Ödsmål, Kville sn, Bohuslän

Hällristning
Fiskare från
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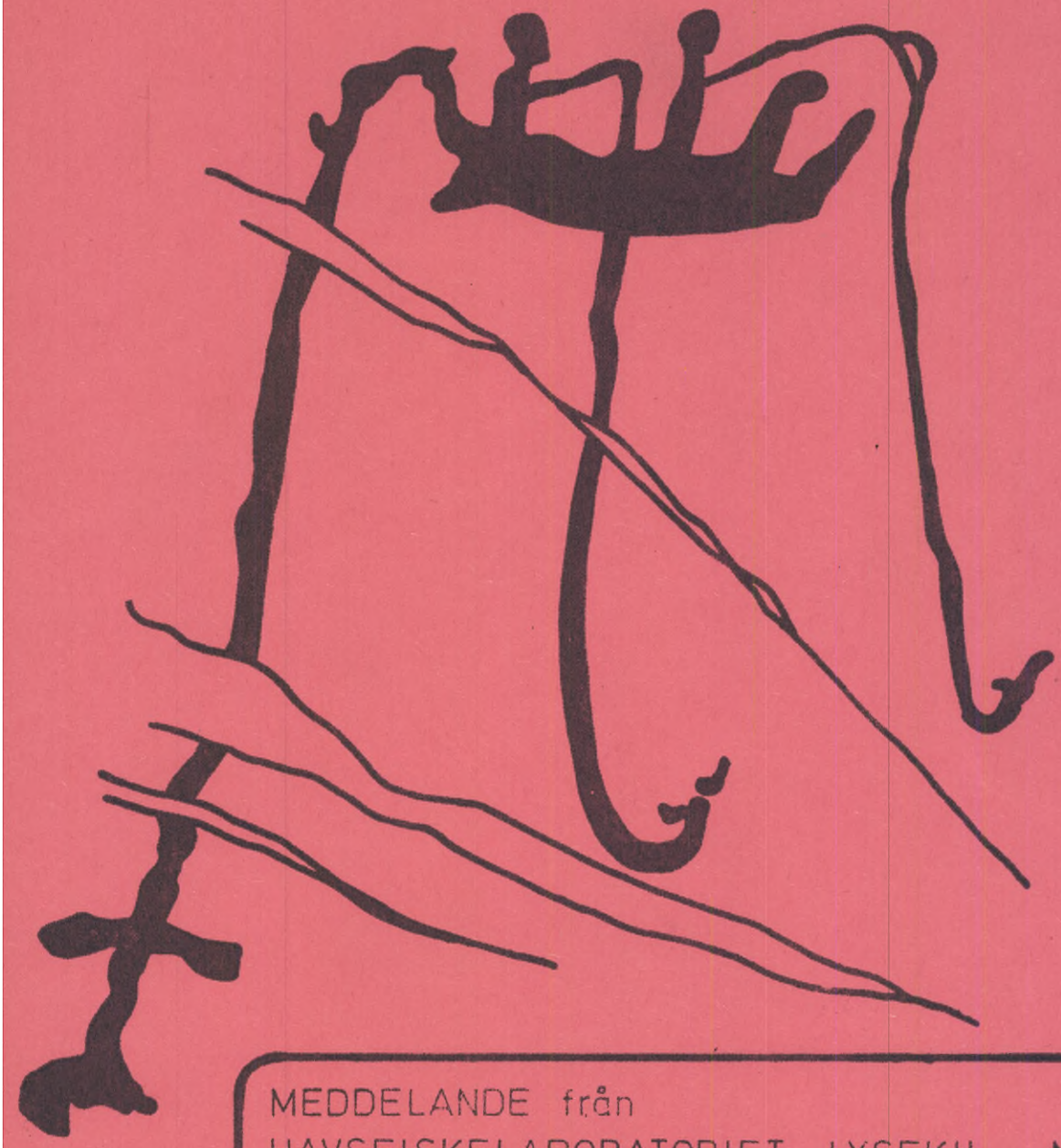
Rock carving
Bronze age
fishermen



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The distribution of urea in the Baltic Sea.

by
Jorge Valderrama

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Jorge C. Valderrama

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THE DISTRIBUTION OF UREA IN THE BALTIC SEA

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SWEDEN

ABSTRACT

The vertical distribution of urea has been determined during a five - year period (from June 1976 to May 1981) at 21 different stations in the Baltic Sea on samples collected during 20 cruises. Results show pronounced seasonal variations with the highest concentrations (up to 1.86 µM) toward the end of spring, while the lowest (down to 0.10 µM) were found during winter months. A total average of 0.32 µM was calculated. Except for some stations in the western Baltic Sea (Arkona basin, Hanö bight and Bornholm deep) the concentrations were notably higher above the halocline than below it. Areas around the Gulf of Finland and the Hanö bight show elevated average concentrations (0.48 and 0.36 µM respectively) while the lowest average were found in the central part of the Baltic i.e. north of the Gotland deep (0.27 µM).

SOMMAIRE

La distribution verticale de l'urée a été determiné pendant une période de cinq ans (Juin 1976 à Mai 1981) dans 21 différentes stations dans la Baltique sur des échantillons recueillis dans 20 croisières. Les résultats montrent des variations saisonniéres trés distinctes, avec les plus hautes concentrations (jusqu'à 1,86 µM) vers la fin du printemps, alors que les plus

basses (jusqu'à 0,10 µM) ont été trouvées durant les mois d'hiver. Une moyenne totale de 0,32 µM a été calculée. Sauf dans quelques stations en Baltique occidentale (le bassin d'Arkona, la baie d'Hanö et le trou de Bornholm) les concentrations étaient notablement plus hautes au-dessus de l'halocline qu'au dessous. Certaines zones autour du Golfe de Finlande et de la baie d'Hanö montrent une moyenne plus elevée de concentrations (0,48 et 0,36 µM, respectivement) tandis que les moyennes les plus basses ont été trouvées dans la partie centrale de la Baltique, c'est-á-dire au nord du le trou de Gotland (0,27 µM).

INTRODUCTION

Urea (carbamid or carbonyldiamide), $H_2N - CO - NH_2$, is excreted into the environment as an end product of nitrogen metabolism by many higher organisms and as a product of microbial action on amino acids, purines and pyrimidines.

A considerable amount of urea found in some coastal marine environments may be added by freshwater discharges, especially through sewage from densely populated areas, since man and other terrestrial vertebrates represent a primary source of urea. In addition, drainage from agricultural regions also might contribute heavily if urea-based fertilizers are used (Remsen et al. 1974).

Urea-decomposing bacteria have been shown to be present in both freshwater and marine environments (Steinmann, 1976). Marine phytoplankters have also been shown to utilize urea as a source of nitrogen. Most of these are inhabitants of estuaries or inshore areas (Carpenter, 1972), which suggest that urea should be considered as an important part of the nitrogen reserve in coastal waters, especially where nitrogen is the limitating factor, and during periods when nitrate levels in the euphotic layer are minimal (Vaccaro, 1963).

During the two last decades, the distribution of urea in coastal and other oceanic waters has been studied. Newell (1967) found concentrations as high as 1.54 µM in surface waters of the English Channel; Mc Carthy (1972) reported 0.27

to 0.50 µM in waters off La Jolla, California, and values up to 0.34 µM in surface waters along the Peruvian coast; Remsen (1971) found values from 0.27 to 2.50 µM in surface waters off the continental shelf between Panamá and Callao, Perú, and from 0.12 µM on the 1830 m depth line between Cape Cod and Cape May along the continental shelf of the northeast United States to high of 5.60 µM within New York Harbor; Koroleff (1974) in a preliminary study in Baltic waters reported values from 0.05 to 1.00 µM, and more recently, Steinmann (1976) reported levels for the Kiel bight from 0.01 to 4.52 µM. To date, there have been rather few measurenments of urea in the Baltic Sea.

The present report attempts to outline the results of a five-year study of urea levels at different stations in the Baltic Sea. For convenience, the area under investigation has been divided into section A, from Arkona basin (BY 2) through Karlsö deep (BY 38) to Landsort deep (BY 31), and section B, from Bornholm deep (BY 5) through Gotland deep (BY 15) to the Gulf of Finland (BY 23), as described in figure 1. Some stations were visited only few times. For that reason they have been grouped in order to get more representative values (BY 29/28, BY 27/26 and BY 25/24/23).

About 4000 samples, from 21 stations, obtained during the course of 20 cruises carried out during different seasons from June 1976 to May 1981, were analyzed.

MATERIALS AND METHODS

Urea was determined by the spectrophotometric method originally proposed by Newell et al. (1967) and modified mainly by Koroleff (1976). It is based on the reaction with diacetylmonoxime and semicarbazide in the presence of controlled amounts of a weak oxidant in a strongly acidic medium where chloride ions are included in excess to sensitize the reaction. Manganous ions stabilize the resultant magenta coloured molecular complex and the presence of phosphate ions enables reasonable reproducibility to be achieved. Reaction takes place under heating at 70 °C. It is positive for compounds having the general formula

$R_1 - NH - CO - NH - R_2$, where R_1 is hydrogen or a single aliphatic radical and R_2 not an acyl radical. The reaction is quantitative for urea. Maximun absorbance occurs at 520 nm. When a 5 cm cell is used, concentrations from 0.10 to 10.0 µM of urea can be measured. At the 2 µM level the relative standard deviation is ± 2.6 %, whereas at the 0.2 µM level it has been estimated to be ± 15 %. Even if at the Baltic Intercalibration Workshop in Kiel (March 1977), no statistical treatment of the data were done, the deviations from the true values were within the error of the method (Grasshoff, 1977).

The common ions present in the natural waters do not interfere, nor are there interferences by ammonia, leucine, tyrosine, cystine, arginine, lysine, histidine, taurine or uric acid. Thiourea and biurea react to some extent as do allantoine and citrulline. That might cause some problems in water samples having a high animal production (Remsen, 1971), but all these compounds normally are not present in natural waters in large enough amounts to interfere with the method (Koroleff, 1976). No interference from hydrogen sulphide in anoxic waters has been detected (Valderrama, 1979).

The samples were collected directly from the Hydro - Bios TPN polycarbonate water samplers together with samples for analysis of other nutrients, from the standard depths generally used in the Baltic. Aliquots of 100 ml were poured into glass bottles and 0.5 ml of a saturated $HgCl_2$ solution was used as preservative. The samples were analyzed 4 to 6 weeks after collection in 25 ml replicates. Preservation tests showed that ures samples remain unalterable for at least two months after sampling using this procedure (Valderrama, 1979).

With each series of samples replicates of blank and standard solutions at different concentrations (0.2, 0.5, 1.0, and 2.0 µM) were analyzed in order to calculate the concentration factor of reagents, which for a 5 cm cell should be close to 9.

RESULTS

Table I gives mean values of the vertical profile concentration of urea determined during each of the 20 cruises showing results for sections A and B, as for the total studied area (T). At the left of each column values in the water masses above (upper figure) and below (lower figure) the halocline, and at the right the total mean values for the all area are shown. Values are plotted in figures 2 and 3. Except for the cruise on June 1976 all measurenments show higher levels of concentration above than below the halocline.

From the Table I and figures 2 and 3 a pronounced seasonal variation of the concentration can be observed. The highest values were determined during May and June and they may reach up to 0.49 µM (on an average) but some isolated values may reach up to 1.86 µM. The lowest levels were determined in January and on an average they may reach down to 0.17 µM with some isolated values down to 0.10 µM.

When a graph with the values obtained during all the different cruises is plotted for a "representative" year the figure 4 is obtained. During spring and early summer urea levels reach a maximun which decreases later during autumn and winter with two smaller maximums during late summer and autumn - early winter (respectively September and November - December).

Tables II and III and figures 5 and 6 give a picture of the seasonal variation and distribution of the concentration above and below the halocline for the different stations included in the two sections. The Hanö bight (station HB in the section A) and the Gulf of Finland (Stations BY 25/24/23 in the section B) were the areas having the highest levels of concentration, which is especially outstanding during spring months, respectively 0.55 and 0.60 µM. In the Gulf of Finland these high levels were observed even during all other periods. Stations as Norköping deep (BY 32), Fårö deep (BY 20) and Ryssh̊alan (BY 8) presented the lowest average concentrations even during spring.

Figure 7 show the average concentrations found during the entire investigated period for each station indicating values above and below the halocline. The concentration average of all samples (section A 0.32 µM and section B 0.31 µM) even as for the levels above and below the halocline (section A respectively 0.34 and 0.29 µM and section B respectively 0.35 and 0.27 µM). A total average of 0.32 µM for the entire investigated area was calculated, 0.35 and 0.28 µM for respectively above and below the halocline.

Figure 8 shows the integrated values of concentration levels for the two sections during the four seasonal periods, they are nearly similar for both sections.

Except for stations BY 2 (during spring, summer and autumn), HB (during spring and summer), BY 39 (during spring), and BY 5 (during spring) all other stations exhibit the highest concentrations above the halocline (Tables II and III, and figures 6 and 7). The mentioned stations are located in the south-western part, that is near the only communications (through the Belts and Öresund) that the Baltic Sea has with the rest of the world ocean, and where the halocline is more pronounced, and where heavy salt water from the Kattegatt flows easterly as a botton current below the outflowing brackish surface water.

The differences in concentration levels of urea between the two water layers separated by the halocline are higher toward the eastern areas of the Baltic, especially during spring and summer. These differences may reach up to 77% in the station BY 27/26 during spring and 78% in the station BY 29/28 during summer (Table III and figure 6).

Figures 9 and 10 show the concentration isoplates in a vertical profile for respectively section A and section B during a typical spring period. The halocline level is indicated with a segmented line.

The results obtained during the investigated period suggest that the high urea levels measured above the

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Page 6, line 4, between "of" and "all", it should be said:
... the two sections were nearly the same as the average of ...

halocline and especially during spring and, to some extent, during autumn months, are connected with the primary production, and in areas such as the Gulf of Finland and the Hanö bight even with freshwater discharges from the surrounding densely populated areas. It is more difficult to explain why this pattern is inverted in the south-western part of the Baltic. As a preliminary explanation it may be assumed that it is connected with inputs arising from Öresund which represents another high populated area.

In the Baltic, nutrients such as nitrate, nitrite and ammonium build up during the winter months and in the euphotic zone they are consumed during a few weeks in spring. An intensive primary production then occurs and the system becomes nitrogen limited during the end of spring and summer (Rönner, 1983). Therefore, urea may be considered an important nitrogen reserve source in the Baltic Sea.

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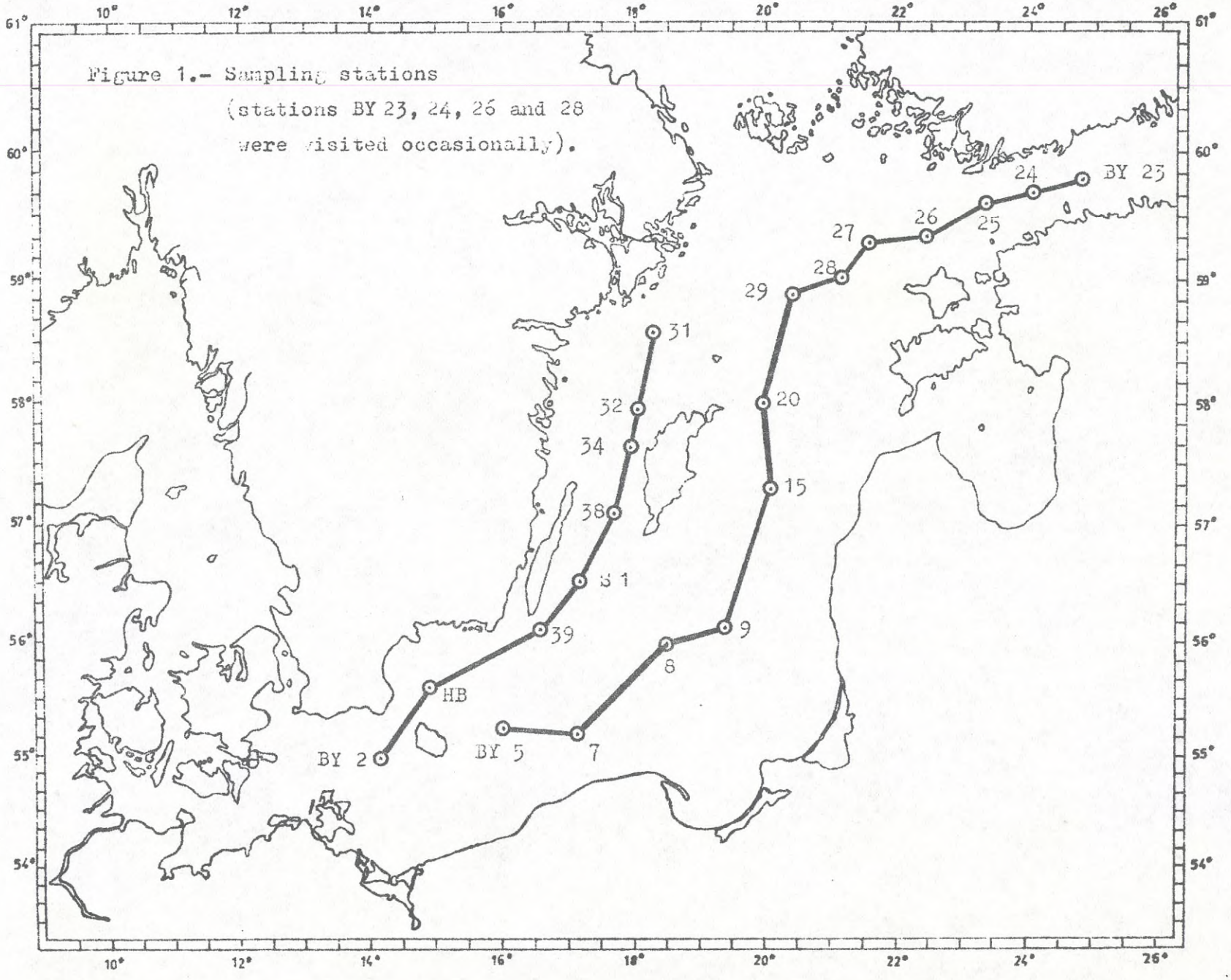

Figure 1.- Sampling stations
(stations BY 23, 24, 26 and 28
were visited occasionally).

TABLE I.- Average concentrations of urea (in μM) during 20 cruises to the Baltic Sea, pointing out the levels above and below the halocline.

Cruise	Section A		Section B		TOTAL (T)	
1976.06.16 - 06.23	0.41 0.42	0.42	0.45 0.40	0.43	0.44 0.41	0.43
08.24 - 09.08	0.31 0.24	0.28	0.32 0.24	0.28	0.32 0.24	0.28
11.22 - 12.04	0.33 0.32	0.32	0.30 0.30	0.30	0.31 0.31	0.31
1977.06.01 - 06.14	0.44 0.35	0.41	0.40 0.30	0.36	0.42 0.32	0.38
08.30 - 09.20	0.32 0.30	0.31	0.37 0.28	0.33	0.34 0.30	0.32
11.22 - 12.03	0.40 0.30	0.36	0.32 0.29	0.30	0.36 0.29	0.33
1978.01.24 - 01.31	0.28 0.23	0.25	0.27 0.20	0.24	0.28 0.21	0.24
03.18 - 03.29	0.41 0.38	0.40	0.44 0.37	0.40	0.42 0.38	0.40
05.17 - 06.01	0.49 0.37	0.45	0.47 0.29	0.39	0.48 0.32	0.42
08.22 - 09.06	0.27 0.25	0.26	0.39 0.25	0.32	0.34 0.25	0.30
11.14 - 11.23	0.32 0.31	0.31	0.34 0.29	0.32	0.33 0.30	0.31
1979.01.16 - 01.19	0.31 0.22	0.28	0.34 0.26	0.31	0.33 0.25	0.30
05.29 - 06.16	0.38 0.33	0.36	0.39 0.30	0.34	0.38 0.31	0.35
08.21 - 08.24	0.27 0.23	0.26	0.27 0.19	0.24	0.27 0.21	0.25
11.06 - 11.28	0.28 0.27	0.27	0.27 0.20	0.24	0.28 0.23	0.25

TABLE I (cont.).-

	Section A		Section B		TOTAL (T)	
1980.01.15 - 01.22	0.27 0.20	0.24	0.20 0.17	0.19	0.23 0.18	0.21
05.28 - 06.13	0.46 0.40	0.44	0.48 0.34	0.42	0.47 0.36	0.43
10.27 - 11.13	0.24 0.20	0.22	0.22 0.20	0.21	0.23 0.20	0.22
1981.03.10 - 03.13	0.25 0.22	0.24	0.21 0.18	0.20	0.23 0.20	0.22
05.12 - 05.31	0.38 0.37	0.38	0.36 0.34	0.35	0.37 0.35	0.36
TOTAL AVERAGE	0.34 0.29	0.32	0.35 0.27	0.31	0.35 0.28	0.32

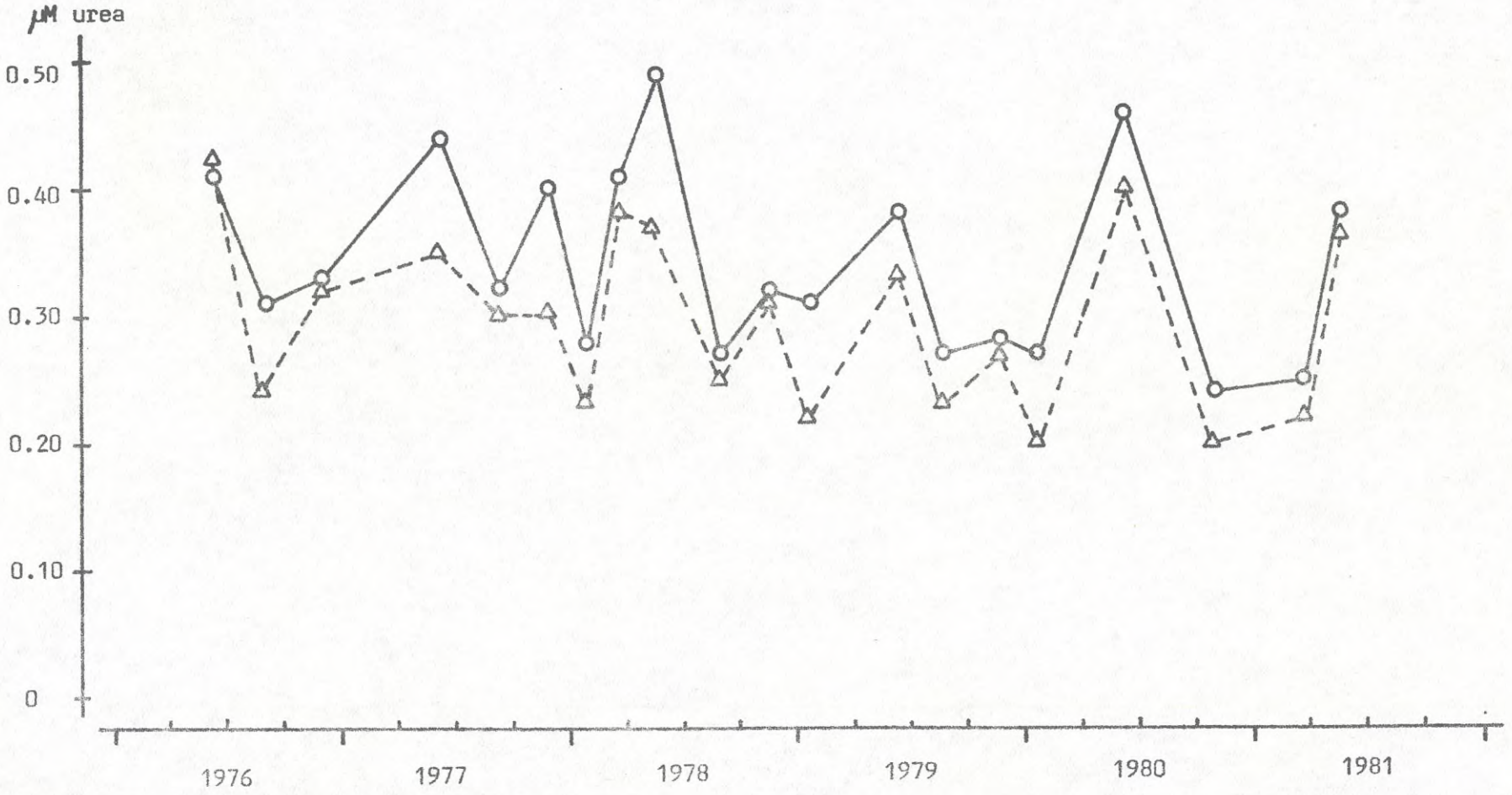

Figure 2.- Average concentrations of urea measured during 20 cruises to the Baltic Sea pointing out the levels above (O——O) and below (Δ- -Δ) the halocline. Section A.

Figure 3.- Average concentrations of urea measured during 20 cruises to the Baltic Sea pointing out the levels above (O——O) and below (Δ- -Δ) the halocline. Section B.

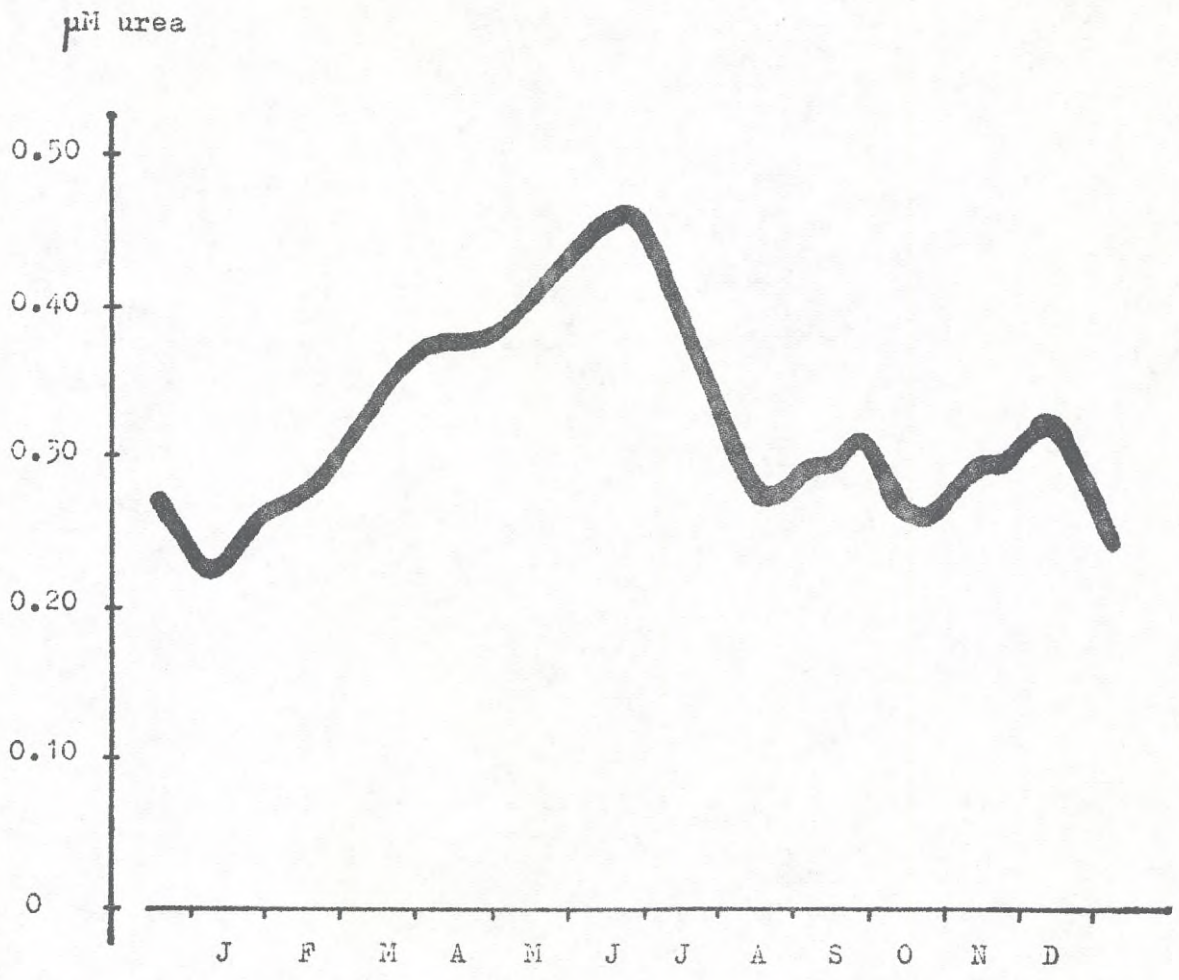

Figure 4.- Characteristic mean values for the vertical profile concentration of urea in the Baltic Sea during a "representative" year, based on measurenments done during 5 years (June 1976 to May 1981).

TABLE II .- Seasonal distribution of the concentrations of urea above and below the halocline. Mean values, in μM. Section A.

Station	depth m	number of samples	Jan	Feb	Mar	Winter	Apr	May	Jun	Spring	Jul	Aug	Sep	Summer	Oct	Nov	Dec	Autumn	TOTAL
BY 2	48	168	0.32		0.27	0.30	0.32		0.50	0.38	0.30		0.31	0.31	0.26		0.38	0.30	0.30 / 0.36 / 0.32
Hanö bight	82	205	0.26		0.24	0.25	0.54		0.57	0.55	0.28		0.36	0.31	0.34		0.30	0.32	0.36 / 0.37 / 0.36
BY 39	50	128	0.27		0.23	0.26	0.38		0.40	0.39	0.34		0.26	0.32	0.28		0.22	0.28	0.32 / 0.31 / 0.32
Segerstad 1	72	148	0.30		0.21	0.29	0.41		0.38	0.40	0.32		0.25	0.30	0.34		0.32	0.33	0.35 / 0.32 / 0.34
BY 38	112	272	0.32		0.25	0.29	0.45		0.40	0.44	0.28		0.23	0.26	0.31		0.28	0.30	0.36 / 0.29 / 0.33
BY 34	105	223	0.31		0.27	0.30	0.48		0.33	0.43	0.27		0.19	0.23	0.33		0.27	0.30	0.37 / 0.27 / 0.33
BY 32	205	196	0.26		0.21	0.23	0.40		0.29	0.34	0.26		0.20	0.23	0.32		0.29	0.31	0.33 / 0.26 / 0.29
BY 31	459	389	0.31		0.26	0.28	0.40		0.33	0.36	0.30		0.26	0.27	0.28		0.24	0.26	0.33 / 0.27 / 0.30
TOTAL Section A		1729	0.30		0.25	0.28	0.43		0.37	0.40	0.29		0.26	0.28	0.30		0.28	0.29	0.34 / 0.29 / 0.32

TABLE III.- Seasonal distribution of the concentration of urea above and below the halocline.
Mean values, in μM. Section B.

Station	depth m	number of samples	Jan	Feb	Mar	Winter	Apr	May	Jun	Spring	Jul	Aug	Sept	Summer	Oct	Nov	Dec	Autumn	TOTAL
BY 5	91	233	0.24			0.22	0.32			0.34	0.37			0.34	0.24			0.24	0.30
			0.20				0.36				0.28				0.24				0.28	0.29
BY 7	83	192	0.29			0.29	0.32			0.31	0.35			0.34	0.26			0.26	0.31
			0.28				0.30				0.32				0.26				0.30	0.30
BY 8	109	132	0.26			0.25	0.35			0.34	0.29			0.26	0.24			0.23	0.30
			0.23				0.33				0.19				0.21				0.26	0.29
BY 9	127	264	0.31			0.27	0.39			0.36	0.32			0.29	0.22			0.22	0.32
			0.22				0.31				0.25				0.21				0.25	0.29
BY 15	249	350	0.29			0.26	0.43			0.37	0.38			0.31	0.30			0.28	0.36
			0.24				0.30				0.24				0.27				0.27	0.31
BY 20	203	306	0.30			0.26	0.36			0.32	0.27			0.23	0.28			0.25	0.31
			0.23				0.27				0.19				0.23				0.23	0.27
BY 29/28	170/200	260/32	0.31			0.27	0.39			0.36	0.32			0.25	0.31			0.28	0.35
			0.23				0.32				0.18				0.26				0.27	0.31
BY 27/26	176/113	274/24	0.25			0.24	0.55			0.44	0.29			0.23	0.32			0.30	0.39
			0.23				0.31				0.17				0.27				0.26	0.33
BY 25/24/23	73/73/80	87/27/20	0.28			0.27	0.68			0.60	0.40			0.38	0.37			0.36	0.51
			0.25				0.47				0.30				0.33				0.42	0.48
TOTAL Section B		2174	0.28			0.26	0.42			0.38	0.34			0.29	0.29			0.27	0.35
			0.23				0.32				0.23				0.25				0.27	0.31

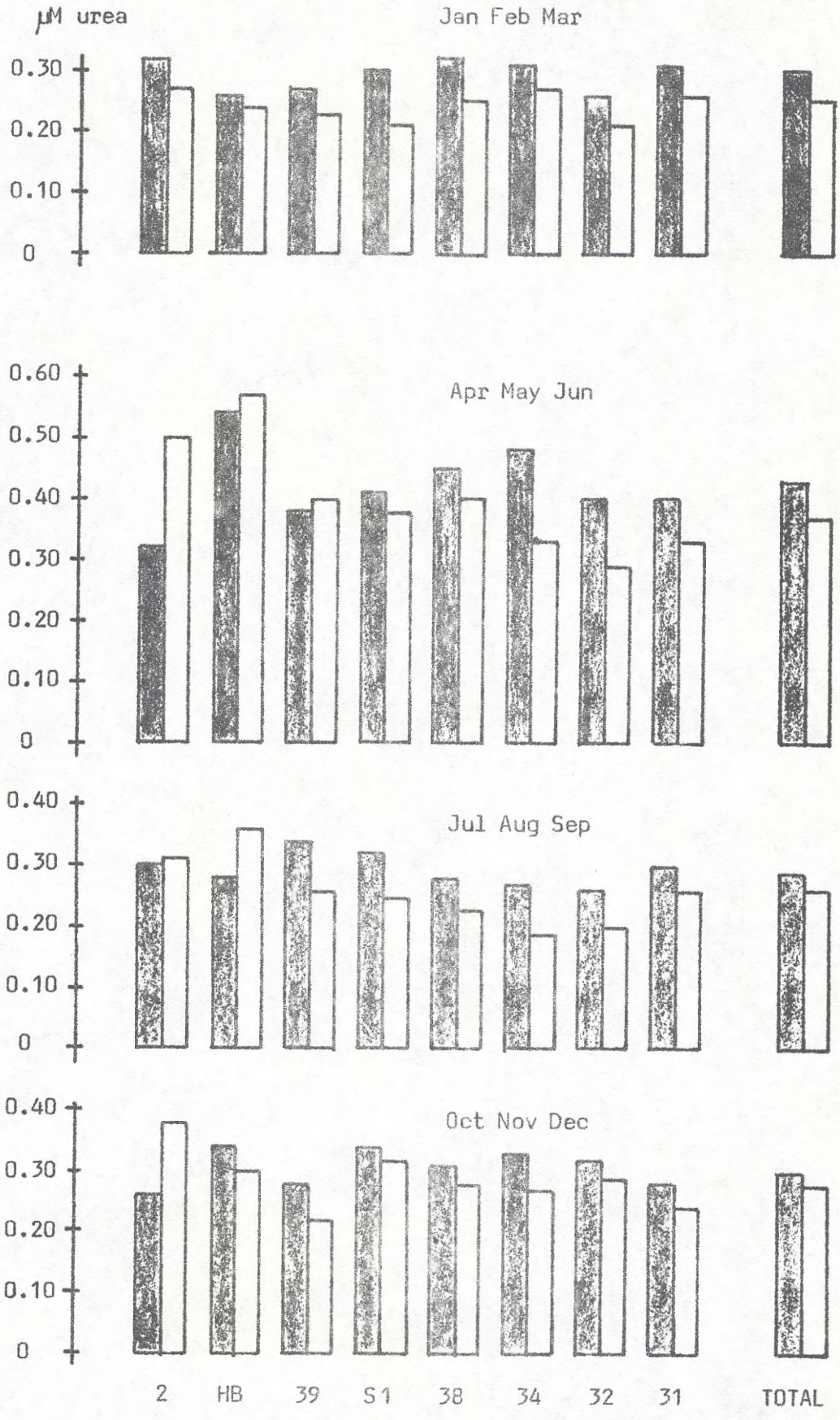

Figure 5.- Seasonal variations of the average concentration of urea on section A stations (June 1976 - May 1981), above (■) and below (□) the halocline.

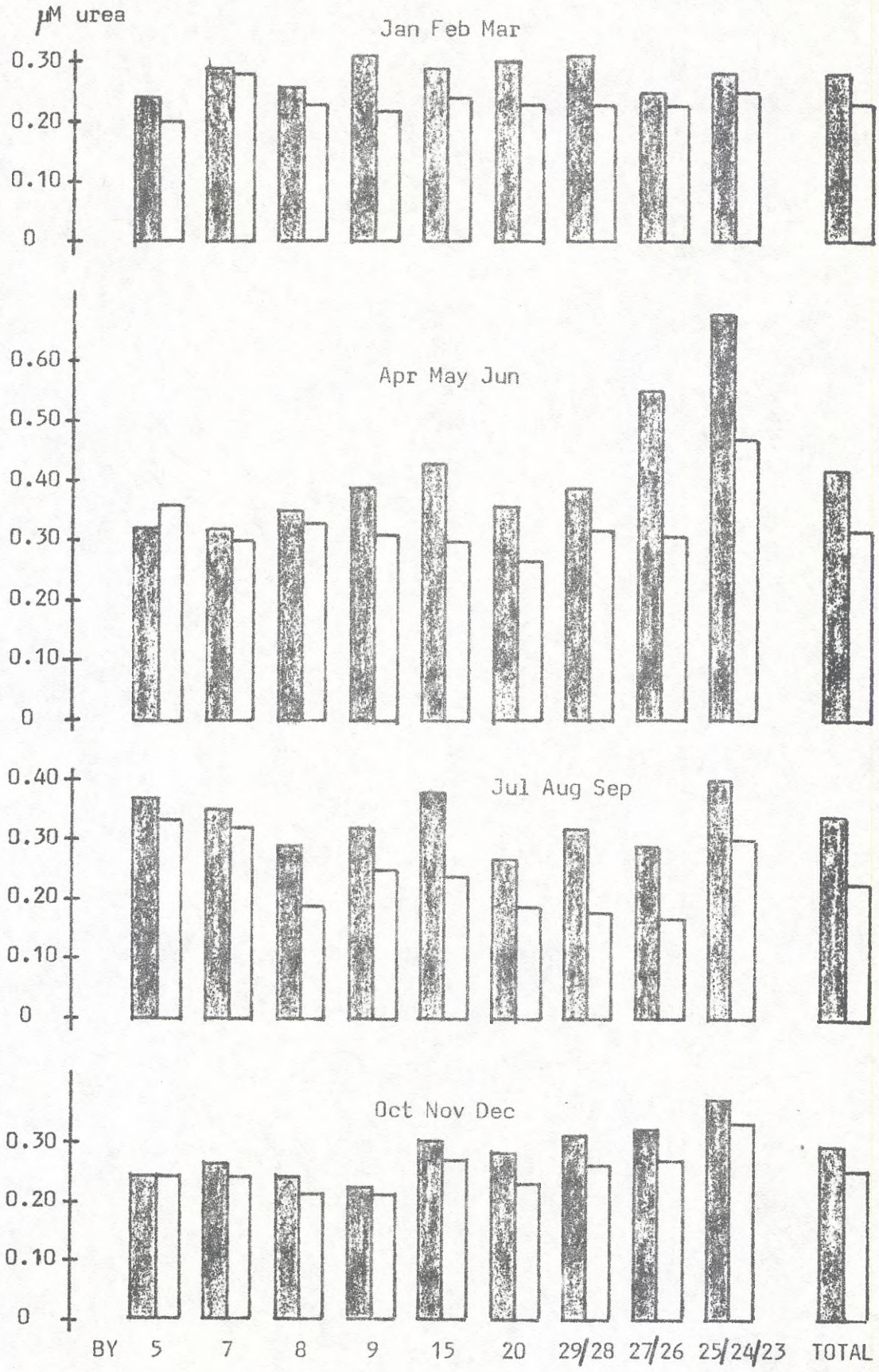

Figure 6.- Seasonal variations of the average concentration of urea on section B stations (June 1976 - May 1981), above (■) and below (□) the halocline.

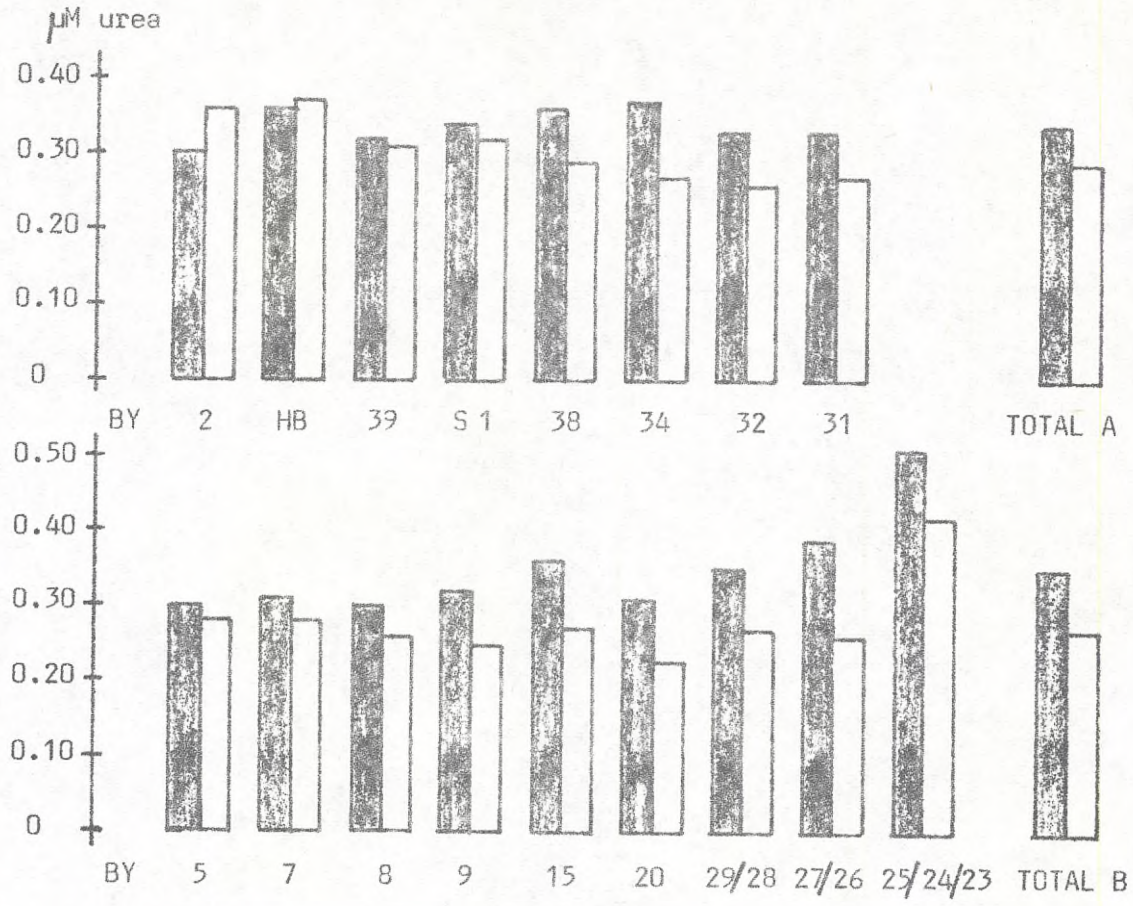

Figure 7.- Average concentration of urea in different stations of the Baltic Sea from June 1976 to May 1981, above (■) and below (□) the halocline.

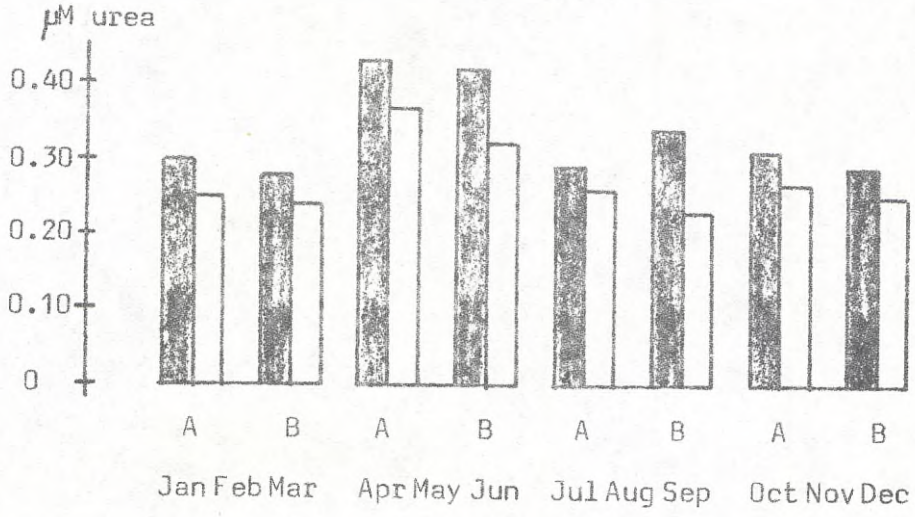

Figure 8.- Seasonal variation of the average concentration of urea in the Baltic Sea from June 1976 to May 1981, above (■) and below (□) the halocline.

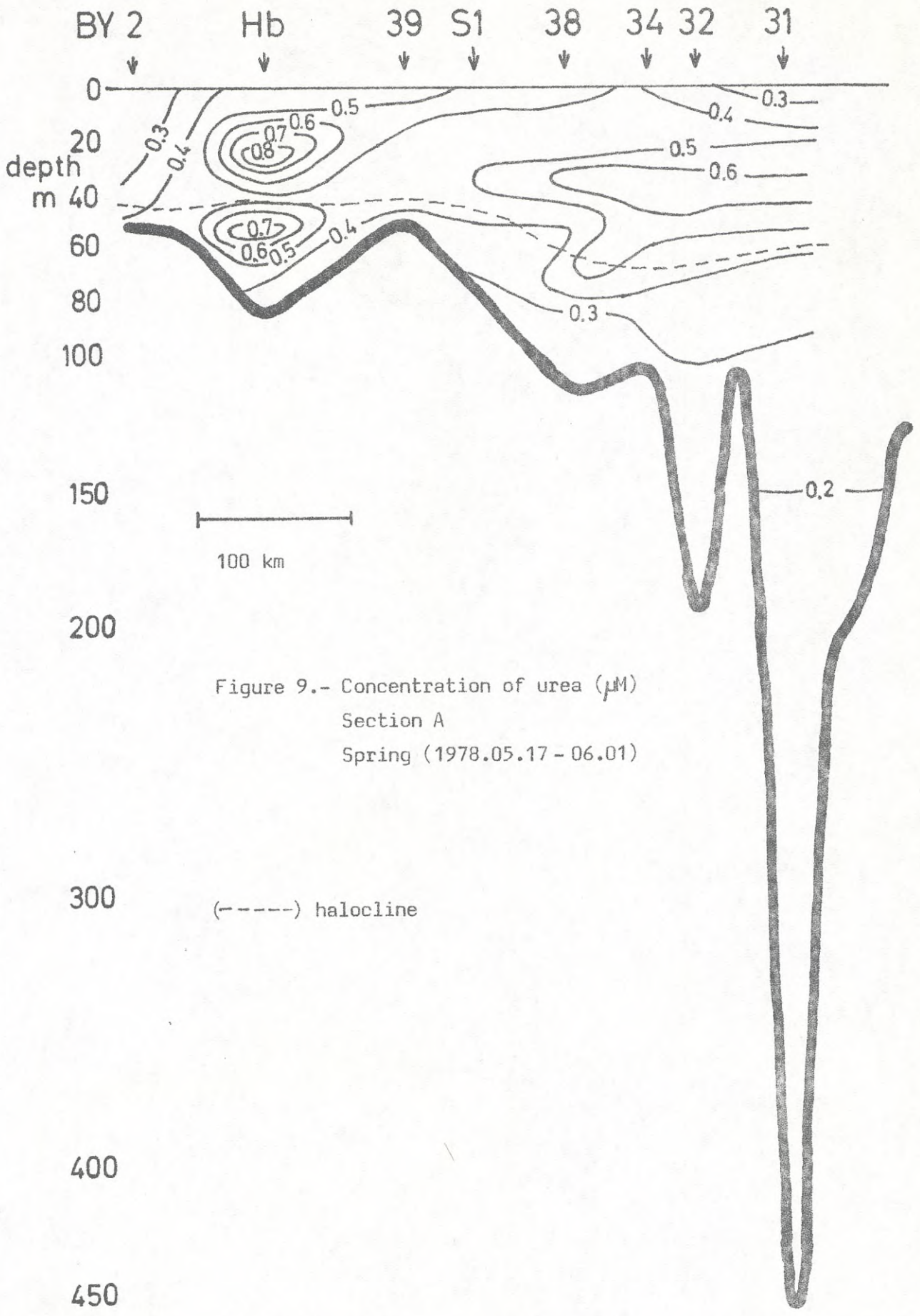

Figure 9.- Concentration of urea (μM)
Section A
Spring (1978.05.17 - 06.01)

(- - - - -) halocline

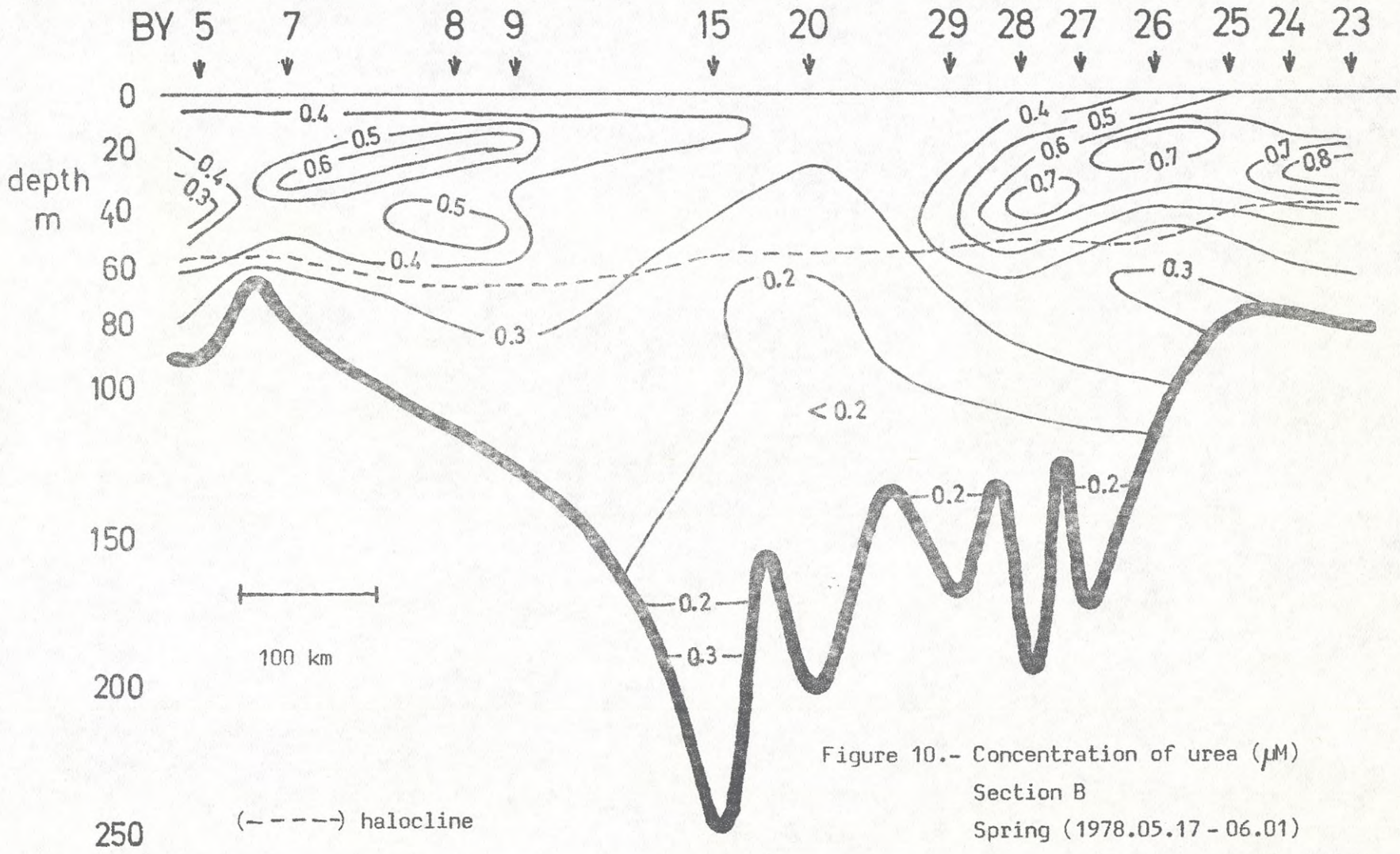

Figure 10.- Concentration of urea (μM)
Section B
Spring (1978.05.17 - 06.01)