

RESULTS OF A FIVE YEAR SURVEY OF THE DISTRIBUTION OF UREA IN THE BALTIC SEA

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Title (and Subtitle) Results of a five year survey of the distribution of urea in the Baltic Sea.		
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 the spring, while the lowest (down to 0.08 μM) were found during winter months. 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 while the lowest concentrations were found in the central part of the Baltic Sea. During the late spring and summer it may reach up to 80% of the nitrogen nutrient reserve on the higher levels of water.		
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INTRODUCTION

Urea or carbamide, $\text{CO}(\text{NH}_2)_2$, 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.

High values of urea found in upwelling waters seem to be a consequence of excretions by the natural population of organisms and not a result of terrestrial pollution (Remsen, 1971). It has been reported that as much as 10 percent of the total nitrogen excreted by *Calanus helgolandicus* (Corner and Newell, 1967) and 5 percent in *Mytilus edulis* (Bayne, 1973) may be in the form of urea, and in the ocean up to 14 percent of the total nitrogen excreted by shrimp, crayfish and mussels is in the form of urea (Parry, 1960) while some elasmobranchs excrete up to 70-80 percent of their total nitrogen in the form of urea (Huggins et al., 1969).

A considerable amount found in some coastal marine environments may originate from 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.

Urea-decomposing bacteria, present in both freshwater and marine environment, and phytoplankton organisms may utilize urea. The former play an important role in its breakdown in the open sea, while phytoplankton plays a more dominant role in the utilization and/or decomposition of urea in estuaries or inshore areas, which suggests that it should be considered as an important part of the nitrogen reserve in coastal waters, especially where nitrogen is the limiting factor, and during periods when nitrate levels in the euphotic layer are minimal (Vaccaro, 1963, Sahlsten, 1984).

Some phytoplankton organisms can grow using urea as a sole nitrogen source while others cannot. This may alter the species composition of phytoplankton, because if nitrogen is limiting, the presence of urea in sufficient quantities will increase the growth rates of those species that can use it while not affecting those that cannot (Remsen et al., 1974).

During the two last decades, the distribution of urea in coastal and oceanic waters has been studied. Newell (1967) found concentrations as high as $1.54 \mu\text{M}$ in surface waters of the English Channel; McCarthy (1972) reported 0.27 to $0.50 \mu\text{M}$ in waters off La Jolla, California; Remsen (1971) found values up to $2.50 \mu\text{M}$ in surface waters off the continental shelf between Panama and Callao, and from $0.12 \mu\text{M}$ at the 1830 m depth line between Cape May along the continental shelf of the NE United States up to $5.60 \mu\text{M}$ within New York Harbor; Verlencar (1980) found values from 0.15 to $3.88 \mu\text{M}$ off the West Coast of India.

Koroleff (1974) in a preliminary study in Baltic waters reported values from 0.05 to 1.0 μM , and Steinmann (1976) reported levels for the Kiel Bight up to 4.52 μM . Today there have been rather few measurements of urea in the Baltic Sea.

The present work 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 the Arkona Basin (BY 2) through the Karlsö Deep (BY 38) to the Landsort Deep (BY 31), and section B, from the Bornholm Deep (BY 5) through the Gotland Deep (BY 15) to the Gulf of Finland (BY 23), as described in figure 1. Some stations were visited only a 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).

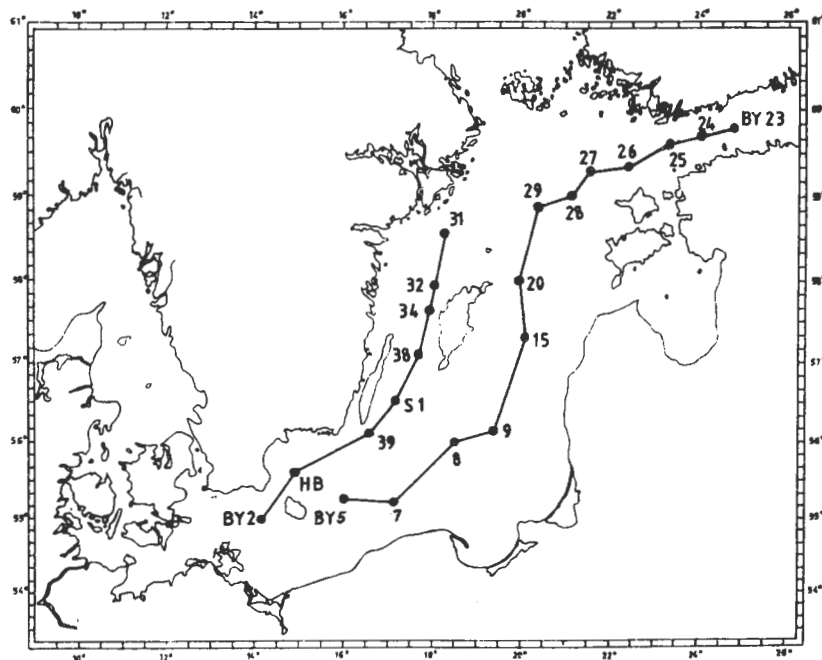


Figure 1.- Sampling stations

Section A : from BY 2 to BY 31

Section B : from BY 5 to BY 23

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

In the Baltic Sea, two different water layers are present, a light surface layer with a low salinity and a heavier deep layer with a higher salinity, separated by a halocline which is an impediment to the mixing or exchange between these two layers (Fonselius, 1970). An important contribution of urea of a terrestrial origin is added to the marine environments by freshwater discharges to the surface water. Therefore it was of interest to consider values above and below the halocline separately.

All data given as mean values are available in a report presented as a contribution to the ICES 1983 Statutory Meeting and published in the Institute of Hydrographic Research Series (Valderrama, 1983).

MATERIAL AND METHODS

Urea was determined by the spectrophotometric method originally proposed by Newell et al. (1967) and modified 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 acid medium where chloride ions are included in excess to sensitize the reaction. Manganese(II) ions stabilize the resulting magenta coloured molecular complex and the presence of phosphate ions enables reasonable reproducibility to be achieved. The reaction takes place under heating at 72°C. This is positive for compounds having the general formula $R_1 \cdot NH \cdot CO \cdot NH \cdot R_2$, where R_1 is hydrogen or a single aliphatic radical and R_2 is not an acyl radical. The reaction is quantitative for urea (Koroleff 1976). Maximum absorbance occurs at 520 nm. When a 5 cm cell is used, concentrations from 0.05 to 10.0 μM of urea can be measured. At the 2 μM level the relative standard deviation is + 2.6 percent whereas at the 0.2 μM level it has been estimated to be + 15 percent. Even if no statistical treatment of the data was done at the Baltic Intercalibration Workshop in Kiel (March 1977), 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 alantoine and citrulline (Koroleff 1976). That might cause some problems in water samples having high animal production (Remsen, 1971), but all these compounds are normally not present in natural waters in amounts large enough to interfere with the method (Koroleff, 1983). No interference of hydrogen sulphide in anoxic waters has been detected (Valderrama, 1979).

Another method to determine urea has been proposed by McCarthy (1970). It is based on a decomposition of urea to ammonia in the presence of a specific enzyme, urease, which acts as a catalyst for the reaction. The resulting ammonia is determined by the indophenol method. Even if this urease technique is recommended as specific and more sensitive for urea than the direct chemical method (Parsons et al., 1984) its success largely depends on the preparation of the urease solution, on a complete urease reaction which is affected by the chance presence of

cationic inhibitors, lead or mercury and finally, the procedure requires a separate blank for each sample tested. Schroeder and Remsen (unpublished work cited in Carpenter et al., 1972) have compared both methods and found the diacetylmonoxime technique to be both more precise and more free from errors.

The samples were collected directly from the Hydro-Bios TPN polycarbonate water sampler together with samples for analysis of other nutrients, at the standard depths generally used in the Baltic. Aliquots of 100 cm³ were poured into glass bottles and 0.5 cm³ of a saturated HgCl₂ solution was used as preservative. The samples were analysed 4 to 6² weeks after collection in 25 cm³ replicates. Preservation tests showed that urea samples remain unchanged for at least two months after sampling using this procedure (Valderrama, 1979).

With each series of samples replicates of blank and standard solutions were analyzed in order to calculate the calibration factor of the reagents, which for a 5 cm cell should be closed to 9.

RESULTS

Figure 2 gives mean values of the vertical profile concentrations of urea determined during each of the 20 cruises showing results for the total studied area and pointing out the levels above and below the halocline.

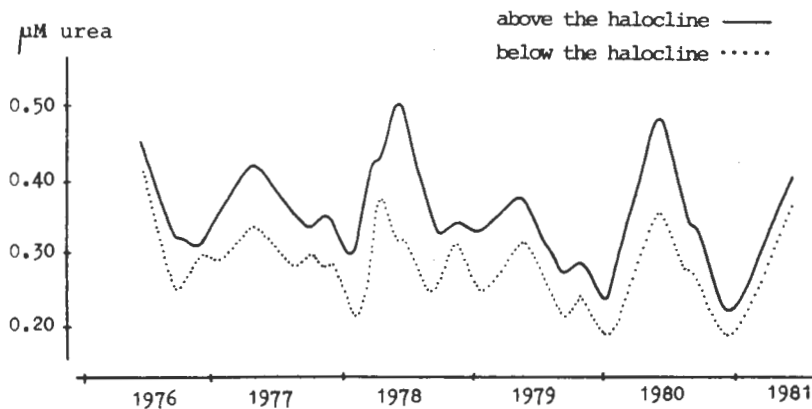


Figure 2.-

A pronounced seasonal variation of the concentrations can be observed. Values below the halocline are always lower than the ones above and they show the same variations.

The highest values were found during May and June reaching up to 0.51 μM above and 0.42 μM below the halocline (on an average), but isolated values may reach respectively 1.86 and 0.98 μM . The lowest levels were found in January and on average they may go down to respectively 0.23 and 0.18 μM with some isolated values down to 0.10 and 0.08 μM .

During autumn an increase of urea levels may be observed but rather small as compared to those observed in spring.

When a graph with the values obtained during all cruises is plotted for a "representative" year the figure 3 is obtained. During spring and early summer, urea levels reach a maximum which decreases later during autumn and winter with two smaller maximums during late summer and autumn-early winter, September and November-December respectively.

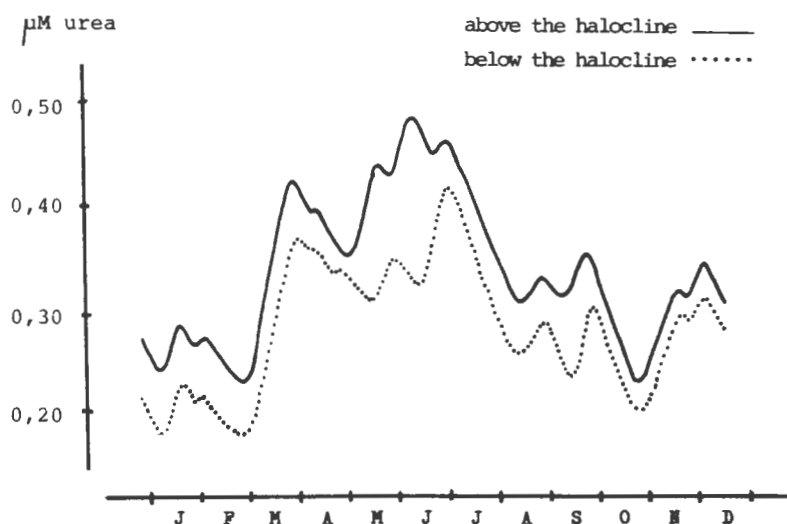


Figure 3.-

Figures 4 and 5 give a picture of the seasonal variation and distribution of the concentrations above and below the halocline for the different stations included in the two sections. The Hanö (HB in the section A) and the Gulf of Finland (BY 25/24/23 in the section B) were areas having the highest concentration levels, which is especially outstanding during spring months, 0.55 and 0.60 μM respectively. In the Gulf of Finland these high levels were observed also during all the other periods. Stations as BY 32 and especially BY 7, BY 8, BY 9 and BY 20, in the central part of the Baltic showed the lowest average concentrations even during spring.

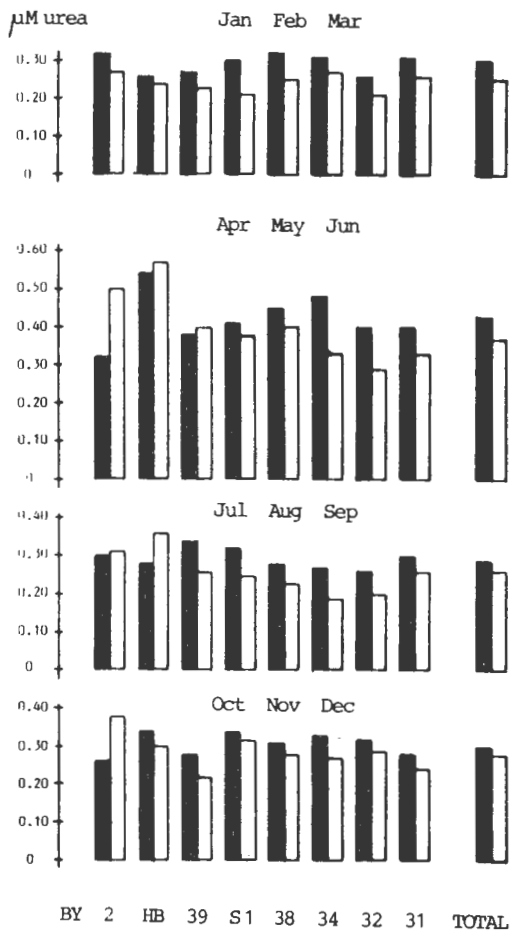


Figure 4.-

Seasonal variation of the average concentrations of urea on Section A stations, from June 1976 to May 1981, above (■) and below (□) the halocline.

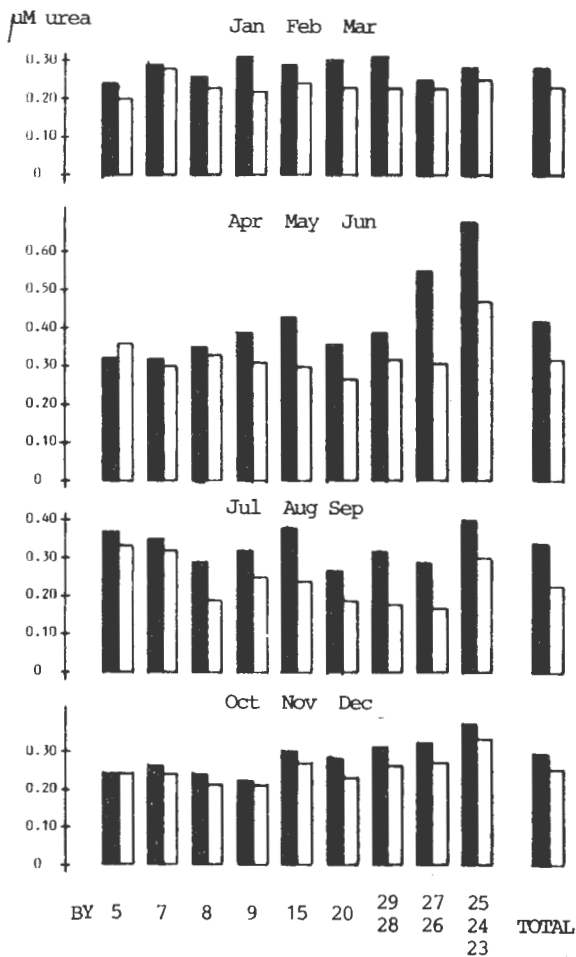


Figure 5.-

Seasonal variation of the average concentrations of urea on Section B stations, from June 1976 to May 1981, above (■) and below (□) the halocline.

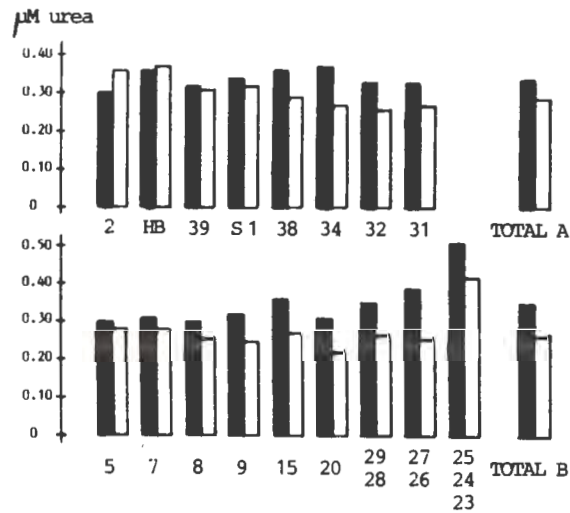


Figure 6.- Average concentration of urea in different stations of the Baltic Sea from June 1976 to May 1981, above (■) and below (□) the halocline.

Figure 6 shows the average concentrations found for each station during the entire investigated period indicating values above and below the halocline. The concentration average of the two sections were nearly the same as the 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 0.34 µM and 0.29 µM and section B 0.35 µM and 0.27 µM respectively). A total average of 0.32 µM for the entire investigation area was calculated, with 0.35 µM and 0.28 µM for above and below the halocline respectively.

Figure 7 shows the integrated values of concentration levels for the two sections during the four seasonal periods. They are nearly similar for both sections.

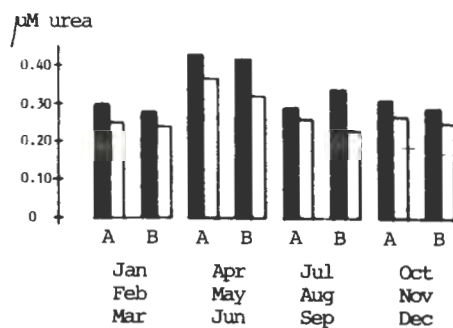


Figure 7.- Seasonal variation of the average concentration of urea in the Baltic Sea from June 1976 to May 1981, for sections A and B, above (■) and below (□) the halocline.

Except for stations BY 2 (during spring, summer and autumn), H8 (during spring and summer), BY 39 (during spring) and BY 5 (during spring) all other stations show the highest concentrations above the halocline (figure 5 and 6). The stations mentioned above are located in the south-western part, that is near the only communication (through the Belts and the Öresund) the Baltic Sea has with the world ocean, and where the halocline is more pronounced, and where heavy salt water from the Kattegatt flows easterly as a bottom current below the outflowing brackish surface water.

The differences in concentration levels of urea between the two 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 at the stations BY 27/26 during spring and 78 per cent at the stations BY 29/28 during summer (figure 5).

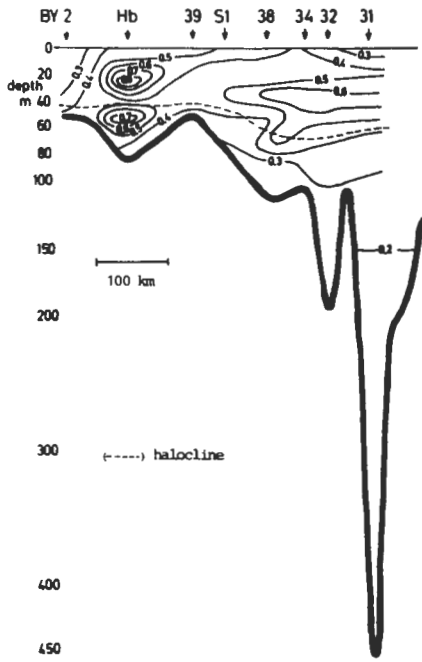


Figure 8.- Concentration of urea (μM) on Section A during a typical spring period. (1978.05.17 - 06.01)

Figures 8 and 9 show the concentration isolines in a vertical profile for section A and section B respectively during a typical spring period. The halocline level is indicated by a dashed line.

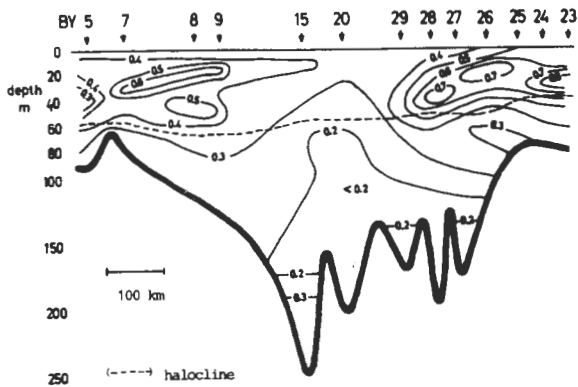


Figure 9.- Concentration of urea (μM) on Section B during a typical spring period. (1978.05.17 - 06.01)

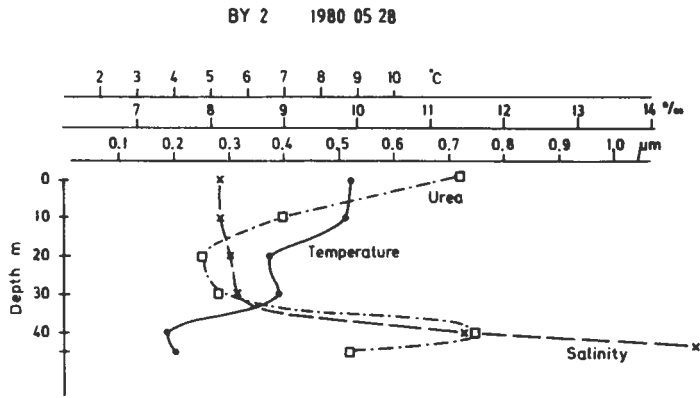


Figure 10.-

Vertical distribution of urea, salinity and temperature in station BY 2.

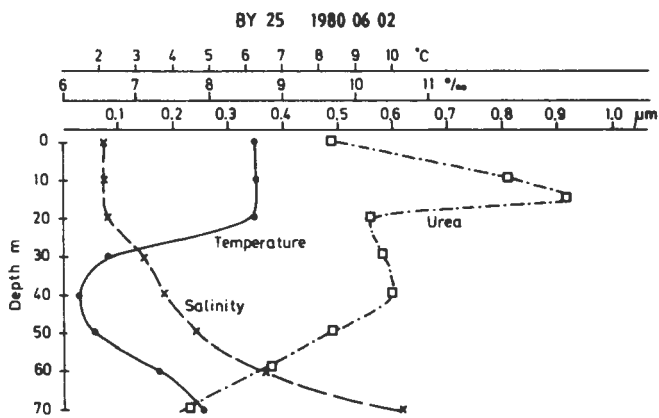


Figure 11.-

Vertical distribution of urea, salinity and temperature in station BY 25.

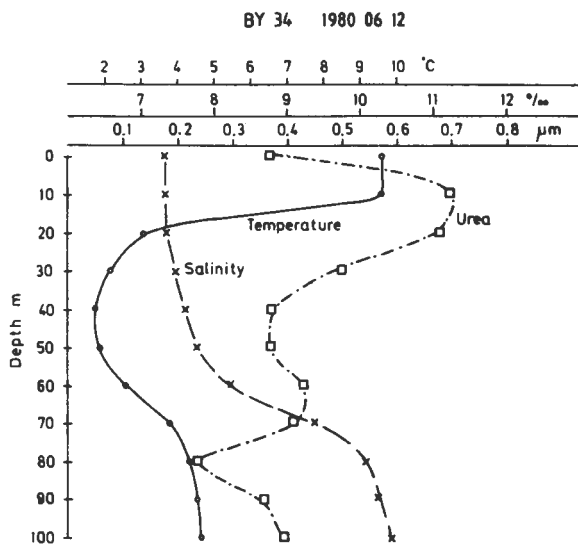


Figure 12.-

Vertical distribution of urea, salinity and temperature in station BY 34.

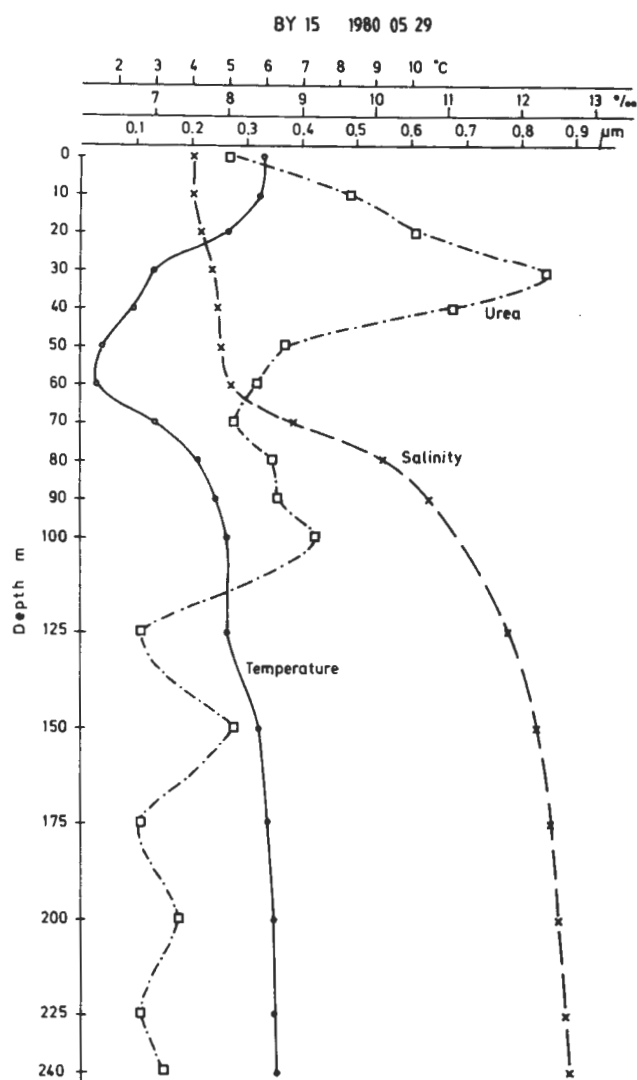


Figure 13.-

Vertical distribution of urea, salinity and temperature in station BY 15.

Figures 10 to 13 show different vertical distributions of the concentration of urea, salinity and temperature in four representative stations during the late spring of 1980. They exhibit that except for the Arkona Basin (BY 2) the levels of urea are notably higher above the halocline and lower just at the surface; below the halocline the concentrations fall down. The vertical distribution of urea at the Arkona Basin follow another pattern, high values at the surface and below the halocline. This pattern is characteristic for samples taken during May-June. The vertical profile concentrations of urea in all stations exhibit a definite dependence with the halocline levels, but there are not clear ones with the thermocline.

The results obtained during the period of investigation suggest that the high urea levels measured above the 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 the Öresund and the Kattegatt which represent influence from densely populated areas.

In the Baltic Sea the concentrations of 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. This becomes evident in figures 14 to 18 that show different vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, during five different samplings in the year 1978, at the Gotland Deep (BY 15). Specially figures 16 and 17, which correspond to the late spring and late summer respectively, show the important contribution that ammonium and urea do to the nitrogen reserve source, and on the other hand, the inverse correlation existing between them on the upper levels, i.e. above the halocline, possibly as a result of the hydrolysis of the urea to give ammonium and carbon dioxide (Dyrssen and Gundersen, 1976).

Figures 19 and 20, which correspond to the same samplings shown in the figures 16 and 17, show now the vertical distribution of the concentrations of the four parameters under consideration. In spite of the rather small contribution of the concentration of urea to the total nitrogen as compared with the nitrate one, it is significant in relative terms on the higher levels of water. Figures 16 and 17 show that in the euphotic zone, urea may reach up to 80 percent of the nutrient nitrogen available, since even if it is present mainly as excretion product it may be used as nitrogen reserve for phytoplankton so long as the other ones have become exhausted (Sörenson, 1987).

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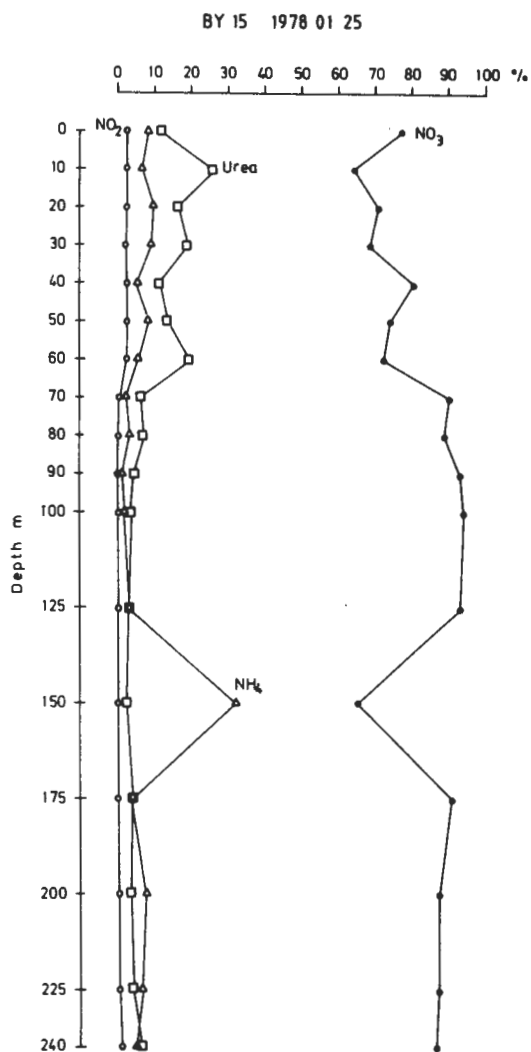
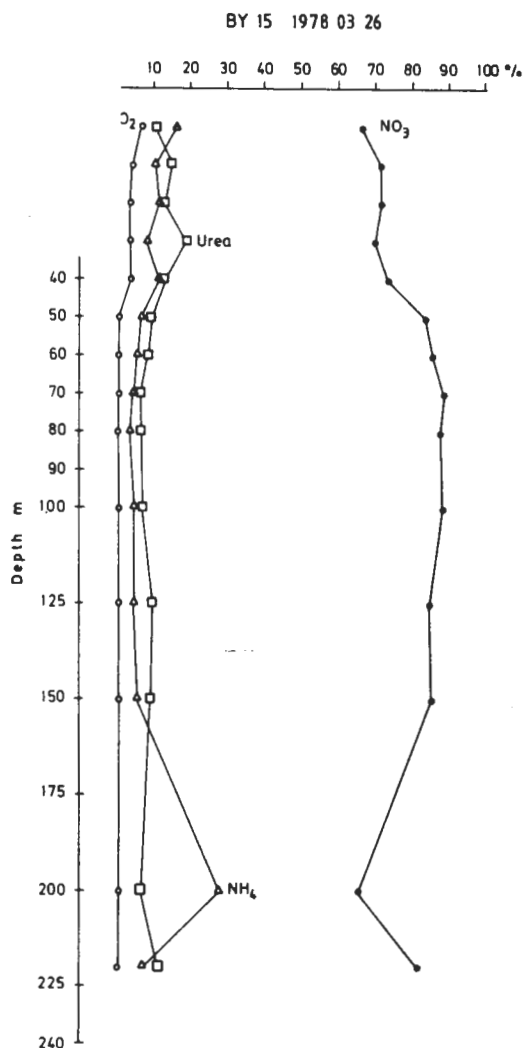


Figure 14.-

Vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, in station BY 15, on 1978.01.25.

Figure 15.-

Vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, in station BY 15, on 1978.03.26.



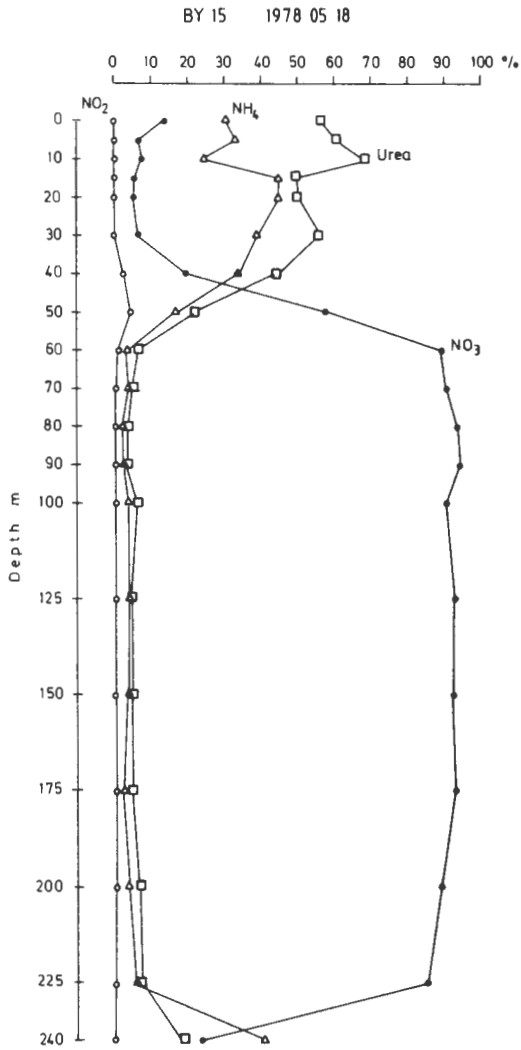
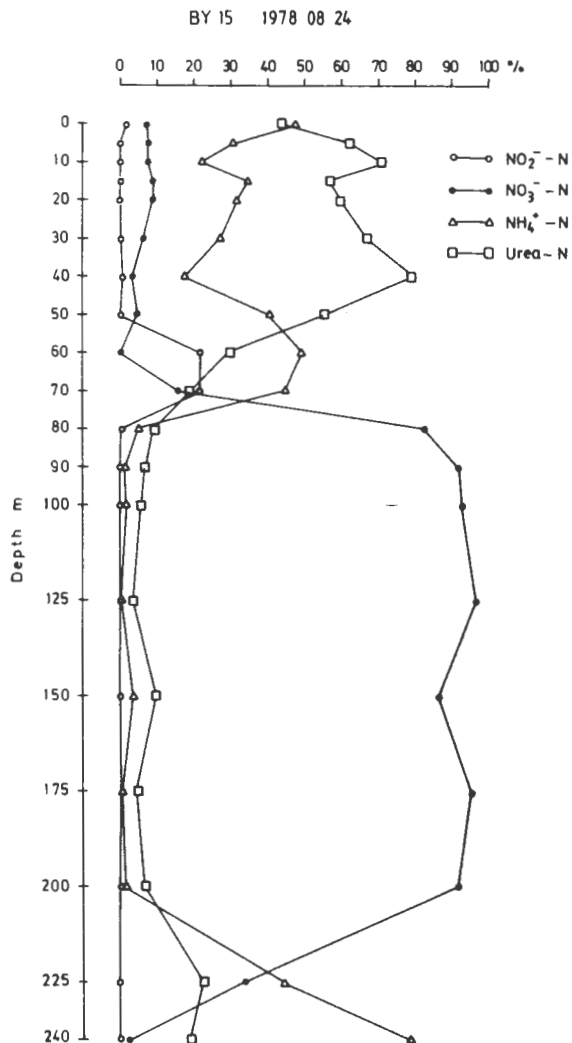


Figure 16.-

Vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, in station BY 15, on 1978.05.18.

Figure 17.-

Vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, in station BY 15, on 1978.08.24.



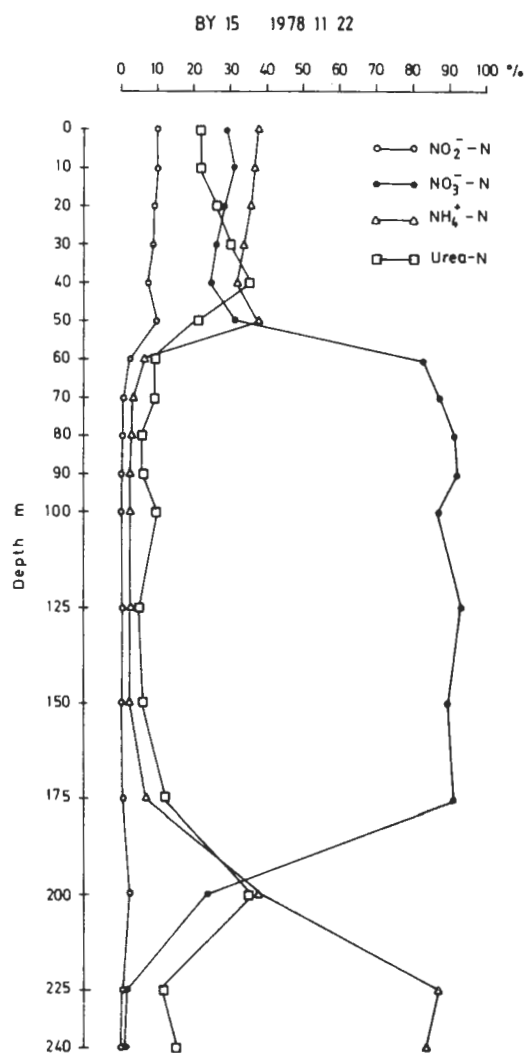


Figure 18.-

Vertical distribution of nitrite, nitrate, ammonium and urea (expressed as nitrogen) as a percentage of their total sum, in station BY 15, on 1978.11.22.

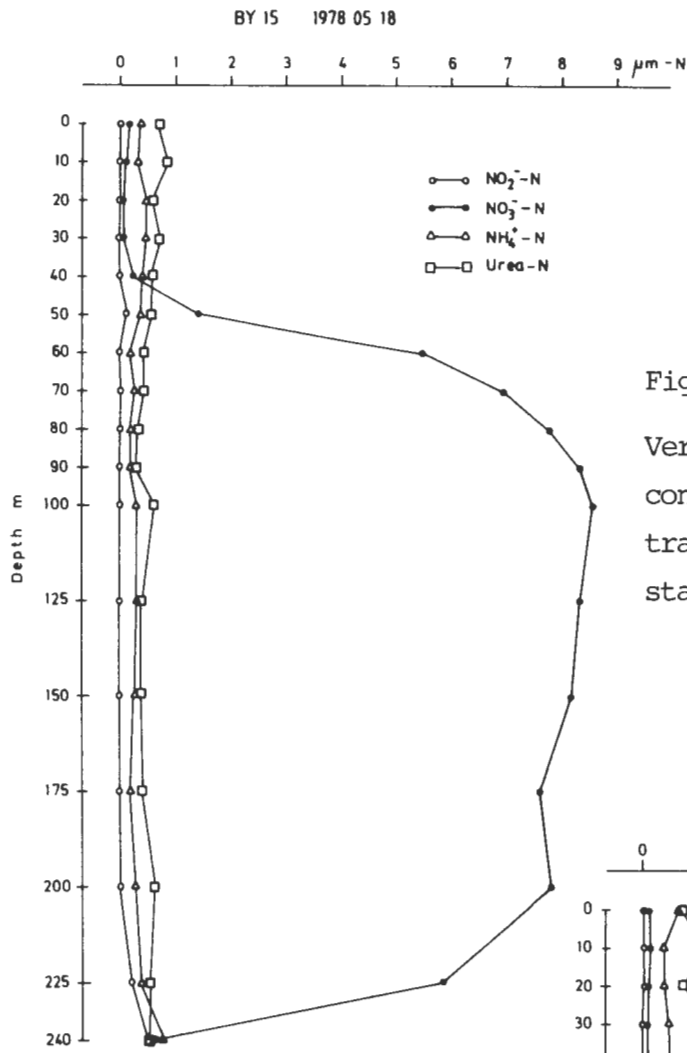
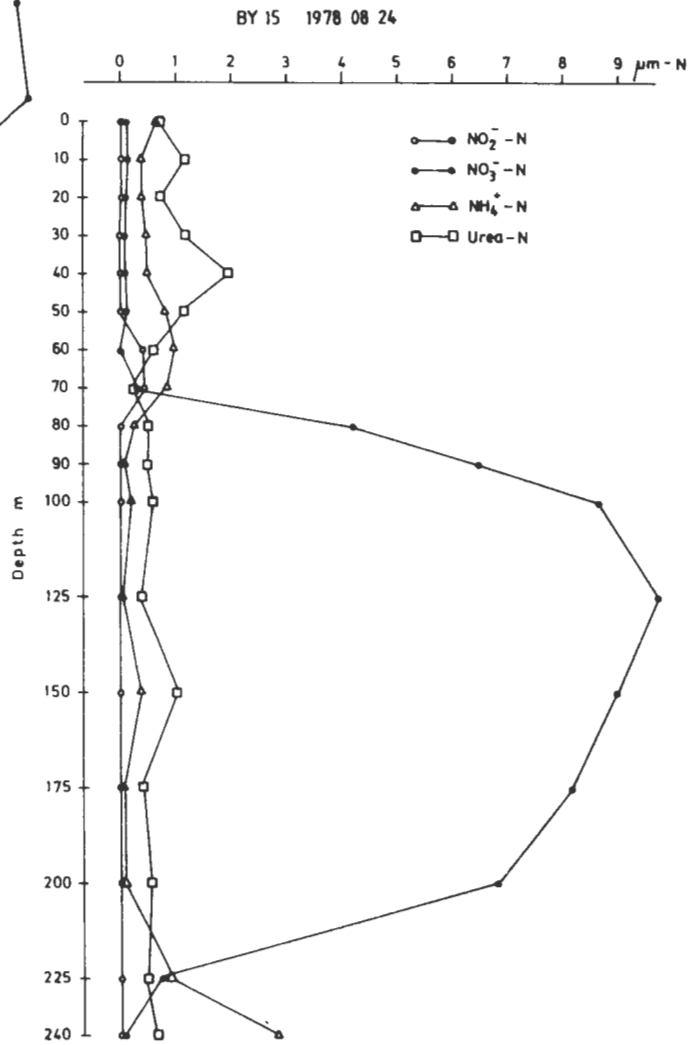


Figure 19.-
Vertical distribution of the concentrations of nitrite, nitrate, ammonium and urea in station BY 15, on 1978.05.18.

Figure 20.-
Vertical distribution of the concentrations of nitrite, nitrate, ammonium and urea in station BY 15, on 1978.08.24.



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