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DISTRIBUTION OF DISSOLVED AND PARTICULATE ORGANIC CARBON IN ALASKAN POLAR, SUB-POLAR AND ESTUARINE WATERS

A

DISSERTATION

Presented to the Faculty of the
University of Alaska in Partial Fulfillment
of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By

Theodore C. Loder, III, A. B., M. S.

College, Alaska

May 1971

DISTRIBUTION OF DISSOLVED AND PARTICULATE ORGANIC CARBON IN ALASKAN POLAR, SUB-POLAR AND ESTUARINE WATERS

APPROVED:

John J Goering

Robert J Barsdate

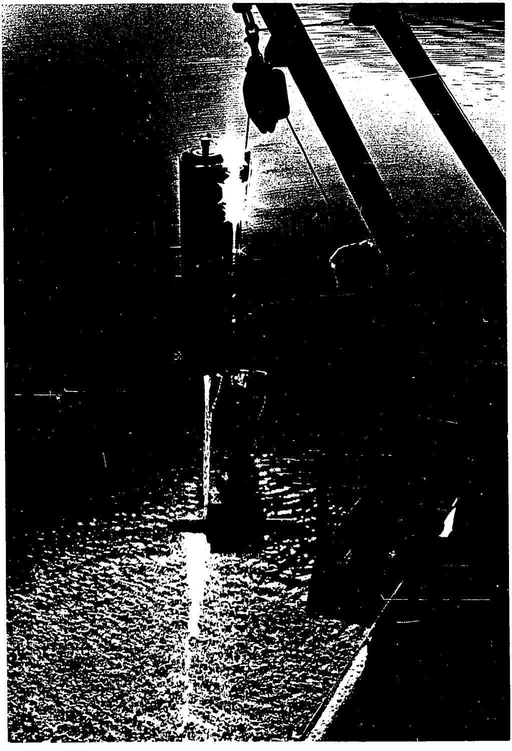
Daniel B. Hawkins

D Warren Smith

Donald W Hood
Chairman and Department Head

Date May 15, 1971

Vice President for Research and Advanced Study



Frontispiece

The early morning sun sparkles on the still waters of Endicott Arm as a 30 liter Niskin bottle is emptied.

ABSTRACT

The distribution and significance of particulate (POC) and dissolved (DOC) organic carbon were determined in six areas of Alaskan waters including: Southeast Alaska, Cook Inlet, Kodiak Island shelf, southeast Bering Sea - Unimak Pass, Bering Strait - Chukchi Sea, and the Arctic Ocean. Support data for most of the samples included: particulate nitrogen (PN), particulate matter, inorganic nutrients and hydrographic data.

The highest POC values (∿100 - several 1000 μg C/liter) were found in glacial inlets and Cook Inlet. High values (∿200 - ∿1000 μg C/liter) were also found near Kodiak Island and in the Bering and Chukchi Seas in localized areas. Low values (20 - 50 μg C/liter) were found in Southeast Alaska in the winter; the lowest values (2 - 14 μg C/liter) were found in the Arctic Ocean. Nearly all DOC values were between 0.5 and 2.0 mg C/liter. A few Cook Inlet values were greater than 2 mg C/liter and glacial runoff values were less than 0.5 mg C/liter.

Principal component (factor) analysis was used to determine the relationships of POC and DOC to other chemical and hydrographic parameters in several areas. DOC correlated poorly with all parameters except in the Chukchi Sea area-where there was a high positive correlation with POC, PN, and dissolved oxygen overall, but a very low correlation with these parameters in phytoplankton blooms. POC correlated well with different parameters such as salinity, DOC, and PN depending on the area. In general, however, the values of POC and DOC correlated poorly with other oceanographic parameters because they are the end results of complex biological and physical interactions.

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Mr. Frank J. O'Hara designed and helped build the raft used for the beginning work in North Dawes Inlet. Mrs. Gulser G. Wood helped collect and process samples in North Dawes. Miss Kathy L. Kendrick helped with calculations and key punching and Mrs. Judith Henshaw drew most of the figures. Captain Kenneth R. Turner and the crew of the R/V Acona provided able assistance in procuring samples as did Mr. Peter Nice, Captain of the Maybeso, and the crew of the USCGC Northwind. I also thank the other members of the Institute of Marine Science both faculty and staff who have helped in matters big and small concerned with the completion of this work.

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INTRODUCTION

I.1. Summary of recent work

Organic matter in sea water is mainly derived from the decomposition of marine organisms and the excretion of various compounds by living organisms. Other sources such as diffusion from sediments on the sea floor and wind-borne terrestrial material add only minor amounts of organic matter (Hood 1963 and Riley 1970). Water-borne terrestrial material, mainly humic substances, may add considerable amounts of organic matter to near shore water (Breger 1970), but areas where this occurs represent less than 1% of the world oceans (Riley 1970).

Since the late 1950s there has been a great increase in the studies of organic matter in sea water. Although the photosynthetic origin of organic matter is reasonably well known, the ultimate fate is only partially understood. Recent reviews by Parsons (1963), Hood (1963, 1966 and 1970), Wangersky (1965), Duursma (1965), Wagner (1969), Williams (1969b) and Riley (1970) have summarized both historical and recent work on the distribution and role of organic matter is sea water.

Historically Natterer (1892-1894) was one of the first investigators to report the presence of organic matter in sea water and found about 2 mg of dissolved organic matter per liter in the near surface water of the open sea (from Duursma 1965). Pütter (1909) suggested that dissolved organic matter was a main source of food for many marine animals, but Krogh (1934) found this not to be the case. By the late 1950s, due to the increasing use of chromatographic techniques, a number of individual organic compounds had been identified in sea water (Vallentyne 1957). Duursma (1961) published the first major study on the distribution of dissolved organic matter in sea water based on his studies of the North Atlantic.

Since it is relatively easy to measure, organic carbon is generally used as an indication of the amount of total organic matter present in sea water. Its use makes data comparison easier because organic matter is of such variable composition. Dissolved organic carbon (referred to as DOC) can be defined theoretically as "all the biogenic carbon compounds in true solution in sea water" (Barber 1967); particulate organic carbon (referred to as POC) could be defined as all biogenic carbon compounds not in true solution in sea water. However, DOC is usually defined on the basis of the physical techniques used to remove the particulate organic matter from the water. Early definitions included not precipitatable at a pH of 1 in 24 hours, not readily separated by centrifugation and not coprecipitated with aluminum hydroxide (Hood 1966) or aluminum sulfate (Skopintsev, Romenskaya and Sokolova 1968).

Today DOC is considered to be the amount of carbon in organic matter which passes through a filter: either a very fine glass-fiber filter (Gelman, Type A or Whatman GF/C with a nominal pore size of 0.3-1.0 µ), a silver membrane filter of varying porosities (Selas Flotronics 0.5, 0.8 or 1.2 µ pore size) or a cellulose ester membrane filter (0.45-μ Millipore). Sheldon and Sutcliffe (1969) reported that filters of a stated pore size often retain a large percentage of particles smaller than the stated range. Consequently, the lower size limit for particulate organic matter is between 0.25 and 1 μ. Thus DOC includes the organic carbon in organic matter in true solution as well as colloidal material and particles up to about 0.5 μ in size. The upper size limit is generally 0.5-2 mm and excludes zooplankton which in this study were either removed by prefiltering the sample through 125-μ stainless steel mesh or removing the zooplankton from the filter with forceps.

One of the major problems which beset early workers in analyzing DOC was the presence of about 35 g/liter of inorganic salts which interfered with the accurate analysis of a few mg/liter of organic matter. These problems were partially solved by the introduction of wet combustion methods by Parsons and Strickland (1959) and Duursma (1961), but the analysis still required considerable time per sample. Rapid determination of POC and DOC in sea water became possible when the persulfate oxidation in sealed glass ampoules method was developed by Menzel and Vaccaro (1964) and Fredericks and Hood (1965). This permitted the running of a large number of samples for determining the general distribution and significance of organic carbon in the world oceans. Szekielka (1967a) reviewed the development of analytical techniques, and recent papers by Holm-Hansen et. al. (1967), Strickland and Parsons (1968), P. J. LeB. Williams (1969), Ehrhardt (1969) and Gordon (1969) discuss some of the problems and modification of the methods.

There have been a number of studies on the distribution of both DOC and POC in the world's oceans. Some in the Atlantic Ocean include work by Duursma (1961), Menzel and Ryther (1964), Riley, Wangersky and Van Hemert (1964), Riley, Van Hemert and Wangersky (1965), Skopintsev, Romenskaya and Sokolova (1968), Menzel and Ryther (1968), Hobson and Menzel (1969) and Gordon (1970a, b). Some Pacific Ocean studies have been done by Holm-Hansen, Strickland and Williams (1966), Hobson (1967), Barber (1967), Holm-Hansen (1969), Nakajima (1969) and Gordon (1970c). Work in the Indian Ocean has included Menzel (1964), Starikova (1967), Szekielda (1967), Newell and Kerr (1968) and Newell (1969).

There is general agreement among most of the authors cited as to the concentrations of DOC and POC both near the ocean surface and at depth with two exceptions: (1) The DOC results of Skopintsev and co-workers are several times higher than found by other workers although their range of variations is similar. They use dry combustion of an evaporated sample. (2) There has been a trend toward finding smaller amounts of POC in the deep sea than was earlier reported; this is probably due to more careful sample preparation, larger samples and more precise methods.

From surface to about 300 m (100-400 m) the DOC concentration is about 1.0 mg C/liter (range 0.3-2.0) and the POC concentration is about 100 μg C/liter (range 30-300). In dense plankton blooms, however, DOC values may temporarily reach 3-5 mg C/liter and POC values 1000-2000 μg C/liter. Below this surface zone DOC values are relatively constant with an average of 0.5 mg C/liter (range 0.2-0.8 mg C/liter) and POC values averaging about 10 μg C/liter (range 2-30 μg C/liter).

The composition of the deep water particulate organic matter appears to be mainly carbohydrates and proteinaceous material (Parsons and Strickland 1962, Gordon 1970a and Handa 1970). There have been conflicting reports as to the nutritional value of this material. Menzel and Goering (1966) found that particulate organic matter is uniformly resistant to biological decomposition while Gordon (1968) found that 19-26% of the material (mostly protein could be removed with a mixture of digestive enzymes. Lorenzen (1968) found that although Artemia nauplii did not survive feeding on concentrated deep water particulate organic matter, nevertheless, 43% of the POC was lost when concentrated and allowed to sit for 90 days at 20C in the dark. Deep water zooplankton do ingest organic aggregates (G. Harding, personal communication 1970), but whether or not they digest them is unknown.

In the surface layers the particulate organic matter consists mainly of detritus from the death of organisms and organic aggregates described by Riley (1963, 1970). Living matter only contributes about 10% of the total. The ratio of DOC/POC ranges from about 3-10 in the surface layers to 200-300 for some deep water (Chapter VII). The deep water average is about 50 (Williams 1969b).

Dissolved organic matter appears to have small portions (< 20%) of the following compounds present: amino acids (free and combined)

(Degens 1970, Pocklington 1970); sugars (free) (Handa 1970); fatty acids and hydrocarbons (Jeffrey 1970, Blumer 1970); urea (free) (Degens 1970); as well as smaller amounts of aromatics (substituted phenols); and vitamins (Natarajan 1968). The amount of these compounds present in the near surface waters is quite variable because of changes in biological activity involving both uptake and liberation of extracellular products and decomposition (Parsons and Seki 1970). Both Williams (1969b) and Degens (1970) feel that these compounds make up only a small per cent (10-25) of the total amount of DOC. Based on low C/N ratios reported by several workers, Degens (1970) proposed that most of the remaining dissolved organic material is in the form of "heteropolycondensates", a clathrate-type molecular structure. Williams (1969b), however, suggests that the remaining material is "humus" or "lignin-type" material and is refractory to microbial and chemical oxidiation. Barber (1968) found that bacteria would not utilize this DOC from deep water even when it was five-fold concentrated.

Duursma (1961, 1965) and later Menzel and Ryther (1968, 1970) have suggested that DOC in deep waters appears to be a conservative property and can therefore be used to trace water masses. Menzel and Ryther (1968) concluded from their study of the Antarctic Intermediate Water that oxygen concentrations observed in the water as it moved north were a function of mixing and not oxidation of entrapped organic matter. They suggest that dissolved organic matter is conservative in nature once water masses sink below the surface and the organic matter cycling is almost entirely restricted to relatively shallow surface water. However, their mixing theory does not explain how average differences of 0.35-0.70 mg C/liter or more are maintained at depth.

Carbon-14 dating and stable isotope studies (carbon-13: carbon-12 ratios) have provided further insight into organic carbon in sea water and its age. Williams and Gordon (1970) reported that the range of $^{13}C/^{12}C$ ratios for both POC and DOC was between -22.0 and -24.4°/₀₀ relative to the PDB_1 standard, meaning the carbon is relatively depleted in ^{13}C. They found that the ratios are constant with depth, sample location and time in the northeast Pacific. In addition they reported that the ratios found for both DOC and POC most closely approximate the cellulose and "lignin" fractions of surface plankton and concluded that particulate organic matter is similar in composition to dissolved organic matter. Williams, Oeschger and Kinney (1969) have reported an average age of 3400 yrs. (b.p.) for the total organic matter in 2 samples taken at 2000 m off southern California using carbon-14 dating techniques. This value is almost twice that of inorganic carbon suggesting different input and utilization pathways for the two fractions.

With the concept of the inert nature of sea water organics in mind, a review of other evidence suggests that rather than being totally inert, a portion of organic material at depth is in dynamic equilibrium. There are a number of problems that are unanswered by Menzel, Williams and their co-workers. Some of these include the seasonal and spatial variation of POC and DOC in the sea (Hobson 1967, Menzel 1964 and Gordon 1970a,c), and the possible DOC to POC transformation and subsequent role as a food source for deep sea filter feeders.

The role of DOC to POC transformations is still not well understood although it is generally accepted that under the proper conditions particulate organic matter does form from part of the dissolved fraction. Baylor, Sutcliffe and Hirschfeld (1962) found that phosphate adsorbed to bubbles passing through sea water. The next year Baylor and Sutcliffe (1963) found that cultures of Artemia could survive on particles produced by the bubbling of sea water. Sutcliffe, Baylor and Menzel (1963) suggested this process might be associated with Langmuir circulation and be a source of organic food particles in the sea. Riley, Van Hemert and Wangersky (1965) found that particles could be produced by bubbling both surface and deep water from the Sargasso Sea although deep water produced fewer particles.

Menzel (1966) in re-evaluating bubbling found by using ignited and filtered air and 3-times-filtered sea water, that bubbling is not a likely mechanism for the production of carbon containing particles. Barber (1966) reported that he was unable to produce significant particulate carbon by bubbling sea water "sterilized" by filtration through 0.22-μ filters and concluded bacteria played a role in particle formation. Batoosingh, Riley and Keshwar (1969) explained these apparent contradictions with a set of very carefully controlled experiments. They found that small particles (0.22-1.2 μ in size) are important as nuclei in formation of larger particles during the bubbling process and that the concentration of particles inhibits further formation until particles are removed. Thus it appears that entrapment of bubbles near the sea surface may play an important role in production of organic particles suitable for food for the small grazing organisms. However, this does not provide particles for the deep sea.

Riley, Van Hemert and Wangersky (1965) proposed that there is a dynamic balance between utilization of particles and further adsorption from the filterable fraction. Sheldon, Evelyn and Parsons (1967) and Parson and Seki (1970) describe the formation of particles and the possible role of bacteria in particle formation and enlargement by bacterial clumping. Khaylov and Finenko (1968) found that dissolved high-molecular weight compounds are sorbed onto detritus, broken down by enzymatic-hydrolysis and then utilized by bacteria populating the detritus. This would move dissolved organic matter into the particulate phase and make it available to filter feeding organisms. The role of adsorption of organic molecules by inorganic particles has been shown by several workers (Bader, Hood and Smith 1960, Chave 1965, 1970 and Degens and Matheja 1967), but the extent of their importance in particle formation is unknown. These then are some of the problems concerning the relationship of DOC to POC.

Several theories have been suggested concerning the source of food for deep living zooplankton: 1) Non-living particulate organic material may settle slowly out of the euphotic zone and provide a continuous supply of food material. 2) Migrating zooplankton populations may utilize food materials above them in the water column and in turn are eaten by organisms below them in a series of overlapping food chains (Vinogradov 1962). 3) Detrital organic matter, some of which originates in the euphotic zone, settles in the water column in a state of dynamic equilibrium with the dissolved organic matter through a series of interactions perhaps mediated by heterotrophic microorganisms and/or physical adsorption (Riley, Wangersky and Van Hemert 1964, Sheldon, Evelyn and Parsons 1967, and Riley 1963, 1970). 4) High concentrations of particulate matter may exist at various depths perhaps at discontinuity layers for short periods of time providing a concentrated food source (Parsons and Seki 1970). Since data has been found to support all of these theories to a certain extent, I suggest that the actual mechanisms are a combination of some or all of these theories with the amount of food contributed by each mechanism still unknown.

Several recent studies on the role of POC and DOC in sea water may help in our understanding of the very complex role played by organic matter. Organisms may release natural organic chelators which are necessary for increased phytoplankton growth (Barber and Ryther 1969). Surface charge studies on organic particles may give insight into aggregate formation (Wangersky 1968). Studies on the release of dissolved organic matter by both phytoplankton (Anderson and Zeutschel 1970) and zooplankton (Johannes and Webb 1970) suggest additional sources of DOC. The work on the ATP content of sea water

(Holm-Hansen 1970) gives an estimate of biomass. This then is a review of some of the history and recent work done toward a fuller understanding of the role of particulate and dissolved organic matter in sea water.

I.2. Purpose of this study

Prior to this study no work had been done on the distribution of organic carbon in polar and sub-polar waters around Alaska. In addition, the significance of DOC and POC as chemical parameters in sea water was only partly understood. Consequently this study was undertaken to determine the distributions of DOC and POC in Alaskan waters and compare them with distributions in other areas of the world as well as determine their significance relative to: particulate nitrogen (referred to as PN), total suspended or particulate matter (referred to as PM), the inorganic nutrients, and hydrographic parameters. To analyze some of the data I chose principal component (factor) analysis, a technique of interpreting data that prior to this study had not been used for oceanographic data. Finally a detailed study of organic matter in glacial inlets was carried out to determine the role of clay-organic matter relationships in a natural environment unpolluted by man.

The data used in this study were collected on 14 cruises in six major areas of Alaskan waters (Table 1.1). The general locations of these areas are shown in Fig. 1.1 except for Ice Island T-3 which is shown in Fig. 7.1. Station location data for nearly all stations are given in the appendix.

Table 1.1. Cruises used in this study

Cruise Number	Ship	Area Studied	Date	Station Numbers	Samples Prepared By:	Number of Sample Locations	Number of Carbon Samples
027	R/V Acona	Unimak Pass	07/24-08/10/66	701-741	Loder	20	83
030	"	S. E. Alaska	11/4-18/66	807-881	Verhagen	8	32
031	"	Endicott Arm	11/26-30/66	888-896	Loder	9	27
032	"	S. E. Alaska	02/12-24/67	905-995	Short	10	30
045	"	Kodiak I.	06/21-30/67	1364-1444	Loder	25	57
---	Maybeso	North Dawes	07/17-23/67	ND-1-ND-5	Loder	5	12
053	R/V Acona	North Dawes Endicott Arm	09/17-21/67	ND-1-ND-6	Loder	7	22
056		S. E. Alaska	11/13-18/67	1986-2013	Loder	19	22
065	"	Cook Inlet	05/21-30/68	2242-2296	Groves	11	23
751	USCGC Northwind	Chukchi Sea	07/27-08/01/68	CC-1-CC-25	Loder	18	38
074	R/V Acona	Glacier Bay	09/17-20/68	2639-2646	Loder	5	10
075	R/V Acona	North Dawes Endicott Arm	09/23-27/68	2648-2659	Loder	13	25
703	Ice Island T-3	Arctic Ocean	03/29-04/06/68		Kinney	1	9
704	Ice Island T-3	Arctic Ocean	04/30-05/08/68		Loder	1	10

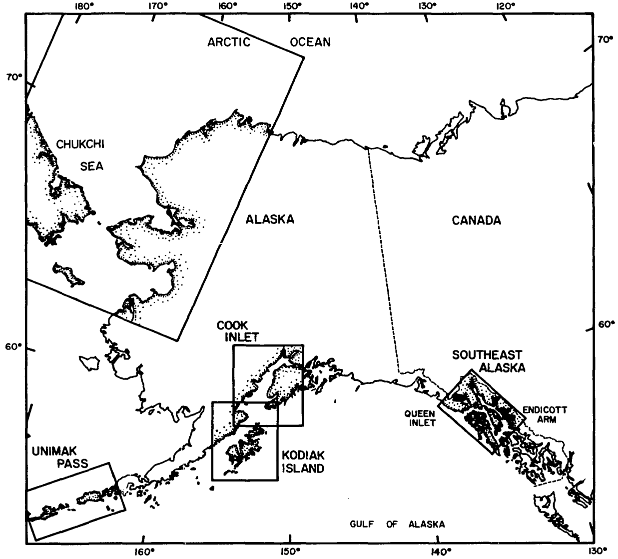

Fig. 1.1. Alaska map showing study areas.

Chapter II

EXPERIMENTAL METHODS (FIELD)

Chapter II

EXPERIMENTAL METHODS (FIELD)

Procedures used in collecting and preparing samples for POC, DOC, PN, PM, nutrients, and oxygen analyses are described in this chapter. These procedures were carried out in the field as soon as practical after samples were collected. Some nutrient analyses and all oxygen analyses were completed at this time.

II.1. Organic Carbon Samples

Water samples for organic carbon analysis were collected with Nansen bottles, large volume samplers, and pumps. The Nansen bottles were used on cruises 030 and 032 early in the study and were replaced because of the possibility of contamination. A large volume (10 liter) glass and Teflon sampler, designed by Dr. David Menzel of Woods Hole Oceanographic Institute, was used for cruises 027, 031, and 045. A 5 liter polyvinylchloride (PVC) sampler (CM^2 Model 806) was used on cruises 074 and 075. With the exception of surface layer samples in North Dawes, Queen and Reid Inlets, the remainder of the water samples were collected with a 30 liter PVC sampler (CM^2 Model 808). The samplers were rinsed by flushing up and down on the hydro wire prior to sampling.

Water samples from surface layers in North Dawes, Queen and Reid Inlets were collected with an onboard pump attached to a plastic garden hose lowered to the desired level. Using this system it was possible to obtain samples from a few centimeters to several meters below the surface. A Jabsco pump (20 liters/min) was used during the July and September, 1967 North Dawes cruises. It was replaced with an easier to prime Vanton Flexiliner pump (20 liters/min) for the September, 1968 cruise. To purge the pump and hose of contamination, water was pumped for several hours prior to sampling. A comparison of the 5 liter PVC sampler and the pumping system was made (Table 2.1). The PM and C/N ratios are similar indicating little or no contamination. The slight variations of DOC, POC and PN may be due to different sampling times and/or analytical errors.

The collected water was stored in glass bottles or polyethylene Cubitainers prior to processing. Mercuric chloride was added (final concentration $\simeq$ 10 ppm Hg^{++}) to retard biological activity in samples stored for more than one hour. The bottles were cleaned with hot chromic acid at the start of the cruise and rinsed with distilled water between samples. The Cubitainers were cleaned with hot soap and water, acid rinsed and soaked with sea water for a day prior to use. There were no significant changes in DOC due to storage in different containers (Table 2.2).

Three methods of filtration were used. On cruise 027 samples were filtered by vacuum ($\simeq$50 cm Hg) through a one inch glass-fiber filter (Reeve Angel 984-H) in a Gelman plastic filter holder. On later cruises (030, 032, 045, 046, 053, 056, and 751) a pressure system was utilized. The sample was placed in a stainless steel

Table 2.1. Comparison of sampling methods on 5 m sample, EN-25, September 24, 1968

Sample Method	DOC (µg/liter)	POC (µg/liter)	PN (µg/liter)	PM (mg/liter)	C/N
Flexiliner pump	0.81	15	1.88	0.94	8.0
PVC sampler	0.87	21	2.54	0.93	8.3

Table 2.2. Effect of storage on POC concentrations

Location	Date collected	Container	Time stored	DOC (mg/liter)
North Dawes River	9-26-68	Cubitainer	2-3 hr	0.24
North Dawes River	9-26-68	Cubitainer	4 d	0.24
En-15, 5m*	9-23-68	glass	1-2 hr	0.92
En-15, 5m*	9-23-68	glass	12 hr	0.91
En-20, 5m*	9-23-68	glass	1-2 hr	0.83
En-20, 5m*	9-23-68	glass	12 hr	0.89

* filtered sample

pressure tube and pushed at 13 lbs/in^2 through two 25-mm filters. On the remainder of the cruises the samples were filtered by vacuum (∿50 cm Hg) through two 47-mm glass-fiber filters (Gelman, Type A) in a glass Millipore filter holder. Prior to sampling all filters were heated to 475C for 4 hours or more and stored in plastic Millipore petri dishes.

The amount of water filtered depended on the amounts of suspended material present and ranged from 100-200 ml in silt and clay laden waters of glacial inlets and Cook Inlet to 2000-4000 ml for deep water in the Arctic Ocean. For most "normal" samples 500-1000 ml were filtered.

Each filter was rolled and inserted in a 10 ml glass ampoule (Kimble-Neutraglas) which had been baked at 575C for 4 or more hours and stored top to top connected by a short piece of clean Tygon tubing. Approximately 0.1g $K_2S_2O_8$ and 0.25 ml H_3PO_4 (3%) were added to each ampoule. In addition 5 ml of organic free distilled water or filtrate were added to provide a liquid necessary for oxidation.

After flushing for 5 minutes with purified oxygen the ampoules were sealed using an apparatus built by Mr. Alan D. Fredericks of Texas A & M University.

For DOC determinations, 5 ml of the filtrate were added to an ampoule with the above reagents, flushed and sealed. DOC samples were prepared in quadruplicate; POC in duplicate or triplicate. The above method is described in more detail by Menzel and Vaccaro (1964), Fredericks and Hood (1965) and more recently by Strickland and Parsons

(1968). Details on blank determinations and the laboratory procedures are in section III.1.1.

Filters for the POC determinations by the dry combustion method were prepared by filtering 0.2-1.0 liters (for cruises 074 and 075) or 8-16 liters (for cruise 704) through precombusted 47-mm Gelman Type A glass-fiber filters. The filters were dried at 30-40C over anhydrous $CaCl_2$ or silica gel and stored in plastic dishes. No attempt was made to remove carbonates on the cruise 704 samples as there is very little contribution of CO_2 from carbonates in open ocean carbon samples (Newell and Kerr 1968). However, the cruise 075 samples were acid treated with 10 ml of approximately 5% HCl which was sucked through the sample and filter to remove any readily soluble carbonates. There was a slight loss in carbon content as shown in Table 2.3.

Table 2.3. Loss of measured carbon content due to acid treatment on POC samples analyzed by the dry combustion method

Sample Location	Depth	POC (no acid) (μg/liter)	POC (acid) (μg/liter)	Loss (%)
North Dawes River 10/24/68	surf.	651	612	6
ND-4 10/25/68	2 m	145	120	17

II.2. Particulate Nitrogen Samples

Water samples for particulate nitrogen analysis were collected using either the large water samplers or pumping system described in section II.1. Various amounts of water (1-2 liters in glacial inlets, 3-6 liters in coastal waters, and 26-52 liters for the Arctic Ocean (T-3)) were filtered through 47-mm glass-fiber filters (Reeve Angel 984-H or Gelman, Type A). These were dried and stored in glassine envelopes or plastic dishes.

II.3. Particulate Matter

Water samples for total particulate matter (suspended load) were collected using either the large water samplers or pumping system described in section II.1. Measured amounts (0.2-26.0 liters) of the sample were filtered through carefully washed and tared HA Millipore filters (0.45-μ pore diam.). Ten ml of filtered distilled water were sucked through the sample to remove salts. The filters were dried and stored in plastic dishes (method of Strickland and Parsons 1968).

II.4. Transmissivity

Transmissivity profiles were run during cruise 027 using a 1 m transmissometer (Hydro Products Model 412-T) lowered to 55 m and read at 5 m intervals. The portable deck readout indicated per cent transmittance relative to 100 per cent transmittance in distilled water.

A 10 cm transmissometer (Hydro Products Model 411) was used in a similar manner in North Dawes Inlet and Endicott Arm. The values of per cent transmittance were consistant for a given profile, but because of the difficulty in standardizing the instrument between profiles different stations should be compared only in the shape of the profiles.

For cruise 027 the data are presented as:

$$\text{absorbance} = \log\left(\frac{100}{\%\ \text{transmittance}}\right)$$

In the glacial inlets data are presented as turbidity or relative % absorption (100-% transmittance).

II.5. Nutrients, Oxygen, Salinity, and Temperature

Samples for nutrient analysis were collected with Nansen bottles and analyzed on board ship or stored in 500-ml polyethylene bottles containing 1 ml of $HgCl_2$ (4%) solution until later analysis. North Dawes samples were collected by pumping and stored until analyzed. All nutrient analysis was performed by either Mr. David Wallen or Mr. Martin Arhelger of the Institute of Marine Science using methods of Wallen (1967). These methods are based on a slight modification of those of Murphy and Riley (1962) for phosphate-phosphorus; Grasshoff (1964a) for silicate-silica; Grasshoff (1964b) and Wood, Armstrong, and Richards (1967) for nitrate-nitrogen; and Bendschneider and Robinson (1952) for nitrite-nitrogen.

Salinity and dissolved oxygen samples were collected using Nansen bottles equipped with reversing thermometers. Oxygen samples were determined by a modified Winkler method (Wallen 1967). Salinity samples were stored in sealed glass bottles, returned to the laboratory and analyzed with a Hytech Model 6220 induction salinometer.

The pumped samples obtained in North Dawes, were analyzed for salinity by means of hydrometer readings on spot samples. Temperature was determined with a standard laboratory thermometer (-20 to 110C) to the nearest 0.5C.

II.6. Bottom Grab and Core Samples

Sediment samples were collected in North Dawes Inlet, Endicott Arm, and Queen Inlet. Grab samples, taken with a Shipek grab, were examined and described. Sediment cores, taken with gravity or piston corers, were stored in plastic core liners until extrusion, usually within 12 hours after collection. The cores, extruded onto aluminum foil, were measured, photographed, and described. Representative portions of the grab and core samples were sealed in plastic bags and frozen for later analysis.

Chapter III

EXPERIMENTAL METHODS (LABORATORY)

Chapter III

EXPERIMENTAL METHODS (LABORATORY)

III.1. Sample Analysis

This section describes the laboratory methods used to analyze samples collected and prepared in the field. The carbon methods are discussed in detail because of the controversial nature of some of the techniques. The nutrient, salinity, and oxygen methods were discussed in Chapter II and are not included here.

III.1.1. Dissolved and Particulate Organic Carbon (Wet Combustion)

The organic carbon content of the sealed ampoules (section II.1) was measured by heating the ampoule to oxidize the organic carbon and then measuring the resultant CO_2 by passing it through an infrared CO_2 analyzer. The recorded peak area was proportional to the amount of CO_2. This method was first described by Menzel and Vaccaro (1964) and later in more detail by Strickland and Parsons (1968).

Early in this study ampoules were heated to 175C for 24 hours in a steel pressure container to complete oxidation (Fredericks and Hood, 1965). I later found that heating the ampoules in an autoclave to 130C for 4 hours was adequate (section III.1.1.3).

An ampoule was prepared for analysis by placing a piece of rubber tubing (20-mm x 8-mm ID) over the neck. A flared glass tube containing a sliding "O-ring-sealed" crusher, stainless steel cannula and gas outflow tube was placed tightly against the rubber tubing on the ampoule neck. The enclosed space above the ampoule was flushed with CO_2-free nitrogen and the infrared analyzer zeroed. The gas flow was turned off, the tip of the ampoule crushed, and the cannula pushed into the ampoule. The nitrogen was turned on and the ampoule flushed at exactly 250 ml per minute. The gas was passed through Anhydrone ($Mg(ClO_4)_2$) to remove water vapor and then into a Beckman infrared analyzer (Model IR215) with 10 inch cells. A Sargent recorder (Model SR) equipped with a Disc integrator recorded the sample peaks. An average sample required 1-2 minutes to pass through the system and 20-24 ampoules could be run per hour for DOC samples; 16-20 for POC samples. A flow meter was attached to the outflow of the IR analyzer. The ampoule crushing and flushing apparatus was designed and built by Mr. Alan D. Fredericks of Texas A&M University.

Although Menzel and Vaccaro (1964) suggest the use of a KI-sulfuric acid solution to remove chlorine gas produced during the oxidation of sea water samples, I did not find this necessary. Menzel no longer uses the KI solution since the chlorine gas has no effect on the IR readings (personal communication 1969).

For DOC samples the recorder scale was adjusted using a variable potentiometer so that full scale deflection was approximately equivalent to 3 mg C/liter in the standard or 15 μg carbon in the ampoule. For POC samples the full scale deflection was equivalent to about 1000 μg C in the ampoule.

III.1.1.1. Standard Dextrose Solutions

"Organic free water" necessary for the preparation of carbon standards was made in 3 liter batches by adding $K_2S_2O_8$ and H_3PO_4 to double distilled water, refluxing and distilling. This water contained less than 0.1 mg C/liter when analyzed by the persulfate oxidation method using standard additions of dextrose.

The carbon standards were prepared by dilution of a standard dextrose solution (200 mg C/liter) to the desired carbon concentration. DOC standard ampoules were prepared with $K_2S_2O_8$ and H_3PO_4 reagents and 5 ml of water containing the equivalent of 0.0, 0.2, 0.5, 0.75, 1.0, 1.5, 2.0, and 3.0 mg C/liter. Most or all of these concentrations were used to determine a calibration curve. The peak area vs. carbon concentrations were plotted on linear graph paper to determine a reagents plus water blank. This blank had an equivalent value of 0.29 mg C/liter (for a group of standards prepared in March 1969) based on the 5 ml sample. This blank value was added to the carbon concentration values and the calibration curve was plotted (Fig. 3.1). The calibration curve was checked daily while running the DOC ampoules and did not change significantly.

Standards for POC analysis were prepared as above except that carbon concentrations were 0.75, 1.0, 3.0, 4.0, 5.0, 7.0, 10, 15, 20, 30, 40, 50, 75, 100, 150, and 200 mg C/liter. Unlike the nearly linear DOC curve, the POC calibration curve was nearly logrithmic and plotted on a log-log graph (Fig. 3.2). The POC calibration curve was recalculated daily with dextrose standards because of small daily changes. (< 6%).

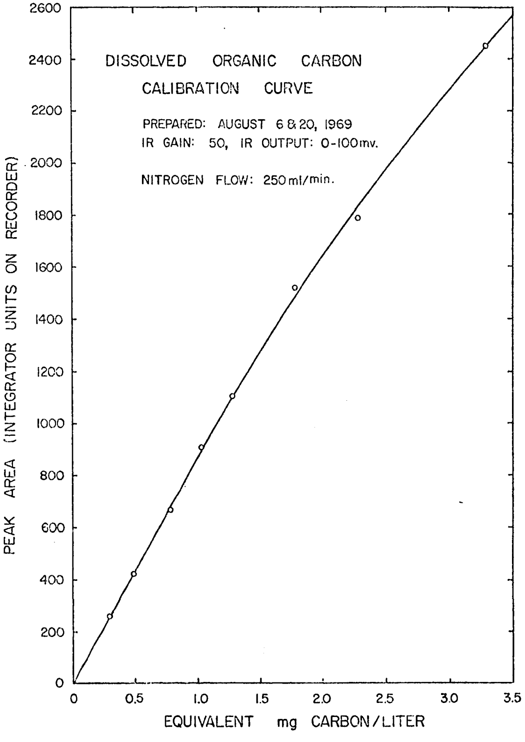

Fig. 3.1. Calibration curve for dissolved organic carbon samples.

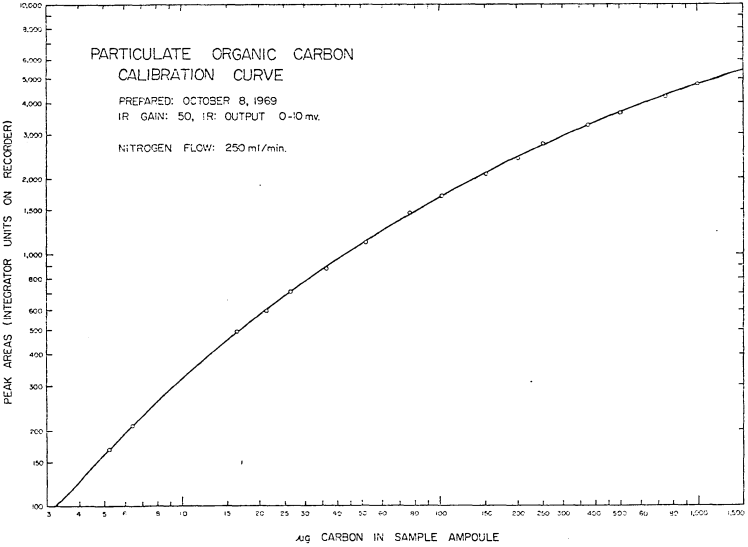

Fig. 3.2. Calibration curve for particulate organic carbon samples (wet oxidation).

III.1.1.2. Reagent Blanks

The determination of an accurate reagent blank is a major factor in the accuracy of the wet combustion carbon method. The usual method, suggested by Menzel and Vaccaro (1964), is to make duplicate or triplicate determinations on different amounts of low carbon sea water. The amounts of carbon obtained are plotted against ml of sample and the curve extrapolated to zero. The values obtained may range from 0.15 mg C/liter (Strickland and Parsons 1968) to 1.00 mg C/liter or more (Table 3.1). The high values for reagent blanks were found on samples collected early in this study and not analyzed for over two years. The low value reagent blanks were found on recently collected samples and analyzed in a few months to one year. These results may be due to the length of storage of the ampuoles or improvement in the analytical technique.

Another method of determining the reagent blank is to place just the reagents themselves (0.1g $K_2S_2O_8$ and 0.25ml H_3PO_4 (3%)) in the ampoule and process normally. This results in a reagent blank slightly lower than that obtained by the first method. For example: 0.29 mg C/liter vs. 0.37 mg C/liter for the cruise 751 data. Perhaps the presence of the water increases the reagent blank because of its solvent properties.

Two experiments were run investigating the reagent blank problem. In the first, 24 ampoules were prepared with normal reagents in the first six, twice normal in the second six, and up to 4 times normal in the last six ampoules. These were heated to 130C for 4 hours and analyzed for CO_2 in the normal manner.

Table 3.1. Values of reagent blank carbon in equivalent mg C/liter reported by different authors

Author	Reagent Blank Equivalent to mg C/liter
Menzel and Vaccaro (1964)	0.52-0.54
Fredericks (1968)	0.22
Strickland and Parsons (1968)	0.15-0.30
Loder (this study)	
Total range	0.25-1.09
4 recent reagent blanks	0.31 (ave.)
4 old reagent blanks	0.82 (ave.)

Table 3.2. Reagent blank experiment 1. Result of increased amounts of normal reagents

Ampoule contents	Total carbon in ampoule* equivalent to mg C/liter
1 x normal reagents ≠	0.33 ± 0.03
2 x normal reagents	0.35 ± 0.02
3 x normal reagents	0.38 ± 0.03
4 x normal reagents	0.44 ± 0.04

* Data are from two series of tests.

≠ Normal reagents are 0.1 g $K_2S_2O_8$ and 0.25 ml H_3PO_4 (3%).

Instead of the blanks doubling with double the reagents, they increased only by about 10% indicating that the reagents themselves contribute only a small part of the reagent blank value (Table 3.2). Since the $K_2S_2O_8$ was not recrystallized as suggested by Strickland and Parsons (1968), this step appears to be unnecessary.

The results of a second experiment suggest that most of the reagent blank CO_2 comes from the glass ampoule itself (Table 3.3). The reagent blank, determined by extrapolation, was 0.29 mg C/liter. Approximately 0.17 mg C/liter was obtained with only acid and water in the ampoule. By using ampoules boiled in 50% H_3PO_4 the amount of CO_2 released with water and acid was reduced. When just $K_2S_2O_8$ was added to water in an acid treated ampoule only 0.23 mg C/liter equivalents were produced. The sum of these last two values is 0.40 mg C/liter which is nearly the same as the equivalent 0.38 mg C/liter obtained with normal oxidation procedures.

Thus it appears that a large fraction of the reagent blank is due to the releasing of CO_2 either physically or chemically bound on the surface of the glass ampoule. Since the amount of carbon involved is on the order of 1-3 μg, this possibility is not unlikely.

III.1.1.3. Ampoule Combustion Temperature and Time

Potassium persulfate in aqueous solution undergoes slow decomposition at room temperature and complete rapid decomposition at 100C (The Merck Index 1960) producing a very strong oxidizer, the

Table 3.3. Reagent blank experiment 2. Determination of the source of reagent blank carbon in glass ampuoles

Ampoule contents	Autoclave 130C, 4 hours	Total carbon equivalent to mg C/liter*
5 ml DH_2O**, normal reagents†	yes	0.38 ± 0.01
4 ml DH_2O, normal reagents†	yes	0.35 ± 0.01
3 ml DH_2O, normal reagents†	yes	0.30 ± 0.02
2 ml DH_2O, normal reagents†	yes	0.33 ± 0.03
1 ml DH_2O, normal reagents†	yes	0.31 ± 0.01
empty ampoule, flushed with oxygen	no	0.01
5 ml DH_2O, 0.25 ml H_3PO_4 (3%)	no	0.06 ± 0.03
5 ml DH_2O, 0.25 ml H_3PO_4 (3%)	yes	0.17 ± 0.12
5 ml DH_2O, 0.25 ml H_3PO_4 (3%)‡	yes	0.08 ± 0.04
5 ml DH_2O, 0.1 g $K_2S_2O_8$‡	yes	0.23 ± 0.02

* Three to six replicates per determination.

** All DH_2O in this table is "organic free distilled water".

† Data used to determine normal reagent blank equivalent to 0.29 mg C/liter

‡ After normal precombustion these ampoules were boiled in 50% H_3PO_4 and rinsed with organic free water.

oxygen radical (O^+). Various authors recommend combustion temperatures and times ranging from 100C for 2.5 hours to 175C for 24 hours (Table 3.4).

I used a temperature-time combination of 175C for 24 hours early in this study, but after several tests (Table 3.5) decided to use 130C for 4 hours. This combination seemed to oxidize as much carbon as the higher temperature and was more convenient.

III.1.1.4. Filter Blanks

The method of determining a filter blank for POC analysis is highly controversial. Menzel (1966, 1967) suggests that both glass-fiber filters and silver filters adsorb a small amount of carbon (20-40 µg for 47-mm filters) from the dissolved organic fraction, thus adding to the value of POC reported. I also have found (by the method described below) adsorption onto glass-fiber filters (25-mm) ranging from 0-10 µg C/filter in glacial inlets and deep water to almost 35 µg C/filter in areas of high productivity.

Menzel (1967) suggests that the amounts adsorbed are a function of differential adsorption of specific dissolved organic compounds. He found no adsorption for deep water samples. Perhaps the adsorbed materials are compounds produced near the surface in association with the production of particulate organic matter. Most other authors, except for Fredericks (1968), do not take the adsorption effect into account in reporting POC data.

Instead of filtering different volumes of water and extrapolating to determine the adsorbed carbon (Menzel 1966), I filtered

Table 3.4. Temperature-time combinations recommended by various authors for oxidation of seawater with $K_2S_2O_8$ in glass ampoules

Author	Temperature	Time
Williams (1969)	100C	2.5 hr
Menzel and Vaccaro (1964)	130C	30 min
Holm-Hansen et al. (1967)	130C	40 min
Strickland and Parsons (1968)	130C	40 min
Fredericks and Hood (1965)	175C	16 hr
Fredericks (personal communication, 1967)	175C	24 hr
Loder (this study)	175C	24 hr
Loder (this study)	130C	4 hr

Table 3.5. Effect of oxidation time-temperature variations on amount of carbon (peak areas) in identical seawater samples. Samples collected near Point Retreat, Chatham Straits, S.E. Alaska on July 7, 1967. All ampoules analyzed on February 22, 1968

Oxidation time and temperature	Number of samples	Average Peak area	Sample variation
1 hr, 130 C	6	1135	± 1.9%
4 hr, 130 C	5	1187	± 4.7 %
12 hr, 175 C	6	1207	± 1.9 %
24 hr, 175 C	6	1191	± 5.7 %
48 hr, 175 C	5	1303	± 6.0 %

the sample through two filters placed in a single filter holder. The value of carbon on the bottom or second filter was subtracted from the top filter value to obtain the POC value for the sample. This was repeated for each sample since the filter blank varied, the highest occurring in high DOC, POC water. A criticism of this method is that the carbon value of the second filter is due only to the passage of particulate matter through the top filter and entrapment on the second filter (G. A. Riley, personal communication, 1969). Thus the adsorbed carbon would be only a function of the particulate carbon in the sample. Although this may be partly true, several experiments I have conducted indicate that the carbon value for the bottom filter is more a function of the water type than POC concentration.

In the first experiment, a closed filtering system was used to filter (vacuum ∿ 35 cm) water from different areas through 5 glass-fiber filters (Gelman, Type A, 47-mm, precombusted at 475C for 5 hours). The experiment was repeated on the same water and water from different areas. The filters were dried at 40C and their carbon content analyzed using the dry combustion method (section III.1.1.6). The carbon content of a blank filter (∿ 3μg) was subtracted from each filter value. In all cases the carbon value of the first filter was high and filters 2-5 were low and nearly equal to each other for a given water type (Fig. 3.3). Since the amount of filter carbon did not decrease significantly from filter 2 to 5, it appears that the carbon on those filters may be adsorbed from

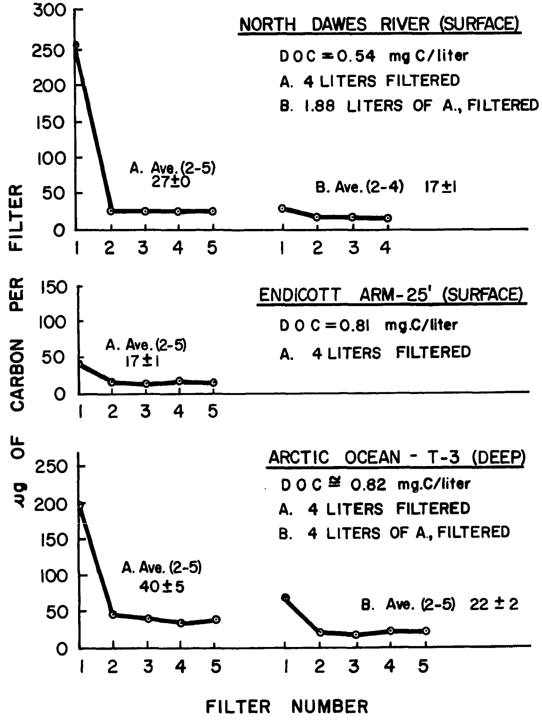

Fig. 3.3. Filter adsorption experiment 1 showing amount of carbon adsorbed to stacked filters after filtering water from different locations.

the dissolved fraction and not from the particulate fraction. Filters 2-5 had different carbon values for water from different areas, ranging from an average of 17 ± 1 to 40 ± 5 μg C/liter for the 4 filters. When the filtered water was refiltered through a second set of filters, a lower 2-5 filter carbon average was obtained. Conclusions suggested by this experiment are: 1. Waters of different origin may contain a variety of adsorbable organic compounds in different concentrations. 2. The amount of organic carbon a filter can adsorb may be limited. 3. The amount of organic adsorption is probably concentration dependent.

In the second experiment, using cruise 751 data, total carbon in the ampoule containing the bottom filter (BFC) was correlated with the total carbon in the top filter ampoule (TFC) and with the DOC content of the water filtered (Table 3.6). Although not significant at the 95% confidence level, there was both a higher correlation coefficient for BFC and TPC than for BFC and DOC as well as a slightly higher intercept value for BFC and TFC (Fig. 3.4a and 3.4b). This suggests that perhaps in the surface waters where high POC values result from high biological activity, the "adsorbed carbon" values obtained may also include a small fraction of the particulate material.

Generally, adsorbed carbon will have a small effect on the final POC value reported, lowering the uncorrected value by less than 6% except in surface waters with low POC values. In deep water with very low POC values, such as 2-9 μg C/liter in the Arctic Ocean (cruise 704), an adsorbed carbon value of 2-3 μg C/liter has lowered

Table 3.6. Linear correlation coefficients for filter adsorption experiment 2

	Bottom filter carbon (BFC)	Top filter carbon (TFC)	DOC
BFC	1.000	0.620	0.516
TFC	0.620	1.000	0.710
DOC	0.516	0.710	1.000

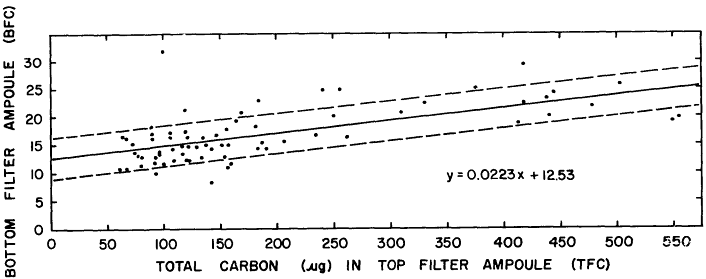

Fig. 3.4a. Filter adsorption experiment 2. TFC vs. BFC for cruise 751 data.

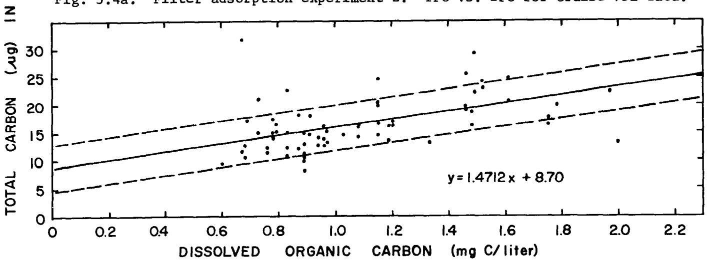

Fig. 3.4b. Filter adsorption experiment 2. DOC vs. BFC for cruise 751 data.

the final POC value by as much as 30-50%.

All POC data in this study except for cruise 027 had an adsorbed carbon blank subtracted. Thus the values are slightly lower than data of some other authors.

III.1.1.5. Precision and Accuracy

Both precision and accuracy of DOC and POC data are a matter of concern if the data of various authors are to be meaningfully compared. Menzel and Vaccaro (1964) reported a precision of ± 0.1 mg C/liter for their DOC method. In spite of more recent reports of greater precision (less than ± 0.06 mg C/liter by Strickland and Parsons (1968) and ± 5% by Fredericks (1968)) Menzel still feels that ± 0.1 mg C/liter is the best precision attainable on natural samples (personal communication, 1969).

I found that greater precision was possible with distilled or fresh-water samples than with sea water samples. The variation between identical samples carefully prepared in the laboratory was on the average between ± 0.03 and ± 0.06 mg C/liter (Tables 3.3 and 3.7). Instrument variation was the equivalent of ± 0.02 mg C/liter or less (Table 3.7). However, the variation between replicate (3-4) salt water samples collected at sea was ± 0.04 to 0.2 mg C/liter or more, with an average of about ± 0.1 mg C/liter or ± 5 to 15% depending on the sample size.

The higher variations on field samples (see Table 3.8) were probably a result of non-ideal working conditions found aboard

Table 3.7. DOC contents and precision of laboratory distilled water and $KHCO_3$ standards

Water type	Number of samples	mg C/liter	Variation %
Lab distilled	5	2.10 ± 0.06***	± 3
Redistilled Lab distilled	4	1.04 ± 0.06	± 6
Distilled tap (holding jug)‡	5	0.21 ± 0.04	± 8
Distilled tap (receiving jug)	6	0.15 ± 0.03	± 6
$KHCO_3$ solution*	5 groups**	2.0 ± 0.02†	± 1.2

* 100 µl of a $KHCO_3$ solution were squirted into 5 ml of 50% H_3PO_4, and the CO_2 carried through the IR analyzer. Since the technique was reproducible, it was used to determine instrument reproducibility which was equivalent to ± 0.02 mg C/liter or better.

** Each group consisted of 3-6 separate samples.

† This value is approximate because the shape of the peak was different than those peaks produced by dextrose standards or samples.

‡ Glass distilled tap water (single distillation of laboratory tap water in Corning glass still).

*** This high value is due to the use of an organic chelator added to the steam line. University heating steam was condensed to make laboratory distilled water.

Table 3.8. Average variations for replicate DOC and POC determinations

Cruise Number	Area studied	Number of DOC samples	Average variation per sample (%)	Number of replicate POC samples	Average variation per sample (%)
027	Unimak Pass	91	± 7.8	7	± 8.7
045	Kodiak Island	54	± 6.2	31	± 5.8
751	Chukchi Sea	38	± 6.6	36	± 5.8
074 075	Glacier Bay North Dawes Endicott Arm	36	± 8.6	15*	± 4.5
704	Arctic Ocean, T-3	10	± 9.5	10	± 23

* Dry combustion method used, only 075 data reported.

most ships where crowded conditions, dust, smoke and diesel fumes provide opportunities for contamination. This is a trace analysis and at the 1 mg C/liter level, a contamination of 0.5 μg carbon is equivalent to 0.1 mg C/liter.

P. J. LeB. Williams (1969) suggested that the variation among replicate samples is due to differences in the initial rate of heating when the ampoules are combusted. Since my sea water samples prepared in the laboratory generally showed less variation between replicates than those prepared at sea and all ampoules were heated in the same manner, this possibility does not seem likely.

There are many sources of error affecting both the precision and accuracy of POC determinations. These include sampling and handling errors, filter blank determinations, and instrument error. Because the distribution of particulate matter may be somewhat nonhomogenous, <u>in situ</u> sampling errors may be quite high. Newell and Kerr (1968) report a coefficient of variation of ± 35% between sample pairs taken simultaneously with separate samplers. Gordon (1968) found no significant difference in average POC concentrations between two different types of samplers placed 15 m apart, but there was a significant difference between individual comparisons. He attributes the differences to variations in the vertical distribution of particulate organic carbon. In surface waters, particularly in glacial inlets or areas of high productivity, I have found large vertical variations in POC. Thus the POC values obtained are only approximations.

Handling errors probably account for most of the variation between replicate portions of a sample. Mixing of the sample prior to measuring, measuring of the sample, and handling of the filters can all account for variations in the final value of POC. Holm-Hansen (1969) obtained much lower POC values for deep water when he stopped using plastic containers and stopped shaking samples vigorously prior to measuring the samples for filtration. He suggested that vigorous shaking might form particulate matter from the dissolved fraction, resulting in much higher POC values. Contamination of the filter by air-borne dust is possible while the filter is being folded and placed in an ampoule or while the filter is drying.

For samples containing very low amounts of particulate organic carbon, filtering a large sample (5-20 liters) provides a more representative sample than just 1-2 liters. Also systematic errors are probably less for larger samples. This may explain why lower, but more consistant POC values for Arctic Ocean deep water were obtained with the dry combustion method (16 liters filtered) than with the wet combustion method (2-4 liters filtered).

The handling errors are difficult to estimate. For duplicate samples the average variation is less than ± 6% (Table 3.8) on large samples (>50 μg C/liter). For cruise 751, POC samples had an average variation of ± 5.8% or ± 19 μg C/liter based on 500 ml samples. Deep water POC samples (cruise 704) showed an average variation between triplicate samples of ± 23%. But the POC values ranged from only 2-9 μg/liter, so the variation was only ± 1-2 μg C/liter.

Gordon (1968) reports that his largest source of error (about ± 13.5 μg C) came from filter handling. I found the carbon content of the precombusted filters to be low, 3-6 μg C/47 mm filter and less for the 1 inch (25.4-mm) filters, having little effect on the variation between replicates.

Instrument error was less than ± 1 μg C for the wet combustion method. Instrument error for the dry combustion method is discussed in section III.1.1.6.

The accuracy of the persulfate oxidation method depends on the precision of the analysis, discussed above, and the degree of completion of oxidation. Several authors (Menzel and Vaccaro 1964; Fredericks and Hood 1965; and Holm-Hansen et al. 1967) have tested the degree of completion of oxidation. Oxidizing a known amount of an organic compound, they determined the per cent recovered as CO_2. A criticism of this technique is that the compound must be added to the water in concentrations 100 to 1000 times its natural concentration in sea water possibly affecting the kinetics of oxidation (P. J. LeB. Williams, 1969). P. J. LeB. Williams (1969) refined this method by using a radiochemical procedure in which he utilized ^{14}C labeled compounds and measured the amount of residual radioactivity left in solution after the persulfate oxidation. He oxidized various compounds at natural level concentrations and found 95-100% oxidation. Menzel and Vaccaro (1964) and Fredericks and Hood (1965) both report greater than 95% oxidation for most compounds.

The complete oxidation of fatty acids or long chain hydrocarbons still remains questionable. Fredericks and Hood (1965) found that only an average of 77% recovery was possible when they oxidized methyl-12-hydroxystearate for 1 hour at 175C. P. J. LeB. Williams (1969) obtained about 95% oxidation of linolenic acid after oxidation for 1 hour at 130C. Holm-Hansen et al. (1967) reports essentially total recovery of a mixture of cellular lipids as CO_2 by oxidation for 40 minutes at 130C.

In spite of the fact that some of the lipid fraction is not totally oxidized by the persulfate method, it generally has little effect on the final value of DOC reported for natural samples. Jeffrey (1970) reported that lipid carbon (chloroform extractable) represented only 10-20% of the total DOC in Gulf of Mexico samples. If only 80% of the lipids were oxidized in a normal sea water sample of 1.5 mg C/liter, this would mean that at the most 4% of the original DOC would remain unoxidized. This is well within the precision of the method.

Thus it appears that the oxidation of dissolved organic compounds in sea water by persulfate is greater than 95% complete. This could be verified with the use of ^{14}C labeled natural organic compounds produced by growing diatoms in ^{14}C-carbonate media. The residual radioactivity, checked by the method of P. J. LeB. Williams (1969), would provide an estimate of oxidation completion. A similar solution of labeled natural organics could be used to determine the amount of volatile dissolved organic carbon lost during the bubbling of the seawater sample prior to sealing of the ampoule (section III.1.1.1.).

P. J. LeB. Williams (1969) reports essentially no loss (0.1%) of volatile combustion products, but he used only a mixture of amino acids and a glucose solution and not sea water containing natural organics. Corwin (1970) reports that as much as 0.3 ppm of volatile hydrocarbons can be present in sea water. These volatiles may be mostly removed during the purging of the water sample to remove inorganic CO_2. Thus the volatiles would not be included in our present estimates of dissolved organic carbon.

Another method of checking the accuracy of the persulfate oxidation is to compare DOC values obtained by this method of analysis with those of another method. P. M. Williams (1969) compared the persulfate oxidation with an ultraviolet oxidation method of Armstrong et al. (1966) and Williams (1968). He found that DOC values obtained with the UV method were 0.07 mg C/liter (average of 24 samples) higher than duplicate samples run by the persulfate method. He concluded that the persulfate method is not "missing" an appreciable amount of dissolved organic carbon. I found that heating the ampoules for 4 hours instead of 1 hour oxidized about 4% more carbon (Table 3.5). Perhaps this may be why Williams using a 40 minute oxidation time found slightly less dissolved organic carbon oxidized.

Since particulate organic matter in sea water has a somewhat different composition than the dissolved organic matter, I felt it necessary to determine the degree of completion of its oxidation by the persulfate method. This was done by comparing POC values on duplicate sets of samples run by both the wet (persulfate) oxidation and dry combustion methods (section III.1.1.6). The first set of samples was collected in North Dawes Inlet and Endicott Arm (cruise 076) and included a wide range of values of POC (22-1237 μg C/liter). The average coefficient of variance between samples run by the two methods was only ± 10.6%. The values obtained by persulfate oxidation were generally slightly higher than those obtained by dry combustion (for samples with >100 μg C/liter) (Table 3.9 and Fig. 3.5). Perhaps more volatiles associated with the particulate matter are lost with the dry than the wet combustion method. This extra loss may have occurred when the filters were dried at 40C overnight prior to storage in glass vials.

For the second set of samples collected in the Arctic Ocean (cruise 704), the average coefficient of variation was ± 26% which although quite high represents only an average range between duplicates of 2.4 μg C/liter (Table 3.9). Slightly higher values were obtained with dry combustion for sample values greater than 8 μg C/liter and lower for sample values less than 4 μg C/liter. There is no apparent reason for these differences.

In spite of the errors in handling and analysis in both the persulfate and dry oxidation methods, there is sufficient agreement between values obtained on duplicate samples to indicate that the persulfate method is oxidizing essentially all of the particulate

Table 3.9. Comparison of wet oxidation (persulfate method) and dry combustion methods on duplicate particulate organic carbon samples

Cruise	Sample area	Number of samples	Range of sample values (µg C/liter)	Average variation between samples (%)	Average variation between samples (µg C/liter)	Average coefficient of variation** (%)
076	North Dawes Endicott Arm	18	22 - 1237	± 7.5	(N. A.*)	± 10.6
704	Arctic Ocean	8	2.7 - 10.7	± 18.4	(2.4)	± 26.0
	Total	26	2.7 - 1237	± 10.9	(N. A.)	± 15.3

* Not applicable because of large range of values.

**Coefficient of variation = [(Standard deviation) (100) / mean].

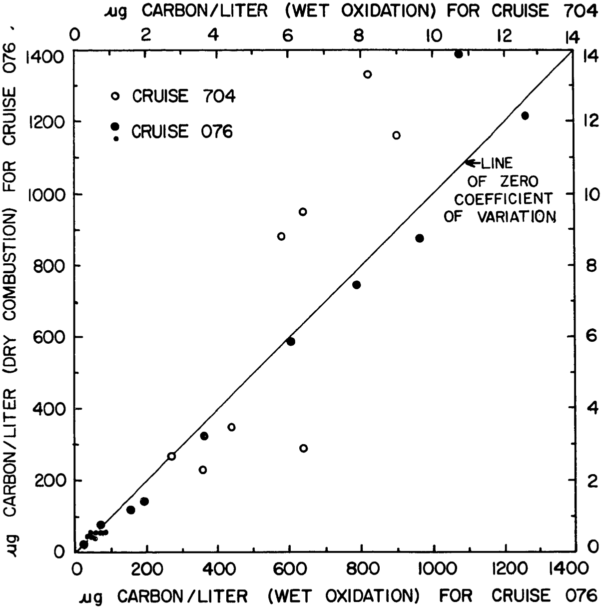

Fig. 3.5. Comparison of wet oxidation (persulfate method) and dry combustion methods on duplicate particulate organic carbon samples.

organic matter. Thus, data obtained by the two different methods are quite comparable.

The persulfate method of wet combustion is able to oxidize at least 95% of the non-volatile dissolved and particulate organic matter in natural waters giving us a good indication of the natural organic carbon levels found there.

III.1.1.6. Dry Combustion Carbon Analyzer

A dry combustion carbon analyzer utilizing high temperatures and an oxygen atmosphere to oxidize the carbon to CO_2 was built to check the accuracy of the persulfate oxidation method and determine the organic carbon content of sediments. The design was a modification of a carbon analyzer built by Dr. David W. Menzel of Woods Hole Oceanographic Institute. Fig. 3.6 is a schematic diagram and Plate 3.1 shows the completed analyzer.

Several construction features are worthy of mention. The combustion tube holder was movable in two directions allowing the tube to be moved in and out of the furnace as well as back and forth within the furnace. Two- and three-way solenoid valves (Valcor Engineering Corporation) were used for all on-off and directional flow changes. This enabled all operations except combustion tube position changes to be made from one set of switches, increasing reproducibility, reducing the possibility of stopcock breakage, and preventing the burning of the operator on the hot oven (not entirely foolproof). Finally, the analyzer was constructed on a single piece

Legend for Fig. 3.6. Schematic for dry combustion analyzer.

---

1. Valves for adjusting O_2 flow.
2. Solenoid (2-way Valcor Model P/N 61P18C2) for increasing flushing flow rate. All solenoid valves from Valcor Engineering Corporation, 365 Carnegie Ave., Kenilworth, N. J., 07033.
3. Flowmeter (0-90 ml/min).
4. Drying tube filled with Anhydrone ($Mg(ClO_4)_2$) and Indicarb to remove CO_2 from oxygen stream.
5. Movable tube support with rubber gasket, Coleman Nitrogen II Analyzer part #9486-J and coil spring #9485-J.
6. Sample placed inside quartz tubing (12-mm O.D., 10-mm I. D.).
7. Quartz wool (fine).
8. Partly ground cupric oxide, wire form.
9. Furnance (E. H. Sargent and Col., Chicago, Cat. No. S-36400).
10. Sationary tube support with rubber gasket, Coleman Nitrogen II Analyzer part #9482-J.
11. Drying tube filled with Anhydrone to remove water vapor.
12. Solenoid (3-way directional Valcor Model P/N 54P18D2B) for diverting gas flow to exhaust.
13. Exhaust tubing used during precombustion flushing.
14. Cartesian-diver manostat to provide even flow into gas bulb.
15. Solenoid (3-way) for diverting vacuum bulb to IR analyzer.
16. Solenoid (2-way) for reducing vacuum to atmospheric pressure.
17. Drying tube filled with Ascarite to remove CO_2.
18. Glass vacuum bulb (1200 ml).
19. Vacuum gauge.
20. Solenoid (2-way).

Legend for Fig. 3.6. continued

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21. Solenoid (3-way) used to divert gas bulb contents through Ascarite to remove CO_2 from sample (23).

22. Dyna pump for circulating CO_2 through IR analyzer.

23. Drying tube with Ascarite.

24. Infrared CO_2 analyzer Beckman Model IR-215 with 10 inch cells.

25. Solenoid (2-way) opens gass bulb to vacuum pump.

26. Vacuum pump.

27. Multiple outlet box with 7 switches. The solenoids and pumps controlled by switches are indicated.

28. Tygon tubing (1/4-inch I.D., 3/32-inch wall) used throughout analyzer.

29. Plywood base (3/4 inch thick).

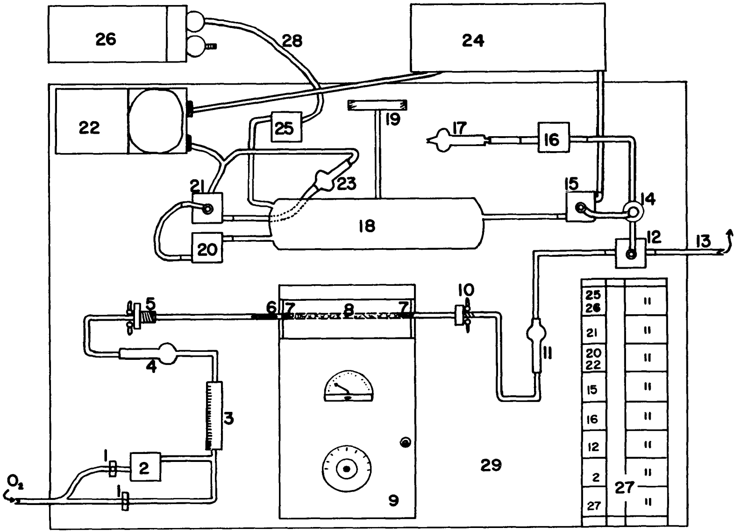


Fig. 3.6. Schematic drawing for the dry combustion carbon analyzer.

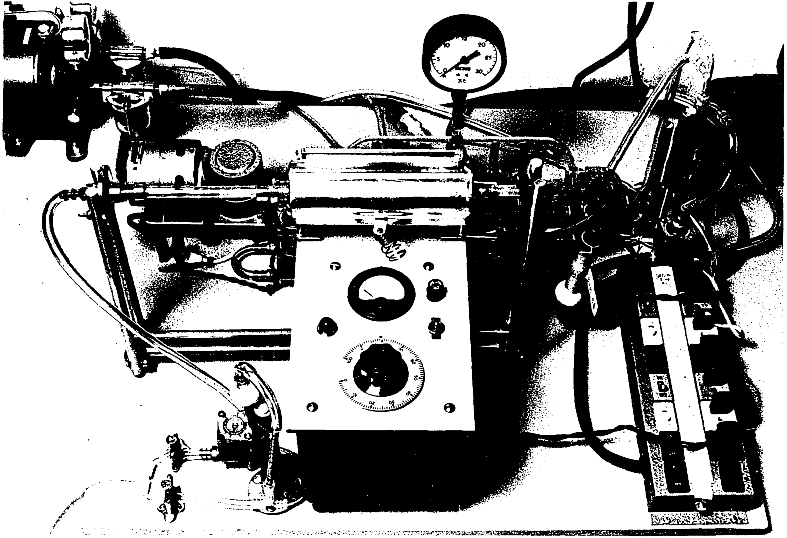


Plate 3.1. Dry combustion carbon analyzer.

of plywood for portability.

A sample was placed in a 38.1 cm quartz combustion tube (10-mm ID, 12-mm OD). The tube was packed with 18 cm of wire-form reagent cupric oxide (Baker No. 1820) placed 5 cm from the exit end and held in place with quartz wool. The cupric oxide was reused throughout the life of the quartz tube (30-40 samples).

For POC determinations the glass-fiber filters were carefully rolled with 2 pairs of forceps, sliced down the middle with a razor blade, and inserted into the tube up to the quartz wool. Cupric oxide, which had been partially ground up and heated in oxygen at 850C for 15 minutes at the start of each day, was poured into the tube surrounding the glass-fiber filter. This was necessary to prevent the filter from melting into a ball and sticking to the side of the combustion tube.

Dried sediment samples with carbonates removed were weighed into porcelain boats (Coors, Size 0000) for small samples (< 100 mg) or into aluminum boats (Coleman #29-412) for large samples (400-800 mg). The combustion tube with sample was placed in its holder and moved into the hot oven so that just the cupric oxide was heated. The tube was flushed with oxygen at 4 lbs/in^2 at 100 ml/min for 3 minutes while the cupric oxide reached temperature (800C) and the CO_2 from the previous sample was removed from the collection bulb. Then the IR analyzer was zeroed and a vacuum pulled on the collection bulb (51 cm Hg). The oxygen flow was reduced to 40-50 ml/min for combustion and diverted into the collection bulb through a tube of Anhydrone ($Mg(ClO_4)_2$) to remove water and through a Cartesian diver manostat to keep the flow rate constant.

The sample was then moved into the furnace and positioned so that about one half of the cupric oxide remained in the furnace. After 2 minutes of combustion the tube was flushed (oxygen flow rate increased to >100 ml/min) for about 3 minutes until the collection bulb vacuum reached 13 cm Hg. The vacuum was reduced to room pressure by allowing CO_2-free air to leak into the bulb. Then the sample gases were circulated (∿ 3 liters/min) with a Dyna pump through the IR analyzer until equilibrium was reached in 30-45 seconds. The pump was turned off and the output dial on the IR analyzer was read to the nearest 0.1 microampere D.C. and converted to μg C using a calibration curve (Fig. 3.7). A sample could be run every 13-14 minutes including preparation and all calculations.

The calibration curve was prepared by combusting known amounts of several organic compounds including urea, dextrose and nitrilotriacetic acid to determine the upper part of the curve (>100 μl CO_2). Then a substandard, a clayey sediment containing 0.245 ± 0.006% organic carbon, was used to determine the calibration curve at lower concentrations. The curve, checked every other day, did not change for the several months that samples were run.

A total blank, made up of an oxygen, tube, and boat or cupric oxide blank, was subtracted from each sample. This had a value of about 8-10 μg C (Table 3.10). Error in reading the output dial on the IR analyzer was about ± 0.1 microampere D.C. This was equivalent

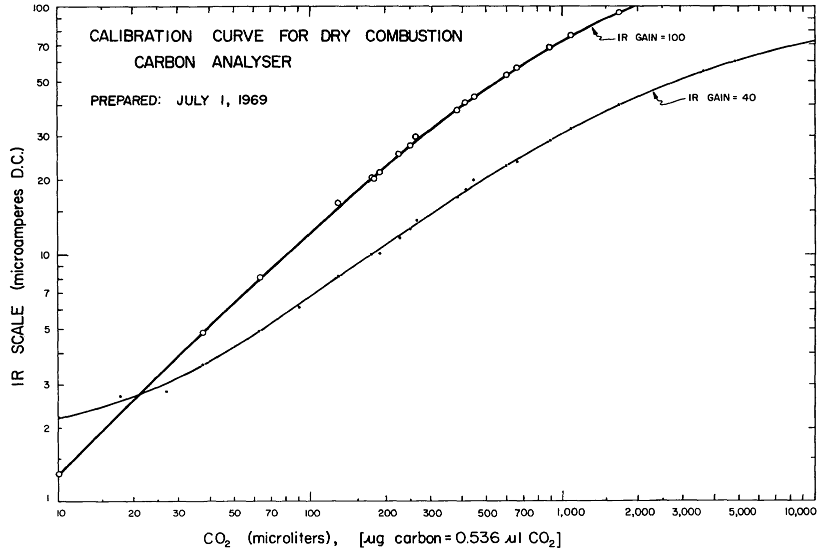


Fig. 3.7. Calibration curve for the dry combustion method.

Table 3.10. Contributions of various sources to blank values for the dry combustion carbon analyzer

Carbon blank source	CO_2 (µl)	Carbon (µg)
Oxygen (about 600 ml)	3 - 5	2 - 3
Tube (empty tube cooled and rerun)	5 - 12	3 - 6
Fine cupric oxide (used around filters)	4 - 6	3
Gelman filter (precombusted at 457C for 4-5 hr.)	7 - 10	3 - 5
Porcelain boat (pre-combusted each day at 850C for 15 min.)	1 - 3	1 - 2
Aluminum boat	7 - 10	3 - 5
Gelman filter (Ave. Total)	23	12
Porcelain boat (Ave. Total)	14	8
Aluminum boat (Ave. Total)	23	12

to about ± 5 μg C at the 500 μg C level, ± 1 μg C at the 150 μg C level, and ± 0.5 μg C at the 25 μg C level or about ± 1-2% of the sample value.

The weighing error (included weighing of a boat twice and adsorption of water) and was estimated to be a maximum of ± 0.06 mg for sediment samples. This was less than ± 0.1% for typical sediment samples of 100 mg but about ± 4-5% for a typical urea standard. Thus the accuracy of the analyzer is probably limited to ± 4% or the accuracy of the calibration curve. Precision on replicate samples of fine grained homogeneous sediment was even better, being about ± 2-4% or about ± 4 μg C.

III.1.2. Particulate Nitrogen

The particulate nitrogen samples, collected on glass-fiber filters as described in section II.2 were analyzed for total nitrogen content with a Model 29 Coleman automatic nitrogen analyzer utilizing the Micro-Dumas method. A filter was prepared for analysis by grinding it with about 20 grams of Cuprox (cupric oxide, wire form) before it was placed in the combustion tube and analyzed by the method suggested by Coleman.

The volume of sample nitrogen produced was read (on the analyzer dial) to the nearest 1 μl of nitrogen, which is equivalent to about 1 μg of nitrogen. The instrument precision is probably about ± 1 μg nitrogen and the per cent error would depend on sample size. Ammonium sulfate standards were run; there was essentially 100% recovery of the nitrogen.

The largest source of error affecting accuracy of the method was probably the accurate determination of a filter plus tube blank. This blank value ranged from 9-25 μl of nitrogen and had to be redetermined several times during a day's run of samples. Since the average blank value had a variation of ± 1-2 μl nitrogen, this probably limited the precision of any determination to ± 2 μl nitrogen or about ± 2 μg nitrogen/sample. There was no detectable adsorption of nitrogen onto filters as there was with carbon (section III.1.1.4).

The problems of obtaining identical samples of particulate matter were the same for nitrogen samples as those discussed under POC methods (section III.1.1.5) and are not discussed here. Variation between duplicate samples from both cruise 751 (Chukchi Sea) and 056 (North Dawes Inlet) was less than ± 10%. But the average variation for duplicate Arctic Ocean samples (cruise 704) was about ± 15% because of the very low particulate nitrogen content of the water (range 0.08-1.06 μg N/liter).

The particulate nitrogen values (in μg N/liter) were computed by the method suggested in the Coleman analyzer instruction manual. The calculation, including the number of μl of nitrogen in the sample and blank, the temperature of the sample gas and temperature changes during readings, the volume of sample gas in the syringe, the number of liters filtered, and the atmospheric pressure, was made by an IBM-1620 computer using a program provided by Dr. Vera Alexander.

III.1.3. Particulate Matter (Suspended Load)

The method for determining total particulate matter by Strickland and Parsons (1968) was followed with only slight modification. Dried filters containing the particulate matter collected in the field (section II.3) were redried at 60-65C for 1 hour and desiccated under a partial vacuum (40 cm Hg) for 16-24 hours. The filters were carefully weighed to the nearest 0.01 mg on a Mettler balance while using a radioactive ionizer (polonium strip) to reduce electrostatic effects. Each set of 12 sample filters had 3 control filters weighed with them to determine changes due to humidity fluctuations. The average change in weight for the control filters was generally less than ± 0.5 mg and the average variation between the 3 filters was less than 0.2 mg.

Precision of the method, based on variation between control filters, was from ± 4 μg/liter for large volume samples (20-25 liters) to about ± 0.2 mg/liter for small volume samples (500 ml). Variations between duplicate samples are given in Table 3.11.

III.1.4. Sediment Analysis (Grab and Core Samples)

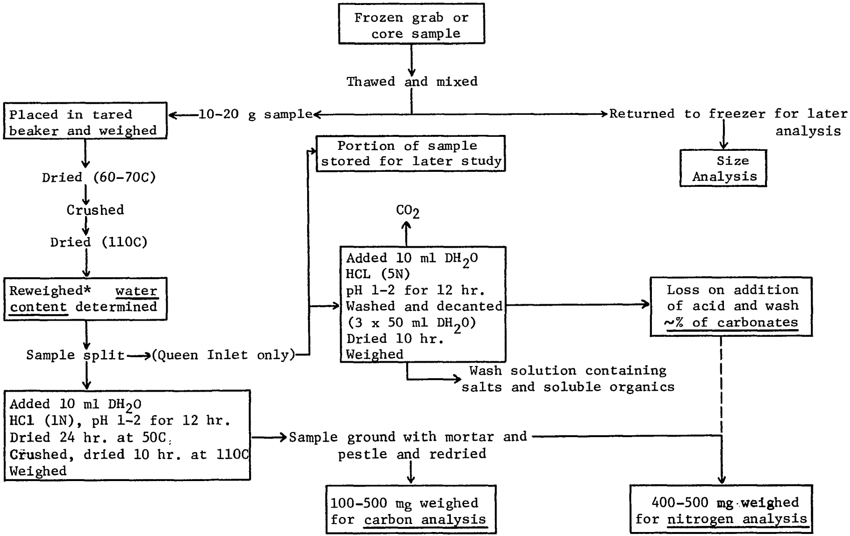
The sediment samples sealed in plastic bags were kept frozen at -10C until preparation for analysis. The samples were thawed for 24 hours at room temperature, thoroughly mixed, and prepared for carbon and nitrogen analysis (Fig.3.8). A portion of the sample (10-20 g wet weight) was placed in a tared 50 ml glass beaker and weighed. The remainder of the sample was refrozen for later

Table 3.11. Duplicate sample variations for particulate matter (PM) determinations

Cruise area	Approximate range of PM values (mg/liter)	Average variation (± mg/liter)	(± %)
North Dawes, 7/67	4 - 350	4.0	3*
Chukchi Sea	0.4 - 4.0	0.13	8/

* for 8 duplicate samples.

/ for 7 duplicate samples.



* Percent carbonate, carbon, and nitrogen based on this dry weight.

Fig. 3.8 Flow chart for sediment analysis

analysis. The samples were dried for several hours at 60-70C, crushed with a spatula, and dried completely at 110C for 12 hours. They were then reweighed to determine the original water content. All carbon, nitrogen, and carbonate (loss on addition of acid) contents were calculated on the basis of the sample weight at this point in the analysis.

Carbonates were removed by adding 10 ml of distilled water to the sample and then slowly adding 1 N HCl drop-by-drop (5 N HCl was used for the Glacier Bay samples with high carbonate content). After fizzing stopped, the pH (checked with Hydrion pH paper) was lowered to 1-2 for 10-12 hours, then the samples were dried directly or were decanted, washed, and dried at 50C for 24 hours and weighed. After further grinding with morter and pestle the samples were stored in small glass or plastic vials until carbon and nitrogen analysis. Only unwashed samples were used for carbon and nitrogen analysis because about 24% (average of 6 Queen Inlet samples) of the organic carbon content was lost by the washing procedure. The samples were prepared for carbon analysis by grinding and redrying at 110C.

The carbon content of the sediments were determined with the dry combustion carbon analyzer (section III.1.1.6). The average variation between replicate samples was less than 10% (average of 24 samples) for fine grained sediments and less than 35% (average of 4 samples) for sand and silty sediments. The high variation for coarser sediments was due to their generally lower carbon content and their inhomogeneity. Since the average carbon content of the fine grained sediments was about 0.1%, the variation for the percentage values reported is about ± 0.005% carbon.

Samples were prepared for nitrogen analysis by grinding 400-500 mg of dried sediment with 10 g of Cuprox. The sample was then analyzed in the Coleman nitrogen analyzer (section III.1.2). The average variation between duplicates was less than 15%.

III.2. Data Analysis

Routine data calculations and analyses were performed on a Friden Model 1151 desktop calculator; some correlation coefficients were determined on a Hewlett Packard 9100A calculator. The more complex statistical calculations including correlation, regression and factor analysis (principal component analysis) were performed on the University of Alaska's IBM-System 360-40G computer.

III.2.1. Linear Regression Analysis

The method used to determine the regression coefficients and their standard error of estimate was that described by Ostle (1954) and Cooley and Lohnes (1962). The Gauss-Jordon method was used in the solution of the normal equations.

The computer program MULTR, used for the regression analysis, was written in IBM Fortran IV E and was obtained from the IBM-scientific Sub-Routine Package (360A-CM-03X, Version III).

III.2.2. Correlation Analysis

The correlation coefficient is a measure of the degree to which 2 variables tend to be related in a linear fashion. A variable may be any parameter which has a different value at different observation points. For an oceanographic station the temperature, depth, DOC, POC, etc., are variables.

The correlation coefficient is designated as r or r_{ij} (where i and j represent two different variables) and has values ranging from -1 to +1 (Klovan 1968). A value of -1 indicates perfect negative correlation; a value of 0 indicates no correlation between variables; and a value of +1 indicates perfect positive correlation.

The value of r_{ij} is dimensionless and equal to:

$$r_{ij} = \pm\sqrt{\frac{\text{explained variation.}}{\text{total variation}}} \qquad (3.1)$$

The mathematical formula for the correlation coefficient is:

$$r_{ij} = \frac{\sum_{k=1}^{N} (X_{ki} - \bar{X}_i)(X_{kj} - \bar{X}_j)}{\sqrt{\sum_{k=1}^{N} (X_{ki} - \bar{X}_i)^2}\ \sqrt{\sum_{k=1}^{N} (X_{kj} - \bar{X}_j)^2}}. \qquad (3.2)$$

In this formula, K = 1, 2, ..., N and is the number of an observation; N is the total number of observations; X_{ki} and X_{kj} are the values of variables i and j at a specific observation point k; and

$\overline{X}_i$ and $\overline{X}_j$ are the mean values of the variables i and j. The mean value for the variable i is defined as:

$$\overline{X}_i = \frac{\sum_{k=1}^{N} X_{ki}}{N}. \tag{3.3}$$

The correlation coefficient contains all the information concerning the relationship between two variables in the original data matrix. The above description has been modified from Klovan (1968).

A correlation coefficient matrix is calculated from a data matrix consisting of a number of different variables by correlating all possible pairs of variables. Since the correlation between variable 3 and 6, for example, is the same as between variable 6 and 3, the resulting matrix is symmetrical and the lower left half is a mirror image of the upper right half. This technique was applied to data matrices consisting of a number of oceanographic stations (observations) and the values for 11-16 variables recorded at each station (Tables 5.2, 5.6 and 6.2).

The correlation matrices were calculated by the IBM-360-40G computer using program CORRE taken from the IBM-Scientific Sub-Routine Package (op. cit.). The correlation coefficients were also calculated by the two different factor analysis programs to be used as the starting point in the factor analysis.

III.2.3. Factor Analysis (Principal Component Analysis)

Factor analysis aids in explaining the variance in a data matrix by placing related variables (R-mode) or related samples

(Q-mode) into groups called "factors". Only R-mode factor analysis was used in this study. The basis for the grouping is the correlation coefficient matrix. These factors provide a simple interpretation of the original data matrix permitting a more fundamental description of the particular set of variables analyzed. The number of variables in a factor depends on the original data, but may be partially controlled by the number of factors requested during the varimax rotation described below.

The 11-16 variables used in this study were grouped into 2-5 factors explaining 75-85% of the total variance. Nearly all the variance (98-100%) can be explained when the number of factors approaches the number of variables.

A description in general terms of how the factors are determined is as follows: The correlation matrix is computed (section III.2.2) and treated by the method of principal components, producing the eigenvalues and eigenvectors for the correlation matrix. The eigenvalues are roots of a series of partial differential simultaneous equations and tell us the importance of each factor. Generally the amount of variance "explained by" each factor is also given in per cent of the total variance of the original correlation matrix. For example, for the Chukchi data, the first 4 factors had eigenvalues greater than 1.0 and explained 84.8% of the total variance (Table 6.3).

Whereas 2 variables plotted in 2 dimensions form a line or ellipse and 3 variables plotted in 3 dimensions form a line or and ellipsoid, N variables plotted in N-dimensional space will form a series of hyperellipsoids which can only be described algebraically. The eigenvectors represent the major and minor axes of these hyperellipsoids. A correlation coefficient is the cosine of the angle formed by the vectors of the two variables in N-space (Harman 1967 and Klovan 1968).

In addition to the eigenvalues and vectors, a principal factor matrix is computed showing the composition of the factors in terms of the original variables. This matrix is not often used without rotation since the contributions of many variables in a factor are often of nearly the same value.

The principal factor axes are mathematically rotated to maximize the loading (the proportion of the variance of a variable contributing to a given factor) for a specific number of factors requested. Rotation clarifies a factor's composition in terms of the original variables by producing a varimax factor matrix in which each factor is composed of one or several variables with high loadings and the remaining variables with low loadings.

The effect of rotation can be seen more clearly by comparison of an unrotated and varimax rotated factor matrix in Chapter VI (Tables 6.4 and 6.5). The varimax factor matrix is the important result of a factor analysis. The individual numbers or loadings in a column beneath a factor indicate the relative contribution of a particular variable to the makeup of that factor. These numbers when squared are the per cent of variance of the original variable contributing to an individual factor. Factor analysis reduces the original number of variables to only 3 or 4 new variables (factors), simplifying the description of the original data considerably.

At this point it is necessary to examine the composition of the factors in terms of their "variable" composition and the original correlation matrix. The relationship of the variables in a factor should "make sense" in terms of the original data. Choosing the "correct" or significant number of common factors for the above mentioned varimax rotation is a subjective problem in factor analysis and has no correct answer. Dr. R. B. McCammon of the University of Illinois at Chicago Circle suggests two rules of thumb based on practical experience (personal communication to Dr. D. B. Hawkins, January 27, 1970): 1) "The number of common factors should be equal to the number of eigenvalues greater than one and 2) if, after 75 per cent of the total variance is accounted for, any additional factor accounts for less than five per cent, it should not be retained."

Another method for choosing the number of factors is to determine nearly all the eigenvalues and plot them vs. the factor number (Figs. 3.9a and b). A break in slope of the curve, representing a change in per cent of the total variance explained by a factor, may also indicate the best number of factors. For the Chukchi data (Chapter VI) both McCammon's rules and the break in slope criteria indicate that 4 factors be rotated. The resulting factors "make sense" both in terms of the original data and our knowledge of oceanographic processes. For the Kodiak data (Chapter V), either 2 or 4

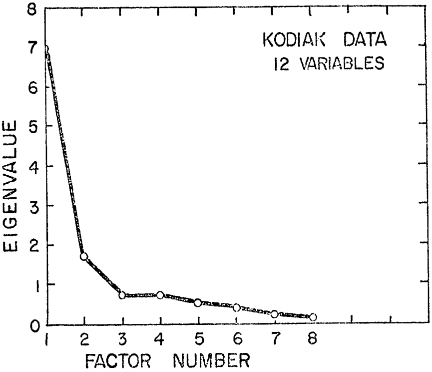


Fig. 3.9a. Eigenvalues (>0.1) plotted in order of extraction from the factor matrix for Kodiak data. Five factors were chosen.

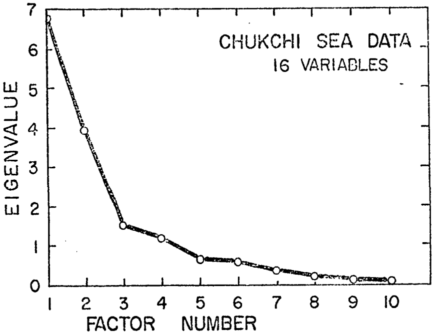


Fig. 3.9b. Eigenvalues (>0.1) plotted in order of extraction from the factor matrix for Chukchi data. Four factors were chosen.

factors are indicated. Using the "make sense" criterion on the results, however, I found that 5 factors explained the data best. The different factor compositions made by varying the number of factors rotated are given in Tables 5.10a and b. This shows the need for a "make sense" criterion when dealing with factor analysis of data from a natural system.

Once the "correct" number of factors is determined a varimax factor scores matrix is computed giving us the weight or influence of each factor at each observation point, in effect a factor analysis of the samples similar to Q-mode factor analysis. The new variables (factors) are then plotted on the original map and contoured (Figs. 6.6 - 6.9).

I felt the above somewhat lengthy discussion was necessary because factor analysis is not a familiar tool in the field of oceanography although it has been used recently by marine geologists (McManus et al. 1969) and biologists (Cassie and Michael 1968). For a more detailed mathematical discussion of factor (principal component) analysis refer to Harman (1960, 1967) or the computer program references cited below.

Two different computer programs were used in this study. The first program, found in the IBM-Scientific Sub-Routine Package (op. cit.), consisted of 7 sub-routines. They were DATA, which read raw data; FACTO, which was the main program (method of Dixon 1964); CORRE, which performed the correlation analysis (section III.2.2); EIGEN, which computed eigenvalues and vectors by the Jacobi method (Greenstadt

1960); TRACE, which selected the specified number of eigenvalues; LOAD, which computed a factor matrix; and VARMX, which performed a varimax rotation of the factor matrix (method of Kaiser 1959).

The second program, that of Cameron (1967), used similar techniques to determine factors, and in addition, computed factor scores by Harman's (1960) method of ideal variables. Cameron's program was used after the number of factors required was determined by the shorter (less expensive) first program.

Chapter IV

ALEXANDER ARCHIPELAGO (SOUTHEASTERN ALASKA)

Chapter IV

ALEXANDER ARCHIPELAGO (SOUTHEASTERN ALASKA)

IV.1. Introduction

The Alexander Archipelago consists of numerous mountainous islands, estuaries and interconnecting waterways associated with the deeply embayed and glaciated Coast Mountains located in the panhandle or southeastern part of Alaska. Most of the estuaries in this area have been formed by the drowning of glacially eroded valleys and are termed fiord estuaries.

There have been several recent articles on the geochemistry of glacial fiords including Burrell, Hoskin and Rosenberg (1967), Burrell, O'Brien and Sharma (1968), Kunze, Knowles and Kitano (1968), and Sharma (1970). All have dealt in part with the inorganic reactions and composition of the suspended material and the sediments. Wallen and Hood (1968) reported the general distribution of nutrients in several inlets and fiords in Southeast Alaska as well as the distribution of nutrients in surface mixing layers (0-1 m depth). They report that the nutrient mixing profiles are quite complex and are affected by tidal cycles, amount of fresh water drainage, suspended sediment load and biological activity.

The first study in this area was undertaken to determine the distribution and significance of organic carbon in glacial inlets where large amounts of glacially produced detrital material are added by glacial runoff. The general distribution of organic carbon was also determined for a number of selected areas throughout the Alexander Archipelago.

IV.2. Organic Matter in Glacial Fiords

The dynamic systems of an estuary are responsible for the change from an essentially terrigenous environment to that of the normal marine environment. I undertook this study to determine the effect of various processes on the concentration of organic carbon in these estuarine waters.

IV.2.1. North Dawes Inlet and Endicott Arm - Introduction

North Dawes Inlet, a small extension of Endicott Arm, is a typical fiord located in southeast Alaska (Fig. 4.1). This inlet was chosen because of its relatively small size (0.5 km wide and 1.6 km long) which allowed sampling at close intervals in the transition from fresh to nearly normal estuarine water. The proximity of Endicott Arm to the Douglas Marine Station and the availability of data from others working in the arm also influenced the decision to work here. In addition this inlet is unpolluted by man.

At the head of North Dawes Inlet is a prograding mud-flat delta (Fig. 4.2 and Plate 4.1) deposited by the North Dawes River which flows from the receeding North Dawes Glacier, located about 3.4 km from the inlet with its terminous about 200 m elevation above sea level. Most of the glacial debris carried by the river is deposited on the delta or in the inlet while the remainder is carried into Endicott Arm and deposited. From aerial observations and PM determinations almost none of the PM is carried out of Endicott Arm. The

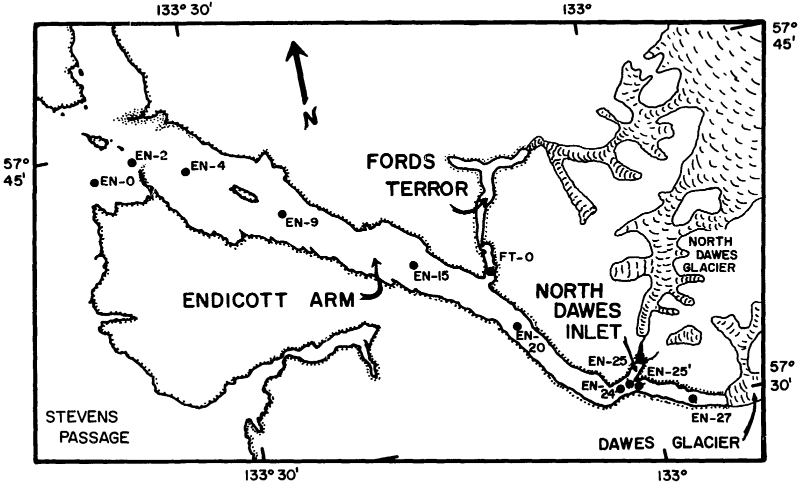


Fig. 4.1. Station locations for Endicott Arm.

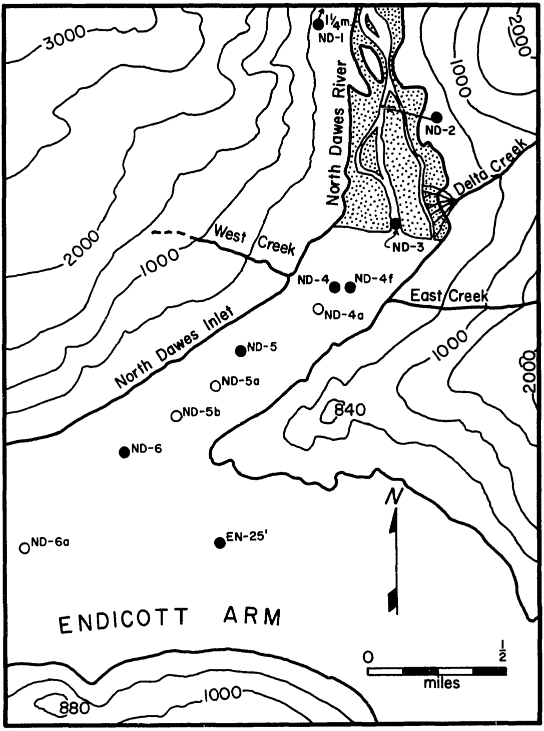


Fig. 4.2. Station locations in North Dawes Inlet and adjacent Endicott Arm.

Plate 4.1. Aerial view of North Dawes Inlet at low tide. White areas in the foreground are small bergs in Endicott Arm. Top of the picture is approximately north.

Plate 4.2. Aerial view of North Dawes River delta at the head of North Dawes Inlet at low tide. Top of picture is approximately east.

average tidal range is 4 - 5 m, enough to expose the tidal delta and allow resuspension of deposited material. This is apparent in Plate 4.2 where dark areas on either side of the river plume at low tide indicate resuspended deltaic material with a high percentage (25 - 45%) of heavy minerals (D. E. Buckley, personal communication 1970).

The bottom topography of North Dawes can be described as a narrow, almost V-shaped trough having a maximum depth of 150 m. The bottom rises sharply at the head where the delta is prograding. At the junction of North Dawes Inlet with Endicott Arm there is a small sill rising about 30 m above the bottom on the inlet side and plunging to a depth greater than 220 m in Endicott Arm.

The topography surrounding the inlet is ruggedly mountainous with 600 m altitude within 1 km of the inlet and peaks 1500 - 1800 m high surrounding the almost 100 square km drainage basin. Vegetation is sparse and located at lower altitudes near the inlet.

The river flow is highest during the early summer (May to July) due to melting snow and during the fall (September to December) due to heavy precipitation (Wallen and Hood 1968).

North Dawes and Endicott Arm were sampled on 5 separate cruises from November 1966 to September 1968. Samples within North Dawes Inlet were taken prior to low tide. The work on the first three cruises was done with the help of Mr. Dale E. Buckley of the Bedford Institute, Dartmouth, Nova Scotia, Canada, who is completing his dissertation on the clay-inorganic associations on samples from North Dawes Inlet.

IV.2.2. North Dawes Inlet and Endicott Arm - Results and Discussion

The results for DOC, POC, PN and PM values in North Dawes are given in Tables 4.1 to 4.4. Tables 4.3, 4.5 and 4.6 contain data for Endicott Arm. The station locations are shown in Figs. 4.1 and 4.2.

The North Dawes River with its low DOC content and high suspended load flows into the North Dawes Inlet forming a fresh water lens on the surface. The lens is generally less than 2 m thick and has very strong gradients of all of the above parameters. The lens becomes more diffused as mixing occurs and the particulate materials settles out. Figure 4.3 shows the distribution of the several parameters through the mixing zone for ND-4 and ND-5 in July 1967.

The DOC concentration for the North Dawes River was about 0.5 mg C/liter during the July and two September cruises. A much lower value of 0.15 mg C/liter was found in November 1967 (Table 4.3) suggesting that the DOC content of the river varies seasonally. Further evidence for this variability was found on cruise 075 (Table 4.6) when the river was sampled on both September 24 and 26. The first sample contained 0.53 mg C/liter and two days later the value had dropped to 0.24 mg C/liter. The only explanation for the sudden drop is dilution by rain water. Although no measurements were made, considerable rain fell during the interval between sampling times. Since there is very little vegetative cover in the drainage area, rapid runoff occurred and the river and smaller streams were noticeably higher. If we assume the DOC content of rain is near zero, then

Table 4.1. Organic and particulate data for North Dawes cruise, July 17-23, 1967

Station and Date	Depth	DOC (mg/liter)	POC (μg/liter)	PN (μg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N	Salinity (°/₀₀)
ND-1, 7-18	Surf	0.57	109	-	196	0.05	-	0
ND-2, 7-19	Surf	0.50	1220	56	354	0.34	21.8	0
ND-3, 7-20	10 cm	0.37	435	28	147	0.30	15.5	2
	50 cm	0.90	630	47	124	0.51	13.4	12
ND-4, 7-21	10 cm	0.54	214	23	83	0.26	9.3	5-6
	50 cm	1.0	312	57	54	0.58	5.5	16
	5 m	1.3	180	23	10.8	1.7	7.8	29
ND-5, 7-22	10 cm	0.54	132	-	29	0.45	-	7
	30 cm	0.70	116	7.6	42	0.28	15.3	15
	2.5 m	1.6	263	55	6.4	4.1	4.8	-
	5 m	1.4	87	4.8	3.5	2.5	18.1	-
	20 m	1.3	70	7.0	4.3	1.6	10.0	-

† Hydrometer used to determine salinity.

Table 4.2. Organic and particulate data for cruise 053, September 17-21, 1967

Station and Date	Depth	DOC (mg/liter)	POC (μg/liter)	PN (μg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N	Salinity (°/₀₀)
ND-4f, 9-9	10 cm	0.52	567	34	-	-	17	3-5≁
	1 m	0.78	404	(12)*	223	0.18	(34)*	14.68
	10 m	0.96	652	32	167	0.39	20	27.13
	40 m	0.87	97	(17)	55	0.18	(6)	-
ND-6, 9-18	10 cm	-	140	(17)	69	0.20	(8)	6≁
	0.5 m	0.80	145	(13)	77	0.19	(11)	15≁
	3 m	1.16	84	17	8.0	0.11	4.9	28≁
	10 m	1.10	63	3.6	11	0.57	17	-
	19 m	0.98	55	(2.2)	26	0.21	(25)	-
	50 m	1.04	52	(28)	75	0.71	(2)	-
	190 m	1.24	161	(6)	186	0.87	(27)	-
En-25', 9-20	10 cm	0.92	48	(15)	5.2	0.92	(3)	24≁
	10 m	0.82	87	9.6	1.6	0.54	9.1	-
	50 m	1.20	108	(17)	116	0.93	(6)	28.72
	190 m	0.82	64	4.3	51	0.13	15	-
	220 m	1.08	51	-	46	0.11	-	-

* PN and C/N values in ( ) are only approximate.

≁ Hydrometer used to determine salinity; the remainer were determined by chlorinity titration.

Table 4.3. Organic and particulate data for Endicott Arm, North Dawes area, cruise 056, November 16-18, 1967

Station and Date	Depth	DOC (mg/liter)	POC (μg/liter)	PN (μg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N
N. Dawes R., 11-17	Surf	0.15	237	2.2	147	0.16	107
2009, ND-4, 11-17	75 cm	0.25	178	16	62	0.29	11
	5 m	0.65	35	4.9	2.9	1.2	7.1
Delta Creek, 11-17	Surf	0.90	20	2.4	0.95	2.1	8.3
West Creek, 11-17	Surf	-	-	4.1	0.38	-	-
2010, En-25', 11-18	25 m	-	-	1.8	0.92	-	-
	68 m	-	-	3.2	2.38	-	-
2013, En-15	25 m	0.45	20	3.8	0.42	4.8	5.3

Table 4.4. Data for cruise 075, North Dawes Inlet, September 24-26, 1968

IMS Ref. number Station and Date	Depth	DOC (mg/liter)	POC* (μg/liter)	PN (μg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N	Salinity (°/₀₀)
N. Dawes R., 9-24	Surf	0.53	680^D	31.8	263	0.23	19.1	0.0
N. Dawes R., 9-26	Surf	0.24	1235	78.2	803	0.15	15.8	0.0
75652	5 cm	0.39	1237	72.1	435	0.28	17.2	5-6†
ND-4, 9-25	50 cm	0.83	595	34.4	253	0.24	17.3	19†
	2 m	0.89	138	14.5	53	0.26	9.5	28†
	5 m	1.07	-	-	21	-	-	28.827
	10 m	-	-	-	14	-	-	29.397
	20 m	1.00	64	-	7.3	0.88	-	29.694
	30 m	-	-	-	5.7	-	-	29.918
	50 m	-	43^D	-	10.1	0.43	-	30.210
75653	5 cm	0.56	915	48.2	394	0.23	19.0	7†
ND-4, 9-26	40 cm	0.75	766	45.0	361	0.21	17.0	15†
	5 m	1.04	169	11.0	72	0.23	15.4	26†
75654	5 cm	0.37	344	19.3	128	0.27	17.8	4†
ND-5, 9-26	20 m	1.10	65	-	6.2	1.05	-	28.934
	50 m	0.80	40^W	-	9.4	0.43	-	29.928
	100 m	0.98	49	-	24	0.20	-	-
West Creek, 9-26	Surf	-	75	-	1.45	5.2	-	0.0
East Creek, 9-26	Surf	1.59	47	4.49	1.25	3.8	10.5	0.0
Delta Creek, 9-26	Surf	0.83	22	1.08	3.4	6.5	20.4	0.0

* POC values are an average of values determined by both the wet and dry combustion methods unless indicated otherwise.

D Dry combustion only. W Wet combustion only. † Hydrometer used to determine salinity.

Table 4.5. Data for cruise 031, Endicott Arm, November 26-30, 1966

Station Location & Number	Depth (m)	DOC (mg/liter)	POC (μg/liter)	PM (mg/liter)	POC/PM (x 100)
En-27, 888	0-1	0.78	32	1.13	2.8
	10	0.76	17	1.42	1.2
	50	0.70	20	4.37	0.46
	150	0.73	25	-	-
En-24, 889	0-1	0.69	23	1.26	1.8
	50	0.75	-	2.29	-
En-20, 890	0-1	0.63	-	0.87	-
	10	0.69	22	0.43	5.1
	50	0.67	17	0.48	3.5
	200	0.71	29	-	-
Ft-0, 891	0-1	0.61	38	-	-
	75	0.50	25	-	-
En-15, 892	0-1	0.63	23	0.58	4.0
	10	0.70	15	0.60	2.5
En-9, 894	0-1	0.66	28	0.68	4.1
	10	0.60	-	0.54	-
	150	0.69	23	0.38	6.1
En-4, 893	0-1	0.67	27	0.51	5.3
	10	0.70	27	0.33	8.2
	250	0.69	24	-	-
En-2, 895	0-1	-	30	0.43	7.0
	10	-	26	0.43	6.0
	25	-	25	-	-
	75	-	110	-	-
En-0, 896	0-1	0.73	30	0.29	10
	10	0.75	19	0.34	5.6
	150	0.69	16	-	-

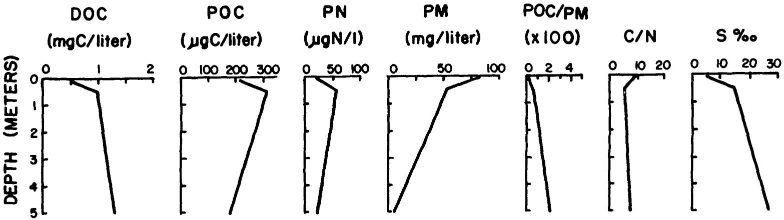
Table 4.6. Data for cruise 075, Endicott Arm, September 23-27, 1968

IMS Ref. Number Station and Date	Depth	DOC (mg/liter)	POC* (μg/liter)	PN (μg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N	Salinity (°/oo)
75659, En-4, 9-27	5 m	1.04	53	10.4	0.60	8.7	5.1	28.32
75658, En-12, 9-27	5 m	0.97	52	-	1.64	3.1	-	-
75648, En-15, 9-23	5 m	0.92	27^{D}	-	1.01	2.7	-	-
75649, En-20, 9-23	5 m	0.83	36^{D}	-	0.74	4.8	-	
75657, En-20, 9-27	5 m	0.98	42	5.0	2.44	1.7	8.4	27.79
75656, En-25, 9-27	5 m	1.14	44	2.9	5.44	0.81	15.2	27.88
75650, En-25'† 9-27	5 m	0.84	18	2.2	0.93	1.9	8.2	-

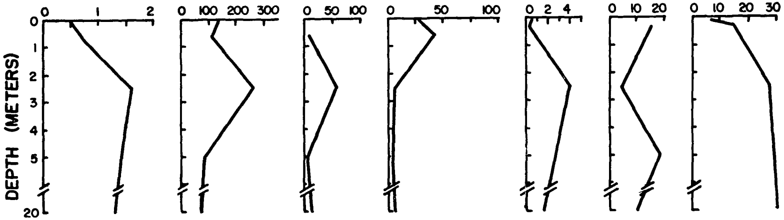
* POC values are an average of values determined by both the wet and dry combustion methods unless indicated otherwise.

D Dry combustion only.

† Values are an average of PVC and pumped samples.



STATION ND-4, JULY 21, 1967



STATION ND-5, JULY 22, 1967

Fig. 4.3. Near surface profiles for stations ND-4 and ND-5, July 1967.

the North Dawes River probably more than doubled in volume. During the same time the values for POC, PN and PM increased probably due to increased turbulence in the swollen river.

DOC usually increased with salinity and its value in the mixing layer could be approximated on the basis of salinity values and mixing. For 5 samples tested 3 were found with observed DOC values higher than was predicted on mixing alone but within the error of the DOC method. One observed value (ND-5, 30 cm, July 1967) was 25% lower than predicted and one was equal to the predicted value (ND-4, 40 cm, September 1968). This suggests that if clays are releasing or adsorbing dissolved organic materials, the quantity is small or the process is a slow one. This contrasts with Seki, Stephens, and Parsons (1969) who reported apparent removal of DOC from particle surfaces as the particles entered sea water; this was based on a decrease in POC and no decrease in PM across the salinity gradient in a small bay off the Strait of Georgia, Canada. However, Khaylov and Finenko (1968) reported apparent uptake of dissolved macromolecules by microorganism-populated natural detritus. This process would probably take several days to reach equilibrium since the particles are going from fresh to salt water environment, but might play a very important role in clay organic interactions in Endicott Arm itself. The DOC concentration rose sharply to greater than 1 mg C/liter just below the mixing layer at stations ND-5, July 1967 and ND-6, September 1967 and then dropped several tenths of a mg C/liter with increasing depth.

The DOC content of the normal estuarine water dropped during the fall from about 0.8 - 1.0 mg C/liter in September (Table 4.6) down to 0.45 - 0.7 in November (Tables 4.3 and 4.5). Thermo-haline convection occurs during the fall and winter and mixes the water column in Endicott Arm resulting in a reasonably uniform distribution of DOC with respect to depth and length of the arm. This is shown by the DOC and POC data for cruise 030 (November 1966) which are given in Table 4.5. These values are slightly higher than those reported by Loder and Hood (1967) because of a calculation error in the orginal data.

The POC values for North Dawes River generally varied with the quantity of PM in the river. They ranged from about 100 μg C/liter to greater than 1000 μg C/liter depending on sample location, river flow and time of year. Referring to the samples collected on September 24 and 26, 1968 (Table 4.4) the large rainfall and increased river flow doubled the POC content in 2 days. The low POC content (109 μg C/liter, ND-1, July 1967) of the water flowing out of the glacier suggests that much of the particulate organic matter must be picked up during the river's travel from the glacier to the inlet.

POC values in the normal estuarine water of North Dawes Inlet were generally greatest just below the mixing layer in a layer I term the "biologically active layer" (BAL) which will be discussed below. The samples collected in September 1968 (Table 4.4) were an exception to this and showed decreasing POC with increasing salinity approximating expected values from normal dilution. In addition, the percentage of organic carbon in the particulate matter (POC/PM x 100) did not increase with depth suggesting dilution rather than preferential settling of inorganic matter over organic matter. This was probably due to the large concentration of POC and PM being carried into the inlet overwhelming any effects of biologically produced marine organic matter.

The highest value of POC in the estuarine water (263 μg C/liter) was found at 2.5 m (July 1967) in the BAL where the high DOC values were also found. POC values for September were about 30 - 60 μg C/liter for most of Endicott Arm and the normal estuarine water under the mixed layer in North Dawes Inlet. There were higher values in deep nepheloid layers such as the one found at En-25' at 50 m (Table 4.2). By late fall (November, Tables 4.3 and 4.5) the values of POC in the normal estuarine water dropped to about 15-30 μg C/liter and were uniform throughout the water column. These POC values were extremely low for near shore surface waters and reflect the essentially zero productivity, low detrital input during the winter and a well-mixed water column. Low fall-winter values were also found throughout much of the rest of southeastern Alaska (section IV.3).

PN values are given in the tables for most of the samples. Some of the low values for North Dawes Inlet are only approximations because of the difficulty in filtering enough sediment-laden water to obtain a sufficiently large sample. In spite of this difficulty several trends in the PN content and C/N (POC/PN) ratio for the particulate organic matter were evident.

In general the PN distribution was similar to the POC distribution, that is, high in the river and mixing layer and lower in the rest of the samples. The resulting C/N ratios are more useful in determining the origin of the organic matter than the PN value alone. The C/N ratio of the particulate matter carried into the inlet by the river averaged between 15 and 20, reflecting its terrestrial origin. The C/N ratios for normal marine particulate organic matter range from about 5 to 7. The BAL at ND-4 and ND-5 for July 1967 had ratios of about 5, indicating that essentially all of the particulate organic matter in the layer was marine derived. A low C/N ratio was also found in September (Table 4.2) at ND-6 (3 m) with a high DOC value at the same depth. Perhaps the strongest evidence in support of this BAL was the greenish-gray color of the filtered particulate matter collected at ND-5 (2.5 m) in July 1967. Since all of the stations for North Dawes Inlet were sampled just prior to low tide, it appears that the BAL is not carried out by the tide but moves back and forth within the inlet. Thus the biologically active layer is chemically characterized by high POC, PN and DOC values and low PM and C/N values (Fig. 4.3). Nutrient values (discussed below) vary within the layer.

Although the surface mixing layer had much suspended matter in it, the BAL had very low amounts indicating that the suspended material was confined to a shallow depth at the surface at ND-4, ND-5

ND-6. A turbidity profile (Fig. 4.4) for ND-6 (cruise 053) showed a high at the surface, a low from 3-15 m and then an increase into one large partially split nepheloid layer down to 50 m or more. These layers were probably deeper than the 1% light penetration level and would have little effect on the biological activity. Light penetration values determined with a photometer at different levels for ND-4 and ND-5 (cruise 056) are given in Table 4.7 and show that the 25% light level was at about 1 m. This value probably drops below 10% during the summer months with the higher runoff and suspended matter. Thus ample light for phytoplankton growth is available beneath the mixed layer. Light penetration at En-15 was equivalent or greater than values for the open ocean except for some tropical areas.

An examination of the PM data indicates that large variations occur at a given station. The variation in the river ranged from about 100 to 800 mg/liter and nearly tripled with increased river flow for the September 26 (cruise 075) sample. The range of values at the surface at station ND-4 was 83 to 435 mg/liter depending on the stage of the tide and river flow. These values were higher than the river because of resuspension of material deposited on the delta during high tide (Plate 4.2).

In the inlet, high PM values were associated with the fresh water at the surface and diminished rapidly below the surface. However, at some locations such as ND-6 (Table 4.2) the PM values increased with depth well below the mixing layer, approaching values

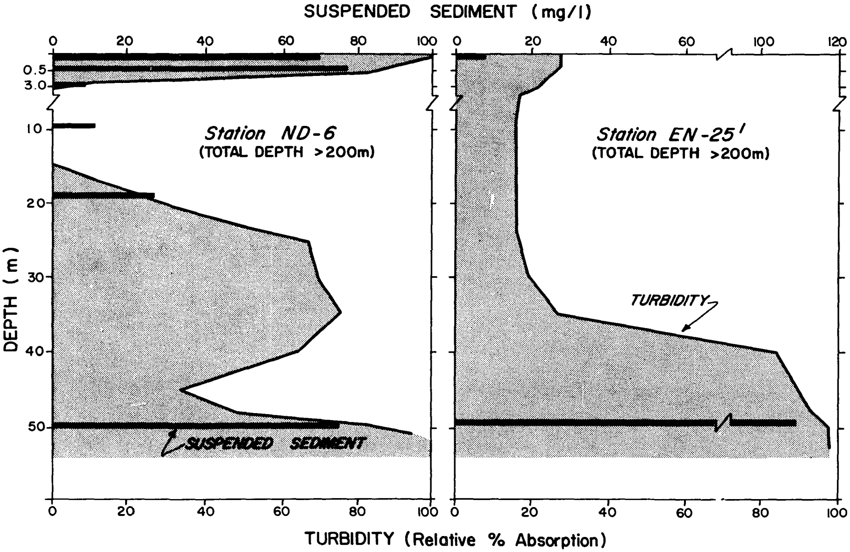


Fig. 4.4. Turbidity and suspended sediment (PM) profiles for stations ND-6 and En-25', September, 1967.

Table 4.7. Approximate* light penetration values for selected stations in North Dawes and Endicott Arm, cruise 056, November 1967

Station, Date and Time	Depth	% Light Penetration
ND-4, 11-17, 1600 hr	Surface	100
	23 cm	50
	90 cm	25
	2.3 m	10
ND-5, 11-17, 1630 hr	Surface	100
	28 cm	50
	1 m	25
	2.3 m	10
En-15, 11-18, 1420 hr	Surface	100
	2.7 m	50
	5.7 m	25
	11.0 m	10
	30 m	1

* The values for ND-4 and 5 are approximate because of the shifting currents at the surface causing changes in the density and thickness of the mixing layer.

found at the surface. At En-25' for the same cruise a very sharp boundary was found at 37 m with the PM value increasing rapidly. The PM values (suspended sediment) are shown in Fig. 4.4 with the turbidity of the layer superimposed. These data indicate that the water column consists of a series of layers constantly changing during a tidal cycle. The layers contained a high percentage of fine silt and clay and the percentage of POC in the PM of these layers was higher than values found in the mixed layer or the river. PM values for near surface samples dropped rapidly outside the inlet and ranged from less than 1 to about 5 mg/liter for samples taken from a 5 m depth at En-4 to En-25' (Table 4.4). In general values were less than 1 mg/liter for Endicott Arm samples collected in November (Table 4.3 and 4.5).

The percentage of POC in the total PM (POC/PM x 100) and in the different size fractions of the PM was determined for ND-4 and ND-5, July 1967 (Table 4.8). The value of these percentages was obtained by filtering the samples through a set of breaker sieves constructed of polyethylene beakers with bottoms removed and fitted with stainless steel or nylon screening (Buckley and Loder 1968). In general the values ranged from about 0.15 - 0.34% in the river to several per cent in the BAL. Values from 1 to almost 9% were found for Endicott Arm. The values in the mixing layer usually increased with depth probably due to less turbulence and settling of the larger sized particles. As larger particles settled, the percentage of fine silt and clay in the suspended material increased both with depth at station and increasing distance from the river source.

Table 4.8. PM and POC values for different size fractions of the suspended matter in North Dawes Inlet, July 1967

Station & Date	Depth	Part. Size (μ)	PM (mg/liter)	% in Size Class	POC (μg/liter)	% in Size Class	POC/PM (x 100)
ND-3 7-20	10 cm	total	147	100	435	100	0.30
		62	-	-	45	10	-
		25	-	-	59	14	-
		10*	-	-	(99)	(23)	-
		0.45	-	-	232	53	-
ND-4 7-21	10 cm	total	83		214		0.26
		62	0.8	1	12	6	1.5
		25	16.6	20	39	18	0.23
		10	(36.6)	(47)	(105)	(49)	(0.27)
		0.45	27.0	32	58	27	0.21
	50 cm	total	54	100	312	100	0.58
		62	4.5	8	30	10	0.67
		25	26.2	48	105	34	0.40
		10	(9.9)	(18)	(41)	(12)	(0.41)
		0.45	14.8	27	136	44	0.92
	5 m	total	10.8	100	180	100	1.7
		62	0.7	7	27	15	3.9
		25	3.0	28	48	27	1.6
		10	(2.6)	(24)	(12)	(7)	(0.46)
		0.45	4.4	41	93	52	2.1

Table 4.8. continued

Station & Date	Depth	Part. Size (µ)	PM (mg/liter)	% in Size Class	POC (µg/liter)	% in Size Class	POC/PM (x 100)
ND-5	10 cm	total	29	100	132	100	0.45
7-22		10	(3.7)	(12)	(36)	(27)	(0.97)
		0.45	25.8	88	96	73	0.37
	30 cm	total	42	100	116	100	0.28
		25	-	-	11	9	-
		10	(13.6)	(32)	(26)	(22)	(0.19)
		0.45	28.5	68	79	68	0.28
	2.5 m	total	6.4	100	263	100	4.1
		62	-	-	31	12	-
		25	-	-	73	28	-
		10	(4.0)	(63)	(74)	(28)	(1.8)
		0.45	2.4	37	85	32	3.5

* Values in parentheses for the > 10 µ and < 25 µ size were determined by difference and thus are only approximate.

Most of the incoming POC was found in the size fractions less than 25 µ (e.g. ND-3, 10 cm, Table 4.8). Organic material settled slowly increasing the percentage of organic carbon in both the total PM and the PM fraction less than 25 µ. The total amount of POC decreased with depth probably due to mixing and dilution. This suggests that most of the particulate organic matter carried into North Dawes Inlet by the river is carried out of the inlet in the fine fractions and deposited in Endicott Arm. The organic carbon content of sediments in North Dawes Inlet (average 0.09%, range 0.07 - 0.12%) was substantially lower than the organic content of the suspended matter in the North Dawes River (average 0.22%, range 0.15 - 0.34%). Based on the percentages of organic carbon in the river PM, the inlet PM and the bottom sediments, about half or more of the organic matter brought into North Dawes Inlet is carried through the inlet and deposited in Endicott Arm. Since river flow rates were not determined, the total amount of organic matter added to Endicott Arm is not known; however, it may be significant when compared to the annual amount added by primary productivity.

The inorganic nutrients were determined for the July 1967 stations in North Dawes Inlet (Table 4.9). The values given are approximations because of several problems. Silicate-Si values are higher for non-centrifuged samples in which the suspended material was left for several months prior to analysis than for the centrifuged ones from which the suspended material had been removed soon after collection. This difference was probably due to partial solution of suspended clays

Table 4.9. Chemical nutrient data for North Dawes cruise, July 1967 and cruise 053, September 1967

(All concentrations in microgram atoms/liter)

Station	Depth (m)	PO_4-P	SiO_3-Si	NO_3-N	NO_2-N	NH_3-N
July - 1967						
ND-1	0	0.26 (0.12)*	17.5 (11.5)	0.22 (0.29)	0.37 (0.37)	0.0 (0.0)
ND-2	0	0.18 (1.40)	22.0 (14.2)	0.16 (0.44)	0.46 (0.39)	0.0 (1.3)
ND-3	0	0.52 (0.11)	23.2 (13.1)	- (0.74)	0.52(0.40)	0.0 (0.0)
	0.5	1.30 (0.68)	31.9 (23.6)	2.82 (3.96)	0.67 (0.51)	0.0 (0.0)
ND-4	0	0.51 (0.49)	22.7 (19.9)	2.32 (2.55)	0.44 (0.40)	0.0 (0.3)
	0.5	0.83 (0.28)	32.4 (27.3)	1.64 (0.12)	0.29 (0.05)	1.8 (0.7)
	5.0	1.95 (1.74)	43.9 (41.4)	7.19 (8.35)	0.46 (0.91)	1.4 (1.0)
ND-5	0	0.72 (0.51)	23.1 (16.7)	2.07 (2.48)	0.63 (0.35)	0.4 (0.6)
	0.3	1.50 (0.91)	30.3 (23.0)	3.18 (4.10)	0.48 (0.22)	0.7 (0.6)
	2.0	1.54 (1.28)	48.9 (34.8)	1.60 (4.49)	1.13 (1.01)	1.6 (0.6)
September - 1967						
ND-4f	0	0.55	29.6	0.85	0.44	0.0
	1	0.90	34.1	1.93	1.54	0.0
	10	0.43	46.9	0.03	0.09	0.7
ND-6	0	0.83	29.6	2.28	0.61	0.0
	0.5	1.42	37.4	3.15	0.81	0.2
	3.0	0.38	42.3	0.10	0.06	0.6
EN-25	0	0.15	39.4	0.05	0.04	1.1
	10	0.66	41.8	1.61	1.00	0.8
	50	1.15	50.0	2.96	0.22	0.6

* Values in parentheses were run on the outflow from the continuous flow centrifuge.

in the non-centrifuged samples thereby increasing the silicate-Si content. Nevertheless the values are low for the sediment-laden river water (about 10 - 20 μg A/liter) and increase with salinity to about 40 - 50 μg A/liter for the normal estuarine water in North Dawes.

Wallen and Hood (1968) reported that the technique used to determine nitrate-nitrogen was not reliable because of interference problems from the nitrate to nitrite reduction. Thus the nitrate data run by Wallen prior to 1968 are again approximations. However, several trends are apparent. Nitrate values were low for the inflowing river water and high at depth. The normal increase with salinity noted for silicate-Si was not found for nitrate-N and nitrite-N. Both low nitrate and nitrite values and a high ammonia value were found at ND-4, 50 cm and a similar decrease in nitrate and increase in ammonia was found at ND-5, 2 m for July 1967. Phosphate followed similar trends. This suggests nutrient-clay interactions or phytoplankton uptake. The later seems more likely in light of the other evidence of biological activity in the near surface layers.

Mr. David Wallen (personal communication 1970) has also found strong evidence for a biologically active water layer near the surface in several other inlets with strong haloclines in southeastern Alaska. Since biological activity appears to be occurring in North Dawes Inlet, a measurement of the primary productivity would be useful. Standard ^{14}C uptake techniques might be used, but the presence of the large amounts of clays might affect the results by adsorbing labeled dissolved organics usually not counted in the standard ^{14}C productivity technique.

The values of the various parameters except nutrients were also obtained for 3 streams flowing into North Dawes Inlet: Delta Creek, East and West Creeks. In general the values for the particulate parameters were low and DOC high compared with the North Dawes River. Since the volume of these streams was low compared to the North Dawes River, their contribution to the organic matter of the inlet was quite low on a percentage basis.

IV.2.3. Sediments of North Dawes Inlet and Endicott Arm

Most sediment studies in active glacial fiords have been concerned with the sedimentological and geochemical aspects of the bottom sediments. Little or no mention of the organic matter in these sediments has been made except that there is very little present (D. C. Burrell, personal communication 1970).

Glacially derived marine sediments have been termed periglacial sediments by Wright and Sharma (personal communication 1969) and in general tend to consist of clayey silts or silty clays which do not exhibit any unique qualities that may be associated with glacial influence. They are characterized by low concentrations of organic matter and the clay fractions contain essentially unaltered layered silicates. In North Dawes the clay fractions contained unaltered biotite, chlorite, plagioclase feldspars, hornblende and quartz (D. E. Buckley, personal communication 1970).

In order to determine the relationship of the organic carbon associated with particulate matter in the suspended load and the sediments, a series of grabs and cores were taken in North Dawes Inlet.

The grab samples and their organic carbon and nitrogen contents are listed in Table 4.10.

The bottom sediments in the inlet follow the classic depositional sequence with respect to size distribution, i.e., coarse material is deposited near the sediment source and fine material away from the source. Near the delta the sediments consisted of fine sands with a low organic carbon content and high C/N ratio. Further away from the delta the sediment became increasingly fine with only fine silt and clays comprising the bottom sediment at ND-5 and ND-5a. The sediment then became coarser from ND-5b (silty mud) to ND-6a (dark medium-fine sand). This increase in coarseness indicates that there are strong tidal or turbidity currents present near the bottom at the mouth of North Dawes Inlet which winnow the sediment, leaving the coarser material. The east-west cross section at the mouth of the inlet between ND-5b and ND-6 is almost V-shaped near the bottom. This would constrict currents, increasing their velocity and may be one cause of the suspended material found in the nephalitic or turbid layers. The organic carbon content of the sandy sediments at ND-6 and ND-6a was very low.

Short gravity cores were taken at ND-5a, ND-5b and En-25'. The ND-5a core (Table 4.11) consisted of a series of 1-4 cm thick alternating layers comprised of either brown silty layers or fine gray-brown mud. Both graded and sharp contacts were present between the layers probably a result of episodic increase and decreases such as observed on September 24 and 26, 1968 (section IV.2.2). Similar layers were

Table 4.10. Organic carbon and nitrogen contents of grab samples from North Dawes Inlet and Endicott Arm

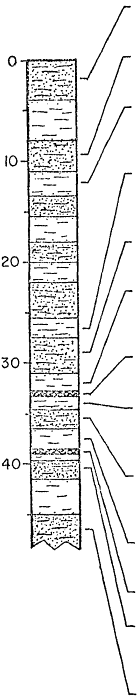
Sample Location	Depth (m)	Sediment Description	% Carbon	% Nitrogen	C/N
North Dawes Inlet					
N. D. Glacier #1	Surf.	Sandy silt	0.014	-	-
N. D. Glacier #2	Surf.	Muddy silt	0.085	-	-
ND-4	32	Fine sand	0.070	0.0035	20
ND-4a	70	Sandy mud	0.091	-	-
ND-5	80	Brownish-gray mud	0.117	0.0078	15
ND-5a	85	Gray mud	0.091	0.0045	20
ND-5b	150	Silty gray mud	0.069	-	-
ND-6	193	Fine dark sand	0.015	-	-
ND-6a	215	Dark sand	0.007	-	-
Endicott Arm					
En-25'	220	Light brown mud	0.094	0.0096	9.8
En-15	250	Fine light brown mud	0.424	0.042	10

found in the ND-5b core (Table 4.12). If these layers do represent episodic changes in the river flow and not simple yearly variations, then the sedimentation rate in the middle of North Dawes Inlet would be on the order of several tens of cm/yr. This rate probably increases to several meters near the delta.

The water content of the different layers ranged from 25-35% and showed no apparent variation with respect to either the depth in the core or the type of layer. The carbonate content based on observed "fizzing" and weight changes on addition of acid was very low (< 2%). The organic carbon content of the cores was low and ranged from 0.0057 to 0.149% with an average of about 0.090%. The organic nitrogen content was determined for some of the layers and ranged from 0.0022 to 0.0085% resulting in C/N ratios of 10-32. None of the organic parameters showed significant correlation with depth of the core or sediment type.

A core was collected at En-25' (Table 4.13) for comparison with the North Dawes cores since En-25' is in the main channel of Endicott Arm and away from the direct sedimentary influence of the North Dawes River and Inlet. The core consisted of fine muds instead of the sands found in Endicott Arm less than 2 km away at ND-6a. The fine muds of the core were light olive brown near the top and changed to light grayish brown with depth. There were no alternating layers of coarse and fine material as were found in the North Dawes cores, but there were several dark gray layers. The dark gray or "black layers" were generally less than a cm in thickness and ranged

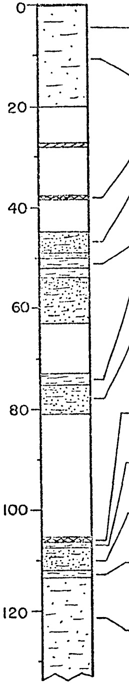
Table 4.11. Organic carbon and nitrogen content of core from North Dawes Inlet taken at ND-5a



Depth (cm)	Sample Interval	Sediment Description	% Carbon	% Nitrogen	C/N
	Surface	Gray mud	0.091	0.0045	20
	8-11 cm	Brown silty mud	0.087	-	-
	11-13.5 cm	Fine gray-brown mud	0.106	0.0077	14
	25.5-27.5 cm	Fine gray-brown mud	0.101	-	-
	27.5-31 cm	Brown silty mud	0.125	0.0085	15
	31-33 cm	Fine gray-brown mud	0.070	0.0022	32
	33 cm	Dark gray mud	0.066	0.0051	13
	33-34.5 cm	Fine gray-brown mud	0.057	0.0039	14
	34.5-36.5 cm	Brown silty mud	0.149	-	-
	36.5-38.5 cm	Fine gray-brown mud	0.092	-	-
	38.5 cm	Black mud	0.079	0.0076	10
	39-41.5 cm	Gray brown silty mud	0.112	-	-
	45-48 cm	Brown silty mud	0.092	0.0050	18

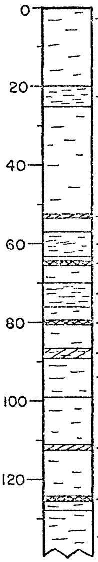
Table 4.12. Organic carbon and nitrogen content of core from North Dawes Inlet taken at ND-5b

Depth (cm)



Sample Interval	Sediment Description	% Carbon	% Nitrogen	C/N
Surface	Silty gray mud	0.069	-	-
0-20 cm	Silty gray mud	0.107	-	-
38 cm	Black mud	0.098	-	-
45-49 cm	Silty gray mud	0.071	-	-
50-52 cm	Fine gray mud	0.061	-	-
73-75 cm	Fine gray mud	0.059	-	-
76-81 cm	Silty brown mud	0.130	-	-
106 cm	Black mud	0.120	0.0068	18
106-107 cm	Fine gray mud	0.084	-	-
107-112 cm	Silty brown mud	0.095	-	-
112-113 cm	Fine gray mud	0.126	-	-
113-133 cm	Mixture of silty and fine layers	0.104	-	-

Table 4.13. Organic carbon and nitrogen content of core from Endicott Arm taken at En-25'



Sample Interval	Sediment Description	% Carbon	% Nitrogen	C/N
Surface	Light brown mud	0.094	0.0096	9.8
20-25 cm	Light brown mud	0.058	-	-
53 cm	Dark gray mud			
57-63 cm	Dark gray mud	0.117	0.0104	11
65 cm	Black mud	0.098	0.0104	9.4
70-76 cm	Dark gray mud	0.067	0.0030	22
80 cm	Black mud	0.109	0.0112	9.7
87-89 cm	Dark gray mud			
90-99 cm	Light gray-brown mud	0.122	-	-
112 cm	Dark gray mud			
125 cm	Black mud	0.117	0.0121	9.7
128-138 cm	Light gray-brown mud	0.075	0.0089	8.5

from 7-23 cm (average 15 cm) apart in the core. Similar layers were reported for Queen Inlet (Hoskin and Burrell 1968) and Rendu Inlet (D. C. Burrell, personal communication 1969) in Glacier Bay, but there the spacing between layers was on the order of 30 cm to greater than 100 cm. For Queen Inlet the spacing between layers decreased with increasing distance from the head of the inlet. The gray-black layers found in the cores at ND-5a and ND-5b always occurred in the fine mud layers which graded into more silty layers above and below. If the En-25' black layers are of a similar origin they may be related to quiet periods of deposition suggesting a periodic or seasonal phenomenon.

The origin and chemical nature of the layers has not yet been fully determined, but several observations have been made by myself and others at the University of Alaska. The black color of the layer disappeared when exposed to air for a short period of time. When dilute HCl was added to a sample black layer, an H_2S odor was detectable. The carbon and nitrogen contents of the black layers were not significantly different than the layers above and below them although the black layers in En-25' had slightly lower C/N ratios than the rest of the core. However, the organic carbon content of the black layers from Queen Inlet and Rendu Inlet (D. C. Burrell, unpublished data 1969) were slightly higher than the rest of the core. Ethanol (95%) extracts of black layers from Rendu Inlet were green and had a medium sharp absorption peak at about 660 mμ and a strong broad absorption peak at 410-425 mμ (R. Hadley, personal communciation 1969).

This absorption curve suggests the presence of chlorophyll a or a bacterio-chlorophyll such as chlorobium chlorophyll 660 from the green sulfur bacteria of the genera, Chlorobium (Goedheer 1966). Further work is necessary before the nature and origin of the black layers is fully understood.

IV.2.4. Queen and Reid Inlets, Glacier Bay

In order to compare observations in North Dawes Inlet with other glacial systems, two glacial inlets in Glacier Bay were sampled on cruise 074 (Fig. 4.5).

Queen Inlet is a typical glaciated fiord with high steep rock walls and a receding valley glacier (Carroll Glacier). An outwash fan in front of the Carroll Glacier has been built across the head of the inlet and is criss-crossed by melt water streams (Hoskin and Burrell 1968). The amount of PM and POC carried by the outwash streams was an order of magnitude greater than in the North Dawes River, but the amount of POC in the PM was 0.08% or about equal to that for North Dawes River in front of the North Dawes Glacier (Table 4.1). The DOC values for the runoff water in Queen Inlet as well as Reid Inlet was very low (0.11 - 0.14 mg C/liter) probably due to the lack of vegetation in the runoff area (Table 4.14).

The mixing layer at QI-10 was thicker than 10 m and its DOC content ranged from 0.18 mg C/liter at 5 cm to 0.84 mg C/liter at 10 m. A similar pattern was found in Reid Inlet. In both inlets the amount of DOC found in layers of intermediate salinity could be predicted on the basis of mixing alone.

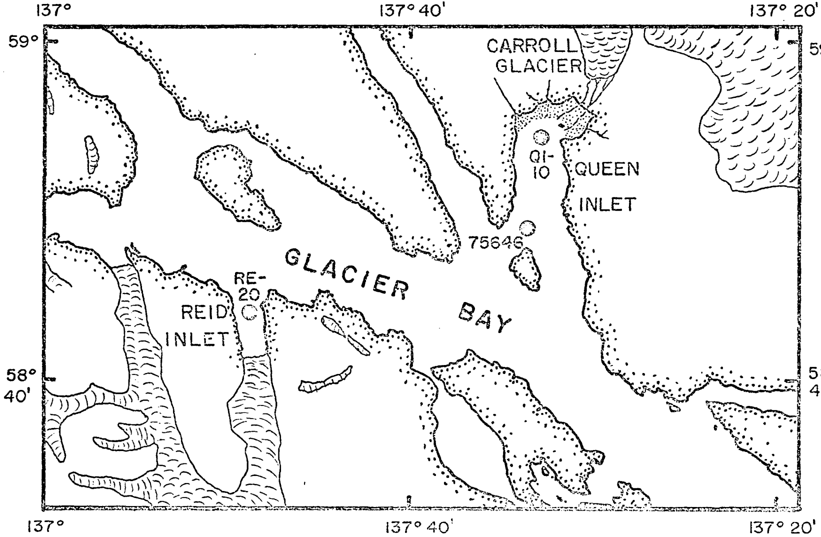


Fig. 4.5. Station locations in Glacier Bay for cruise 074, September, 1968.

Table 4.14. Data for cruise 074, Reid and Queen Inlets, Glacier Bay, September 17-20, 1968

IMS Ref. Number	Station Name	Date	Depth	DOC (mg/liter)	POC* (μg/liter)	PM (mg/liter)	POC/PM (x 100)	Salinity† (°/oo)
-	Reid Inlet Stream	9-17	Surf	0.11	-	113	-	0.0
74638	RE-20	9-17	5 cm	0.28	-	46	-	5.7
	RE-20	9-17	50 cm	-	-	63	-	11.4
	RE-20	9-17	2 m	-	-	21	-	22.7
	RE-20	9-17	4 m	0.98	-	14	-	27.5
-	Queen Inlet Stream	9-19	Surf	0.14	3590	4690	0.08	0.0
74639	QI-10	9-18	5 m	0.18	113	71	0.16	1.5
	QI-10	9-18	20 cm	-	51	40	0.13	3.9
	QI-10	9-18	50 cm	0.55	906	751	0.12	15.5
	QI-10	9-18	1 m	0.71	1320	1130	0.12	21.3
	QI-10	9-18	3 m	-	541	1170	0.05	24.5
	QI-10	9-18	5 m	0.84	1260	1150	0.11	24.5
	QI-10	9-18	10 m	-	-	-	-	27.1
74646	Queen Inlet	9-20	30 m	0.94	66	-	2.07	3.2

* Based on dry combustion of filters treated with 50% HCl to remove the carbonates. The acid was dried on the filters.

† Salinity based on hydrometer determinations.

The amount of POC and PM in the mixing layer did not decrease with depth as in North Dawes, but there was a very sharp increase of both parameters from a low of 51 µg C/liter and 40 mg/liter at 20 cm to 1320 µg C/liter and 1130 mg/liter at 1 m depth (Fig. 4.6). The percentage of organic carbon in the PM decreased slightly with the greater than 20 fold increase in PM. This is in contrast with North Dawes Inlet where the percentage increased with depth in the mixing layer. The consistant value of the POC/PM (x 100) probably resulted from the continued suspension of the coarser material throughout the mixing layer by strong currents. This is substantiated by Burrell and Gatto (1969) who reported no correlation of size distribution of the sub-surface suspended sediments with depth in Queen Inlet. The sudden drop of POC at 3 m and return to the 1 m value at 5 m suggests that the 3 m POC value is suspect (Fig. 4.6).

A surface grab and a 220 cm core sample were taken at QI-10 and analyzed for carbonate and organic carbon content. Although QI-10 is near the outwash plain, the core did not exhibit the alternating coarse and fine layers as found in North Dawes Inlet, but three "black layers" were present approximately 1 m apart. The carbonate content (% loss on addition of acid and washing with distilled water) ranged from 23 - 24% for 3 samples near the top down to 17 - 21% for 3 samples near the bottom of the core. The average carbon content for 4 non-black layers was 0.11% while that of the black layers was 0.15%.

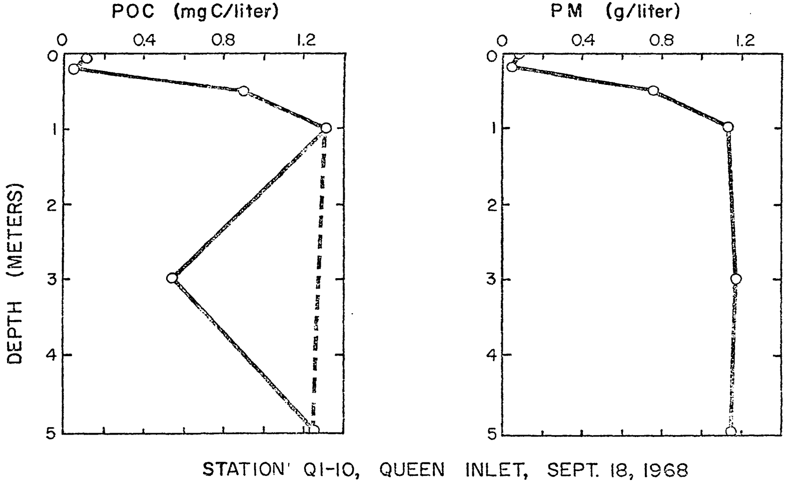


Fig. 4.6. Particulate organic carbon (POC) and particulate matter (PM) profiles at station QI-10.

In additon to the normal procedure for preparing sediment samples for organic carbon analysis (Fig. 3.8), a second group of the samples were prepared by repeated washing after addition of acid to remove carbonates. The washing procedure removed about 25% of the organic carbon found by the normal procedure. The organic carbon content of the sediment was about the same as that of the PM, suggesting that essentally all the POC in the PM was deposited with the sediment. This contrasts with North Dawes Inlet where a portion of the POC was separated from the suspended material and carried out of the inlet. Since the final concentration of organic matter in the sediments of North Dawes Inlet and Queen Inlet was the same, the different values in the PM just discussed may be due to differences in the nature of the organic matter involved.

IV.2.5. Glacial Fiords, Conclusion

Based on the studies of North Dawes Inlet, Endicott Arm and Queen Inlet I have concluded the following about the distribution and significance of organic matter in glacial fiords:

1. Although the POC content of the glacial runoff is high, it represents but a small fraction of the total glacial detritus.

2. The DOC and inorganic nutrient values of glacial meltwater are low compared to the estuarine water.

3. In North Dawes Inlet about half of the POC entering is not deposited in the inlet but is carried out in suspension. In Queen Inlet, however, the POC appears to be deposited in the inlet with the sediment.

4. There is significant biological activity (growth of phytoplankton, etc) in a layer just beneath the surface "mixing layer". This layer has been named the "biologically active layer" (BAL) and is characterized by almost normal salinity, low PM, high DOC and POC and low C/N ratios. In addition some of the inorganic nutrients may be depleted in this layer. This BAL is absent at the head of Queen Inlet, possibly due to the thickness of the mixing layer. It is probably present near the mouth of Queen Inlet where the mixing layer is thinner.

5. During the winter months of low runoff, low productivity and vertical mixing in Endicott Arm the amount of organic carbon approaches the low values found in the deep ocean and is relatively homogeneous with respect to both depth and length of the inlet.

6. The rate of sedimentation is quite rapid in North Dawes Inlet. The finer sediments are characterized by alternating layers of silty and clayey muds. The normal and reverse graded bedding found between layers is probably due to episodic variations in river flow. In addition, there are "black layers" present which may be seasonal in the nature of their deposition.

7. Adsorption or release of organic compounds (in terms of organic carbon) by the glacial clays in the mixing layer is presently undetectable within the precision of the methods used in this study.

IV.3. Organic Matter in Marine Waters in Winter

The winter distribution of organic carbon was determined for selected areas in the Alexander Archipelago on cruises 030, 032 and

056. The data for cruise 056 are given in Table 4.15. and the station locations are shown in Fig. 4.7. The specific data for cruises 030 and 032 are not given although they will be discussed in general terms.

For cruise 056 (November 1967) the values of DOC ranged from 0.40-1.75 mg C/liter. Low values of DOC were found in the larger open straits (Chatham Straits, Stephens Passage) whereas higher more variable values were found in several of the inlets such as Tenakee Inlet and Peril Straits.

POC values were low ranging from 27-64 μg C/liter and PN values ranged from 6-11 μg N/liter resulting in C/N ratios of 3.3-7.6 with an average of 5.4. This C/N ratio is normal for open marine water and reflects the marine source of most of the particulate matter. The PM values were low ranging from 0.25-0.83 mg/liter.

The POC values determined on cruises 030 and 032 were also low ranging on the average from 20-50 μg C/liter. There was a slight decrease in POC with depth for most of the 12 stations sampled. High surface values of POC (>100 μg C/liter) were found at three locations, the heads of Snettisham Arm and Tenakee Inlet and in the middle of Glacier Bay. All three of these locations had reduced surface salinities suggesting that the high POC values were due to stream runoff.

Several streams were sampled for the various organic parameters (Table 4.15) indicating wide variation between streams. All the streams except Cannery Creek had as high or higher values of DOC, POC, PN and PM than the marine water into which they flowed. This suggests

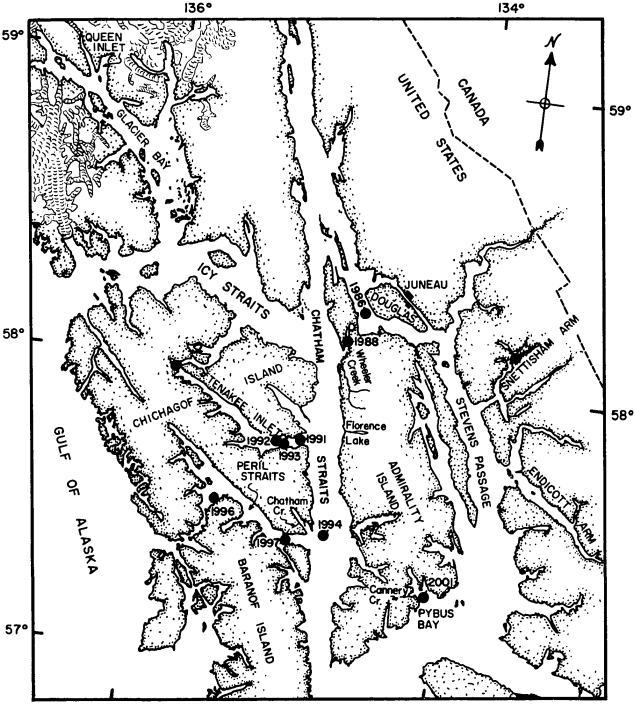


Fig. 4.7. Station locations in the Alexander Archipelago (Southeastern Alaska) for cruise 056, November, 1967.

Table 4.15. Organic and particulate data for Admiralty Island area, cruise 056, November 13-16, 1967

Station and Date	Depth	DOC (mg/liter)	POC (µg/liter)	PN (µg/liter)	PM (mg/liter)	POC/PM (x 100)	C/N
1986, 11-13	2 m	0.50	64	11	0.69	9.3	5.8
	10 m	0.65	36	11	0.25	14.4	3.3
1988, 11-13	2 m	0.55	60	7.9	0.60	10.0	7.6
1991, 11-14	10 m	0.55	30	-	0.48	6.2	-
1992, 11-14	2 m	1.00	54	9.1	0.36	15.2	5.9
1993, 11-14	3 m	1.20	52	-	0.38	13.7	-
1994, 11-14	3 m	0.40	56	9.8	0.68	8.2	5.7
	300 m	0.50	27	6.0	0.59	4.6	4.5
1996, 11-15	10 m	0.80	36	9.0	0.34	10.6	4.0
1997, 11-15	3 m	1.75	55	9.4	0.36	15.3	5.9
2001, 11-16	10 m	0.50	38	7.2	0.42	9.0	5.3
	50 m	0.45	46	7.6	0.83	5.5	6.1
Fresh Water Streams							
Wheeler Creek, 11-14	Surf	2.2	220	7.6	1.24	17.7	29
Florence Creek, 11-14	Surf	2.6	90	13	0.61	14.8	6.9
Chatham Creek, 11-15	Surf	6.0	256	33	2.46	10.4	7.8
Cannery Creek, 11-16	Surf	0.55	32	2.4	0.18	17.8	13

that the organic matter in runoff, particularly the POC, might be an important source of detritus for zooplankton in selected areas during the early winter months of high rainfall. A large budgetary study of seasonal runoff and its organic content, the marine water and its organic content, primary productivity and zooplankton populations would have to be undertaken before this could be shown conclusively.

Chapter V

PACIFIC RIM AREAS

Chapter V

PACIFIC RIM AREAS

The distribution of organic carbon and other chemical and physical parameters were determined for two different areas adjacent to the Gulf of Alaska; Cook Inlet and the shelf area around Kodiak Island. A third area investigated was the southeastern part of the Bering Sea just north of Unimak Pass.

Correlation and factor analysis were used to interpret the data from the first two areas showing the relationship of organic carbon to various commonly measured parameters and determining its significance in the specific areas studied. Organic carbon data from the area north of Unimak Pass are presented with only minimal discussion because of a lack of support data.

V.1. Cook Inlet

Cook Inlet, a major tidal estuary located in southcentral Alaska (Fig. 5.1), is more than 150 n miles long and approximately 50 n miles wide at the mouth. The head of the inlet is divided into two arms, Turnagain Arm which is 43 n miles long and Knik Arm which is 45 n miles long. The inlet is divided into two natural regions, a northern portion and a southern portion, by a topographic feature, the Forelands, which extend part way into the inlet from both the east and west sides causing a natural constriction (Rosenberg et al., 1967).

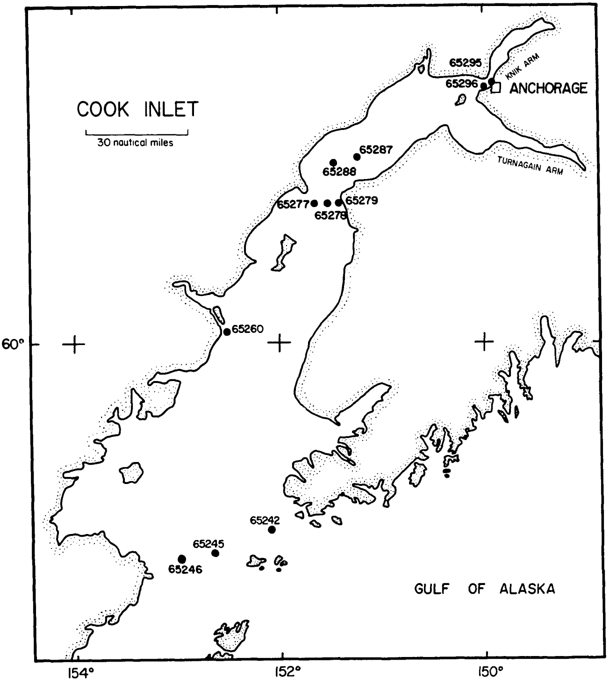


Fig. 5.1. Station locations in Cook Inlet, cruise 065, May 21-30, 1968.

Tides in the inlet are large, ranging from a mean diurnal range of 4.2 m at the mouth to 9.0 m at the city of Anchorage on Knik Arm. These large tidal ranges produce moderate to high current velocities with maximum velocities in the range of 2.8 to 3.0 knots and velocities tend to keep in suspension essentially all the fine suspended material carried into the inlet north of the Forelands (Burrell, Rosenberg and Hood 1967).

Two glacially fed rivers, the Susitna and the Knik, provide 70-80% of the input of fresh water to the inlet. More than half the annual input occurs during the three summer months (Burrell, Rosenberg and Hood 1967). Total flushing of the inlet by tidal and river driven flushing is 90% complete in about 10 months (Kinney, Button and Schell 1969).

V.1.1 Introduction

The data for the physical and nutrient parameters were collected by Institute of Marine Science personnel on R/V Acona cruise 065 from May 21 to 30, 1968. The carbon samples were prepared and analyzed by Miss Joanne Groves of the Institute of Marine Science.

Station locations are shown in Fig. 5.1 and the data are given in Table 5.1. All of the variables except PM and POC/PM were used in the correlation and factor analyses. These two were not used because data were missing for a number of samples which would bias the final results; missing data are given a value of zero in the computer analysis.

IMS REF NUMBER	DEPTH METERS	TEMP C DEG	SAL PPT	OXY ML/L	PO4 µG-A/L	NH3 µG-A/L	NO2 µG-A/L	NO3 µG-A/L	SIO3 µG-A/L	DOC MG-C/L	POC µG-C/L	PM MG/L	POC/PM (x100)
65242	1	5.97	31.66	8.40	0.97	0.40	0.22	7.90	17	0.79	97	-	-
	74	4.93	31.91	7.34	1.33	1.40	0.20	13.90	25	0.70	92	1.00	9.20
	147	4.94	32.02	7.32	1.37	1.20	0.24	13.70	23	0.51	84	0.16	52.50
65245	1	5.89	31.81	8.65	1.03	1.40	0.18	7.80	17	0.67	139	-	-
	50	4.97	31.92	7.33	1.29	1.20	0.19	13.60	22	0.45	350	-	-
65246	1	6.37	31.65	9.98	0.50	1.30	0.06	0.20	10	1.15	190	0.71	26.80
	75	5.02	31.94	7.38	1.32	1.30	0.17	13.20	21	0.94	37	0.51	7.20
65260	1	5.26	30.21	7.66	1.34	1.10	0.24	11.70	22	1.02	106	-	-
	30	4.98	30.61	7.80	1.52	1.50	0.27	11.20	21	0.84	94	-	-
	49	4.99	30.63	7.84	1.58	1.20	0.30	11.30	21	0.77	91	-	-
65277	1	4.90	28.13	7.76	1.11	1.80	0.17	13.80	40	8.80	763	-	-
	10	4.89	28.13	7.81	1.07	0.01	0.16	13.90	40	1.45	900	-	-
65278	1	5.06	27.37	7.81	0.99	0.60	0.15	14.20	48	5.10	2050	194.00	1.05
	20	5.06	27.38	7.80	1.04	0.70	0.18	14.30	44	12.80	1225	146.00	0.84
65279	1	5.60	27.19	7.79	1.10	1.10	0.11	14.40	49	1.03	1880	-	-
	10	5.55	27.20	7.81	1.11	0.70	0.13	14.30	49	1.23	2520	-	-
65287	1	5.00	25.27	7.91	0.98	0.50	0.20	13.00	48	5.60	327	125.00	0.26
65288	1	4.90	25.96	7.89	1.02	1.20	0.42	12.90	49	9.40	894	155.00	0.58
	20	4.89	25.98	7.91	1.01	1.20	0.38	15.00	49	10.20	822	149.00	0.55
	50	4.90	25.78	8.12	1.04	1.10	0.25	14.70	1	2.00	1690	198.00	0.85
65295	1	8.58	17.65	7.55	0.67	0.80	0.27	15.10	68	6.00	2740	390.00	0.70
65296	1	8.74	17.55	7.52	0.62	0.40	0.23	17.00	64	8.50	1805	480.00	0.38
	30	8.12	17.63	7.96	0.76	0.90	0.16	17.60	71	2.70	4800	1350.00	0.36

Table 5.1. Data for cruise 065, Cook Inlet. All variables except PM and POC/PM were used in correlation and factor analyses

V.1.2. Results and Discussion

On the basis of the data the inlet may be divided into 3 areas. The area near the mouth is characterized by nearly normal ocean salinity (31-32 ppt.) and nutrients with some depletion of nutrients at the surface such as seen at stations 65-242, 245 and -246. The DOC and POC values are normal for spring-summer ocean water not supporting a large phytoplankton bloom.

The areas both north and south of the Forelands are characterized by strong currents and vertical mixing of the water column resulting in salinity values that are nearly the same vertically at a given station but decrease toward the head of the inlet. DOC, POC and PM data showed great variability which may be due in part to drifting at station by the the ship causing the sampling of different water masses since samples were taken with a single sampler sometimes at large time intervals (10-30 min.). Salinity values would not show this variability because the samples are taken almost simultaneously with Nansen bottles (P. J. Kinney, personal communication 1970). The linear correlation between POC and PM is r = 0.927 (13 samples) suggesting a common source and a generally similar response to mixing processes in the inlet. The high values of POC and PM in the Forelands area and their POC/PM (x 100) ratio suggest that not only mixing and dilution are occurring, but also sedimentation and resuspension. The finer sediments which usually contain higher percentages of organic matter are probably resuspended by strong tidal currents increasing the POC/PM (x 100) ratio.

The two stations in Knik Arm were characterized by higher temperatures, silicate, nitrate, DOC, POC and PM values and lower salinities than the rest of the inlet because of the influx of fresh water from the river. The very high nitrate, DOC and POC values for the river input and the fact that these samples were taken in late May prior to the major summer runoff suggests that much of the runoff water was melt from lowlands which would include large amounts of organic matter. In addition, the percentage of organic carbon in the PM (POC/PM x 100) was 2-4 times higher than was found in glacial runoff in Southeastern Alaska (Chapter IV). Since most of the PM in the Knik and Susitna Rivers is of glacial origin, the organic matter is probably added to the river from the lowland areas. Although there are a number of oil wells in the area just north of the Forelands which might be considered a pollution source of organic matter, the high DOC values are probably not due to oil pollution since hydrocarbons are undetectable in the water and suspended sediment except in the immediate vicinity of an oil spill (Kinney, Button and Schell 1969).

A factor analysis was run on the correlation matrix (Table 5.2) with the chosen 4 factors explaining 84.4% of the total variance (Tables 5.3 and 5.4). As might be expected from the above discussion of the processes in Cook Inlet, the variables most strongly affected by the dynamic freshwater-saltwater mixing processes in the inlet are mainly in factor I and include salinity, temperature and POC. The signs indicate that salinity is inversely proportional to temperature and

Table 5.2. Correlation matrix for Cook Inlet data, cruise 065

	DEP	TEMP	SAL	OXY	PO4	NH3	NO2	NO3	SIO3	DOC	POC
DEP	1.000	-0.289	0.355	-0.408	0.530	0.306	0.102	0.170	-0.368	-0.352	-0.247
TEMP	-0.289	1.000	-0.753	0.111	-0.700	-0.293	-0.121	0.139	0.548	0.115	0.612
SAL	0.355	-0.753	1.000	0.161	0.627	0.398	-0.153	-0.584	-0.818	-0.497	-0.809
OXY	-0.408	0.111	0.161	1.000	-0.509	0.057	-0.315	-0.824	-0.321	-0.111	-0.093
PO4	0.530	-0.700	0.627	-0.509	1.000	0.384	0.242	0.112	-0.455	-0.378	-0.510
NH3	0.306	-0.293	0.398	0.057	0.384	1.000	0.138	-0.229	-0.401	-0.119	-0.320
NO2	0.102	-0.121	-0.153	-0.315	0.242	0.138	1.000	0.259	0.079	0.373	-0.163
NO3	0.170	0.139	-0.584	-0.824	0.112	-0.229	0.259	1.000	0.622	0.352	0.551
SIO3	-0.368	0.548	-0.818	-0.321	-0.455	-0.401	0.079	0.622	1.000	0.563	0.718
DOC	-0.352	0.115	-0.497	-0.111	-0.378	-0.119	0.373	0.352	0.563	1.000	0.216
POC	-0.247	0.613	-0.809	-0.093	-0.510	-0.320	-0.163	0.551	0.718	0.216	1.000

Table 5.3. Primary composition of 4 factors for Cook Inlet data based on the varimax matrix with percentages of the total variance "explained" by each factor

Factors							
I (33.5%)		II (22.2%)		III (15.6%)		IV (13.4%)	
SAL	0.887	OXY	-0.949	DOC	0.841	NH3	0.887
TEMP	-0.885	NO3	0.842	NO2	0.759		
POC	-0.873						
SIO3	-0.719						
PO4	0.704						

Table 5.4. Eigenvalues and percent variance "explained" for Cook Inlet data

Factor	Eigenvalue*	Percent*	Cumulative Percent
I	4.54	41.3	41.3
II	2.59	23.5	64.8
III	1.34	12.1	76.9
IV	0.86	7.8	84.7
V	0.62	5.7	90.4
VI	0.44	4.0	94.4
VII	0.32	2.9	97.3
VIII	0.16	1.4	98.7
IX	0.08	0.7	99.4
X	0.05	0.5	99.9
XI	0.01	0.1	100.0

* These values are for the unrotated factor matrix.

POC. Silicate and phosphate are also included in factor I although their correlation with salinity was lower than temperature and POC Tables 5.2 and 5.3). This suggests that the concentrations of silicate and phosphate are controlled more by the physical mixing process than the biological. Factor I, mainly the physical mixing processes, accounted for 33.5% of the variance of the data collected in the inlet.

Factor II was mainly composed of 2 variables, oxygen and nitrate, which are negatively correlated. The grouping of these two variables in one factor suggests that the amount of nitrate and dissolved oxygen are at least partially controlled by the same process, i.e. biological processes. This is particularly true at the inlet mouth where phytoplankton growth has reduced the surface nitrate and increased the oxygen content.

Factor III was mainly composed of DOC and nitrite; they have a low correlation coefficient of 0.352 (Table 5.2), however, indicating that there is little relationship between them. Perhaps the restriction of chosing only 4 factors for the rotation "forced" these two variables together. Thus their appearance may not be representative of a fundamental relationship between them. DOC and nitrite are essentially independent variables as is ammonia in factor IV. If more factors had been requested for varimax rotation, the rest of the variables would each fit into a factor showing that except for the 7 variables found related in factors I and II, the rest of the variables are independent, unrelated to each other and affected by processes for which related variables were not measured.

V.1.3. Conclusions

Although the Cook Inlet data were limited, several tentative conclusions can be made:

1. The physical mixing processes, including the inflow of fresh sediment-laden water and subsequent turbulent mixing with the inlet waters, are the most important processes and "explain" about 33.5% of the variance in the data. The variables most affected are salinity, temperature, POC, silicate and phosphate.

2. The only other well correlated variables are nitrate and oxygen which as factor II "explain" about 22.2% of the variance in the data and are affected by phytoplankton growth near the mouth of the inlet. Nitrate values are also somewhat influenced by the river mixing and show a negative correlation (-0.584) with salinity.

3. The remainder of the variables, DOC, nitrite, ammonia and depth, are independent variables. Although DOC correlates somewhat with salinity (-0.497) due to the high DOC values in the river input, the correlation was low because of the large variability of DOC values (ranging from 1-13 mg C/liter) in the Forelands area. Consequently it is difficult to determine if other than mixing processes affect the distribution of DOC.

V.2. Kodiak Shelf

Kodiak Island, located in the western part of the Gulf of Alaska, is surrounded by the Gulf of Alaska on the east, Cook Inlet on the north, Shelikof Strait and the Alaska Peninsula on the west and the

Pacific Ocean on the south. Because of its location and broad shelf areas, the waters surrounding the island are very productive and support a large fishing and crabbing industry.

V.2.1. Introduction

The standard physical and chemical oceanographic parameters were determined by Institute of Marine Science personnel for the shelf waters surrounding Kodiak on R/V Acona cruise 045 from June 21-30, 1967. I determined the DOC and POC for the stations located on Fig. 5.2. Samples from 3 depths (2 surface and 1 deep) were determined for 12 stations and 2 near surface depths for 5 stations totaling 46 observations for the 17 stations. This data (Table 5.5) was used in a correlation and factor analyses to determine the relationship of DOC and POC to the standard oceanographic parameters and their significance in a highly productive area.

V.2.2. Results and Discussion

For most of the stations sampled the 1 and 10 m samples were above the thermocline and were depleted in nutrients, notably silicate, nitrate and phosphate. Several stations i.e., 45-372, -382 and -383, had high nutrient values and low temperatures at the surface indicating recent vertical mixing and upwelling. The values for the nutrients in deep water were generally high with the highest values at stations 45-420, -409 and -364. The surface layers were generally oxygen supersaturated with an average of 117% saturation (1 and 10 m samples) while the deep samples were slightly undersaturated with an average of 97% saturation (50, 75 or 100 m samples).

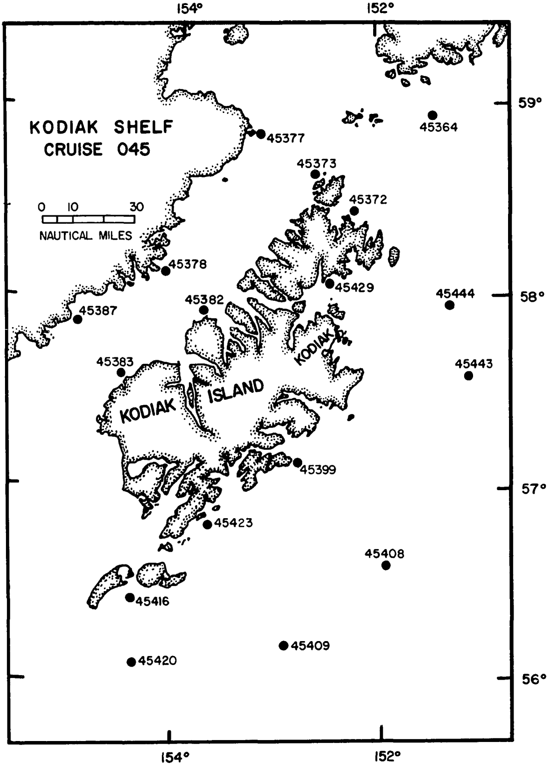


Fig. 5.2. Station locations for Kodiak Shelf, cruise 045, June 21-30, 1967.

IMS REF NUMBER	1.DEPTH METERS	2.TEMP C DEG.	3. SAL PPT	4.OXY ML/L	5. PO4 µG-A/L	6. NH3 µG-A/L	7. NO2 µG-A/L	8.NO3 µG-A/L	9.SIO3 µG-A/L	10.DOC MG-C/L	11.POC µG-C/L	12.SIG T
45364.	1.	9.49	32.140	7.33	0.57	0.60	0.03	0.01	1.	1.23	368.0	24.83
45364.	10.	9.35	32.150	7.31	0.37	0.30	0.01	0.10	1.	1.14	332.0	24.86
45364.	100.	4.75	32.450	6.50	1.56	1.90	0.14	7.60	26.	0.82	40.0	25.71
45372.	1.	5.95	32.120	7.58	1.02	2.00	0.17	2.40	15.	0.99	232.0	25.31
45372.	10.	5.76	32.140	7.53	1.02	1.80	0.16	2.60	16.	0.93	289.0	25.35
45372.	75.	5.73	32.230	7.47	1.18	2.40	0.14	3.80	17.	0.78	215.0	25.42
45373.	1.	8.11	32.000	8.49	0.24	0.70	0.02	0.01	2.	1.13	744.0	24.93
45373.	10.	6.77	32.040	7.99	0.57	1.80	0.09	0.90	6.	1.33	723.0	25.14
45373.	100.	5.12	32.260	6.77	1.44	3.30	0.15	4.40	22.	0.78	44.1	25.52
45377.	1.	8.48	30.460	8.03	0.47	1.30	0.10	0.30	9.	1.00	414.0	23.67
45377.	10.	7.75	30.620	7.76	0.63	0.90	0.13	1.00	10.	0.82	423.0	23.90
45377.	99.	6.08	32.050	7.13	1.07	3.80	0.15	1.90	12.	0.85	88.3	25.08
45378.	1.	9.07	31.160	9.73	0.20	1.30	0.06	0.01	1.	0.87	1392.0	24.06
45378.	10.	8.84	31.180	9.96	0.23	1.30	0.05	0.01	1.	1.21	1067.0	24.10
45378.	100.	5.12	32.160	7.16	1.30	3.20	0.21	3.00	18.	0.97	61.7	25.44
45382.	1.	5.83	31.990	7.69	0.87	0.90	0.16	2.30	12.	0.82	567.0	25.22
45382.	10.	5.03	32.240	7.24	1.25	2.60	0.18	3.50	15.	0.88	266.0	25.51
45383.	1.	7.92	32.220	7.25	0.58	1.60	0.05	0.01	13.	1.27	175.0	25.13
45383.	10.	7.52	32.300	7.26	0.61	1.70	0.07	0.10	12.	1.07	167.0	25.25
45383.	50.	6.84	32.360	7.22	0.74	1.70	0.11	0.60	14.	1.13	117.0	25.39
45387.	1.	8.29	31.160	8.52	0.30	0.80	0.05	0.01	2.	1.15	553.0	24.24
45387.	10.	8.16	31.180	8.22	0.30	1.90	0.05	0.01	1.	1.07	479.0	24.28
45387.	99.	5.35	32.110	7.17	1.25	4.20	0.20	3.60	15.	0.93	55.6	25.38
45399.	1.	7.38	30.700	8.21	0.47	1.00	0.06	0.10	5.	1.57	447.0	24.00
45399.	10.	6.57	31.030	8.32	0.55	1.20	0.08	0.20	7.	1.47	340.0	24.37
45399.	75.	5.45	32.500	6.94	1.20	5.50	0.15	2.60	18.	1.26	123.0	25.66
45408.	1.	9.28	32.290	7.67	0.55	1.20	0.03	0.01	2.	1.22	482.0	24.98
45408.	10.	7.90	32.350	7.61	0.52	0.60	0.07	0.40	1.	1.51	429.0	25.23
45409.	1.	9.18	32.320	7.24	0.51	0.50	0.06	0.30	1.	1.51	148.0	25.02
45409.	10.	8.73	32.370	7.49	0.53	0.50	0.06	0.30	1.	1.01	151.0	25.12
45409.	75.	4.78	32.780	6.24	1.72	1.00	0.15	7.50	31.	1.07	44.2	25.96
45416.	1.	8.53	32.930	7.24	0.73	0.30	0.09	0.30	9.	1.13	222.0	25.59
45416.	10.	8.13	32.940	7.21	0.62	1.70	0.09	0.30	7.	0.96	162.0	25.66
45420.	1.	9.32	32.250	7.35	0.41	1.60	0.02	0.01	2.	0.79	248.0	24.94
45420.	10.	8.31	32.320	7.79	0.41	1.30	0.01	0.01	2.	0.82	249.0	25.15
45420.	100.	4.72	32.880	5.64	1.82	2.60	0.20	8.20	36.	0.63	32.8	26.05
45423.	1.	9.27	32.290	7.48	0.34	1.20	0.01	0.10	2.	1.12	195.0	24.98
45423.	10.	8.27	32.380	7.63	0.35	1.70	0.01	0.01	0.	1.10	230.0	25.20
45429.	1.	9.76	31.470	7.96	0.50	0.80	0.24	0.01	3.	1.01	663.0	24.26
45429.	10.	6.47	32.150	7.67	0.87	2.70	0.12	1.10	8.	0.95	600.0	25.27
45443.	1.	7.47	32.070	8.77	0.57	2.00	0.10	0.40	8.	1.11	604.0	25.07
45443.	10.	6.55	32.080	7.92	0.78	2.80	0.16	1.00	12.	0.74	167.0	25.20
45443.	75.	5.56	32.140	7.12	1.19	4.10	0.28	2.70	18.	0.88	133.0	25.37
45444.	1.	7.11	32.115	9.32	0.42	2.00	0.05	0.01	3.	0.93	183.0	25.15
45444.	10.	5.76	32.165	9.15	0.94	2.90	0.24	1.30	15.	1.05	132.0	25.36
45444.	75.	5.19	32.139	7.53	1.12	2.70	0.28	2.10	16.	0.84	69.4	25.39

Table 5.5. Data for Kodiak Shelf, cruise 045

The values for DOC ranged from 0.63-1.57 mg C/liter and had an average of 0.91 mg C/liter for deep water and 1.09 mg C/liter for the surface waters. The high DOC values were not found at the high POC stations but off the southeast coast of Kodiak Island at stations 45-399, -408 and -409. The highest values of DOC (station 45-399) were found near shore which suggests an extraneous source of DOC. One such source might be the exudates of littoral algae such as reported by Sieburth and Jensen (1970). However, values nearly as high were also found at substantial distances off shore so this may be only a partial contribution to the high DOC values. Although average values of DOC were 20% higher in the surface waters than deep water, they do not correlate well with any of the other parameters measured (Table 5.6).

The POC values ranged from 33-1390 μg C/liter and had an average of 85 μg C/liter for deep water samples and 398 μg C/liter for surface waters. POC correlated reasonably well ($r = 0.721$) with only one variable, dissolved oxygen (Table 5.6). When per cent oxygen satuation was correlated with POC, the coefficient was only slightly higher ($r = 0.756$). The surface layers with the highest POC values had almost 150% oxygen saturation, a result of the high rate of productivity, yet the DOC values were about average (station 45-378). Most of the high POC values occurred in the Shelikof Strait on the northwestern side of Kodiak Island.

A factor analysis was run in order to provide a better basis for interpreting the processes affecting the parameters measured. The eigenvalues are given in Table 5.7 and Fig. 3.9a. Unlike the Cook

	DEP	TEMP	SAL	OXY	PO4	NH3	NO2	NO3	SIO3	DOC	POC	SIGT
DEP	1.000	-0.722	0.315	-0.573	0.815	0.669	0.574	0.773	0.751	-0.404	-0.523	0.519
TEMP	-0.722	1.000	-0.263	0.403	-0.876	-0.676	-0.722	-0.795	-0.859	0.387	0.476	-0.598
SAL	0.315	-0.263	1.000	-0.582	0.449	0.203	0.108	0.373	0.356	-0.184	-0.544	0.930
OXY	-0.573	0.403	-0.582	1.000	-0.683	-0.229	-0.275	-0.627	-0.616	0.225	0.721	-0.639
PO4	0.815	-0.876	0.449	-0.683	1.000	0.587	0.729	0.929	0.943	-0.450	-0.593	0.700
NH3	0.669	-0.676	0.203	-0.229	0.587	1.000	0.597	0.415	0.529	-0.367	-0.381	0.417
NO2	0.574	-0.722	0.108	-0.275	0.729	0.597	1.000	0.569	0.689	-0.434	-0.327	0.359
NO3	0.773	-0.795	0.373	-0.627	0.929	0.415	0.569	1.000	0.907	-0.462	-0.446	0.606
SIO3	0.751	-0.859	0.356	-0.616	0.943	0.529	0.689	0.907	1.000	-0.454	-0.538	0.620
DOC	-0.404	0.387	-0.184	0.225	-0.450	-0.367	-0.434	-0.462	-0.454	1.000	0.207	-0.291
POC	-0.523	0.476	-0.544	0.721	-0.593	-0.381	-0.327	-0.446	-0.538	0.207	1.000	-0.640
SIGT	0.519	-0.598	0.930	-0.639	0.700	0.417	0.359	0.606	0.620	-0.291	-0.640	1.000

Table 5.6. Correlation matrix for Kodiak Shelf data, cruise 045

Table 5.7. Eigenvalues and percent variance "explained" for Kodiak data

Factor	Eigenvalue*	Percent*	Cumulative Percent
I	7.15	59.5	59.5
II	1.72	14.4	73.9
III	0.78	6.5	80.4
IV	0.75	6.2	86.6
V	0.58	4.8	91.4
VI	0.42	3.5	95.0
VII	0.27	2.3	97.2
VIII	0.17	1.4	98.6
IX	0.09	0.7	99.4
X	0.06	0.5	99.9
XI	0.02	0.1	100.0
XII	-0.00	-0.0	100.0

* These values are for the unrotated factor matrix.

Inlet data where factor I accounted for only 41% of the variance, for the Kodiak data it accounted for almost 60%. The unrotated factor matrix (Table 5.8) shows high loadings on almost every variable for factor I. After varimax rotation (Table 5.9) the high loadings are restricted to only the related variables and factor I accounts for only 35.2% of the total variance.

The composition of a factor in terms of variables depends in part on the number of factors requested for the varimax rotation (section III.2.3). This is seen in Tables 5.10a and 5.10b showing composition of factors when the number of factors requested were 2, 3, 4, 5 and 8. Several trends are evident. In all cases except where four factors were rotated the first factor was made up of the nutrients and the second factor consisted mainly of salinity and sigma-t. With the rotation of an increasing number of factors the variables in the factors tended to become grouped more significantly according to the relationships between variables noted in the original correlation matrix (Table 5.6).

The criteria for choosing the correct number of factors (section III.2.3) suggested the use of 4 factors whose compositions are given in Table 5.10a. However, when 4 factors were rotated, the compositions of factors I and IV were reversed placing ammonia as the most important variable in factor I. This does not "make sense" in terms of the original data or correlation matrix. Thus 5 factors (Table 5.10b) were chosen. In addition to returning the nutrients to factor I, POC and oxygen were moved from factor II (salinity and sigma-t) to factor V,

Variable	FACTORS I	II	III	IV	V
DEP	0.846	0.166	-0.110	-0.077	0.170
TEMP	-0.869	-0.296	0.067	0.135	0.194
SAL	0.555	-0.724	0.323	-0.052	-0.217
OXY	-0.716	0.463	0.273	-0.170	-0.275
PO4	0.971	0.088	-0.133	0.069	-0.088
NH3	0.659	0.342	0.279	-0.519	0.152
NO2	0.706	0.469	0.056	-0.107	-0.066
NO3	0.884	0.102	-0.206	0.296	-0.165
SIO3	0.921	0.151	-0.174	0.140	-0.109
DOC	-0.508	-0.274	-0.586	-0.503	-0.256
POC	-0.688	0.412	0.098	0.190	-0.431
SIGT	0.787	-0.498	0.236	-0.096	-0.255

Table 5.8. Unrotated factor matrix for 5 factors for Kodiak data

	Variable	FACTORS I	II	III	IV	V
SUM OF SQUARES		4.230	2.101	1.080	1.692	1.869
0.790	DEP	0.634	-0.092	0.156	-0.418	0.425
0.902	TEMP	-0.800	0.191	-0.060	0.461	-0.099
0.986	SAL	0.093	-0.948	0.067	-0.022	0.273
0.906	OXY	-0.404	0.339	-0.070	-0.092	-0.783
0.981	PO4	0.838	-0.279	0.152	-0.262	0.329
0.922	NH3	0.307	-0.117	0.136	-0.883	0.127
0.737	NO2	0.654	-0.003	0.203	-0.518	0.006
0.948	NO3	0.892	-0.215	0.200	-0.026	0.257
0.933	SIO3	0.865	-0.201	0.165	-0.197	0.280
0.995	DOC	-0.265	0.089	-0.942	0.162	-0.058
0.875	POC	-0.188	0.338	-0.024	0.280	-0.804
0.997	SIGT	0.377	-0.862	0.070	-0.187	0.268

Table 5.9. "Variable" loading for rotated (varimax) factor matrix for 5 factors for Kodiak data. (Sum of squares is the fraction of the total variance of a variable accounted for by the 5 factors shown.)

Table 5.10a. Selection of factors for Kodiak data, cruise 045

Number of factors	Factors** I		II		III		IV	
2	TEMP	-0.871*	SAL	0.912				
	NO_2	0.847	SIGT	0.870				
	PO_4	0.828	OXY	-0.804				
	SIO_3	0.826	POC	-0.745				
	DEP	0.775	PO_4	0.514				
	NO_3	0.767						
	NH_3	0.733						
3	SIO_3	0.867	SAL	0.941	DOC	0.793		
	PO_4	0.863	SIGT	0.864				
	TEMP	-0.851	OXY	-0.741	NH_3	-0.533		
	NO_3	0.825	POC	-0.702				
	DEP	0.790						
	NO_2	0.748						
4	NH_3	0.907	SAL	0.953	DOC	0.908	NO_3	-0.873
			SIGT	0.864			SIO_3	-0.835
	NO_3	0.634					PO_4	-0.809
	TEMP	-0.609	POC	-0.686				
			OXY	-0.650			DEP	-0.667
							TEMP	0.667
							OXY	0.630
8	NO_3	0.880	SAL	0.965	DOC	0.947	NH_3	0.901
	SIO_3	0.848	SIGT	0.861				
	TEMP	-0.821						
	PO_4	0.793						
	Dep	0.580						
	V		VI		VII		VIII	
	POC	0.840	NO_2	0.808	OXY	0.746	DEP	0.615

* These data were obtained using the IBM program. The signs should be reversed to make it comparable with the factor scores program of Cameron (1967).

** The primary composition of the factors are given based on the varimax rotated factor matrix.

Table 5.10b. Selection of factors for Kodiak data, cruise 045. Primary composition of 5 factors based on the varimax factor matrix with the percentages of the total variance "explained" by each factor

		FACTORS			
I (35.2%)		II (17.5%)		III (9.0%)	
NO_3	0.891	SAL	0.946	DOC	0.942
SIO_3	0.865	SIGT	0.860		
PO_4	0.838				
TEMP	-0.799	IV (14.1%)		V (15.8%)	
NO_3	0.654	NH_3	0.883	POC	0.803
DEP	0.634			OXY	0.781

which makes more sense in terms of their correlation coeffiencts (Table 5.6).

Factor I, consisting mainly of the nutrients (nitrate, silicate and phosphate) and temperature, accounted for about 35.2% of the data variance. This relationship can be seen in the original data; at most stations thermoclines were developed and there was nutrient depletion in the surface layer. This is similar to what was found in the Chukchi Sea except there the nutrients did not correlate with temperature (section VI.2). This contrasts with Cook Inlet where factor I consisted of physical properties (salinity and temperature) and mixing processes were the most important.

Factor II accounted for about 17.5% of the data variance and consisted mainly of salinity and sigma-t showing that salinity was independent of most of the other variables and more effective than temperature in controlling the density distribution (sigma-t) in the water column.

DOC and ammonia were in factors III and IV respectively and as in Cook Inlet were unrelated to any of the other variables in terms of processes affecting them.

POC and oxygen in factor V are related because of the positive effect of a phytoplankton bloom on the oxygen content of the water. The placement of POC and oxygen alone in a factor shows that they are not as related to other variables such as the nutrients or DOC as might be though from a cursory examination of the original data (Table 5.5).

V.2.3. Conclusions

1. Most of the marine waters surrounding Kodiak Island have stabilized by late June allowing rapid phytoplankton growth and the resulting reduction of nutrients (nitrate, silicate and phosphate). The nutrients and temperature were negatively correlated and in a factor analysis of the data were the most important group of variables "explaining" about 35% of the total data variance.

2. DOC (factor III) showed very low correlation with the other parameters measured including POC. However, the DOC values were on the average higher in the surface layers (ave. 1.09 mg C/liter) than in the deep water (ave. 0.91 mg C/liter).

3. POC values averaged much higher in the surface waters (ave. 398 μg C/liter) than in the deep water (ave. 85 μg C/liter) but showed a very low correlation with DOC ($r = 0.207$). POC did show a medium high correlation with dissolved oxygen ($r = 0.721$) and these two variables were found in a separate factor (V).

4. The 12 variables used in the Kodiak data analysis were reduced by factor analysis to 5 factors "explaining" 91% of the data variance.

V.3. Unimak Pass

Unimak Pass is the easternmost major pass in the Aleutian chain of islands that separates the Bering Sea and the northern Pacific Ocean (Fig. 1.1 and 5.3). In the area south of the pass surface currents partly composed of Alaskan coastal water with low salinity and depleted nutrients flow east to west along the coast as part of the

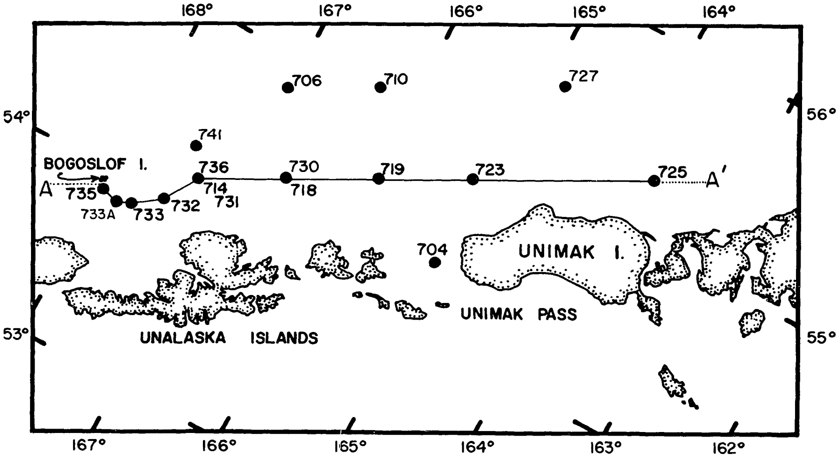


Fig. 5.3. Station locations for samples taken north of Unimak Pass in the southeastern Bering Sea on cruise 027, July 26 - August 8, 1966.

Alaskan Stream (Dodimead, Favorite and Hirano 1963). A portion of this current flows north into the Bering Sea along the east side of the relatively shallow Unimak Pass. This water mixes in and just north of the pass with higher salinity, nutrient-rich water that flows northeast along the north side of the chain in this area. These two currents and the presence of the continental shelf edge just northwest of the pass are the probable cause of a strong upwelling in this area. This upwelling water, apparently from about the 200 m depth in the Bering Sea (J. Goering, personal communication 1970), is high in nutrients and supports a very high level of primary productivity. Holms (1958) reported Unimak Pass to have the highest level of primary productivity in the North Pacific.

V.3.1. Introduction

The Institute of Marine Science has supported several cruises to the southeastern Bering Sea and Aleutian chain since 1965. The data discussed here were collected by myself on R/V Acona cruise 027 from July 27-August 9, 1966. Data (from 16 stations) for organic carbon (DOC and POC), absorbance, and standard euphotic depths are given in Table 5.11. The support data (nutrients and hydrographic) were not completely processed and therefore not discussed.

Station locations are shown in Fig. 5.3. Two locations were sampled several times during the cruise. These were stations 714, 731 and 736 and stations 718 and 730.

Table 5.11. DOC and POC data for Unimak Pass area in the Bering Sea, cruise 027, July 27 to August 9, 1966

Station Date	Depth (m)	Light Penetration (Per cent)	DOC (mg C/liter)	POC (μg C/liter)	Absorbance
704	0	-	1.65	234	-
7-27	10	-	1.15	164	-
	20	-	1.10	148	-
	30	-	1.10	129	-
	50	-	-	96	-
706	0	100	1.40	716	0.49
7-27	2	50	0.80	596	0.48
	5	25	1.25	528	0.46
	7	10	1.25	541	0.47
	17	1	1.20	569	0.36
710	0	100	1.35	150	0.22
7-28	5	50	1.45	152	0.19
	12	25	1.00	118	0.18
	20	10	1.10	142	0.17
	50	1	1.00	86	0.10
	100	-	0.70	108	-
714	0	100	1.00	196	-
7-29	3	50	0.85	211	-
	7	25	1.25	231	-
	17	10	0.70	154	-
	42	1	0.90	89	-
	100	-	-	43	-
	200	-	-	27	-
	500	-	0.75	19	-
	1000	-	0.75	15	-
718	0	100	1.25	367	-
8-2	2	50	1.35	409	-
	6	25	1.15	427	-
	12	10	1.55	450	-
	30	1	1.25	79	-
	100	-	1.15	52	-
719	0	100	1.00	297	-
8-2	3	50	1.30	419	-
	7	25	1.35	389	-
	12	10	1.00	283	-
	27	1	1.25	216	-
	50	-	1.30	98	-
	100	-	1.10	51	-

Table 5.11. (Continued)

Station Date	Depth (m)	Light Penetration (Per cent)	DOC (mg C/liter)	POC (µg C/liter)	Absorbance
723 8-4	0	100	1.45	381	-
	3	50	1.00	303	-
	5	25	1.45	343	-
	10	10	1.60	343	-
	23	1	1.30	220	-
	50	-	1.45	135	-
	100	-	1.10	-	-
725 8-4	0	100	1.85	731	0.40
	2	50	1.00	747	0.38
	4	25	1.15	731	0.37
	7	10	1.10	746	0.37
	16	1	1.70	751	0.36
	50	-	1.50	104	0.12
727 8-5	0	100	1.10	221	0.38
	3	50	1.90	185	0.22
	8	25	1.40	180	0.21
	17	10	1.15	197	0.20
	37	1	0.70	58	0.11
	50	-	0.60	55	0.09
730 8-6	0	100	1.10	811	-
	3	50	1.05	468	-
	15	1	1.20	749	-
731 8-6	0	100	1.30	442	0.34
	4	50	1.40	486	0.34
	30	1	1.05	114	0.15
732 8-7	4	-	1.30	651	0.46
733 8-7	0	100	1.20	504	0.57
	8	10	1.40	507	0.55
	22	1	0.95	196	0.27
733A 8-7	1500	-	1.00	12	-
735 8-8	0	100	1.30	652	-
	2	50	1.35	747	-
	13	1	1.55	277	-
	50	-	0.75	80	-
736 8-9	2	-	1.75	686	-

V.3.2. Results and Discussion

DOC values were quite scattered in the surface waters and ranged from 0.60-1.90 mg C/liter with an average of 1.20 mg C/liter for depths less than 100 m. Only three deep samples were taken (stations 714 and 733A); the DOC values (0.75 and 1.00 mg C/liter) were not as low as I found near the surface for several stations or as low as the average value of 0.5 mg C/liter reported for the western North Pacific water by Ogura (1970a).

Large variations in DOC values were found at several stations. However, POC values at these stations showed little variation suggesting that the top layer above the thermocline was quite well mixed. For example, at station 725 (Table 5.11) POC values did not vary more than 1.2 per cent from a mean of 741 μg C/liter in the upper 16 m (above thermocline), and yet the DOC values varied from 1.00-1.85 mg C/liter or almost 30% from the mean of 1.35 mg C/liter. This was my first cruise and the analytical techniques were not as precise as in later cruises which may explain some of the variation. However, near-surface DOC samples taken later in both the Kodiak area (section V.2) and the Chukchi area (Chapter VI) also showed wide variation. In addition, DOC showed a very low correlation with POC ($r = 0.377$) for this data as it did in the Kodiak area ($r = 0.207$). Thus, unless all the observed variation in DOC concentrations are due to analytical error, it appears that high variations in DOC may occur in the productive surface layers.

DOC data given by Barber (1967) also show large variations in the euphotic zone. However, he found a negative correlation between POC and DOC when following an upwelled water mass off the coast of Peru for five days. Anderson and Zeutschel (1970) found a positive correlation between the production of particulate organic matter and the release of dissolved organic matter in productivity experiments run off the northwest coast of the United States. This problem is discussed further in Chapter VIII.

The POC values ranged from 43-811 μg C/liter for 68 surface layer (< 100 m) samples and 12-27 μg C/liter for 4 deep (>100 m) samples. The deep water values agree reasonably well with those found by Nakajima (1969) in the south-central Bering just north of the Aleutian chain. My POC data does not include a correction for glass filter-adsorbed carbon because the second filter method (section III.1.1.4) had not been initiated at the time these samples were taken. However, a value of 5.4 μg C/filter for deep water was determined using the method of filtering different volumes and extrapolating through zero (Menzel 1966). Thus a value of 5 μg C/liter should be subtracted from the deep water samples. The adsorption in the surface water (< 100 m deep) was about 8 μg C/filter; since 500 ml were filtered, then 16 μg C should be subtracted from these surface samples.

As expected, high POC values were found in thermally stabilized upwelled water north of the islands permitting high rates of productivity. Lower POC values were found in the area north of Unimak Pass and northwest of Akutan Pass due to current mixing. The distribution of POC along a cross-section A-A; is shown in Fig. 5.4. Both stations 714 and 718 showed substantial POC increases at the surface the second time these stations were sampled although only the first stations are shown on the cross-section.

The transmissivity of the surface waters was measured at seven stations (29 samples) and the results are given as absorbance in Table 5.11. The absorbance of the water correlated very well ($r = 0.881$) with log (POC) as shown in Fig. 5.5. There was a high amount of scatter in absorbance for POC values above about 200 µg C/liter. At low concentrations of suspended matter in sea water the concentration of different size (apparent-diameter) particles is about the same. However, at higher concentrations the distribution is uneven or patchy due to large number of individuals from different species of plankton (W. H. Sutcliffe, personal communication 1971). This patchiness is a possible explanation for the absorbance scatter at high POC concentrations. A second explanation might be that there is a variable production of particles less than one micron in size at different stages in a plankton bloom. Beardsley et al. (1970) suggest these particles cause about one-half of the total light scatter yet comprise only about one-tenth of the total volume of the suspended matter. Ogura (1970b) found that in near surface water the amount of organic carbon in the nominally 0.5-0.1 µ range was on the order of ± 0.05 mg C/liter, the precision of his methods. More precise techniques will be necessary before the importance of this size fraction can be determined.

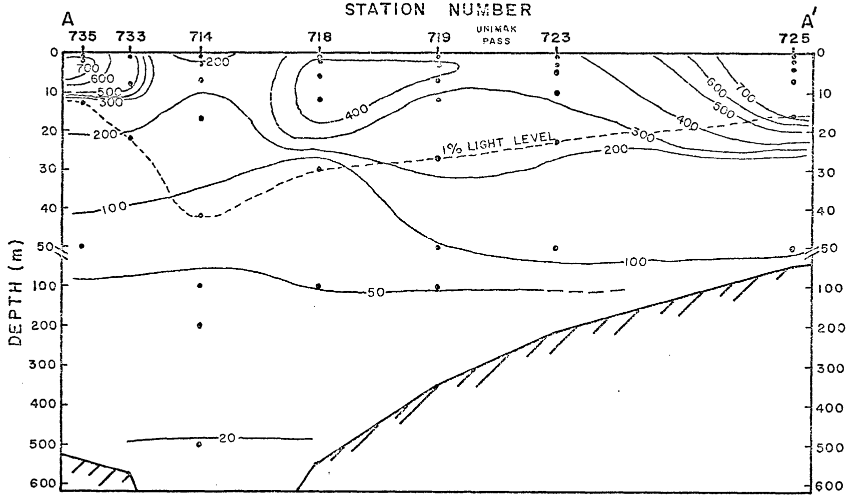


Fig. 5.4. The distribution of POC (µg C/liter) along the west-east section A---A' (Fig. 5.3). The depth of the euphotic zone is shown by the dotted line representing the 1% light penetration level.

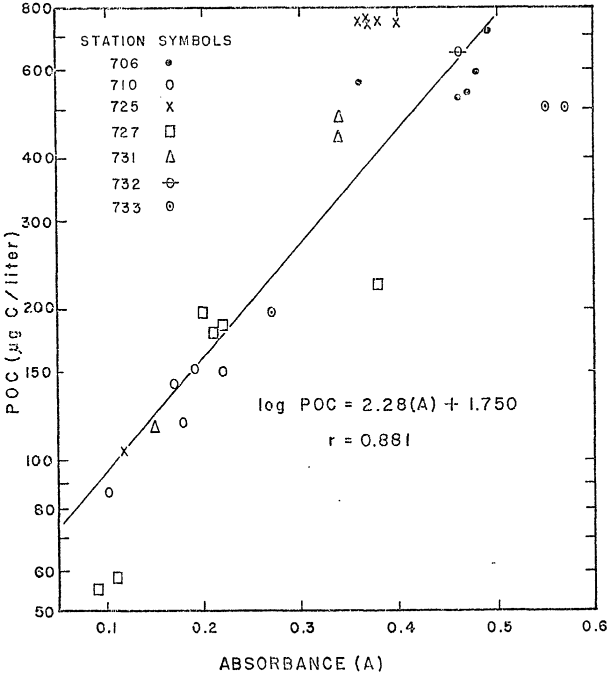


Fig. 5.5. Scatter diagram showing the correlation between log POC and absorbance for 29 near surface (<50 m) samples.

Two sub-surface profiles (0-1 m) were sampled for POC and DOC with a sampler made by suspending on two fiberglass floats a stainless steel rod with Tygon tubing attached at 7 different levels. Water was sucked into 1 liter bottles supported by the floats. The POC values for the profile (Table 5.12) agreed reasonably well with the surface sample taken with the glass-Teflon sampler (station 730); the variation of samples was well within the average variation of duplicate POC samples. The average standard deviation for the 7 samples in each profile was about 6.1%. This indicates that the top meter can be very homogeneous with respect to POC. Higher organic matter values reported by Williams (1967) only occur in the surface slick (top 150 μ layer) not sampled in this study.

Surface layer DOC values showed much greater variation (Table 5.12) than the POC values and were slightly higher than the DOC values obtained from samples taken with the normal glass-Teflon sampler although this amount may not be significant. The DOC samples may have been contaminated, but the POC values do not give any indication of this. Thus it appears that even on a small scale, large DOC variations are possible while the concentration of POC can be quite homogeneous in the near surface layers.

V.3.3. Conclusions

1. The surface waters in the southeastern Bering Sea just north of Unimak Pass contain high amounts of particulate organic matter whose distribution is affected by both the upwelling and northerly currents in the area. At several stations POC concentrations were found to be

Table 5.12. DOC and POC data for the surface to 1 meter samples taken at stations 730 and 741

Station 730, 8-6-66

Depth (cm)	DOC (mg C/liter)	POC (μg C/liter)
0-1	1.20	756
3	1.00	701
6	1.40	769
10	1.45	831
20	1.10	721
50	1.25	741
100	1.20	831

DOC Ave.: 1.25 mg C/liter
Standard Deviation: 0.16 (12.8%)
Standard Sampler: 1.10 mg C/liter

POC Ave.: 764 μg C/liter
Standard Deviation: 51 (6.6%)
Standard Sampler: 811 μg C/liter

Station 741, 8-11-66

Depth (cm)	DOC (mg C/liter)	POC (μg C/liter)
0-1	1.40	963
3	1.25	1071
6	1.40	1111
10	1.15	1021
20	1.65	1071
50	1.50	1011
100	1.40	963

DOC Ave.: 1.40 mg C/liter
Standard Deviation: 0.16 (11.6%)

POC Ave.: 1030 μg C/liter
Standard Deviation: 57 (5.5%)

reasonably homogeneous above the thermocline or down to the 10% euphotic level. At other stations distributions were almost random although values were higher above the thermocline than below it.

2. DOC values were generally higher above the thermocline, but showed an unhomogeneous distribution within the euphotic zone. The linear correlation between all DOC and POC values was low ($r = 0.377$).

3. Absorbance due to particle scattering was measured for 29 samples and was found to correlate quite well ($r = 0.881$) with the log of the POC concentration. The regression was log POC = 2.28(A) + 1.750.

4. Two sets of subsurface samples were taken at 7 intervals between 1 cm and 1 m depth. POC values were reasonably homogeneous while DOC values were almost random and showed larger variation than expected from precision of the analysis.

Chapter VI

CHUKCHI SEA

Chapter VI

CHUKCHI SEA

The Chukchi Sea is a large shallow sea extending southward from the Arctic Ocean basin, bounded on the east by the northern half of Alaska and on the west by the northeast coast of Siberia and Wrangell Island. The Bering Strait, a feature only 45 n miles wide and less than 55 m deep bounds the Chukchi Sea on the south.

The chemical, physical and biological features of the Chukchi Sea are dominated by the properties of the water in the northern Bering Sea because of the continual northerly flow of the water through the strait.

VI.1. Introduction

The first oceanographic observations of the Bering Strait and Chukchi Sea were probably made by Captain James Cook in 1778 who noted a pronounced northerly flow through the Bering Strait which was nearly independent of tidal effects (Lloyd 1949). Later explorers noted that the water on the eastern side of the Bering Strait was considerably fresher than on the western side probably due to the northerly flow of fresh water from the large rivers located south of the strait (Aagaard and Coachman 1964).

Based on previous work as well as their own Aagaard and Coachman (1964) concluded the following about the physical oceanography of the Chukchi Sea.

1. The average flow of water through the Bering Strait to the Chukchi Sea is about 1 million cubic meters per second.

2. The water flowing through the strait shows strong horizontal gradients of both temperature and salinity with fresher warmer water on the east side following the Alaskan coast north of the strait.

3. There is a flow of cold water to the southeast along the Siberian coast.

4. Winter freezing and summer melting of ice are local processes which create distinct water masses in the area.

5. Because of the shallowness of the Chukchi Sea, wind and tidal mixing are effective resulting in a complex water structure and circulation pattern.

Almost all of the studies on which these conclusions were based were made during the summer or early fall when there was little or no ice cover in the area.

The water of the southeastern Chukchi Sea has a residence time of about 10 days (Fleming and Heggarty 1966). It continues north finally forming a near-surface layer (50-200 m) of the Arctic Ocean (Chapter VII).

The Chukchi Sea provides an ideal area for study of the mixing of several water masses from different sources and the effect of biological activity on both the nutrients and organic carbon.

The data used in this study were collected by Martin Arhelger of the University of Alaska and myself during a 5-day period on the USCGC NORTHWIND from July 27 to August 2, 1968 (cruise 751). All stations located in Fig. 6.1 except number 10 were sampled for organic carbon, PN and PM as well as the usual physical and nutrient parameters. The

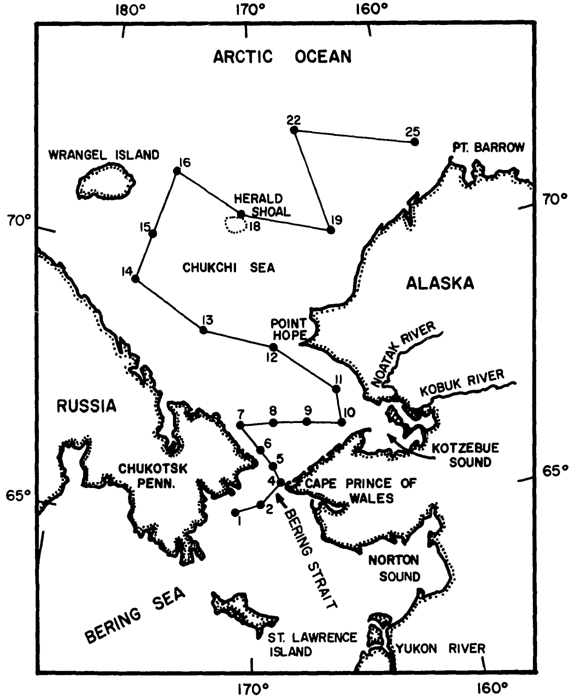


Fig. 6.1. Station locations for Chukchi Sea, cruise 751, July 28-August 2, 1968.

station locations are given in the Appendix.

VI.2. Results of factor analysis

A shallow thermocline (10-15 m) was present at most of the stations. Samples were taken both above it at 1 or 5 m (surface) and below it at 25-40 m (deep) depending on the depth of the water, which ranged from 32 to 55 m. The samples taken in the thermocline at 10 m were considered surface for the purpose of the data analysis.

In order to determine the relationship of the various parameters to each other as well as the significance of organic carbon in this physically and biologically dynamic area, I used both correlation and factor analyses. The 16 variables used in these analyses are given in Table 6.1 and represent a total of 38 observations or sets of samples from 18 stations. The values given for NH_3 and NO_3 are given to one significant figure more than usual so that 0.01 μg-A could be reported for zero concentrations. This was done because Fortran does not distinguish between a missing value and a zero value for a given observation. For the same reason zero meters depth is given as 1 m. A correlation matrix is given in Table 6.2. Nutrient and physical data for these stations as well as those not sampled for organic carbon, PN and PM are discussed by Kinney, Burrell, Arhelger and Loder (1970).

The eigenvalues and per cent variance for each factor are presented in Table 6.3. I chose 4 factors with eigenvalues greater than 1 and per cent variance greater than 5 as discussed in sections III.2.3 and V.2.2. The unrotated factor matrix for 4 factors is given in Table 6.4. The "variable" composition of the 4 factors taken from the rotated factor

IMS REF NUMBER	1.DEPTH METERS	2.TEMP C DEG.	3. SAL PPT	4.OXY ML/L	5. PO4 µG-A/L	6. NH3 µG-A/L	7. NO2 µG-A/L	8.NO3 µG-A/L	9.SIO3 µG-A/L	10.DOC MG-C/L	11.POC µG-C/L	12.PN µG-N/L	13.PM MG/L	14.C/N PLC/PN	15.C/PM X100	16SIG-T
751001.	10.	2.90	32.938	7.01	1.92	3.50	0.27	16.80	47.	1.08	333.0	81.44	1.25	4.1	26.6	26.27
751001.	40.	2.56	32.995	6.45	2.28	4.20	0.35	18.70	53.	0.94	261.0	44.67	3.30	5.8	7.9	26.35
751002.	1.	6.03	32.281	10.22	0.89	1.00	0.15	0.50	35.	1.57	835.0	189.85	2.80	4.4	29.8	25.43
751002.	10.	2.70	32.789	7.26	1.70	0.80	0.15	16.80	28.	1.33	197.0	37.21	1.55	5.3	12.7	26.17
751002.	35.	1.53	32.922	6.66	2.20	2.10	0.23	19.80	48.	0.99	133.0	17.81	1.75	7.5	7.6	26.36
751004.	5.	10.27	28.796	6.90	0.63	0.01	0.09	0.01	22.	1.75	267.0	34.00	1.95	7.9	13.6	22.10
751004.	35.	4.95	32.392	7.80	0.83	0.01	0.12	0.10	8.	1.17	172.0	23.38	1.85	7.4	9.2	25.64
751005.	1.	5.75	32.432	11.28	0.52	1.60	0.14	0.01	17.	1.97	1206.0	229.70	4.10	5.2	29.4	25.58
751005.	10.	2.50	32.701	8.38	1.38	1.50	0.32	11.30	38.	1.49	891.0	176.86	3.70	5.0	23.8	26.12
751005.	45.	2.00	32.792	7.00	2.04	4.40	0.20	15.40	51.	0.89	178.0	29.20	1.95	6.1	9.1	26.23
751006.	5.	2.69	32.814	9.35	0.88	1.40	0.15	10.70	36.	1.78	876.0	180.79	3.95	4.8	22.1	26.19
751006.	35.	1.65	32.877	6.94	2.26	3.10	0.18	19.10	48.	0.76	185.0	42.47	2.00	4.4	9.2	26.32
751007.	10.	3.04	32.989	7.44	1.85	2.40	0.24	15.20	44.	1.15	447.0	77.81	1.70	5.7	26.2	26.30
751007.	40.	2.57	33.033	7.01	2.09	2.80	0.30	17.70	48.	0.87	219.0	45.68	2.55	4.8	8.5	26.38
751008.	5.	9.06	31.289	8.35	0.27	0.10	0.09	0.01	12.	1.51	577.0	83.62	2.40	6.9	24.0	24.23
751009.	5.	6.85	31.787	8.76	0.61	0.60	0.10	0.01	8.	1.48	801.0	102.73	2.90	7.8	27.6	24.93
751009.	27.	6.53	32.663	7.53	0.93	1.00	0.18	0.40	13.	0.94	366.0	61.32	9.85	6.0	3.7	25.19
751011.	5.	7.38	31.354	7.01	0.86	0.70	0.07	0.01	14.	1.08	223.0	39.82	1.65	5.6	13.5	24.52
751011.	25.	6.42	31.789	6.99	1.00	0.90	0.12	0.20	13.	0.96	161.0	22.35	3.00	7.2	5.3	24.99
751012.	5.	5.85	32.951	11.13	0.80	1.50	0.21	0.10	20.	1.46	1753.0	320.22	5.35	5.5	32.7	25.98
751012.	35.	3.91	33.063	6.63	2.20	5.20	0.37	15.40	54.	0.68	118.0	22.33	1.10	5.3	10.7	26.28
751013.	5.	6.99	29.663	6.63	0.36	0.60	0.06	0.01	5.	0.87	204.0	40.18	0.85	5.1	24.0	23.41
751013.	35.	3.00	33.157	6.4[illegible]	2.19	7.10	0.36	12.90	36.	0.67	191.0	35.17	2.65	5.4	7.2	26.44
751014.	5.	7.76	30.060	7.28	0.47	0.40	0.07	0.02	8.	1.20	73.2	14.35	0.65	5.1	11.2	23.46
751014.	10.	6.44	30.468	7.46	0.44	0.40	0.04	0.01	10.	0.96	55.6	13.30	0.65	4.2	8.5	23.95
751014.	35.	-0.10	33.214	9.32	1.09	2.20	0.09	0.20	7.	0.79	70.1	20.30	0.60	3.5	11.6	26.68
751015.	5.	7.80	30.495	7.08	0.44	0.20	0.01	0.01	6.	0.89	157.0	27.06	0.65	5.8	24.1	23.79
751015.	35.	1.70	32.944	6.16	2.04	3.20	0.26	8.60	1.	0.93	232.0	29.08	2.50	8.0	9.2	26.37
751016.	5.	7.73	31.150	7.02	0.40	0.01	0.01	0.01	9.	1.15	214.0	40.03	0.80	5.3	26.7	24.32
751016.	40.	0.80	32.908	7.75	1.32	2.00	0.12	1.30	11.	0.78	110.0	18.57	1.05	5.9	10.4	26.40
751018.	5.	4.00	29.738	7.80	0.37	0.01	0.02	0.01	9.	0.73	99.6	18.74	0.40	5.3	24.9	23.63
751018.	31.	-1.23	32.915	10.73	1.02	0.60	0.07	0.40	9.	1.15	338.0	73.88	1.65	4.6	20.4	26.49
751019.	5.	6.88	30.284	7.32	0.53	0.01	0.03	0.01	12.	1.03	130.0	25.52	0.50	5.1	26.0	23.75
751019.	39.	-0.86	32.648	8.46	1.58	1.30	0.21	5.30	29.	0.97	168.0	28.75	3.15	5.8	5.3	26.27
751022.	5.	0.83	28.963	8.81	0.47	0.01	0.02	0.01	15.	0.78	125.0	21.06	0.55	5.9	22.7	23.23
751022.	35.	-1.66	33.092	7.00	2.24	2.60	0.20	18.00	58.	0.69	176.0	36.17	2.45	4.9	7.1	26.65
751025.	5.	1.97	30.021	8.84	0.73	0.01	0.04	0.01	23.	0.83	139.0	20.52	0.55	6.8	25.2	24.02
751025.	35.	-1.65	32.160	7.49	1.73	1.00	0.18	9.80	37.	0.91	88.9	15.13	0.55	5.9	16.1	25.89

Table 6.1. Data for Chukchi Sea, cruise 751, July 28 - August 2, 1968.

	DEP	TEMP	SAL	OXY	PO4	NH3	NO2	NO3	SIO3	DOC	POC	PN	PM	C/N	C/PM	SIGT
DEP	1.000	-0.636	0.616	-0.339	0.746	0.571	0.547	0.519	0.412	-0.572	-0.407	-0.402	0.090	0.065	-0.770	0.669
TEMP	-0.636	1.000	-0.537	-0.074	-0.632	-0.367	-0.370	-0.513	-0.447	0.454	0.215	0.159	0.111	0.232	0.292	-0.687
SAL	0.616	-0.537	1.000	0.078	0.732	0.592	0.726	0.615	0.525	-0.050	0.241	0.273	0.351	-0.199	-0.280	0.981
OXY	-0.339	-0.074	0.078	1.000	-0.422	-0.364	-0.242	-0.441	-0.229	0.553	0.699	0.720	0.245	-0.231	0.556	0.078
PO4	0.746	-0.632	0.732	-0.422	1.000	0.753	0.834	0.910	0.797	-0.419	-0.203	-0.172	0.082	-0.052	-0.527	0.776
NH3	0.571	-0.367	0.592	-0.364	0.753	1.000	0.752	0.597	0.416	-0.351	-0.063	-0.056	0.122	0.039	-0.380	0.601
NO2	0.547	-0.370	0.726	-0.242	0.834	0.752	1.000	0.765	0.730	-0.120	0.161	0.179	0.367	-0.028	-0.341	0.715
NO3	0.519	-0.513	0.615	-0.441	0.910	0.597	0.765	1.000	0.879	-0.265	-0.138	-0.100	0.028	-0.136	-0.361	0.653
SIO3	0.412	-0.447	0.525	-0.229	0.797	0.416	0.730	0.879	1.000	-0.143	0.009	0.067	0.091	-0.214	-0.225	0.557
DOC	-0.572	0.454	-0.050	0.553	-0.419	-0.351	-0.120	-0.265	-0.143	1.000	0.720	0.699	0.316	0.108	0.500	-0.155
POC	-0.407	0.215	0.241	0.699	-0.203	-0.063	0.161	-0.138	0.009	0.720	1.000	0.983	0.547	-0.039	0.585	0.159
PN	-0.402	0.159	0.273	0.720	-0.172	-0.056	0.179	-0.100	0.067	0.699	0.983	1.000	0.520	-0.181	0.590	0.201
PM	0.090	0.111	0.351	0.245	0.082	0.122	0.367	0.028	0.091	0.316	0.547	0.520	1.000	0.118	-0.134	0.275
C/N	0.065	0.232	-0.199	-0.231	-0.052	0.039	-0.028	-0.136	-0.214	0.108	-0.039	-0.181	0.118	1.000	-0.147	-0.228
C/PM	-0.770	0.292	-0.280	0.556	-0.527	-0.380	-0.341	-0.361	-0.225	0.500	0.585	0.590	-0.134	-0.147	1.000	-0.302
SIGT	0.669	-0.687	0.981	0.078	0.776	0.601	0.715	0.653	0.557	-0.155	0.159	0.201	0.275	-0.228	-0.302	1.000

Table 6.2. Correlation matrix for Chukchi Sea, cruise 751, July 28 - August 2, 1968.

Table 6.3. Eigenvalues and per cent variance "explained" for Chukchi Sea data

Factor	Eigenvalue*	Percent*	Cumulative Percent
I	6.84	42.7	42.7
II	3.98	24.8	67.6
III	1.54	9.6	77.2
IV	1.21	7.6	84.8
V	0.70	4.4	89.2
VI	0.62	3.9	93.0
VII	0.40	2.5	95.5
VIII	0.23	1.5	97.0
IX	0.18	1.1	98.1
X	0.10	0.6	98.7
XI	0.08	0.5	99.2
XII	0.06	0.4	99.6
XIII	0.03	0.2	99.8
XIV	0.02	0.1	100.0
XV	0.01	0.0	100.0
XVI	0.00	0.0	100.0

* These values are for the unrotated factor matrix.

Variable	FACTORS I	II	III	IV
DEP	0.843	0.194	0.057	0.410
TEMP	-0.677	0.029	0.510	-0.297
SAL	0.759	-0.513	-0.056	0.214
OXY	-0.427	-0.681	-0.357	0.375
PO4	0.974	-0.060	0.026	-0.145
NH3	0.760	-0.091	0.213	-0.057
NO2	0.813	-0.377	0.245	-0.197
NO3	0.858	-0.106	-0.029	-0.427
SIO3	0.730	-0.243	-0.098	-0.478
DOC	-0.506	-0.651	0.221	-0.143
POC	-0.276	-0.931	0.120	-0.022
PN	-0.241	-0.951	0.007	-0.049
PM	0.100	-0.590	0.531	0.305
C/N	-0.095	0.199	0.748	0.116
C/PM	-0.626	-0.449	-0.314	-0.330
SIGT	0.809	-0.448	-0.165	0.240

Table 6.4. Unrotated factor matrix for 4 factors for Chukchi Sea data.

	Variable	FACTORS I	II	III	IV
SUM OF SQUARES		4.733	4.207	1.539	3.087
0.919	DEP	0.377	0.419	0.193	0.751
0.807	TEMP	-0.288	-0.203	0.403	-0.721
0.888	SAL	0.580	-0.266	-0.019	0.693
0.914	OXY	-0.429	-0.757	-0.315	0.241
0.974	PO4	0.853	0.231	0.012	0.439
0.634	NH3	0.671	0.122	0.207	0.356
0.901	NO2	0.865	-0.133	0.184	0.318
0.931	NO3	0.928	0.164	-0.116	0.173
0.830	SIO3	0.881	0.002	-0.209	0.097
0.750	DOC	-0.120	-0.782	0.116	-0.331
0.958	POC	0.042	-0.977	0.033	-0.039
0.966	PN	0.073	-0.976	-0.082	-0.015
0.733	PM	0.120	-0.580	0.547	0.289
0.622	C/N	-0.082	0.102	0.764	-0.147
0.800	C/PM	-0.230	-0.580	-0.435	-0.471
0.940	SIGT	0.573	-0.182	-0.112	0.753

Table 6.5. Variable loading for rotated (varimax rotation) factor matrix for 4 factors for Chukchi Sea data.

matrix (Table 6.5) is given in Table 6.6.

Factor I consisted mainly of the nutrients: nitrate, silicate, nitrite and phosphate explaining about 29.6% of the total variance. In general, the nutrients were somewhat depleted at the surface although nitrate was the only major nutrient reduced to essentially zero in most of the samples where nutrient depletion occurred. Temperature did not correlate well with the nutrients as was found on the Kodiak Shelf (section V.2) because other processes than surface warming and biological depletion affected the distribution of the nutrients. In addition, both upwelling areas and recent ice melting tended to lower the temperature at the surface, but had opposite effects on the nutrients.

Factor II (explaining 26.3% of the variance) mainly consisted of the biologically affected variables: POC, PN, DOC and oxygen and is referred to as the organic factor. POC and PN are the major contributors to the factor and have a very high correlation of 0.983 reflecting the relatively narrow range of C/N ratios for most of the samples. Unlike the DOC in both Cook Inlet and Kodiak Shelf, DOC correlated reasonable well with both POC (0.720) and PN (0.699) indicating an increase of dissolved organic matter with the increase of particulate organic matter.

Oxygen values showed a positive correlation with POC and were well over 100% saturation at several stations, i.e. station 12, 5 m sample, >150% saturation.

The C/N ratio, ranging from 3.5 to 8.0 with an average of 5.7 for the 38 observations, was the main component of factor III with PM

Table 6.6. Primary composition of 4 factors for Chukchi Sea data based on the varimax factor matrix. The percentages of the total variance "explained" by each factor are given

FACTORS							
I (29.6%)		II (26.3%)		III (9.6%)		IV (19.3%)	
NO_3	0.928	POC	-0.997	C/N	0.764	SIGT	0.753
SIO_3	0.881	PN	-0.976	(PM)	0.547	DEP	0.751
NO_2	0.865	DOC	-0.782			TEMP	-0.721
PO_4	0.852	OXY	-0.757			SAL	0.693
(NH_3)	0.671						

contributing about half as much. Finding C/N essentially alone in a factor is not surprising since it does not have a high correlation coefficient with any other variable (Table 6.2). The underlying relationship between C/N and PM is not readily apparent although examination of factor scores in section VI.3 suggests that both these variables are affected by the influence of river water and detritus. However C/N and PM only make up about 57% of factor III with the rest of the factor divided among the remaining variables.

Factor IV, accounting for 19.3% of the total variance, mainly consisted of what might be termed the physical or advective variables: sigma-t, depth, temperature and salinity with temperature showing reverse correlation with the other three. Salinity had a much greater effect on the density than temperature for the low temperature ranges found in the Chukchi Sea, resulting in a higher correlation between salinity and sigma-t than temperature and sigma-t. Removing depth as a variable from the factor analysis did not change the composition of the factors. Thus it was retained although the factor scores were separated and plotted by depth and area in section VI.3.

These then are the compositions of the 4 factors chosen which "make sense" in terms of the original data and the correlation matrix. The original number of 16 variables is reduced to 4 factors including 14 of the original variables and explaining about 85% of the total variance.

VI.3. Results and Discussion of Factor Scores

Now that the factors are determined, it is possible to return to the original data matrix and determine a factor score for each factor at an observation point. This factor score is a single number taking into account the influence of all the variables at a given observation point. The influence of a variable on the factor score depends on its contribution to a given factor. For example, in factor II four variables listed in Table 6.6 comprise 73.4% of the factor and thus the factor score value is mainly determined by the values of these four variables.

The factor scores are listed in Table 6.7. It is not necessary to understand the absolute meaning of each factor score, but only its value relative to the others. The relative meaning becomes clear upon examination of the original data matrix (Table 6.1) and the correlation matrix (Table 6.2). For example, a large negative number for factor II at the surface implies that the values of POC, PN, DOC and oxygen are high for that sample (Table 6.8). Because a factor score is based on a group of variables related by one or more processes, it is useful for plotting one group of variables vs. a second to define or determine water types. Assuming that variables in a water mass from a given area are similar, I chose to separate the observations into 4 separate categories: stations 1-12, surface (above thermocline) and deep (below thermocline) and stations 13-25, surface and deep. However, stations 1-12 (deep) were separated into 2 water masses when some of the variables or factors were plotted (Figs. 6.2, 6.4 and 6.5).

Several authors (Menzel 1964, Barber 1967, and Menzel and Ryther 1968) have suggested that DOC is a quasi-conservative property and can be used to identify water masses. Figure 6.2 is a plot of DOC vs. sigma-t with 5 fields enclosed, stations 1-12, surface and deep and

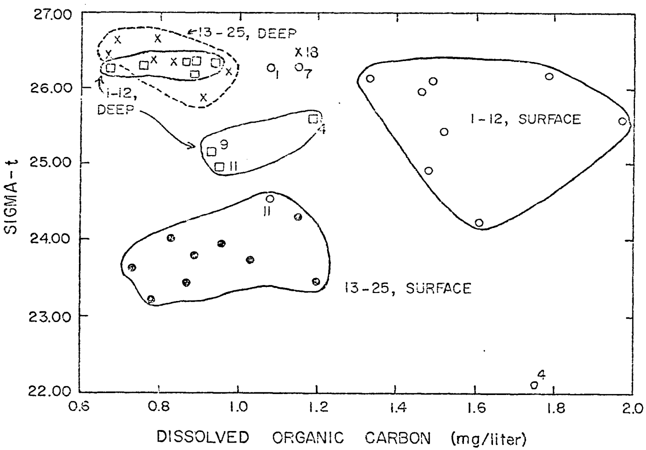


Fig. 6.2. Plot of DOC versus sigma-t for Chukchi Sea data.

Table 6.7. Factor scores for Chukchi Sea data

Station Number	Depth (m)	Factors I	II	III	IV
751 001	10	1.698	-0.189	-1.441	-0.809
751 001	40	1.760	0.291	0.645	0.194
751 002	1	0.006	-1.747	-1.014	-0.391
751 002	10	0.648	0.134	-0.487	-0.221
751 002	35	1.225	0.700	0.683	0.187
751 004	5	-0.171	0.207	1.876	-2.399
751 004	35	-1.004	0.324	1.283	0.828
751 005	1	-0.475	-2.648	-0.148	0.084
751 005	10	1.045	-1.519	-0.348	-0.260
751 005	45	1.079	0.597	0.277	0.500
751 006	5	0.372	-1.774	-0.545	0.003
751 006	35	1.161	0.593	-0.752	0.414
751 007	10	1.354	-0.373	-0.664	-0.650
751 007	40	1.297	0.359	-0.158	0.438
751 008	5	-0.569	-0.750	0.909	-1.071
751 009	5	-0.596	-1.071	1.117	-0.516
751 009	27	-0.779	-0.512	2.709	1.174
751 011	5	-0.482	0.344	0.305	-0.682
751 011	25	-0.672	0.523	1.674	0.283
751 012	5	-0.160	-3.261	0.135	0.398
751 012	35	1.792	0.691	-0.065	-0.087
751 013	5	-0.681	0.624	-0.347	-1.304

Table 6.7. (Continued)

Station Number	Depth (m)	Factors			
		I	II	III	IV
751 013	35	1.417	0.539	0.681	0.534
751 014	5	-0.752	0.687	0.047	-1.087
751 014	10	-0.972	0.843	-0.507	-0.447
751 014	35	-1.265	0.480	-1.513	2.161
751 015	5	-0.834	0.609	-0.170	-1.125
751 015	35	0.522	0.580	2.136	0.989
751 016	5	-0.698	0.261	-0.428	-1.080
751 016	40	-0.861	0.693	0.010	1.631
751 018	5	-1.071	0.783	-0.947	-0.757
751 018	31	-1.472	-0.439	-1.353	2.098
751 019	5	-0.690	0.527	-0.691	-1.210
751 019	39	-0.373	0.281	0.248	1.682
751 022	5	-1.228	0.733	-0.981	-0.500
751 022	35	1.136	0.624	-0.751	0.853
751 025	5	-0.905	0.526	-0.642	-0.490
751 025	35	0.199	0.730	-0.785	0.638

Table 6.8. Interpretation of factor scores for Chukchi Sea data

Factor	FACTOR SCORES Negative	Positive
I	Low nutrients	High nutrients
II	High organic	Low organic
III	Low C/N (PM)	High C/N (PM)
IV	High temperature Low salinity	High salinity Low temperature

stations 13-25, surface and deep. As can be seen the deep water at stations 4, 9 and 11 is half way between the other major fields in both density and DOC content. This method of plotting was unable to separate the deep water in the Bering Strait and southern Chukchi Sea from the deep water in the central Chukchi Sea. If factor scores for factor II (organic) and factor IV (physical) are plotted, these two deep water masses are then separated, because stations 1-12 deep water had higher temperatures and lower salinities than stations 13-25 deep (Fig. 6.3). Several of the points fall outside the enclosed fields. These represent samples taken in areas that do not fall into the arbitrary stations 1-12, 13-25 categories or are the result of current mixing. For example, station 4 surface has high temperature and low salinity due to the influence of mixing with Yukon or other river water. Also the surface water at station 11 is more characteristic of the Chukchi than the Bering Strait water. The fact that station 12 surface represents upwelled highly productive water can also be clearly seen.

When factor I (nutrient) is plotted vs. factor II (organic) and factor IV (physical), a separate field is again found for deep water at stations 4, 9 and 11 (Figs. 6.4 and 6.5) due to the nutrient reduction in this water mass. However, when factor I and factor II are plotted (Fig. 6.4), separate water masses are not well defined suggesting a poor relationship between these two factors in a given water mass although both are affected directly by biological processes. It should be noted that all the 13-25 surface samples and some of the 1-12 and 13-25 deep samples have lower nutrient values than the 1-12 surface samples where the high

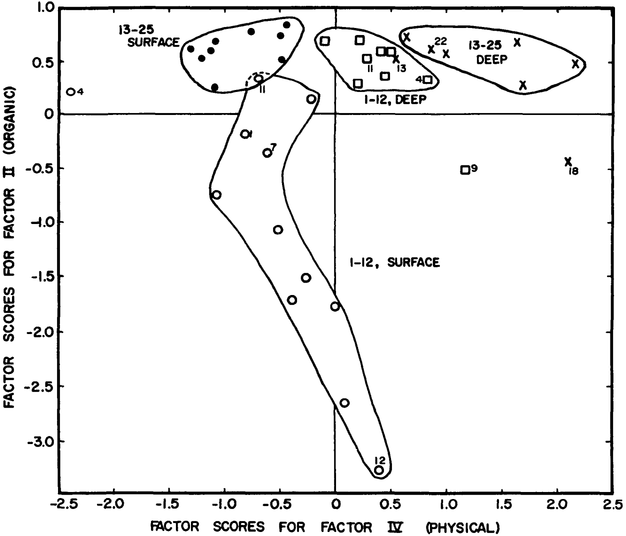


Fig. 6.3. Factor score plot for factors II and IV for Chukchi Sea data.

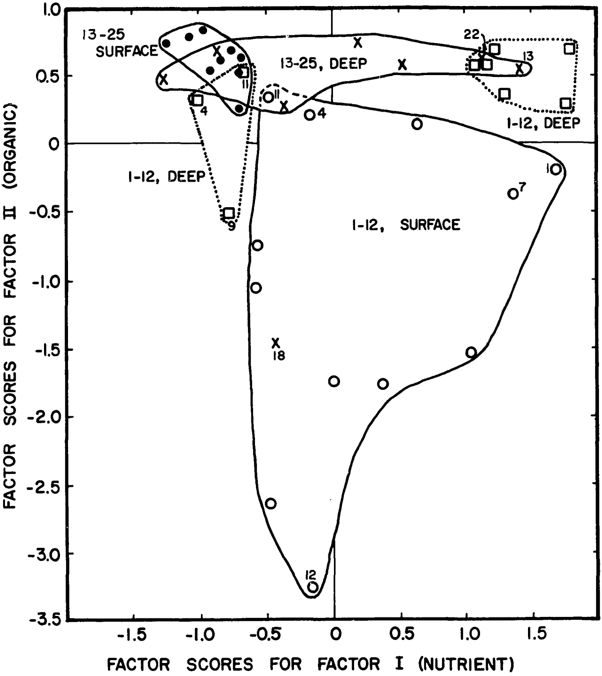


Fig. 6.4. Factor scores plot for factors I and II for Chukchi Sea data.

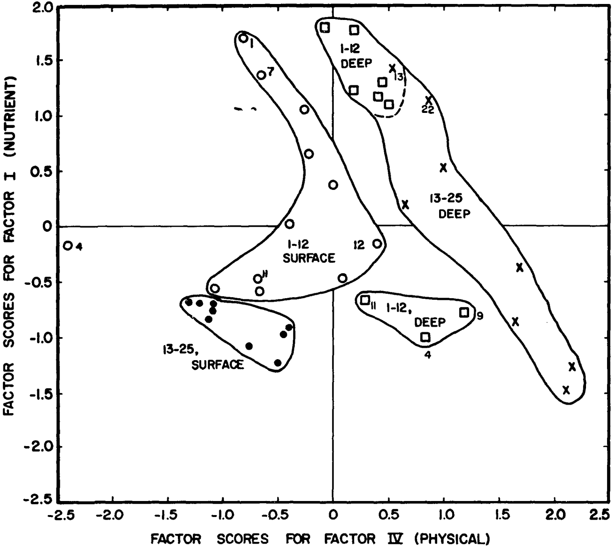


Fig. 6.5. Factor scores plot for factors I and IV for Chukchi Sea data.

values of organic matter were found. The above suggests that the physical or advective variables have a stronger influence on the organic variables than do the nutrients. This is supported by the large role (29.6%) which the nutrients play in defining the variance of the total system while the physical factors play a smaller role (19.3%). Stated simply the organic variables are more dependent on the physical than on the nutrient variables.

The physical oceanography of the area and the distribution of nutrients and organics may be better understood by plotting and contouring the values of the factor scores on a map (Figs. 6.6a & b - 6.9a & b). In general, the surface waters (above the thermocline) were quite different in their physical and chemical properties than the deep (below thermocline) waters. There were several exceptions to this which will be apparent as the area is discussed in detail.

There were four characteristic water masses moving north through the Bering Strait. The first water mass type was located on the western side and in the deep water of the center of the strait; it was characterized by high nutrients (Fig. 6.6), low organics (Fig. 6.7), high salinity and low temperatures (Fig. 6.9). In the central part of the straits this water mass continued northward and made up the bottom water of the central and western part of the southern Chukchi Sea (Fig. 6.6b).

The second water mass type was found at the surface in the central part of the Strait. It was characterized by high values for the factor II variables (DOC, POC, PN and oxygen), partially depleted nutrients and varying temperature and salinity. This area of intensive biological activity extended northward to the upwelling area at station 12 formed

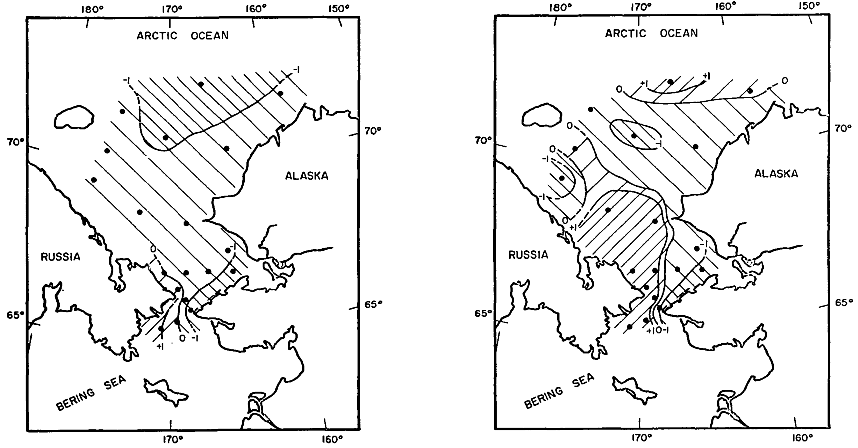


Fig. 6.6a. Surface.

Fig. 6.6b. Deep.

Figs. 6.6a and 6.6b. Contour maps of factor scores for factor I. Positive values indicate high nutrient values.

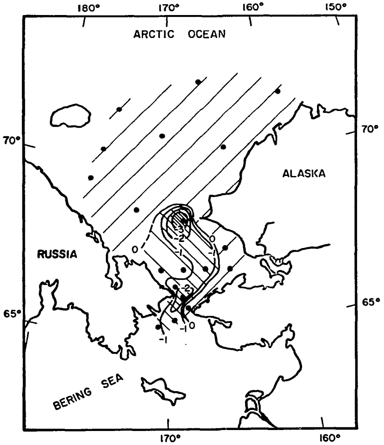


Fig. 6.7a. Surface.

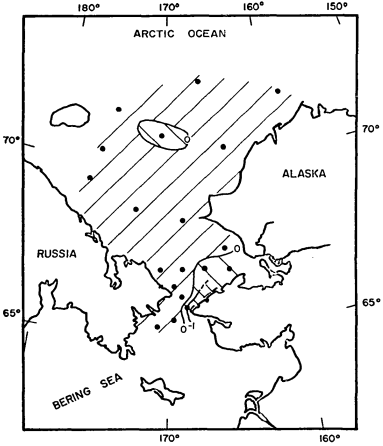


Fig. 6.7b. Deep.

Figs. 6.7a and 6.7b. Contour maps of factor scores for factor II. Negative values indicate high organic variables and dissolved oxygen.

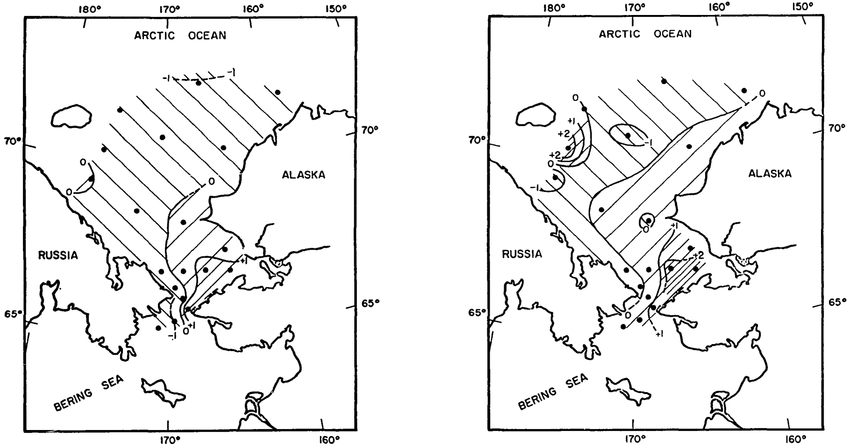


Fig. 6.8a. Surface.

Fig. 6.8b. Deep.

Figs. 6.8a and 6.8b. Contour maps of factor scores for factor III. Positive values indicate slightly higher C/N and PM.

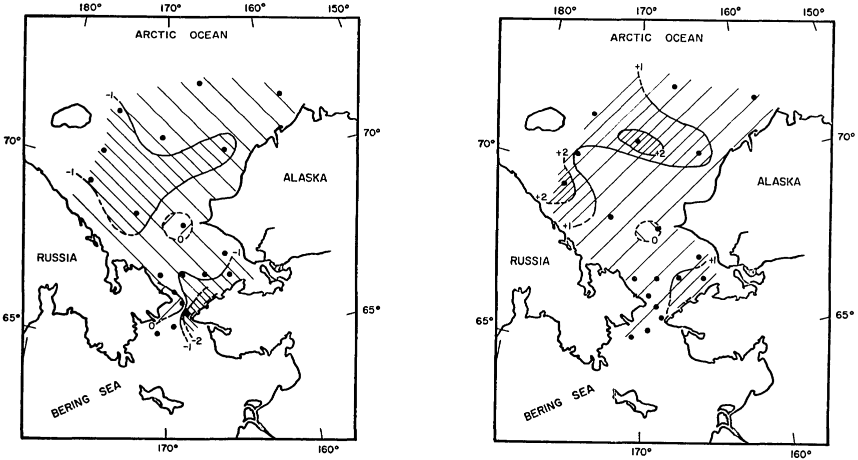


Fig. 6.9a. Surface.

Fig. 6.9b. Deep.

Figs. 6.9a and 6.9b. Contour maps of factor scores for factor IV. Positive values indicate high salinity and low temperature.

by a counterclockwise gyre (Arhelger, personal communication 1970) (Figs. 6.7a and 6.9a & b). The highest values for POC and PN were found here. The relationship between the biological variables and other variables are discussed in section VI.4.

The third and fourth water mass types are located on the east side of the strait at the surface and at depth. The surface water had high temperatures and low salinities due to the influence of fresh water from the Yukon and rivers south of the strait (Fig. 6.9a) and had nutrient depletion and low organics (Fig. 6.7a) separating it from the surface water in the central part of the strait. The deep water, although slightly less dense than the deep water in the central strait area was nutrient depleted but high in organics (Fig. 6.7b) making it a separate water mass type. The north-south trends of the separate water mass types is also shown by factors III (Fig. 6.8a & b) although the exact reasons why factor III is affected are not clear.

Most of the stations representing the central Chukchi Sea were dominated by a well developed pycnocline resulting from recent ice melting and subsequent surface warming. Generally the surface waters were characterized by low nutrients, organics, and salinities, and high temperatures.

The deep water at station 18 appears anomolous on all maps showing contoured factor scores (Figs. 6.6b - 6.9b). It is characterized by depleted nutrients, high organics, low C/N, high salinity and very low temperature. These properties suggest that this water was upwelled somewhere in the central Chukchi Sea, supported a phytoplankton bloom, was then cooled as it moved north and sank below the less dense melting ice pack at the surface. This appears to have occurred within a short period of time prior to sampling (approx. one week or less) because of the very high oxygen values and high POC content of the water. Current data, reported by Aagaard and Coachman (1964) supports this hypothesis. An alternate hypothesis would be the in situ production of the high organics and oxygen due to the shallowness of the water and clarity of the surface waters.

The influence of an outside source of water was found in the area south of Wrangel Island at station 14. This water, moving southeast along the Siberian coast, was characterized by low temperature and high salinity (Fig. 6.9b), low organics and low nutrients (Fig. 6.6b).

VI.4. Discussion

In the results above I showed how the factor scores could be used to describe and define various water mass types. Now that we have the physical setting in mind I shall discuss the organic variables.

Averages for DOC, POC and C/N ratios are given in Table 6.9 for different parts of the area studied. In addition to the natural groupings of stations 1-12 and 13-25, seven observations at the surface and five observations at depth in the biologically active area designated by factor II (Fig. 6.7a) were chosen. Although several other samples had high POC or DOC, only the seven chosen had higher than normal values for all factor II variables (POC, PN, DOC and oxygen) indicative of high productivity.

The DOC values were generally higher at the surface than at depth although surface values were substantially lower for stations 13-25 than

Table 6.9. Average values for DOC, POC and C/N data for 4 groups of samples from surface and depth in the Chukchi Sea

Sample Locations	Surface		Deep	
	No. of samples	Average DOC (mg C/liter)	No. of samples	Average DOC (mg C/liter)
Central Bering Strait	7*	1.62	5**	0.83
Stations 1 to 12	11	1.51	10	0.92
Stations 13 to 25	9	0.94	8	0.85
Stations 1 to 25	20	1.25	18	0.89

	No. of samples	Average POC (μg C/liter)	No. of samples	Average POC (μg C/liter)
Central Bering Strait	7*	990	5*	156
Stations 1 to 12	11	733	10	213
Stations 13 to 25	9	133	8	172
Stations 1 to 25	20	463	18	194

	No. of samples	Average C/N	No. of samples	Average C/N
Central Bering Strait	7*	5.7	5*	5.9
Stations 1 to 12	11	5.8	10	5.9
Stations 13 to 25	9	5.4	8	5.5
Stations 1 to 25	20	5.6	18	5.7

* These 7 samples were from stations: 2, 5, 6, 8, 9 and 12.

** These 5 samples were from stations: 2, 5, 6, 9 and 12 stations 1-12. At depth the DOC values were less than 1.0 mg C/liter and similar throughout the whole area studied. The only exception was station 18 where downwelling of surface water may have occurred. POC followed a similar pattern and consequently the correlation between DOC and POC (and PN) was reasonably high (Table 6.2). However, if DOC and POC from the central strait area where production was high are correlated (7 samples), then I find no correlation between DOC and POC (r = -0.01). This is probably due to the fact that the areas sampled were at different stages in blooming and that sampling times occurred during different times of the day and night. This is supported by Barber (1967) who found that DOC values were highest at the start of a bloom and then decreased as heterotrophic organisms increased their utilization of the dissolved organic matter even though chlorophyll a and primary production increased throughout the studied period of the bloom of 5 days.

Thus it appears that there are several levels of DOC concentrations in water masses with each successively lower concentration being more stable than the previous one. DOC levels between approximately 1.5 and 2 mg C/liter or higher (Barber 1967) are commonly found in plankton blooms or areas of high productivity. However, these DOC levels are reduced rapidly (several days or less) to levels of 1 to 1.5 mg C/liter once nutrient limitation has occurred. There were very few samples in this category in the Chukchi Sea because of the time of year, although many surface samples in the Kodiak area (Chapter IV) fit this category.

The second level values are then reduced to the third level of degradation with DOC values ranging approximately from 0.7 - 1 mg C/liter.

This level is reached after a period of several months to a year, a period of time in which the nutrients are partially regenerated. Degradation below these values is very slow and values may remain at this level for several decades with most of the dissolved organic matter possibly made up of humic acids (Williams 1969b). Further degradation occurs very slowly and its mechanisms are discussed in Chapter VIII.

The distribution of POC is similar to DOC with the highest average values found in the central strait area at the surface. The lowest average values were found both at the surface in the central Chukchi and at depth throughout the area studied (Table 6.9). POC correlated with dissolved oxygen reasonably well ($r = 0.699$) for allstations and even better for the seven surface stations discussed above ($r = 0.790$) suggesting that the amount of POC was related closely to the productivity based on photosynthesis and oxygen release while DOC was not.

The values for POC dropped rapidly as did the values for DOC although several 100 mg C/liter was usual for most of the area. There was essentially no increase in POC values for deep water beneath the central strait area suggesting that little or no particulate matter produced at the surface sank below the thermocline. This supports recent findings by both Menzel and Ryther (1970) and Barber (1967).

Although the values for C/N ratios based on weight values ranged from 3.5 to 8.0, the average values for the different areas ranged from 5.4 to 5.9 (Table 6.9). These values agree with an average C/N ratio of 5.7 found by Parsons and Strickland (1962) for surface water in the temperate north Pacific. Holm-Hansen et al. (1966) found an average C/N ratio of 5.5 in the surface layer at their station off the California coast. The narrow range of values found in this study suggest that most of the organic matter found both at surface and depth in the Chukchi Sea is of marine origin and recent. Values well above the 5.7 average, such as found at stations 4 and 9, may have been due to either the addition of land derived plant detritus with much higher C/N ratios or differences in organism types or growth stages.

Most values for the amount of organic carbon in the total particulate matter (POC/PM x 100) fall between 20 and 30% for the surface waters and 3-10% for deep waters (Table 6.1). Assuming that the amount of organic matter is approximately twice the POC value, then many of the surface waters contained 40-60% organic matter in their total PM. This is quite high for a near shore area and reflects the high rate of production in the Bering Strait area and a limited source of suspended matter for the central Chukchi Sea. The low values for deep water are probably due to resuspension of bottom sediments and limited source of particulate organic matter. Most published data has been collected in open ocean areas and in general values are lower. Gordon (1969) found that organic matter averaged about one-third the total dry weight for samples taken in the central North Atlantic. Hobson (1967) at his North Pacific stations found that organic carbon comprised an average of 20% of the total particulate matter present.

VI.5. Conclusions

The following conclusions are summarized from the above discussion on the Chukchi Sea. Several of these conclusions are discussed in more detail in Chapter VIII.

1. Sixteen oceanographic variables for the Bering Strait - Chukchi Sea area were analyzed by factor analysis and reduced to 4 factors explaining about 85% of the data variance. The 4 factors were I-Nutrients, II-Organics, III-C/N and PM and IV-Physical.

2. The distribution of POC, PN, DOC and oxygen (factor II) was more strongly influenced by the physical or advective variables than the nutrients. The variables in factor II are a much better indication of productivity than the nutrients.

3. When factor scores were plotted against each other, 4 or 5 water mass types were distinguished.

4. Plotting factors against each other may be more useful in defining water mass types than plotting individual variables.

5. Four physically and chemically identifiable water masses were found moving northward in the Bering Strait.

6. POC and PN showed a very high degree of correlation with an average POC/PN (C/N) ratio of 5.7 indicating planktonic origin for the organic matter.

7. DOC correlated reasonably well with POC (0.722) and PN for all samples and poorly with all other variables. However, DOC and POC showed no correlation ($r = -0.01$) in the highly productive region in the central Bering Strait area.

8. Several levels of DOC concentrations occur and are semi-stable for increasing lengths of time as the concentration is reduced. Thus DOC may be used as a quasi-conservative water-mass property, but only in a limited sense.

9. In the highly productive area there was no evidence of sinking particulate organic matter below the thermocline.

10. High values for the percent organic carbon in the total PM were found (20-30% in surface waters) reflecting high productive rates and a low input of land derived suspended matter.

Chapter VII

ARCTIC OCEAN

Chapter VII

ARCTIC OCEAN

VII.1. Introduction

This chapter deals with the distribution of organic and particulate matter in the Amerasian Basin in the Arctic Ocean. Samples were collected from Fletcher's Ice Island, T-3, which is operated and supplied by the Naval Arctic Research Laboratory at Barrow, Alaska, and supported by the Office of Naval Research. This study was accomplished with the help of Dr. P. J. Kinney and Miss J. E. Groves of the University of Alaska and has been submitted for publication (see Kinney, Loder, and Groves 1971).

The distribution of DOC and POC has been determined by a number of investigators (Chapter I) for the Atlantic, Pacific, and Indian Oceans. Many of these investigators (Menzel and Goering 1966, Menzel 1967, Holm-Hansen 1969, Hobson and Menzel 1969, and Menzel and Ryther 1970) have found that although the values of POC may vary widely in the surface layers, below 200-300 m the values are low and remain relatively constant with increasing depth. Gordon (1968), Szekielda (1967), Hobson (1967), Dal Pont and Newell (1964), and Holm-Hansen et al. (1966), however, show vertical differences in concentration of POC which could be correlated with hydrographic features; Riley et al. (1965) show seasonal variations.

Although systematic DOC determinations in the oceans have been few, the vertical distribution appears to be similar, that is variable at the surface and relatively constant at depth. But DOC values at depth may vary widely from location to location (Menzel 1964).

No values for organic carbon have been reported for the Arctic Ocean. This ocean is unique in several aspects including the low, seasonal nature of its surface primary productivity (English 1961 and Appollonio 1959) and the distinctive water masses from diverse sources at depth, including an oxygen minimum layer. Thus it was of interest to run vertical profiles for DOC, POC, PN, and PM. Samples were collected and analyzed as described in Chapters II and III. Because of the time necessary to filter the large amounts of water required for analysis, only 2-3 depths were sampled each day. Ice island movement of 1-3 miles a day probably did not affect the results because of the uniformity over large areas of the distribution with depth of the various water layers (Dr. P. J. Kinney, personal communication 1969).

Station locations for T-3-703 and T-3-704 are shown in Fig. 7.1. Organic matter samples were collected by Dr. P. J. Kinney for station T-3-703 and myself for station T-3-704. The detailed hydrographic and chemical nutrient data were provided by Mr. M. E. Arhelger of the University of Alaska.

VII.2. Results and Discussion

Several diverse water masses present in the Amerasian Basin are apparent from the vertical profiles of temperature, salinity, oxygen, and chemical nutrients shown in Figs. 7.2 and 7.3. Although the data shown were from station T-3-703, the profile for T-3-704 is the same except for very slight variations in depth. The depth locations and descriptions of the specific water masses are based on Coachman and Barnes (1961, 1962, 1963) and Kinney, Arhelger and Burrell (1970).

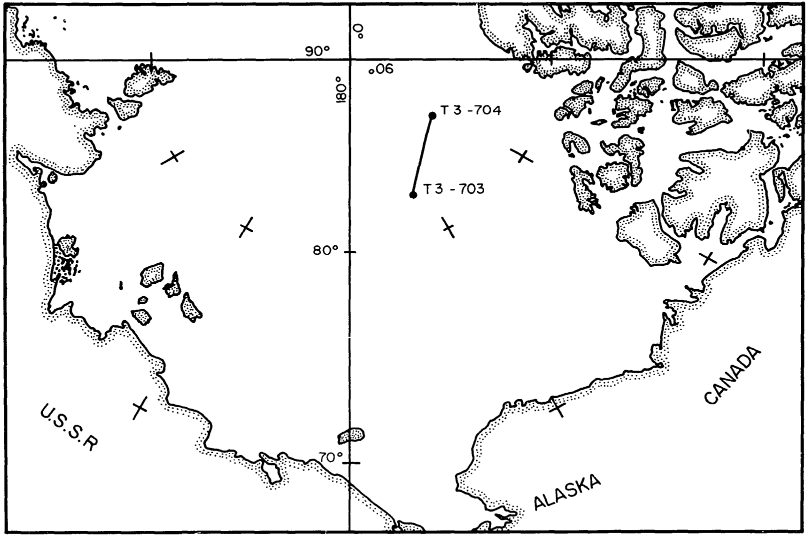


Fig. 7.1. Station locations for T-3-703 and T-3-704 in the Amerasian Basin of the Arctic Ocean.

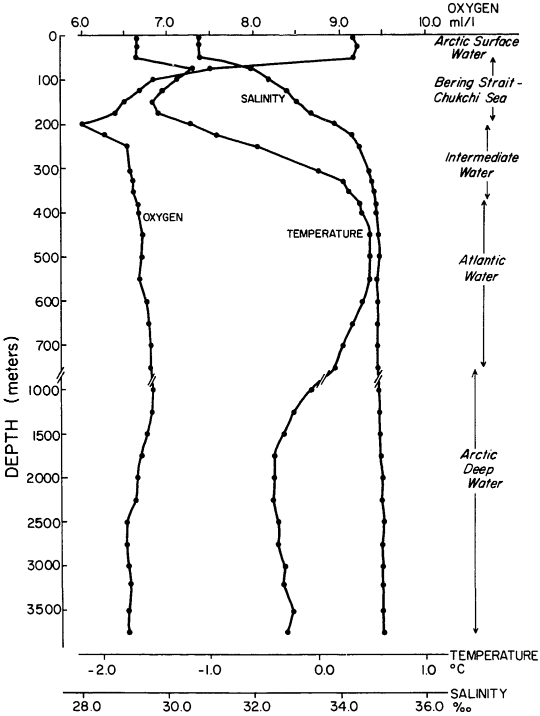


Fig. 7.2. Temperature, salinity and oxygen structure for Arctic Ocean Station T-3-703.

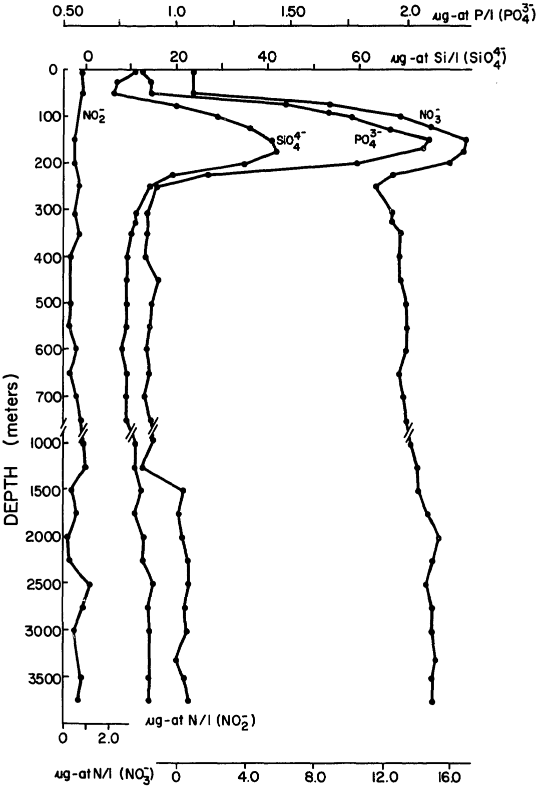


Fig. 7.3. Nutrient profiles for Arctic Ocean Station T-3-703. Spring 1968.

The Arctic surface water, generally at or near the freezing point, is relatively dilute and well mixed down to approximately 50 m where both salinity and temperature increase sharply with depth (Fig. 7.2). From 50 to about 200 m the water contains both a temperature maximum and minimum and a nutrient minimum. This water is postulated to be of Bering Strait-Chukchi Sea origin with the 75 m water representing summer origin and 150 m water representing winter origin. The intermediate water with a core at 230 m based on temperature-salinity plots of Kinney, Arhelger, and Burrell (1970), appears to be mixing with the above Chukchi water and below with the Atlantic water. They concluded that the sharp oxygen minimum at about 200 m contained in the intermediate layer is at least partly due to advection of water into the basin rather than *in situ* oxidation alone. The fact that there was no significant change in DOC concentration at 200 m supports this hypothesis.

The core of water of Atlantic origin appears at approximately 500 m and extends down to 800-900 m. Below the Atlantic layer lies the Arctic deep water of the Amerasian Basin with temperatures less than 0C and salinities ranging from 34.93 to 34.99°/$_{oo}$.

Values for PM, POC, PN, DOC, and various ratios are tabulated in Tables 7.1 and 7.2. The PM concentrations (Fig. 7.4) varied from about 32 μg/liter in the upper layers to 7-9 μg/liter at depth. The highest concentration of 55 μg/liter occurred near the strong pycnocline at the bottom of the well mixed Arctic surface water. These values compare very well with similar values obtained by a centrifugation technique

Table 7.1. Organic matter in the water of the Amerasian Basin of the Arctic Ocean at Station T-3-703, 82°N, 157°W, from March 29 to April 6, 1968

Depth (m)	POC (μg/liter) Wet Combustion	DOC (mg/liter)	DOC/POC
5	11.0	1.31	119
30	11.0	1.14	106
60	7.1	1.31	185
200	14.0	1.20	86
250	8.8	1.26	143
500	5.5	0.77	140
1500	6.4	0.76	119
2500	14.0	0.80	57
3500	6.9	0.75	109

Table 7.2. Organic matter in the water of the Amerasian Basin of the Arctic Ocean at Station T-3-704, 85°N, 125°W, from April 30 to May 8, 1969

		POC (μg/liter)							
Depth (m)	PM (μg/liter)	Wet Combustion	Dry Combustion	PN (μg/liter)	DOC (mg/liter)	POC/PM* (x 100)	PN/PM (x 100)	POC/PN*	DOC/POC*
5	31	7.5	-	0.60	1.49	24†	1.9	13†	199†
20	32	8.2	13.0	0.36	1.05	41	1.1	39	81
50	55	14.0	-	1.06	1.04	25†	1.9	13†	74†
75	30	6.4	9.5	0.30	0.90	32	1.0	32	95
100	22	9.0	12.0	0.12	0.74	55	0.5	97	62
140	18	5.8	8.8	0.29	0.92	48	1.6	30	105
200	10	4.4	3.5	0.32	0.93	35	3.2	11	266
500	15	6.4	2.9	0.11	0.96	19	0.7	26	331
750	10	3.6	2.3	0.22	0.82	23	2.2	10	357
1100	9	2.7	2.7	0.09	0.72	30	1.0	30	267

* Based on dry combustion method unless indicated otherwise.

† Wet combustion method.

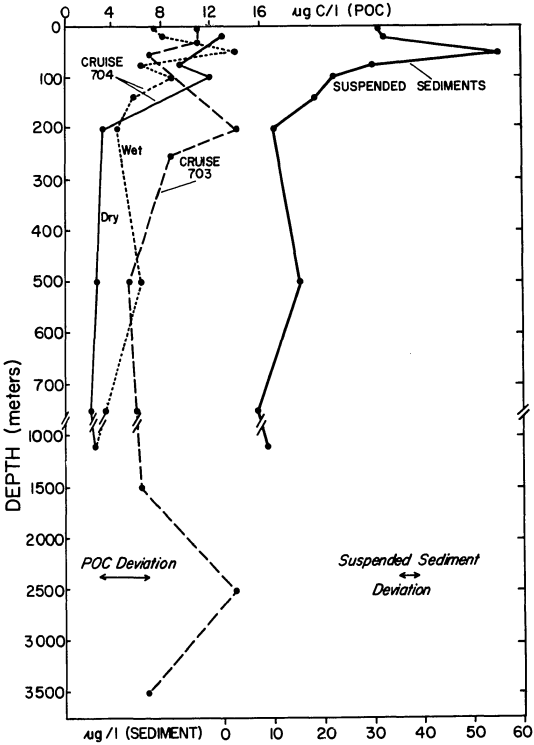


Fig. 7.4. Vertical distribution of suspended sediments (PM) and POC for Arctic Ocean Stations T-3-703 and T-3-704.

(Jacobs and Ewing 1969) with the exception that the very high value for Atlantic core water (49 µg/liter) was not repeated. In comparison with the other oceans the PM values for the Arctic Ocean are the lowest reported (Jacobs and Ewing 1969) with the possible exception of the south Pacific. Both available profiles indicate lower values in deep water than in the Arctic surface water, the Chukchi, or Atlantic water masses.

The POC values were very low, ranging from 2-13 µg C/liter (Fig. 7.4). Although there was a slight difference in values obtained by the wet and dry combustion methods (section III.1.1.5), the values are comparable with the lowest reported by Menzel (1967), Hobson and Menzel (1969), and Holm-Hansen (1969) for the Atlantic and Pacific deep water. The POC values were higher in the surface waters above 200 m than in the deeper water masses. These higher values might be expected from consideration of the higher surface values found in other oceans, but the absolute concentration is still quite low. This is not surprising considering the very low primary productivity in the surface layer, 0.6 g C/m^2/yr estimated by Appollonio (1959) which is limited to the months of July, August and early September (English 1961). Also, both sets of samples in this study were collected in the spring, 7 to 8 months after the end of the previous year's summer productivity.

Very high percentages of organic carbon in the particulate matter (POC/PM x 100) were found (19-55%). These values were substantially higher than the 3-7% found by Hobson and Menzel (1969) for deep water off South America and the deep water average of 15-20% reported by

Wangersky (1965). The source water in the Bering Strait-Chukchi Sea had high values (20-25%) only in surface waters where there was high biological activity. These two facts suggest that the particulate matter in the surface waters is settling out of the water column which is not unlikely considering the long transit time of about 30 years between Chukchi Sea and T-3-703 and 704 (Coachman and Barnes 1961, Giletti and Kulp 1959). In addition the input of airborne dust and river-carried inorganic material is probably very low. This is supported by Clark (1969) who reported apparent slow sedimentation rates of 1-3 mm per 1000 years for the Arctic Basin.

The particulate nitrogen values were very low ranging from 0.09-1.06 μg/liter with slightly higher values in the top 200 m. The highest value was found at the 50 m level corresponding to the high values of POC and PM also found there. By comparison, Holm-Hansen et al. (1966), report from 2-24 μg N/liter for their Pacific station; Holm-Hansen (1969), 0.3-1.0 μg N/liter for deep water off the coast of California; Menzel (1964), 2-3 μg N/liter for the western Atlantic; and Hobson and Menzel (1969), 0.08-1.8 μg N/liter for the area off the east coast of South America. Although the present absolute concentrations (0.1-1.0 μg N/liter) in this study are fairly reliable, large percentage errors in the low values introduce large variations in the resulting carbon/nitrogen (POC/PN) ratios (Table 7.2). Large values are indicated, however, supporting more recent results of Holm-Hansen et al. (1966), Hobson and Menzel (1969) and Holm-Hansen (1969).

The concentration of dissolved organic carbon was unexpectedly high (Tables 7.1 and 7.2, Fig. 7.5) both in surface and deep layers.

The high DOC values found in the surface layers are comparable with those found in the surface waters of the Chukchi Sea during the summer (Chapter VI). The deep water values of 0.72-0.96 mg C/liter for Atlantic and Arctic bottom waters are almost twice that for comparabledepths in other oceans (Menzel and Ryther 1970). Perhaps this reflects the shallow source in the Atlantic for these waters and the relatively slow decomposition rate compared to relatively rapid turnover of the Arctic Ocean, probably on the order of 50-150 years (Pickard 1964). This is an order of magnitude faster than the turnover rates for the northeast Pacific Ocean where the apparent age of the deep water dissolved organic matter as determined by ^{14}C dating is approximately 3400 years (b.p.) (Williams, Oeschger, and Kinney 1969). The proposed dating of the Arctic water masses (P. J. Kinney, personal communication 1969) should help solve this problem.

The reason for the differences in DOC values at the two stations is not readily evident. These differences may represent the seasonal variations in the source waters of the Bering Strait-Chukchi Sea and the North Atlantic. The very high DOC value of 1.45 mg/liter at 5 m for T-3-704 seems anomalous considering how well the Arctic surface water is mixed as shown by almost all the other parameters. Contamination is a possibility since this sample was taken just beneath a 4 m hole in the ice, although the particulate parameters do not indicate contamination.

With the exception of the 100 m sample the DOC values remained approximately equal with depth increase through the Bering Strait-Chukchi Sea summer and winter water, the intermediate water which contained the oxygen minimum and nutrient maximum, and the Atlantic water.

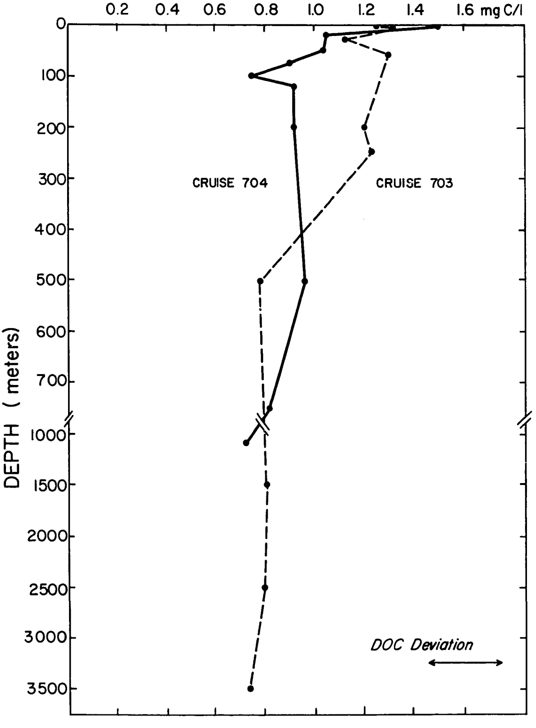


Fig. 7.5. Vertical distribution of DOC for Arctic Ocean Stations T-3-703 and T-3-704.

The slightly lower DOC values for the Arctic deep water were about the same (~0.7 mg/liter) for both stations. These values lend support to Menzel and Ryther's (1970) suggestion that DOC is a quasi-conservative parameter over significant periods of time.

The high ratios of DOC to POC ranging from about 60 to 360 are a result of the higher than normal DOC values at depth and POC values which are as low or lower than other ocean values. These ratios are substantially higher than an average ratio of 50 reported by Williams (1969) for other oceans. Sheldon, Evelyn, and Parsons (1967) and others have suggested that POC may be formed from the DOC pool by bacterial activity, bubbling, and/or adsorption of DOC onto inorganic or biologically inert surfaces. Perhaps the almost year around ice cover preventing wave action and bubble entrapment and the extremely low import of detrital material limiting available bacterial substrates, reduces the possibility of DOC to POC transformations and permits the high DOC/POC values to remain.

VII.3. Conclusions

The limited available data on organic matter in the Amerasian Basin of the Arctic Ocean suggest the following conclusions:

1. The low PM values and the high percentage of organics in the particulate matter indicate that there may be a low input of airborne and river carried inorganic material to all the Arctic water masses. In addition a lowering in the concentration of particulate matter (both organic and inorganic) must be occurring in the source waters as they are incorporated into the Amerasian Basin water circulation since there

are incorporated into the Amerasian Basin water circulation since there is little or no influence on POC concentrations at T-3-703, 704 by the original POC concentrations of the water masses. This may be caused by oxidation, re-solution, settling, mixing and dilution, or a combination of these processes.

2. The low values of POC and their low correlation with hydrographic features support the more recent findings of Hobson and Menzel (1969) for Atlantic deep water and Menzel (1967) and Holm-Hansen (1969) for Pacific deep water. The low surface values reflect the seasonal nature of the low primary productivity.

3. The high DOC values in the Arctic may reflect the youth of the water masses relative to their surface sources as compared with the cases for the other oceans. This suggests that the DOC is a quasi-conservative parameter over a period of time greater than the turnover for the Arctic Ocean.

4. The high DOC/POC ratios compared to other oceans may imply differences in decomposition rates, DOC to POC transformation rates, or methods of transport of particulate and dissolved organic material at depth.

5. The high C/N ratios (>10) for particulate matter support the recent findings of Holm-Hansen et al. (1966), Hobson and Menzel (1969) and Holm-Hansen (1969).

Thus the Arctic Ocean appears to be somewhat unique in its distribution of organic matter.

Chapter VIII

SUMMARY AND CONCLUSIONS

Chapter VIII

SUMMARY AND CONCLUSIONS

Samples for dissolved organic carbon (DOC), particulate organic carbon (POC) and some particulate nitrogen (PN) and particulate matter (PM) analyses were collected from 6 major areas around Alaska. These included Southeastern Alaska (including glacial inlets), Cook Inlet, Kodiak Island shelf, Unimak Pass-Southeast Bering Sea, Chukchi Sea and the Arctic Ocean (T-3).

All DOC samples were oxidized by wet combustion (potassium persulfate oxidation) and most POC by wet combustion of glass-fiber filters; the resulting CO_2 was analyzed by an IR analyzer. Some POC samples were analyzed by dry combustion; the resultswere comparable to those obtained with the wet combustion method. The glass-fiber filters were found to adsorb a variable amount of DOC depending on the origin of the water filtered.

Linear regression and principal component (factor) analyses were used to determine the relationship of POC and DOC to the other chemical and hydrographic parameters in Cook Inlet, the Kodiak area and the Chukchi Sea. Factor analysis was useful in reducing the data (12-16 variables) to 4 or 5 factors (groups of variables) based on processes affecting the distribution of the data. It was most effective on the Chukchi Sea data for which distribution patterns were clearly defined by factor scores determined by factor analysis. This appears to be a very useful technique in analyzing oceanographic data and will probably be used by more workers in the field as they become aware of it.

Detailed conclusions for the individual areas are summarized at the ends of Chapters IV-VII, however, a short summary is as follows:

Glacial runoff in southeast Alaska contained very low amounts of DOC (0.2-0.5 mg C/liter) and variable amounts of POC (several 100-several 1000 µg C/liter) depending on the season and amount of local rainfall. In North Dawes Inlet, a glacial inlet studied in detail, about half of the POC entering the inlet in glacial runoff was carried out of the inlet in suspension. During the late summer a biologically active layer (BAL) was found a few meters below the surface mixing layer of glacial runoff and normal estuarine water. The adsorption or release of organic compounds (in terms of DOC) by the glacial clays in the mixing layer was undetectable although adsorption may occur after longer time intervals.

In Cook Inlet mixing was the most important process affecting the distribution of organic matter. POC values ranged from 37-4800 µg C/liter while the DOC ranged from 0.45-12.80 mg C/liter. The high values were found near the head of the inlet due to river inflow.

The marine waters surrounding Kodiak Island were sampled in late June when most of the water had stabilized and nutrient concentrations had been reduced in the euphotic zone. POC values averaged much higher in surface waters (0-10 m, 398 µg C/liter) than in the deep water (50-100 m, 85 µg C/liter). POC showed a high correlation with dissolved oxygen and a very low correlation with DOC. Although DOC was higher in surface than in deep water (ave. 1.09 vs 0.91 mg C/liter), it showed a very low correlation with all other parameters measured in this study.

During mid-summer the surface waters in the southeastern Bering Sea just north of Unimak Pass continued high concentrations of POC whose distribution was affected by both upwelling and northerly currents through the passes. POC values ranged from 43-811 μg C/liter for near surface (< 100 m) samples and 12-27 μg C/liter for deep samples (>100 m) and were reasonably homogeneous above the thermocline. DOC values were scattered in near-surface samples (0.60-1.90 mg C/liter) and showed a low correlation with POC values.

During late July in the Bering Strait and southern Chukchi Sea, high POC, PN, DOC and dissolved oxygen values, a result of high productivity, were found in the surface waters above the thermocline. All of these parameters correlated well with each other as contrasted with Kodiak and Umimak Pass where POC and DOC showed only a low correlation.

However, in the central Bering Strait area where the highest values for all four parameters were found, POC and DOC showed no correlation. Although Anderson and Zeutschel (1970) found a log-log relationship between the rates of production of DOC and POC, it appears from my data that there is almost no relationship between the amounts of DOC and POC present in productive surface waters. However, in an upwelling area off Peru, Lorenzen (1968) found a high correlation between the concentrations of POC and chlorophyll. Anderson and Zeutschel (1970) found no relationship between chlorophyll and the DOC production rate. This suggests that although released DOC is related to produced

POC, there are other processes affecting the observed DOC concentrations in the water. Barber (1967) proposed that heterotrophic utilization of dissolved organic matter increased during a bloom, and DOC values actually decreased as primary production increased. He also found a strong diurnal cycle in the concentrations of DOC. This may explain why DOC showed such a low correlation with all the parameters in this study except in the Chukchi on an overall scale. Consequently the measurement of DOC is generally of little utility because DOC concentration is the result of a number of diverse processes which include hetertrophic utilization, adsorption to particulate matter, DOC to POC transformations, and extracellular excretion by living plants and animals as well as decomposition of dead organisms.

Two vertical profiles were sampled for DOC and POC in the Arctic Ocean at T-3; on the second profile PN and PM were also sampled. POC values (2-13 μg C/liter) were as low or lower than any reported for the rest of the world's oceans (Menzel and Ryther 1970) as were the PN and PM values. This indicates that there is little detrital input to the Arctic Ocean and a very low production of organic particles probably due to the low seasonal productivity and the almost year around ice cover. DOC values (0.72-0.96 mg C/liter) in the deep water were almost twice those for comparable depths in other oceans as reported by Menzel and Ryther (1970). The resulting higher than normal DOC/POC ratios (60-360) may reflect the youth of the water masses relative to their surface sources or be due to different decomposition rates. A more plausible explanation is that DOC to POC transformations may occur at much lower rates because of a lack of particle production at the surface due to almost continual ice cover and the low input of detrital material which might aid these transformations by providing an adsorption substrate.

Thus it appears that the distributions of DOC and POC are controlled by different processes in different areas at different depths. Although the concentrations of both DOC and POC are generally higher in surface waters than at depth, there are so many controlling processes that the resulting concentrations do not appear to be related to any other single parameter.

Some general observations may be made. It appears that there are several levels of DOC concentrations in water masses with each successively lower concentration being more stable (resistant to degradation) than the previous one. The values given for DOC are based on the wet combustion technique. High DOC levels (about 1.5-2.0 mg C/liter or higher (Barber 1967)) are found in plankton blooms or areas of high productivity. These levels are reduced rapidly in one-half to several days to concentrations of 1-1.5 mg C/liter which are common in areas of medium productivity during summer months. The reduction of DOC might occur by heterotrophic utilization or adsorption to particles which are more available in a maturing bloom than in the initial phases. These second level values are then reduced to the third level of degradation where DOC values are about 0.7-1.0 mg C/liter. This level, reached after several months to a year, is probably a result of both slower DOC to POC transformations. This third level was not reached during the 8-9 month winter in the Arctic Ocean in the near surface waters, yet was attained in 3 months or less in Endicott Arm in Southeast Alaska where wind-stirred surface waters and high inputs of particulate matter could provide easy removal of DOC by DOC to POC transformations.

The lowest levels of DOC concentration (about 0.3-0.7 mg C/liter) generally are found in deep ocean water that has been removed from the surface for an extended period (perhaps several decades to centuries) and represents the "stable or resistant fraction" of the organic matter. Although this organic matter appears to be totally inert in short term experiments (Menzel and Goering 1966, Barber 1968), there must be some mechanism for reducing the low value of 0.4 mg C/liter down to about 0.2 mg C/liter such as reported by Menzel (1964) in the Indian Ocean. Several possible mechanisms are (1) adsorption onto clay surfaces or other inorganic or organic particles by either an abiotic or biotic process with subsequent removal by settling or ingestion into particle feeders, (2) abiotic oxidation to CO_2, and (3) direct uptake and utilization by organisms. The importance of any or all of these mechanisms is unknown.

A similar time degradation-concentration scale can be constructed for POC with ranges from several 1000 μg C/liter down to 2-6 μg C/liter. So it can be seen that the concentrations of DOC can be used as quasi-conservative properties for any given water mass, but the time period involved must be understood.

This study has been useful in describing the distribution of DOC and POC in different areas under natural conditions as well as determining their significance as chemical parameters. Generally the values of

DOC and POC correlate poorly with other oceanographic parameters because they are the result of a complex series of biological and physicochemical interactions. Consequently the values of DOC and POC cannot be easily predicted from nutrient and hydrographic data, but must be determined specifically whenever this information is desired.

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APPENDIX

Station Locations - Cruise 027

Unimak Pass - Southeastern Bering Sea

Station Number	Date	Time-hours (Greenwich)	Latitude (Deg. Min.)		Longitude (Deg. Min.)		Sonic Depth (m)
027704	27/07/66	06.1	54	23.5 N	165	04.5 W	91
027706	27/07/66	19.3	54	29.4	166	59.5	329
0227710	28/07/66	17.8	55	04.0	166	17.0	137
027714	29/07/66	23.6	54	11.0	167	17.5	1750
027718	02/08/66	04.2	54	25.0	166	36.0	550
027723	04/08/66	05.7	54	52.0	165	09.0	109
027725	04/08/66	19.0	55	18.2	163	43.6	58
027727	05/08/66	04.2	55	31.5	164	50.4	95
027730	06/08/66	06.4	54	25.0	166	36.1	560
027731	06/08/66	18.4	54	11.5	167	18.4	1700
027732	07/08/66	08.4	54	01.0	167	28.6	1700
027733	07/08/66	20.8	53	54.9	167	41.6	1664
027733A	07/08/66	20.8	53	54.9	167	41.6	1664
027735	08/08/66	17.7	53	55.0	168	00.0	540
027736	09/08/66	01.1	54	11.1	167	18.9	600
027741	11/08/66	00.6	54	38.5	165	53.0	380

APPENDIX

Station Locations - Cruises 031, 056 & 075 Endicott Arm

Station	Latitude (Deg. Min.)	Longitude (Deg. Min.)
En-0	57 44.0 N	133 39.1 W
En-2	57 44.6	133 35.5
En-4	57 43.8	133 31.7
En-9	57 41.0	133 24.9
En-15	57 37.8	133 15.6
En-FT	57 37.3	133 10.2
En-20	57 34.3	133 08.7
En-25	57 31.2	133 01.3
En-27	57 30.7	132 58.5

APPENDIX

Station Locations - Cruise 045

Kodiak Island Shelf

Station Number	Date	Time-hours (Greenwich)	Latitude (Deg. Min.)	Longitude (Deg. Min.)	Sonic Depth (m)
045 364	22/06/67	09.7	58 55.0 N	151 21.7 W	0146
045 372	22/06/67	07.2	58 27.4	152 10.6	0109
045 373	22/06/67	17.7	58. 40.0	152 39.0	0135
045 377	22/06/67	22.4	58 49.7	153 12.0	0146
045 378	23/06/67	04.9	58 07.5	154 12.0	0137
045 382	23/06/67	10.2	57 54.2	153 45.0	0054
045 383	23/06/67	14.3	57 35.0	154 32.3	0073
045 387	23/06/67	20.1	57 49.0	155 05.0	0285
045 396	25/06/67	16.3	57 44.4	152 23.4	0033
045 399	26/06/67	01.1	57 08.0	152 50.5	0082
045 408	26/06/67	10.6	56 36.5	151 52.0	0400
045 409	26/06/67	16.9	56 13.1	152 52.0	0640
045 416	27/06/67	04.5	56 25.0	154 25.5	0024
045 420	27/06/67	08.6	56 05.0	154 25.5	0128
045 423	26/06/67	16.9	56 50.5	153 40.0	0044
045 429	28/06/67	20.8	58 04.6	152 31.6	0046
045 433	30/06/67	07.4	54 36.3	151 00.0	0077
045 444	30/06/67	10.7	57 57.6	151 09.6	0086

APPENDIX

Station locations - Cruise 056 Admiralty Island area

Station Number	Date	Latitude (Deg.	Min.)	Longitude (Deg.	Min.)
1986	13/11/67	58	10.5 N	134	18.5 W
1988	13/11/67	58	08	134	45
1991	14/11/67	57	46.9	134	58.7
1992	14/11/67	57	46	135	08
1993	14/11/67	57	45.8	135	07.8
1994	14/11/67	57	28.5	134	44.5
1996	15/11/67	57	33	135	28
1997	15/11/67	57	26	134	59
2001	16/11/67	57	18	134	04

APPENDIX

Station Locations - Cruise 065 Cook Inlet

Station Number	Date	Time-hours (Greenwich)	Latitude (Deg. Min.)	Longitude (Deg. Min.)	Sonic Depth (m)
065 242	21/05/68	22.8	59 04.9 N	152 05.6 W	177
065 245	22/05/68	09.3	58 58.5	152 39.0	148
065 246	22/05/68	12.4	58 57.0	152 58.5	163
065 260	24/05/68	11.2	60 03.0	152 31.1	62
065 277	26/05/68	17.3	60 40.3	151 40.5	18
065 278	26/05/68	18.7	60 40.3	151 32.7	29
065 279	26/05/68	20.5	60 40.3	151 25.2	18
065 287	27/05/68	16.9	60 53.9	151 14.6	31
065 288	27/05/68	19.6	60 52.6	151 29.0	55
065 295	28/05/68	17.0	61 15.4	149 53.3	26
065 296	28/05/68	18.2	61 13.3	149 59.2	50

APPENDIX

Station Locations - Cruise 751

Bering Strait - Chukchi Sea

Station Number	Date	Time-hours (Greenwich)	Latitude (Deg. Min.)	Longitude (Deg. Min.)	Sonic Depth (m)
751 001	27/07/68	19.4	65 11 N	170 38 W	0045
751 002	28/07/68	00.4	65 20	169 35	0042
751 004	28/07/68	05.2	68 48	168 19	0054
751 006	28/07/68	13.8	66 26	169 20	0052
751 007	28/07/68	18.0	66 46	170 19	0046
751 008	28/07/68	23.7	66 46	168 49	0043
751 009	29/07/68	03.0	66 46	167 16	0032
751 011	29/07/68	10.1	67 19	165 38	0032
751 012	29/07/68	17.8	68 05	168 52	0057
751 013	30/07/68	02.3	68 28	172 20	0054
751 014	30/07/68	11.4	69 20	176 22	0054
751 015	30/07/68	16.4	70 06	175 41	0054
751 016	31/07/68	00.0	71 16	174 27	0046
751 018	31/07/68	09.8	70 35	170 14	0036
751 019	31/07/68	19.4	70 24	165 16	0044
751 022	01/08/68	07.5	72 20	167 05	0050
751 025	02/08/68	04.0	71 36	159 10	0055

APPENDIX

Station Locations - Cruise 074 Glacier Bay

Station Number	Date	Time-hours (Local)	Latitude (Deg. Min.)	Longitude (Deg. Min.)
74638	17/09/68	10.0	58 51.0 N	136 48.7 W
74639	18/09/68	19.0	58 57.3	136 33.0
74646	20/09/68	07.0	58 54.8	136 34.2