7 (continued)

Species	Deposit feeders		Suspension feeder	Predator	Scavenger	Ectoparasite	Data source <sup>a</sup>
	Selective	Non-selective					
<i>Goniada annulata</i>			X	Δ			3, 7, 8
<i>Lumbrineris similabris</i>		X					3, 4, 9, 15, 17
<i>Haptoscoloplos panamensis</i>			X				9
<i>Aricidea suecica</i>			X				17
<i>Prionospio malmgreni</i>			X				9
<i>Chaetozone setosa</i>	X		X				3, 4, 9
<i>Tharyx monilaris</i>			X				4, 15, 17
<i>Tharyx parvus?</i>			X				4, 17
<i>Sternaspis scutata</i>		X					16, 17
<i>Heteromastus filiformis</i>		X					3, 17
<i>Praxillella gracilis</i>		X					7, 16
<i>Amphicteis scaphobranchiata</i>	X						4, 8, 16, 17
<i>Lysippe labiata</i>	X						3, 15
<i>Melinna cristata</i>	X						
<i>Pista cristata</i>	X						
<i>Myxicola infundibulum</i>					X		
<i>Cosswa longicirrata</i>			X				16

<sup>a</sup>Data source (citation omissions above represent unpublished observations of H. M. Feder and colleagues):

1. Abbott 1954
2. Baer 1951
3. Baggé 1969
4. Banse and Hobson 1968
5. Boooloottian 1966
6. Clark 1962
7. Hartman 1950
8. Hunt 1925
9. Lie 1968
10. MacGinitie and MacGinitie 1949
11. Morton 1958
12. Newell 1970
13. Purchon 1968
14. Reid and Reid 1969
15. Sanders 1960
16. Semenov 1965
17. Young and Rhoads 1971

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Addendum  
9.8 THE VAN VEEN GRAB

A discussion of its effectiveness as a  
quantitative instrument for benthic study in Valdez Arm

by  
H. M. Feder

*Introduction*

The van Veen grab, the quantitative instrument chosen to sample the bottom fauna of Port Valdez and vicinity, is a modification of the initial Petersen grab (Thamdrup 1938) that marked the advent of quantitative ecology (Petersen and Jensen 1911).

There is little agreement as to what is the most suitable apparatus for benthic sampling, and it is rare to find the same devices used by workers in different laboratories (Longhurst 1964). It is widely recognized that a variety of gear should be employed to obtain adequate faunal samples of a deposit substrate; no single sampler is able to collect all types of organisms which range from small abundant fauna to rarer and more widely dispersed epifauna. Petersen himself recognized this problem in devising the first set of instruments, the most effective of which was his grab mechanism that remains in use today in variously modified forms. Although the Petersen grab is an effective instrument, it has two major faults: it samples only a relatively small area, and the depth to which it penetrates depends upon the nature of the substrate (it is most effective on soft bottoms). A number of workers have modified the original grab. Van Veen added long scissors-like arms to close the instrument by lever action (see Thamdrup 1938), thereby improving its efficiency significantly (Ursin 1954). Smith and McIntyre (1954) mounted a van Veen type of grab equipped with two trigger plates in a frame in such a manner that the open grab could be thrust into the substrate by the action of two strong helical springs. The investigators indicated that this modification enhanced the quality of performance. Birkett (1958) used the van Veen modification of the grab but weighted it heavily with lead plates to assist its drive into the deposits, and thus he claimed better results than with the original grab. Several other samplers have been designed and used with varying effectiveness (Holme 1949; Hartman 1955; Vinogradova 1962; Jones 1969).

Various sorts of core samplers have been developed for deep penetration into hard sandy ground (Hunt 1926; Knudsen 1927; Barnes 1959; Holme 1971). Each has the capability limitation of extremely small spatial coverage, even relative to that of a Petersen grab, and none has been widely used.

In addition to grabs and corers, sampling instruments have been developed to collect organisms situated deep in the substrate as well as larger, more widely dispersed epifaunal specimens. Perhaps the most successful instrument of this type is Forster's anchor dredge, which is capable of digging a single bite in the hardest sandy deposits to about a 10-cm depth (Forster 1953). This was found to sample so uniformly in all deposits that it was put to quantitative use (Sanders 1956, 1958, 1960; Sanders et al. 1965). Larger epifaunal organisms have been sampled with runner-dredges or sea sleds such as the detritus sledge of Ocklemaun (1964).

In recent years increased attention has been called to the use of optical sampling methods: direct observation, photography, and closed circuit television. Perhaps SCUBA represents the device that has given the greatest impetus to direct investigation of benthic

fauna. As Longhurst (1964) has pointed out, however, it is not clear whether SCUBA is practical in the study of sedimentary substrates—whether it is "... practicable for a diver to perform a quadrant survey on the burrowing infaunal animals more efficiently than can a grab operated from the surface." As an example, it was not possible for divers to survey sedimentary substrates near Montague Island, Prince William Sound, for fauna fed upon by sea otters living in the area because of turbidity induced by diver activity (Calkins 1972). A series of submersibles with viewing and photographic ports have been developed in recent years with great potentialities for their practical usage. Despite the desirability of submersibles and underwater television, however, the heavy initial expenditures, specialized maintenance staff, and equipment needed for both methods put them out of the reach of most laboratories. It seems evident that the less sophisticated collecting gear, costing a fraction of the optical apparatus, will remain the mainstay in the foreseeable future.

*Advantage of the van Veen grab for Port Valdez sampling*

When the benthic sampling program was planned for Port Valdez, two samplers were considered: the van Veen and the Smith-McIntyre bottom grabs. The Institute of Marine Science, University of Alaska, had only a van Veen grab available for quantitative benthic work; acquisition of a Smith-McIntyre grab could have required as much as a year's time (Lie 1968). The urgency of the project demanded the choice of the sampler at hand.

Consideration of samplers for this project has not indicated that use of the Smith-McIntyre grab would have enhanced the sampling program. The major advantage of the latter sampler is its superior performance in heavy seas; although strong winds occasionally prevailed in Port Valdez, swells over a few feet were rare.

The Smith-McIntyre grab is more complex to operate, and its spring loading poses an additional hazard for sampler operation. The van Veen grab, on the other hand, is extremely easy to operate with few moving parts subject to malfunction, and it is relatively safe in the type of weather typical of Port Valdez; it is always far easier to cock than the Smith-McIntyre grab.

Smith and McIntyre (1954) studied the difference in catching power between the van Veen and the Smith-McIntyre grabs. They found that the latter grab consistently collected larger volumes of sediment than the former, although the volume they obtained was still extremely small for sedimentary samples collected (3.2 liters mud, 3.25 and 2.25 liters muddy sand). On similar bottom types sampled by Lie (1968) in Puget Sound, the van Veen grab sampled 20 liters and about 10 liters, respectively. The majority of the samples obtained in Port Valdez were volumes of 16-20 liters. A few samples contained less sediment than this, but none were less than 5 liters. The latter samples were all taken in rocky or cobbly areas where one cannot expect an effective performance from any sampler. In sandy areas there is the possibility that the greater driving force of the Smith-McIntyre might result in larger volumes, but no such areas were found during the Valdez investigation. All stations sampled, with the exception of cobble or rock areas, contained very soft mud. Thus, according to the work of Lie (1968) and from experience incurred in this study, the van Veen grab with its ability to dig deeper than the Smith-McIntyre sampler was the superior choice for use in Port Valdez.

One criticism of the van Veen grab by Birkett (1958) is that it supposedly makes a semicircular cut in the substrate and is said to introduce bias, because it would result in a

depth-differential effect in sampling animals inhabiting different layers of the substrate (Longhurst 1959). Experimental field studies by Lie and Pamatmat (1965) indicated that under ideal sampling conditions on sand, however, the van Veen grab makes a *horizontal* rather than a semicircular cut. On the other hand, when the grab is used on muddy bottom, the depth of penetration is considerably deeper than on sand and sufficiently deep to catch the majority of the fauna; it is therefore immaterial whether the cut is horizontal or semicircular.

Experimental work by Wigley (1967) in comparing the van Veen and Smith-McIntyre bottom samplers has suggested that the former creates strong hydraulic disturbance (shock wave) as it descends, while the latter creates only weak, oscillatory shock waves. Trials with ping pong balls, confetti paper, and formalin-preserved invertebrate animals demonstrated that these objects were pushed aside by the descending van Veen sampler. In terms of the Valdez sampling program, the major intent was to examine the infaunal residents of the area. The shock waves alluded to by Wigley (1967) would affect only epifauna—if, in fact, they do actually at all induce lateral movement in most *living* epifaunal organisms. The experimental data presented by Wigley would be of more significance if he had used living epibenthic forms, since most such organisms have abilities to attach themselves to the sediment with varying tenacities. Also, Lie and Pamatmat (1965) have shown experimentally that the van Veen shock waves do not affect the infauna and the epifaunal forms such as ophiuroids that partially embed themselves in the substrate. Sedimentary surfaces observed through the doors of the field sampler in the Valdez study always appeared intact, and the grab samples included some epifaunal species. Wigley (1967) indicated that the shock waves of the sampler are related to the small area (45 cm<sup>2</sup>) of screen openings on the tops of the van Veen grab compared with 826 cm<sup>2</sup> for the Smith-McIntyre sampler. The instrument used in the Valdez study had 200 cm<sup>2</sup> screen surface area.

A grab-sampling simulation program written to simulate multiple grab-sampling of the benthic organisms in Port Valdez showed that the most abundant species were adequately sampled in the first two or three samples taken by a van Veen grab (see text 9.5.1).

### Conclusion

As indicated by the above discussion, the van Veen sampler used in this project was effective for the weather conditions and substrate characteristic of the Port Valdez area.

Limited funds budgeted for ship time during the research period did not allow for dilution of efforts in a comparative sampling study between the van Veen and the Smith-McIntyre grabs, especially when the van Veen sampler functioned effectively.

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# PART III

## HYDROCARBON INVOLVEMENT



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# *Chapter 10*

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## BASELINE HYDROCARBON CONCENTRATIONS





## 10. BASELINE HYDROCARBON CONCENTRATIONS

by

P. J. Kinney

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### 10.1 Introduction

Progress is reported on measurements of baseline hydrocarbon concentrations in sediment, biota and water of Port Valdez for use in future crude-oil pollution detection or monitoring efforts after proposed tanker terminal development in the Port. Although assay methods sensitive to analysis of petroleum hydrocarbon samples collected from the environment are still under development, progress is sufficient that the direct chemical measurement of these contaminants in the environment is often possible.

Samples of sediments and biological material supplied by geologists and biologists working in Port Valdez have been analyzed for hydrocarbons by a gas chromatographic technique. Seawater has also been sampled for similar hydrocarbon analyses.

As development of the Valdez tanker facility progresses, additional hydrocarbon measurements should be made in order to extend the pre-existing data base and apply it to monitoring capability. Background data on certain organisms and stations should be standardized for this purpose. Modification and standardization of techniques for field monitoring applications progress slowly because of the inevitably time-consuming nature of such development efforts. From results to date, however, it is clear that standardized hydrocarbon type-analysis and work with the non-volatile (high-molecular weight) fractions should be integral to insure that monitoring techniques will measure those variables that are important in the actual environment.

### 10.2 Methods

Slightly modified extraction and gas chromatographic methods of Blumer et al. (1970) were used in this work. Kudaar evaporators were used rather than the vacuum method, and the Dexsil 300 high-temperature, silicone grease chromatographic column packing was used rather than Apiezon L vacuum grease.

Sediment samples obtained by Shipek bottom grab were each immediately transferred from the surface into a 1-liter wide-mouth glass jar (with screw cap) that had been

previously washed with a sulfuric acid-dichromate cleaning solution. The samples were then rinsed with hydrocarbon-free distilled water followed by methanol and frozen until analysis.

Biological samples were obtained by various techniques; some were hand-picked on beaches, while others were collected by hook and line or by crab pot. Specimens were placed in jars as in the case of the sediment samples, or they were frozen in methanol-extracted aluminum foil.

Water samples were obtained by a 20-liter glass sampler and taken immediately to the shore laboratory. Twelve liters were then extracted in a large separatory funnel with three 160-ml portions of hexane solvent. The hexane extracts were returned to the Fairbanks laboratory in glass-stoppered bottles that had been cleaned as described above.

After thawing, 50-g (wet wt) samples of sediment were used for methanol extraction. Biological samples were chopped with a cleaned knife (after shucking in the case of shellfish) into 50-g (wet wt) samples, which were then extracted for 18 hours with refluxing methanol in Soxhlet extractors. The extracts were centrifuged free of solids, and both extracts and solids were extracted three times with hexane. The hexane extracts were then combined, water-washed, and dried with sodium sulfate. Elemental sulfur was removed from sediment extracts on a column of precipitated copper following a method described by Blumer (1957). The dried extracts were then evaporated to approximately 5 ml in a Kudarr evaporator.

Samples were next chromatographed on a (2.5 x 30.5 cm) column consisting of three parts of silica gel (Davidson, grade 922, through 200 mesh, activated at 120C, deactivated with 5 wt-percent water) and 2 parts of alumina (Harshaw, 0102-P, activated at 250C, deactivated with 5 wt-percent water) packed in hexane with the alumina layer on top. The samples were then eluted with 400 ml hexane (about 2.5 column volumes) according to the methods of Hirsh et al. (1972) and Koons and Monaghan (1969) for saturated hydrocarbons.

Samples were evaporated into 25- $\mu$ l capillaries on the bottom of the Kudarr evaporators and analyzed on a Varian 1520 Gas Chromatograph using a 48-min 80-285C linear temperature program and a flame-ionization detector. The 12-ft column used was 1/8 inch in diameter, packed with 2.5 wt-percent Dexsil 300 GC silicone grease on 70-80 mesh Chromosorb W.

### 10.3 Results

Hydrocarbon data obtained by means of the slightly modified Blumer technique were based on sediment samples collected in Port Valdez at locations shown in Figure 10.1.

In order to quantify the amount of hydrocarbons present, an n-alkane standard provided by British Petroleum Company Limited was used to calibrate the gas chromatograph. Quantification was obtained by measuring the total area under the peaks, relative to the baseline due to the slight column bleed, and comparing this area with that obtained from chromatographing a known amount of the n-alkane standard. Suitable corrections were made for instrument attenuation changes and for the proportion of the total sample injected (as measured by microliter syringes). The n-alkane standard was used also as an internal standard to determine recoveries throughout the complex analytical procedures; these recoveries varied from 30-90 percent over the C-14 to C-28 range with an average of 60 percent. Figure 10.2 illustrates a gas chromatograph of the standard n-alkane mixture and the baseline obtained by single-column operation, 80-285C program, with the Dexsil 300 GC column packing.

The gas chromatographic signature obtained by processing 10  $\mu$ l of Prudhoe Bay crude oil throughout the same analytical procedure as was used for the sediment samples (Figure 10.3) may be used for comparative purposes with sample spectra that follow.

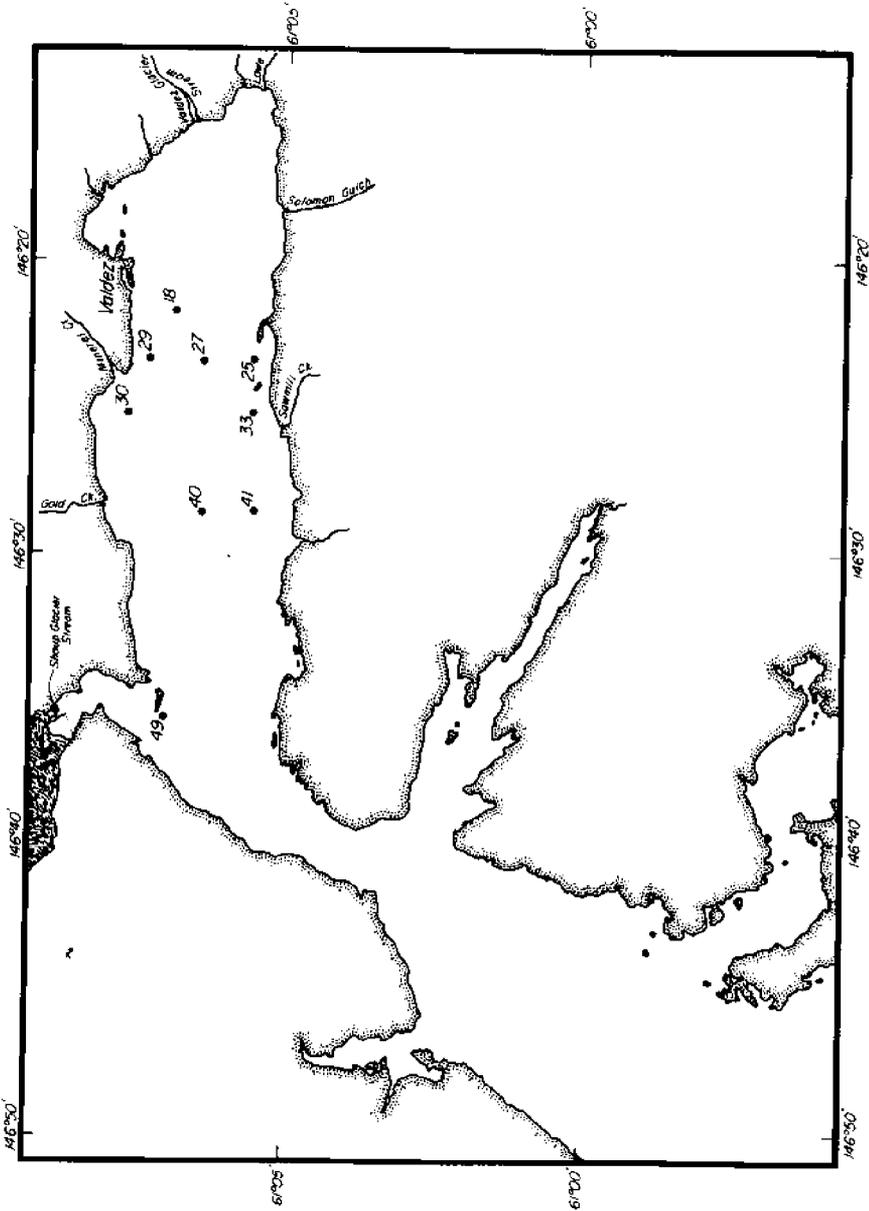


Figure 10.1 Sampling locations for sediments analyzed for hydrocarbons by the Blumer technique.

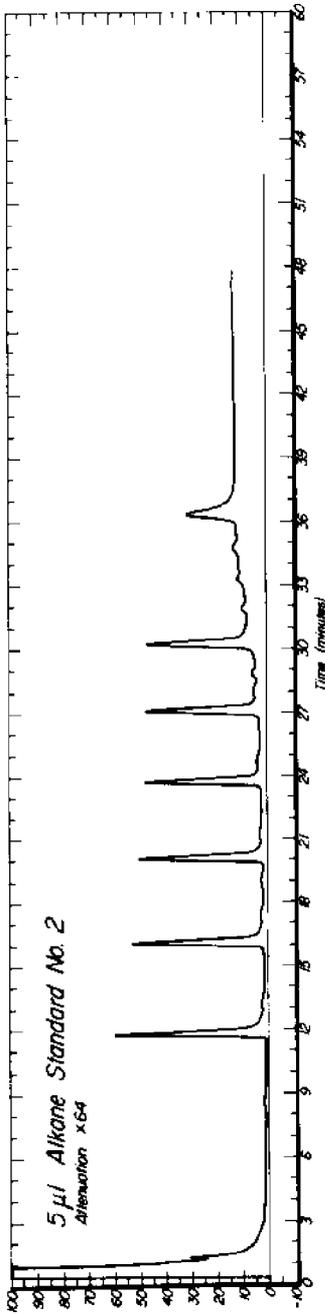


Figure 10.2 Gas chromatograph of n-alkane standard in hexane used for calibration and internal standardization of C-14, C-16, C-18, C-20, C-22, C-24 and C-28 measurements with 80-285°C temperature program.

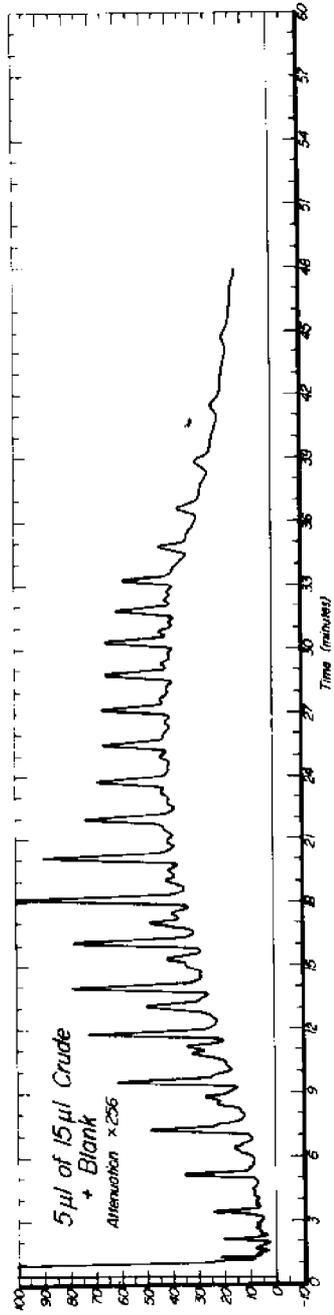


Figure 10.3 Gas chromatograph of Prudhoe Bay crude oil subjected to same analytical procedure as used with sediment samples (Figures 10.4-10.9).

Shown in Figures 10.4-10.9 are samples of gas chromatographs obtained from the sediment samples. Quantification of the hydrocarbons was arbitrarily limited to the C-16 through C-28 range in order to standardize the procedure in the range of molecular weights for which the method is most applicable. Table 10.1 below gives resulting hydrocarbon concentrations for this range as determined by the above method:

**Table 10.1 Hydrocarbon concentrations (C-16 through C-28) in Port Valdez sediments**

Station	C-16 through C-28 hydrocarbons (ppm by wet wt)
18	0.47
25	0.72
27	1.8
29	1.3
30	2.3
33	1.4
40	1.0
41	1.3
49	2.5

The concentrations in the Port Valdez sediments were in the 0.5-2.5 ppm range, and similar concentrations were measured for some biological materials collected in the Port:

**Table 10.2 Hydrocarbon concentrations (C-16 through C-28) in Port Valdez organisms**

Sample	C-16 through C-28 hydrocarbons (ppm by wet wt)
Mya clams, Mineral Creek Flats, 9 September 1971	1.1
Mussels, Mineral Creek Flats, 9 September 1971	1.9
Starfish (I) from Crabpot, Station 24, 30 August 1971	0.80
Starfish (II) from Crabpot, Station 24, 30 August 1971	12.4
Yellowfin Sole, Genus <i>Lamanda</i> , Station 24, August 1971	0.51
Yellowfin Sole, Genus <i>Lamanda</i> , Station 24, August 1971	0.97

The C-16 to C-28 hydrocarbon concentrations measured in organisms varied from 0.5-1.9 ppm, with the exception of one starfish that was apparently contaminated during shipboard sampling. Examples of gas chromatographic signatures of the biological materials are shown in Figures 10.10-10.15.



perch samples measured for hydrocarbon content in tissue

#### BASELINE HYDROCARBON STUDIES



gas chromatograph

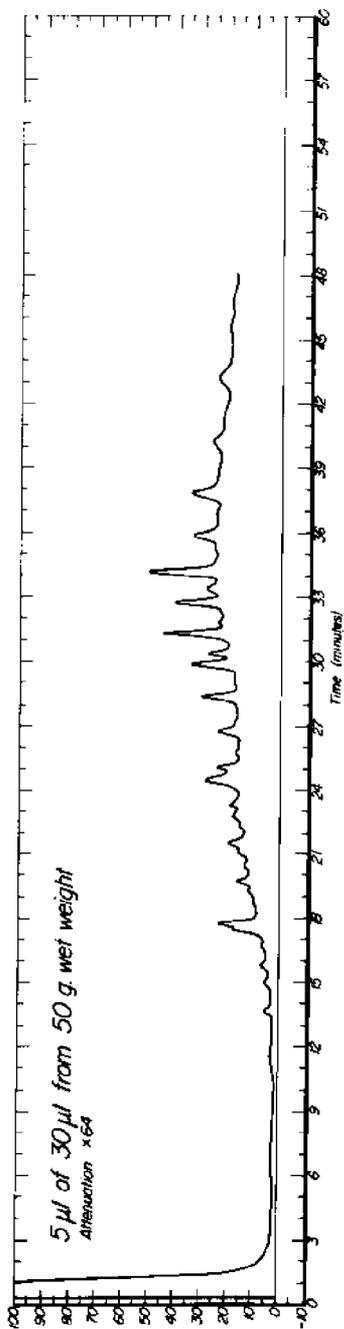


Figure 10.4 Gas chromatograph of hydrocarbons from sediment at station 49.

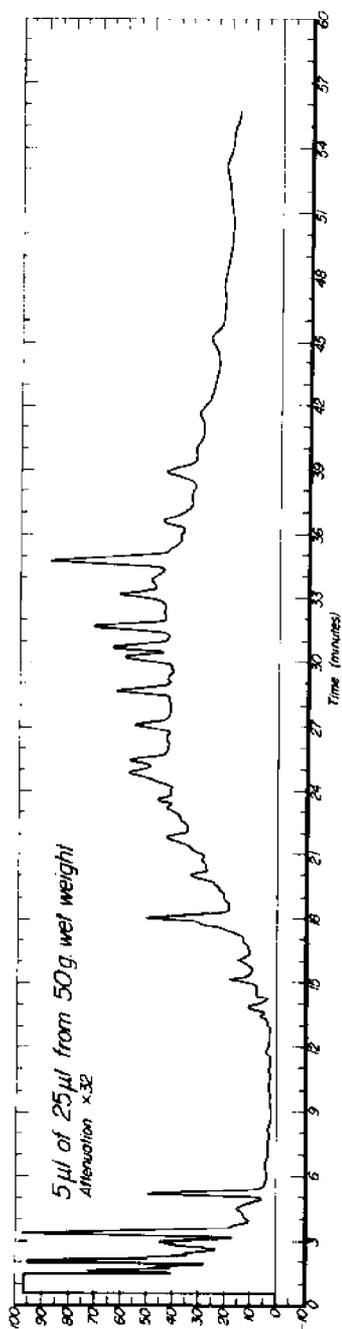


Figure 10.5 Gas chromatograph of hydrocarbons from sediment at station 30.

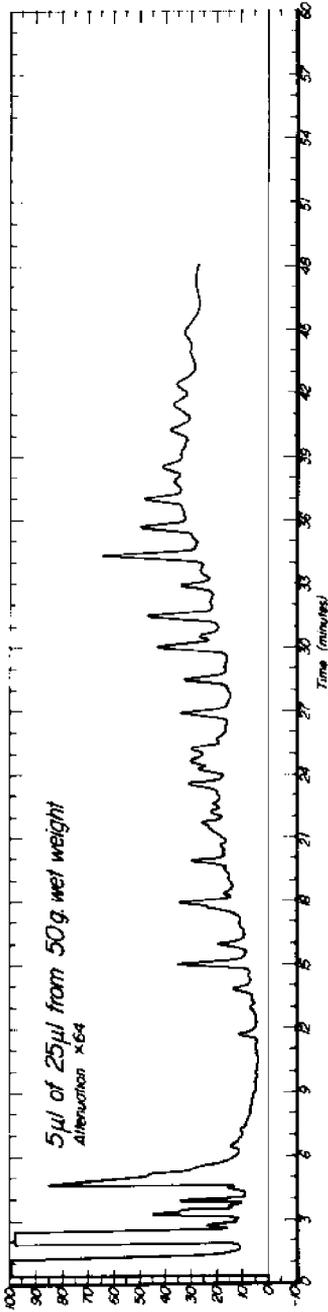


Figure 10.6 Gas chromatograph of hydrocarbons from sediment at station 27.

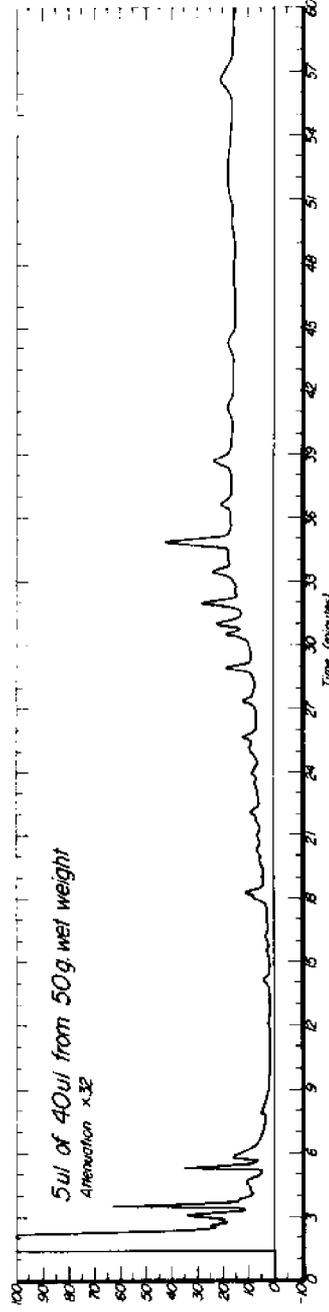


Figure 10.7 Gas chromatograph of hydrocarbons from sediment at station 40.

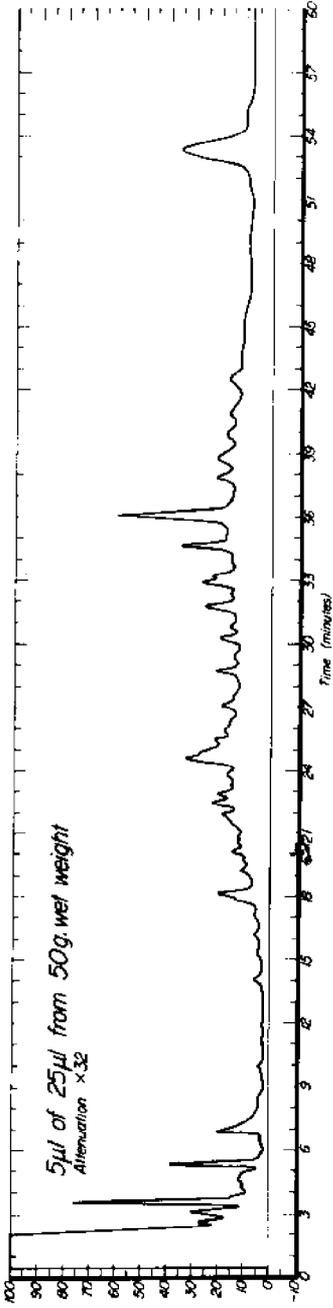


Figure 10.8 Gas chromatograph of hydrocarbons from sediment at station 33.

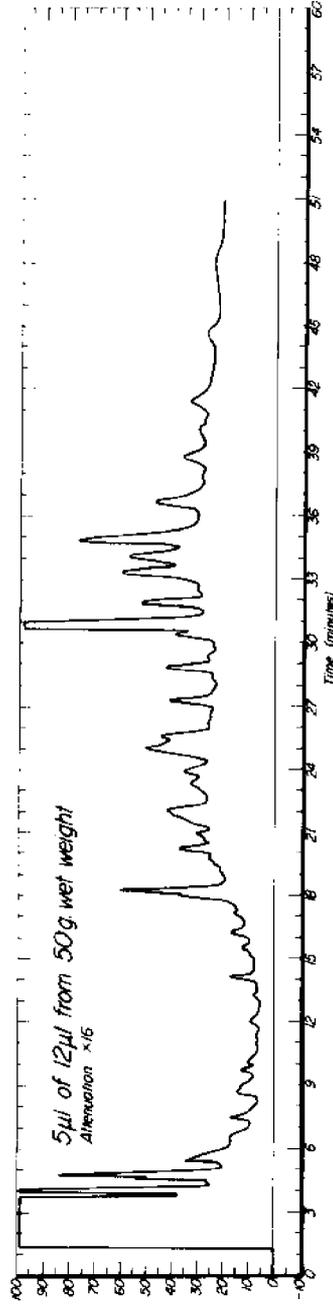


Figure 10.9 Gas chromatograph of hydrocarbons from sediment at station 29.

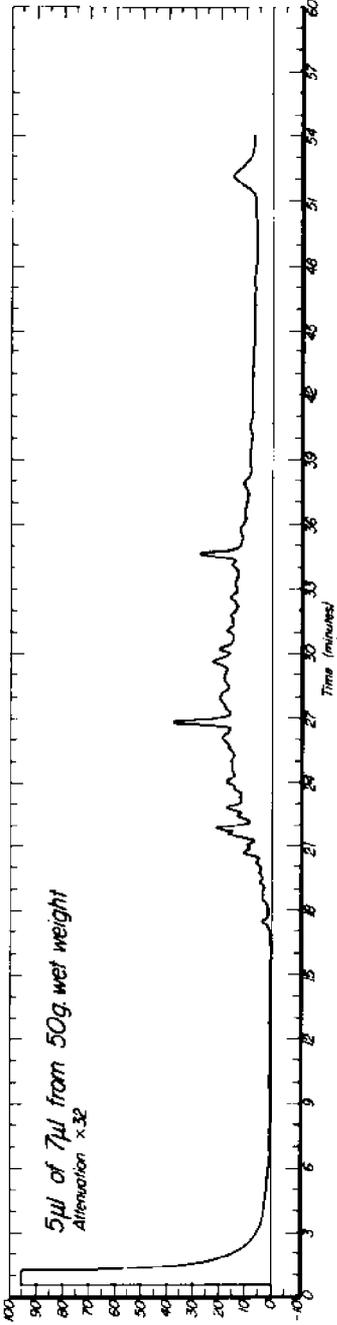


Figure 10.10 Gas chromatograph of hydrocarbons from *Myz* clams collected at Mineral Creek Flats, 9 September 1971.

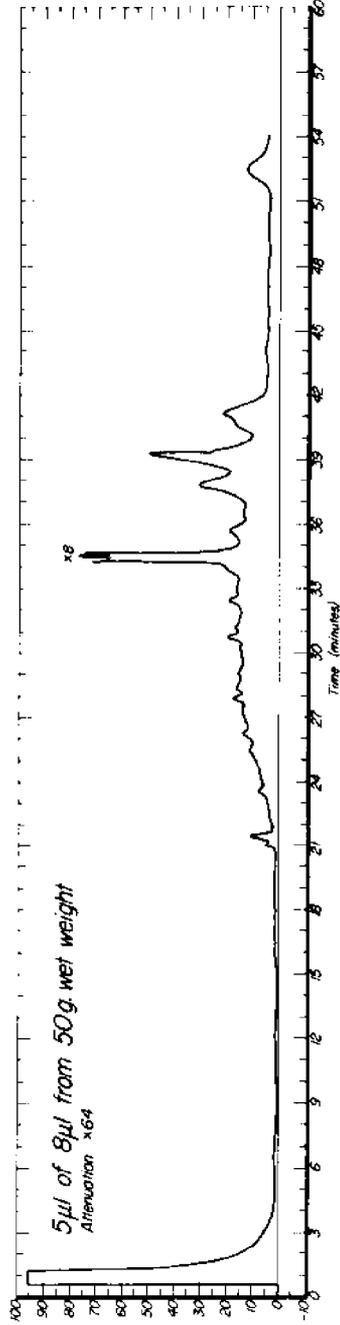


Figure 10.11 Gas chromatograph of hydrocarbons from mussels collected at Mineral Creek Flats, 9 September 1971.

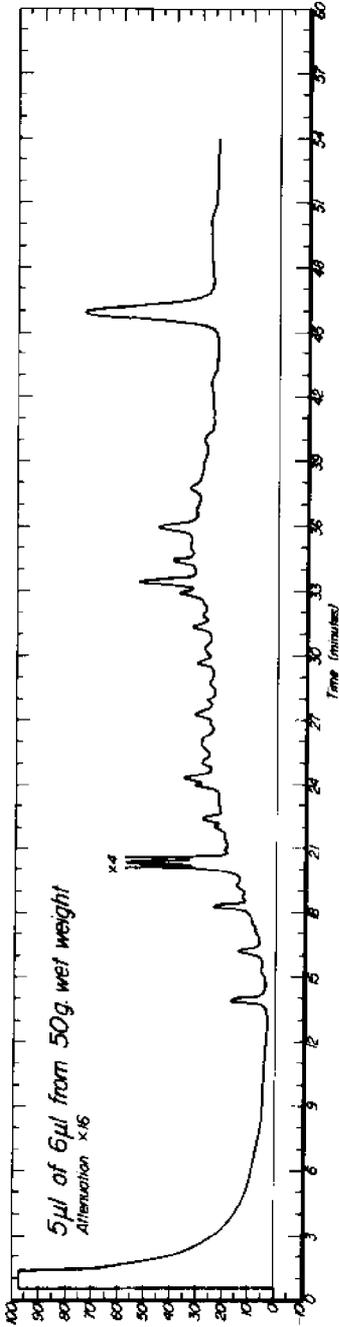


Figure 10.12 Gas chromatograph of hydrocarbons from starfish (I) collected in crabpot at station 24, 29 August 1971.

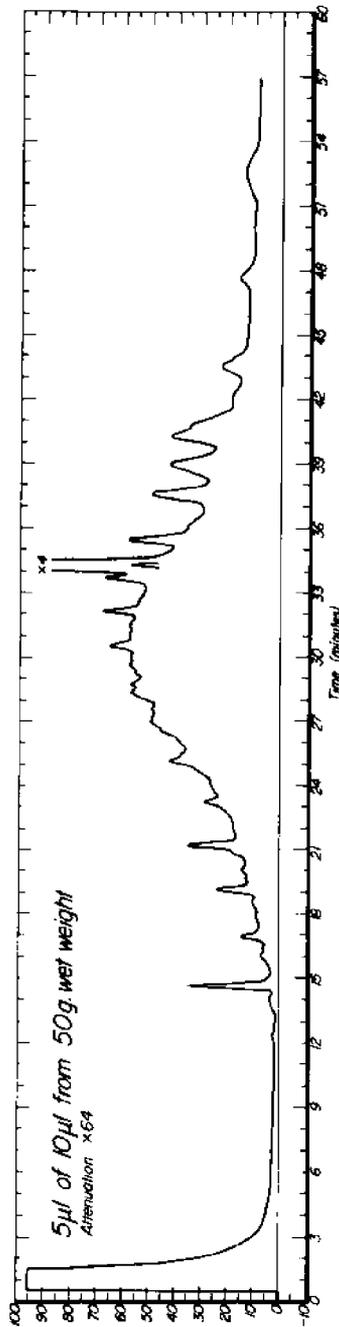


Figure 10.13 Gas chromatograph of hydrocarbons from starfish (II) collected in crabpot at station 24, 30 August 1971.

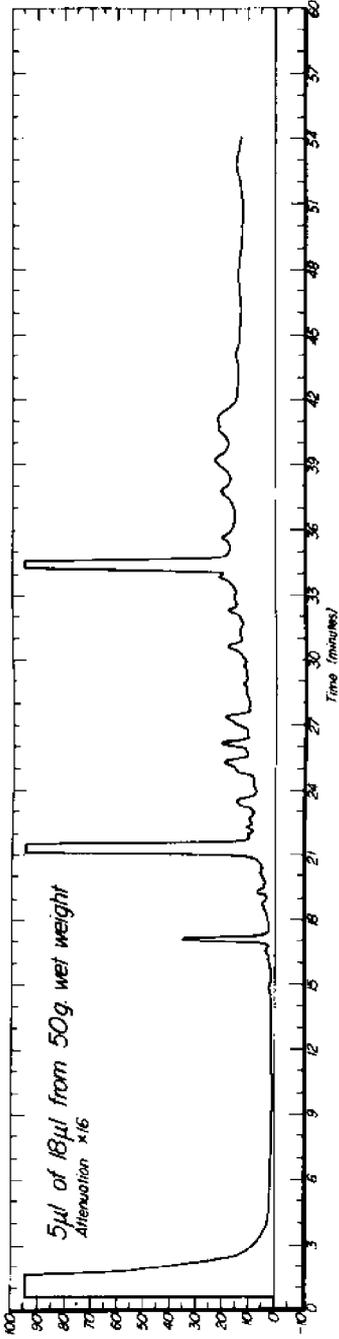


Figure 10.14 Gas chromatograph of hydrocarbons from yellowfin sole, genus *Lamanda*, collected at station 24.

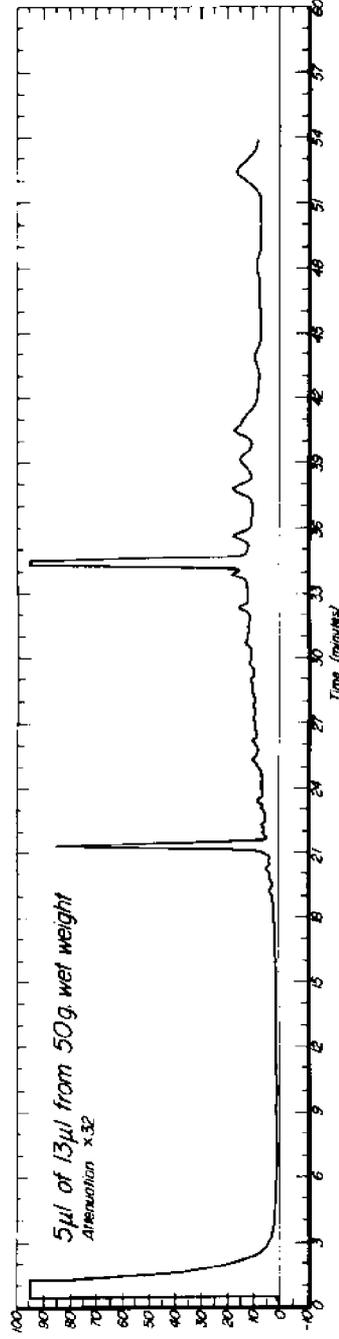


Figure 10.15 Gas chromatograph of hydrocarbons from poacher fish collected at station 24 on 30 August 1971.

Water samples taken from outside the Narrows, off the Jackson Point terminal site and off Mineral Creek have been chromatographed. Carefully controlled blank samples were processed together with these water analyses for precision in detecting the extremely low values inherent. Large (12-liter) samples were processed to minimize blank errors. The values obtained were in the range of 0.02 ppb hydrocarbons, but further work is needed to establish the individual hydrocarbon concentrations and the variability in these on a seasonal basis.

#### 10.4 Summary

The difference between gas chromatographic signatures from the Prudhoe Bay crude oil samples and those obtained from sediment or biological samples is remarkably distinct, thus bearing out the potential validity of the chemical method of discrimination between hydrocarbon pollution and natural background content.

Comparisons of the hydrocarbon concentrations measured in Port Valdez with those reported elsewhere indicate slightly lower but comparable values. Literature values for *total* hydrocarbons typically run from 10-100 ppm (Meinschein 1959; Hunt 1961), with Blumer and Sass (1972) reporting 20-100 ppm for unpolluted Buzzards Bay (Massachusetts) sediments. Values of 3-6 ppm were reported by Kvenvolden (1962) for n-hydrocarbons in San Francisco Bay sediments; Clark and Blumer (1967) reported 1.7 ppm n-paraffins for a recent sediment. Port Valdez values of 0.5-2.5 ppm, using the modified elution method of Hirsh et al. (1972) and Koons and Monaghan (1969) for saturated hydrocarbons, thus seem reasonable. Values of 0.5-1.9 ppm obtained for biological materials in the Port compare with those of Blumer and Sass (1970) of 5 ppm in unpolluted oysters and with values of 2-18 ppm for n-paraffins in an Alaskan sanddollar, flounder and starfish (P. L. Parker, personal communication, 1972).

Port Valdez water samples have yet to be chromatographed. Reliable hydrocarbon values for water are scarce; however, Peake and Hodgson (1966) report 0.2-3.8 ppb (parts per billion) n-alkanes in fresh water and <0.2 ppb for two seawater samples. Parker and Winters (1972) have found 0.63 ppb n-paraffins for Louisiana coast samples, and earlier results in Cook Inlet were <0.02 ppb (Kinney et al. 1969). Thus blank and contamination problems have to be checked carefully on such low values in order to reliably measure the natural background levels.

## 10.5 References

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# *Chapter 11*

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## CRUDE OIL PHYTOTOXICITY STUDIES





PLANTS OF ALASKA, U.S.A.

*Algis tenuifolia* Setchell, in Collins and Setchell, 1901

Attached to stern of USSR ship, V  
boat harbor (probably brought up  
S.E. Alaska) ca. 61°07' N, 146°16'

7 May 1972

Collected by R.E. Lohr, Identifier  
Mueller

UNIVERSITY OF ALASKA HERBARIUM  
College, Alaska

## 11. CRUDE OIL PHYTOTOXICITY STUDIES

by

W. E. Shiels, J. J. Goering and D. W. Hood

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### 11.1 Introduction

Toxicological studies were undertaken in this project to determine the effect of crude oil on the marine primary producers: the phytoplankton and seaweeds, which form the base of the food-chain and as such are critical components of the marine ecosystem. The effects of oil and other toxic substances on aquatic organisms have been well documented in the literature (Mackin 1950; Currier and Peoples 1954; Hood et al. 1960; McCauley 1966; Pickering and Henderson 1966; Carthy and Arthur 1968; Mironov 1968; Smith 1968; Baker 1970, 1971; Blumer et al. 1970; LaRoche et al. 1970; Allen 1971; Dickman 1971; Straughan 1971; and Mosser et al. 1972). Few investigators, however, have examined the effects of petroleum on marine algae (Galtsoff 1935; Clendenning 1959; Mironov 1967; Mironov and Lanskaya 1968; Lacaze 1969; and Strand et al. 1971).

As an initial effort to indicate basic trends in plant response to crude oil under varying environmental conditions, toxicological studies of the marine flora in Port Valdez were conducted over a 1-year period (May 1971 to June 1972). Experiments were designed to evaluate the effects of crude oil on phytoplankton and important species of macrophyte algae at concentrations in the range expected to result from treated ballast-water discharge (0.003-10 ppm).

## METHODS

### 11.2 Crude Oil Stock

Prudhoe Bay crude oil (AFS-SR 101A, B. P. Alaska, Inc.) was used in phytotoxicity experiments conducted on natural phytoplankton populations and on major species of seaweeds during five cruises of the *R/V Acona* in Port Valdez and two subsequent field trips to the area. Certain modifications were made to methods and techniques as the study developed.

### 11.2.1 Preparation of oil-treated seawater

Crude oil was applied to marine algae in three ways: emulsion, volume additions and oil slick. In all cases the oil was at room temperature ( $\sim 22$  C) before it was added to seawater and was stored frozen when not in use.

### 11.2.2 Oil-seawater emulsion

One hundred percent oil-saturated seawater was prepared by 1) filtering raw seawater through 0.45- $\mu\text{m}$  Millipore or glass fiber filters, 2) pasteurizing it at 60 C for 2 or more hours, 3) adding an excess of oil (i.e., at least 50 ml) to 2 liters of the seawater, 4) shaking (wrist-action shaker) for at least 24 hours in a tightly stoppered glass bottle, and 5) draining the water from the bottom of the bottle through a spout after the oil-seawater mixture had stood for 12 or more hours. This oil-treated seawater is referred to as *oil-saturated seawater*, which was used full strength or serially diluted in the toxicity experiments.

### 11.2.3 Volume additions of oil to seawater

Volume to volume additions of oil to seawater were made by 1) filtering and pasteurizing raw seawater, 2) adding a known volume of oil to a measured volume of seawater, 3) shaking the mixture for 24 hours and then using it immediately in toxicity experiments. This stock solution was diluted to half with raw seawater in some experiments, or it was first serially diluted with filtered seawater and then diluted to half strength with raw seawater. The oil concentrations reported in the various experiments represent the amount of oil *added to seawater but not necessarily dissolved in it*.

### 11.2.4 Oil slick on seawater

Oil was added to the surface of seawater in incubation vessels during two types of experiments. In one method, referred to as the "Dickman experiments" (Dickman 1971), 5 ml of oil was added to 125 ml of raw seawater. In the species succession experiment, on the other hand, small volumes of oil (0.01 ml and 1.0 ml) were added to 1-liter samples of raw seawater.

## 11.3 Hydrocarbon Analysis

Quantitative analysis of oil-treated seawater used in phytotoxicity experiments was conducted independently by the Institute of Marine Science (IMS), University of Alaska, and the Valdez facility of Battelle Northwest Laboratories.

### 11.3.1 Dissolved organic carbon method

Analysis of crude-oil samples at IMS employed the method of Menzel and Vaccaro (1964), which entails the oxidation of dissolved organic carbon (DOC) to  $\text{CO}_2$  and its measurement by infrared spectrophotometric analysis. Collection of samples for DOC analysis was made by adding 5 ml of seawater to a 10-ml ampoule containing  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_3\text{PO}_4$  (3%) and distilled water, then flushing with oxygen for 5 min before sealing the ampoule. Previously the ampoules had been baked at 575C for at least 4 hours. The organic carbon content in seawater was measured by autoclaving the sealed ampoule to oxidize the organic carbon and then measuring the resultant  $\text{CO}_2$  by passing it through a Beckman

Model IR215 CO<sub>2</sub> Infrared Analyzer. Concentrations of carbon were converted to crude oil concentrations by assuming an average crude oil carbon content of 86 percent by weight (Hobson 1967).

### 11.3.2 Battelle method

Samples analyzed by Battelle were collected in pre-treated glass jars and extracted with carbon tetrachloride (CCl<sub>4</sub>) within an hour after collection. Three extractions were made on each seawater sample; an aliquot of the combined CCl<sub>4</sub> fraction was placed in a KBr volatile liquid cell and read on a Beckman Model IR-20 Infrared Analyzer from 2400-4000 wave numbers. The intensity of the CH<sub>2</sub> bond-stretching was recorded and compared to crude oil standards. This method is reported to reliably measure hydrocarbon levels as low as 1 ppm in seawater (E. Wolf, personal communication).

### 11.4 Collection and Identification of Algae

Phytoplankton standing stock was determined by collecting seawater samples in a polyvinyl chloride (PVC) bottle, preserving the samples with 4% formalin buffered with sodium acetate, and counting by the Utermöhl inverted microscope technique (Utermöhl 1931). Qualitative sampling consisted of taking vertical tows from the bottom of the euphotic zone to the surface with a 0.5-m, no. 25 mesh net towed at 13 m/min. Samples were preserved with buffered formalin until species identifications were made using a Zeiss phase-contrast microscope. A detailed account of methods and results of the Valdez phytoplankton study is given by Horner et al. in Chapter 7 of this volume.

Seaweed samples were collected near Jackson Point by hand (intertidal) or by dredge (subtidal), placed in fresh seawater and kept in subdued light until used in toxicity experiments. Identification of seaweeds was made at the Invertebrate and Marine Collection Center, University of Alaska Museum. Accession numbers are given in Table 11.1 for voucher specimens of all the seaweeds used in the oil toxicity experiments except *Enteromorpha intestinalis*.

### 11.5 Preparation of Plant Material

Plant material used in oil toxicity experiments was tested as soon after collection as possible, usually less than an hour in the case of phytoplankton and not more than 4 hours for the seaweed species.

**Table 11.1** Species of seaweeds studied in crude oil toxicity experiments in Port Valdez, Alaska, from July 1971 to May 1972

Taxa	Accession No.
<b>Chlorophyta</b>	
<i>Cladophora stimpsonii</i> Harvey, 1859	50584
<i>Enteromorpha intestinalis</i> (L.) Link, 1820	--
<i>Ulva fenestrata</i> Postels and Ruprecht, 1840	50583
<b>Phacophyta</b>	
<i>Alaria tenuifolia</i> Setchell, in Collins, Holden and Setchell, 1901	50582
<i>Costaria costata</i> (Turner) Saunders, 1895	50580
<i>Fucus distichus</i> Linnaeus, 1753	50579
<i>Laminaria saccharina</i> (L.) Lamouroux, 1813	50581
<b>Rhodophyta</b>	
<i>Rhodymenia palmata</i> (L.) Greville, 1830	50586
<i>Halosaccion glandiforme</i> (Gmelin) Ruprecht, 1851	50585

### 11.5.1 Phytoplankton

Phytoplankton were usually collected in a 30-liter PVC, non-toxic sampling bottle (General Oceanics Inc., Model 1010). On a few occasions samples were obtained from the ship's PVC non-toxic seawater system, which has an intake port location 2.5 m below the surface. In either case the water sample was used as soon after collection as possible with precautions to avoid any changes in temperature or exposure to intense light. During the summer and fall cruises, toxicity experiments were carried out with net plankton. Plankton were collected with horizontal tows of a no. 25 mesh (0.048-mm) net at selected depths and strained through a no. 0 mesh (0.571-mm) net for removal of the larger zooplankton; that material which passed through the mesh was suspended in fresh seawater and designated *phytoplankton soup*.

### 11.5.2 Seaweeds

Marine macrophyte algae, or seaweeds, were collected from the intertidal and subtidal zones near Jackson Point in Port Valdez. *Alaria tenuifolia* however, was collected in the Valdez small boat harbor from the hull of a ship and may not be indigenous to Port Valdez. This species was selected because it was in an early growth stage, with fronds 6-9 cm in length, which could be used whole in toxicity experiments. Small pieces were cut from the larger fronds of *Costaria costata*, *Fucus distichus*, *Laminaria saccharina* and *Ulva fenestrata*, and *Cladophora stimpsonii*, *Enteromorpha intestinalis*, *Halosaccion glandiforme* and *Rhodymenia palmata* were used either as whole plants or single fronds, depending on the plant size. Prior to experimental use, the plants were kept in a fresh supply of seawater in low light.

## 11.6 Measurements of Metabolism

Two methods were used to measure the effects of crude oil on photosynthesis and respiration by marine plants. The  $^{14}\text{C}$  method was used in both seaweed and phytoplankton studies, employing Geiger-Mueller (G-M) counting (Strickland and Parsons 1968) or the liquid scintillation counting (LSC) technique (Schindler 1966; Wolfe and Schelske 1967). In some seaweed experiments photosynthesis was measured by the light and dark bottle method (Strickland 1960) using a modification of the Winkler oxygen titration procedure (Wallen and Hood 1968).

The techniques used to evaluate oil toxicity in these studies were taken in part from the work done by Hood et al. (1960) and by Strand et al. (1971).

### 11.6.1 Dissolved oxygen method

Plant material was added to glass incubation bottles containing control samples of filtered seawater alone or test samples of filtered seawater with crude oil. Bottles with no plant material were incubated along with bottles containing seaweed to correct for non-plant oxygen changes. After 4-hour incubation the plant material in each bottle was removed and dried at 105°C for 12 hours prior to being weighed, and the oxygen content of the seawater was determined. Photosynthetic rates were computed from  $\text{O}_2$  differences between light and dark bottles (Strickland 1960).

### 11.6.2 Carbon-14 method

In studying oil toxicity by use of the  $^{14}\text{C}$  method, raw seawater containing phytoplankton was placed into either 125 ml clear glass or totally darkened reagent bottles, crude oil was applied as specified by the particular experiment, and  $5\ \mu\text{C}$  of  $^{14}\text{C-HCO}_3^-$  was added. The bottles were then stoppered and placed in a seawater-cooled incubator under natural light or under artificial light at ambient seawater temperatures. After 2.5-9 hours' incubation, the contents of each bottle were filtered through  $0.45\text{-}\mu\text{m}$  Millipore cellulose-acetate filters and rinsed with 5 ml of 0.005 N HCl made with filtered seawater. The filters were then placed in ventilated plastic petri dishes, dried, mounted on aluminum planchets and counted on a Picker low-background  $\beta$ -counter.

The LSC technique was used in experiments conducted on two *R/V Acona* cruises (128 and 131) and on two subsequent field trips to Valdez. Instead of undergoing desiccation, the filters were placed directly into scintillation vials containing 10 ml of Aquasol (NEF-934, New England Nuclear, Boston, Mass.), a scintillation cocktail mixture. After 12-24 hours the filters became nearly transparent; if the contents were shaken several times within 1-2 days of filter addition, the filter remnants were negligible and posed no interference with accurate  $^{14}\text{C}$  counting. The samples were then ready for counting upon the addition of 2.3 ml distilled water for gel formation.

Seaweed photosynthesis was tested also with the  $^{14}\text{C}$  method. The experimental procedure was similar to that used for phytoplankton, except only the LSC counting technique was used. Filtered, pasteurized seawater (oil-treated and untreated) was added to 125-ml reagent bottles, one light and one dark bottle for each oil concentration plus a light and a dark bottle for the controls, followed by the addition of healthy seaweed material. Two ml of seawater were removed and  $5\ \mu\text{C}$   $^{14}\text{C-HCO}_3^-$  added. The bottles were placed in a seawater-cooled incubator for 2-4 hours under natural light, then removed and shaken at half-hour intervals. Following incubation the plant material was removed, rinsed first in filtered seawater and then in dilute acid (0.005 N HCl), blotted dry and placed in glassine envelopes. In the laboratory, the dried seaweed samples were ground with a mortar and pestle and weighed, or they were weighed and then digested in a mixture of Protosol (New England Nuclear, Boston, Mass.) and NCS<sup>TM</sup> (Amersham/Searle Corp., Arlington Heights, Ill.). After treatment with Aquasol, the contents in each scintillation vial were mixed by shaking and allowed to stand for at least 48 hours before addition of distilled water.

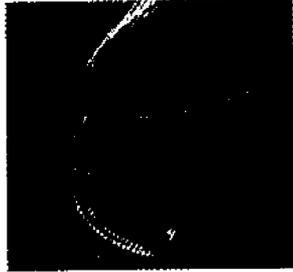
Scintillation vials containing the phytoplankton or seaweed material were wiped clean and counted in a Nuclear Chicago Model 6848 Liquid Scintillation System. The external standard mode of operation, using Barium-133 as the gamma source, was used for quench measurement as opposed to the channels ratio mode. Quenched standards were made up in Aquasol using  $\text{CCl}_4$  as the quenching agent. The external standard ratio (ESR) and corresponding counting efficiency (EFF) value for each quenched standard were plotted and a standard curve drawn.

After plant samples were counted, ESRs were calculated and the corresponding EFFs taken from the standard curve. Since the filters often contained relatively large quantities of oil, color quenching became significant. Chlorophyll *a* and other plant pigments also produced color quenching and thus reduced the counting efficiency when experiments were conducted with seaweeds or with high standing stocks of phytoplankton. With a reliable quenched standard curve, however, an accurate EFF value may be obtained for each sample; and, if EFF plus background-corrected counts per minute (CPM) are known for the sample, sample activity in disintegrations per minute (DPM) may be determined. Such a quenched standard curve was used to obtain reliable  $^{14}\text{C}$  activity measurements.

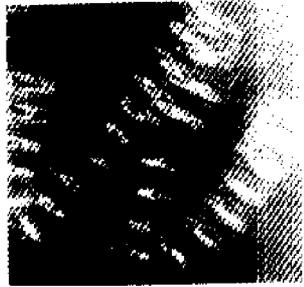
PHYTOTOXICITY  
STUDIES



*Alaria*



*Ceratium*



*Chaetoceros*



Niskin water sample bottle

Phytoplankton and marine macrophyte algae are subjected to treatment with Prudhoe Bay crude oil under varying environmental conditions; subsequent changes in plant metabolism are monitored by use of  $^{14}\text{C}$  technique.



*Fucus*

### 11.7 Statistical Analysis

The statistical tests applied to the data from various oil toxicity experiments followed those described by Snedecor (1962).

## RESULTS

### 11.8 General Discussion

Prudhoe Bay crude oil was used in toxicity experiments on five cruises of the *R/V Acona* in Port Valdez during July 1971-April 1972 and during two field trips in spring and summer. The purpose of the investigation was to determine the concentrations of oil in seawater that caused inhibition or toxicity as manifested by a depressed photosynthetic rate in natural marine phytoplankton populations under differing temperature, light intensities and exposure times. The toxicity of crude oil at several concentrations to 8 species of predominant intertidal and subtidal seaweeds was also tested.

Analytical determinations of oil content in seawater were made in most experiments. In cases where directed measurements were not made, however, the concentrations were estimated according to the known oil content of similarly prepared oil-treated seawater.

The results of the experiments are presented as differences in carbon assimilated, measured as the CPM or DPM per volume of seawater, as dry weight (g) or as the amount of oxygen liberated (ml O<sub>2</sub>/g dry wt). Pertinent data from toxicity experiments in which the <sup>14</sup>C method was used have been tabulated (Shiels 1973).

In this study, low concentrations of fresh (unweathered) crude oil were applied to natural populations of marine phytoplankton or seaweeds for relatively short incubation or exposure times under simulated natural light and temperature conditions. Photosynthesis was usually estimated by the <sup>14</sup>C method in experiments conducted in the field.

Previous studies on the effects of oil pollution on marine algae are difficult to compare to this study due to such discrepancies as treatment of the algae with *non*-crude oils (bunker oil, diesel oil, and other refined petroleum products), treatment of the algae with crude oil plus a dispersant chemical, differences in method of applying oil (emulsion, surface film, aqueous phase of oil-seawater mixture), the amount of oil used, the manner in which algal metabolism is reported (primary productivity, cell counts, dehydrogenase activity), forms of test organisms used (unialgal, axenic cultures, mixed populations) and the location and nature of testing (laboratory, field, *in situ* or chemostatic).

### 11.9 Effects of Oil on Phytoplankton

The growth response of phytoplankton to crude oil contamination is difficult to accurately assess in ecological studies where attempts are made to simulate the natural environment. Even in controlled laboratory experiments it is difficult to determine if an observed change in phytoplankton metabolism is due directly to oil contamination or whether it results from a combination of other factors such as light, temperature, salinity and dissolved nutrients superimposed upon the effects of crude oil.

The main difficulty in an ecological study using natural populations of phytoplankton is that species abundances differ with the time of year. A study of temporal changes in phytoplankton toxicity levels, therefore, might reflect only the changes in species composition in a population and their responses to crude oil rather than changes due to seasonal variations of natural physico-chemical events. Each experiment conducted in this study should be evaluated on its own to consider all such environmental parameters.

Toxicity tests conducted with indigenous phytoplankton during the spring bloom, for example, under natural conditions of light, temperature and water chemistry, would be of greater value in predicting consequences of crude oil pollution in the marine ecosystem than studies with monocultures of plankton algae in laboratory chemostats. The value of the laboratory studies is in their ability to provide information emphasizing the *mechanisms* rather than immediate consequences of oil toxicity.

#### 11.9.1 Oil concentration and toxicity

Toxicity experiments were carried out to determine the effects of varying concentrations of crude oil on phytoplankton photosynthesis in the range expected to occur in treated tanker ballast water (0.001-10 ppm).

*December 1971 experiment:* During December (cruise 125) nutrient concentrations were relatively high (e.g.,  $6 \mu\text{g-atoms NO}_3^- \text{-N/liter}$ ); phytoplankton primary production ( $0.2 \text{ mg C/m}^3\text{-hr}$ ) and standing stocks ( $0.2 \text{ mg Chl } a/\text{m}^3$ ) were low. The most common species of phytoplankton in the water were small unidentified flagellates and the diatoms *Nitzschia closterium*, *Rhizosolenia stolterfothii* and *Skeletonema costatum*.

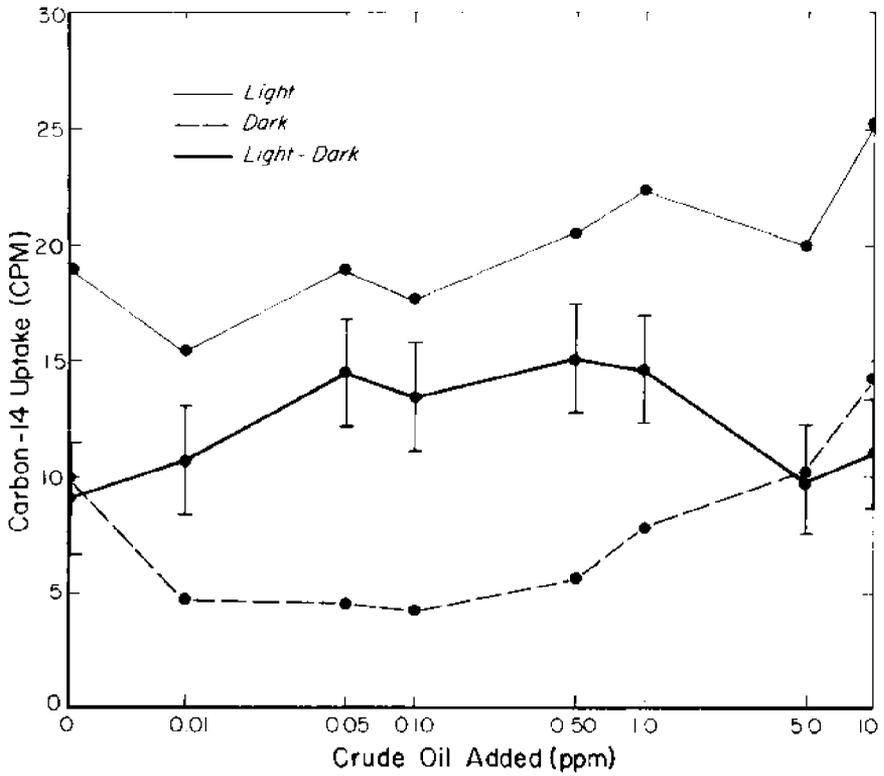
Seawater collected from the ship's non-toxic seawater system was incubated for 6 hours at sea-surface temperatures under artificial light. Light intensity approximated the average maximum natural level of  $0.10 \text{ ly/min}$ . The estimated concentration of the 10 ppm (v/v) oil-seawater mixture was between 0.8-2.0 ppm, and a mean of 1.4 ppm was assumed.

A one-way analysis of variance was performed on the December experiment data (Figure 11.1) and demonstrated a significant oil concentration effect with respect to phytoplankton photosynthesis ( $P = 0.05$ ). Dark values were assumed to be representative and were subtracted from each of the three corresponding light values for each oil concentration. The 95-percent confidence limits were then calculated for points on the light-minus-dark curve. Phytoplankton photosynthesis was found not to differ significantly between the control and 1.4 ppm sample (Figure 11.1). At concentrations between 0.007-0.14 ppm, however, a 50-percent stimulation in photosynthetic rate was observed at about 0.05 ppm of oil.

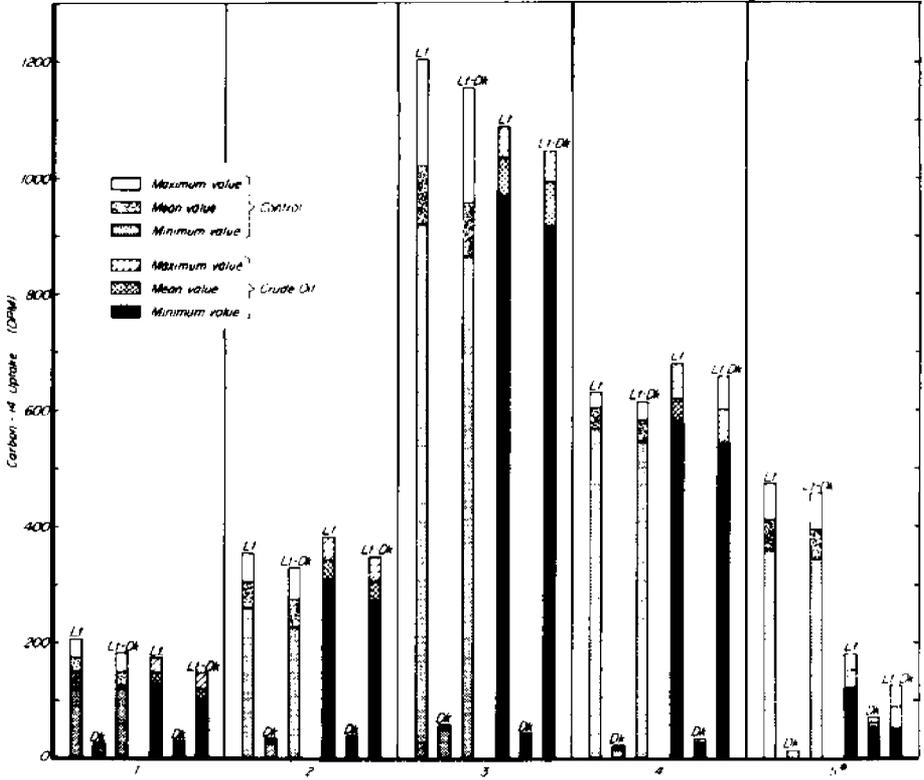
*March and April 1972 Dickman experiments:* Four experiments were conducted during March (cruise 128) and one during April (cruise 131) following the procedure outlined by Dickman (1971) for testing the effects of crude oil on phytoplankton photosynthesis. During March nutrients were high (e.g.,  $20 \mu\text{g-atoms NO}_3^- \text{-N/liter}$ ), and standing stock was low ( $0.1 \text{ mg Chl } a/\text{m}^3$ ). In contrast, nutrient levels during April were low ( $<1 \mu\text{g-atom NO}_3^- \text{-N/liter}$ ) but standing stocks very high ( $\sim 9 \text{ mg Chl } a/\text{m}^3$ ). The species composition also differed markedly between the two periods. In March small flagellates were abundant with some diatoms present, predominantly *Nitzschia closterium*, and in April typical forms included the chrysophyte *Phaeocystis pouchetii*, the choanoflagellate *Monosiga marina* and the diatoms *Thalassiosira nordenskiöldii*, *Fragilariopsis* sp. and *Chaetoceros debilis*.

In each experiment 5 light and 2 dark bottles were used for both the control and oil-treated sets. Bottles were filled with raw seawater collected at about the 2.5-m depth near Jackson Point, except in the boat harbor. After both sets had been inoculated with  $^{14}\text{C}$  and one set had been treated with oil, the bottles were placed for 4 hours in a seawater-cooled incubator under natural light and sea-surface temperature.

Samples collected in the Valdez boat harbor indicated a higher photosynthetic rate than the three samples from Jackson Point (Figure 11.2). None of the four March experiments indicated any statistical oil inhibition of photosynthesis. During April, however, photosynthesis was inhibited by about 80 percent in oil-treated samples.



**Figure 11.1** Photosynthesis by phytoplankton incubated for 6 hours under artificial light and natural seawater temperature in relation to additions to crude oil during December 1971 in Port Valdez. Mean values of three replicate determinations and their 95-percent confidence limits are presented for the light-minus-dark values.



**Figure 11.2** Photosynthesis by phytoplankton incubated for 4 hours under natural conditions of light and temperature in relation to crude oil added (5 ml/125 ml) in four experiments conducted during March and one in April 1972 in Port Valdez. DPM values for Experiment 5 (April) are  $10^{-1}$  of actual.

*April 1972 experiment:* Predominant species in Port Valdez waters during the spring phytoplankton bloom (cruise 131) were the chrysophyte *Phaeocystis pouchetii*, the choanoflagellate *Monosiga marina* and the diatoms *Fragilariopsis* sp., *Thalassiosira nordenskiöldii* and *Chaetoceros debilis*. Primary productivity and standing stock conditions are the same as indicated above.

Seawater collected from the 5-m depth near Jackson Point was incubated for 2.5 hours under natural light at sea-surface temperature. An oil concentration of 3.1 ppm was measured by the DOC method in the 50-percent oil-seawater mixture. Stimulation was again apparent at a concentration of about 0.003 ppm, representing about a 30-percent increase in photosynthesis (Figure 11.3). Inhibition occurred at concentrations greater than about 0.2 ppm and was about 35 percent at 3.1 ppm crude oil.

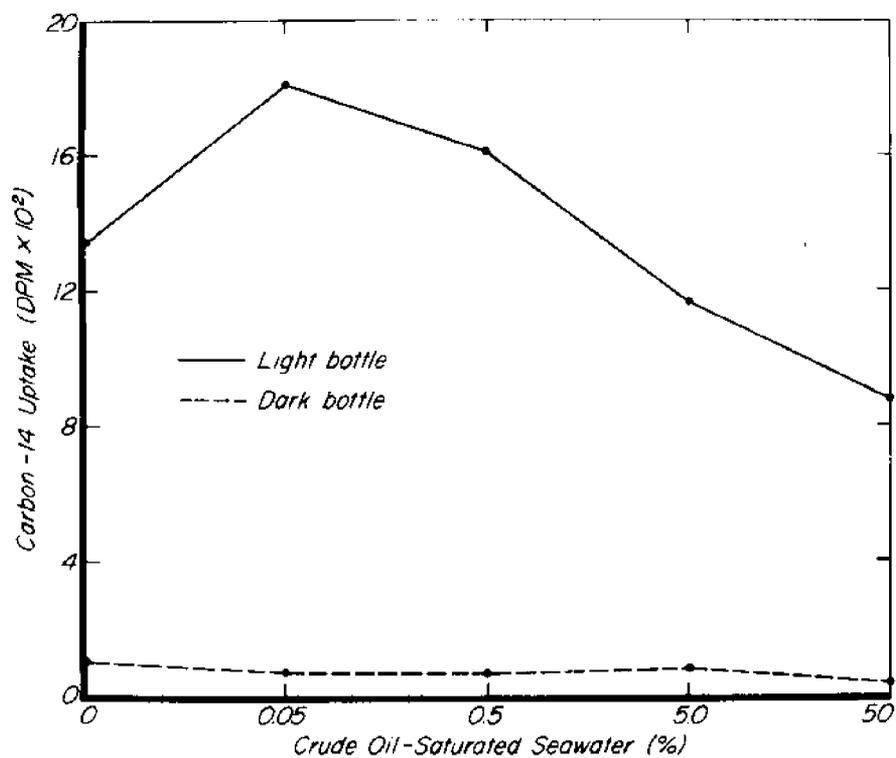
Carbon-14 uptake values for all oil-treated samples represent single determinations; control values are the mean values of duplicates. Assuming that similar errors are associated with oil-treated and control samples and that data points on Figures 11.3 and 11.4 are representative for oil-treated samples, the error associated with each point was estimated. The coefficient of variation for oil-treated and control sets in the Dickman experiments (Figure 11.2), where 5 replicates were tested for each set, did not differ significantly ( $P = 0.05$ ). On this basis the 95-percent confidence limits for the April and June experiments (Figures 11.3 and 11.4) were  $\pm 6\%$  and  $\pm 19\%$ , respectively.

*June 1971 experiment:* During summer (mid-June) phytoplankton species composition and nutrient levels were different from those encountered in spring. Productivity was about 25 percent higher during June than in April. Nutrient concentrations were very low (e.g., 0.7  $\mu\text{g-atoms NO}_3\text{-N/liter}$  as compared to 20  $\mu\text{g-at}$  in March). The numerically dominant (90 percent) phytoplankton was the diatom *Thalassiosira decipiens*; the diatoms *Nitzschia* sp. and *Chaetoceros* sp. were also present.

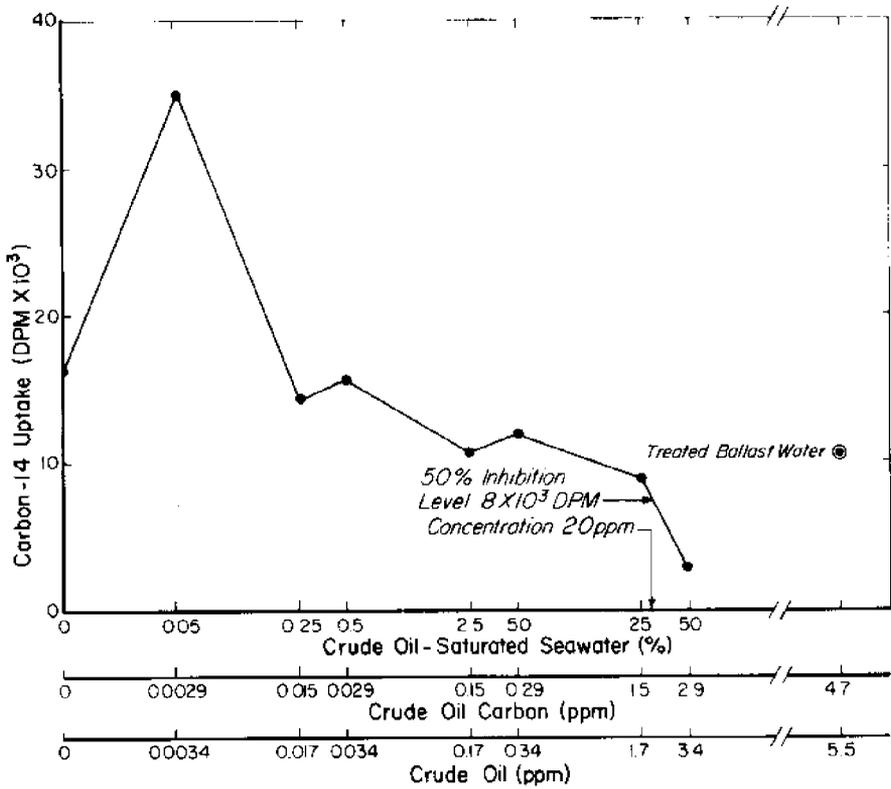
Seawater samples collected from the 2-m depth near Jackson Point were diluted to half with filtered seawater (controls) or an oil-seawater mixture and incubated 4 hours at sea-surface temperature (12C) under natural light. The phytoplankton were subjected to a wide range of crude oil concentrations and to simulated treated tanker ballast water furnished by the Battelle Northwest Laboratories field station at Valdez. The concentration of crude oil was 3.4 ppm in the 50-percent oil-seawater mixture and 5.5 ppm in the treated ballast water after 50-percent dilution with raw seawater (Figure 11.4).

Stimulation of photosynthesis, about double the control rate, again occurred at a concentration of 0.003 ppm. Oil concentrations greater than about 0.06 ppm had an inhibitory effect on photosynthesis (about 80 percent at 3.4 ppm). The oil concentration level at which 50-percent inhibition occurred was about 2 ppm. The toxicity of crude oil in treated ballast water was about one-tenth that of fresh crude oil; that is, about the same low photosynthetic rate was observed when ballast water crude oil was at 5.5 ppm and fresh crude oil at 0.67 ppm.

Analysis for crude oil by the DOC method gave concentrations of 1.2-1.6 ppm ambient organic carbon in filtered untreated seawater. These relatively high DOC values resulted possibly from increased phytoplankton activity during the spring phytoplankton bloom. The oil-saturated seawater mixture contained between 6.1-7.1 ppm carbon, or 4.5-5.9 ppm crude-oil carbon. Since crude oil is about 86 percent carbon by weight (Hobson 1967), the concentration was 5.2-6.9 ppm crude oil. Analysis of the same oil-saturated seawater by Battelle showed 7.5 ppm crude oil; the hydrocarbon content of the untreated seawater was negligible. The concentration of crude oil in the oil-saturated mixture was assumed to be 6.8 ppm (3.4 ppm for the 50-percent mixture), the mean of values obtained by the two methods. The treated ballast water was analyzed for crude oil content by Battelle and found to contain 10.9 ppm, or 5.5 ppm after 50-percent dilution with raw seawater.



**Figure 11.3** Photosynthesis by phytoplankton incubated for 2.5 hours under natural conditions of light and temperature in relation to dilutions of seawater saturated with crude oil during April 1972 in Port Valdez.



**Figure 11.4** Photosynthesis by phytoplankton incubated for 4 hours under natural conditions of light and temperature in relation to dilutions of seawater saturated with crude oil during June 1972 in Port Valdez.

*Discussion:* Crude oil was increasingly toxic to phytoplankton from December 1971 through June 1971. Oceanographic conditions differed appreciably during each period of investigation. Environmental factors such as temperature, dissolved nutrients, solar radiation and species composition varied markedly and could possibly account for the differences in magnitude of inhibition or stimulation.

Crafts and Reiber (1948) have reported that peroxides and acids form in oils exposed to light and that both substances cause acute plant injury. The mean amounts of maximum daily light intensity measured for 7-day periods in Valdez were 0.10 ly/min for December 1971, 0.53 ly/min for March 1972 and 0.98 ly/min for April 1972. These data would suggest that light intensity can act as a factor in toxicity, since the April experiments showed greater toxicities than December and March experiments at equal oil concentrations. This does not preclude the contribution of other factors such as temperature, nutrients, mixing action and species composition.

Photosynthetic stimulation at low oil concentrations was observed in three experiments (Figures 11.1, 11.3-11.4) during this study and has been reported by other investigators: Galtsoff et al. (1935) found that the diatom *Nitzschia closterium*, later reclassified as *Phaeodactylum tricorutum* (Lacaze 1969), showed growth stimulation (by cell counts) when treated with the aqueous extract of a 12-percent mixture of crude oil and seawater. In studying the effects of crude-oil oil-dispersant mixtures on natural phytoplankton populations, Strand et al. (1971) found a significant increase in the photosynthetic rate at a 1-ppm oil concentration after an 8 hour incubation. The inconsistency between oil concentrations which resulted in stimulation (1 ppm vs. 0.003 ppm in this study) may be due to the absence of tests at concentrations lower than 1 ppm in Strand's work, the difference in incubation time (8 vs. 4 hours), and the method by which the crude oil concentrations were determined. The mechanism of stimulation of algal photosynthesis at low concentration is unknown. It is perhaps due to transition metals in crude oil acting as micro-nutrients at very low concentrations (Hufford 1971).

Treated ballast water appeared to be less toxic than fresh crude oil. It is not known whether the treatment process detoxified the oil or if the several-day shaking and venting process of simulating the ballast water was the cause. Only treated ballast water was tested. The treatment process removes about 75 percent of the paraffins and 55 percent of the aromatics in the C<sub>1</sub>-C<sub>10</sub> fraction from simulated tanker ballast water without chemically changing or concentrating any of the hydrocarbon components (D. E. Brandon, personal communication; Table 11.2).

Table 11.2 Results of gas partitioning analyses of simulated Puget Sound ballast water containing Prudhoe Bay crude oil (based on analyses performed by D. Johnson of Esso Production Research Company, Houston, Texas)

Hydrocarbons	Before treatment (ppb)	After treatment (ppb)
i-C <sub>4</sub>	0.06	Trace
n-C <sub>4</sub>	0.32	0.03
n-C <sub>5</sub>	2.70	0.60
n-C <sub>6</sub>	6.20	1.40
n-C <sub>7</sub>	9.44	2.65
n-C <sub>8</sub>	0.05	0.05
n-C <sub>9</sub>	0.42	0.14
Benzene	4,069.00	1,729.00
Toluene	4,069.00	2,034.00
m and p-Xylenc	1,627.00	498.00
o-Xylene	559.00	290.00
C <sub>9</sub> aromatics	765.00	285.00
C <sub>10</sub> aromatics	173.00	204.00
Total	11,281.19	5,044.87

Aromatics are generally considered the most phytotoxic components of crude oil and the straight-chain paraffins least toxic (Currier and Peoples 1954). The removal of a large percentage of aromatics as well as paraffins in the range  $C_1 - C_{10}$  would likely mitigate the toxic effects of crude oil. A significant loss of volatiles may occur also from the oil in tanker ballast, if the tanks are vented in transport. Smith (1968) reported that up to 25 percent by weight of crude oil spilled on the sea surface may evaporate within a few days after release. The loss of volatiles with the concomitant auto- and bio-oxidation could significantly alter the composition of crude oil in tanker ballast water. The rate of change would depend upon temperature, available oxygen, degree of agitation, the physical state of the oil and the water chemistry (Pilpel 1968).

### 11.9.2 Temperature and oil toxicity

Phytotoxicity experiments were conducted to study whether temperatures in the 0-20°C range affect phytoplankton metabolism at low crude oil concentrations.

*August 1971 experiment:* During August (cruise 117) nutrient levels, phytoplankton primary production and standing stock were moderately low (e.g., 2  $\mu\text{g-atoms NO}_3^- \text{-N/liter}$ , 2  $\text{mg C/m}^3 \text{-hr}$  and 0.2  $\text{mg Chl a/m}^3$ ). Dinoflagellates dominated the phytoplankton, and the genera *Ceratium* and *Peridinium* were most predominant.

Reagent bottles were inoculated with phytoplankton soup (net plankton) and incubated for 6 hours under natural light at different temperatures and oil concentrations. The oil concentration of the 100-percent oil-seawater mixture was estimated to be 10-12 ppm (Figure 11.5).

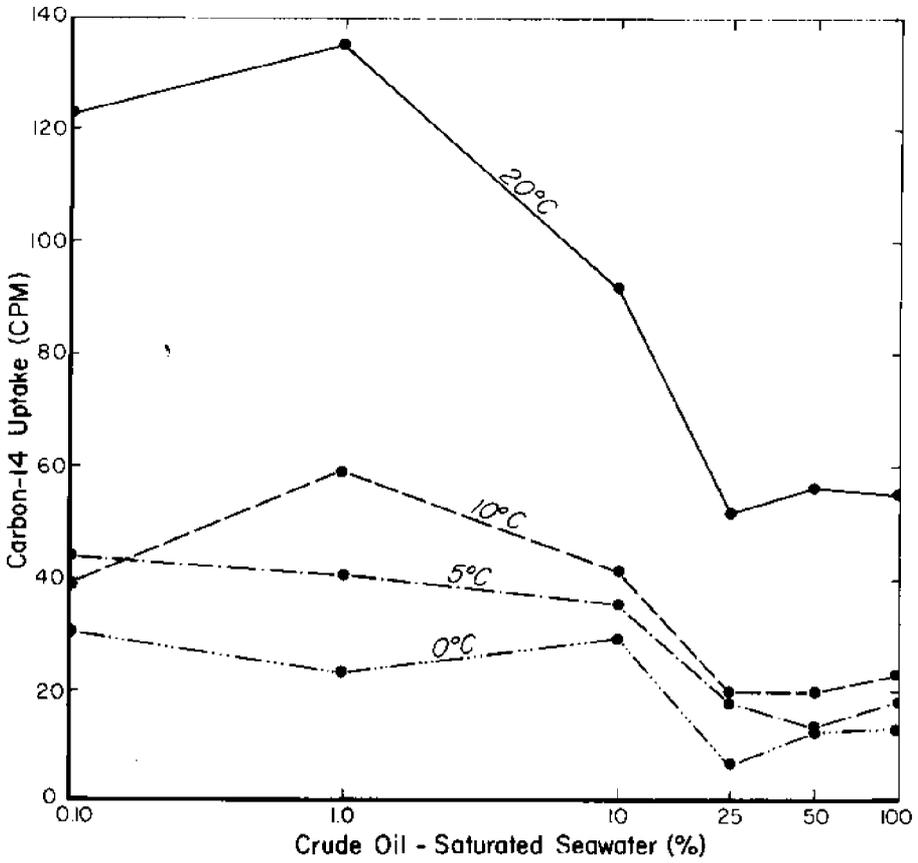
Precise temperature control was not maintained; however, an increase in photosynthesis with increased temperature was indicated at each oil concentration tested. Although it cannot be shown statistically, the greatest inhibition appeared to occur not at the 100-percent level but rather at the 25-percent concentration. A similar trend was noted in an experiment with *Fucus distichus* (Figure 11.12).

*October 1971 experiment:* During October (cruise 122) nutrient concentrations were moderately low (e.g., 1  $\mu\text{g-atom NO}_3^- \text{-N/liter}$ ), and primary production and standing stock were moderately low (2  $\text{mg C/m}^3 \text{-hr}$  and 0.5  $\text{mg Chl a/m}^3$ ). Predominant phytoplankton species were *Nitzschia closterium*, *Skeletonema costatum*, *Leptocylindrus danicus* and *Thalassiosira gravida*.

Reagent bottles containing an oil-seawater mixture were inoculated with phytoplankton soup and incubated for 9 hours under natural light at temperatures of 5, 6 and 10°C (Table 11.3).

**Table 11.3** Photosynthetic inhibition (light values only) for net plankton incubated under natural light conditions for 9 hours in relation to temperature at a crude-oil concentration of 9 ppm (oil added) during October 1971 in Port Valdez, Alaska

Sample	Temperature ( $\pm 1$ C)	CPM	Crude oil inhibition	
			%	% ( $^{\circ}\text{C}^{-1}$ )
Control	5	326	42	8.4
Oil	5	136		
Control	6	294	50	8.3
Oil	6	148		
Control	10	671	80	8.1
Oil	10	125		



**Figure 11.5** Photosynthesis (light values only) by phytoplankton incubated for 6 hours under natural light conditions in relation to temperature and dilutions of seawater saturated with crude oil during August 1971 in Port Valdez.

The oil concentration in the seawater was not measured, but the mixture was 10 ppm (v/v) or about 9 ppm (w/v), since Prudhoe Bay crude oil has a specific gravity of 0.893 (Thompson et al. 1971). The data suggest that an increase in temperature resulted in an increase in oil toxicity between 5-10C, with 80-percent inhibition at 10C or an average inhibition of 8.3 percent per degree C.

*March 1972 experiment:* During March (cruise 128) nutrient levels were very high (e.g., 20  $\mu\text{g-atoms NO}_3^-/\text{liter}$ ), primary productivity was 0.2 mg C/m<sup>3</sup>-hr and standing stock was 0.1 mg Chl *a*/m<sup>3</sup>. Most of the phytoplankton cells were small flagellates; *Nitzschia closterium* was the predominant diatom.

Seawater samples were mixed half and half with either a 20-ppm oil-seawater mixture or filtered seawater and incubated for 3 hours under artificial light at different temperatures. The experimental oil concentration was 1.3-3.6 ppm.

Controls indicated a 10C photosynthetic optimum with zero net photosynthesis (light-minus-dark uptake) at 20C (Figure 11.6, bottom). Oil-treated samples suggested an inverse relationship between temperature and photosynthetic rate—that is, decreased photosynthesis with increased temperature.

*April 1972 experiment:* During April (cruise 131) nutrient levels were quite low (<1  $\mu\text{g-atom NO}_3^-/\text{liter}$ ). Primary productivity and standing stock were 20 mg C/m<sup>3</sup>-hr and ~9 mg Chl *a*/m<sup>3</sup>, respectively. Predominant species of phytoplankton were *Monosiga marina*, *Phaeocystis pouchetii*, *Chaetoceros debilis*, *Fragilariopsis* sp. and *Thalassiosira nordenskiöldii*.

Seawater samples were treated in a manner identical to the March experiment, and the oil concentration was also the same (1.3-3.6 ppm). In this experiment (Figure 11.6, top), the control samples again indicated a 10C photosynthetic optimum. A 10C or possibly higher optimum is also suggested for the oil-treated samples with net photosynthesis decreasing to near zero at 20C. The rate of photosynthesis was similar for control and oil-treated samples at 3C, the ambient seawater temperature.

*Discussion:* Phytoplankton treated with crude oil showed maximum carbon uptake (light values) at 5, 10-15 and 20C during March, April and August, respectively, at oil concentrations between 1-4 ppm. This pattern reflected differences in phytoplankton species composition, as well as temperature, light, and possibly nutrient levels.

The toxicity experiments in this study were all carried out in closed systems. This was particularly significant in the temperature experiments, where at higher temperatures more low-boiling petroleum fractions were retained than would have normally been in seawater (Pilpel 1968); these low-boiling fractions are known to cause plant injury when present in sufficient quantities (Currier and Peoples 1954). Because the loss of volatiles seems improbable in a closed system, serious errors may occur if efforts are made to relate these studies to the natural environment. In the case of treated tanker ballast water, however, the results from closed-system experiments may not differ considerably from natural systems, since the depth of treated ballast-water entry into the Port is planned to be well below the surface.

### 11.9.3 Light intensity and oil toxicity

The depth of the euphotic zone is variable, and in Port Valdez the factors most heavily affecting it are suspended sediment load and phytoplankton. It is therefore not only the seasonal changes in solar radiation which determine light intensity at a particular depth beneath the sea surface but the events that these changes trigger as well.

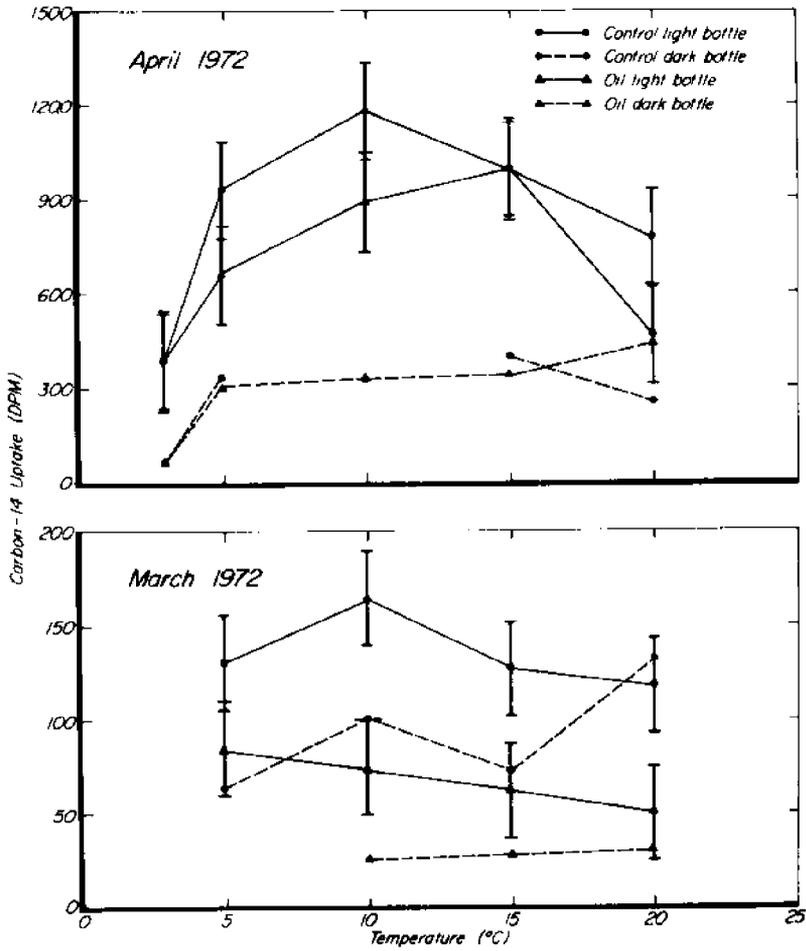


Figure 11.6 Photosynthesis by phytoplankton during March 1972 (bottom) and April (top) in relation to temperature and at a crude oil concentration of 1.3-3.6 ppm in Port Valdez. Mean values of three replicate determinations and their 95-percent confidence limits are presented for light bottle values.

*Valdez experiment:* During April 1972 (cruise 131) nutrient concentrations were low, (e.g.,  $<1 \mu\text{g-at NO}_3\text{-N/liter}$ ), and phytoplankton primary production and standing stock were very high ( $20 \text{ mg C/m}^3\text{-hr}$  and  $\sim 9 \text{ mg Chl } a/\text{m}^3$ , respectively). Predominant forms of phytoplankton were *Monosiga marina*, *Phaeocystis pouchetii*, *Chaetoceros debilis*, *Fragilariopsis* sp. and *Thalassiosira nordenskiöldii* during this phase of the bloom.

Seawater for this experiment was collected from the 2.5-m depth near Jackson Point, mixed half and half with either an oil-seawater mixture or filtered seawater and placed for 5 hours in a seawater-cooled incubator at 100, 50, 25, 10 and 1 percent of the incident surface solar radiation ( $I_0$ ) (Figure 11.7). The oil concentration of the 50-percent oil-seawater mixture was 3.1 ppm. Maximum solar radiation during the experiment was 0.9 ly/min and averaged about 0.7 ly/min.

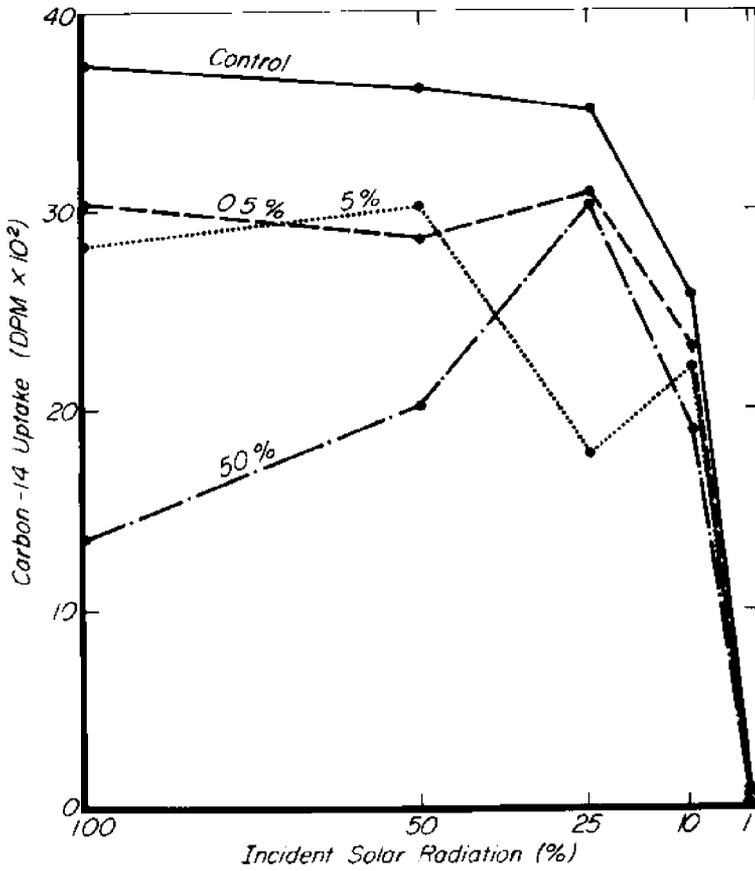
At 3.1 ppm crude oil a 65-percent reduction in net photosynthesis was observed at full light intensity (100 percent), as opposed to a 20-percent reduction observed under the same light conditions at a level of 0.03 ppm (0.5% oil-seawater mixture). At the 25-percent light level and below, no significant difference was noted between oil-treated and control samples.

*Georgia experiment:* During March 1972 a light intensity versus oil toxicity experiment, similar to that conducted in Valdez, was carried out on natural marine phytoplankton populations collected at the Skidaway Institute of Oceanography in Savannah, Georgia (J. J. Goering, personal communication). Fifty-milliliter bottles were filled with 40 ml raw seawater, followed by the addition of 10 ml of an oil-seawater mixture, 5 ml oil mixture plus 5 ml filtered seawater (same used to prepare oil mixture), 1 ml oil mixture plus 9 ml filtered seawater and 10 ml filtered seawater (control). Each of these four samples, designated as 10-ml, 5-ml, 1-ml and control, were tested in duplicate at various light intensities (100, 50, 25, 12, 6, 3 and 0-percent  $I_0$ ). Crude oil concentration of the 10-ml sample was estimated to be about 1.6 ppm. After addition of the oil-saturated mixture, the bottles were incubated for 3 hours at 19.5C under high-intensity artificial illumination at the seven different light intensities.

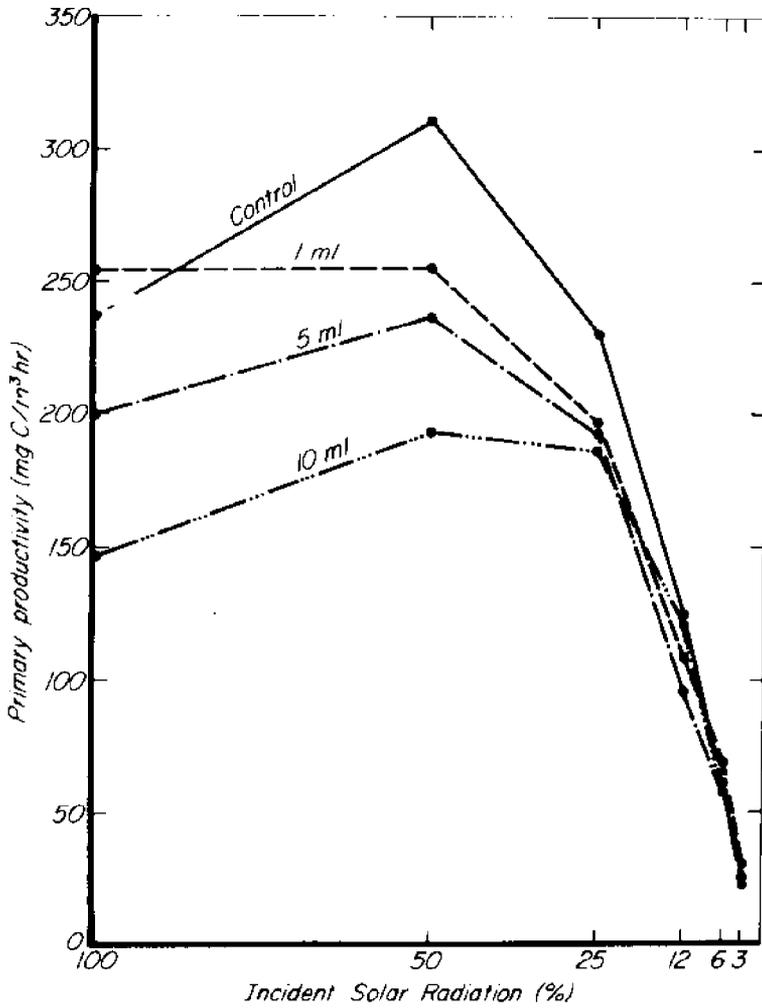
Each data point in Figure 11.8 represents the mean of two samples. The control exhibited photo-inhibition at 100-percent intensity, in contrast to the treated samples which apparently underwent slight stimulation at the same intensity. At 100-percent light intensity the 1-ml sample indicated a higher photosynthetic rate than the control. At the 25-percent and lower light levels, however, differences between control and oil-treated samples were probably not significant.

*Discussion:* Photo-oxidation of crude oil may form organic acids (e.g., cyclohexane carboxylic acid) and peroxides which are known to be harmful to algae (Crafts and Reiber 1948). Either ultraviolet rays or sunlight may initiate this auto-oxidation, or it may occur spontaneously without light in the presence of adequate oxygen (Pilpel 1968). If photo-oxidation is proportionate to light intensity, then toxicity may be likewise entailed. As shown in Figures 11.7 and 11.8, the greatest differences in toxicity between control and oil-treated samples were normally noted at high light intensity (100 percent  $I_0$ ). In the Georgia experiment, however, the rate of photosynthesis was lower at 100-percent than at 50-percent  $I_0$  for the control and about the same for these light intensities in the 1-ml sample. Three processes, occurring simultaneously, may explain this observation. First, photosynthetic inhibition probably occurred as a direct result of chemical interference by crude oil. Secondly, a reduced photo-inhibition caused by light absorbance by crude oil may have resulted in an *apparent* photosynthetic stimulation. And finally, the phenomenon of photosynthetic stimulation at low oil concentrations (see section 11.9.1) may have increased photosynthesis.

Despite the differences in marine environments between Port Valdez, Alaska, and Savannah, Georgia, the results from both experiments demonstrated similar light-toxicity response patterns.



**Figure 11.7** Photosynthesis by phytoplankton incubated for 5 hours under natural temperature conditions in relation to light intensity and to dilutions of seawater saturated with crude oil during April 1972 in Port Valdez.



**Figure 11.8** Photosynthesis by phytoplankton incubated for 3 hours under artificial conditions of light and temperature in relation to light intensity and crude oil concentration during March 1972 in Savannah, Georgia.

#### 11.9.4 Exposure time and oil toxicity

Experiments have been conducted with natural populations of phytoplankton to test the effects of prolonged exposure to oil. Incubation periods routinely used in primary productivity experiments (2-6 hours) may not be long enough to allow the full potential of damage by oil to occur. Also, oil-induced changes in the species composition of a phytoplankton community may occur given sufficient time and are not detectable through routine acute toxicity tests.

*December 1971 experiment:* During December (cruise 125) nutrient concentrations were moderately high (6-8  $\mu\text{g-atoms NO}_3^- \text{-N/liter}$ ), and primary production and standing stock were low (0.2 mg C/m<sup>3</sup>-hr and 0.2 mg Chl *a*/m<sup>3</sup>). Predominant phytoplankton species were *Nitzschia closterium*, *Skeletonema costatum* and *Rhizosolenia stolterforhtii*.

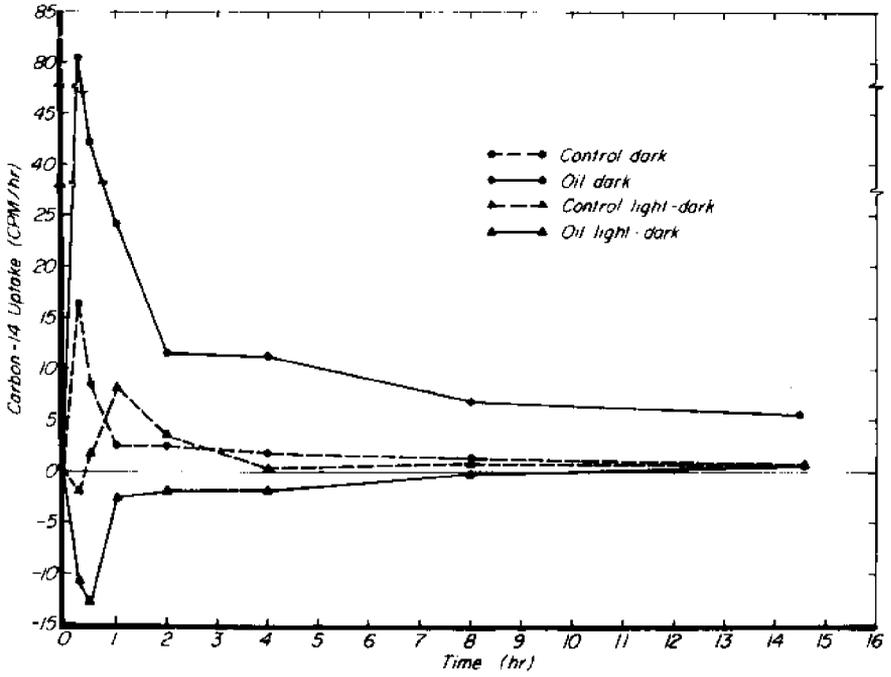
Seawater was collected from 2.5 m near Jackson Point by the ship's non-toxic seawater system and diluted to half with an oil-seawater mixture or with filtered seawater. Crude oil concentration was estimated at 0.8-2.0 ppm for the 10 ppm (v/v) oil-to-seawater mixture. Incubations were carried out for periods of 0.25, 0.5, 1, 2, 4, 8 and 14.5 hours under artificial light at surface seawater temperature. Light intensity during incubation simulated natural levels (0.10 ly/min).

In the controls, uptake of carbon in the dark was high during the first hour and then leveled off (Figure 11.9), whereas uptake in the light (represented by light-minus-dark values) indicated a high rate for the first hour and then gradually decreased. From 8-14.5 hours, uptake appeared to be constant. In the oil-treated samples, uptake of carbon in the dark was initially very high, 300 percent greater than the control, and appeared to be greater than in the light until 10 hours when net photosynthesis became positive.

*May 1971 experiment:* During early summer (mid-May) no measurements were made for nutrients, primary production or standing stock (Chl *a*); however, cell counts indicated that the standing stock was nearly as high as was measured during April studies (Homer et al., Chapter 7 this volume and Hood et al. 1973). Besides the phytoplankton species listed in Figure 11.10, the following were also presented during May: *Dietyocha fibula*, *Monosiga marina*, *Bacterosira fragilis*, *Coscinosira polychorda*, *Fragilariopsis* sp., *Skeletonema costatum*, *Stephanopyxis nipponica*, *Thalassiosira decipiens* and *T. gravida*.

Seawater was collected from 5 m near Jackson Point and randomly dispensed into four 1-liter bottles. Contents of one bottle were immediately preserved with buffered formalin (initial); the others were incubated 48 hours under natural light and temperature conditions. Of the three bottles incubated, one contained 1 ml oil per liter (1000 ppm), another 0.01 ml per liter (10 ppm), and the third contained no oil (control). Following incubation the bottles were removed without agitating or disturbing the contents, and 300-ml aliquots were siphoned from the half-full level of each bottle and preserved with formalin for species identification and counting. The concentration of crude oil in the seawater of the incubated samples was not measured.

Errors associated with counting are considered to be small relative to sampling errors (Lund et al. 1958) and are dependent upon the number of cells counted. The accuracy associated with counts for *Phaeocystis pouchetii* and *Thalassiosira nordenskiöldii* (Figure 11.10) was about  $\pm 10\%$  ( $P = 0.05$ ); in the case of *Nitzschia closterium*, however, the accuracy was as low as  $\pm 75\%$ . Since relatively few cells were counted for *N. closterium* and the small unidentified pennate diatom, conclusions were not drawn as to oil effects on growth for these species. Counting errors of  $\pm 20\%$  or less were associated with the remaining 5 species or groups. Sampling errors cannot be estimated since replicates were not taken; however, the interest in this experiment was in relative differences between treated and untreated samples and not in spatial and temporal differences in species abundances in the marine environment. Sampling errors were therefore probably not serious.



**Figure 11.9** Photosynthesis by phytoplankton incubated under artificial light and natural seawater temperature and at a crude oil concentration of 1.3-3.6 ppm in relation to incubation time during December 1971 in Port Valdez.

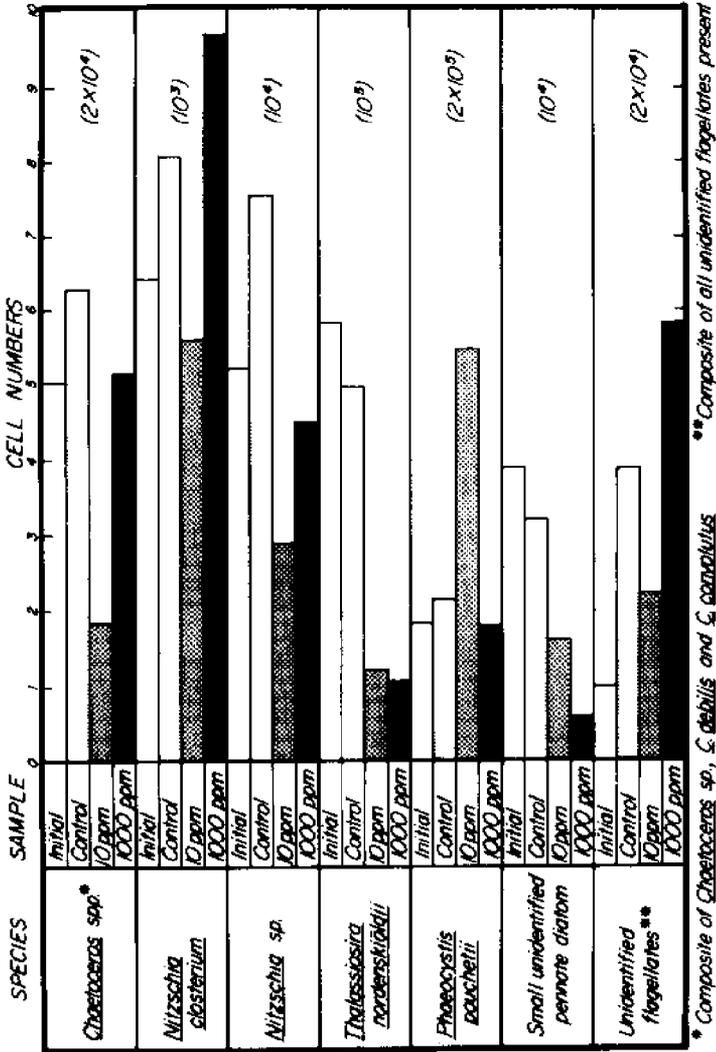


Figure 11.10 Relative abundance of seven major phytoplankton species, or species groups, in relation to additions of crude oil (v/v) in experiments incubated for 48 hours under natural conditions of light and temperature during May 1972 in Port Valdez. Standing stocks (cells/liter) are computed by multiplying the cell number by the factor given in each row.

\* Composite of *Chaetoceros* sp., *C. debilis* and *C. canaliculus*  
 \*\* Composite of all unidentified flagellates present

Each species or species group of phytoplankton tested indicated a different growth response to crude oil at the two concentrations. The flagellates indicated greater growth rates at 1000 ppm than at 10 ppm crude oil, whereas the opposite was true for *Phaeocystis pouchetii*, which was apparently stimulated by the presence of the lower concentration of oil and showed a 150-percent increase in photosynthesis over the control. *Thalassiosira nordenskiöldii* was severely inhibited by both crude oil concentrations, as evidenced by a 75-percent reduction in cell numbers.

*Discussion:* The high uptake rates of carbon in both oil-treated and control-sample dark bottles suggest significant bacterial activity (Figure 11.9). In the oil-treated samples photosynthesis after about 10 hours became positive, indicating that photosynthetic processes were still functional or that bacterial uptake was decreasing in the dark relative to the light bottles. The reason for the higher rates of carbon uptake in the dark than in the light remains unclear. Possibly light inhibition of heterotrophic growth occurred, but further studies would certainly be necessary to test this contention. Additional investigations are also needed in which both the species composition and rates of photosynthesis would be studied concurrently in crude-oil exposure-time experiments to examine possible interactions between these parameters.

Interruption in the natural species succession in a phytoplankton community is likely to have profound effects on high food-chain organisms. An understanding of how the species succession might be altered by man-made and natural influences is essential if reliable and necessary predictions of the ecological consequences of oil pollution are to be made.

Little information is available on the relative toxicities of crude oil to various phytoplankton species. Mironov and Lanskaya (1968) reported a difference in the rate of cell division between *Melosira moniliformis* and *Ditylum brightwellii* of from three to four orders of magnitude under the same conditions of exposure to kerosene, with *D. brightwellii* exhibiting the greatest sensitivity. Tests with crude oil showed similar results. Both of these species are common in Port Valdez waters (as reported by Horner et al. in Chapter 7 this volume and in Hood et al. 1973).

Other important members of the phytoplankton community, such as the dinoflagellates and the yeast-like organism reported in Chapter 7 should be investigated in a manner similar to that used in the May experiment. The relatively high standing stocks of dinoflagellates which occurred during late summer and fall suggest their importance as members of the phytoplankton community. The yeast-like organism appeared during early spring, early summer and late summer, and it often occurred in very large numbers (e.g.,  $1.67 \times 10^8$  cells/liter).

Several physical and chemical factors such as light, temperature, salinity, nutrients and dissolved substances may cause changes in the species composition of phytoplankton communities and may act with oil in either an adverse synergistic way or in such a manner as to promote vigorous growth.

## 11.10 Effects of Oil on Seaweeds

### 11.10.1 General

The near-shore area of Port Valdez, beneath which seaweeds occur, is small compared to the total surface area of the Port. The importance of this region to the entire marine ecosystem, however, is relatively large. Although the annual primary production of seaweeds is probably less than 1 percent of phytoplankton production in this region, the seaweeds are perhaps equal in importance to the phytoplankton in the overall ecology of the system. Intertidal and subtidal seaweeds provide substrates upon which fish and invertebrate eggs may be deposited, animal habitats for a myriad of species, protective nursery areas and often serve as a direct food source.

Estimates of algal cover in the intertidal zone of Port Valdez were made during the month of August by McRoy and Stoker (1969). In some areas dense stands of *Fucus distichus* were found to cover 65 percent of the beach area with concurrent high animal biomass estimates, suggesting the importance of this community as an animal habitat. During late spring and summer the green algae *Cladophora*, *Enteromorpha*, *Monostroma* and others were found to be predominant in many areas of the intertidal region at Jackson Point, and several species of red and brown algae were also present (e.g., *Halosaccion*, *Odonthalia*, *Rhododymenia*, *Alaria* and *Fucus*). Below the intertidal zone, large brown algae were found as apparently important habitat features for many invertebrates and fishes. *Alaria marginata*, *Costaria costata*, *Desmarestia* sp., *Laminaria groenlandica* and *L. saccharina* were obvious components of the subtidal zone and have been estimated to cover from 90 to 100 percent of the bottom to a depth of several meters in the region of Jackson Point (G. J. Mueller, personal communication).

#### 11.10.2 Oil concentration and toxicity

Toxicity experiments were carried out to determine the effects of varying concentrations of crude oil (0.007-12 ppm) on photosynthesis in some predominant species of intertidal and shallow subtidal seaweeds.

*July 1971 experiment:* During late July (cruise 117) the nutrient content in the seawater was moderately low (e.g., 2  $\mu\text{g-atoms NO}_3^- \text{-N/liter}$ ), and water temperatures ranged from 5.5C at the surface to 11.5C at the 5-m depth near Jackson Point.

Specimens of *Enteromorpha intestinalis*, collected from the intertidal zone at Jackson Point, were incubated both in oil-saturated seawater estimated to contain 10-12 ppm crude oil and in filtered untreated seawater for 4 hours under natural light at near-sea-surface temperatures (2.5 m). The light and dark bottle oxygen method was used to assess the damage to this species by oil.

Initial oxygen concentration was lower in the oil-seawater mixture than in the filtered seawater (Figure 11.11). Gross photosynthesis (light-minus-dark oxygen value) was reduced 95 percent when the algae were exposed to oil; net photosynthesis was zero.

*October 1971 experiment:* During early October (cruise 122) nutrients were low ( $\sim 1 \mu\text{g-atom NO}_3^- \text{-N/liter}$ ), and surface-water temperatures ranged from 6.5-9.5C.

Specimens of *Fucus distichus*, collected from the intertidal zone at Jackson Point, were incubated in seawater containing various concentrations of crude oil under the same conditions as described for the July *Enteromorpha intestinalis* experiment.

Dissolved oxygen concentration in initial bottles was inversely proportional to oil concentration (Figure 11.12). Gross photosynthesis showed relatively little change over the concentration range of oil tested. The highest rate of photosynthesis appeared in the 100-percent mixture (10-12 ppm), and the lowest rate was noted for an intermediate oil concentration of 25 percent.

*April 1971 experiment:* During late April (cruise 131) the nutrient content was very low ( $< 1 \mu\text{g-atom NO}_3^- \text{/liter}$ ), and seawater temperature ranged from 2-3C in the euphotic zone.

The  $^{14}\text{C}$  method was used to test 8 species of seaweeds for toxicity of crude oil. The plants were incubated 2-4 hours in filtered seawater containing various concentrations of crude oil under natural conditions of temperature and light. Oil concentration of the 100-percent oil-seawater mixture was 7 ppm.

It is uncertain how representative the curves shown in Figure 11.13 are to the species tested, since only healthy specimens were selected for testing and replicates were not taken. The systematic errors, however, may be estimated by assuming that the standard deviation for five subsamples of *Rhododymenia palmata* (incubated in the light at 0.007 ppm crude oil) is representative for all species at all oil concentrations. The 95-percent confidence limits calculated for the mean and applied to the other plant species is  $\pm 4$  percent.

SAMPLE	Initial O <sub>2</sub>	Final O <sub>2</sub>		Dry Weight (gm)	
		Lt.	Dk.	Lt.	Dk.
Seawater (SW)	6.27	6.44	5.47		
Algae + S.W.	6.27	12.01	4.64	.3116	.3850
S.W./Oil	4.57	5.72	4.58		
Algae + S.W./Oil	4.57	5.12	3.51	.2783	.3284

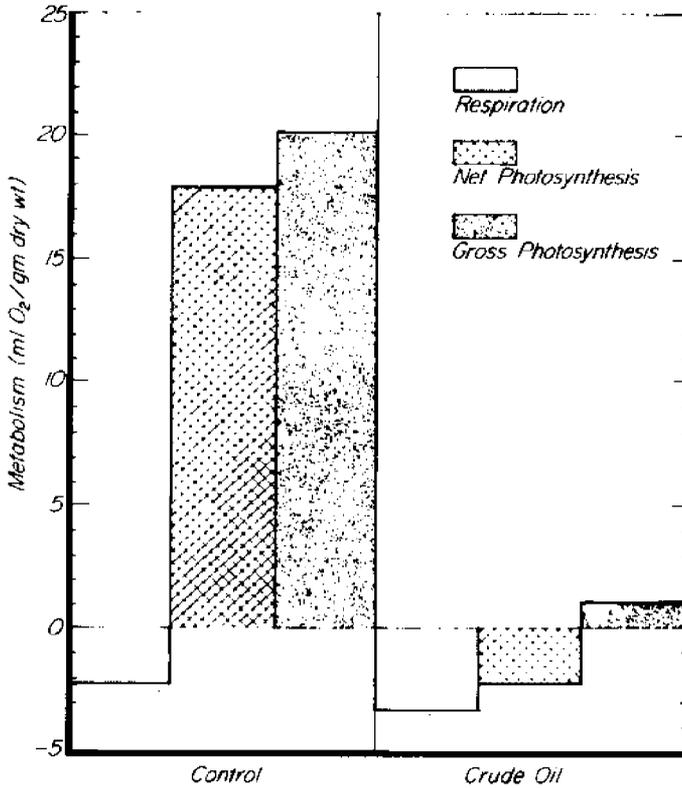


Figure 11.11 Metabolism of the green seaweed *Enteromorpha intestinalis* incubated for 4 hours under natural conditions of light and temperature in relation to seawater saturated with crude oil as measured by the light and dark bottle oxygen method during July 1971 in Port Valdez.

CRUDE OIL SATURATION	DISSOLVED OXYGEN (ml/l)			PLANT DRY WEIGHT (gm)		METABOLISM		
	TB	LB	DB	LB	DB	GP	NP	R
100%	3.22	16.65	2.21	2.01	2.35	7.11	6.68	0.43
25%	5.09	20.76	4.63	2.83	2.68	5.71	5.54	0.17
10%	5.30	22.33	5.06	3.65	4.01	4.73	4.67	0.06
1%	5.43	17.21	3.65	2.05	3.99	6.19	5.75	0.45
0.1%	5.59	17.66	4.60	2.36	2.40	5.53	5.11	0.41

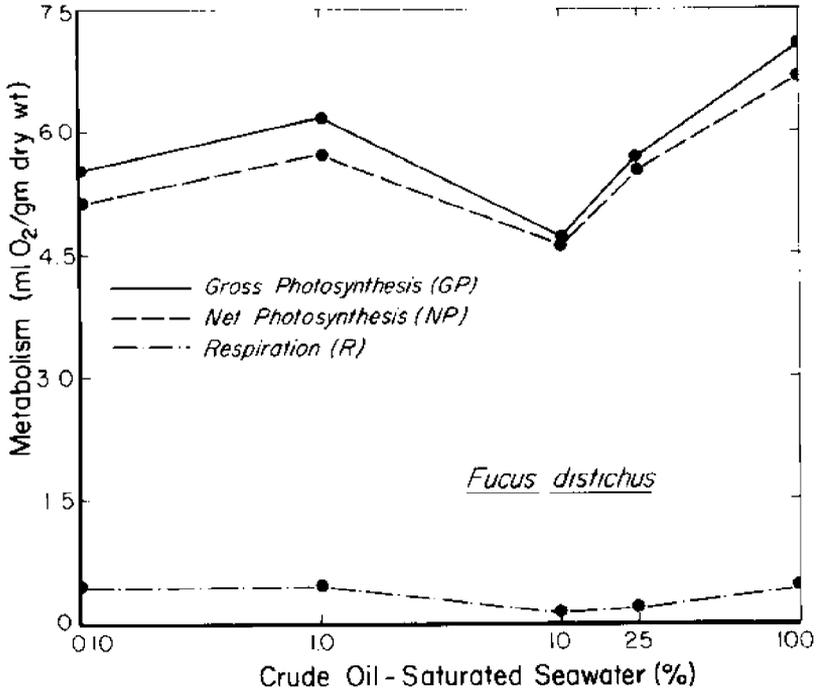


Figure 11.12 Metabolism of the brown seaweed *Fucus distichus* incubated for 4 hours under natural conditions of light and temperature in relation to dilutions of seawater saturated with crude oil as measured by the light and dark bottle oxygen method during October 1971 in Port Valdez.

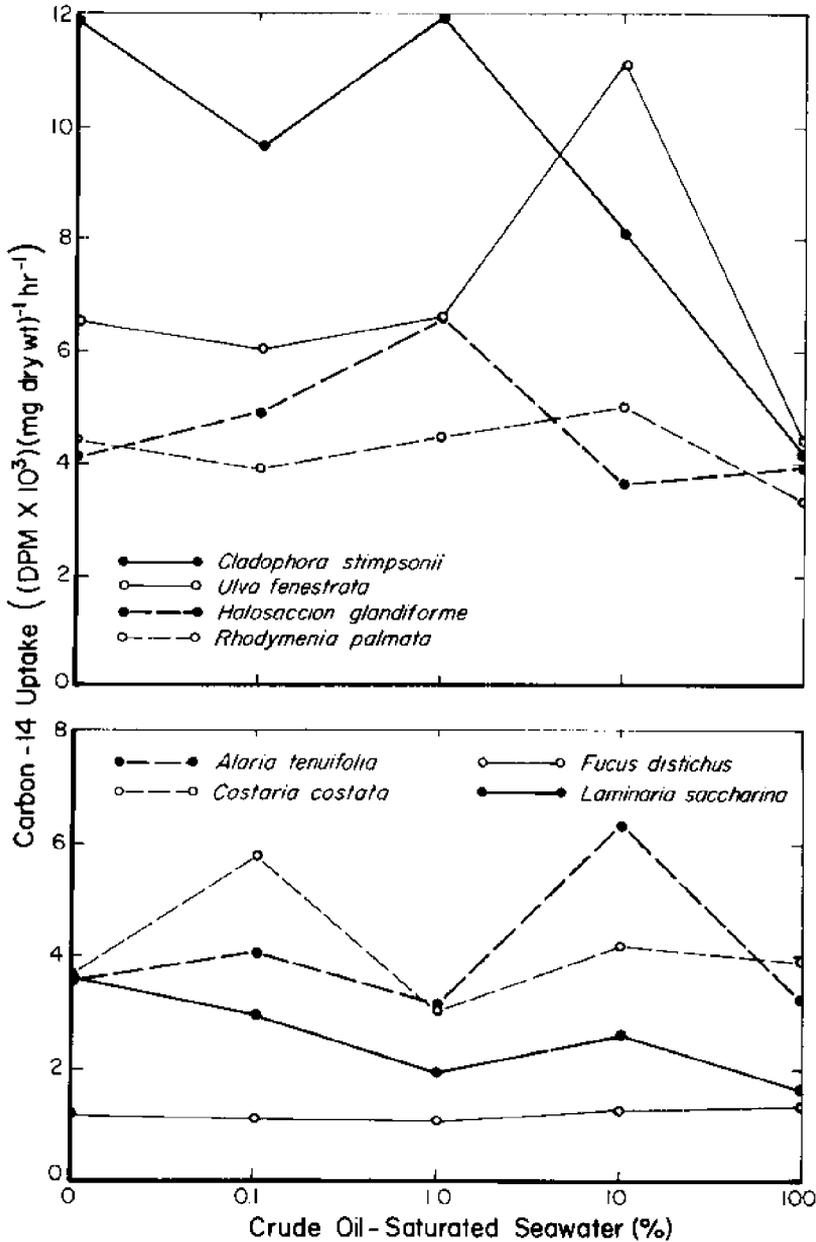


Figure 11.13 Photosynthesis by eight species of seaweeds incubated for 2-4 hours under natural conditions of light and temperature in relation to dilutions of seawater saturated with crude oil during March or April 1972 in Port Valdez. Actual DPM values for *Alaria tenuifolia* are twice those indicated.

Photosynthetic response to oil-treated seawater was different for each species; some showed inhibition at 7 ppm, while others appeared unaffected. *Cladophora stimpsonii* indicated a 65-percent photosynthetic reduction at 7 ppm while *Costaria costata* appeared to be unaffected at the same concentration. Photosynthetic stimulation by crude oil was suggested for some species; at 0.7 ppm *Ulva fenestrata* had a rate nearly twice that of the control.

*Discussion:* Literature on the effects of petroleum products on seaweeds is primarily from studies of economically important species. In tests with the giant brown alga, *Macrocystis pyrifera*, Clendenning (1959) found that diesel oil, emulsified in seawater to give a 1-percent by volume oil concentration, reduced photosynthetic capacity 25 percent after 24 hours and 100 percent after 72 hours of exposure. If the kelp were exposed to a diesel oil emulsion for a period of 6 hours, irreversible damage was done, presumably because at least that much time was required for penetration of the oil into the cytoplasmic membrane (Van Overbeek and Blondeau 1954). Since no experiments in this study were conducted for periods that long, it is not likely that the effects were thoroughly observed.

The green alga *Enteromorpha intestinalis* is considered a very hardy species, being both eurythermal and euryhaline (Biebl 1962). Gross photosynthesis was greatly reduced, however, when the plant was exposed to 10 ppm crude oil for 4 hours (Figure 11.11).

The biochemical oxygen demand (BOD) was observed to be higher in both experiments employing the oxygen method (Figures 11.11 and 11.12). Since the seawater used to prepare the oil-seawater mixture was Millipore-filtered and pasteurized and the crude oil that was used is thought to be nearly sterile (D. K. Button, personal communication), auto- rather than bio-oxidation probably accounted for the higher BOD.

Rates of photosynthesis determined by the oxygen and  $^{14}\text{C}$  methods cannot be reliably compared, since the photosynthetic quotient that must be known in the oxygen method depends upon the physiological state of the organism and the immediate environmental conditions. For example, with the rate of carbon dioxide assimilation constant, the amount of oxygen evolved by algae may vary whether nitrate or ammonia serves as the nitrogen source with higher oxygen evolution resulting from nitrate utilization (Strickland 1960).

In the  $^{14}\text{C}$  experiments, each species of algae appeared to respond differently to the various crude oil concentrations. Crude-oil inhibition of photosynthesis by the green alga *Cladophora stimpsonii* was higher (~60 percent at 7 ppm) than in the case of other species tested. The higher surface-to-volume ratio of this species and the absence of the thick mucilaginous covering typical of other algae may explain these results. The mucilage associated with many algal species is known to protect them from petroleum substances over short exposure periods (Clendenning 1959; Schramm 1971).

Seaweed toxicity experiments conducted in this study were limited by the length of exposure time (2-4 hours) and the absence of information on the toxic effects of oil to reproductive forms of the algae such as gametes and zoospores. Since the protective covering of mucilage typical of mature plants is often absent in reproductive forms, severe damage to a seaweed population could occur if seawater were polluted by oil during the time of year when gametes are released.

### 11.11 Summary

The effects of crude oil as a contaminant in the Port Valdez marine environment were investigated with respect to oil toxicity to photosynthesis by indigenous populations of phytoplankton and important seaweed species. Toxicity experiments were conducted during various times of the year and thus under differing environmental conditions. Experimental results can be summarized as follows:

1. The concentrations of crude oil in seawater necessary to cause a specific degree of photosynthetic inhibition apparently change seasonally depending on physical and chemical factors and on the species composition and relative abundances. During June a 50-percent inhibition to phytoplankton photosynthesis occurred at approximately 2.0 ppm crude oil.

2. Crude oil in very low concentrations in seawater stimulated phytoplankton photosynthesis over short incubation periods during December, April and June. The photosynthetic rate of June phytoplankton exposed to a concentration of about 0.003 ppm crude oil was more than double the rate for phytoplankton in seawater containing no oil.

3. Crude oil in treated ballast water appeared to be about one-tenth as inhibitory to photosynthesis as fresh crude oil when tested on phytoplankton collected in June.

4. The effects of temperature on oil toxicity to phytoplankton were varied. The temperature optimum for photosynthesis differed between experiments. Phytoplankton treated with crude oil showed maximum photosynthesis (light uptake) at 5C during March, 10-15C during April, and 20C during August at crude oil concentrations between 1-4 ppm. The patterns for the oil-contaminated samples did not follow that of the controls. During March the oil-treated samples showed decreased photosynthesis with increasing temperature; controls indicated an optimum temperature for photosynthesis at about 10C. In contrast, during April the oil-treated samples showed a maximum rate of photosynthesis at 10-15C compared to a 10C optimum for controls.

5. The rate of light intensity in oil toxicity to phytoplankton was examined. At high natural-light levels, crude-oil toxicity appeared to be acute. Phytoplankton exposed to about 5.5 ppm crude oil showed a 65-percent reduction in photosynthesis at full light intensity (maximum of 0.89 ly/min), although phytoplankton exposed to the same concentration of crude oil at one-fourth this intensity showed only 20-percent reduction. A similar pattern was observed during tests with phytoplankton from a contrasting marine environment (Savannah, Georgia) that had been subjected to the same crude oil.

6. The relative species composition in a natural phytoplankton population may be altered by crude oil, resulting in a decrease in the abundance of some species and an increase in others. This effect is apparently dependent upon the amount of oil present. During May *Phaeocystis pouchetii* cells more than doubled in number after a 48-hour exposure to a crude oil concentration of 10 ppm (0.01 ml oil/added liter). In contrast, the number of *Thalassiosira nordenskiöldii* cells was reduced about 75 percent.

7. Seaweed oil-toxicity experiments, in which the  $^{14}\text{C}$  method was used to measure photosynthesis, indicated no pattern that was common to all species. Photosynthetic inhibition was indicated for *Cladophora stimpsonii*, *Ulva fenestrata* and *Laminaria saccharina* at 7 ppm crude oil, whereas other species were not significantly affected at this concentration. Photosynthetic stimulation was noted for several algae at different concentrations (~80-percent photosynthetic increase by *Ulva* and *Alaria* at 0.7 ppm crude oil; ~30-percent increase by *Costaria* at 0.007 ppm). *Enteromorpha intestinalis* showed an 80-percent reduction in oxygen production when exposed to 10-12 ppm oil.

The marine plant populations in Port Valdez, Alaska, showed varied photosynthetic responses to crude-oil contamination. These responses seemed to result from a complex interaction of several physical, chemical and biological factors that can apparently act in either an adverse or beneficial way.

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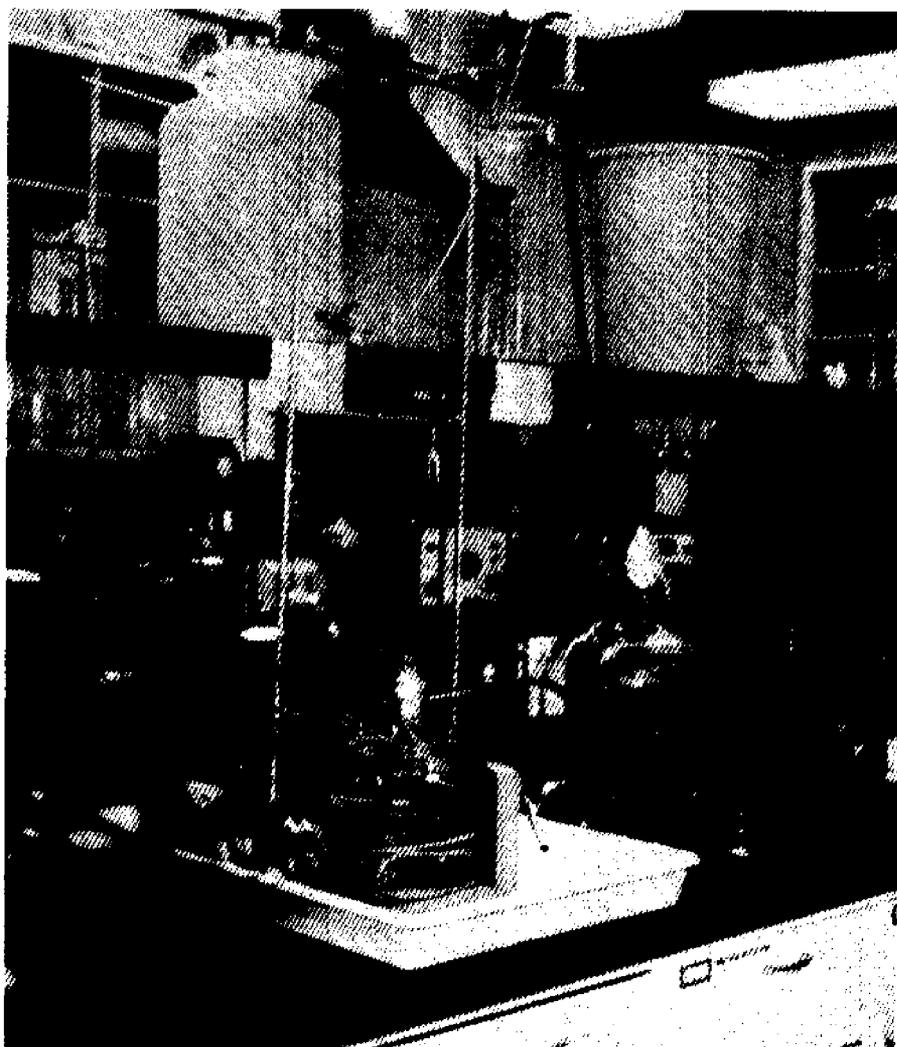
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# *Chapter 12*

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## HYDROCARBON BIODEGRADATION





## 12. HYDROCARBON BIODEGRADATION

by

B. R. Robertson, S. D. Arhelger, R. A. T. Law and D. K. Button

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### 12.1 Introduction

An assessment of biodegradation rates in Port Valdez is presented in response to the suggestion that the inlet may receive an increased hydrocarbon load from the proposed pipeline. Techniques developed and used in this study were based on results obtained earlier in Cook Inlet (Kinney et al. 1969), at which time hydrocarbon biodegradation was not widely recognized as an important marine oil removal mechanism; it had not yet been determined, in fact, whether such a process even occurred in the water column to a significant extent. The Cook Inlet study confirmed that hydrocarbon-oxidizing organisms did indeed exist as part of the marine flora, whether or not in response to frequent oil spills there. Mixing energy appeared to be dominant, and suspended silt as it occurs in Alaskan coastal waters seemed of little consequence in dissipating oil slicks for subsequent biodegradation.

Information obtained during the Cook Inlet study led to the development of two new techniques for estimating potential biodegradation rates. Slicks on water samples quickly dispersed when agitated with seawater containing populations of hydrocarbon-oxidizing organisms, but this was not the case when sterile water was used. An estimate of the indigenous hydrocarbon-oxidizing population was made by observing how large a volume of seawater was necessary to contain sufficient organisms to initiate the biodegradation process. Since biodegradation appeared to occur in the water column, this process was studied by introducing radioactive oil and measuring the rate of resulting metabolic product formation. A general estimate was thus made of the hydrocarbon-oxidizing microflora population in Port Valdez and the rate at which it can be expected to metabolize oil. Sampling locations were located as indicated in Figure 12.1.

### 12.2 Materials and Methods

#### 12.2.1 Plate counts of *in situ* populations

Microbiological samples were taken from rubber bulb type bacteriological water samplers (CM<sup>2</sup> Inc., Mountain View Calif.), evacuated, and triggered to fill at depth.

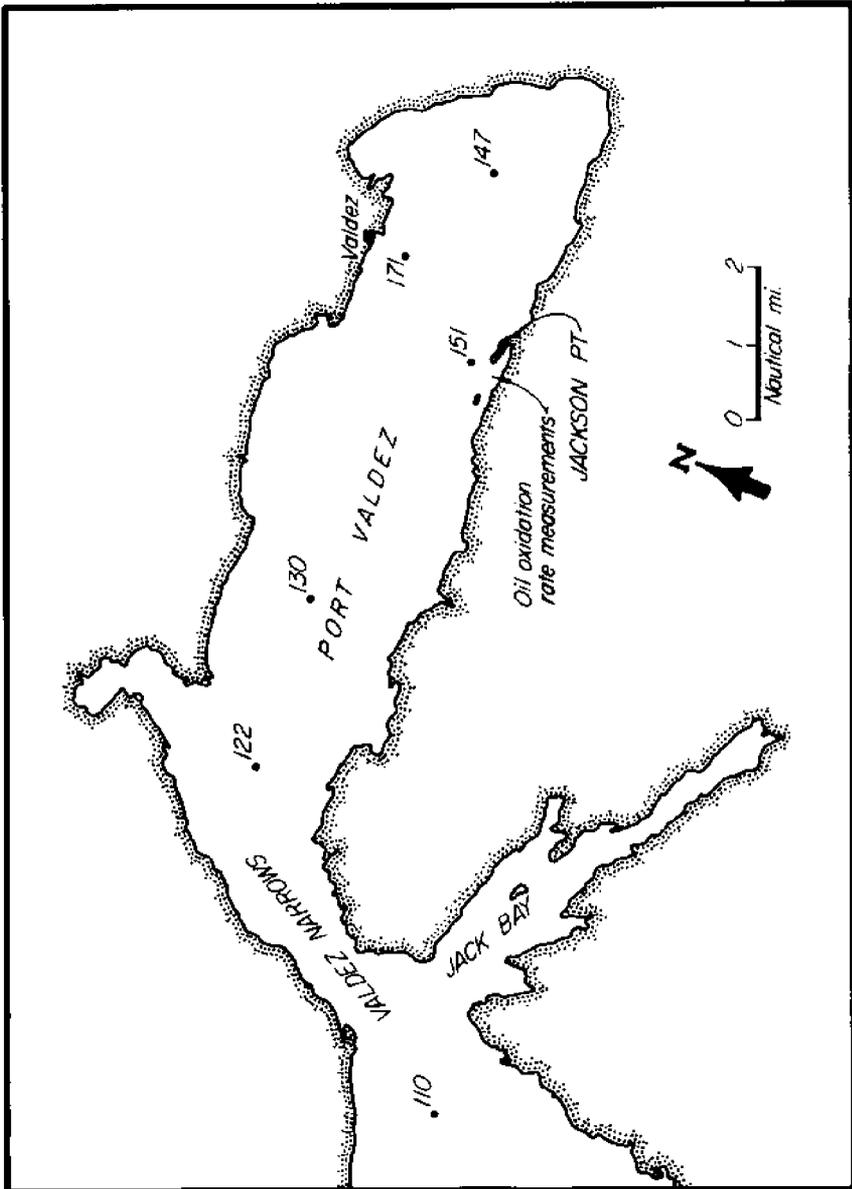


Figure 1.2.1 Port Valdez sampling locations used in hydrocarbon biodegradation studies.

Samplers were autoclaved (121C, 15 min) prior to hydrographic casts. Seawater in 0.1 to 50-ml samples was transferred in a glove box to discourage airborne contamination and were then filtered. Resulting filters (0.45- $\mu$ m pore size) of organisms collected were transferred to agar plates and incubated at 10C for subsequent counting.

#### 12.2.2 Agar media

Agar media had the following composition per liter: 15 g agar; 30 g NaCl; 2 g  $\text{Na}_2\text{HPO}_4$ ; 60 mg  $(\text{NH}_4)_2\text{SO}_4$ ; 40 mg KCl; 25 mg  $\text{MgSO}_4$ ; 5 mg  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ; 5 mg  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; 07  $\mu\text{g}$   $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; 25 ng  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 1.5 ng  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ ; 1.5 ng  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ; 0.5 ng  $\text{MoO}_3$ ; vitamins  $\text{B}_1$ ,  $\text{B}_{12}$  and biotin.  $10^{-10}$  moles. Half of the agar mixture contained 1 g/liter of both yeast extract and succinic acid, and the other half of the medium contained no further additions. The pH was adjusted to 7.3 in both media, which were then autoclaved for 15 min at 15 psi.

At each station, seawater samples were collected and filtered from depths of 0, 5, 10, 25 and 50 m. For each depth at each dilution there were four plates with filtered samples: two yeast extract-succinic acid plates and two plain agar plates. The amount of sample passed through the filters was 0.1, 1.0 or 10.0 ml for the yeast extract-succinic acid plates and 1.0, 10.0 and 50 ml for the plain agar plates. The filters were incubated on the agar surfaces after the samples had passed through them. Crude oil was added to one sterile filter paper situated on the inner top of the culture dish. The plates were inspected periodically for the appearance of colonies on the filters.

#### 12.2.3 Minimum sample volume for oil slick disruption

A nutrient-supplemented seawater medium was prepared by adding 100 mg/liter  $(\text{NH}_4)_2\text{SO}_4$ , 4 mg/liter  $\text{Na}_2\text{HPO}_4$ , and  $10^{-5}$  moles/liter EDTA to 20 liters of seawater, which was taken in October 1971 from a depth of 10 m in Valdez Narrows. The pH was adjusted to 7.3, and the carboy was autoclaved for 25 min at 15 psi. After the medium cooled, 20 ml of Prudhoe Bay crude oil, sterilized at 121C in sealed ampoules, was added to the carboy. The mixture was shaken vigorously for several minutes and left to equilibrate for 24 hours, during which time the oil phase separated out on top. Without disturbing the oil phase, 100 ml of oil-equilibrated medium were siphoned into each of 200 sterile 250-ml screw-cap bottles. Care was taken to keep the medium sterile during transfer.

Seawater samples of 1, 10 or 100 ml were introduced into the bottles. After a 1-week incubation, the bottles were charged with an oil slick by adding 3 drops (about 30  $\mu\text{l}$ ) of the sterile Prudhoe Bay crude oil.

#### 12.2.4 Plating procedure (minimum volume experiments)

Two weeks after crude oil had been added to the sample bottles (3 weeks after sample introduction and storage at 10C), the medium from each bottle was streaked by means of a nichrome wire loop onto each of two yeast extract and succinic acid agar plates and two plain agar plates (see section 12.2.2). To one of each type of plate, 3 drops of sterile crude oil were pipetted onto a sterile piece of filter paper situated inside the culture dish lid. The plates were incubated at 10C and checked periodically for the appearance of colonies and evidence of growth stimulation or inhibition.

#### 12.2.5 Tar oxidation rates

The tar fraction was prepared by distilling Prudhoe Bay crude oil at 300C until only dry chalky tar remained in the boiling flask. This solid fraction was then ground into a fine powder.

The growth medium for tar oxidation consisted of 20 liters of raw Valdez Harbor seawater supplemented with 100 mg/liter  $(\text{NH}_4)_2\text{SO}_4$ , 3 mg/liter  $\text{Na}_2\text{HPO}_4$  and 100 mg/liter tar. After 2 months' incubation at 10°C with stirring, 10-ml samples taken from the carboy were filtered through preweighed 13-mm diameter 0.45- $\mu$  Millipore filters, which were then rinsed with distilled water to remove the salts. The filters were dried and reweighed on a Cahn electrobalance under 50 mm Hg vacuum at 70°C. ATP extractions were made according to the procedure outlined below.

#### 12.2.6 ATP assay procedure

##### *Enzyme preparation*

A vial containing 50 mg of firefly lantern extract (FLE-50, Sigma Chemical Co.) was rehydrated with 5 ml of 0.02 M pH 7.75 Tris (hydroxymethyl) amino methane buffer and allowed to stand at 25°C for 2 hours. Each vial contained the dried extract of 50 mg firefly lantern in  $\text{MgSO}_4$  and  $\text{K}_2\text{HAsO}_4$ . The mixture was then centrifuged at 40,000 times gravity for 1 min. The supernatant was pipetted into 0.2-ml scintillation vials, the pellet was discarded, and the vials with the lantern extract were stored at 0°C until used.

##### *Sample preparation*

A 10-ml sample was filtered through a 0.45- $\mu\text{m}$  Millipore filter, which was then placed in a small test tube containing 2 ml of boiling Tris buffer and boiled for 10 min; the resulting ATP extract was poured into a dry test tube. The filter was boiled again with 1 ml of buffer, and the extracts were pooled. The total volume of the extraction was recorded, and the sample was frozen for future ATP assays. Determinations (Stroehler and McElroy 1957) were made on a Beckman  $\beta$ -mate scintillation counter using one photomultiplier tube.

#### 12.2.7 *In situ* oxidation rates

Either dodecane,  $^{14}\text{C}$ -l- or an amino acid mixture uniformly labelled with  $^{14}\text{C}$ , was added to 1-liter seawater samples. After substrate addition, all samples were incubated *in situ* from 0-35 days. The  $\text{CO}_2$  was then extracted from the sample, collected in alkali and precipitated as  $\text{BaCO}_3$ . The radioactivity of the  $\text{BaCO}_3$  precipitate was measured to quantitate the amount of substrate respired during incubation. The amount of particulate and dissolved  $^{14}\text{C}$ -substrate remaining after each incubation period was also measured.

##### *Incubation procedures*

Two uniformly labelled solutions were prepared:  $^{14}\text{C}$ -amino acid mixture, specific activity 54 mg/m atom-C (Amersham Searle, Arlington Heights, Ill.) containing 2.5  $\mu\text{c}$  and 550 ng C per ml; and  $^{14}\text{C}$ -dodecane specific activity 1.86 mc/m mole (ICN Tracerlab, Waltham, Mass.) containing 825 nc and 75.5  $\mu\text{g}$  dodecane in 0.125  $\mu\text{l}$ . The radiochemicals were autoclaved and stored in sealed ampoules.

Samples of coastal water (30 m total depth) were pumped from 10 m to fill dark incubation bottles. The pump consisted of a PVC hard plastic bilge pump fixed to 10 m of 2.5-cm of o.d. polypropylene tubing. The tubing was weighted to remain at depth. The whole system was flushed in 95 percent ethyl alcohol before use and then with large volumes of seawater from sample ethyl alcohol before use and then with large volumes of seawater from sample depth. Samples were divided into two experimental sets as follows:

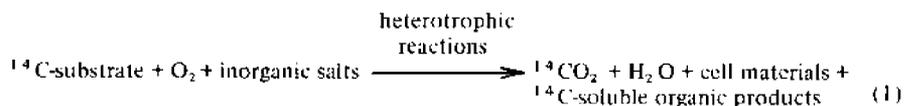
bottles with amino acid mixture, each containing 2.5  $\mu\text{C}$  and 550  $\text{ngC}$  and 1 liter of seawater; and bottles with dodecane, each containing 825  $\text{ng}$  and 75.5  $\mu\text{g}$  dodecane and 1 liter of seawater.

Immediately after the addition of substrates, the samples were lowered and left to incubate for 0-35 days. An arrangement of buoys, nylon line and anchors kept the bottles submerged at 10 m during incubation.

### *CO<sub>2</sub> extraction*

When selected incubation periods were completed, the reactions were stopped with addition of 6 ml of 50% orthophosphoric acid. After acidification, CO<sub>2</sub> was stripped from the sample with a stream of finely divided nitrogen bubbles flowing at 50 ml/min. The gaseous stream that left the reactor passed through an aerosol trap and bubbled into a series of three traps, each of which contained 200 ml of 1N NaOH. After 45 min of continuous flow, 5 ml of 1M BaCl<sub>2</sub> and 1M NH<sub>4</sub> Cl were added to each trap to obtain BaCO<sub>3</sub> precipitate. An outline of the reactions in the water sample follows:

#### a) Addition of <sup>14</sup>C-substrate



#### b) <sup>14</sup>CO<sub>2</sub> in seawater participates in carbonate equilibrium reactions:



#### c) Addition of acid displaces equilibria toward free CO<sub>2</sub>.

#### d) The nitrogen stream strips CO<sub>2</sub> from the sample and drives it into the NaOH traps where it forms Na<sub>2</sub><sup>14</sup>CO<sub>3</sub>, then



The precipitate was collected on glass fiber filter paper (Reeve Angel, grade 9-873, 2.4 cm), dried and weighed.

## OIL BIODEGRADATION

Microbial population media are prepared, Organisms are collected for counting, and water samples are incubated with oil to determine the rate and extent of oil slick disruption.



oil and water emulsion



Electron photomicrograph of hydrocarbon oxidizing bacterium capable of growth both inside and outside the oil phase.



media preparation

### *Particulate and dissolved fractions of the substrates*

When the procedures to obtain  $\text{BaCO}_3$  were completed, the particulate material of the  $\text{CO}_2$ -free water sample was collected on Millipore membrane filters. After filtration, the filters were dried and the filtrate collected. Filters and filtrates were stored in a freezer until counting procedures began.

### *Counting procedures*

Carbonates were suspended in a liquid scintillation solution to which 6% by weight of Cab-O-Sil (Cabot Corporation, Boston, Mass.) was added. The liquid scintillation solution had the following composition per liter of toluene: 5 g of 2,5-diphenyloxazole and 200 mg of 1,4-bis[2-(phenyloxazolyl)] benzene. All samples were counted in a Nuclear Chicago Scintillation Spectrometer.

### 12.2.8 Inhibition of phosphate uptake by hydrocarbons

Samples from a phosphate-limited continuous culture of *Rhodotorula rubra* were equilibrated with hydrocarbons and the phosphate uptake rate subsequently measured as previously reported (Button 1971a). Samples were mixed with sufficient oil for saturation in a 15-ml test tube immediately after sampling. The sample tube contained a pipette for subsequent removal of the lower aqueous phase. After a 30-min incubation period at 25C, during which time the residual phosphate was depleted and the excess oil separated, the aqueous sample was removed from below the slick and charged with radioactive phosphate at  $5 \times 10^{-7}$  M.

## 12.3 Results

### 12.3.1 Hydrocarbon-oxidizing populations

Direct plate counts were made from casts taken at various stations and depths. Colonies developing on yeast extract and hydrocarbon media were inoculated into bottles each containing an oil slick and supplemented seawater media. Bottles were later examined for the presence of a bacterial population developed in response to inoculation with samples and for the disruption or disappearance of the oil slick added. Duplicate casts and samples, taken at all depths for the May 1972 determinations, were in excellent agreement. Many blanks and controls were run using control plates and bottles not inoculated. All controls remained sterile throughout the incubation. Most organisms present were thought to actually have come from the depths sampled rather than through procedural contamination at some point.

The questions arises as to whether colonies developing on plate-count medium use, tolerate, or are inhibited by oil. From the agar counting plates, 177 colonies were distributed among four plates: a yeast extract medium, a mineral salts medium, mineral salts medium supplemented with crude oil, and yeast extract medium supplemented with crude oil. Results presented in Table 12.1 show that all colonies isolated would grow to some extent on agar plates without an oil or other carbon source supplement. Hydrocarbon vapors were in no case inhibitory to colonies growing on yeast extract medium and in only one case on the mineral salts medium. In only 2 of 177 cases were colonies stimulated by the addition of hydrocarbons. This fairly conclusive test for the ability of an organism to utilize hydrocarbons was more frequently positive in the previous Cook Inlet study, indicating a higher indigenous hydrocarbon-oxidizing microflora there than in Port Valdez.

Table 12.1 Response of isolated colonies to crude oil

Station	Depth	Medium	Source Transferred	Yeast Extract		Yeast Extract & Oil		Hydrocarbon		Hydrocarbon & Oil	
				Colonies Appearing	Colony <sup>1</sup> Size	Colonies Appearing	Colony Size	Colonies Appearing	Colony Size	Colonies Appearing	Colony Size
110	0	YE	6	6	+++	6	+++	6	++	6	++
	0	Oil	4	4	+++	4	+++	4	++	4	+
	10	YE	3	3	+++	3	+++	3	+	3	+
	10	YF	6	6	+++	6	+++	6	+	6	+
	10	Oil	1	1	+++	1	+++	1	+	1	+
122	0	YE	23	22	+++	22	+++	20	++	23	++
	0	Oil	3	2	+++	1	+++	2	++	1	++
	0	Oil	8	8	+++	8	+++	8	+	8	+
	10	YE	8	7	+++	7	+++	4	++	7	++
	20	YE	4	4	+++	4	+++	4	+	4	++
130	0	Oil	1	1	+++	1	+++	1	++	1	++
	20	Oil	2	2	+++	2	+++	2	++	2	++
	30	Oil	2	1	+++	1	+++	1	++	1	++
	0	YE	19	16	+++	16	+++	18	++	18	++
	10	YE	1	1	+++	1	+++	0	+	4	+
130	10	YE	4	4	+++	4	+++	4	+	4	+
	10	Oil	1	1	+++	1	+++	0	++	—	++
	20	YE	3	3	+++	3	+++	2	++	1	++
	30	YE	1	1	+++	1	+++	1	+	1	++

<sup>1</sup> Colony size; + = pinpoint colonies; ++ = 0.2 mm colonies; +++ = 1-2 mm colonies

Table 12.1 (continued)

Station	Depth	Medium	Source Transferred	Yeast Extract		Yeast Extract & Oil		Hydrocarbon		Hydrocarbon & Oil	
				Colonies Appearing	Colony <sup>†</sup> Size	Colonies Appearing	Colony Size	Colonies Appearing	Colony Size	Colonies Appearing	Colony Size
147	0	YE	15	15	+++	15	+++	15	++	15	++
	0	YE	2	2	+++	2	+++	1	++	1	++
	10	YE	4	3	+++	3	+++	4	++	4	++
	10	Oil	1	1	+++	1	+++	1	++	1	++
	20	YE	3	3	+++	3	+++	3	++	3	++
	30	YE	4	4	+++	4	+++	4	++	4	++
151	0	YE	10	9	+++	9	+++	9	++	9	++
	0	Oil	2	1	+++	2	+++	1	+	1	++
	0	Oil	4	4	+++	4	+++	3	++	3	++
	30	YE	1	1	+++	1	+++	1	++	1	++
	30	Oil	2	1	+++	1	+++	1	++	1	++
	171	0	YE	10	7	+++	6	+++	5	++	6
						1	++				
	0(50)	Oil	3	1	+++	3	+++	1	++	1	++
	10(50)	Oil	2	2	+++	2	+++	2	++	2	++
	20	YE	3	3	+++	3	+++	3	++	3	++
	20(50)	Oil	1	-							
	30(10)	YE	1	1	+++	1	+++	1	++	1	++

<sup>†</sup> Colony size: + = pinpoint colonies; ++ = 0.2 mm colonies; +++ = 1-2 mm colonies

Table 12.2 summarizes the plate counts and appearance of populations in oil slick disruption bottles resulting from various samples throughout Port Valdez. Spring and fall data are included. Oil slicks in almost all experiments were affected by addition of a 1 to 10-ml seawater sample during the fall cruise as compared to uninoculated controls. Subsequent experiments (not shown here), in which six replicate "disruption bottles" were prepared at each of five dilutions of a single Port Valdez seawater sample, showed fairly good dilution. Complete slick removal was apparent in many cases with sample dilution. Complete slick removal was apparent in many cases during a 45-day incubation at 10C. The "consistency change" reported is an abundantly apparent oil miscibility resulting from the developing bacterial population. This miscibility is probable due to a number of factors: the general emulsification capacity of microbial metabolic processes as well as the organisms themselves, the increased slick density due to partial oxidation of this oil, the water in oil emulsions formed and the penetration of the oil itself by organisms. Populations developed were streaked out on various media. None of these showed stimulated growth by added oil (column 11 {HC + oil} of Table 12.2); however, the population present clearly reduced the stability of the added oil slick. By ATP measurements, the 45-day populations which developed were in the range of 8-32 mg/liter (dry weight); assuming all were heterotrophic organisms, they must have grown at the expense of the oil oxidized. This appeared even in cases where enrichment plates did not prove the presence of hydrocarbon-oxidizing organisms. Had the ATP content been a product of photosynthetic activity, this level of biomass would have produced a green population rather than the white filamentous populations observed. Subsequent samples from Valdez incubated in the dark also generated substantial ATP from added oil.

Stations are located in Figure 12.1; population trends are shown in Figure 12.2 (May) and Figure 12.3 (October). Populations clearly decreased with depth. Figure 12.4 shows that the ratio of organisms capable of growth on hydrocarbon media to a rich media increased with depth. These data may reflect the addition of terrestrial heterotrophs at the surface to the normal indigenous population distributed throughout the water column.

### 12.3.2 Bacteria in sediments

A fresh core was sampled from the central Port Valdez area between stations 151 and 171. Consisting of finely divided gray silt, this core was sampled at the surface and at depths of 2, 4 and 6 cm. The sediment (5-10 mg) was streaked on agar plates and exposed to oil vapors. Only seven colonies developed, however, and all these were from the surface sample. Clearly, in terms of biomass, there did not appear to be large amounts of heterotrophic organisms (hydrocarbon oxidizers or other) in the subsurface sediments. Even if they were anaerobic, the subsurface samples should have produced some facultative organisms which would grow on the media supplied had there been large numbers present. Surface sediment sample plates using similar techniques in Cook Inlet were quickly overgrown with large numbers of colonies.

### 12.3.3 *In situ* hydrocarbon biodegradation rates

General baseline levels of heterotrophic activity were measured by recovering <sup>14</sup>C-carbon dioxide from labelled substrates. These were added to otherwise unaltered seawater samples and incubated at depth in Port Valdez. Incubations were 100 m offshore near station 153 and at a depth of 10 m. Tables 12.3 and 12.4 show the results of 42 such incubations lasting up to 35 days. Material balances (Tables 12.5 and 12.6) show that a significant portion of the substrate added was recovered in the various fractions: particulate, dissolved, and respired CO<sub>2</sub>. Where radioactivity was added as oil, much of it remained on the filter paper to which it was originally supplied. The solubility of this C<sub>12</sub> hydrocarbon is



Table 12.2 (continued)

Date	Station	Depth (m)	Sample Volume ml <sup>1</sup>	Plate Counts <sup>2</sup>		Slick Disruption Bottles				Heterotrophic Population Estimates					
				YE	Oil	Flocculation <sup>3</sup>	Oil Slick	Dissipation	Population Developed <sup>4</sup>		Plates	Disruption Bottles	Hydrocarbon Oxidizers		
									YE	Oil				HC + Oil	ATP gm/liter × 10 <sup>7</sup>
5/72	130	0	0.1	3											
			1.0	0	±	-		+	+						
			10.0	4	±	-		+	+		10.1	0.1	>1	>1	
			50.0	0											
			100.0		+		-	+	+	+					
													6.0		
	5	5	0.1	2											
			1.0	0	±	-		+	+						
			10.0	3.5	+	+		+	+		6.8	0.3	>1	>1	
			50.0	14											
			100.0		+			+	+	+					
													4.6		
	10	10	0.1	2											
			1.0	0.5	+	+		+	+						
			10.0	3	+	+		+	+		6.9	0.5	>1	>1	
			50.0	20											
			100.0		+			+	+	+					
													16		
	25	25	0.1	0.5											
			1.0	0.5	±	-		+	+						
			10.0	1	+	-		+	+		1.9	0.2	>1	>1	
			50.0	10											
			100.0		+			+	+	+					
													4.2		
	50	50	0.1	0											
			1.0	0	±	-		+	+						
			10.0	0.5	+	-		+	+		0.02	.01	>1	>1	
			50.0	2											
			100.0		+			+	+	+					
													13		

Table 12.2 (continued)

				Plate Counts <sup>2</sup>		Slick Disruption Bottles				Heterotrophic Population Estimates					
Date	Station	Depth (m)	Sample Volume ml <sup>1</sup>	YE	Oil	Floc-culation <sup>3</sup>	Oil Slick		Population Developed <sup>4</sup>			Plates		Hydrocarbon Oxidizers	
				YE	Oil		Dissipa-tion	YE	Oil	HC + Oil	ATP gm/liter X 10 <sup>7</sup>	YE	Oil		Total
5/72	147	0	0.1	43		+	+	+	+						
			1.0	36	40	+	+	+	+						
			10.0	208	200	+	+	+	+			162.3	30	>1	>1
			50.0	+++		+	-	-	+	+					
		5	0.1	8	0	+	+	+	+						
			1.0	8	40	+	+	+	+						
			10.0	106	200	+	+	+	+			32.9	2.7	>1	>1
			50.0			+	-	-	+	+					
		10	0.1	4		+	+	+	+						
			1.0	0.5	0	+	+	+	+						
			10.0	13	6	+	+	+	+			13.9	0.4	>1	>1
			50.0		25	+	-	-	+	+					
		25	0.0	2		+	+	+	+						
			1.0	0	0	+	+	+	+						
			10.0	30	25	+	+	+	+			7.7	2.2	>1	>1
			50.0		200	+	-	-	+	+					
		50	0.0	1.5		+	+	+	+						
			1.0	1.5	0.5	+	+	+	+						
			10.0	34	6.5	+	+	+	+			0.7	1.1	>1	>1
			50.0		100	+	-	-	+	+					
			100.0			+	-	-	+	+					



Table 12.2 (continued)

Date	Station	Depth (m)	Sample Volume ml <sup>1</sup>	Plate Counts <sup>2</sup>		Slick Disruption Bottles			Heterotrophic Population Estimates					
				YE	Oil	Flocculation <sup>3</sup>	Oil Slick	Population Developed <sup>4</sup>			Plates	Disruption Bottles		
								YE	Oil	HC+ Oil			ATP gm/liter X 10 <sup>7</sup>	Oil
		20	0.1	-	-									
			1.0	1	-									
			10.0 50.0	3	-		+	+	+			0.3	<0.1	<0.1
		30	0.1	-	-									
			1.0	-	-									
			10.0 50.0	-	-		+	+	+			0	<0.1	>1
10/71	130	0	0.1	2	-									
			1.0	6	-									
			10.0 50.0	25	-		+	+				2.5	0	>1
		10	0.1	-	-									
			1.0	1	-									
			10.0 50.0	10	-		+					1	>0.1	>0.1
		20	0.1	-	-									
			1.0	-	-									
			10.0 50.0	3	-		+	+				0.3	0	>1







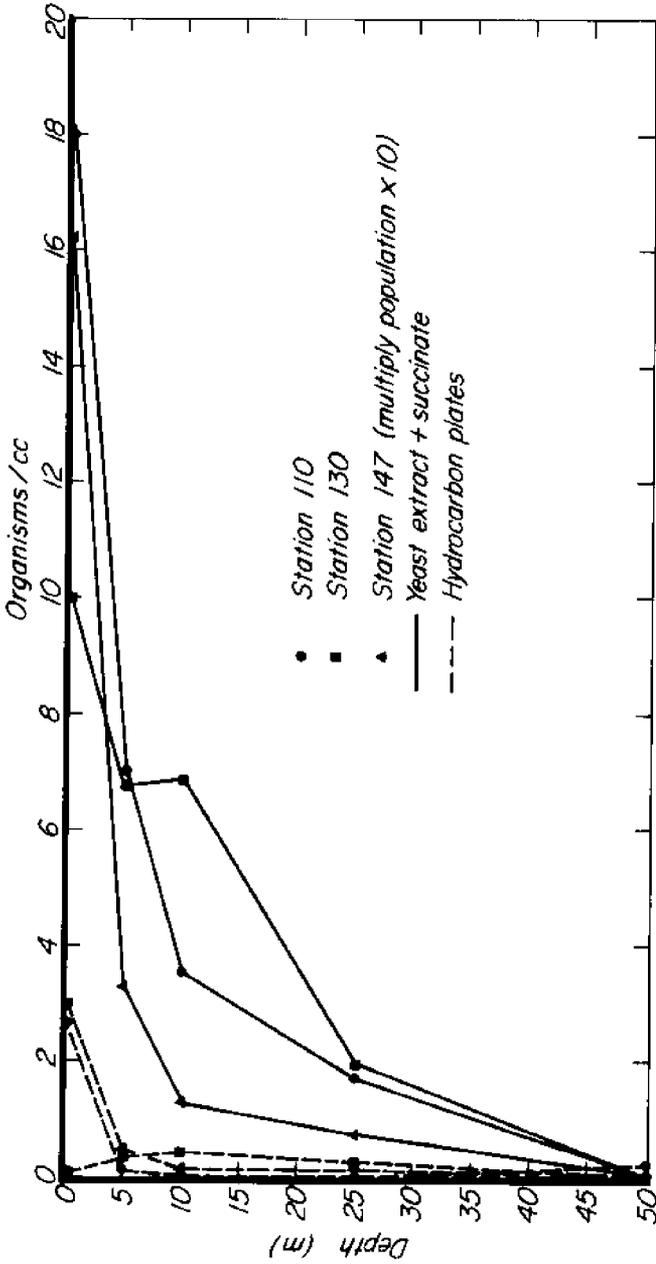


Figure 12.2 Heterotrophic population distribution with respect to depth at three stations in May 1971.

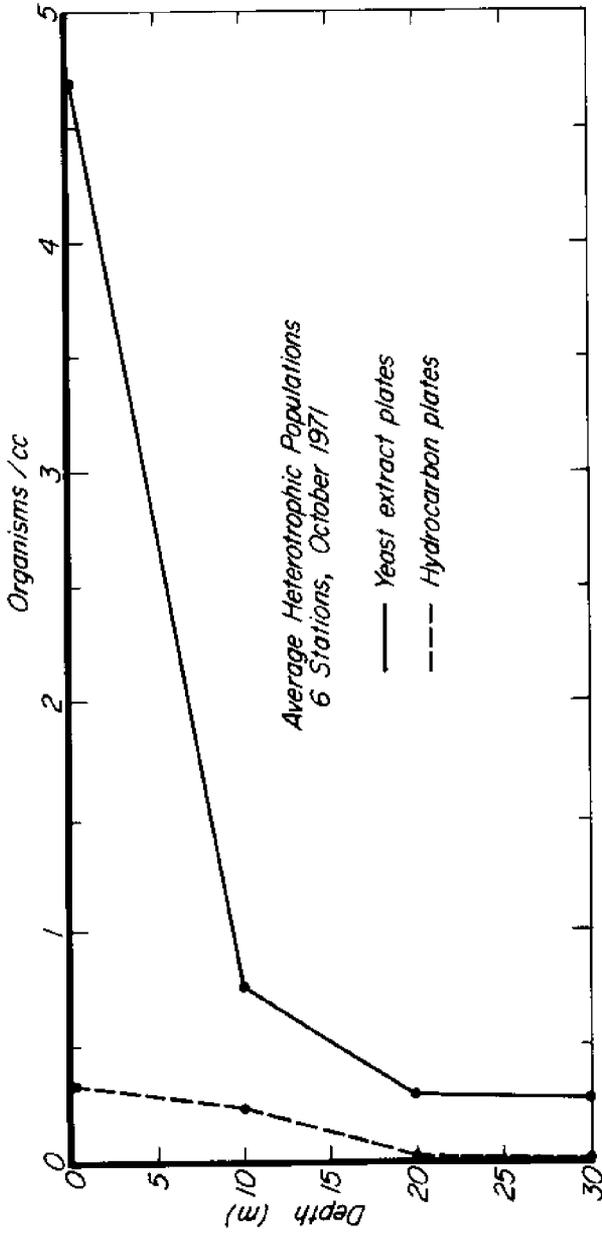


Figure 12.3 Average heterotrophic populations from six stations growing on oil mineral salts plates and growing on complete medium plates, with respect to depths.

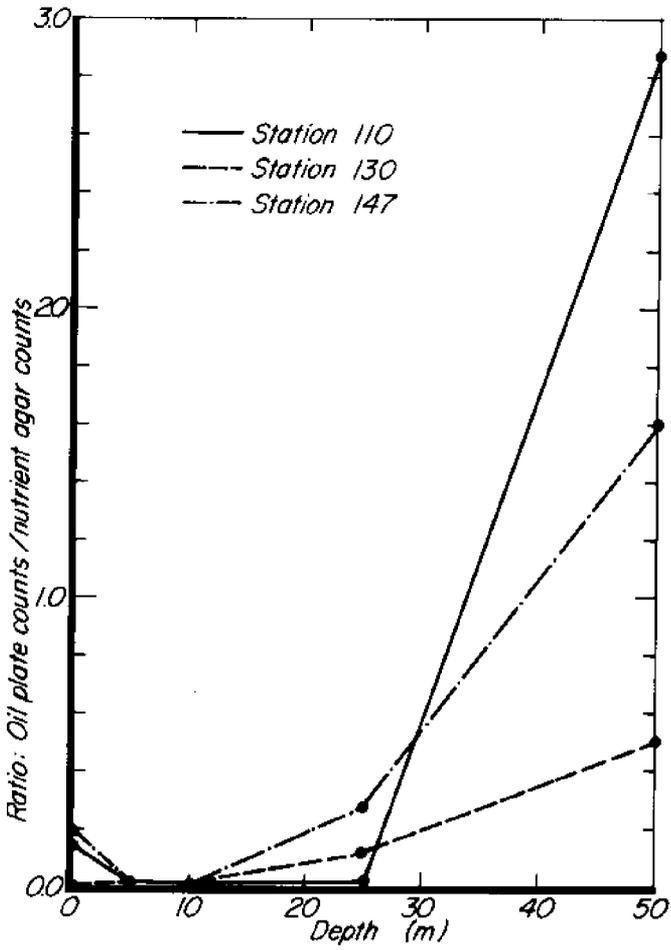


Figure 12.4 Ratio of colonies appearing on plates supplied only with oil to those supplied with a complete medium.

Table 12.3 *In situ* incubation of  $^{14}\text{C}$ -dodecane in Port Valdez

Incubation number	Incubation time (days)	Total precipitate mmole/liter	BaCO <sub>3</sub> formed			Date collected
			Specific activity nci/mmole	Substrate <sup>1</sup> $\mu\text{g}$ dodecane/liter	Average rate <sup>2</sup> $\mu\text{g}$ dodecane/liter-day	
23	0.00	2.5	1.0	0.30	—	Aug. 29, 71
24	0.00	3.9	0.7	0.24	—	Oct. 5, 71
25	0.00	2.9	0.2	0.05	—	May 17, 72
26	0.00	2.7	7.0	1.74 <sup>3</sup>	—	May 17, 72
27	0.12	2.3	1.7	0.36	1.42	Oct. 5, 71
28	0.95	3.1	1.7	0.50	0.33	May 17, 72
29	2.83	2.8	3.2	0.82	0.22	May 17, 72
30	2.99	2.5	1.1	0.24	0.02	May 18, 72
31	3.00	3.4	2.4	0.51	0.11	Aug. 26, 71
32	3.92	2.9	2.7	0.70	0.13	May 17, 72
33	4.00	2.4	77.6	17.05 <sup>4</sup>	—	Aug. 26, 71
34	4.76	2.8	2.9	0.75	0.12	May 17, 72
35	5.66	2.9	6.4	1.70	0.27	May 17, 72
36	5.66	3.0	2.4	0.66	0.08	May 17, 72
37	6.64	3.1	7.1	2.03	0.28	May 17, 72
38	6.64	3.0	3.7	1.02	0.13	May 17, 72
39	6.81	3.2	11.0	3.24	0.45	May 18, 72
40	7.61	3.2	3.0	0.90	0.09	May 17, 72
41	7.63	3.0	2.7	0.75	0.07	May 17, 72
42	7.63	3.4	7.3	2.30	0.28	May 17, 72
43	35.00	2.4	233.8	51.38	1.46	Aug. 30, 71

<sup>1</sup> Carbon dioxide collected from the oxidation of  $^{14}\text{C}$ -dodecane, specific activity 1.86 mci/mmole and concentration 92.4  $\mu\text{g/liter}$ .

<sup>2</sup> Net average rate of dodecane oxidation. A rate of 0.19  $\mu\text{gC}/(\text{liter} \cdot \text{day})$  was taken as average for zero-day incubations. The rates reported in this column are those above zero-day incubations.

<sup>3</sup> and <sup>4</sup> These values were unacceptable and not considered in calculations.

Table 12.4 *In situ* incubation of  $^{14}\text{C}$ -amino acids in Port Valdez

Incubation number	Incubation time (days)	Total precipitate mmole/liter	BaCO <sub>3</sub> formed			Average rate <sup>2</sup> ng-C/(liter-day)	Date collected
			Specific activity nci/mmmole	Substrate <sup>1</sup> ng-C/liter	from		
1	0.00	2.8	0.3	0.2	-	May 17, 72	
2	0.00	2.7	0.8	0.5	-	May 17, 72	
3	0.00	3.4	0.4	0.3	-	Oct. 5, 71	
4	0.12	1.9	1.3	0.5	1.7	Oct. 5, 71	
5	0.91	2.3	104.8	53.5	58.5	May 17, 72	
6	0.99	3.0	78.3	52.2	52.4	May 17, 72	
7	1.64	2.9	104.7	67.5	41.0	May 17, 72	
8	1.69	3.0	80.2	53.4	31.4	May 17, 72	
9	2.89	2.9	125.5	80.9	27.9	May 17, 72	
10	3.00	2.6	115.0	66.4	22.0	Aug. 26, 72	
11	3.98	3.2	105.2	74.8	18.7	May 17, 72	
12	3.98	2.0	209.8	93.5	23.4	Aug. 26, 72	
13	4.75	3.2	115.9	82.4	17.3	May 17, 72	
14	4.77	3.1	164.8	113.5	23.7	May 17, 72	
15	5.66	3.0	175.1	116.7	20.6	May 17, 72	
16	5.66	3.0	162.9	108.6	19.1	May 17, 72	
17	6.64	2.9	103.9	67.0	10.0	May 17, 72	
18	6.64	2.9	112.3	72.3	10.8	May 17, 72	
19	6.81	3.4	65.8	49.7	7.3	May 17, 72	
20	6.81	3.3	88.9	62.2	9.1	May 18, 72	
21	34.99	2.2	313.1	153.1	4.4	May 18, 72	
22	35.34	3.5	293.7	228.7	6.5	Aug. 30, 71	
						Aug. 30, 71	

<sup>1</sup> Carbon dioxide collected from the oxidation of a uniformly labelled mixture of  $^{14}\text{C}$ -amino acids, specific activity 54 mCi/m atom C and concentration 555 ng-C/liter.

<sup>2</sup> Net average rate of amino acid oxidation. A rate of 0.3 ng-C/(liter · day) was taken as average for zero-day incubations. The rates reported in this column are those above zero-day incubations.

Table 12.5 Material balance of incubation with  $^{14}\text{C}$ -dodecane<sup>1</sup>

Incubator number	Incubation time (days)	Respired $\mu\text{g/liter}^2$	Particulate $\mu\text{g/liter}$	Dissolved residual $\mu\text{g/liter}$	Total substrate recovered $\mu\text{g/liter}$	Recovery %
6A	0.00	0.30	0.05	0.27	0.62	0.67
18A	0.00	0.24	2.47	0.44	3.15	3.41
20A	0.12	0.36	2.49	0.35	3.20	3.46
2A	3.00	0.51	2.04	0.73	3.28	3.55
9A <sup>3</sup>	4.00	17.05	2.46	0.81	20.32	78.00
13A <sup>4</sup>	35.00	51.38	40.04	4.11	95.53	110.00

<sup>1</sup> Initial  $^{14}\text{C}$ -dodecane concentration was 92.4  $\mu\text{g/liter}$ .

<sup>2</sup> Carbon dioxide recovered expressed as weight of dodecane oxidized.

<sup>3</sup> Radioactivity remaining on membrane filter section (used as a vehicle substrate to add dodecane) after experimental interval was equivalent to 53.1  $\mu\text{g/liter}$  dodecane.

<sup>4</sup> Residual radioactivity on filter bearing substrate was equivalent to 6.2  $\mu\text{g/liter}$  dodecane.

Table 12.6 Material balance of incubations with  $^{14}\text{C}$ -amino acids (initial concentration 555 ng C/liter).

Incubation number	Incubation time (days)	Respired ng C/liter	Particulate ng C/liter	Dissolved residual ng C/liter	Total substrate recovered ng C/liter	Recovery %
3	0.00	0.3	1.3	460	461.6	83.2
4	0.12	0.5	7.5	440	448.0	80.7
10	3.00	66.4	58.7	13.3	258.1	46.5
12	3.98	93.5	57.0	35	185.5	33.4
21	34.99	153.1	20.5	40	213.6	38.5
22	35.34	228.7	45.3	37	311.0	56.0

about 8  $\mu\text{g/liter}$  or about 10 percent of the total oil added. Although most of the oil added was recovered after the experimental period, either as a product or the original material, only about one-third of the amino acids were recovered. At normal growth rates, however, the particulate biomass produced from amino acids should be approximately equal to the  $\text{CO}_2$  respired. The deficiency here is in the particulate carbon fraction and is probably the result of organisms adhering to the vessel walls and especially to the rubber stoppers used to close the reactor. Material balances generally reflected that most of the carbon dioxide produced from the substrates was recovered and accountable by the procedures used.

Substrate degradation rates are shown in Figure 12.5 by the slope of accumulated radio- $\text{CO}_2$  versus time plots. Amino acid degradation rates were about 0.2  $\mu\text{g/liter-day}$  while those of dodecane were about 1  $\mu\text{g/liter-day}$ . The lower amino acid oxidation rate is due to the lower amino acid concentration, 0.64  $\mu\text{g/l}$ , as opposed to 91  $\mu\text{g/l}$  dodecane. Also local dodecane concentrations were much higher, since most of this material remained in the oil phase. These rates strongly indicate the extent of *in situ* microbial heterotrophic activity.

#### 12.3.4 Tar oxidation rates

Port Valdez water was supplemented with nutrients and provided with the high-molecular weight fractions of Prudhoe Bay crude oil. Twenty liters of this culture was rapidly stirred at 10C. Of the 100 mg/liter oil added initially, only 55.5 mg/liter was present after 2 months. In addition, the concentration of ATP had increased to  $4.02 \times 10^{-7}$   $\mu\text{g/l}$ . This is equivalent to about 2 mg/liter of organisms dry weight.

Four-liter quantities of Cook Inlet water supplemented with 84 mg of crude oil were incubated 36 months at 10C. Only a few brown pieces remained entwined in sheets of fungal mycelia and were almost unrecognizable as crude oil. All visual traces of tar had disappeared in bottles containing 6 mg of crude oil.

#### 12.3.5 Oil toxicity

Certain mechanisms appeared to be dominant in short-term oil toxicity microorganisms: In some cases organisms coalesced with oil droplets on contact such that the microenvironment of part or all of their functional exterior surface entered an oil phase rather than the usual aqueous phase. The second response was to hydrocarbons in the  $\text{C}_5$ - $\text{C}_8$  range (see Button 1971b for review), a third mechanism observed was inhibition of chemotactic response by hydrocarbons toward attractants (Mitchell and Walsh 1972). The latter mechanism is also thought to interfere with pheromone communication in marine invertebrates (Kittredge 1972). Many heterotrophs grow on these low-molecular weight hydrocarbons when supplied at low concentrations, although hydrocarbon concentrations approaching aqueous saturation inhibit growth. This is probably due to solution of phospholipid membrane components in locally high-hydrocarbon collected by partitioning against the hydrophobic cell surface. Alteration in the important capacity to perform metabolite specific osmotic work would be expected.

Different species might be expected to differ in their tolerance thresholds toward these solvents. Reduction in a randomly mixed continuous-culture heterotrophic population has been induced by additions of crude oil to the feed (Kinney et al. 1969). These experiments were designed to test oil toxicity on a specific membrane function, that of active transport into a marine yeast. This system has been found to be exceedingly sensitive toward various naturally occurring inhibitors (Button 1971a).

Table 12.7 shows that saturated aqueous solutions of the lower-molecular weight solvents, all constituents of crude oil, produced grossly inhibited transport rates. In the several experiments shown, however, no response was noted with crude oil additions. This

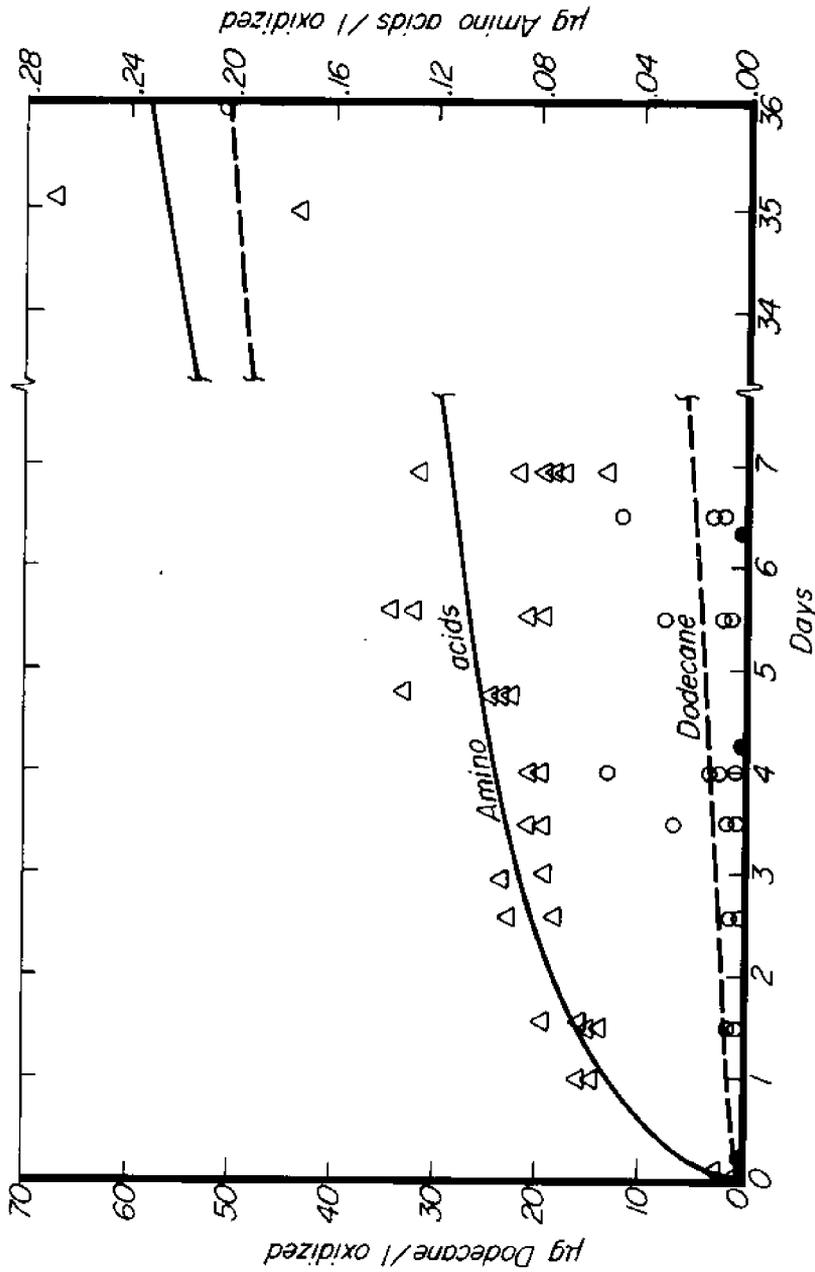


Figure 12.5 Radioactive carbon dioxide recovered from amino acids and from dodecane incubated for various times with indigenous population *in situ*.

Table 12.7 Inhibition of phosphate transport by various hydrocarbons in a marine yeast

Component	Flux $\mu\text{mole PO}_4/\text{gm cells-min}$	% Control
Control	13.0	100
Prudhoe Bay crude	13.0	100
Toluene	0.0	0
Xylene	0.3	2.3
Napthalene	4.0	31.0
Cyclohexane	7.0	54.0
Benzene	9.0	69.0
Pentane	12.0	92.0
Dodecane	12.5	96.0

Table 12.8 Response of algal continuous culture to perturbation by oil added to its medium supply

Hours in culture	Substrate	Algae/ml	Bacteria/ml
480	oil free	$1.1 \times 10^5$	
490	oil free	$1.0 \times 10^5$	
504	oil free	$1.1 \times 10^5$	$5 \times 10^4$
528	oil added	$1.1 \times 10^5$	
540	oil added	$1.2 \times 10^5$	
548	oil added	$1.2 \times 10^5$	$12 \times 10^4$

would indicate that the mole fraction of solvent components in the crude oil samples was insufficient to result in the dissolved aqueous concentrations necessary for major membrane disorientation in this system.

Perturbation by crude oil of an algal culture growing continuously was attempted in a manner similar to that reported for mixed bacterial cultures (Kinney et al. 1969). In this experiment, however, the population was maintained constant by adjusting the feed rate equal to the maximum growth rate of the culture ( $0.041 \text{ hr}^{-1}$ ). The culture was then growing at its maximum rate. The size of the population studied (*S. capricornutum*) was  $1.1 \times 10^7$ /ml or about 0.7 mg/liter (Table 12.8). The steady-state algal culture was unchanged in population after perturbation with oil. This showed that the maximum growth rate of the organisms under conditions of both light and nutrient saturation was not reduced by soluble crude oil components as they exist when the growth medium is partitioned against the many components of crude in the oil phase. Bacterial populations in the uni-algal culture did increase as shown. The numbers of different heterotrophic species comprising the total population, however, decreased markedly as evidenced by the number of colony types appearing on plates.

Hydrocarbons in the oil phase were carefully omitted in the above experiment. Where oil is present as an emulsion, it is probable that this hydrophobic phase will separate the contained organismal surfaces from aqueous contact. As noted earlier, some hydrocarbon-oxidizing organisms have the ability to pass into and metabolize inside the oil phase. The three microorganisms commonly used in the laboratory were a hydrocarbon-oxidizing bacterium (isolate 198), a marine yeast (*Rhodotorula rubra*), and a fresh water alga (*Selenastrum capricornutum*). These organisms were seen to collect around oil droplets upon microscopic examination. The extent of their preference for the oil phase varied greatly in the order listed. The preference of the bacterium is so extensive that where an oil phase was present in a growing culture, organisms were difficult to collect from the underlying medium. Oil droplets in the yeast culture were densely coated with organisms to the exclusion of nearby medium. The algae could be seen in contact with crude oil droplets when medium and oil were shaken together. It would thus appear that effects of oil emulsions on microbial processes would be due in part to their propensity for hydrophobic surface adhesion and concomitant alteration of the organisms' immediate external chemical environment. Microbial surfaces, normally exposed to aqueous chemistry, contact oil when present. In that such organisms are sustained by functional transport systems on their surfaces which concentrate required metabolites, part of the effects of emulsified oil on microbial metabolism (sometimes noted) might be one of physical exclusion of the aqueous medium. Local oil concentration at the surface of the organism would then increase by a factor of several million.

#### 12.4 Discussion and Conclusions

At most points sampled near Valdez, a sufficient microflora existed for each cubic centimeter of water to initiate hydrocarbon biodegradation in the spring season. Populations were somewhat lower in the fall, possibly due to carbon source depletion during the summer. Spring populations would respond to the winter nutrient accumulation. This was borne out by the frequency in which populations developed in sterile seawater media supplemented with nutrients and oil, then inoculated with seawater samples. These general population estimates were substantiated by direct plate counts. ATP assays on populations developed in inoculated bottles suggest that many organisms developing therein, while not responding to hydrocarbon vapors on plate counts, did indeed grow at the expense of oil. Their effects on slicks were substantial.

Carbon dioxide recovered from radioactive oil incubated in place at depth clearly defined the presence of hydrocarbon biodegradation as a normal ongoing process. The rate measured averaged approximately 0.3  $\mu\text{g/liter-day}$  over a range of incubation times. Somewhat lower amino acid oxidation rates at the low amino acid concentrations used, together with recoveries, confirmed the suitability of this technique.

Some conditions might be expected to affect this oxidation rate. This second-order rate is dependent upon both the concentration of the oil and the population of organisms at a given temperature. Of course, the population increases in response to the oil, but hydrocarbon-oxidizing populations can be expected to respond to many things in addition to oil. One is a suitable oxidant. The oxidation of 1 g of oil yields about 1 g of cells (dry weight) and requires about 2 g of oxygen. In addition 10 g of nitrogen and 1 g of phosphorus are required. These nutrients are all essentially nonconservative over a short time interval and deplete the nutrient supplies to the extent of the oil supplied in a ratio set by the respective cell yields involved. Thus, rates of metabolism in areas of high oil density might be affected by nutrient (oxygen, nitrogen, phosphate and water) penetration rates.

Complete removal of tar would be anticipated from observation of oil added to seawater and observed over a 3-year period. The process is slow. Tar probably has a half life of 1 year or longer when in large lumps protected from weathering, but removal is probably complete. Floating tar balls contain a substantial microflora of bacteria and protozoa living on its contents (Finnerty 1972). Limited observations showed surprisingly few organisms in sediments sampled, due perhaps to a rather shallow aerobic layer in the comparatively impermeable sediment. Large pieces of tar settled in sediment could be expected to be rather well preserved due to a lack of oxidation and fragmentation processes.

Apparent crude oil toxicity appears to depend on a number of circumstances. Organisms which have been observed are prone to remain with or inside oil droplets contacted. This eliminates the water phase in the area between oil and organisms contact. Since microorganisms depend on their surface functions for all nutritional functions, such contact is bound to alter metabolic capacity. Where the oil phase was eliminated from test media, no change was found in the very efficient transport capacity of a heterotrophic system tested in response to dissolved crude oil. Crude oil components did, however, produce inhibition in solution as the mole fraction of more soluble low-molecular weight components was allowed to increase.

Soluble crude oil components had no apparent effect on algal growth rate in the steady-state system tested. A decrease in the number of heterotrophic species and an increase in the total count was observed, however, when the non-photosynthetic portion of the uni-algal culture population was examined. One might expect this eventuality in Port Valdez in response to oil addition; i.e., a decrease in total species and an increase in total heterotrophic biomass would result in response to the addition of a new carbon source.

A suitable flora appeared to be indigenous for oil slick inoculation and was contained in the order of each milliliter of water. Slick stability might be anticipated to be a great deal greater than observed in Cook Inlet, however. Relatively low currents would not be expected to provide the order of mixing necessary for rapid slick dissipation in this relatively small protected harbor.

### 12.5 References

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# Summary

D. W. Hood

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## 1 What are the spatial and temporal variations in temperature and salinity?

The salinity and temperature distribution for Port Valdez is controlled by a variety of influences, including tides, winds, surface air temperature and the character of marine source-water available from Prince William Sound. During the May to October period of maximum fresh-water runoff, the waters within Port Valdez were stratified with respect to both temperature and salinity. The maximum annual stratification occurred in July and the minimum in March. Temperature and salinity differences were not observed below the 10-20 m depth between Valdez Arm and Port Valdez, suggesting that horizontal exchange occurs continuously between these two bodies of water. Except at the surface, little horizontal difference in salinity and temperature was found at any season of the year anywhere in Port Valdez, indicating complete horizontal transport of these properties.

## 2 What are the circulation patterns in the Port; what is the velocity of the currents near the outfall site?

The circulation of Port Valdez is driven by winds and tides. Fresh-water input, which heavily influences circulation in estuaries fed by large rivers, is relatively unimportant in Port Valdez, where fresh-water input seldom exceeds 5 percent of the tidal volume. There were few detectable patterns or seasonal variations in circulation at the 15-m (50-ft) depth in the Port. Parachute drogue studies indicated at all times an irregular motion that was heavily dependent on the wind.

Horizontal transport away from the outfall site occurred through small variable currents that changed in direction and velocity with the tidal flow. The currents were consistently found to be stronger at location 1 than at locations 2 and 3 (stations 153, 158 and 157, respectively; Figure 2.1) except in March, when the currents were bimodal in the direction of 81-100°T and 241-280°T (Figure 3.27). The preferred velocity was about 7 cm/sec with maximum currents up to 40 cm/sec. In March the currents were easterly, independent of the state of tide, and had a velocity range of 4-30 cm/sec.

### 3 What are the mixing and flushing rates of Port Valdez?

During the months from April to September, the waters of Port Valdez were vertically stratified; however, at any given depth they were nearly homogeneous throughout the Port, indicating complete horizontal mixing. During late fall cooling of the surface water, coupled with cessations of fresh-water runoff, the stratified waters began to mix vertically and became completely mixed to the bottom by March. Based on climatic data, it is reasonable to expect that vertical mixing is a common winter occurrence.

Based on current meter measurements made in the Valdez Narrows during December 1971 and March 1972, the tidal and non-tidal currents were estimated. Maximum tidal current speeds were about 20 cm/sec. while mean non-tidal currents were 2-3 cm/sec. If cross-channel homogeneity and constancy of currents is assumed, a flushing rate of 40 days was indicated for this season of the year. Tidal currents which involve entrainment of water would shorten this renewal period. The effectiveness of tidal entrainment in water renewal can best be determined by use of physical models, which were not available for this study.

### 4 What are the dilution rates at possible outfall sites; how will the ballast water mix and move away from the discharge site; and will the oil concentration ever build up in the area of the outfall site?

The dilution rates that exist under natural conditions near the three potential outfall sites were measured directly by means of rhodamine-B dye dispersion studies. The mixing which occurred as a result of addition of mechanical energy through pumping was not the purpose of this investigation. (These kinds of data are readily available to the hydraulic engineering profession and since they are not a specific property of the local environment, development of criteria for the outfall design was not included). This study was concerned with that dispersion within the natural water body which effectively lowers the concentration of any added contaminant by mixing new water with the contaminated parcel. Measurements of the natural dilution rates were made by determining the maximum concentration of dye in a dye plume at measured distances from the point of injection. A plot of distance against concentration then allowed an estimate of the maximum concentration of a contaminant that would exist at a given distance from the outfall. The distance of tenfold dilution was computed for the six different times of the year these measurements were made. Measurements were made at three locations (1, 2 and 3) and at 2.5, 15 and 23-m (8, 50 and 75-ft) depths. It was early determined that location 1 (station 153, Figure 2.1) had better characteristics with respect to currents, dilution rates and ease of installation of the outfall equipment. It was found that the average tenfold dilution distance at 2.5 m (8 ft) was 0.56 n. miles; at the 15 and 23-m (50 and 75-ft) depths, the distance required was 0.36 n. miles. Tenfold dilution distances tended to be shorter in the well-mixed waters of the late winter and early spring (0.17 n. miles in December at 15 m (50 ft). In these cases the dye was transported vertically; although the concentrations were low, some of the dye-contaminated water reached the surface. A distance for tenfold dilution of 0.59 n. miles observed in October was the slowest dilution rate found in the study at the 15-m (50-ft) depth. During times when Port Valdez was stratified, the dye plume dispersed horizontally in a layer not more than 2-3 m thick. The dye plume under these conditions developed along the 15-m contour in a northeasterly or northwesterly direction for ebb and flood tide, respectively. Except in the winter, dye dispensed at a depth of 15 m (50 ft) or greater did not pass behind Saw Island. During well-mixed winter conditions, the dye plume developed more randomly and was found at all depths.

including the surface; much of it then passed behind Saw Island. The period for maximum productivity (spring) in Port Valdez corresponded with the period of stratification; thus the surface euphotic zone in which primary production occurs would be relatively lower in hydrocarbon contaminants during this period of maximum growth.

There is no practical evidence or theoretical basis for expecting that petroleum contaminants added to the water through ballast outfall would accumulate in the water column over those levels achieved by the initial dilution. Even though the change of direction of the currents may carry waters that once received hydrocarbons back past the outfall, the contaminant concentration in these waters after a tidal excursion would be several orders of magnitude less than it was originally at the outfall site, due to the turbulent diffusion processes operating. Since the Port is homogeneously mixed horizontally and flushed fairly rapidly, it appears that there would always be sufficient uncontaminated water available to achieve the dilution rates observed from these data.

**5 What is the best practical site for the discharge dispenser pipe to be installed?**

Three sites (1, 2 and 3 at stations 153, 158 and 157, respectively, Figure 2.1) were indicated by Alyeska Pipeline Service Company as locations suitable for construction of a ballast-outfall diffuser. Dye dispersion studies, together with current meter data, indicated that the site at station 153 had the highest current velocities and somewhat better dispersion rates than the other locations. It was found that dispersion was rapid at 15-23 m (50-75 ft) at these locations and that in summer the dye plume which developed from injections at these depths took the shape of an expanding disc in the horizontal plane, thus minimizing surface-water contamination. In the winter when vertical mixing became effective, a tenfold dilution occurred in shorter distances from the discharge point than at other times of the year.

**6 What is the excursion range of pH, alkalinity and total carbon dioxide?**

Near-surface waters of Port Valdez reached a minimum pH value of 8.10 in December and a maximum value of 8.86 in July; the bottom waters reached values as low as 7.96 during the winter. Alkalinity values ranged from 1.69-2.20 mM in the surface waters during May 1971 to values of 2.16-2.28 mM in December. Total carbon dioxide, which is closely related to alkalinity, showed a similar distribution with values as low as 0.72 mM found in the summer associated with fresh-water runoff.

**7 What is the oxygen distribution; what is the extent of oxygen depletion and the probability of low oxygen values resulting from the ballast treatment outfall in the water column, at the sediment water interface and in the sediments?**

Oxygen values were uniformly high in the surface waters throughout the year. During periods of high plant productivity, oxygen reached values as high as 8.0 ml/liter. In winter the surface values were about 6.5 ml/liter. Bottom water of the Port reached its minimum annual oxygen concentration in the winter. Values <5.0 ml/liter were never found in the Valdez Narrows or Port Valdez. A minimum of 5.5 ml/liter was found in the deep water of Port Valdez.

The depletion of oxygen in Port Valdez incurred by oxidation of proposed levels of petroleum hydrocarbons released in the ballast-water treatment plant effluent would be very small. Based on the physical parameters measured during this study and the density profiles observed, it is clear that Port Valdez water undergoes thorough horizontal mixing. Assuming that as much as 8 barrels per day of petroleum hydrocarbons is added in the ballast water effluent and is mixed only into a layer of water 3 m thick throughout the Port with no oxygen-input flushing or biodegradation occurring, the maximum concentration of hydrocarbons can be easily calculated. Since the area of Port Valdez is  $1 \times 10^8 \text{ m}^2$ , the volume of water in a layer 3 m thick would be about  $3 \times 10^8 \text{ m}^3$  or  $3 \times 10^{11}$  liters. Eight 42-gallon barrels of oil per day is equivalent to  $3.65 \times 10^8 \text{ g/yr}$ , to give a hydrocarbon concentration of about 1.2 ppm (mg/liter).

To oxidize the hydrocarbons, about 1.8 mg of oxygen per liter would be required; therefore, the oxygen concentration in the 3-m layer of water would be lowered from 6.5 ml (4.7 mg/liter) to 4.0 ml (3.0 mg/liter). Even under all these unrealistic circumstances, there would still be relatively high values of oxygen in the contaminated layer of water.

If vertical mixing to the bottom were allowed to occur in the model as it did under actual conditions (March 1972), the oxygen depletion would only be 0.03 ml/liter. Considering the fact that oxygen is derived from the atmosphere and photosynthesis and that the Port does flush into Prince William Sound, there appears to be little reason for concern over oxygen depletion in the water column due to hydrocarbon input from the ballast treatment facility.

The sediment-water interface is in contact with high levels of oxygen and is oxygenated; if oxygen were not depleted from the water column, it would not be depleted at the sediment surface. Beneath the surface the sediments are usually low in oxygen under natural conditions. The question of oxygen-sediment relations is covered in Chapter 1 of this study, in which the nature of the bottom sediments is discussed more specifically.

**B What are the variations in nutrients on a seasonal basis; what are their source and rate of regeneration; what are their spatial variations?**

The inorganic nutrients include organic nitrogen (ammonia, nitrite and nitrate), dissolved inorganic phosphate (mostly in the form of monohydrogen phosphoric acid), and soluble silica (in the form of monomeric silicic acid) needed by diatoms. All are required for photosynthetic production of organic matter in the sea. The study showed that concentrations of all these nutrients, except for ammonia, reached a maximum in March after the Port waters had become completely mixed vertically and before the light, temperature and density conditions were yet appropriate for phytoplankton growth. In April, when the waters began to stratify due to surface heating from solar energy input, the spring phytoplankton bloom occurred. By early May the surface water were depleted of nutrients to very low values (0.02  $\mu\text{g-atoms nitrate-N/liter}$ ), except near areas of fresh-water addition by rivers, and they remained low until fall mixing occurred in October. Winter values reached 1.6  $\mu\text{g-atoms phosphate-P/liter}$ , 35  $\mu\text{g-atoms silica-Si/liter}$  and 25  $\mu\text{g-atoms nitrate-N/liter}$ . Ammonium which is produced by metabolic processes, was high in summer (1.5  $\mu\text{g-atoms N/liter}$ ) and low in the winter (0.5  $\mu\text{g-atoms N/liter}$ ).

Horizontal variability in nutrient concentrations below a depth of 20-30 m within the Port system was minimal during the summer months. The surface water concentrations were variable and depended heavily on primary productivity. Nitrate distribution in May showed the lowest values ( $0.4 \mu\text{g-atoms N/liter}$ ) in Port Valdez Narrows and the highest values ( $2.5 \mu\text{g-atoms N/liter}$ ) near the eastern end of Port Valdez, caused probably by lower productivity resulting from high sediment load and from nitrate input from the fresh-water streams.

Nutrients were continuously regenerated in the water column through the digestive processes of grazing organisms and by bacterial action. Although regeneration of nutrients occurred in the euphotic zone during the summer months and supported some phytoplankton growth, major nutrient regeneration occurred below the euphotic zone, causing the accumulation of nutrients which led to the high values typically found in deeper waters of the sea.

**9 What are the phytoplankton growth-limiting factors in this system?**

The phytoplankton bloom that occurred in Port Valdez in April lowered all the inorganic nutrients to values approaching those which limit growth. This condition persisted throughout the summer until fall mixing occurred. It is not clear from the data which of the nutrients were controlling growth. It is likely, however, that the available silicate would control diatom growth at the end of the bloom in April. Winter growth was limited by light, by lack of stability in the water column and possibly by temperature as well.

**10 What are the levels, distribution and seasonal variability of primary productivity; what is the relative importance of benthic and pelagic plants to total productivity?**

Primary productivity reached its maximum value in late April and early May, at which time carbon fixation values as high as  $175 \text{ mg C/m}^2\text{-hour}$  were measured. The winter productivity was low with values of  $0\text{-}2 \text{ mg C/m}^2\text{-hour}$  observed. The average annual production in Port Valdez was about  $150 \text{ g C/m}^2\text{-year}$ , with a range from  $116\text{-}213 \text{ g C/m}^2\text{-year}$ . Daily rates during the spring bloom of up to  $4 \text{ g C/m}^2\text{-day}$  approached the daily rates reported for the most productive marine phytoplankton crops known.

Spring and summer studies of chlorophyll *a* and productivity showed that the Port Valdez waters supported photosynthesis at the level of  $50\text{-}100 \text{ mg C/m}^2\text{-hr}$  in May and only  $2\text{-}14 \text{ mg C/m}^2\text{-hr}$  in July. The difference was attributable in part to the result of turbid fresh-water input that limited light penetration to the upper meter or two of the surface. In much of the Port, therefore, an adequate environment for high production existed only during that period of the year when nutrient concentration was high, when light became sufficient, when water stratification was established and when input of turbid fresh water was minimal. Conversely, the Valdez Arm maintained high rates of production ( $40\text{-}60 \text{ mg C/m}^2\text{-hr}$ ) throughout the summer.

Benthic plants are of minor importance (estimated  $<1$  percent contribution) to productivity in Port Valdez. The stands of submerged macrophytes were usually found on relatively steep beaches, where they provided food, shelter and substrate for a host of marine organisms. Saw Mill Bay, Jack Bay, Galena Bay and Valdez Narrows had relatively large stocks of submerged macrophytes that would be expected to be of major importance to the marine community in those areas.

- 11 What kinds of phytoplankton are responsible for the productivity; what is their distribution and seasonal abundance?**

The spring phytoplankton bloom was composed mainly of diatom species (*Thalassiosira nordenskioldii*, *Chaetoceros debilis*, *Fragilariopsis* sp., *Skeletonema costatum*); however, the chrysophyte *Phaeocystis pouchetii* and choanoflagellate *Monosiga marina* by far represented the greatest number of cells.

The spring diatom bloom in April and May was followed by a summer population composed primarily of small flagellates. Later in the fall dinoflagellates of the genera *Peridinium* and *Ceratium* were predominant.

An unexpected yeast-like organism was found in some of the samples. This organism was especially abundant in Galena Bay at the 1-percent light level in May of 1971, but it was found also at Jackson Point in Port Valdez. Its identification and metabolic behavior are yet to be investigated.

- 12 What kinds of zooplankton exist and how are they associated with the phytoplankton species; what is their seasonal distribution?**

Forty categories of large zooplankton, including 30 genera, were found in samples obtained in vertical hauls taken in Port Valdez, Valdez Arm and contiguous embayments. Calanoid copepods, as expected, contributed the largest number of species of any taxonomic group. Sampling design did not permit a rigorous statistical evaluation of seasonal difference; however, it is suggested by the data that the copepods *Calanus plumchsis* and *C. sp. n.* were numerically most abundant in the spring. During fall and winter, copepods *Metridia lucens* and *M. okhotensis*, along with the chaetognath *Sagitta elegans*, were more abundant. The euphasiid *Thysanoessa raschii* occurred in abundance only in the summer in Galena Bay and Port Valdez. The kinds of organisms found at Jackson Point were about the same as those in other parts of the Port Valdez system. *Calanus sp. n.* and *Metridia lucens* dominated in the summer and winter, respectively. The data on zooplankton were not complete enough to support conclusions concerning the kinds of zooplankton that were associated with specific phytoplankton species.

- 13 What is the present hydrocarbon content of representative water biota and sediments?**

The water in Port Valdez was found to have values of <0.1 ppb for normal paraffin hydrocarbons. Recent sediments were found to contain 0.5-2.5 ppm saturated hydrocarbons, and 0.5-1.9 ppm were measured in the biota. These values are comparable with those found elsewhere in areas of low hydrocarbon exposure.

- 14 How toxic is Prudhoe Bay crude oil to indigenous phytoplankton; what is the toxicity of ballast-treated effluents to these same organisms?**

Prudhoe Bay crude oil was examined in several different kinds of experiments to determine its effects on the photosynthetic ability of indigenous phytoplankton found in the Port Valdez system. Photosynthetic production was measured by the radioactive carbon-14 isotopic technique now recommended by workers in the field as the most acceptable for work in the natural marine area. Under natural light and temperature conditions, the indigenous population of Port Valdez phytoplankton showed 50-percent inhibition to photosynthesis at a fresh crude oil concentration of 2.0 ppm in a 4-hour test in June. At crude oil levels of between 0.05 and 0.2 ppm, little effect was seen in

this preliminary experiment, whereas concentrations  $<0.015$  ppm stimulated growth of these organisms. Experiments made under identical conditions in which treated ballast water containing 5.5 ppm Prudhoe Bay crude oil showed little inhibition to photosynthesis. The reasons for the differences between these results appear to be due to losses of both low-molecular weight and aromatic hydrocarbons during the ballast treatment process. A detailed chemical analysis of the compounds present in each test material has been made by D. Johnson of ESSO Production Research Company, Houston, Texas.

- 15 Will low concentrations of crude oil affect the succession of phytoplankton species; or, how will crude oil affect the species composition of indigenous phytoplankton populations; what is the effect on productivity of prolonged exposure to low concentrations of crude oil; what is the effect of environmental temperature and light intensity on toxicity of oil to phytoplankton?**

Preliminary experiments showed that low concentrations of crude oil (0.005 ppm) stimulate the productivity of a mixed population of indigenous organisms, posing the question of species specificity of this effect. Using control and oil-treated seawater samples under natural light conditions, the species composition was compared after a period of 48-hour incubation. The results indicated that the reaction to oil contamination is different for each organism found in the experimental water. Crude oil depressed to varying degrees the growth of *Chaetoceros* spp., *Nitzschia* sp., *Thalassiosira nordenskiöldii* and a small unidentified pennate diatom. Conversely, the oil appeared to stimulate growth in *Nitzschia closterium* and some unidentified flagellates.

Short-term experiments designed to determine the effect of a toxin on organisms are often misleading, caused largely by the induction time required for organisms to adjust to any change in their environment. In one preliminary experiment with a duration of 14 hours, the organisms exposed to about 3 ppm crude oil appeared to recover from photosynthetic inhibition after about 10 hours and showed growth in excess of that of the controls.

The inhibition of indigenous phytoplankton when exposed to crude oil in the 2.5 ppm range was greater with increasing temperature from 5 to 20°C in the early spring. In late spring, a temperature increase enhanced photosynthesis in oil-contaminated cultures but did so to a lesser degree than in the controls. The differences were due probably to temperature adaptation of the organisms or to a change in the composition of the photosynthesizing species. Under the conditions studied, however, the higher the temperatures the more photosynthesis was inhibited by the presence of oil.

The effect of light intensity on the toxicity of crude oil was examined in an experiment conducted during the April 1972 spring phytoplankton bloom. Seawater samples collected from 2.5 m and exposed to water containing Prudhoe Bay oil showed greater inhibition at high light intensities. At 25 percent of solar incident energy, even 50-percent crude-oil saturated seawater showed little inhibition to phytoplankton growth; at the 100-percent light level, a 60-percent reduction was observed. The 25-percent light level occurred at 3.5 m depth at the time of this experiment, indicating the advantages of dispersing the ballast water well below the sea surface to minimize the adverse effect of high light intensities.

**16 What is the effect of Prudhoe Bay crude oil on the macrophytes of the area?**

Macrophytes in Port Valdez are important habitat features of the littoral and upper sublittoral regions of the Port and constitute a significant segment of the marine ecosystem. Preliminary experiments show a varied photosynthetic response among the species examined when exposed to low concentrations of crude oil. The species *Alaria tenuifolia*, *Fucus distichus* and *Costaria costata* showed no significant effects in water saturated with Prudhoe Bay crude oil; *Laminaria saccharina* and *Ulva fenestrata* showed limited inhibition to photosynthesis at 100-percent saturation, *Ulva* as well as *Alaria* showed considerable stimulation when exposed at the 10-percent saturation level. In one test with *Enteromorpha intestinalis*, a 95-percent reduction in oxygen production (photosynthesis) was noted at 100-percent crude-oil concentration. These data indicate that the macrophytes have variable sensitivity to crude oil exposure, but none of those tested over an oil concentration gradient were affected adversely by concentrations of about 0.01 ppm.

**17 What is the population of hydrocarbon-utilizing organisms?**

Using the conventional plate-counting technique for estimating bacterial populations and a new technique based on oil slick disruption developed in this study, the number of hydrocarbon-utilizing organisms in a liter of Port Valdez water and sediments was estimated. In May 1971 water samples at stations 110, 130 and 147 (Figure 2.1) showed that hydrocarbon-utilizing bacteria were more abundant at the surface (3.0 cells/ml) than at depth (0.5 cells/ml from 10-50 m), whereas the October 1971 the numbers were more uniform with depth (0.5 cells/ml) but did not show the high surface populations. Experiments using a seawater inoculum to test for ability to break oil slicks provided a means to estimate the minimum amount of seawater that contained organisms capable of causing the formation of oil-water emulsions from a surface slick. In nearly all samples examined, an inoculum of 1 or 10 ml of seawater effectively removed the slick during a period of 45 days at 10C. Based on the data obtained in this study, Port Valdez waters contain between 500-3000 cells/liter hydrocarbon-utilizing bacteria. Since cell numbers are usually a function of substrate concentrations, the chronic addition of crude oil to the Port would tend to increase the hydrocarbon-utilizing organisms. This is apparently true for Cook Inlet, in that higher cell numbers are observed in areas where continuous addition of oil has occurred.

**18 What is the rate of hydrocarbon biodegradation under *in situ* conditions?**

Biodegradation experiments were made *in situ* in Port Valdez, utilizing radioactive <sup>14</sup>C-labeled dodecane as the hydrocarbon source in order to estimate the rate of crude oil decomposition. An average rate of 1 µg/liter-day was observed at station 153 at a depth of 10 m over a period of 35 days. This rate is clear indication that the hydrocarbon fraction which reaches the Port water undergoes heterotrophic microbial attack.

**19 What is the toxicity of oil to indigenous micro-organisms; which fractions are most toxic?**

There are three primary mechanisms by which oil has been shown to be toxic to micro-organisms. One results from the coalescence of organisms with oil droplets to change their microenvironment to an oil phase rather than the usual aqueous phase. A second major response is to hydrocarbons in the C<sub>5</sub> - C<sub>8</sub> range when present in concentrations approaching aqueous saturation, or third, to aromatic hydrocarbons such as toluene or naphthalene.

Toxicity to micro-organisms was determined by the inhibition of oil additions to the active transport system of continuous cultures of the marine yeast *Rhodotorula rubra*. It was found that saturated aqueous solutions of pentane, cyclohexane, benzene, toluene, xylene and naphthalene all inhibited membrane transport in varying degrees when added alone to cultures. No response was found with crude oil additions, however, indicating probably that the mole fraction of the toxic components in the Prudhoe Bay crude oil was insufficient to result in the dissolved aqueous concentrations being high enough to cause major disorientation of the membrane. Similar results were obtained using the fresh-water alga *Selenastrum capricornutum* in which case the continuous alga culture was not perturbed by crude-oil components as they exist in solution when the aqueous growth medium is in equilibrium with the many compounds present in the oil phase.

**20 What is the rate of degradation of the tars and other high-molecular weight material?**

Tar, which results from removal of the volatile fractions from crude oil, is often found after long exposure on beaches, in sediments and even in wide distribution as tar balls reported in the Atlantic Ocean. An experiment conducted on the biodegradation rate of lumps of tar showed slow oxidation with a half life of a year or more when protected from surface weathering. In the sediments tar would be well preserved, since physical fractionation, aerobic oxidation and presence of hydrocarbon-utilizing organisms are at a minimum under these conditions.

**21 What is the distribution and abundance of infauna benthic organisms; what is their diversity; which organisms might best be used for monitoring?**

Two hundred and ten species of benthic organisms were collected and identified from Port Valdez. The *Biologically Important Species* (BIS) were selected based on four criteria: representation in 50 percent of the total stations sampled, comprised over 10 percent of the composite population or 10 percent of biomass collected at any one station; its population density was significant at any given station. The BIS listing is presented in Chapter 9, (text 9.4.1 and Table 9.3).

Only nine species were found to be ubiquitous in Port Valdez: *Lumbrineris similabris*, *Prionospio malmgreni*, *Eudorella emarginata*, *Tharyx monilaris*, *Nephtys ciliata*, *Heteromastus filiformis*, *Axinopsis serricata*, *Chaetoderma robusta*, and *Cylichna attonsa*. Only the latter five of these were classified as *Biologically Important Species*.

Monitoring programs for Port Valdez should be especially directed toward detecting changes in the diversity of species with special emphasis on the significant changes in numbers, growth rates and general health of the *Biologically Important Species*.

**22 What is the nature of the sediments, the size distribution patterns, and the rate of sedimentation; can any effect of the Great Alaskan Earthquake of 1964 be identified?**

Three major units of surficial deposits are recognized in Port Valdez. (1) The inshore sediments at the mouth of the Lowe River, Valdez Glacier Stream, Sawmill Creek and sediments in Valdez Narrows are mixtures of silt, sand and gravel; (2) an elongated narrow area extending west-northwest and east-southeast from the head of the inlet to Mineral Creek and Gold Creek is covered with fine to very fine silt; and (3) the predominant unit covering the rest of Port Valdez consists of coarse clay. The size distribution patterns are shown in Figures 1.8 to 1.10.

A profile of cores taken in an east-west direction gave evidence (Figure 1.32) for eight cyclic layers thought to represent annual sediment layers overlying graded sediments derived apparently from the 1964 Alaskan earthquake. The sediments originating at the head of the Inlet during the 1964 slump were deposited at the mouth of Valdez Channel, thus forming Valdez Fan II.

Based on evidence obtained during these studies, all the suspended sediments entering Port Valdez are deposited within the Port.

An average sedimentation rate of 1.67 cm/yr for Port Valdez has been calculated for Port Valdez assuming that all of the  $2.26 \times 10^6$  metric tons of river load sediments are deposited uniformly over the Port. Because of the sediment distribution, however, this rate may be as high as 3.0 cm/year in the eastern third of the Port.

### **23 What is the distribution of suspended sediments in the Port?**

Suspended sediments derived from the major rivers and streams are typically carried into the Port in a 2-10 m surface layer of relatively low-salinity water overlying denser, higher-salinity water. The spatial distribution of these suspended sediments is effected by amount of river input (fresh-water hydraulic head), tides, winds and water dispersion. A typical distribution of surface suspended sediments observed in summer of 1972 showed a well defined plume originating from the Lowe River and Valdez Glacier Stream at the head of the Port. Along the southern shore this plume extended westward to Fort Liscum and extended westward on the north shore to merge with the plume from Mineral Creek. The combined plume then continued west, terminating about 1-2 km west of Gold Creek. A small plume originating in Shoup Bay entered the northwest corner of the Port and tended to move along the western coastline as it passed out of the Narrows.

### **24 What is the relationship between distribution of benthic organisms and the nature of the bottom sediments in which they are found?**

Investigations have revealed the animal-sediment relationships of two specific clastic sedimentary environments in Port Valdez. Hydrodynamics control the distribution and deposition of most detritus introduced into Port Valdez. The area east of Jackson Point consists of bedload and suspended sediments brought in by rivers; the western half of Port Valdez is covered by clayey sediments. Significant differences in percentage composition of the different taxonomic groups in two sedimentary environments are apparent. Nonselective detritus-feeder polychaetes are more abundant in the eastern half of the Port. During summer a continuous rain of sediments provides a better habitat for this group. Crustaceans are more abundant in the western half of Port Valdez, where the rate of sedimentation is relatively low and the inflow of clear ocean water is high. This trend indicates that both the number of species and the number of individual crustaceans decrease with increased turbidity in the water column and mud deposition, the opposite case being true for the polychaetes. Work is currently underway to develop fauna-sediment relationships, the results of which will be published.

**25 What is the maximum concentration that hydrocarbons can reach in the water; what is the probable concentration?**

The maximum concentration of hydrocarbons that can be reached in Port Valdez from the ballast treatment plant can be calculated if certain conservative assumptions are made, as follows. The system flushes at least every 100 days. (The computed value for winter flushing was found to be 40 days); the oil disperses horizontally and sufficiently rapidly so as to prevent pocketing of contaminated water patches (all physical data indicated rapid horizontal dispersion); the vertical mixing from the point of injection to the surface occurs completely in the same order of time as the flushing rate (this certainly occurs within hours in the winter and also reasonably fast under wind stress in the summer).

Assuming a discharge rate of  $1 \times 10^6$  g of oil in ballast water each day, or  $1.1 \times 10^8$  g in 100 days, and the volume of the top 25 m of Port Valdez is  $25 \times 10^8$  m<sup>3</sup> or  $2.5 \times 10^{12}$  liters, then  $4.4 \times 10^{-5}$  g/liter, or 44 ppb, would be the maximum concentration in Port Valdez resulting from the ballast water discharge.

The above computation does not include enhanced flushing through tidal entrainment, mixing of surface water with bottom water, and it neglects biodegradation, adsorption, volatilization and other factors which would reduce the concentration of oil. Biodegradation alone has been found to decompose  $3 \times 10^{-7}$  g/liter-day. The  $2.5 \times 10^{12}$  liters in the upper 25 m alone would decompose  $0.8 \times 10^6$  g of hydrocarbon each day or about the same amount as added from the ballast water. Since biodegradation is not light-dependent and is slowed in high nutrient waters only by lower temperatures, this process would continue at about the same rate throughout the year.

Considering these factors, it seems reasonable to expect that the hydrocarbon content of Port Valdez water would not reach values in excess of a few parts per billion as a result of the ballast water effluent.

**26 What is the probable maximum distance that hydrocarbon levels found inhibitory to indigenous organisms will persist near the outfall?**

There appears to be no data that indicate a deleterious effect due to Prudhoe Bay crude oil hydrocarbons at values of less than 0.05 ppm. Using this minimal value as a target concentration in the vicinity of Jackson Point, the following computations may be made.

The dispersion rates measured at location 1 near Jackson Point showed that a tenfold dilution of an added contaminant occurred at a maximum distance of 0.60 n. miles from the point of injection. The ballast treatment plant is designed to produce effluent water of <10 ppm oil. If this were placed in the bay with no effort to disperse it, it would require about 15 n. miles to reach a concentration of 0.05 ppm. Under the poorest dilution conditions measured in the dye experiments, concentrations of oil >0.05 ppm would develop in an east-northeast or west-northwest direction, depending on the tide, but would not exceed an excursion distance of 1.5 n. miles. The high concentrations would be at a centerline in the plume, which would dilute laterally to ambient concentration at some distance from the center.

Reduced toxicity of the oil, as occurs by ballast water treatment according to data obtained in these studies, or reduction of the total amount of oil in the effluent through such treatment would lead to a much smaller field of contamination that may be deleterious to photosynthesizing organisms.

**27 What dilution of ballast water should be sought through engineering design of ballast water diffusers?**

Engineering technology will permit the dispersion of water from an outfall to a high dilution by forcing the effluent through specially designed nozzles into the seawater. Uncontaminated water would then be entrained, giving rapid dilution of the wastes within a few feet of the outfall. A 100-fold dilution a short distance from the outfall would allow the effective concentration reaching the environment to be 0.1 ppm or less, depending on the level of treatment in the ballast water plant. A disperser of the 100-fold dilution type, coupled with lower toxicity of the crude oil in ballast water over Prudhoe Bay crude oil (5.5 ppm treated ballast water equivalent to 0.67 ppm crude oil) would lead to an operation in which the oil level reaching a distance of more than a few feet would be less than that found to be affective to phytoplankton photosynthesis. The oil discharge from the ballast treatment plant would then be expected to have little effect on the primary productivity of Port Valdez.

*While a complete response to many of the questions posed above is not possible from the results of a one-year study, important insights have been gained towards a better understanding of the complex problems involved.*

*It is not the intent of this section to make recommendations for future research or monitoring of actual effects of the oil terminal operations. Such a plan should logically develop from full consideration of the data presented in this report in association with information available through other agencies such as the National Marine Fisheries Service, Alaska Department of Fish and Game, Environmental Protection Agency, Bureau of Land Management, Alaska State Department of Environmental Conservation, U. S. Geological Survey, Alaska State Geological Survey, U.S. Weather Bureau, National Oceanographic and Atmospheric Administration (other than NMFS), U.S. Army Corps of Engineers, and Battelle Northwest. Private industry and other interests likewise hold concern and responsibilities for the area and its development.*

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THE R/V ACONA UNDERWAY



captain on bridge





first mate



cook

seaman



CREW OF R/V ACONA

chief engineer



