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SOME FACTORS AFFECTING THE CONCENTRATION
AND PROPERTIES OF CARRAGEENAN IN
CHONDRUS CRISPUS STACKHOUSE

by

STEPHEN WILLIAM FULLER
B.S., Cornell University, 1967

A THESIS

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Department of Botany

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This thesis has been examined and approved.

Arthur C. Mathieson
Thesis director, Arthur C. Mathieson,
Assoc. Prof. of Botany

Albion R. Hodgdon
Albion R. Hodgdon, Prof. of Botany

Charlotte G. Mast
Charlotte G. Mast, Prof. of Botany

John J. Sasuer
John J. Sasuer, Assoc. Prof. of Zoology

Richard W. Schreiber
Richard W. Schreiber, Prof. of Botany

Aug. 19, 1971
Date

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ABSTRACT

The concentration, gel strength, viscosity, and ratio of kappa to lambda fractions of carrageenan in Chondrus crispus Stackhouse have been studied in relation to the plant's age, reproduction, habitat, and season of harvest. No correlation was found between gel strength and viscosity, but gel strength and ratio of fractions showed a direct relationship. Plant age, reproduction, vertical position and exposure to wave action had no affect on the quantity or properties of carrageenan. The percent of carrageenan, gel strength, and the size of the kappa fraction were usually greater in plants of coastal than of estuarine locations. In contrast the viscosities showed an opposite trend. Carrageenan concentration, gel strength, and viscosity were highest in late fall-early winter, while the lowest values were recorded during the spring-early summer. A complex interaction of many factors (including temperature, salinity, and nutrients) is probably responsible for the seasonal trends.

INTRODUCTION

Chondrus crispus and several other Gigartinalean algae contain the phycocolloid carrageenan, which is a sulfated polysaccharide (Anderson and Rees, 1965). Carrageenan forms the basis of an extensive phycocolloid industry (Mathieson, 1967; Hoppe and Schmid, 1962), that is an important source of income for New England and the Canadian Maritime provinces. The chemical and physical properties of carrageenan make it useful as a stabilizer, as well as a gelating, stiffening and thickening agent. Food, pharmaceutical, cosmetic, and other industries incorporate carrageenan in products as diverse as tooth paste, chocolate milk, ice cream, insect spray, paint, and cloth sizing (Hoppe and Schmid, 1962).

Among others, Taylor (1957), Hass and Hill (1920-21), Hahre and Mathieson (1970), and Mathieson and Burns (in preparation) have described the general morphology and reproduction of C. crispus. Chondrus is a perennial plant with maximum growth in spring and summer. The fronds are distally expanded and dichotomously branched, giving the plant a tufted habit. The coloration of the fronds varies from bleached white to purlish brown and reddish purple. The reproductive organs are immersed in the blade (Kylin, 1956). Chondrus is abundant in the lower intertidal and subtidal zones of New England (Hahre and Mathieson, 1970). Percival (1968) suggests that carrageenan provides flexible strength and hygroscopic properties to Chondrus, which are beneficial for existence in the marine environment.

Little is known of the role of environmental parameters in determining the concentration and properties of carrageenan in Chondrus crispus. An investigation by Black et al (1965) deals, at least in part, with variations in carrageenan induced by different seasons and habitats. As far

as I am aware, only one other author (Butler, 1936) has reported on the seasonal variations of carrageenan in Chondrus. The paucity of information on carrageenan ecology and the economic importance of the phycocolloid have suggested the need for further investigations. Thus, the present investigation was initiated in order to evaluate the interrelationships between percent carrageenan, gel strength, viscosity, and ratio of kappa to lambda fractions in Chondrus relative to its age, reproduction, habitat, and season of harvest.

DESCRIPTION OF STUDY AREAS

Five sampling areas were selected (Dover Point, Toll Bridge, Jaffrey Point, Rye Harbor, and Rye Ledge). The stations ranged from estuarine to exposed open coastal sites. Unless otherwise noted, these will be the stations referred to in the text.

Dover Point at Hilton State Park is a tidal rapids area. The substrate is rocky with little silt due to the strong currents. The tidal waters from Great Bay and Little Bay pass through this constriction into the Piscataqua River. A current of nearly five knots is produced. The flora closely resembles that of the open coast (Mathieson, Reynolds, and Hehre, in press).

The Maine-New Hampshire Toll Bridge station is located on the Piscataqua River about half way between Dover Point and the mouth of the river at Portsmouth, N.H. The substrate consists of a rock outcrop, which is surrounded by silty mud and scattered small boulders. The paucity of solid substrate limits the flora. However, kelps, fucoids, and gigartinalean species are found there.

Jaffrey Point, or Fort Stark as it is commonly called, is located on New Castle Island at the mouth of the Piscataqua River. The collecting area was a massive rock outcrop. The area is a semi-exposed coastal station because of the prevailing wave patterns. The substrate supports a luxuriant algal community (Mathieson, Hehre, and Reynolds, in press).

Rye Harbor in Rye, N.H. is delineated by two jetties which are perpendicular to the open sea and lie parallel to and opposite each other. The collecting site was on the granite blocks of the northern jetty and the adjacent boulders and cobbles. The flora on the cobbles is limited in density and diversity due to the mobility of the substrate.

Rye Ledge is an extensive rock outcrop lying several hundred yards

offshore. It is accessible only at low tide, by way of a narrow isthmus. The outcrop protrudes a few feet above the level of the water at high tide, and it is banded by a well defined zonation. There is an extensive flora on its seaward face which is consistent with its fully exposed condition.

Three additional stations (Star and Appledore Islands of the Isles of Shoals and Frost Point) were each visited once during the study. Frost Point is located on Little Harbor near the mouth of the Piscataqua River. The Isles of Shoals are a group of nine islands, ten miles off Portsmouth, N.H. Star Island was sampled on the eastern, seaward side. The collection from Appledore Island was made from the most northern point of its shore. Maps and further descriptions of all study areas may be found in Hehre and Mathieson (1970).

METHODS

Physical and Chemical Parameters of the Environment

Monthly salinity and temperature measurements were taken at each of the five stations with a hydrometer and thermometer from September 1968 to January 1970. Bimonthly records were kept at the five stations throughout 1970. Simultaneously, water samples were collected for the determination of total phosphorus, soluble phosphate, nitrate-nitrogen, and nitrite-nitrogen. The methods of nutrient analysis employed were as follows: total phosphorus (Menzel and Corwin, 1965), soluble phosphate (Murphy and Riley, 1962), nitrate-nitrogen (Wood, Armstrong, and Richards, 1967), and nitrite-nitrogen (Bandscheider and Robinson, 1952). A regression model was formulated to fit a curve to the nitrate-nitrogen and soluble phosphate data of each station (Mendenhall, 1968). The equation contains factors to account for linear, quadratic, and cubic effects of time. Coded values to indicate yearly cycle, station, and time-station interactions were also included in the equation. Several 't' tests were run (at the 5% level of significance) on the results of the equation to determine if differences in nutrient levels existed between the stations. The results of the equation were also used in predicting the nutrient concentrations found during January of 1969 and 1970. The standard deviations of these predictions was used to ascertain differences among the stations for these two months. In addition, the nitrate and phosphate data from all stations were averaged together monthly and plotted seasonally.

Salinity, temperature, and nutrients were monitored hourly throughout a tidal cycle at Dover Point and Rye Harbor on successive days, in order to evaluate short term variations of the parameters. A tidal curve was calculated using the method and data presented in the U.S. Department of

Commerce Tide Tables publication (Anon., 1969). Salinity and temperature regimes on either side of the northern jetty at Rye Harbor were also noted.

Physical and Chemical Properties of Carrageenan

Samples of Chondrus were usually collected over a large area in order to minimize population deviations. Some collections were made from specific quadrats (30 x 50 cm.). All of the plants were brought to the laboratory and cleaned of epiphytes and epizooans. The samples were subsequently allowed to dry at room temperature and then stored for varying periods of time before being analyzed. The plants were hydrated again prior to extraction. Each sample was characterized as to its gel strength, viscosity, and ratio of fractions; interactions of these properties were also identified.

Among others, Rose (1950), Black et al (1965), Butler (1934), Young and Goring (1958), and Tsunino (1968) have developed methods of extracting carrageenan from Chondrus. Young and Goring (1958) have also presented procedures for measuring the gel strength and viscosity of carrageenan. Anderson et al (1968) and Smith et al (1954) have developed methods of separation which yield two fractions of carrageenan-kappa and lambda. Demetri Stancioff, of Marine Colloids Inc., Rockland, Maine, and I worked out methods for these analyses which were best suited to this investigation. The procedures ¹⁾ are outlined below:

1) Abbreviations used in procedures outline:

dry equals forced hot air oven at 50°C
 heat equals boiling water bath
 mill equals macerate with blender-stirrer
 filter equals high pressure (to 100 lb.) filter bomb
 i.a. equals isopropyl alcohol

Extraction of carrageenan:

- (1) weigh out approximately 135 g. wet weight Chondrus crispus
 - (2) soak twice for 10 min. each in cold tap water
 - (3) dry for 2 days and then seal in an air tight container
 - (4) weigh out 20 g. of dry Chondrus and place in 1 liter H₂O
 - (5) add 10 ml. of 3% NaOH (maintains pH at approximately 8)
 - (6) cover and heat mixture for 1 hour
 - (7) mill plants until well pasted; keeping them on the heat
 - (8) cover and heat for 16 hours
 - (9) add 200-300 ml. H₂O; for very high viscosity materials divide the sample in half and dilute further to aid in filtration
 - (10) mill the pasted solution again and then stir in 50 g. of Cellite 503 filter aid
 - (11) cover and heat for 1 hour
 - (12) filter with a filter cloth, keeping the filtrate warm to prevent gelation
 - (13) add 15 ml. of 10% NaCl to 300 ml. of near boiling water
 - (14) add filter cake to #13 and reslurry
 - (15) heat the solution for 1 hour
 - (16) filter with a filter cloth and combine the filtrate with that obtained in #12
 - (17) bring the combined filtrates to 40-45°C
 - (18) measure out a volume of 85% i.a. equal to 2.5 times the combined filtrates and add to it 35 ml. of 10% NaCl solution
 - (19) stir the alcohol vigorously and pour the combined filtrates in the alcohol slowly to allow for proper coagulation of carrageenan
 - (20) allow the coagulum (carrageenan) to stand at least 1 hour
 - (21) squeeze the carrageenan damp dry
 - (22) pick the carrageenan apart and place it into 500 ml. of 85% i.a. for 1 hour
 - (23) repeat steps # 21 and 22
 - (24) filter the i.a. used in #19 with a tared #5 Whatman filter paper in a buchner funnel (to collect fine carrageenan fibers)
 - (25) dry the filter paper and carrageenan for 2 days and then determine their weights
 - (26) grind the carrageenan through a 40 mesh/in. screen
- The accuracy of the extraction technique is $\pm 10\%$

Gel strength determination:

- (1) prepare a 1% solution of carrageenan in 1% KCl by heating and stirring until dissolved
- (2) pour the solution into a crystalizing dish
- (3) cool in a 25°C water bath for 2 hours
- (4) invert the gel in the crystalizing dish
- (5) test the gel 4 times on a Cherry-Burrell plunger apparatus with a dietary gram scale

The plunger diameter is 11.0 mm. The speed of compression is 3.0 mm/sec. The accuracy of the gel strength evaluation is $\pm 10\%$.

Viscosity

- (1) prepare a 1.5% solution of carrageenan in distilled H₂O by heating

- and stirring until dissolved
- (2) bring to 75°C
 - (3) measure viscosity at 60 rpm on a Brookfield model LVF viscometer
- The accuracy of the viscosity measurement is $\pm 5\%$.

Fractionation

- (1) measure out 5 g. of carrageenan
- (2) place carrageenan in a 1 liter beaker and add 500 ml. of 2.3% KCl solution
- (3) stir solution for 1 hour
- (4) place mixture in a 25°C water bath for 24 hours
- (5) add 25 g. of Cellite 503 filter aid
- (6) stir for 1 hour
- (7) filter using a #5 Whatman filter paper
- (8) wash the filter cake with 100 ml. of 2.3% KCl solution; save the filter cake
- (9) coagulate the filtrate in 2 volumes of 85% i.a.
- (10) let coagulum stand for 1 hour
- (11) squeeze the coagulum damp dry
- (12) pick coagulum apart and place it in 250 ml of 85% i.a. for ¼ hour
- (13) repeat steps 11 and 12 twice
- (14) filter the coagulating i.a. with a buchner funnel and a tared #5 Whatman filter paper
- (15) dry the coagulum and filter paper used in #14 for 2 days and then determine their weights

The coagulum is the lambda fraction.

- (16) disperse the filter cake from #8 in 400 ml. of distilled H₂O
- (17) heat to 80-85°C
- (18) filter the solution prepared in #16
- (19) wash the filter cake with 100 ml. of distilled water
- (20) repeat steps 9-15

The coagulum is the kappa fraction.

The accuracy of the fractionation techniques is $\pm 10\%$.

Carrageenan Variation

As suggested previously, the physical and chemical properties of carrageenan in Chondrus were studied in relation to a variety of parameters. Each collection was analyzed for percent carrageenan, gel strength, and viscosity.

Seventeen quadrats (30 x 50 cm.) were progressively denuded (one each month) at Rye Ledge between February 1969 to August 1970 (Fig.1-5) in order to evaluate the effects of population age on carrageenan properties. The plants were allowed to regrow until September 1970 when the quadrats were simultaneously denuded. Table I summarizes the denudation dates and maximum age of plants on the quadrats. Two collections of Chondrus made on December 19, 1969 at Rye Ledge were used to evaluate reproductive versus vegetative differences in carrageenan properties.

An investigation of the effects of wave exposure on carrageenan properties was carried out at Rye Harbor. Samples of Chondrus were collected from the sheltered and exposed sides of the northern jetty. Differences in carrageenan properties were evaluated from samples of Chondrus collected vertically (by SCUBA) in the lower intertidal and subtidal zones at Rye Ledge, Frost Point, and Star and Appledore Islands. In addition a smaller transect study of plants from the lower intertidal and upper subtidal zones was conducted at Rye Harbor. Depths were calculated relative to mean low water.

Monthly samples of Chondrus were obtained from five stations in order to evaluate the effects of locations and season of harvest. Specific details of collection dates and locations are summarized in Table II. Collections from Dover Point and Rye Harbor were analyzed for the ratio of kappa to lambda fractions in addition to the other properties. Seasonal

fluctuation of carrageenan content and properties was examined by pooling data from all five stations.

The effects of location on carrageenan properties was also studied by reciprocal transplants of Chondrus between Rye Harbor and Dover Point. Large rocks, carrying substantial Chondrus populations were marked and moved between stations. Small quantities of Chondrus were collected from each group of rocks initially, and then again after 1-2½ months.

RESULTS

Physical and Chemical Parameters of the Environment

Figure 6 illustrates the salinity and temperature regimes found at Dover Point and Rye Ledge. The Rye Ledge plots are typical of the three coastal stations while Dover Point illustrates the situation in the estuary. Specific details of hydrographic records at each station can be found in Table III. The salinities at Dover Point were lower and more erratic than on the coast, while the Toll Bridge values were intermediate between Dover Point and the coastal sites (Table III). Temperatures at the five stations followed a normal seasonal trend with summer maxima and winter minima. The extremes of temperature were generally found at Dover Point.

Seasonal variations of nitrate-nitrogen and soluble phosphate are depicted in Figure 7. The regression model 't' tests indicated no significant differences among the stations; hence the data from all five stations were pooled¹⁾. In general the highest values of nitrates were recorded in the late fall-early winter, whereas phosphates were highest during late summer-fall. Low nutrient levels were generally recorded during spring and early summer. The data for individual stations is summarized in Table III. Table IV lists the computer predicted nutrient concentrations for January of 1969 and 1970. The highest nutrient values and greatest differences between stations were recorded in this month. Although the differences between stations in January were not statistically significant there were trends in nitrate values towards higher concentrations in the estuary.

The tidal cycle results of January 25 and 26, 1970 at Dover Point and Rye Harbor, respectively, are summarized in Figures 8-11. Phosphate and

1) Two soluble phosphate values (Rye Ledge 9-7-70 and Dover Point 7-20-70) were rejected from the analysis as outliers.

nitrate concentrations were higher and they had a greater range at Dover Point than at Rye Harbor (Fig. 8 and 9). The only exception to this observation was the sample taken at 0715 at Rye Harbor, which was probably due to contamination. As depicted in Figures 10 and 11, the temperatures were relatively constant at both stations. In contrast the salinities were higher and more constant at Rye Harbor than at Dover Point.

Table V contains the salinity and temperature data from both sides of the northern jetty at Rye Harbor. The temperatures on the sheltered side of the jetty were consistently higher while the salinities were generally lower.

Physical and Chemical Properties of Carrageenan

Figure 12 is a plot of gel strength versus viscosity for all of the samples. No trend was evident, except that there were very few instances in which both gel strength and viscosity were high in the same sample. Figure 13 depicts the relationship between the ratio of kappa to lambda fractions and the gel strength of the sample. An increase in gel strength corresponded to an increase in the kappa to lambda ratio of fractions.

Figure 14 illustrates the relationship between the viscosity of the sample and the duration of storage prior to extraction. A decrease in viscosity was evident after prolonged storage. Thus, no data were reported for collections stored longer than six months. In Figure 15 the gel strengths of samples stored for varying periods of time are compared. Gel strengths were not influenced by storage.

Carrageenan Variation

Age of plant: Figures 16-18 illustrate the effects of age on the concentration and properties of carrageenan. The percent carrageenan ranged

from 61.7 to 76.0; these values occurred in the 3 and 4 month old populations, respectively (Fig.16). There was no correlation between the age of plants and percent of carrageenan. The viscosity peak was 900 cps in the 11 month old plants; the minimum value was 401 cps in the 18½ month old plants (Fig. 17). Several samples were not illustrated in Figure 17 because they were stored for 7½ months before being analyzed. The latter values are, however, presented in Table VI. There was no correlation between age of plants and carrageenan viscosity. The values of gel strength ranged between 102 and 258 g. in the 16 and 18 month old plants, respectively (Fig.18). One very high value (368) occurred in the 11 month old population. No apparent correlation existed between gel strength and the age of the plants (Fig.18).

Reproductive state: Table VII summarizes the interaction between reproductive state and the concentration and properties of carrageenan. No significant differences were apparent between reproductive and vegetative plants.

Habitat: Table VIII illustrates the effects of wave exposure on the concentration and properties of carrageenan. No significant differences in percent carrageenan or gel strength were apparent between the exposed and sheltered populations. The viscosity values were inconsistent. Figures 19-21 depict the relationships between depth and percent of carrageenan, gel strength, and viscosity, respectively. No correlation existed between depth and any carrageenan properties.

Figure 22 illustrates the variations in percent of carrageenan for coastal and estuarine populations. The coastal plot represents an average of monthly data for Rye Ledge, Rye Harbor, and Jaffrey Point, while the estuarine graph represent similar information for Dover Point and the Toll

Bridge. Figures 23 and 24 summarize similar information for viscosity and gel strength. Specific details of percent of carrageenan, gel strength, and viscosity data for each of the five locations are listed in Table IX. The percent of carrageenan and gel strength were usually highest in coastal populations, except during June and July (Fig. 22 and 24). In contrast the viscosity of estuarine plants was usually higher than that of coastal populations (Fig. 23), except during June and July.

Figure 25 illustrates the fluctuation of percent of kappa carrageenan at Rye Harbor and Dover Point. The estuarine populations usually had a smaller kappa fraction than the coastal plants, except during June and July.

Table X summarizes the data for the transplant experiments. No differences in percent of carrageenan were recorded between Dover Point and Rye Harbor populations either before or after transplantations. No consistent viscosity data was evident. In contrast, the gel strength decreased after all transplants, although the differences were not statistically significant in every case.

Seasonal: Figure 22 illustrates the seasonal variation of percent of carrageenan obtained by pooling data from all five stations. The highest percent of carrageenan was consistently found in the late fall and early winter. Thereafter the carrageenan concentration decreased to a summer minimum. Figures 23 and 24 summarize similar pooled information for gel strength and viscosity. The gel strength and viscosity showed a trend similar to percent of carrageenan.

DISCUSSION

Commercial uses of carrageenan necessitate its characterization as to gel strength, viscosity, and ratio of kappa to lambda fractions. A know-

ledge of the interrelationships between these properties would eliminate the necessity of carrying out some of the analyses. For example, the relationship between gel strength and the ratio of fractions could be employed to this end (compare Fig. 13). Thus, gel strength can be determined in a few hours as compared to fractionation which requires more than a day for completion. Accordingly, the gel strength could be used to predict the ratio of kappa to lambda fractions. The weak correlation between viscosity and gel strength would necessitate separate analyses.

The stability of carrageenan in stored plant material is an important consideration when a uniform product is to be prepared. Young and Goring (1958) found degradation of gel strength and viscosity after storage of Chondrus for a year. I found similar results for viscosity after approximately six months of storage, but no degradation of gel strength was evident after twenty two months. Thus, the use of fresh plant material is of paramount importance when a highly viscous product is needed.

Harvesting Chondrus via raking or gathering weed cast up by storms provides plants with a fairly uniform and large size. Most of the collections for this investigation sought to duplicate commercial harvesting so that the information would be readily applicable. However, the use of only larger fronds raises a question as to possible differences between plants of various ages; consequently sequentially denuded quadrats were established at Rye Ledge. Considering the lack of correlation between carrageenan concentration, viscosity, and gel strength in relation to the age of Chondrus and the impracticality of obtaining younger populations, the use of larger fronds appears to be a commercially sound practice.

Mixed populations of reproductive and vegetative plants of Chondrus crispus are found throughout the year (Mathieson and Burns, in preparation).

It was anticipated that during reproduction the manufacture of carrageenan might be reduced, particularly during the winter when the plants would be least active metabolically. However, there were no differences in carrageenan concentration or properties between reproductive and vegetative plants.

Ross (1953) has reported the presence of cellulose in Chondrus, which Naylor and Russell-Wells (1934) had earlier described as a cell wall component of red algae. Percival (1968) suggests that carrageenan is located in the wall or in intercellular spaces, and that the polysaccharide helps provide flexible strength to the plant. If carrageenan is an important structural component of the wall, it would be reasonable to expect larger concentrations of the polysaccharide in plants growing in exposed areas. However, my results did not show any differences between exposed and sheltered populations with respect to carrageenan properties. Thus, the plant does not appear to respond to wave action by producing larger quantities of carrageenan.

Percival (1968) also suggests that the hygroscopic properties of carrageenan may be important to Chondrus in adapting to desiccation during low tides. Thus, it was expected that larger quantities of carrageenan would be present in intertidal as compared to subtidal plants. However, no correlation was evident between percent of carrageenan, gel strength, or viscosity and elevation. Thus, it can be assumed that carrageenan is not produced in response to physiological stress of desiccation.

The effects of spatial distribution on the properties of carrageenan was investigated at five stations. As was anticipated, the estuarine stations had greater fluctuation of salinity, more extreme temperatures and a trend toward higher nutrients than the coastal stations. Coastal populations of

Chondrus generally had higher gel strengths, percent of carrageenan, percent of kappa carrageenan, and lower viscosities. Two exceptions should be discussed. Foremost, the transplant studies did not correspond to the above generalizations, perhaps because of the short duration of acclimatization. In addition a reversal of the chemical and physical properties of carrageenan was noted during June and July (Fig. 15-17). It is probable that one or more of the above environmental parameters interact in a complex fashion to determine the properties of carrageenan in Chondrus. It is also evident from my findings that coastal populations of Chondrus are more valuable commercially except when a highly viscous product is desired.

Black et al (1965) recorded seasonal fluctuation of carrageenan from Northumberland Strait, Nova Scotia, Canada. Low yields were found during September to November, while the highest concentrations were recorded in July and August. My results indicated that the carrageenan concentrations were greatest during August to December and there was a rapid decline thereafter, with low values found from February to June. None of the physical or chemical parameters monitored fluctuated in correspondence to carrageenan concentration. Thus, a complex interaction of many factors is probably responsible for producing seasonal changes of carrageenan. The closest correspondence seemed to be with nutrients, but further studies should be conducted to determine if a positive correlation exists. If one considers carrageenan as a "typical" reserve product, then the seasonal patterns of concentrations found in New Hampshire as compared to Canada could be explained by differences in environmental parameters (particularly temperature and light) in these areas. Thus, carrageenan production should occur for a shorter period of time and be utilized earlier in a northern (Canada) versus a southern (New Hampshire) location. Further investigations to

establish the presence of carrageenan in Chondrus should be used to test this hypothesis.

The gel strength and viscosity data revealed similar trends to percent carrageenan, with maximum values being recorded during the fall and early winter. In contrast to the findings of Black et al (1965), there did not appear to be a seasonal trend to the ratio of fractions. It is concluded that the most efficient extraction process and the best quality carrageenan will be obtained from plants harvested during the fall.

CONCLUSIONS

- (1) A direct relationship exists between gel strength and ratio of kappa to lambda fractions.
- (2) No relationship exists between viscosity and gel strength.
- (3) Storage of Chondrus for 6 or more months prior to extraction produces a decrease in viscosity.
- (4) A decrease in gel strength was not evident after twenty-two months of storage.
- (5) The age of Chondrus populations had no affect on carrageenan concentration or properties.
- (6) Reproductivity of Chondrus did not alter the concentration or properties of carrageenan.
- (7) Carrageenan concentration and properties are unaffected by exposure to wave action.
- (8) Vertical position on the shore produced no differences in percent carrageenan or its properties.
- (9) The difference in carrageenan concentration and properties at coastal and estuarine locations is produced by a complex interaction of many factors (including temperature, salinity, and nutrients).
- (10) Seasonal variation of carrageenan concentration and properties is also the result of a complex interaction of many factors.

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Table I Denudation dates of quadrats at Rye Ledge, maximum age of plants, and quadrat numbers.

Date Denuded	Maximum Age in Months	Quadrat Number
8-17-70	1	17
7-24-70	2	66
6-20-70	3	15
5-11-70	4½	14
4- 8-70	5½	13
3-13-70	6½	12
2- 4-70	7½	11
12-19-69	9	10
11-24-69	10	9
10-24-69	11	8
9-25-69	12	7
8-21-69	13	6
8- 2-69	15	5
6- 1-69	16	4
5-31-69	16	2
3-14-69	18½	2
2-14-69	19½	1

Table II Collection dates and sites of sample collections.

Date	Rye Ledge	Rye Harbor	Jaffery Point	Toll Bridge	Dover Point
9-26-68			X		
9-29-68		X			
10-21-68			X		
10-24-68		X			
11-24-68	X				
12-17-68	X				
12-19-68			X		
1- 8-69			X		
2-14-69	X				
2-15-69			X		
3-18-69	X		X		
5-31-69	X				
6- 1-69	X				
7-17-69	X				
8- 2-69	X				
8-21-69	X				
9-25-69	X				
10-25-69	X				
11-24-69					
12-19-69	X				
1- 6-70			X		
1-10-70				X	X
1-11-70		X			
1-13-70					X
2- 4-70	X				
2-19-70		X	X	X	X
3-13-70	X				
4- 3-70		X			
4- 4-70					X
4- 8-70	X				
5-11-70	X				
5-12-70		X			
5-24-70			X	X	X
6-20-70	X				X
7-24-70	X				X
8-17-70	X	X	X	X	X
9-26-70	X				
9-27-70		X	X	X	X
10-13-70	X	X	X	X	X
11-15-70	X	X	X	X	X
12-11-70	X	X	X	X	X

Table III Seasonal values of physical and chemical parameters at the five stations.

Date	Salinity ‰	Temperature °C	Phosphate ug at/l	Total Phosphorous ug at/l	Nitrate ug at/l	Nitrite ug at/l
RYE LEDGE						
11-24-68	33.4	5.0	1.00	1.31	5.36	0.32
12-17-68	34.0	3.0				
1- 8-69	33.5	0.5				
2-14-69	33.0	0.0				
3-18-69	32.8	2.5	0.42	0.73	2.21	0.17
4-30-69	26.8	10.0				
5-31-69	31.5					
6- 1-69			0.68	1.10	1.58	0.17
7- 1-69	31.5	12.5				
7-29-69	30.1	16.0	0.47	0.67	1.08	0.32
8- 2-69	30.1	16.5				
8-21-69	31.0	15.0	0.82	1.22	1.13	0.22
9-25-69	30.2	15.5	0.44	0.83	1.04	0.12
10-25-69	30.5	9.5				
11- 1-69	32.0	9.5				
11-24-69	31.5	6.7	0.86	1.06	6.90	0.24
12- 4-69	29.6	4.5	0.95	1.44	5.57	0.23
12-19-69	29.9	4.5	1.07	2.13	6.26	0.23
1- 3-70			0.91	1.11	6.26	0.19
2- 7-70	28.4	3.0	0.87	1.06	7.56	0.14
2-19-70	30.3	6.0	0.84	0.92	8.24	0.14
3- 5-70	31.5	3.0	0.90	1.33	7.28	0.16
3-20-70	31.1	6.0	0.67	0.79	0.07	0.14
4- 8-70	28.1	4.0	0.57	0.76	0.24	0.00
4-23-70	28.8	8.0	0.29	0.50	0.81	0.07
5-10-70	29.9	11.5	1.26	1.78	3.31	0.30
5-22-70	28.4	13.5	0.53	0.78	1.26	0.14
6- 3-70	32.1	10.0	0.56	0.81	5.02	0.14
6-20-70	32.2	9.0	0.41	0.57	1.75	0.06
7- 6-70	32.1	16.1		1.30		
7-20-70	31.7	14.2	0.53	0.77	0.72	0.09
7-24-70		12.8				
8-17-70	31.8	19.2	0.47	0.78	0.00	0.01
9- 7-70	33.1	12.2	1.95	2.20	0.72	0.11
9-28-70	31.7	15.0	0.64	0.89	0.89	0.13
10-13-70	32.0	13.5	0.81	1.28	1.08	0.13
10-27-70	31.5	9.5	1.12	1.63	10.29	0.33
11-15-70	31.4	9.0	1.16	1.75	5.33	0.54
12- 2-70	32.0	8.5	0.96	1.20	9.01	0.43
12-11-70	31.4	5.0	0.95	1.17	9.19	0.40
RYE HARBOR						
9-29-68		16.0				
9-30-68	31.7	13.7				
10-24-68	33.5	10.5	0.85	1.15	1.15	0.53
11-17-68	33.0	3.0				
11-24-68	32.8	5.2	0.90	1.15	3.61	0.30

Date	Salinity ‰	Temperature °C	Phosphate ug at/l	Total Phosphorous ug at/l	Nitrate ug at/l	Nitrite ug at/l
RYE HARBOR						
1- 9-69	34.0	2.0	0.74	0.97	6.31	0.18
2-14-69	32.5	0.0				
3-18-69	31.6	2.5	0.51	0.76	1.10	0.44
4-29-69	28.2	11.5	0.72	1.07	1.59	0.11
5-31-69	29.9	13.0				
7-29-69	30.1	17.0	0.34	0.41	1.01	0.28
8-21-69	31.1	15.0	0.66	0.98	0.98	0.14
9-25-69	30.2	15.5	1.50	2.08	1.73	0.72
10-25-69	31.5	9.5				
11- 1-69	31.7	9.5				
11-29-69			1.14	1.45	5.94	0.38
12- 4-69	29.5	4.5	1.08	1.30	7.08	0.23
12- 7-69	28.6	3.0				
12-21-69	30.0	4.3				
1- 3-70			0.91	1.12	6.26	0.19
2- 7-70	28.6	3.0	0.74	0.94	7.99	0.14
2-19-70	30.8	4.0	0.80	0.85	8.33	0.14
3- 5-70	31.4	3.5	0.70	0.77	5.56	0.12
3-20-70	31.2	6.0	0.72	0.95	0.07	0.14
4- 8-70	28.1	4.0	0.65	0.87	0.14	0.00
4-23-70	27.3	7.0	0.32	0.50	1.28	0.07
5-10-70	30.4	12.5	0.75	1.04	1.59	0.10
5-22-70	28.4	13.5	0.45	0.66	1.01	0.16
6- 3-70	31.2	13.0	0.67	1.01	1.01	0.15
6-20-70	32.2	9.0	0.50	0.74	0.36	0.24
7- 6-70	32.3	15.6				
7-20-70	31.7	13.1	0.92	1.24	0.70	0.06
8-17-70	31.5	19.2	0.76	1.02	0.33	0.06
9- 7-70	32.5	13.1	0.92	1.14	0.82	0.09
9-27-70			0.84	1.12	2.81	0.13
9-28-70	31.6	14.5				
10-13-70	32.0	14.2	0.92	1.28	1.08	0.13
10-27-70	30.9	9.5	1.02	1.41	7.37	0.33
11-15-70	31.4	9.0	1.13	1.63	5.33	0.54
12- 2-70	31.4	8.0	0.95	1.18	8.49	0.43
12-11-70	30.7	5.0	1.00	1.19	8.47	0.33
JAFFREY POINT						
9-26-68		15.0				
10- 7-68	30.4	16.0				
10- 8-68	31.6	9.4	1.00	1.31	6.60	0.04
10-21-68	31.8	9.5	0.50	0.69	0.84	0.13
11-19-68	32.6	6.5	0.94	1.06	3.22	0.18
12-19-68	32.6	4.0				
1- 8-69	32.5	1.5	0.65	0.97	6.51	0.15
2-15-69	32.8	1.0				
3- 8-69			0.55	0.73	5.41	0.18
3-17-69			0.50	0.65	3.61	0.26
3-18-69	31.5	2.0				
4- 8-69			0.45	0.87	4.13	0.21

Date	Salinity ‰	Temperature °C	Phosphate ug at/l	Total Phosphorous ug at/l	Nitrate ug at/l	Nitrite ug at/l
JAFFREY POINT						
4-29-69	28.5	9.0	0.53	0.80	1.05	0.09
5-31-69	28.0	13.0				
7-29-69	31.0	16.0				
8- 1-69			0.55	0.91	1.03	0.18
8-22-69	31.4	14.5	0.77	1.05	1.18	0.44
9-28-69	30.6	14.0				
10-24-69	30.5	9.0	0.76	1.18	9.25	0.42
11- 1-69	31.9	9.0				
11-23-69	30.2	6.0				
12- 4-69	27.5	4.5	1.09	1.39	9.90	0.23
1- 3-70			0.90	1.08	10.13	0.19
2- 7-70	29.2	3.5	0.80	0.99	8.80	0.14
2-19-69	28.1	2.0	0.85	0.99	9.19	0.14
3- 5-70	30.8	2.5	0.80	0.94	8.05	1.12
3-20-70	31.0	4.0	0.82	0.96	0.34	0.14
4-10-70	29.8	4.0	0.51	0.64	0.12	0.12
4-23-70	28.7	6.5	0.23	0.43	0.98	0.06
5-10-70	30.5	7.5	0.65	0.94	2.06	0.12
5-22-70	28.9	12.0	0.43	0.63	1.02	0.16
6- 3-70	30.7	11.5	0.77	1.08	0.81	0.37
6-20-70	31.4	9.0				
7- 6-70	31.3	12.5				
7-20-70	31.2	11.4	0.90	1.39	1.17	0.10
8-17-70	29.9	15.8	1.17	1.35	0.48	0.10
9- 7-70	32.5	11.3	0.92	1.32	1.77	0.19
9-27-70			0.79	1.08	1.63	0.20
9-28-70	31.5	14.0				
10-13-70	32.0	13.0	0.93	1.29	3.10	0.34
10-27-70	29.1	10.5	1.10	1.57	3.53	0.47
11-15-70	31.2	9.5	1.05	1.50	5.64	0.54
12- 2-70	31.4	8.0	0.90	1.12	9.27	0.43
12-11-70	29.9	3.0	0.96	1.20	9.71	0.32
TOLL BRIDGE						
3- 8-69			0.52	0.77	6.02	0.21
3- 9-69			0.68	0.95	10.17	0.24
4- 8-69			0.31	0.56	2.85	0.16
10-24-69			0.76	1.26	6.31	0.27
12- 4-69			1.08	1.45	9.34	0.29
1- 3-70			0.74	1.03	10.13	0.19
2- 7-70			0.79	1.05	10.88	0.17
2-19-70	18.9	1.5	0.76	0.89	9.61	0.15
3- 5-70	25.2	2.0	0.83	1.01	8.68	0.17
3-20-70	26.3	4.0	0.86	1.00	0.51	0.17
4-10-70	19.0	4.0	0.54	0.69	0.30	0.18
4-23-70	27.9	6.0	0.24	0.54	0.98	0.06
5-10-70	30.6	7.0	0.63	0.86	3.43	0.14
5-22-70	27.1	12.0	0.61	0.84	5.52	0.20
6- 3-70	27.9	13.0	0.77	1.05	4.34	0.37
6-20-70	28.5	14.5	0.76	1.03	3.12	0.34

Date	Salinity ‰	Temperature °C	Phosphate ug at/l	Total Phosphorous ug at/l	Nitrate ug at/l	Nitrite ug at/l
TOLL BRIDGE						
7- 6-70	31.2	13.3	0.60	0.86	2.01	0.16
7-20-70	31.2	10.6	1.10	1.52	1.09	0.15
8-17-70	29.5	19.9	1.05	1.29	1.57	0.22
9- 7-70	31.5	14.9	1.50	1.87	4.77	0.39
9-27-70			1.01	1.35	2.69	0.20
9-28-70	31.4	15.0				
10-13-70	31.1	14.5	1.15	1.57	4.35	0.34
10-27-70	24.8	10.5	1.20	1.64	3.84	0.50
11-15-70	27.7	9.5	1.10	1.36	6.33	0.54
12- 2-70	30.6	8.0	0.91	1.15	9.66	0.43
12-11-70	25.9	3.0	1.03	1.30	11.77	0.37
DOVER POINT						
9-28-68			1.28	1.44	2.36	0.26
9-30-68	31.4	16.4				
10- 7-68	16.6	17.4				
10- 8-68	31.4	10.6				
10-24-68	28.8	11.5	1.31	1.62	3.49	0.81
11-17-68	31.0	2.0				
11-23-68	26.0	5.0				
12-17-68	20.3	1.0	1.02	2.18	10.29	0.33
1- 8-69	25.0	-1.0	0.86	1.07	4.25	0.09
2-13-69	26.5	1.0	0.43	0.68	6.85	0.29
3-19-69			0.49	0.70	4.17	0.17
3-21-69	27.3	2.5	0.53	1.07	6.80	0.47
4- 8-69			0.39	0.56	3.79	0.22
4-29-69	18.3	12.0	0.62	1.11	2.65	0.39
5-31-69	2.22	15.0				
7-29-69	26.0	19.0				
8-22-69	28.0	17.5	1.73	2.24	2.64	0.46
9-22-69	28.5	15.5				
10-22-69	29.0	9.5	1.34	1.62	6.86	0.41
11- 1-69	27.2	9.5				
11-26-69	24.6	4.0				
12- 4-69	21.4	2.5	1.09	1.48	8.82	0.35
12-21-69	27.0	4.0	1.19	1.37	11.97	0.37
1- 3-70			0.76	1.00	10.82	0.27
2- 5-70			0.67	0.89	10.96	0.19
2- 7-70	19.4	0.5	0.64	0.83	11.50	0.20
2-19-70	16.8	0.5	0.73	0.80	10.15	0.17
3- 5-70	23.2	2.0	0.75	0.97	8.68	0.17
3-20-70	25.8	6.0	0.57	0.73		0.14
4-10-70	17.2	4.0	0.68	0.91	0.11	0.32
4-23-70	20.3	7.5	0.24	0.53	2.64	0.30
5-10-70	26.8	9.0	0.68	0.88	3.99	0.20
5-22-70	23.4	11.5	0.74	1.00	3.32	0.29
6- 3-70	26.0	15.5	0.85	1.06	4.90	0.47
6-20-70	28.2	15.5	0.81	1.10	2.79	0.33
7- 6-70	30.0	15.0	0.78	1.11	2.52	0.25

Date	Salinity ‰	Temperature °C	Phosphate ug at/l	Total Phosphorous ug at/l	Nitrate ug at/l	Nitrite ug at/l
DOVER POINT						
7-20-70	30.1	15.3	3.01	3.29	1.61	0.22
8-17-70	30.6	20.0	0.91	1.25	1.24	0.16
9- 7-70	30.3	16.0	1.85	2.32	4.82	0.56
9-27-70			1.42	1.90	3.41	0.35
9-28-70	30.5	17.0				
10-13-70	30.8	15.0	1.07	1.46	12.83	0.37
10-27-70	16.7	9.0	1.25	1.72	4.55	0.69
11-15-70	26.5	8.8	1.02	1.33	7.33	0.54
12- 2-70	27.6	7.5	0.97	1.24	9.66	0.43
12-11-70	22.9	2.0	1.00	1.27	12.20	0.38

Table IV Computer predicted nutrient concentrations for January 1969 and 1970.

Station		Computer predicted NO ₃ conc., ug at/1 ± Std.Dev.	Computer predicted PO ₄ conc., ug at/1 ± Std.Dev.
Rye Ledge	1969	8.78 ± 1.95	0.90 ± 0.19
Rye Harbor	"	7.93 ± 1.79	0.86 ± 0.17
Jaffery Point	"	9.04 ± 1.75	0.87 ± 0.17
Toll Bridge	"	10.94 ± 1.91	0.87 ± 0.18
Dover Point	"	10.37 ± 1.66	0.83 ± 0.16
Rye Ledge	1970	8.26 ± 2.09	0.83 ± 0.20
Rye Harbor	"	7.41 ± 1.88	0.80 ± 0.18
Jaffery Point	"	8.52 ± 1.79	0.80 ± 0.17
Toll Bridge	"	10.42 ± 2.00	0.81 ± 0.19
Dover Point	"	9.85 ± 1.70	0.76 ± 0.16

Table V Salinity and temperature data from both sides of Rye Harbor jetty.

Date	Location	Salinity ‰	Temperature °C
9-30-68	Sheltered	31.9	14.2
	Exposed	31.7	13.7
10-24-68	Sheltered	32.8	10.8
	Exposed	33.5	10.5
4-14-71	Sheltered	27.0	6.5
	Exposed	31.0	5.5

Table VI Concentration and properties of carrageenan for various age classes of Chondrus.

Age in months	% Carrageenan	Viscosity (cps)	Gel Strength (gr)
3	61.7	784	125
4½	76.0	713	168
5½	62.1	448	124
6½	72.7	62	126
7½	70.5	202	142
9	75.0	83	132
11	67.1	900	368
12	71.4	38	155
13	73.1	44	166
15	72.1	44	163
16	70.6	170	172
16	73.7	147	102
18½	66.3	401	258
19½	71.2	434	204

Table VII Concentration and properties of carrageenan for reproductive and vegetative materials of Chondrus.

Reproductivity	% Carrageenan	Viscosity (cps)	Gel Strength (gr)
Rep	68.7	212	144
Non-rep	67.8	276	167
Rep	69.9	164	98
Non-rep	69.3	67	104

Table VIII Concentration and properties of carrageenan in Chondrus from different sides of the Rye Harbor jetty.

Date	Side of Jetty	% Carrageenan	Viscosity (cps)	Gel Strength (gr)
1-11-70	Sheltered	66.5	1418	8
	Exposed	74.4	450	0
4-14-71	Sheltered	54.0	31	0
	Exposed	58.7	47	0

Table IX Collection dates and sites with concentration and properties of carrageenan.

Date	Carrageenan %	Viscosity cps.	Gel Strength gr.
RYE LEDGE			
11-24-68	67.9	40	181
12-17-68	75.0	40	103
1-14-69	63.3	127	125
3-18-69	61.9	71	95
5-31-69	68.8	224	141
6- 1-69	66.3	111	81
7-17-69	69.7	91	116
8 -2-69	67.5	123	136
8-21-69	68.6	442	102
9-25-69	70.6	113	197
10-25-69	70.5	164	96
11-24-69	75.8	326	187
12-19-69	67.3	282	156
2- 4-70	61.3	426	148
3-13-70	63.4	259	101
4- 8-70	67.4	108	74
5-11-70	53.3	244	92
6-20-70	55.3	754	66
7-24-70	60.6	432	52
8-17-70	69.0	1154	62
9-26-70	66.3	686	224
10-13-70	72.0	134	151
11-15-70	68.5	496	152
12-11-70	56.8	472	171
RYE HARBOR			
9-26-68	71.4	270	76
10-24-68	66.5	72	149
1-11-70	74.4	500	0
2-19-70	59.8	336	70
4- 3-70	57.9	386	118
5-12-70	62.7	354	142
8-17-70	71.0	839	135
9-27-70	62.2	1995	186
10-13-70	74.0	103	171
11-15-70	71.9	746	124
12-11-70	58.6	679	133
JAFFERY POINT			
9-26-68	63.4	146	91
10-21-68	73.6	192	81
12-19-68	65.5	173	116
1- 8-69	65.2	193	55
2-15-69	63.7	140	106
3-18-69	61.6	180	82
1- 6-70	66.6	69	100

Table IX continued

Date	Carrageenan %	Viscosity cps.	Gel Strength gr.
JAFFERY POINT			
2-19-70	54.7	101	28
5-24-70	59.7	1150	20
8-17-70	76.7	1287	70
9-27-70	61.5	1512	199
10-13-70	71.1	336	151
11-15-70	70.5	1280	138
12-11-70	54.8	666	197
TOLL BRIDGE			
1-10-70	61.6	369	35
2-19-70	52.6	933	43
5-24-70	58.9	582	23
8-17-70	68.5	1101	88
9-27-70	60.9	1762	125
10-13-70	72.3	2410	21
11-15-70	67.5	874	92
12-11-70	64.9	685	132
DOVER POINT			
1-10-70	64.1	371	29
1-13-70	63.3	425	80
2-19-70	55.8	620	92
4- 4-70	53.9	432	27
5-24-70	55.2	907	52
6-20-70	58.2	657	117
7-24-70	62.0	178	126
8-17-70	69.5	1145	32
9-27-70	61.1	2630	82
10-13-70	69.3	1900	57
11-15-70	66.2	1285	93
12-11-70	56.9	1740	63

Table X Concentration and properties of carrageenan before and after transplantation between Rye Harbor and Dover Point.

Transplantation

Before		After	
Rye Harbor 1-12-70	72.0% 241 cps 38 gr	Dover Point 2-19-70	58.0% 999 cps 22 gr
Dover Point 1-13-70	63.3% 425 cps 80 gr	Rye Harbor 2-19-70	56.0% 246 cps 45 gr
Rye Harbor 4-3-70	57.9% 386 cps 118 gr	Dover Point 6-20-70	55.7% 1040 cps 41 gr
Dover Point 4-4-70	53.9% 432 cps 27 gr	Rye Harbor 6-20-70	66.2% 1583 cps 24 gr

% = Carrageenan concentration in plant
 cps = Viscosity in centipoise
 gr = Gel Strength in grams

**Figure 1 Overall view of all quadrats 1-17 at Rye Ledge,
before final denudation on September 26, 1970.**

**Figure 2 Close up of quadrats 1-7 at Rye Ledge, before
final denudation on September 26, 1970.**



10-17

10-17



Figure 3 Close up of quadrats 8 and 9 at Rye Ledge before final denudation on September 26, 1970.

Figure 4 Close up of quadrats 10-17 at Rye Ledge, before final denudation on September 26, 1970.



•
1
2
•
3
4



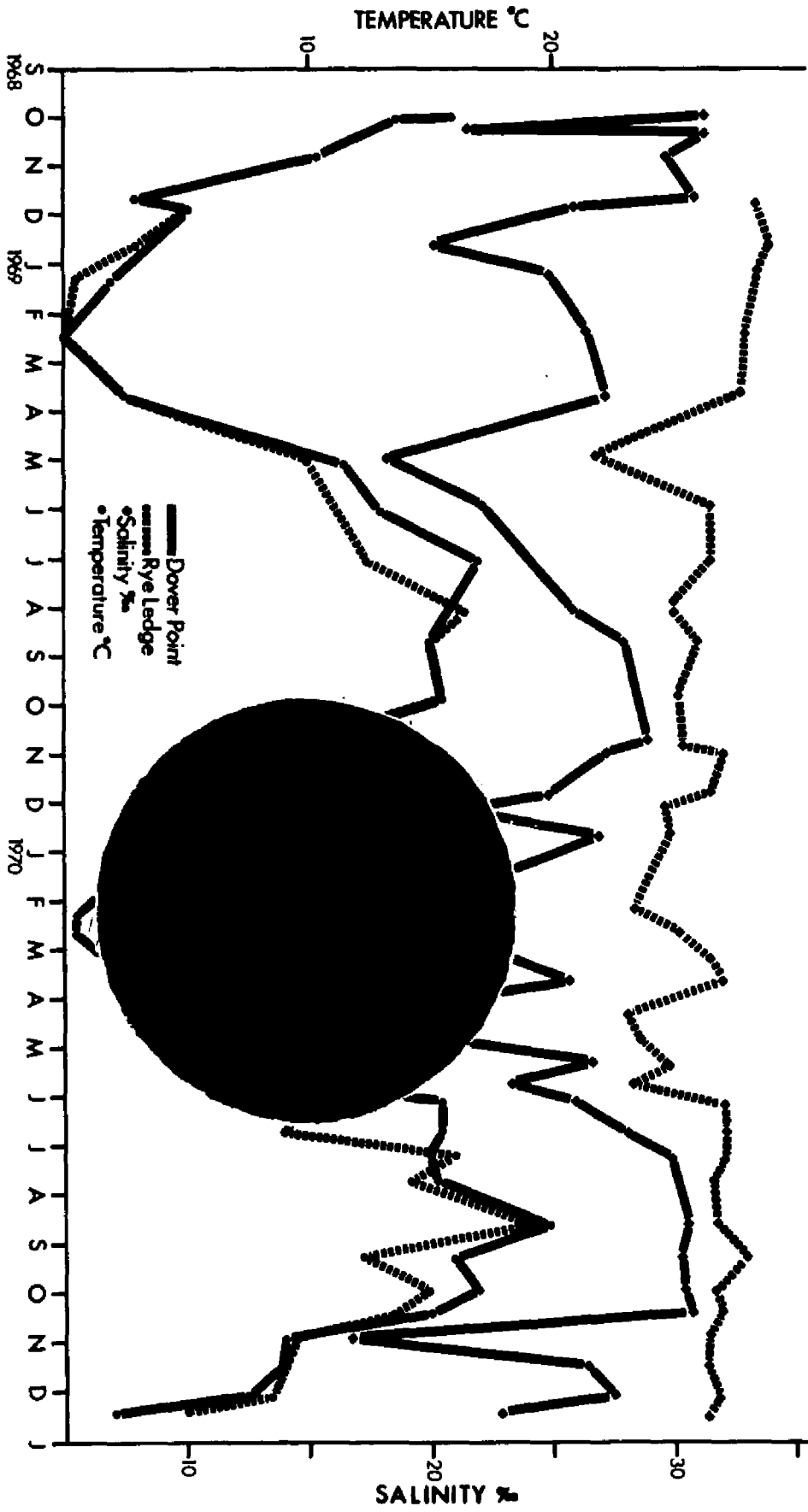
1
2
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3
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Figure 5 Quadrats 1-9 at Rye Ledge, after final denuda-
tion on September 26, 1970.



1
2
•
3
4

Figure 6 Seasonal salinity and temperature regimes at Dover Point and Rye Ledge, 1968-1970.



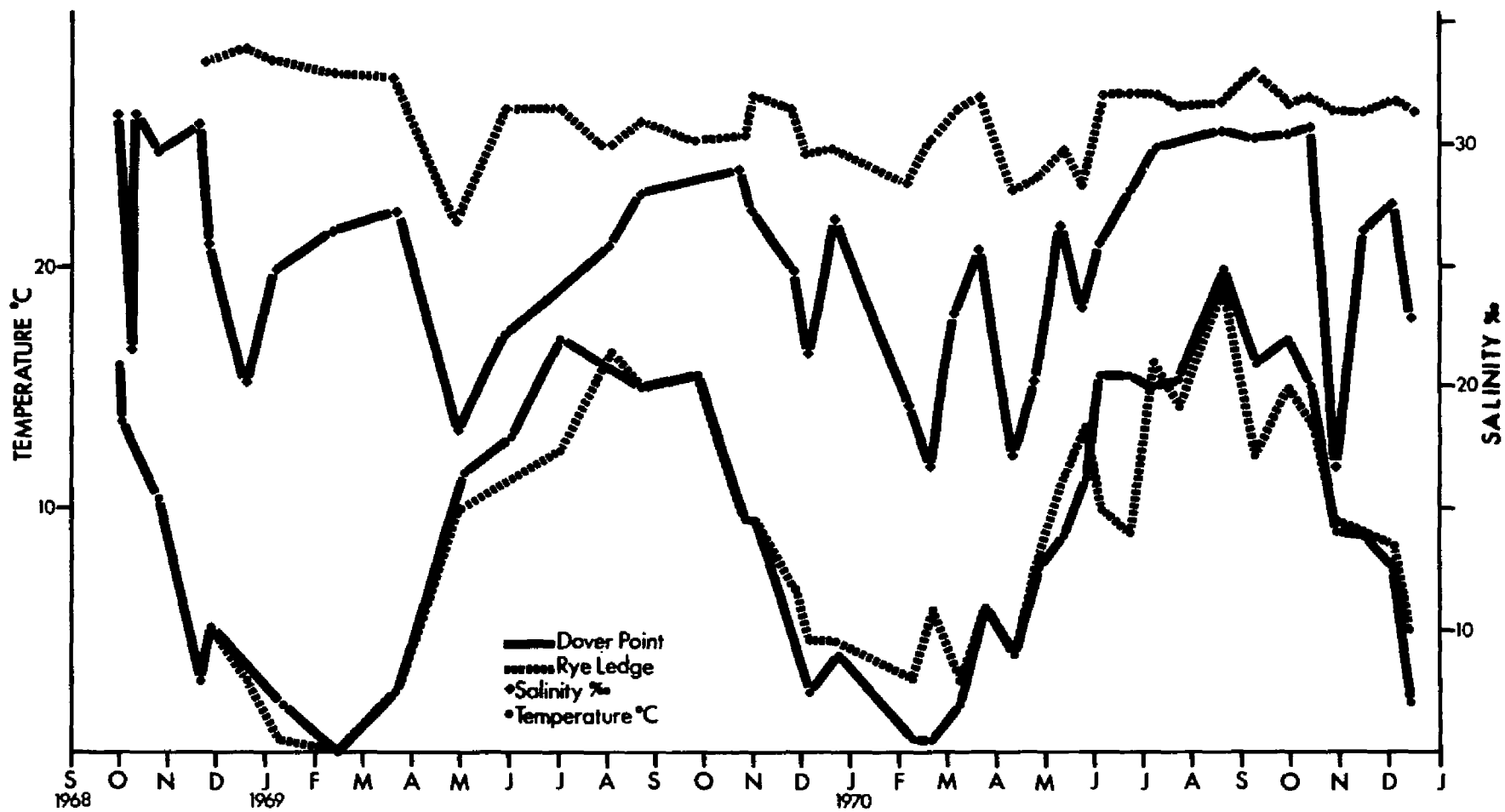


Figure 7 Seasonal nitrate and phosphate regimes at Dover Point and Rye Ledge, 1968-1970.

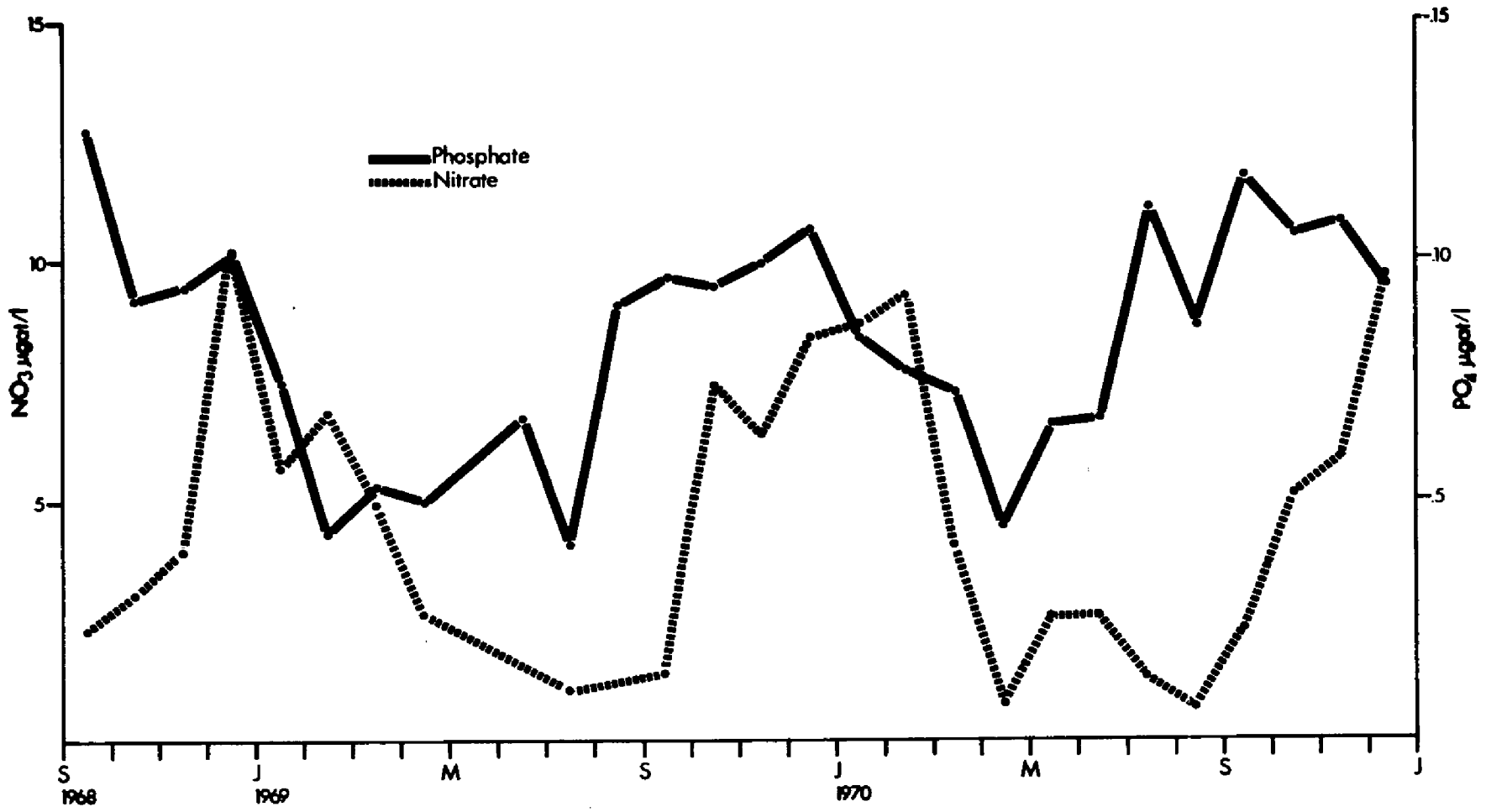


Figure 8 Nutrient regimes at Dover Point during a tidal cycle on January 25, 1970.

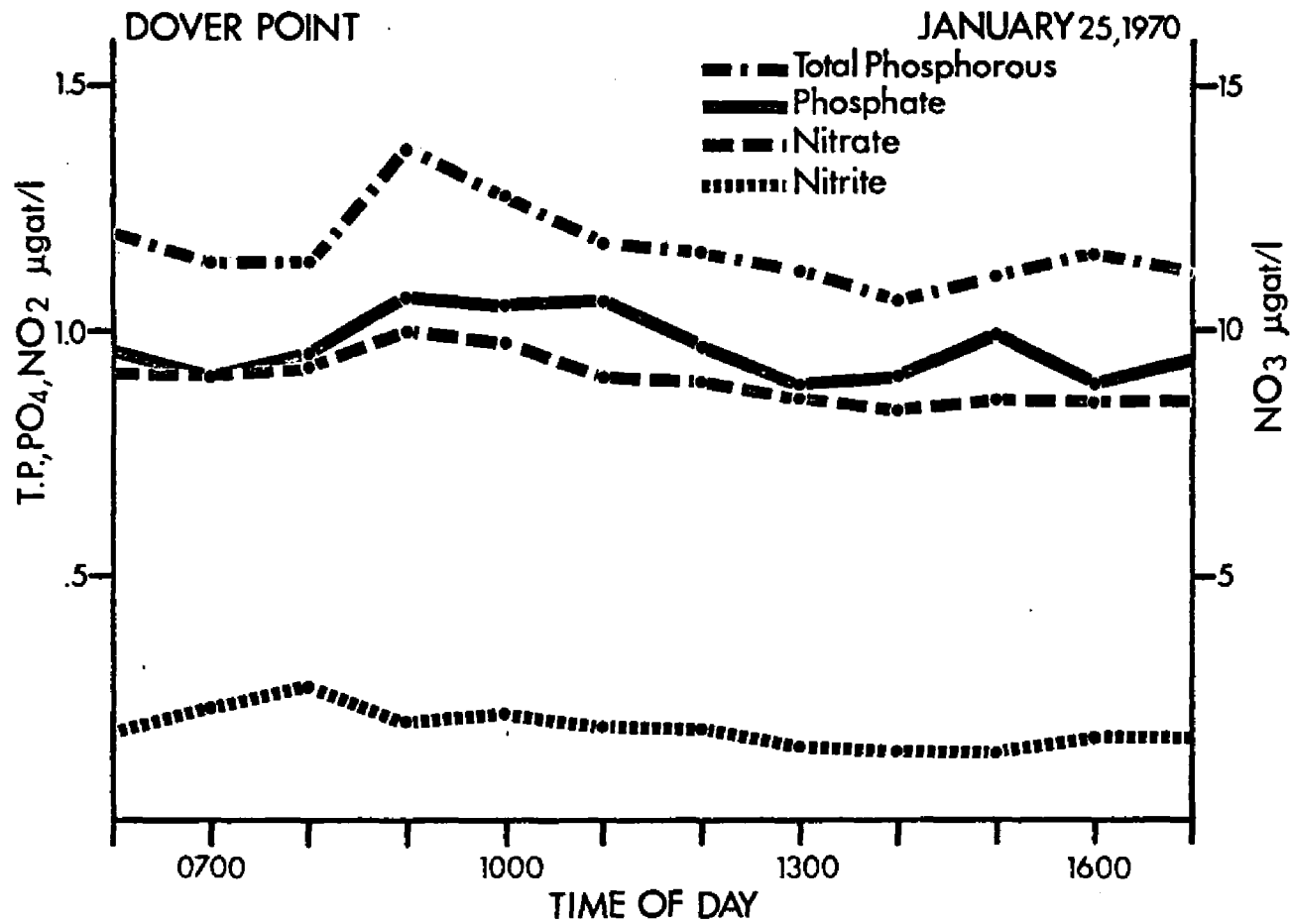


Figure 9 Nutrient regimes at Rye Harbor during a tidal cycle
on January 26, 1970.

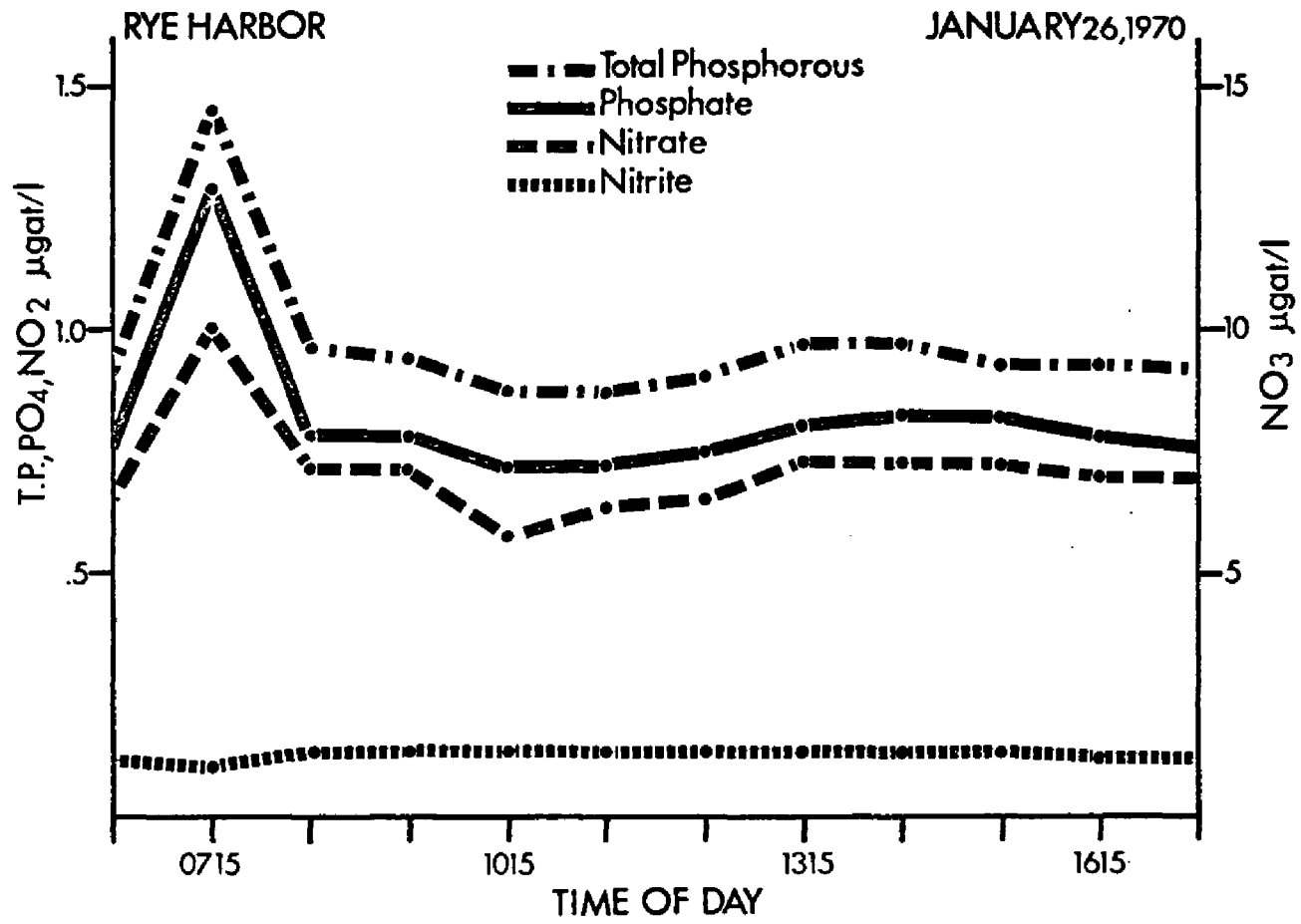


Figure 10 Variations of salinity, temperature and tidal level
at Dover Point during a tidal cycle on January 25,
1970.

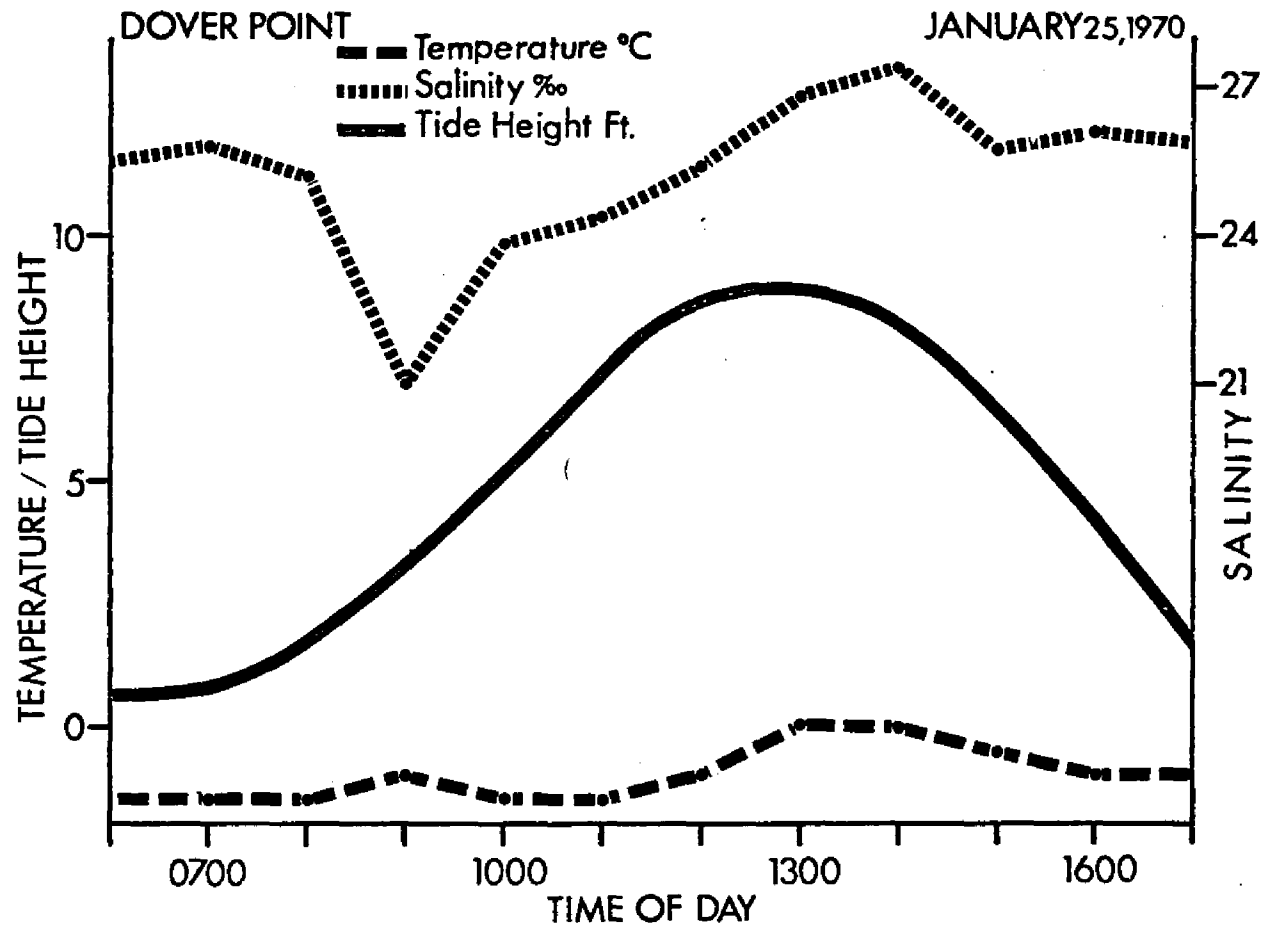


Figure 11 Variations of salinity, temperature and tidal level
at Rye Harbor during a tidal cycle on January 26, 1970.

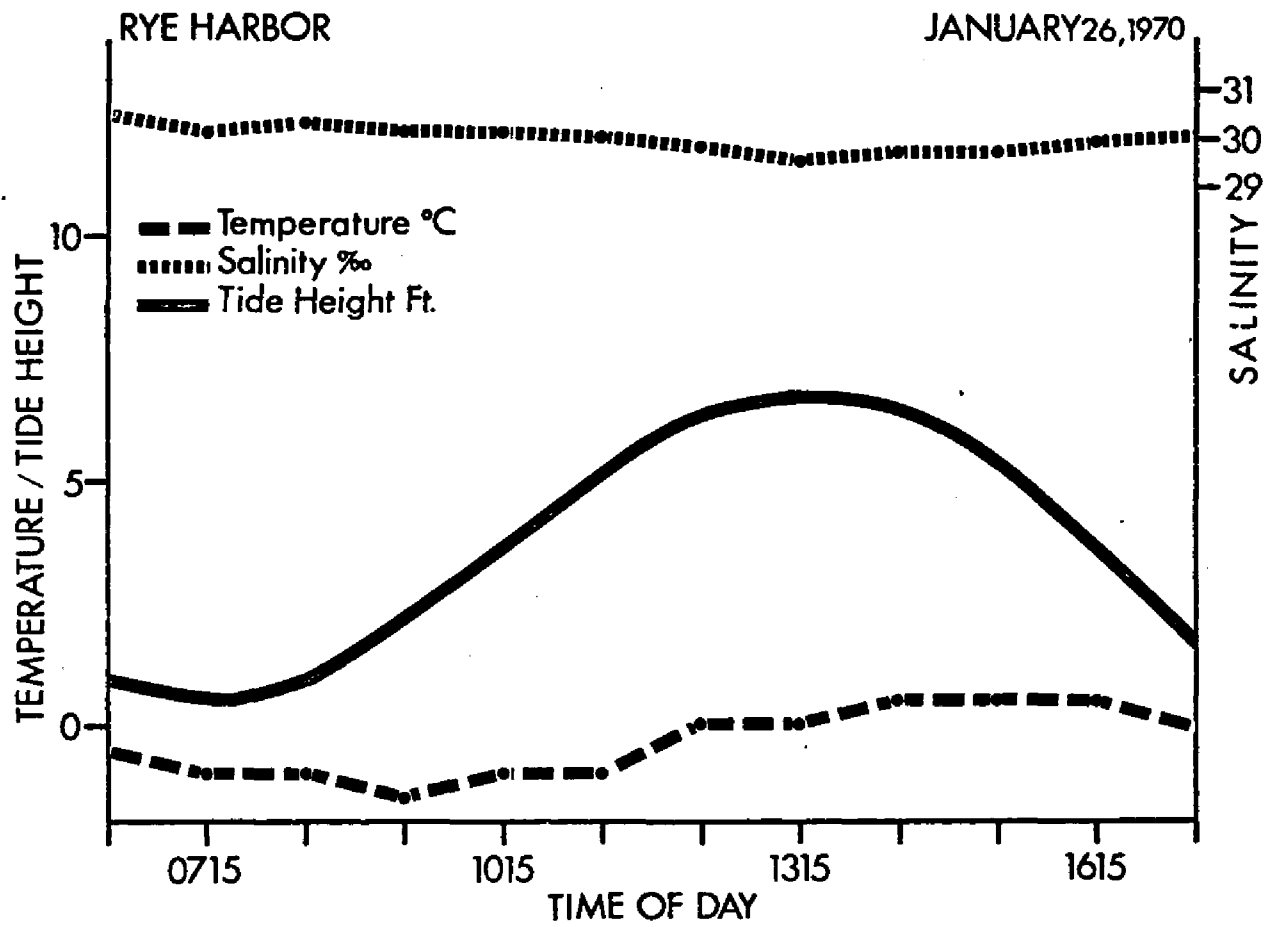


Figure 12 Gel strength versus viscosity.

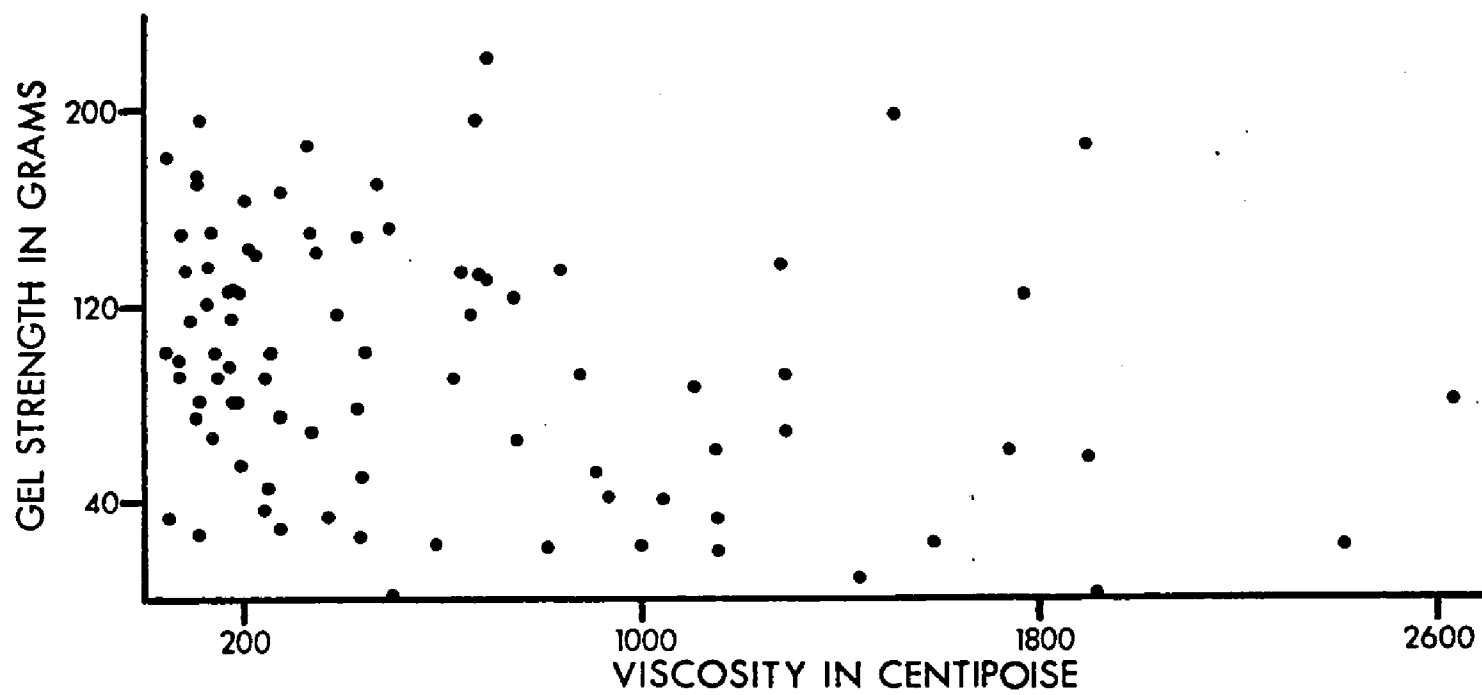


Figure 13 Kappa/lambda fractions versus gel strength.

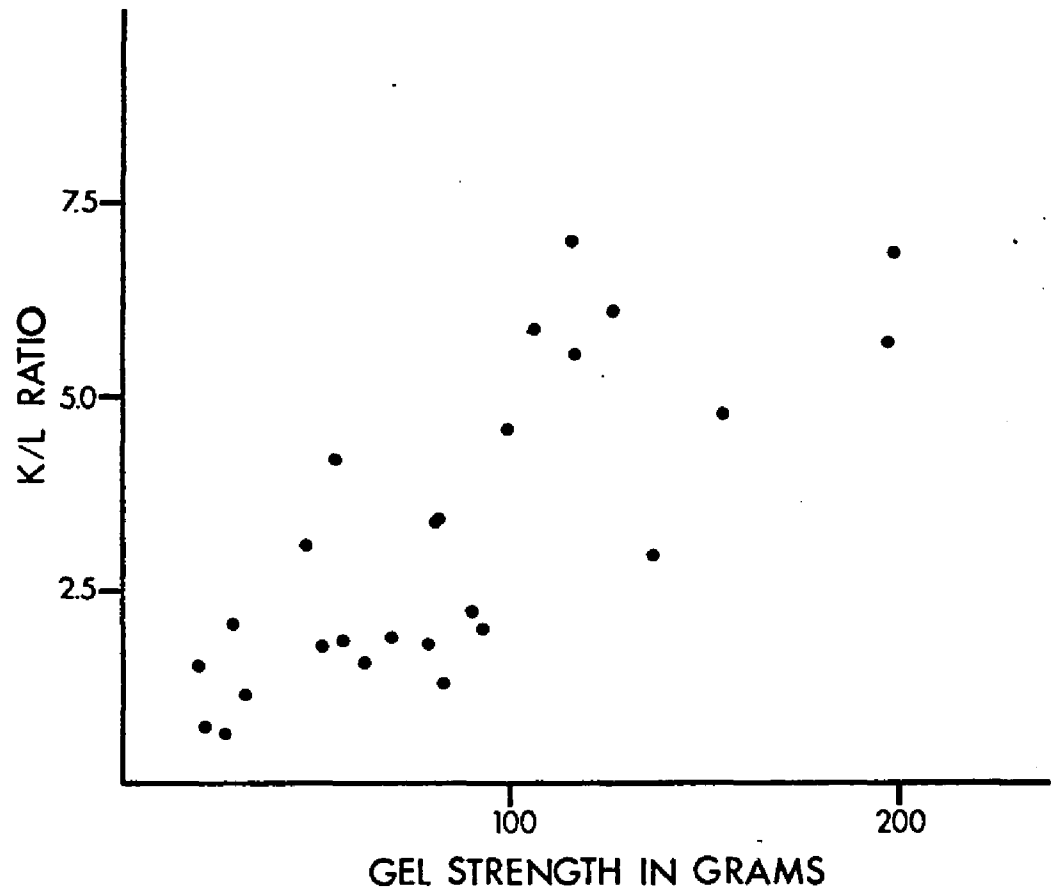


Figure 14 Viscosity versus months of storage prior to extraction.

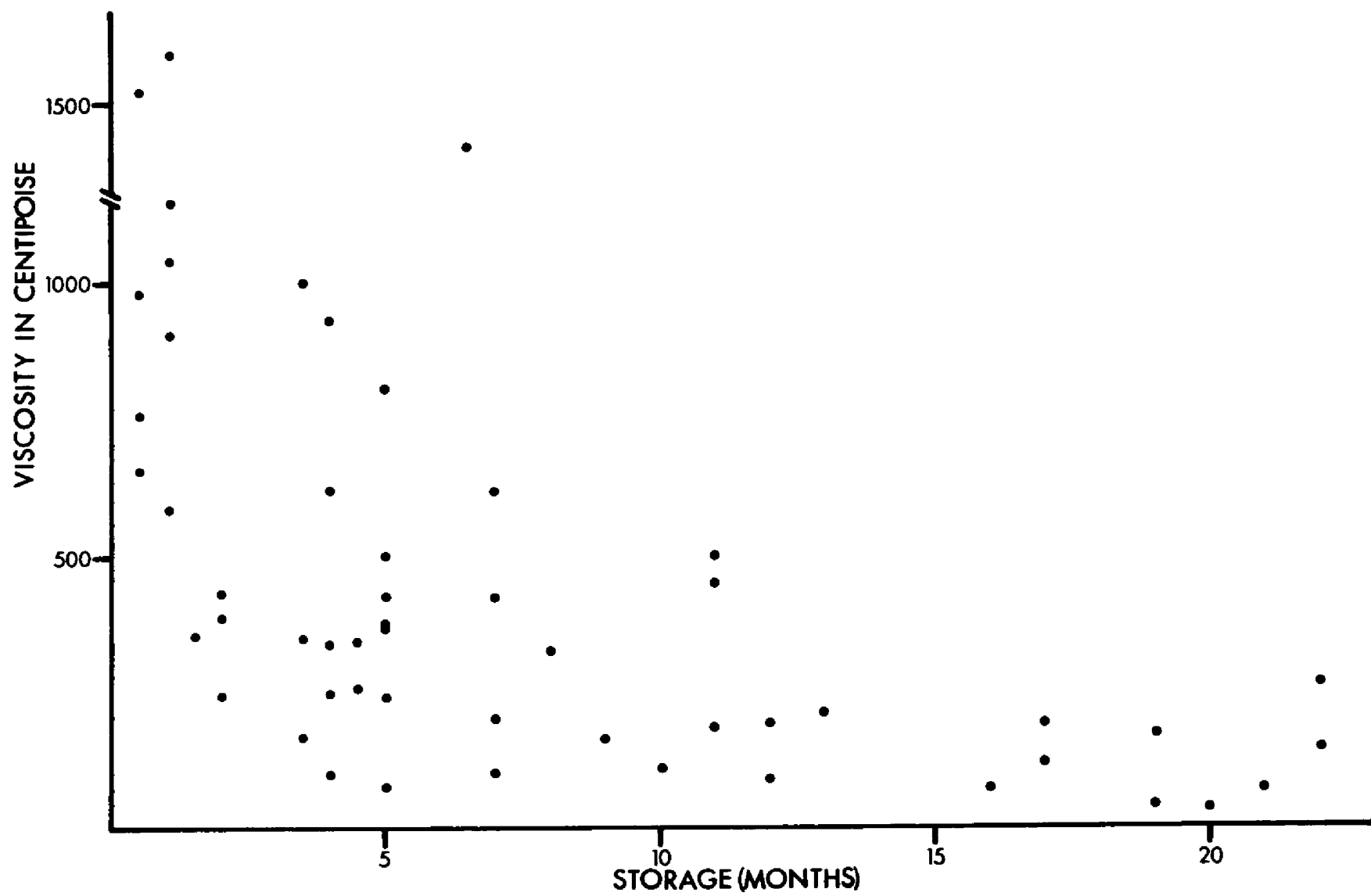


Figure 15 Gel strength versus months of storage prior to extraction.

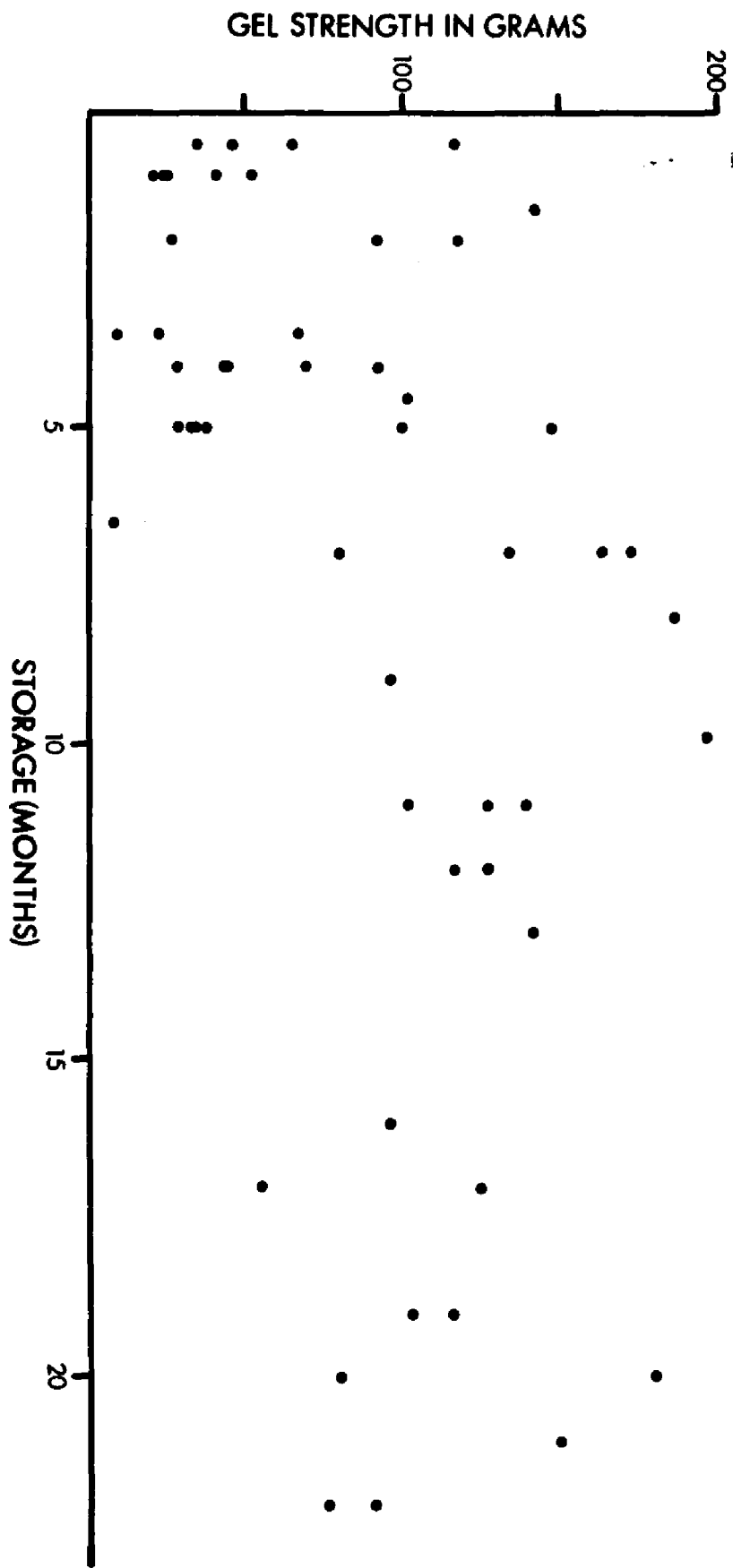


Figure 16 Percent carrageenan versus age of Chondrus.

Figure 17 Viscosity versus age of Chondrus.

Figure 18 Gel strength versus age of Chondrus.

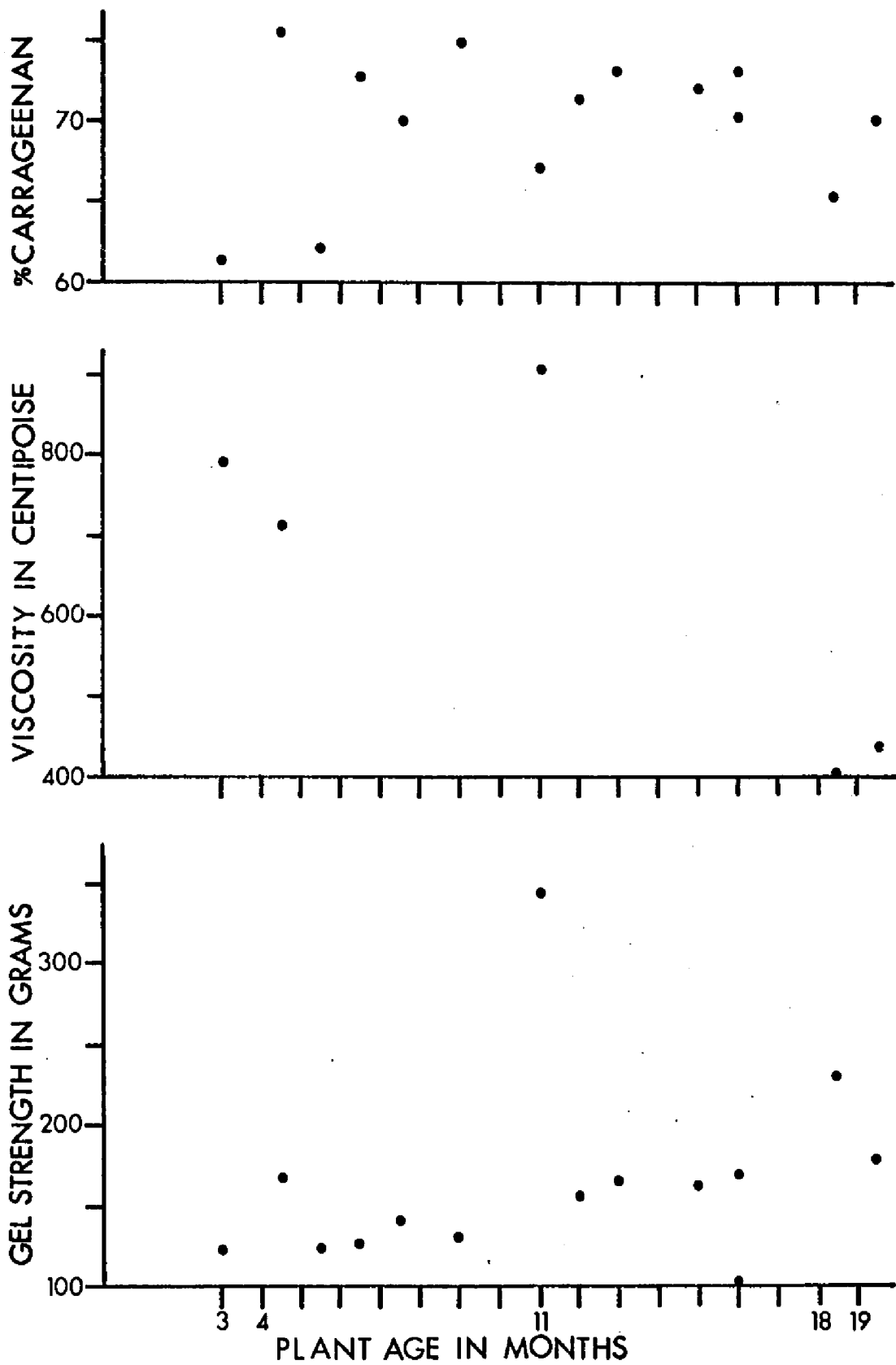


Figure 19 Percent carrageenan in Chondrus relative to depth (feet) below mean low water.

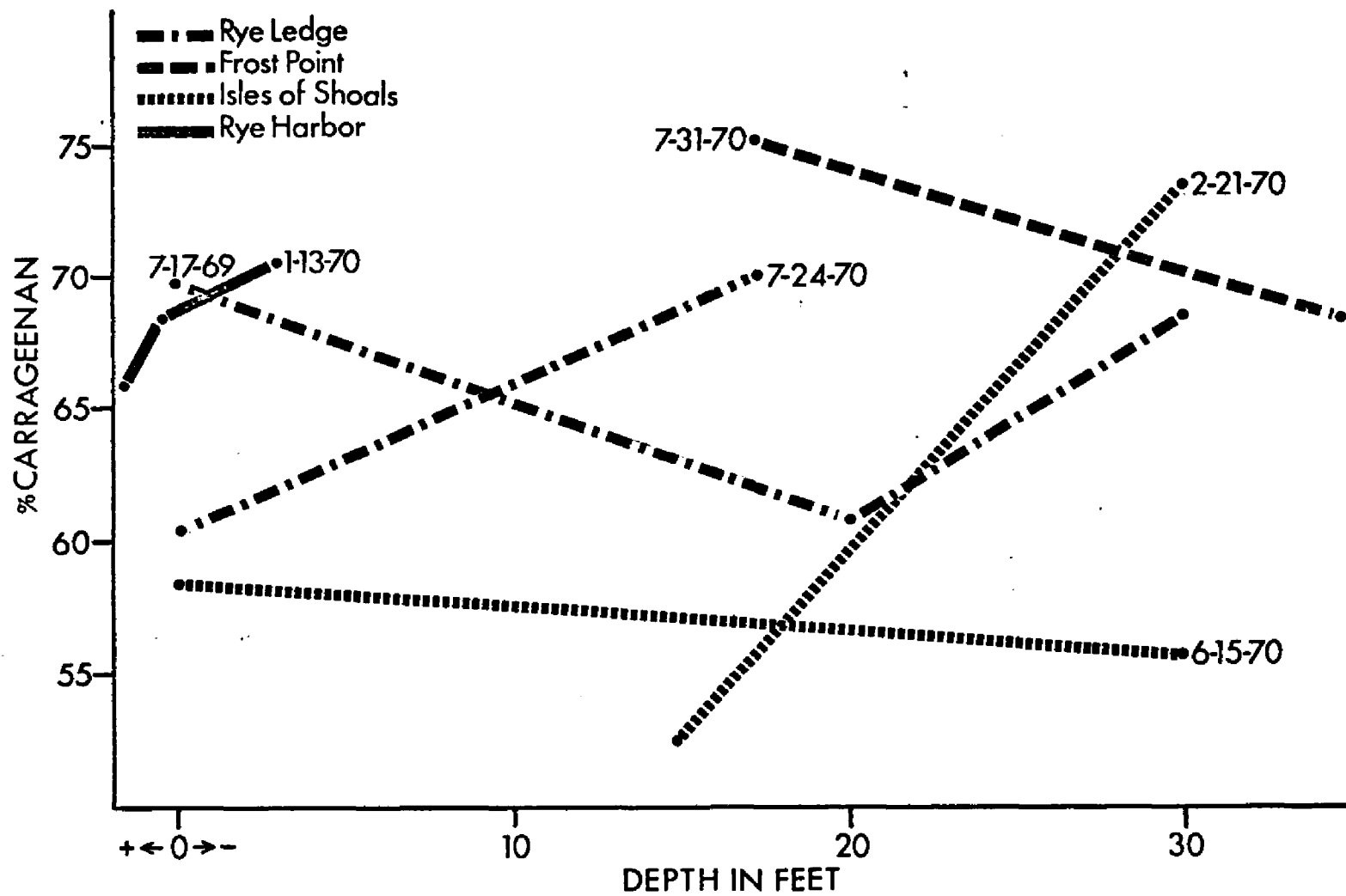


Figure 20 Gel strength in Chondrus relative to depth
(feet) below mean low water.

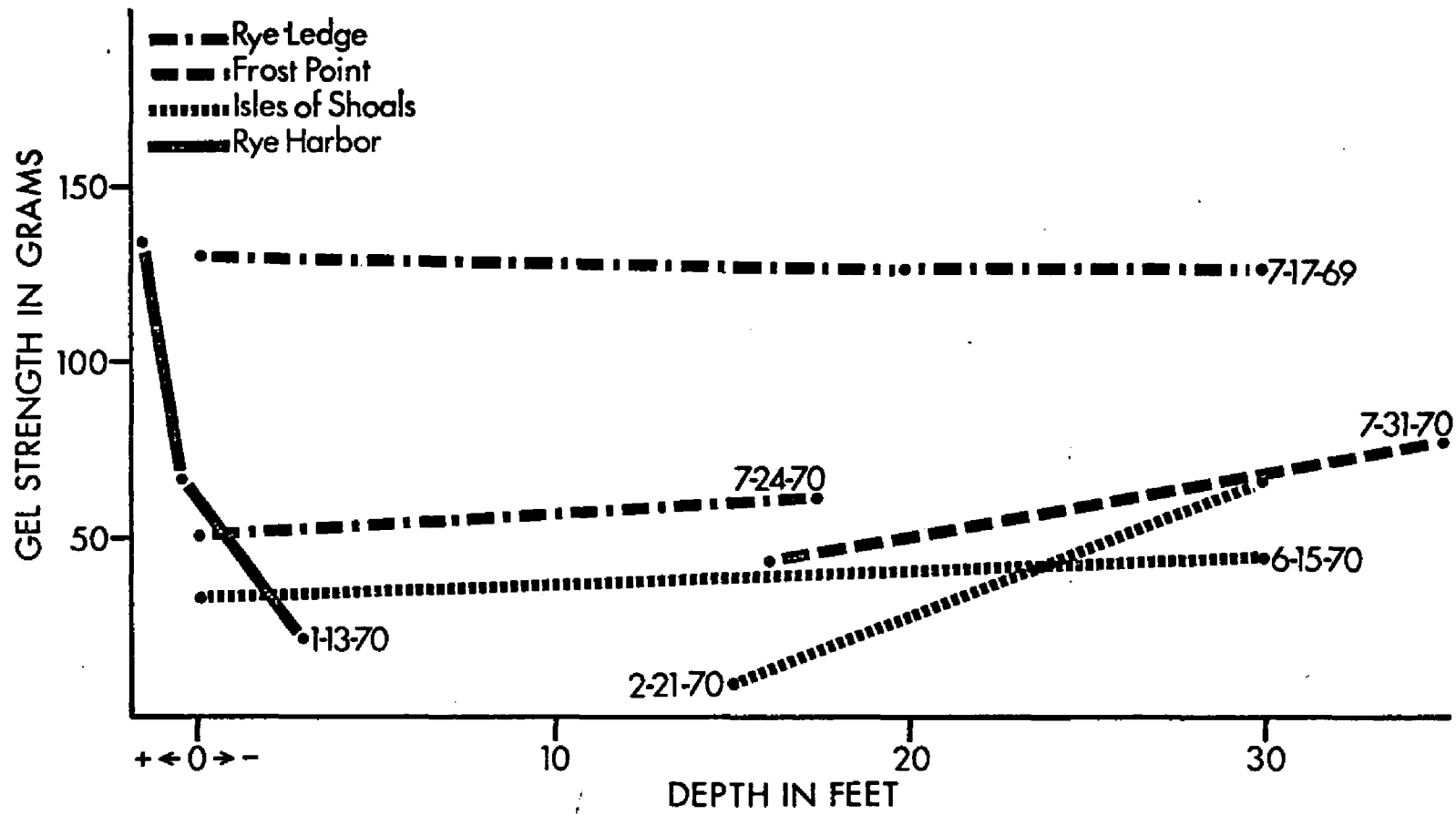


Figure 21 Viscosity in Chondrus relative to depth (feet)
below mean low water.

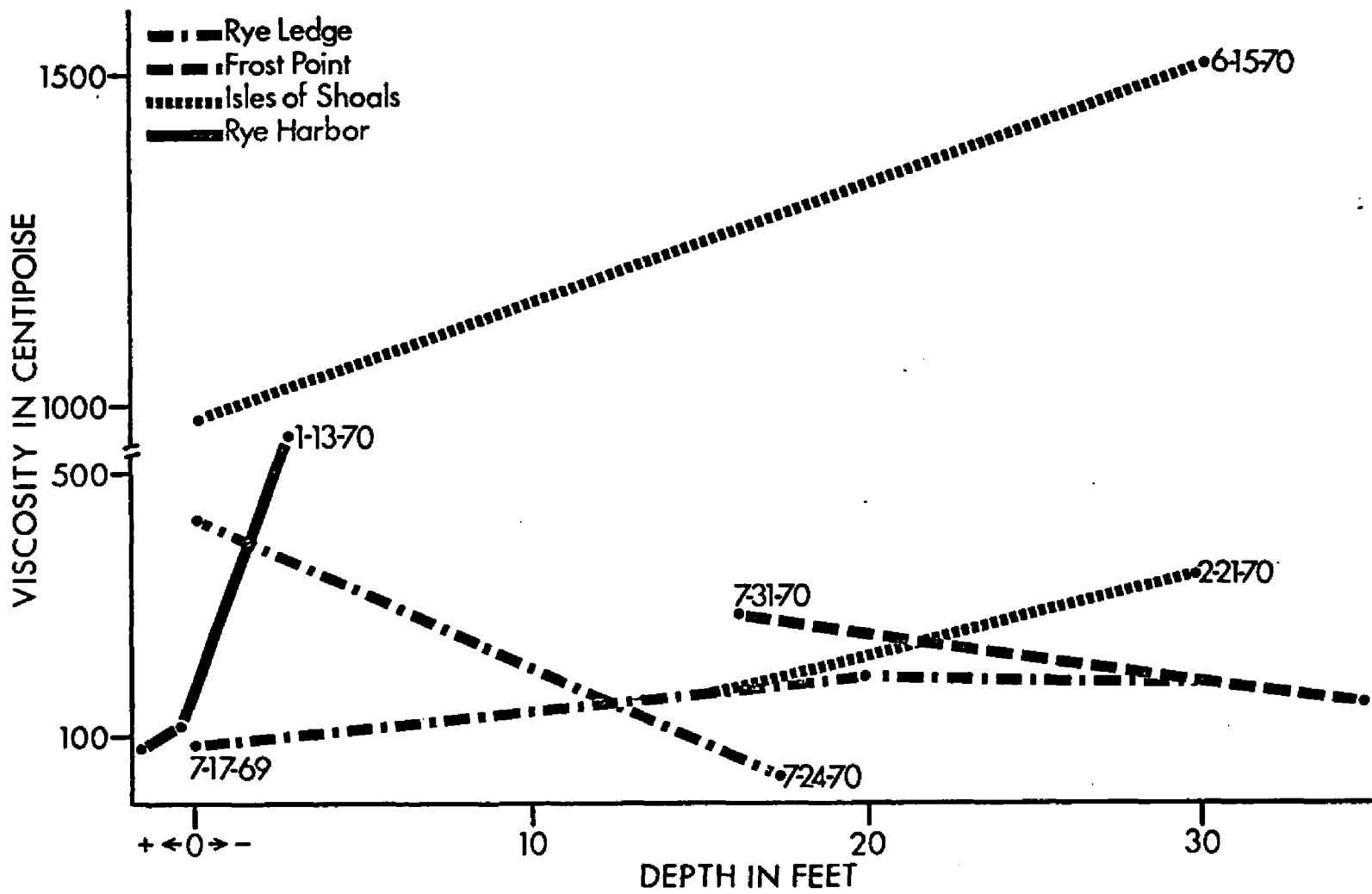


Figure 22 Seasonal fluctuation of percent carrageenan in Chondrus at coastal and estuarine locations.

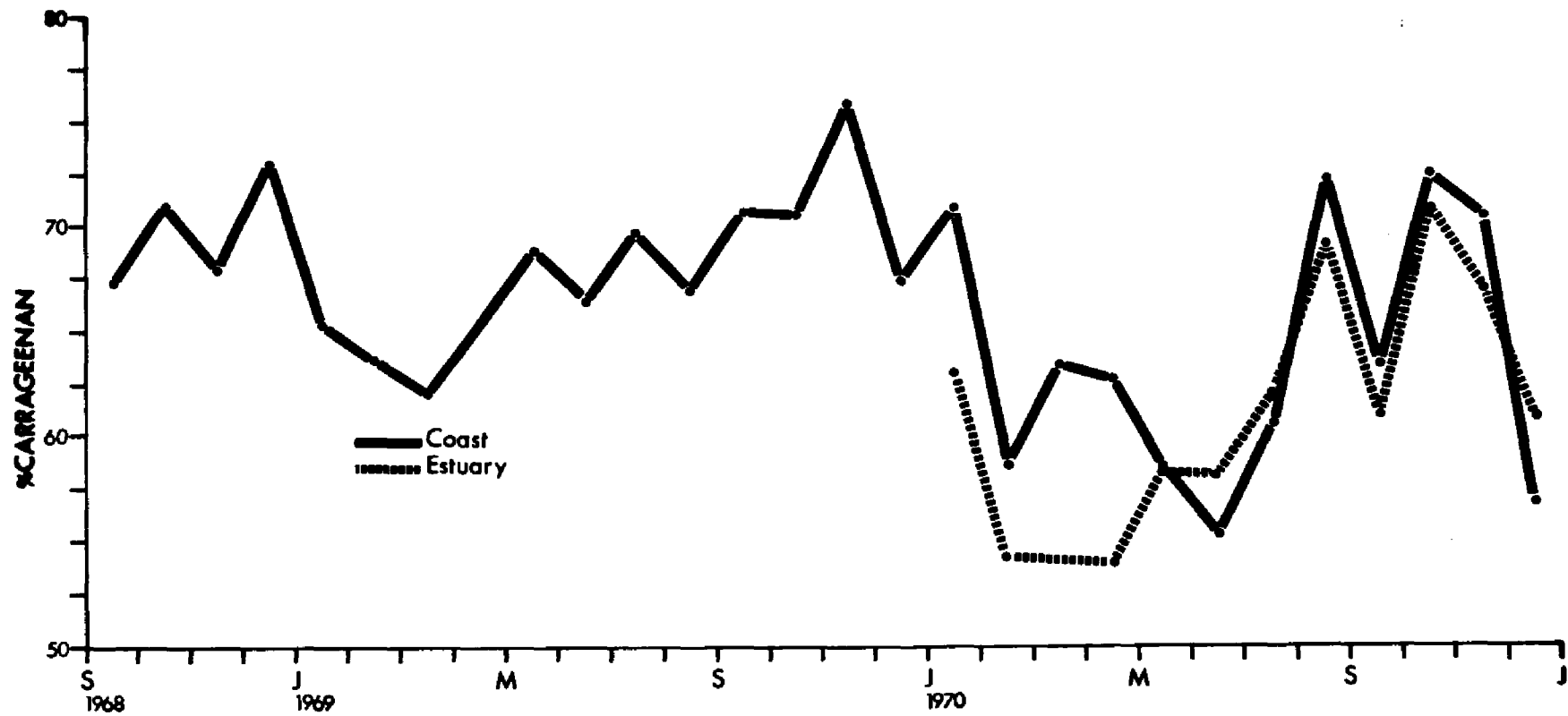


Figure 23 Seasonal fluctuation of viscosity in Chondrus
at coastal and estuarine locations.

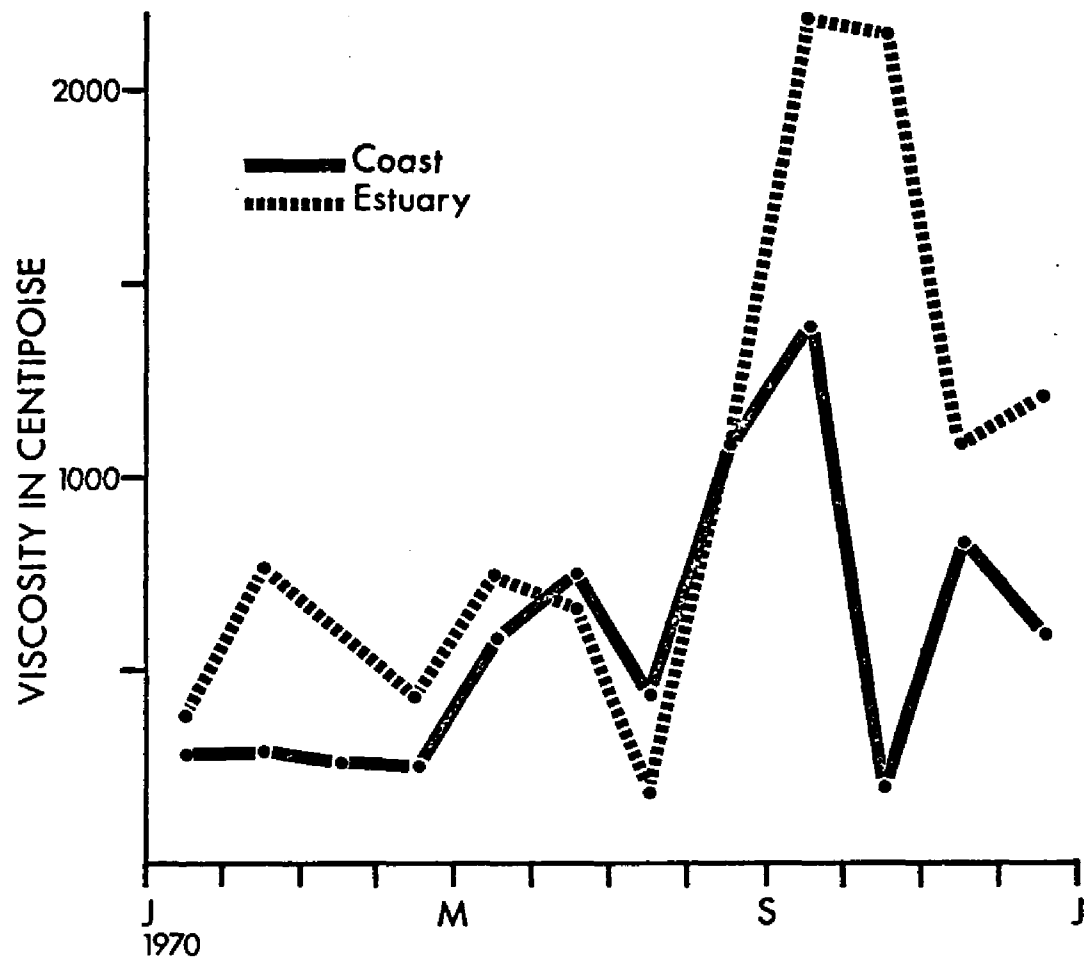


Figure 24 Seasonal fluctuation of gel strength in Chondrus
at coastal and estuarine locations.

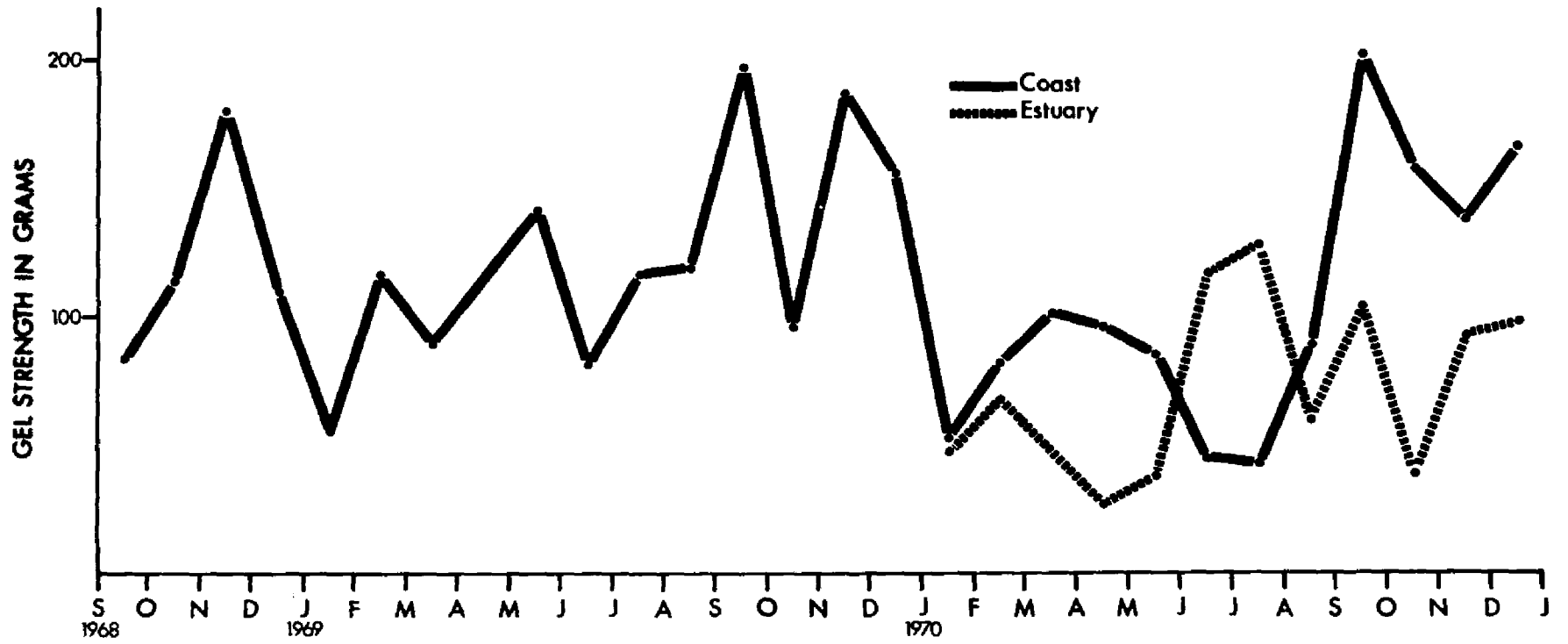


Figure 25 Seasonal fluctuation of percent kappa carrageenan
in Chondrus at Rye Harbor and Dover Point.

