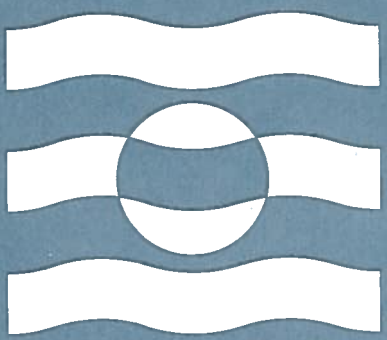
FINNISH MARINE RESEARCH

N:o 257

ISSN 0357-1076



ELIMINATION OF SEASONAL VARIATION FROM LONG-TERM CHANGES OF SOME NUTRIENTS IN THE BALTIC SEA
KIMMO K. KAHMA AND AARNO VOIPIO

LONG-TERM CHANGES IN THE NUTRIENT RESERVES AND PELAGIC PRODUCTION IN THE WESTERN GULF OF FINLAND
LARS GRÖNLUND AND JUHA-MARKKU LEPPÄNEN

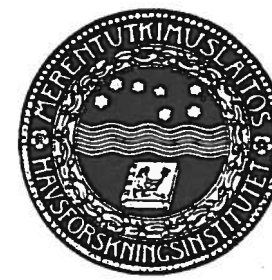
PROPOSAL FOR STANDARDIZATION OF THE WAY OF PRESENTING PHYTOPLANKTON RESULTS
GUY HÄLLFORS AND ÅKE NIEMI

INTERCOMPARISON OF THE MEASUREMENT OF CHLOROPHYLL *a* CONCENTRATION, PRIMARY PRODUCTION CAPACITY, AND PHYTO- AND ZOOPLANKTON ABUNDANCES DURING THE BALTIC SEA PATCHINESS EXPERIMENT (PEX'86)
JUHA-MARKKU LEPPÄNEN, KAISA KONONEN, GERDA BEHRENDS AND GESA HANSEN

PLUTONIUM ISOTOPE RATIOS IN BALTIC SEA SEDIMENTS
PER ÖSTLUND

HELSINKI 1990

FINNISH MARINE RESEARCH No. 257




ELIMINATION OF SEASONAL VARIATION FROM LONG-TERM CHANGES OF SOME NUTRIENTS IN THE BALTIC SEA

Kimmo K. Kahma and Aarno Voipio

LONG-TERM CHANGES IN THE NUTRIENT RESERVES AND PELAGIC PRODUCTION IN THE WESTERN GULF OF FINLAND

Lars Grönlund and Juha-Markku Leppänen

PROPOSAL FOR STANDARDIZATION OF THE WAY OF PRESENTING PHYTOPLANKTON RESULTS

Guy Hällfors and Åke Niemi

INTERCOMPARISON OF THE MEASUREMENT OF CHLOROPHYLL *a* CONCENTRATION, PRIMARY PRODUCTION CAPACITY, AND PHYTO- AND ZOOPLANKTON ABUNDANCES DURING THE BALTIC SEA PATCHINESS EXPERIMENT (PEX'86)

Juha-Markku Leppänen, Kaisa Kononen, Gerda Behrends and Gesa Hansen

PLUTONIUM ISOTOPE RATIOS IN BALTIC SEA SEDIMENTS

Per Östlund

Helsinki 1990

**Aarno Voipio**
**1928-1990**

Professor Aarno Voipio joined the Finnish Institute of Marine Research in 1957. He held the post of Director of the Institute in the years 1975-1990.

CONTENTS

Kimmo K. Kahma and Aarno Voipio: Elimination of seasonal variation from long-term changes of some nutrients in the Baltic Sea . . . . . 3

Lars Grönlund and Juha-Markku Leppänen: Long-term changes in the nutrient reserves and pelagic production in the western Gulf of Finland . . . . . 15

Guy Hällfors and Åke Niemi: Proposal for standardization of the way of presenting phytoplankton results . . . . . 29

Juha-Markku Leppänen, Kaisa Kononen, Gerda Behrends and Gesa Hansen: Intercomparison of the measurement of chlorophyll *a* concentration, primary production capacity, and phyto- and zooplankton abundances during the Baltic Sea Patchiness Experiment (PEX'86) . . . . . 37

Per Östlund: Plutonium isotope ratios in Baltic Sea sediments . . . . . 59

Finnish Marine Research No. 257 (1990):3-14

# ELIMINATION OF SEASONAL VARIATION FROM LONG-TERM CHANGES OF SOME NUTRIENTS IN THE BALTIC SEA

Kimmo K. Kahma and Aarno Voipio †

Finnish Institute of Marine Research
P.O. Box 33, SF-00931 Helsinki, Finland

## ABSTRACT

The seasonal variation in phosphate, total phosphorus and a nitrate-nitrogen levels was investigated using the Finnish observations from the years 1966-1987. Fourier analysis for irregularly timed data was used to determine the first two Fourier coefficients of the seasonal variation. By this method we were able estimate the long-term trends free from the spurious trend which is caused by the systematic changes in the observation times.

In the surface layer (0-10 m) none of the determinants showed any statistically significant long-term change in our analysis. For the layer above the halocline (0-50 m) the trends from our analysis were consistent with the trend reported previously for deep water below the halocline, and suggest no increase in phosphate, a marginal increase in total phosphorus and a clear increase of about 4 % per year in the nitrate-nitrogen concentrations.

Key words: Seasonal variation, irregularly spaced observations, Baltic Sea nutrients

## 1. INTRODUCTION

Various kinds of evidence, both direct and indirect, have been presented which appear to indicate that nutrient concentrations and the primary production in the Baltic Sea, especially in the Gulf of Finland, have changed during recent decades.

This evidence includes, inter alia, the high nutrient load (HELCOM, 1987a) and various reports on increased nutrient concentrations (Perttilä et al., 1980; HELCOM, 1987b) in the Gulf of Finland. There are also some observations of changes in the littoral areas in the Gulf of Finland (e.g. Kangas et al., 1982).

The growing interest in the pollution monitoring of the Baltic Sea has also resulted in more frequent monitoring cruises and a gradual increase in the part of the year covered by such cruises. However, relatively little attention has so far been paid to the details of the seasonal variation of the concentrations of nutrients, especially during the winter in the northernmost parts of the Baltic Sea. This has been at least partly caused by the difficulty and expense of oceanographic operations in ice-covered sea areas.

In the first attempts at this Institute to look at the effect of the seasonal variations on the analysis of long-term trends, data collected at different seasons were separated. The winter season was selected to be from October 15 to April 14, the two other periods reflected the spring bloom and the low summer production. The findings dealing with long-term nutrient concentrations in the Gulf of Finland were calculated from the unevenly distributed data representing the above-mentioned winter season. This kind of data analysis showed marked increasing trends in the nutrient levels (Perttilä et al., 1980; HELCOM, 1987b).

For various practical reasons it has been impossible to carry out samplings each year at exactly the same time, either corresponding to the same phase of the biological production cycle or even on the same calendar day (Fig. 1). Indeed, a consistent delay in sampling days can be found in the Finnish winter observations during the years 1973-1986; i.e. in the main part of the data used in the HELCOM assessment.

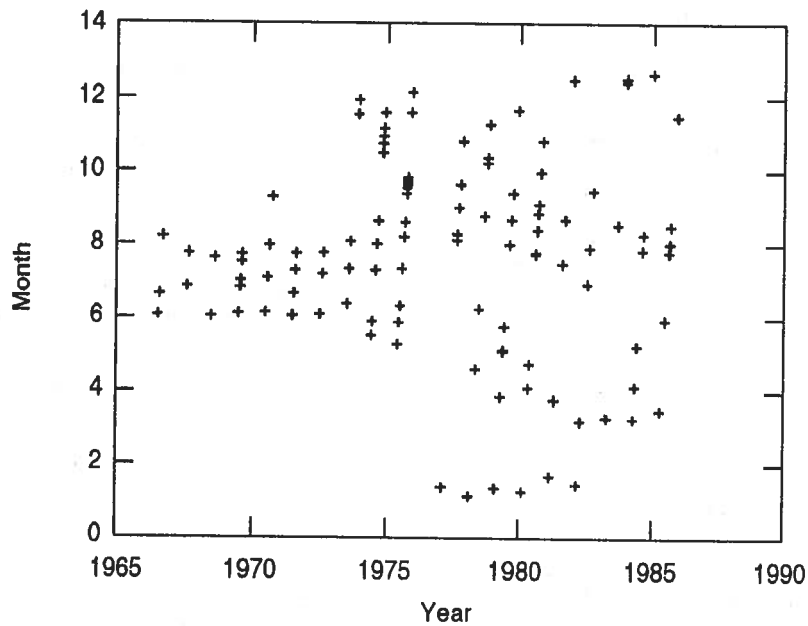



Fig. 1. The sampling time within the year at LL7.

This together with the amount of new nutrient data collected by the same institute and mainly by the same personnel gave us reason to study more closely the seasonal variation of some nutrients and to check whether the increase in nutrients in the Gulf of Finland has been as great as is sometimes assumed.

Part of the results given here have been reported by Voipio and Tervo at the bilateral Finnish-Soviet symposium in Tallinn, August 1988, and at the XVI Conference of the Baltic Oceanographers in Kiel, September 1988.

## 2. RESULTS

The experimental material consists of Finnish data collected during 1966-1986 from stations LL3, LL7, LL12 and LL17. The largest amount of data was available from station LL7, situated in the middle of the Gulf of Finland. Most of the conclusions therefore refer to the situation in that area.

All data referring to station LL7 surface layer above the thermocline (mean values, 0-10 m) and the layer above the halocline (mean values, 0-50 m) were plotted for each determinant against time, and against date disregarding the year. The latter plot gives the seasonal variation of each determinant. (Figs 2-6).

All the determinants show a consistent seasonal variation, not only during the rapid decrease in $PO_4$-P and $NO_3$-N concentrations caused by phytoplankton blooms after the disappearance of the ice cover, and when this vernal diatom bloom is followed by a fairly clear "steady state", but also during the autumn and winter when the nutrient levels increase. The scatter during the summer months reflects, to a great extent, the climatological variation and the succession of the plankton populations. In the surface layer the seasonal variation curve can be defined reasonably accurately even by eye, but in the layer 0-50 m the scatter is so large that an analytical method becomes a necessity.

The increase in the various determinants begins in September-October and continues until midwinter, February-March. This increase is caused by at least three factors: decomposition of biological material, thermal convection, and upwelling through the halocline. This slow increase without a clear "steady state" period around the maximum implies that samplings made at irregular dates can show artificial long-term trends. This phenomenon is closely related to the generation of spurious periodities by so-called aliasing.

In the earlier papers dealing with these long-term trends, all the data collected during the winter period mentioned were considered to form one homogeneous data set. This was the only possible conclusion that could have been drawn in earlier days because the data available was so scarce: the regularity of the seasonal cycle particularly in this season could not have been identified on the basis of these data.

Since the data is now sufficient to identify the details of the seasonal variation, we constructed functions describing the seasonal variation of the nutrients studied. In addition to the biological cycle of 12 months, a component of 6 months, evidently reflecting the thermal convection in spring and autumn, was visible when a Fourier analysis for irregularly spaced data was used. The mathematical procedure is explained in the Appendix.

Functions describing the seasonal variation were then calculated for several data sets representing $NO_3$-N, $PO_4$-P and total P mean concentrations at depths of 0-10 m and 0-50 m for stations LL7 and LL12. We have minimized the contribution of the near zero values which are typical for $NO_3$-N at the surface layer during the summer season.

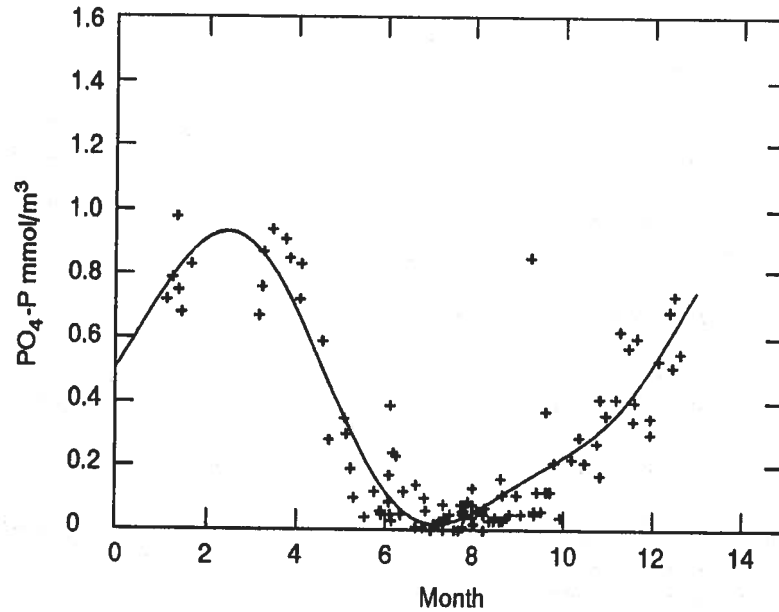



Fig. 2. The seasonal variation of $PO_4$-P in the surface layer 0-10 m at LL7. The seasonal variation function is based on components of 12 and 6 months.

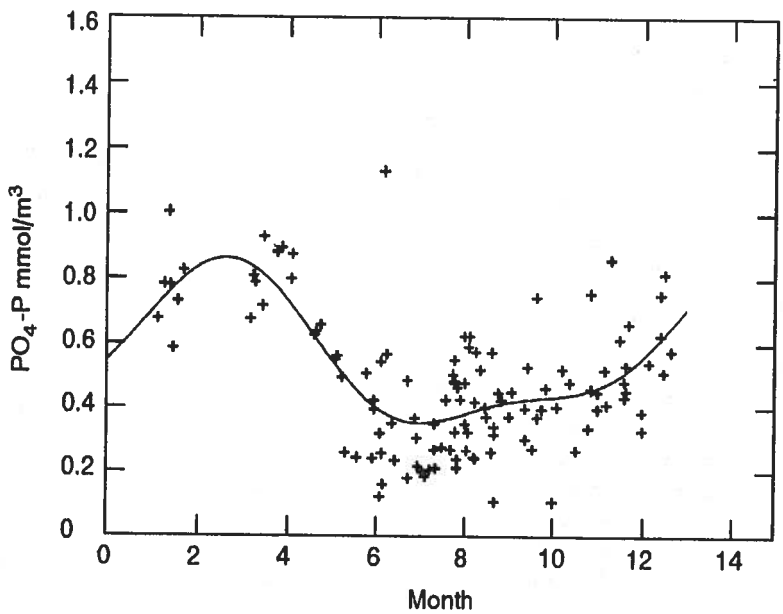



Fig. 3. The seasonal variation of $PO_4$-P in the layer 0-50 m at LL7. The seasonal variation function is based on components of 12 and 6 months.

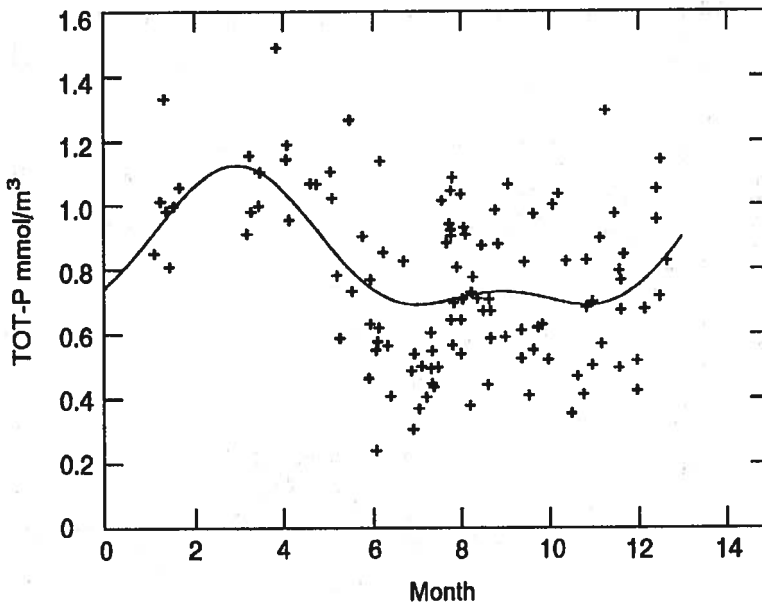



Fig. 4. The seasonal variation of tot-P in the layer 0-50 m at LL7. The seasonal variation function is based on components of 12 and 6 months.

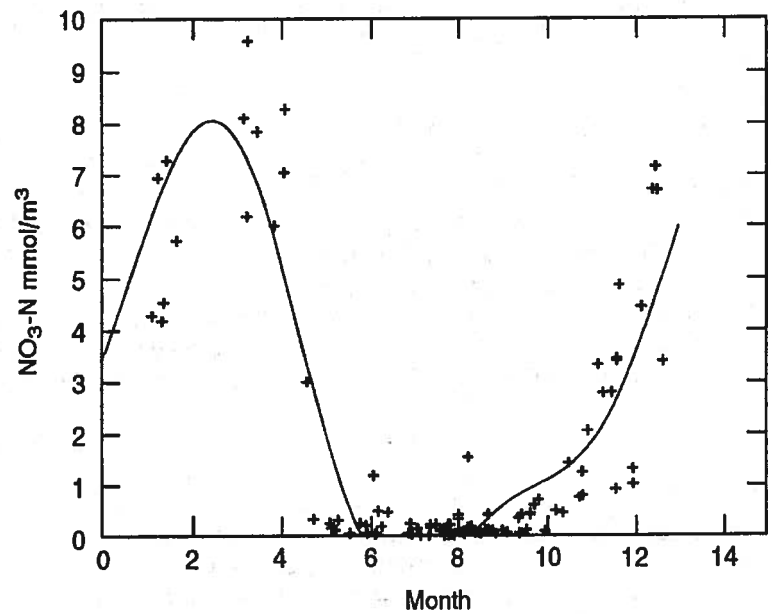



Fig. 5. The seasonal variation of $NO_3$-N in the surface layer 0-10 m at LL7. The seasonal variation function is based on components of 12 and 6 months.

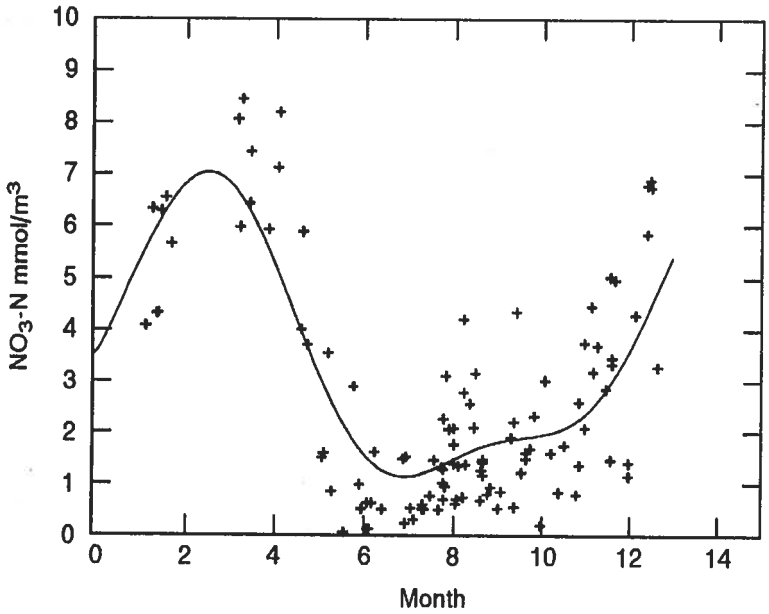



Fig. 6. The seasonal variation of $NO_3$-N in the layer 0-50 m at LL7. The seasonal variation function is based on components of 12 and 6 months.

Furthermore, a "residual concentration", which is regarded as free from most of the seasonal variation, was calculated by subtracting the seasonal variation function from the measured values of each sample. The residual concentrations were finally plotted against time together with the corresponding regression lines.

At station LL7, situated in the middle of the Gulf of Finland, no significant trend of the residuals was found in the $PO_4$-P concentrations in the layers 0-10 m and 0-50 m (Figs. 7 and 8). In the case of tot-P concentrations a small increase (ca. 1.5 % per year) at the 99.9 % confidence level was observed in the layer 0-50 m (Fig. 9). As regards the $NO_3$-N concentrations, no significant trend of residuals was found in the layer 0-10 m, while in the layer 0-50 m a clear increasing trend of ca. 3 % per year at 99.9 % confidence level was found (Figs. 10 and 11). When one ignores the data from the years before 1974 (when only summer samples were available), the trend in $NO_3$-N is found to be ca. 4 % per year.

These trends clearly show that the assumed increase of nutrients ($PO_4$, tot-P, $NO_3$) is not as unequivocal as the earlier results (Perttilä et al., 1980; HELCOM, 1987b) seem to indicate. In particular, at station LL7, from which we have the largest data set, we cannot find any support for the previously reported increasing trends in the surface layer (0-10 m): Eg. Perttilä et al. (1980) concluded that during 1962-1978 the increase in the total phosphorus concentration was 40 % and that of nitrogen 15 % in the surface layer. HELCOM (1987b) correspondingly reports for the years 1967-1983 an approximately 5 % increase per year in $PO_4$-P, tot-P and $NO_3$-N in the surface layer.

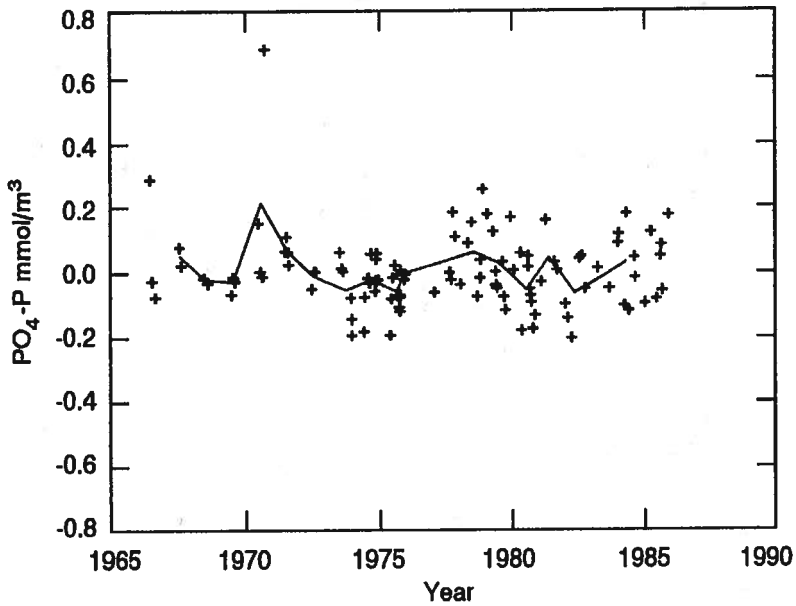



Fig. 7. $PO_4$-P residual in the layer 0-10 m at LL7 Solid line: annual averages. No statistically significant trend.

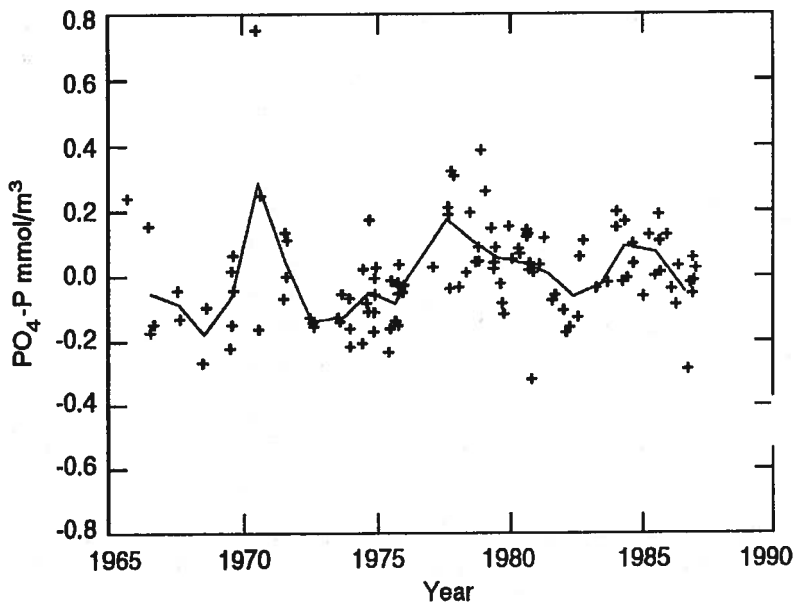



Fig. 8. $PO_4$-P residual in the layer 0-50 m at LL7 Solid line: annual averages. No statistically significant trend.

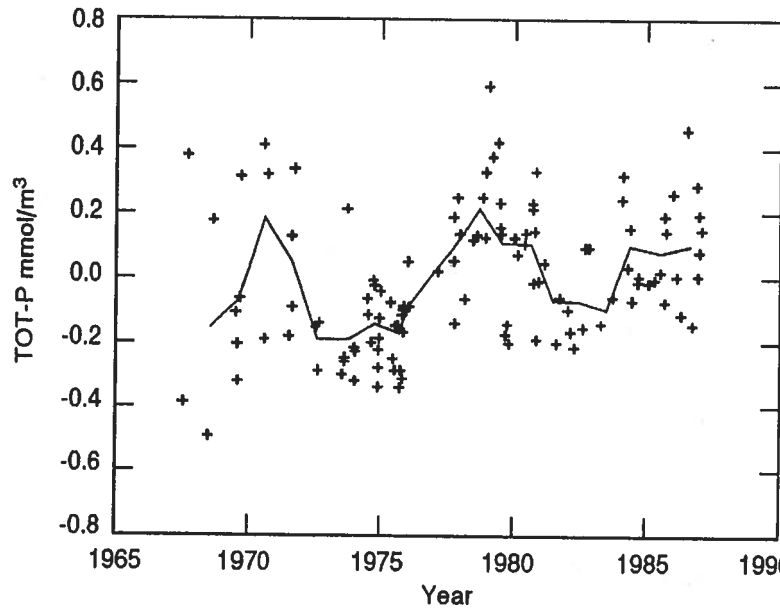



Fig. 9. tot-P residual in the layer 0-50 m at LL7 Solid line: annual averages. Trend: ca. 1.4 % per year.

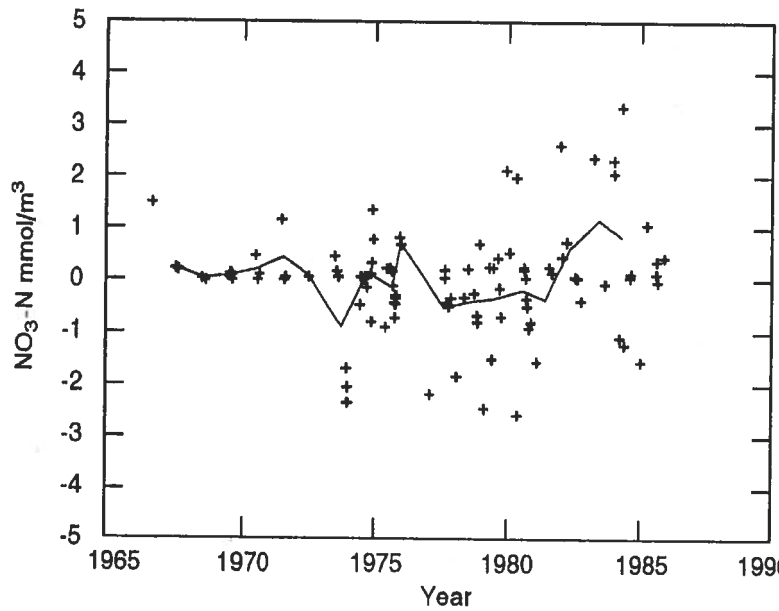



Fig. 10. $NO_3$-N residual in the layer 0-10 m at LL7 Solid line: annual averages. No statistically significant trend.

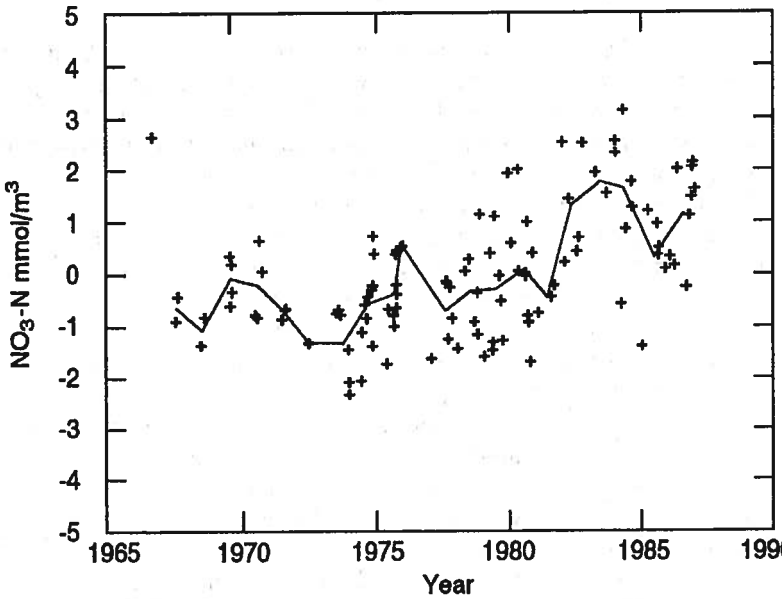



Fig. 11. $NO_3$-N residual in the layer 0-50 m at LL7 Solid line: annual averages. Trend: ca. 3 % per year.

On the other hand, the trends in the layer 0-50 m agree reasonably well with the previously reported trends in deep water below halocline where eg. Perttilä et al. (1980) report no trend for phosphors, while the nitrogen trend is increasing. The explanation why these results agree is probably the following: The mean concentration in the layer 0-50 m is strongly influenced by the concentration at 50 m, which in turn seems to be correlated with the concentration below the halocline. Because the seasonal cycle of nutrients in deep water is different than on the surface, irregular sampling time does not result in the same bias in that data as it does at the surface.

For the other stations in the Gulf of Finland the amount of data was too small for any definite conclusions. However, the shape of the curves was rather similar in all the stations in the Gulf of Finland and in the Northern Baltic, the seasonal variation being smaller in the west than in the middle of the Gulf of Finland. For instance, at station LL12 the $PO_4$-P concentration in the surface layer actually shows a decreasing trend, while tot-P shows an annual increase of ca. 2 % and $NO_3$-N an annual increase of ca. 4 %.

## 3. CONCLUDING REMARKS

The method can be used only when there is sufficient data collected during one year, or preferably during two years, representing the beginning and end phases of the study period, to confirm the shape of the seasonal variation function. Otherwise it is possible to get errors analogous to the cases where the seasonal variation is omitted. In other words, the method requires that the shape of the seasonal variation function does not change substantially with time. The average may vary from year to year, but otherwise the shape has to remain fixed. This assumption is not a critical one, however, because the error introduced by a change in the real seasonal variation is proportional to the difference between the real and the assumed (fixed) seasonal variation function. Therefore, as long as the change in seasonal variation is less than the variation itself, the method still generally reduces the errors in the trend estimates. Particularly in our data, the change in the seasonal variation in the accepted stations was determined to be small, and this source of error therefore clearly is negligible compared with the error which is introduced by the limited accuracy of the seasonal variation function itself. This latter source of error is discussed in more detail in the Appendix.

The above findings once more highlight the importance, for efficient monitoring of the Baltic, of increasing our knowledge about the basic factors which control the processes taking place in sea water. They also indicate that it might be possible to decrease the annual sampling frequency in general, if the seasonal variation function is checked from time to time and the sampling is done around the winter maximum.

## Appendix

The method for approximating the seasonal variation function.

Because seasonal variation has, by definition, a fundamental cycle of one year, it is natural to use a Fourier series as the approximating function. Standard Fourier analysis cannot be applied when the data is irregularly spaced. However, it is possible to use the well known method in which the Fourier coefficients are determined by minimizing the error between the Fourier series and the observations in the least squares sense. This method leads to the standard equations of Fourier analysis if the data is regularly spaced.

Mathematically, this means applying standard multidimensional regression analysis to the equation

$$y_i = \sum_j c_j f_j(x_i) + e_i$$

or, in matrix notation,

$$Y = C\,F + E$$

where $Y = [y_1, y_2 .. y_n]$ is the vector of observations, $E$ is the vector of errors and, in this application,

$$F = \begin{bmatrix} \cos mx_1 & \cos mx_2 & \dots \cos mx_n \\ \sin mx_1 & \sin mx_2 & \dots \sin mx_n \\ \cos(m-1)x_1 & \cos(m-1)x_2 & \dots \cos(m-1)x_n \\ \sin(m-1)x_1 & \sin(m-1)x_2 & \dots \sin(m-1)x_n \\ & & \vdots \\ \cos x_1 & \cos x_2 & \dots \cos x_n \\ \sin x_1 & \sin x_2 & \dots \sin x_n \\ 1 & 1 & \dots 1 \end{bmatrix}.$$

Here $x_i = 2\pi t_i / L$ where $t_i$ is the time of the observation $y_i$, and $L$ is the length of the fundamental cycle, which in our analysis is one year.

The Fourier coefficients $C = [a_m, b_m \dots a_1, b_1, a_0]$ can then be solved in the least squares sense by solving the matrix equation (see eg. Lawson & Hanson 1974)

$$C F F^T = Y F^T,$$

where $F^T$ is the transpose of $F$.

The seasonal variation function is then $f(x) = \sum_{j=1}^{m} c_j f_j(x)$, and the "residual concentration" is $y_i - f(x_i)$. If all the data is used to determine the seasonal variation function $f$, the residual is the error $e_i$.

In the case of $NO_3$-N we did not try to reproduce by the Fourier series the flat zero part of the cycle, which characterizes the summer data in the top 0-10 m layer. Instead, we ignored this part of the data and let the sum of the Fourier series dip below zero concentration in summer. The final seasonal variation function was defined as the maximum of zero and the sum of the Fourier series.

It is important to note that $L$ is one year and not the length of the whole time series. Therefore f is not the Fourier series of the whole time series.

Certain precautions are necessary when seasonal variations are subtracted to study long-term variations. The number of observations must be much larger than the number of estimated Fourier coefficients, and the data should cover sufficiently evenly every part of the year during the whole observation period. Otherwise the function, which should represent the seasonal variations only, may absorb some of the long-term variations also. This error is in fact analogous to the mistake which is introduced when the seasonal variation is ignored.

To illustrate this problem, let us assume that only summer observations were made in the beginning and only winter observations in the end of the period under study. For the purpose of this example we assume further that the nutrient levels have increased. When the seasonal variation function is determined from the data, it will in the winter season be as high as the data is

in the end and in the summer season as low as the data is in the beginning. The residual would then show no trend.

Similarly, if there are too few data points compared with the Fourier coefficients, the seasonal variation function is no longer close to the average of the observation points nearby, but has a complicated structure attempting to go near each individual point. Again, a real trend will not show up in the residual.

To avoid these errors we used only the annual and semiannual cycles in the Fourier series ($m=2$ in the equations above). The seasonal distributions of the observation times were analyzed, and because they were not sufficiently uniform (there were no winter observations in the beginning) the seasonal variation functions were compared with the data from one single year which had the best seasonal coverage. The results were statistically consistent. Only those stations were accepted for which there were enough data to make this comparison reliable.

To determine how much of the long-term trend was absorbed by the seasonal variation function, an artificial trend was added to the data. The analysis showed that more than 70 % of the artificial trend was visible in the residuals. We then subtracted a trend from the original data until the analysis showed no trend in the residuals. This subtracted trend $T(t)$ was considered to be the best estimate of the real trend in the data. Finally a corrected seasonal variation function was calculated from $y_i$-$T(t_i)$. When this corrected seasonal variation function was used, the residuals e (Figs. 7-11) had the trend $T(t)$.

The steps above seem sufficient to recover the true trend in this data. We want to emphasize, however, that the method should not be used with insufficient data or when the seasonal variation function changes substantially. An uncritical use of the method can easily lead to conclusions that are equally incorrect as those obtained when the seasonal variation is ignored.

REFERENCES

Baltic Marine Environment Protection Commission - Helsinki Commission 1987a: First Baltic Sea pollution load compilation. - Baltic Sea Environment Proceedings 20:1-56.

- " - 1987b: First periodic assessment of the state of the marine environment of the Baltic Sea area, 1980-1985; background document. - Baltic Sea Environment Proceedings 17 B:1-351.

Kangas, P., Autio, H., Hällfors, G., Luther, H., Niemi, Å. & Salomaa, H. 1982: A general model of the decline of Fucus vesiculosus at Tvärminne, south coast of Finland in 1977-81. - Acta Botanica Fennica 118:1-27.

Lawson, C.L., Hanson, R.J. 1974: Solving Least Squares Problems. - Prentice-Hall.

Perttilä, M., Tulkki, P. & Pietikäinen, S. 1980: Mean values and trends of hydrographical and chemical properties in the Gulf of Finland 1962-1978. - Finnish Mar. Res. 247:38-50.

Finnish Marine Research 257 (1990):15-27

# LONG-TERM CHANGES IN THE NUTRIENT RESERVES AND PELAGIC PRODUCTION IN THE WESTERN GULF OF FINLAND

Lars Grönlund and Juha-Markku Leppänen

Finnish Institute of Marine Research
P.O. Box 33
SF-00931 Helsinki, Finland.

## ABSTRACT

Long-term data on total phosphorus, total nitrogen, chlorophyll *a*, and daily primary production collected by the Finnish Institute of Marine Research at a coastal site and an adjacent open sea area in the western Gulf of Finland, the Baltic Sea, are evaluated in order to determine whether changes in nutrient reserves and phytoplankton productivity occurred during the period 1968-1988. The peaks of the vernal phytoplankton blooms have become more intensified as a result of the increase in nutrient reserves, but no increase was detected in phytoplankton summer production.

Key words: Long-term changes, total phosphorus, total nitrogen, chlorophyll *a*, primary production, eutrophication, Gulf of Finland, Baltic Sea

## 1. INTRODUCTION

The Gulf of Finland is directly connected to the northern Baltic Proper, and thus the Baltic deep water, rich in phosphorus, is able to flow freely into the area from the west. The Gulf of Finland is affected by both landbased and atmospheric pollution (HELCOM, 1987). Most of the landbased load is discharged into the eastern part of the Gulf of Finland (Pitkänen et al., 1987), but varying degrees of eutrophication have been reported along the coasts (Hällfors et al., 1987; Niemi & Åström, 1987; Järvekülg et al., 1988; Kononen, 1988; Pesonen, 1988).

The aim of this paper is to evaluate the long-term data collected by the Finnish Institute of Marine Research at a coastal site and in an adjacent open sea area of the western Gulf of Finland in order to determine whether changes in nutrient concentrations and phytoplankton productivity occurred during the period 1968-1988.

## 2. MATERIAL AND METHODS

Hydrography, nutrients, chlorophyll *a* and phytoplankton primary production have been measured since 1972 in the sea area off Tvärminne archipelago, at the entrance to the Gulf of Finland. The location of the sampling station was changed in 1976 to a point ca. 5 km closer to the coast (Fig. 1, Stations 1a and 1b). According to Laakkonen et al. (1981), both sampling stations represent the same water masses.

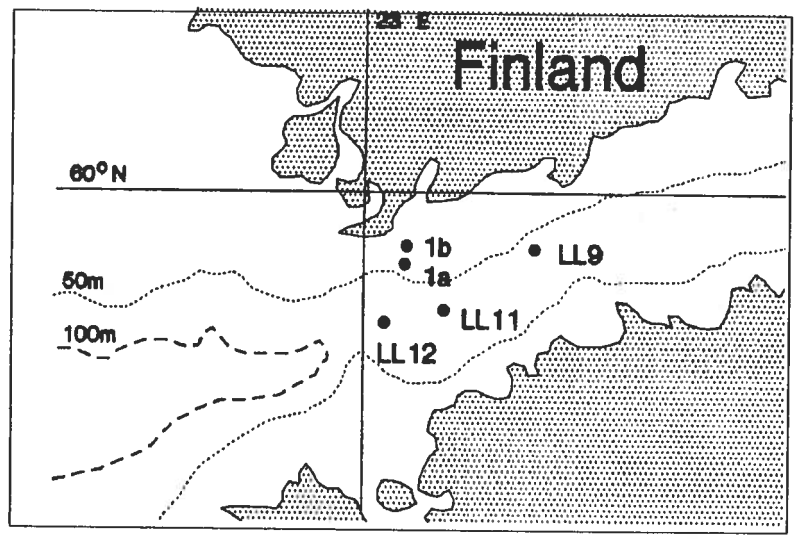



Fig. 1. The locations of the sampling stations. Stations 1a and 1b refer to Tvärminne.

Sampling at stations LL9-LL12 (Fig. 1) in the open western Gulf of Finland, started in 1968. The total number of observations during the period 1972-1988 in the coastal area was ca. 290 for total nutrients, chlorophyll *a* and primary production. The numbers of observation in the open sea area in 1968-1987 were ca. 215 and 178 for total nutrients and chlorophyll *a*, respectively.

Winter sampling has been sparse and irregular, most of the sampling being done during the ice-free period. The data analysis in the following is therefore concentrated on the growing season: in the coastal waters between March and November, and in the open sea between June and September. Attention is restricted to total phosphorus and nitrogen, chlorophyll *a* and daily primary production. The analysis methods of Koroleff (1979) have been used for total phosphorus and nitrogen. The samples for daily primary production were incubated *in situ* for 24 hours as described by Lassig & Niemi (1972). Chlorophyll *a* was determined spectrophotometrically up until 1978 (Niemi et al., 1970), and since then fluorometrically as described in Edler (1979). The slight modifications of the methods have not affected the results. Depth-balanced, integrated average values from 0-10 m were used in the data processing. In order to better illustrate the data (Figs. 3, 4 and 5) annual monthly means were used instead of single values. This was possible because the annual sampling frequency has not changed to any marked extent.

# 3. RESULTS

## 3.1. Coastal area

The seasonal succession of the measured parameters remained similar during 1972-1988. The values for total phosphorus and nitrogen showed an increasing trend (Fig. 2). This tendency was seen throughout the growing season (Fig. 3). The total concentrations of nitrogen and phosphorus in the euphotic layer increased during the observation period by ca. 4.2 and 0.3 mmol*m$^{-3}$, respectively. The vernal concentrations of chlorophyll *a* showed an increase after 1983, while the summer concentrations remained at the same level (Fig. 4). The values for daily primary production behaved more irregularly (Fig. 5), and the annual production values fluctuated markedly (Fig. 6). The increase in total nutrient concentration is clearly indicated by the shift in the

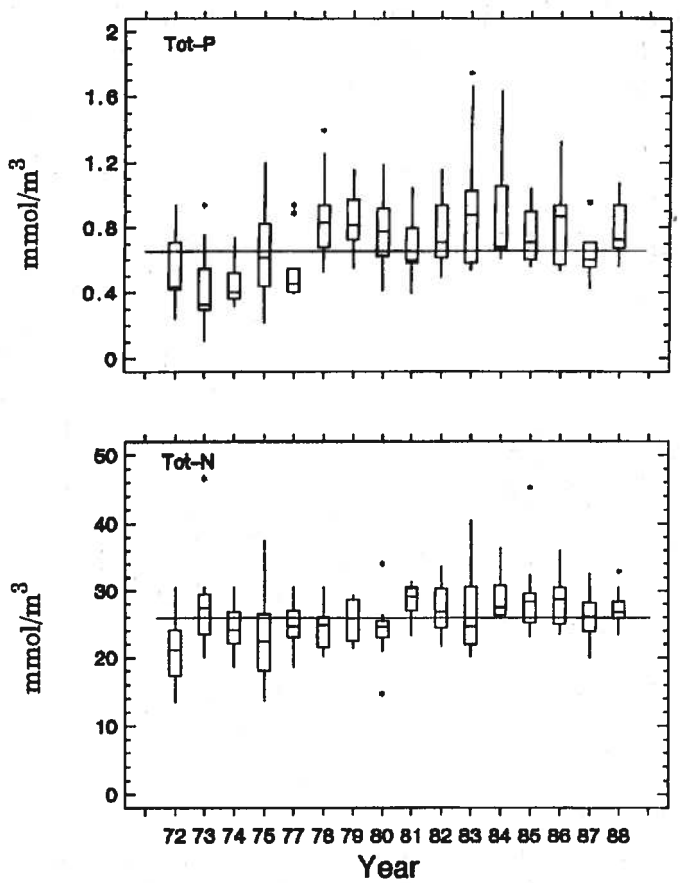



Fig. 2. The annual distribution of total phosphorus and nitrogen in a 0-10 m water layer off Tvärminne archipelago between March and November during 1972-1988. The central box covers the middle 50 % of the data values, between the upper and lower quartiles of the respective year. The 'whiskers' extend to the minimum and maximum values, and the central line is at the median of the annual values. Extreme values are plotted as separate points. The horizontal line represents the median for all the years. (Note that there are no data from 1976!).

frequency distribution of the concentrations between the beginning and the end of the observation period (Fig. 7). According to the t-statistics this increase was significant for nitrogen at the 2.5 % level and for phosphorus at the 0.1 % level.

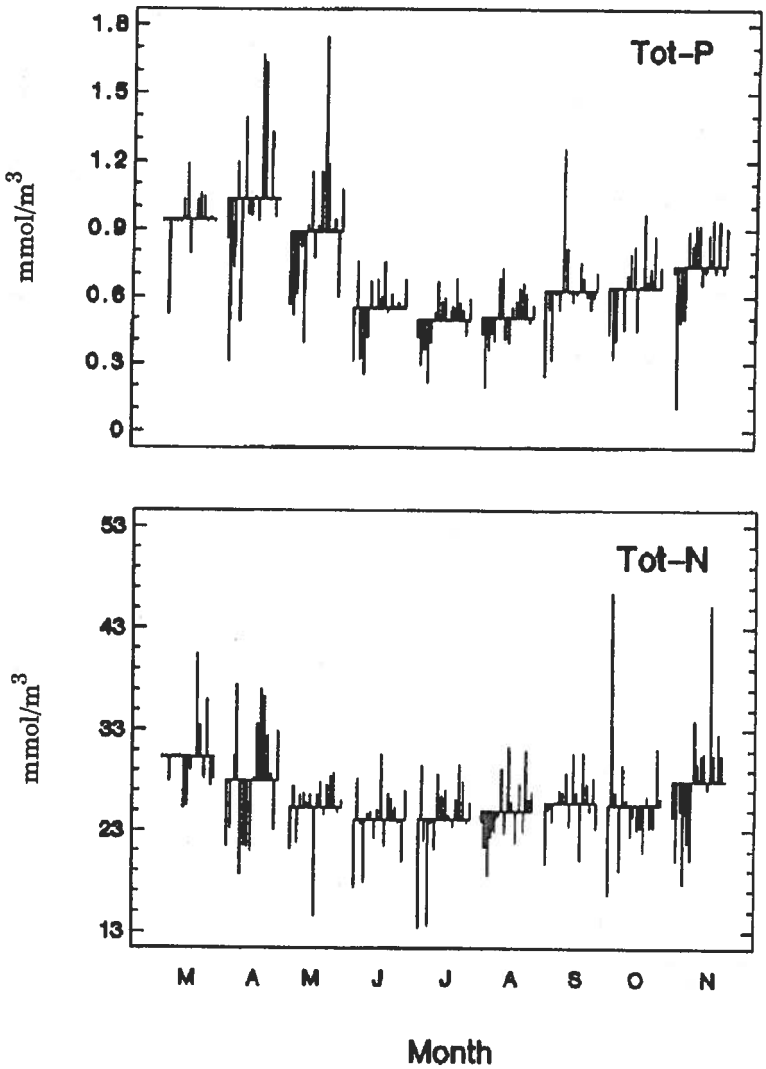



Fig. 3. The concentrations of total phosphorus and total nitrogen grouped by month. The horizontal lines represent the monthly average for the months March-November during the period 1972-1988. Each vertical line represents one year and is plotted from the long-term average to the monthly mean concentrations of the respective year.

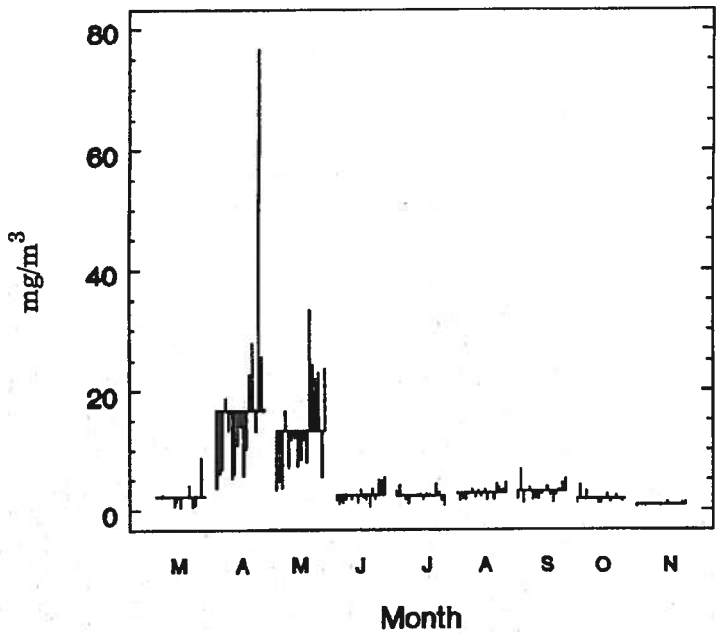



Fig. 4. The concentrations of chlorophyll *a* grouped by month. Horizontal lines represent the monthly average values of the observations for all the years during the period March-November in 1972-1988. Each vertical line represents one year and is plotted from the long-term average to the monthly mean concentrations of the respective year.

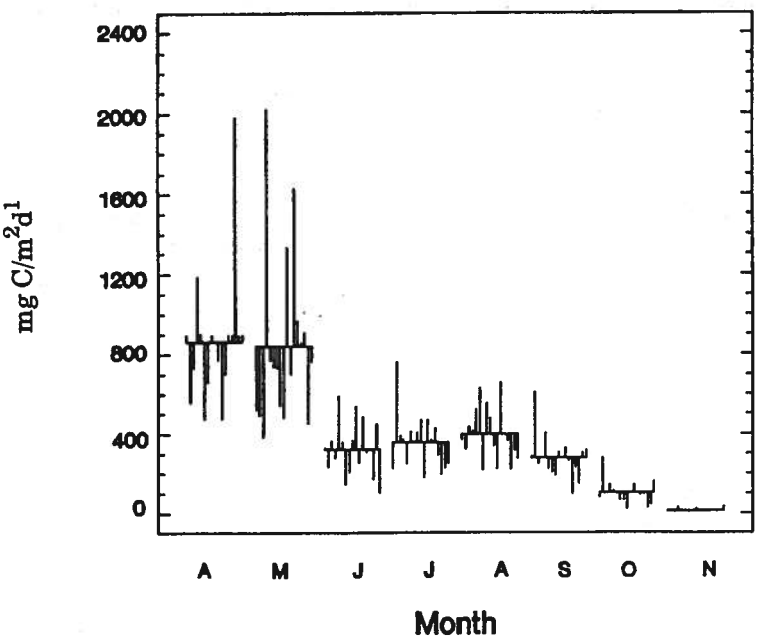



Fig. 5. The daily primary production (mg C $m^{-2}d^{-1}$) values grouped by month. Horizontal lines represent the average values of the observations for all the years during the period 1972-1988. Each vertical line represents one year and is plotted from the long-term average to the monthly mean concentrations of the respective year.

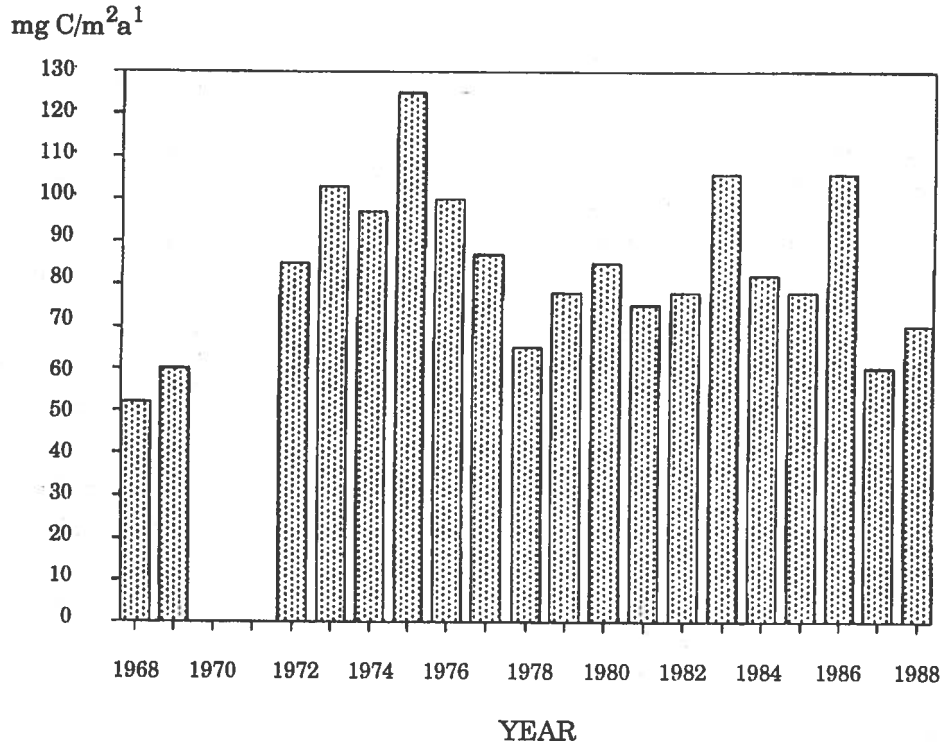



Fig. 6. The annual primary production (mg C $m^{-2}$ $a^{-1}$) during 1968-1988 in the Tvärminne archipelago. The vales for 1968 and 1969 are adapted from Niemi (1975).

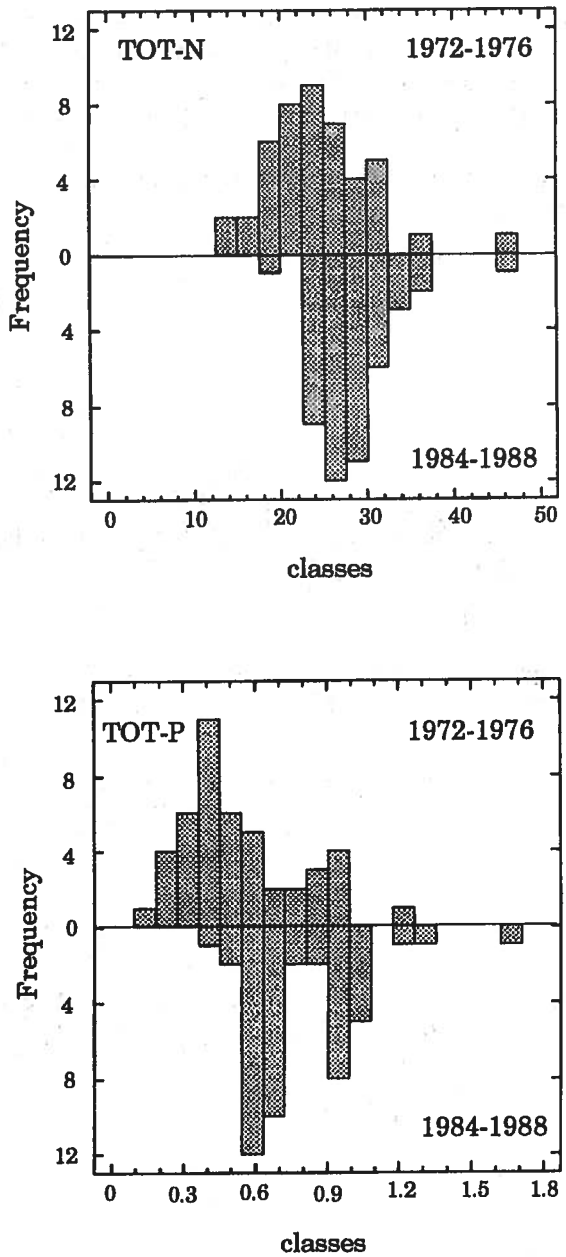



Fig. 7. Frequency histogram for total nitrogen and total phosphorus. The bars above the horizontal line represent the first 5 years of the investigation period and the bars below show the last 5 years of the period 1972-1988.

### 3.2. Open sea

The values for total phosphorus and nitrogen showed an increasing trend similar to that for the coastal waters (Fig. 8). This is clearly indicated by the shift in the frequency distribution of the concentrations between the beginning

and the end of the observation period (Fig. 9). According to the t-statistics this increase was significant for both nitrogen and phosphorus at the 0.1 % level. No increase in the chlorophyll *a* values was detected; the measurements were made only during the summer period (Fig. 10).

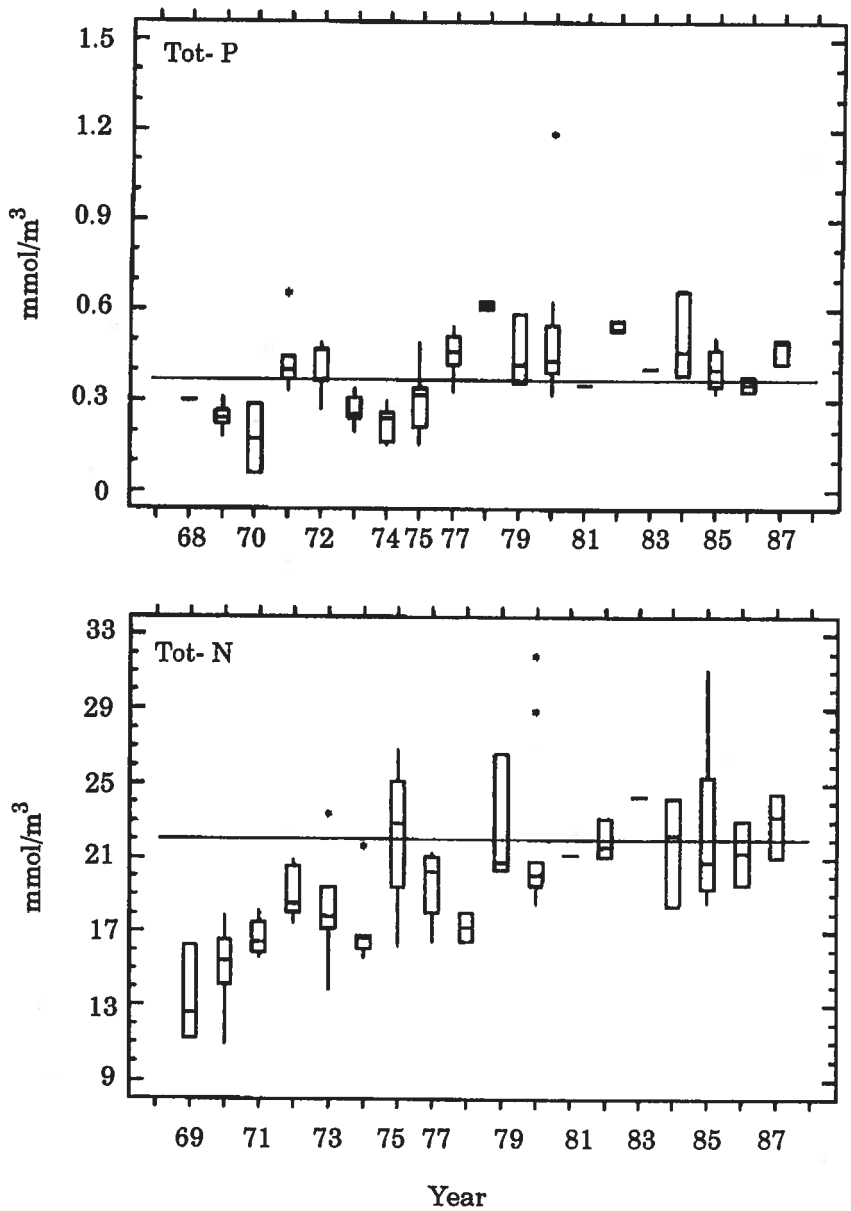



Fig. 8. The annual distribution of total phosphorus and total nitrogen in a 0-10 m water layer in the open western Gulf of Finland between June and September in 1968-1987. The central box covers the middle 50 % of the data values, between the upper and lower quartiles. The 'whiskers' extend to the minimum and maximum values, and the central line is at the median of the annual values. Extreme values are plotted as separate points. (Note that there are no data from 1976 and that tot-P begins from the year 1968 while tot-N begins from 1969!)

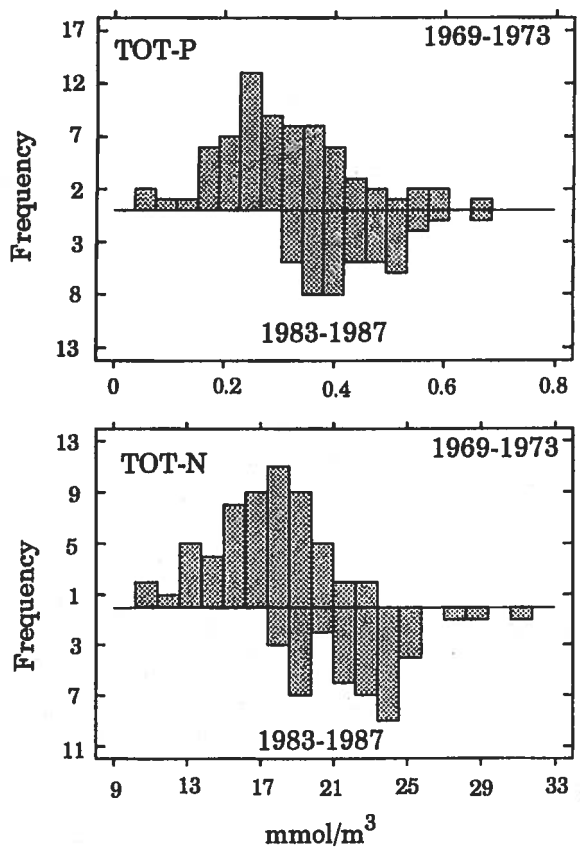



Fig. 9. Comparison of frequency histograms for total phosphorus and total nitrogen concentrations during 1969-1973 and 1983-1987 in the open western Gulf of Finland during the summer months (June-September).

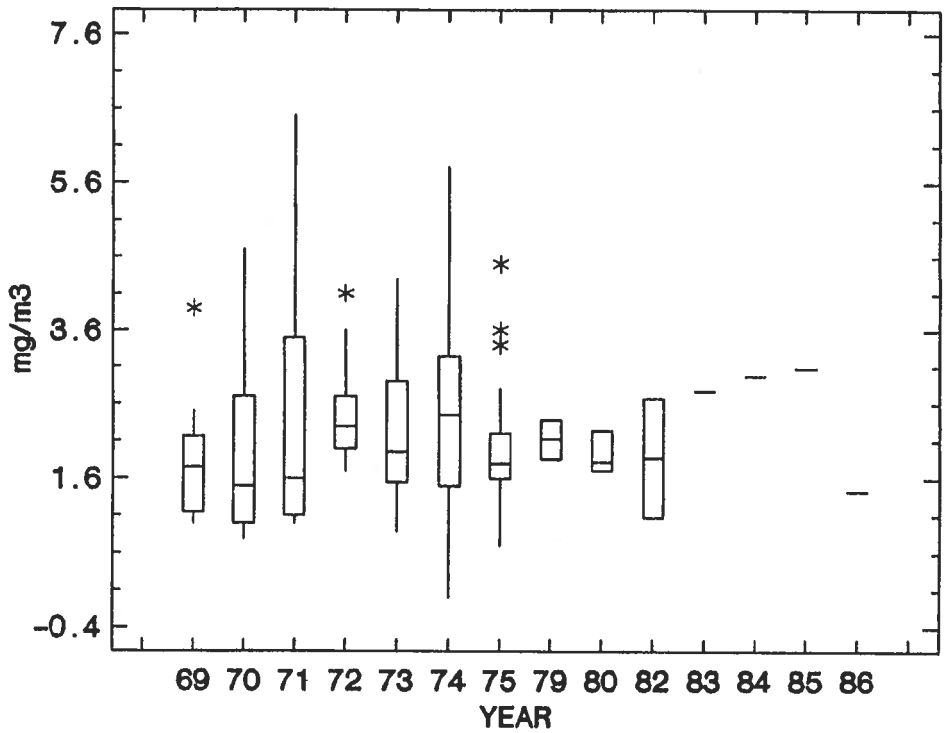



Fig. 10. The annual distribution of chlorophyll *a* concentrations in a 0-10 m water layer in the open western Gulf of Finland between June and September in 1969-1986. The central box covers the middle 50 % of the data values, between the upper and lower quartiles. The 'whiskers' extend to the minimum and maximum values, and the central line is at the median of the annual values. Extreme values are plotted as separate points. The years 1983-1986 consist of single values. (Note the lack of data for the years 1976-1978!)

## 4. DISCUSSION

An increase in nutrient concentrations, enhanced plankton production, depletion of oxygen in deep waters, changes in the composition of the plankton communities, and intensified plankton blooms which are often found to be toxic, have been reported especially in the Southern Baltic Sea and in several coastal areas (Kangas et al., 1982; Yurkovski & Khozioski, 1982; Kononen & Niemi, 1984, 1986; Persson et al., 1984; Nehring, 1985; Ciszewski & Zmudzinski, 1986; Ilus & Keskilato, 1987; Pitkänen et al., 1987; Gerlach, 1988; Järvekülg et al., 1988; Kononen, 1988; Sivonen et al., 1989 and HELCOM, 1990). Changes in the phytoplankton species composition related to the increase in total phosphorus have been reported from the coastal site of this study by Kononen (1988). Increasing phosphorus trends, corresponding to this study area, have been reported from the open Gulf of Finland by HELCOM (1987) and Kahma & Voipio (1989).

An increase in the total nutrient reserves was evident in both the coastal and adjacent open sea areas. The coastal chlorophyll data substantiates the increase in the phytoplankton spring bloom biomass. The decrease or depletion

in the reserves of reactive silicate in the euphotic layer after the spring bloom (Niemi & Åström, 1987), which is a relatively recent observation, indicates enhanced diatom production at that time, too.

The sparsity of spring chlorophyll *a* observations in the adjacent open sea area does not permit verification of any trend. High chlorophyll *a* concentrations, like the values measured in the coastal area of this study, have, however, been observed in the open northern Baltic Proper in 1982 (Leppänen & Kononen, 1988) and in the whole open Gulf of Finland in 1990 (unpublished data of the Finnish Institute of Marine Research). This, and the similar development of the nutrient reserves, indicate an increase in the spring phytoplankton bloom in the open sea as well.

After spring, the bulk of total nutrients is in the form of dissolved organic compounds (Lahdes & Leppänen, 1988), which are not directly utilizable for phytoplankton growth. The phytoplankton production is then mainly based on nutrient recycling (e.g. Tamminen, 1990). The inorganic nutrients limit phytoplankton growth at that time, and the effect of the allochthonous input of these compounds into the system should be clearly seen. Whether such an input from the coast reaches the study area was not investigated. The upwelling events and airborne input may be the main sources of allochthonous nutrients. However, neither the chlorophyll *a* nor the primary production levels have increased during the summer growing period. One explanation for this could be zooplankton grazing. The biomass of copepods and cladocerans reach the annual maximum in summer in this area (Vuorinen & Ranta, 1989). The formation of fecal pellets and their sinking to the bottom might remove the 'new production' (Dugdale & Goering, 1967) rapidly from the euphotic layer.

The fluctuation in both the annual and daily production values was probably due to the light conditions prevailing during in situ incubation. No trend could be detected.

The chlorophyll data show that eutrophication of the sea is not a linear process. The increase in the nutrient reserves first intensifies the algal blooms. Extensive sedimentation of the blooms in spring, zooplankton grazing and rapid sedimentation of fecal pellets, formation of refractory organic compounds, denitrification, and the binding of phosphorus in the sediments, can counteract the eutrophication process. When the accumulation of organic matter reaches a high level, nitrogen starts to accumulate as ammonium rather than be lost through denitrification (Rönner, 1985), and in anoxic conditions phosphorus is released from the sediments. Anomalous nutrient ratios may precede the development of exceptional blooms (Skjoldal & Dundas, 1989).

## 5. CONCLUSIONS

These data show that the pelagic system of the open sea area of the western Gulf of Finland has reached a stage where the increase in the nutrient reserves is intensifying the algal blooms in spring, but changes in summer have not occurred. Continuous anthropogenic discharge and accumulation of nutrients in the deep waters especially, increase the possibility of exceptional algal blooms occurring during the whole growing period.

**Acknowledgements**

The authors wish to thank Dr. Julius Lassig and Prof. Åke Niemi for their farsightedness in starting these studies. We would also like to thank the National Board of Waters and Environment who has financed the coastal study during the last years. Valuable help has been given by the personnel of the Tvärminne Zoological Station.

REFERENCES

Ciszewski, P. & Zmudzinski, L., 1986: The results of the first stage monitoring of the Polish Baltic water. - Baltic Sea Environ. Proc. 19:181-193.

Dugdale, R.C. & Goering, J.J., 1967: Uptake of new and regenerated forms of nitrogen in primary productivity. - Limnol. Oceanogr. 12:196-206.

Edler, L., (ed.) 1979: Recommendations on methods for marine biological studies in the Baltic Sea. Phytoplankton and chlorophyll. - The Baltic Marine Biologists Publ. 5:1-38.

Gerlach, S.A., 1988: "Is the Baltic Sea dying?" - Pollution and nutrients in the Baltic Sea and the alternation of environmental conditions in the last 40 years. - Wasser Boden 40(11):639-644.

HELCOM, 1987: Baltic Marine Environment Protection Commission - Helsinki Commission: First Baltic Sea Pollution Load Compilation. Baltic Sea Environment Proceedings 20:1-56.

- " - 1990: Baltic Marine Environment Protection Commission - Helsinki Commission: Second periodic assessment of the state of the marine environment of the Baltic Sea, 1984-1988; General conclusions. Baltic Sea Environ. Proc. 35A:1-32.

Hällfors, G., Viitasalo, I. & Niemi, Å., 1987: Macrophyte vegetation and trophic status of the Gulf of Finland. - A review of Finnish investigations. - Meri 13:111-158.

Ilus, E. & Keskitalo, J., 1987: Phytoplankton in the sea area around the Loviisa nuclear power station, south coast of Finland. - Ann. Bot. Fennici 24:35-61.

Järvekülg, A., Kukk, E., Kangas, P., Lassig, J., Niemi, Å., Saava, A. & Vuorinen, I., 1988: Changes in the ecological state of the Gulf of Finland from the 1960's to the 1980's. - Symposium of the Gulf of Finland, Tallinn, Sept. 18-22, 1988 (in press).

Kahma, K. & Voipio, A., 1989: Seasonal variation of some nutrients in the Baltic Sea and the interpretation of monitoring results. - ICES, C.M. 1989/C:31.

Kangas, P., Autio, H., Hällfors, G., Luther, H., Niemi, Å. & Salemaa, H., 1982: A general model of the decline of Fucus vesiculosus at Tvärminne, south coast of Finland in 1977-81. - Acta Bot. Fennica 118:1-27.

Kononen, K., 1988: Phytoplankton summer assemblages in relation to environmental factors at the entrance to the Gulf of Finland during 1972-1985. - Kieler Meeresforsch. 6:281-294.

- " - & Niemi, Å., 1984: Long-term variation of the phytoplankton composition at the entrance to the Gulf of Finland. - Ophelia, Suppl. 3:101-110.

- " - & Niemi, Å., 1986: Variation in phytoplankton and hydrography in the outer archipelago at the entrance to the Gulf of Finland in 1968-1975. - Finnish Mar. Res. 253:35-51.

Koroleff, F., 1979: Meriveden yleisimmät kemialliset analyysimenetelmät. - Meri 7:1-60.

Laakkonen, A., Mälkki, P. & Niemi, Å., 1981: Studies on the sinking, degradation and sedimentation of organic matter off Hanko Peninsula, entrance to the Gulf of Finland, in 1979. - Meri 9:1-42.

Lahdes, E. & Leppänen, J.-M., 1988: Cycling of organic matter during the vernal growth period in the open northern Baltic Proper. II. Nutrient development and chemical composition of particulate matter. - Finnish Mar. Res. 255:19-35.

Lassig, J. & Niemi, Å., 1972: Standardization of techniques for measuring phytoplankton primary production by the C-14 method, recommendation for Finnish scientists working on the Baltic. - Merentutkimuslait.Julk. /Havsforsknings inst. Skr. 237:27-30.

Leppänen, J-M. & Kononen, K., 1988: Cycling of organic matter during the vernal growth period in the open northern Baltic proper. III. Phytoplankton composition and estimation rates of phytoplankton production. - Finnish Mar. Res. 255:37-54.

Nehring, D., 1985: Long-time changes of essential nutrients in the central Baltic Sea. - Acta. Hydrochim. Hydrobiol 13:5:591-609.

Niemi, Å. & Åström, A.-M., 1987: Ecology of phytoplankton in the Tvärminne area, SW coast of Finland. IV. Environmental conditions, chlorophyll a and phytoplankton in winter and spring 1984 at Tvärminne Storfjärd. - Ann. Bot. Fennici 24:333-352.

- " - 1975: Ecology of phytoplankton in the Tvärminne area, SW coast of Finland. II. Primary production and environmental conditions in the archipelago zone and sea zone. - Acta Bot. Fennica 105:14-25.

- " - Skuja, H. & Willen, T., 1970: Phytoplankton from the Pojoviken-Tvärminne area, S coast of Finland. - Memoranda Soc. Fauna Flora Fennica 46:14-28.

Persson, P.-E., Sivonen, K., Keto, J., Kononen, K., Niemi, M. & Viljamaa, H., 1984: Potentially toxic blue-green algae (cyanobacteria) in the Finnish natural Waters. - Aqua Fennica 14:147-154.

Pesonen, L., (ed.) 1988: Monitoring of the sea area off Helsinki and Espoo in 1979-1986. - Reports of the Water Conservation Laboratory 17:1-264. Helsinki.

Pitkänen, H., Kangas, P., Miettinen, V. & Ekholm, P., 1987: The state of the Finnish coastal waters in 1979-1983. - Vesi- ja Ympäristöhallinnon Julkaisuja 8:1-167. National Board of Waters and Environment. Helsinki.

Rönner, U., 1985: Nitrogen transformations in the Baltic Proper: denitrification counteracts eutrophication. - Ambio 14:134-138.

Sivonen, K., Kononen, K., Carmichael, W.W., Dahlem, A. M., Rinehart, K. L., Kiviranta, J. & Niemelä, S. I., 1989: Occurrence of the hepatoxic Cyanobacterium Nodularia spumigena in the Baltic Sea and structure of the toxin. - Applied and Environmental Microbiology 55(8):1990-1995.

Skjøldal, H.R. & Dundas, I., (eds.) 1989: The Chrysochromulina polylepis bloom in the Skagerrak and the Kattegat in May-June 1988: Environmental conditions, possible causes, and effects. - ICES, C.M. 1989/L:18, Sess.T+Q.61 pp. (mimeogr.).

Tamminen, T., 1990: Nitrate and ammonium depletion rates and preferences during a Baltic spring bloom: Eutrophication and the Baltic Sea: Studies on phytoplankton, bacterioplankton and pelagic nutrient cycles. - VII:1-11.

Vuorinen, I. & Ranta, E., 1987: Dynamics of marine mesozooplankton at Seili, northern Baltic Sea. - Ophelia, 28(1):31:48.

Yurkovski, A.K. & Khozioski, S.A., 1982: Analysis of vertical, seasonal and long-term dynamics of phosphorus in the Baltic Sea with special reference to the Gotland Deep. - Okeanologiya 22(4):584-589.

Finnish Marine Research 257 (1990):29-36

# PROPOSAL FOR STANDARDIZATION OF THE WAY OF PRESENTING PHYTOPLANKTON RESULTS

Guy Hällfors[1] and Åke Niemi[2]

with the support of Seija Hällfors[1], Maija Huttunen[3], Kaisa Kononen[3], Erich Kukk[4], Harri Kuosa[2], Liisa Lepistö[5], Kai Piirsoo[6] and Hilkka Viljamaa[7]

This paper has been prepared within the Biological Section of the Finnish-Soviet Working Group of the Gulf of Finland.

## ABSTRACT

Intercalibration between laboratories involved in the study of Baltic Sea phytoplankton have revealed differences in the ways results are presented. We are mainly concerned with how to present uncertain cases relating to the identification of a species, the names of collative groups, and how to name and measure definite counting units and size classes.

It is discussed how to treat some taxonomically problematical groups, and the type of microscopy and samples required for the identification of species within these groups.

Key words: Baltic Sea phytoplankton, identification, counting units, size classes, standardization.

The results of phytoplankton intercalibrations (Barinova et al., 1980, Baltic Marine Environment Protection Commission 1983; Niemi et al., 1985; Kukk and Niemi, 1987) have revealed differences between Baltic Sea laboratories. There have been several reasons for these discrepancies. For instance, how to indicate uncertainty regarding species identification, has been a factor making comparison of results between laboratories difficult. Species of several flagellate genera (e.g. *Cryptomonas*, *Gymnodinium*, *Chrysochromulina*, *Pyramimonas*) are mostly impossible to identify on species level with an inverted microscope in an Utermöhl chamber. Because of their great range in size, they

1 Department of Botany, Ecological Laboratories, University of Helsinki
2 Tvärminne Zoological Station, University of Helsinki
3 Finnish Institute of Marine Research, Helsinki
4 Tartu State University, Tartu
5 National Board of Waters and Environment, Helsinki
6 Institute of Zoology and Botany, Academy of Sciences of the Estonian SSR, Tartu
7 Helsinki City Water and Sewage Works, Helsinki

have to be classified in several size groups. This is needed calculating their biomass on volume basis. There is thus a clear need for standardizing several details concerning presentation of phytoplankton results.

An urgent need of standardization was emphazised by the Soviet-Finnish seminar on phytoplankton identification held in Pärnu in October 1987. The seminar also underlined the need to supplement and update the existing Baltic Sea phytoplankton check-list (Edler et al., 1984). This paper is an attempt to fill at least part of the gaps pointed out at the Pärnu seminar.

The topics to be standardized can be grouped as follows:

1. Indication of uncertainty regarding identification of an alga.
2. Problems concerning the names of special collective groups.
3. How to deal with special taxonomical problems.
4. Counting units and size classes.
5. Type of microscopy and quality of phytoplankton material needed for the identification of certain groups of phytoplankton.

## 1. HOW TO INDICATE UNCERTAIN IDENTIFICATION

When using light microscopy and especially when analysing fixed/preserved phytoplankton material, several flagellate groups cannot be identified to species level, many of them, especially flagellates, not even to genus level. The same is valid for several pennate diatoms analysed in an Utermöhl-chamber with an objective of 4x magnification (NA≥0.70). In case of doubtful identification, the lowest reliable taxonomical level should be given. The specimens can be grouped in different size classes (p. 32).

Uncertainty has been indicated in different ways, for instance using cf., parenthesis, quotation marks, or a question-mark before the scientific name or after it. Without a standardized manner there are possibilities of different interpretation of these signs.

It is proposed that when there is uncertainty regarding the species identification, it should be indicated in the following way:

*Uroglena ?americana* Calkins.

If there is uncertainty regarding the genus, one should write as follows:

*?Uroglena.*

If it is certain that there is only one species, one should write:

*Uroglena* sp.

If it is certain that there are more than one species, one should write:

*Uroglena* spp.

If quotation marks, parenthesis or other indications of uncertainty are used, their meaning must be explained.

## 2. PROBLEMS CONCERNING THE NAMES OF SPECIAL COLLECTIVE GROUPS

If fixed material several algal groups, e.g. several diatoms and naked dinoflagellates cannot be identified with certainty to the genus level with the Utermöhl (1958) method.

When using the genus name one should be absolutely sure of the identification of the genus. The diatom genus *Navicula* should not be used for naviculoid diatoms. One should write **naviculoid diatom**. The same is valid for *Nitzschia*. If there is uncertainty regarding the distinction between *Nitzschia, Synedra, Fragilaria* or similar genera, one should write **rod-shaped diatom**.

If naked dinoflagellates cannot be identified to genus level (e.g. *Gymnodinium, Katodinium, Amphidinium*), it is best to write **naked dinoflagellate** - autotrophic respectively heterotrophic.

The genus *Glenodinium* can be used as a working name for dinoflagellates carrying a Peridiniales-type theca, which, however, is so thin that the plate structure is indiscernible.

Small, centric diatoms, whose valve structure cannot be distinguished, should be indicated as centric diatoms and grouped in size classes (p. 33).

With the Utermöhl method picoplanktonic cells, e.g. *Synechoccus, Nannochloropsis* and *Micromonas* are difficult to separate from each other and from mineral particles. It is proposed to write **autotrophic picoplankton**. Small chroococcalean cells (*Synechoccus*) cannot be separated from bacteria using the Utermöhl-technique (epifluorescence microscopy is needed, Kuosa 1988a, see also 1988b). The use of epifluorescence microscopy for the quantification of picoplankton is highly recommended. The exact method employed should be described.

Small nanoplanktonic unidentified flagellates and unflagellated cells should be called **unidentified monads**. They should be grouped as to whether they are autotrophic or heterotrophic, and according to size classes. In case of doubt of their trophic character they should not be included in the total autotrophic biomass.

The taxonomy of small cryptomonads is very difficult and is now in a state of flux; considerable changes in the systematics are expected in the near future. If a determination to species or genus level cannot be made, it is proposed to write **Cryptomonadales spp.**, and give the size classes.

## 3. HOW TO DEAL WITH SPECIAL TAXONOMICAL PROBLEMS

Previous intercalibrations of species identification have revealed several groups of phytoplankton in which taxonomical difficulties were found and discussed by Kukk and Niemi (1987). The following additional comments may be necessary.

*Microcystis reinboldii, Aphanothece, Cyanodictyon* and bacterial colonies may be very difficult to separate from each other. In taxonomical works it is important to inform whether *Chroococcales*-colonies have a mucous envelope or not (this is required for the identification of *Microcystis, Aphanocapsa,*

*Synechocystis*, *Synechococcus*, *Cyanocystis*, *Aphanothece* etc.), and whether they are one-layered (*Merismopedia*) or three-dimensional (*Chroococcus* etc.).

The determination of silica-scaled chrysophytes (e.g. *Mallomonas*, *Synura*, *Paraphysomonas*, *Spiniferomonas*) to the species level, requires information about the structure of the scales, which is frequently obtained only with the aid of electron microscopy.

Dwarf specimens of chain-forming Chaetoceros species (esp. *C. wighamii*) can be very difficult to distinguish from several small solitary species of the genus (*C. calcitrans*, *gracilis*, *muelleri*, *simplex*). When in any doubt of identification it is best to write *Chaetoceros* sp. (solitary), and give the size.

Most *Entomoneis* (*Amphiprora*) species cannot be distinguished with the Utermöhl-technique (p. 33).

The taxonomy of the genus *Scenedesmus* is developing rapidly and there are many recent nomenclatural changes. If specimens are determined to species level, one should refer to the identification literature, and give the authors of the names.

The separation of the genera *Monoraphidium* and *Koliella* is difficult, and reguires considerable experience unless dividing cells are present. If there is any uncertainty it is best to write *Monoraphidium/Koliella*, or e.g. *Monraphidium contortum/Koliella spiralis*.

## 4. COUNTING UNITS AND SIZE CLASSES

In order to achieve uniformity in practical phytoplankton counting the following counting units are recommended (Guidelines for the Baltic Monitoring Programme for the third stage, Baltic Marine Environment Commission, 1989)

| | |
|---|---|
| CELL: | All non-colonial unicellular species |
| | Dinobryon |
| | Uroglena (disintegrated colonies) |
| | Aulacosira |
| | Chaetoceros |
| | Leptocylindrus |
| | Melosira |
| | Skeletonema (and other chain-forming diatoms) |
| | Achnanthes taeniata |
| | Navicula vanhoeffenii |
| | Nitzschia cylindrus |
| | Planktonema (and other filamentous green algae) |
| | Oocystis |
| COLONY: | Aphanothece |
| | Coelosphaerium |
| | Gomphosphaeria |
| | Microcystis (incl. Aphanocapsa) |
| | Gloeotrichia |
| | Uroglena (when colonies well preserved) |
| | Sphaerocystis (and similar genera) |

COENOBIUM, with a ± fixed number of cells (n):

Eudorina (32)
Pandorina (16)
Coelastrum (8, 16, 32, etc.)
Crucigenia (4)
Micractinium (4)
Pediastrum (4, 8, 16,32, etc.)
Scenedesmus (2, 4, 8)

If cell number is variable within a species, the coenobia should be grouped according to the number of cells.

SOME COLONIAL ALGAE are most conveniently counted as groups of four cells, e.g.:

Chroococcus
Merismopedia
Crucigeniella
Dictyosphaerium

FILAMENTS to be counted in lengths of 100 μm:

Achroonema
Anabaena
Anabaenopsis
Aphanizomenon
Beggiatoa
Lyngbya
Nodularia
Oscillatoria
(etc. filamentous blue-green algae).

*Nodularia spumigena* varies very much in width and should be classified as follows in the size groups: < 10 μm, 10-15 and > 15 μm. Many large species are encountered as single filaments or cells and should be measured individually. When the measured dimensions of a taxon are presented, one should give the general range of variation and the extremes as follows: (8)-10-15-(19). Dimensions in μm should generally not be given with more than two significant numbers when using the light microscope.

The grouping of specimens in standardized classes makes the transformation to volume and biomass values easier and makes the results between different laboratories more comparable. The following size classes (length or diameter in μm) are proposed:

Cryptomonads < 5, 5-7, 7-10, 10-15, 15-20, 20-25, 25-30, etc.
Gymnodiniales 6-10, 10-15, 15-20, etc.
Glenodinium 10-15, 15-20, etc.
Chrysochromulina < 4, 4-5, 5-7, 7-10, 10-15, etc.
Chaetoceros, both the length and width of the cell should be taken

into account, as well as the 'window' between cells, when present
small, centric diatoms < 4, 4-5, 5-7, 7-10, 10-15
pennate diatoms should be measured individually
Euglenomonads 10-15, 15-20, etc.
Pyramimonas 3-4, 4-6, 6-8, 8-10, 10-15
Chlamydomonadaceae < 6, 6-7, 7-10, 10-15, 15-20, etc.
unidentified monads 2-3, 3-5, 5-7, 7-10, 10-15, 15-20, etc.
picoplankton < 2 µm.

The methods for calculating volumes/biomasses (and carbon content) have already been standardized for the Baltic Sea (Edler, 1979; Baltic Marine Environment Protection Commission, 1984). Heterotrophic cells should not be included in the total phytoplankton biomass, but their biomass should be reported separately, as should autotrophic zooplankton (e.g. *Mesodinium*).

## 5. TYPES OF MICROSCOPY AND THE QUALITY OF PHYTOPLANKTON MATERIAL NEEDED FOR THE IDENTIFICATION OF CERTAIN GROUPS OF PHYTOPLANKTON

During the last years several new species and genera, even taxa of higher level have been found in Baltic waters (e.g. Hällfors & Niemi, 1974; Thomsen, 1975, 1977, 1979a and b; Thomsen & Oates, 1978; Hällfors & Thomsen, 1979, 1985; Moestrup & Thomsen, 1986; Pedersen et al., 1986, Moestrup et al., 1987; Hällfors et al. (in prep.)). Many algae can be identified using the Utermöhl-technique. However, many nanoplankton species can be identified only using electron microscopy (TEM, occasionally SEM). Some can be identified using good oil immersion optics (NA≥1.30).

The following diatoms require at least diatom preparations and oil immersion microscopy for reliable identification (the list is not exhausted):

*Cyclotella* spp.
*Stephanodiscus* spp.
small *Thalassiosira* spp.
small *Achnanthes* spp.
*Entomoneis* spp.
small *Amphora* spp.
single *Berkeleya* frustules
small *Cocconeis* spp.
most *Fragilaria* spp.
*Grammatophora* spp.
most *Gyrosigma* spp.
*Licmophora* spp.
most *naviculoid* spp.
most *Nitzschia* spp.
*Opephora* spp.
*Pinnularia* spp.
*Pleurosigma* spp.
some *Synedra* spp.
*Tropidoneis* spp.

Species of the following groups can be identified by their scales in dry preparations using oil immersion optics and phase contrast microscopy:

a few Prymnesiophyceae e.g. *Chrysochromulina birgeri* and C. spinifera
*Chrysosphaerella* spp.
most *Mallomonas* spp.
some *Paraphysomonas* spp.

some *Spiniferomonas* spp.
most *Synura* spp.

Identification of the following taxa need electron microscopy:

most Prymnesiophyceae
probably several species in the genera *Cyclotella, Cyclostephanos* and *Stephanodiscus*
the smallest *Thalassiosira* spp.
some small *Nitzschia* spp.
many Prasinophyceae, esp. *Pyramimonas* spp.

The identification of the following taxa, if at all possible, needs living material:

several cryptomonads
naked dinoflagellates, i.e. taxa without a discernible theca
the genus *Pavlova* (most species require TEM of ultrathin sections for determination)
small euglenids
most Chlamydomonadales

As a general fixative for Utermöhl counts acid Lugol's solution is recommended. It should be noted, however, that the colour of most cells changes markedly. In the rare cases when coccolithophorids are present, they should be fixed in an alkaline solution in order to preserve the coccoliths which are essential for identification of the species.

Other fixatives/preservatives (formalin, Keefe's solution) should not be used due to their deleterious effects on cell morphology (Hällfors et al., 1979). Even acid Lugol's solution, however, can cause considerable shrinking of naked cells (cf. Børsheim & Bratbak, 1987). This will require further studies in the Baltic Sea. For blue-green algae fixation with formalin is usually adequate.

A confident identification of several thecate dinoflagellates require a study of the thecal pattern, which requires special preparation methods and oil immersion optics or even SEM.

Thus it is important to state whether the studied material was living of fixed, and if so, what fixative was used. The type of microscope and illumination should also be mentioned.

REFERENCES

Barinova, S.P., Forsskåhl, M., Kukk, E., Melnikova, T., Melvasalo, T., Niemi, Å., Piirsoo, K. & Viljamaa, H. 1980: Phytoplankton. Finnish-Soviet intercalibration of biological parameters used for monitoring the conditions of the Gulf of Finland. - Meri 8:11-23.

Baltic Marine Environment Protection Commission 1983: Second Biological Intercalibration Workshop. - Baltic Sea Environment Proceedings 9:1-95.

- " - 1984: Guidelines for the Baltic Monitoring Programme for the second stage. - Baltic Sea Environment Proceedings 12. - 251 pp.

Baltic Marine Environment Protection Commission 1989: Guidelines for the Baltic Monitoring Programme for the third stage. - Baltic Sea Environment Proceedings 27D. - 161 p.

Børsheim, Y. & Bratbak, G. 1987: Cell volume to cell carbon conversion factors for a bacterivorous Monas sp. enriched from seawater. - Mar. Ecol. Progr. Ser. 36:171-175.

Edler, L. (ed.) 1979: Recommendations on methods for marine biological studies in the Baltic Sea. Phytoplankton and chlorophyll. - The Baltic Marine Biologists. Publ. 5:1-38.

- " - , Hällfors, G. & Niemi, Å. 1984: A preliminary check-list of the phytoplankton of the Baltic Sea. - Acta Bot. Fennica 128:1-26.

Hällfors, G., Hällfors, S. & Thomsen, H.A. (eds.): Electron microscopical observations on nanoplankton flagellates from the Baltic Sea. I-VIII. (in prep.)

- " - & Niemi, Å. 1974: A Chrysochromulina (Haptophyceae) bloom under the ice in the Tvärminne archipelago, southern coast of Finland. - Memoranda Soc. Fauna Flora Fennica 50:89-104.

- " - , Melvasalo, T., Niemi, Å. & Viljamaa, H. 1979: Effect of different fixatives and preservatives on phytoplankton counts. - Publ. Wat. Res. Inst., National Board of Waters, Finland 34:25-34.

- " - & Thomsen, H.A. 1979: Further observations on Chrysochromulina birgeri (Prymnesio-phyceae) from the Tvärminne archipelago, SW coast of Finland. - Acta Bot. Fennica 110:41-46.

- " - & Thomsen, H.A. 1985: Chrysochromulina barchycylindra sp. nov. (Prymnesiophyceae) from Finnish coastal waters. - Nord. J. Bot. 5:499-504.

Kukk, E. & Niemi, Å. 1987: Finnish-Soviet intercalibration of phytoplankton identification used for monitoring the conditions of the Gulf of Finland. - Meri 13:7-42.

Kuosa, H. 1988a: Occurrence of autotrophic picoplankton along an open sea - inner archipelago gradient in the Gulf of Finland, Baltic Sea. - Ophelia 28(2):85-93.

- " - 1988b: Enumeration of autotrophic and heterotrophic flagellates in Baltic Sea samples - a comparison of microscopical methods. - Arch. Hydrobiol. Beih. (Ergenb. Limnol.) 31:301-306.

Moestrup, Ø. & Thomsen, H.A. 1986: Ultrastructure and reconstruction of the flagellar apparatus of Chrysochromulina apheles sp. nov. (Haptophyceae = Prymnesiophyceae). - Can. J. Bot. 64:593-610.

- " - , Hori, T. & Kristiansen, A. 1987: Fine structure of Pyramimonas octopus sp. nov., an octoflagellated benthic species of Pyramimonas (Prasinophyceae), with some observations on its ecology. - Nord. J. Bot. 7:339-352.

Niemi, Å., Melvasalo, T. & Heinonen, P. 1985: Phytoplankton counting techniques and primary production measurements - comment of results of intercalibration. - Aqua Fennica 15(1):89-103.

Pedersen, S.M., Beech, P.L. & Thomsen, H.A. 1986: Parapedinella reticulata gen. et sp. nov. (Chrysophyceae) from Danish waters. - Nord. J. Bot. 6:507-513.

Thomsen, H.A. 1975: An ultrastructural survey of the chrysophycean genus Paraphysomonas under natural conditions. - Br. Phycol. J. 10:113-127.

- " - 1977: Chrysochromulina pyramidosa sp. nov. (Prymnesiophyceae) from Danish coastal waters. - Bot. Notiser 130:147-153.

- " - 1979a: Chrysochromulina cyatophora sp. nov. (Prymnesiophyceae), a new species from Danish coastal waters. - Bot. Notiser 132:71-76.

- " - 1979b: Electron microscopical observations on brackish-water nanoplankton from the Tvärminne area, SW coast of Finland. - Acta Bot. Fennica 110:11-37.

- " - & Oates, K. 1978: Balaniger balticus gen. et sp. nov. (Prymnesiophyceae) from Danish coastal waters. - J. Mar. Biol. Ass. U.K. 58:773-779.

Utermöhl, H. 1958: Zur Vervollkommnung der quantitativen Phytoplankton-Methodik. - Mitt. int. Verein. Limnol. 9:1-38.

Finnish Marine Research 257 (1990):37-57

# INTERCOMPARISON OF THE MEASUREMENT OF CHLOROPHYLL *a* CONCENTRATION, PRIMARY PRODUCTION CAPACITY, AND PHYTO- AND ZOOPLANKTON ABUNDANCES DURING THE BALTIC SEA PATCHINESS EXPERIMENT (PEX'86)

Juha-Markku Leppänen[1)], Kaisa Kononen[1)], Gerda Behrends[2)], Gesa Hansen[2)]

[1)] Finnish Institute of Marine Research
PO.Box 33
SF-00931 Helsinki

[2)] Institut für Meereskunde
Düsternbrooker Weg 20
D-2300 Kiel

## ABSTRACT

Research vessels from most of the countries surrounding the Baltic Sea participated in the investigation on the patchy distribution of biological, chemical and physical parameters (the Baltic Sea Patchiness Experiment - PEX'86). Several exercises were carried out during the investigation period in order to evaluate the comparability of the measurements made on board the ships. This paper summarizes the results of the intercomparisons of the biological determinants. Statistically significant differences were found between the results of the ships for all determinants. Recommendations are given for developing the precision and comparability of the measurements.

Key words: Intercomparison, chlorophyll *a*, primary production, phytoplankton, zooplankton, Baltic Sea

## 1. INTRODUCTION

In order to investigate the methodological variability and the comparability of the results of the ships/laboratories participating in the Baltic Sea Patchiness Experiment (PEX'86, e.g. Dybern & Hansen 1989) several intercomparison exercises were carried out during the course of the experiment in April-May 1986. All the countries surrounding the Baltic Sea, except Denmark, participated in the experiment and, since the same institutions are responsible for the execution of the Baltic Sea Monitoring Programme (BMP), the intercalibration results also provide valuable information to the Helsinki Commission.

## 2. MATERIALS AND METHODS

The following research vessels participated in the intercomparison exercises:

| | |
|---|---|
| Alkor, | Institut für Meerskunde an der Universität Kiel, FRG, |
| Argos, | Swedish Meteorological and Hydrological Institute, Sweden, |
| Aranda, | Finnish Institute of Marine Research, Finland, |
| Arnold Veimer, | Institute of Thermophysics and Electrophysics, Department of the Baltic Sea, Estonian SSR, |
| Gauss, | Deutsches Hydrographisches Institut, FRG, |
| Lev Titov, | Lith. Rep. Board for Hydromet. and Env. Contr., Vilnius, Lithuanian SSR, |
| Oceania, | Academy of Sciences, Institute of Oceanology, Poland, |
| Prof. Albrecht Penck, | Academy of Sciences, Institut für Meerskunde, DDR, |
| Wieczno, | Polish Fisheries Institute, Poland. |

The ships are listed in alphabetical order and does not correspond to the listing of the results presented in the following figures and tables.

The intercomparison samples for all the participating ships were collected and subsampled by one ship. All the analyses were performed according to the Guidelines for the Baltic Monitoring Programme for the Second Stage (HELCOM 1983a).

The intercalibration measurements for chlorophyll *a* and primary production capacity were carried out on April 22, 24 and May 4.

Five replicates from the water samples for chlorophyll *a* analysis were filtered on Whatman GF/C glass fiber filters. 90 % acetone was used as extractant. After homogenization, the extraction time was 2 h in total darkness. The concentration of the extract was determined either spectrophotometrically or fluorometrically. In order to test the precision of these instruments, chromatographically purified chlorophyll *a* extracted in 90 % acetone, prepared by one ship, was submitted to all ships.

Phytoplankton carbon assimilation was measured with the $^{14}C$ method (Steeman Nielsen, 1952) using five replicates. The laboratories used their own $^{14}C$ batches, the activities of which were determined by one laboratory. During the experiment this laboratory also determined the $^{14}C$ activity of all the samples with a liquid scintillation counter (Rackbeta, LKB-Wallac). Lumagel was used as scintillation cocktail. The size of the experimental bottles ranged from 25 to 130 $cm^3$. The samples were incubated for 2 h in constant light incubators. The irradiance in the individual incubators was standardized as far as possible before the experiments started and measured with a Li-lor quantameter equipped with a cosine sensor. The temperature in the incubators was adjusted according to the actual average temperature in the 0-20 m water

column. After incubation, the samples were immediately filtered on membrane filters (Sartorius) with a pore size of 0.4 μm.

Phytoplankton samples were preserved with acid Lugol's solution. Six species were selected for counting on the basis of their dominance in the total phytoplankton biomass. Another important criterion was to avoid misidentification by selecting species which are easy to identify. The species counted were *Gonyaulax catenata*, *Achnanthes taeniata*, *Chaetoceros holsaticus*, *C. wighamii*, *Skeletonema costatum*, *Thalassiosira baltica* and *T. levanderi*. The cells were counted using the inverted microscope technique (Utermöhl, 1958). In every laboratory five subsamples were sedimented (here referred to as subsamples). One subsample was counted five times (here referred to as parallel countings). The samples of ship no. 7, however, were counted using a reverse filtration method (Sournia, 1978) including concentration of the sample and counting in a 0.05 $cm^3$ chamber. If possible, at least 200 cells and 50 chains of each species were counted in a single sample. Due to the identification problems *C.holsaticus* and *C. wighamii* and *Chaetoceros* sp., were all reported as *Chaetoceros* spp.

Three mesozooplankton samples taken with a WP-2 net (mesh size 100 μm) were pooled and then subsampled with a Folsom splitter for each participating ship. The samples were preserved in 4 % formalin buffered with borax. In the laboratories Kott or Folsom splitters were used to produce subsamples. One laboratory used Stempel pipette. In all laboratories except one, at least 2 subsamples and in most cases at least 500 animals per subsample were counted. The following 11 mesozooplankton species were counted: the copepods *Acartia bifilosa*, *A. longiremis*, *Centropages hamatus*, *Temora longicornis* and *Pseudocalanus minutus elongatus*, the cladoceran species *Bosmina coregoni maritima*, *Evadne nordmanni* and *Podon* spec., Polychaeta larvae, the rotifer genus *Synchaeta* spec. and the appendicularian species *Fritillaria borealis*. The copepods were determined for sex if adult and for 3 development stage groups: nauplii, copepodite stage I-III and copepodite stage IV-V. For *Acartia*, development stages were determined only to genus level.

Due to occasional mistakes in the analysis, the ships could not always report the results of all replicates.

The statistical tests were performed by the Student's t-test and one-way and nested analyses of variance.

## 3.RESULTS

### 3.1. Chlorophyll *a*

The results of the chlorophyll *a* intercomparisons are presented in Figs. 1 and 2 and in Tables 1-3. The differences between the ships were significant in all exercises, but the pattern varied. In most cases ship no 6 reported the lowest values and the values of ships 1, 2 and 3 tended to be the highest. The coefficient of variation for a single ship was usually <5 % with some exceptions (Table 2). The coefficients of variation for the means of all ships ranged between 16 and 28 %. The 95 % confidence limits for the means of all ships were ca. ±0.5 mg $m^{-3}$.

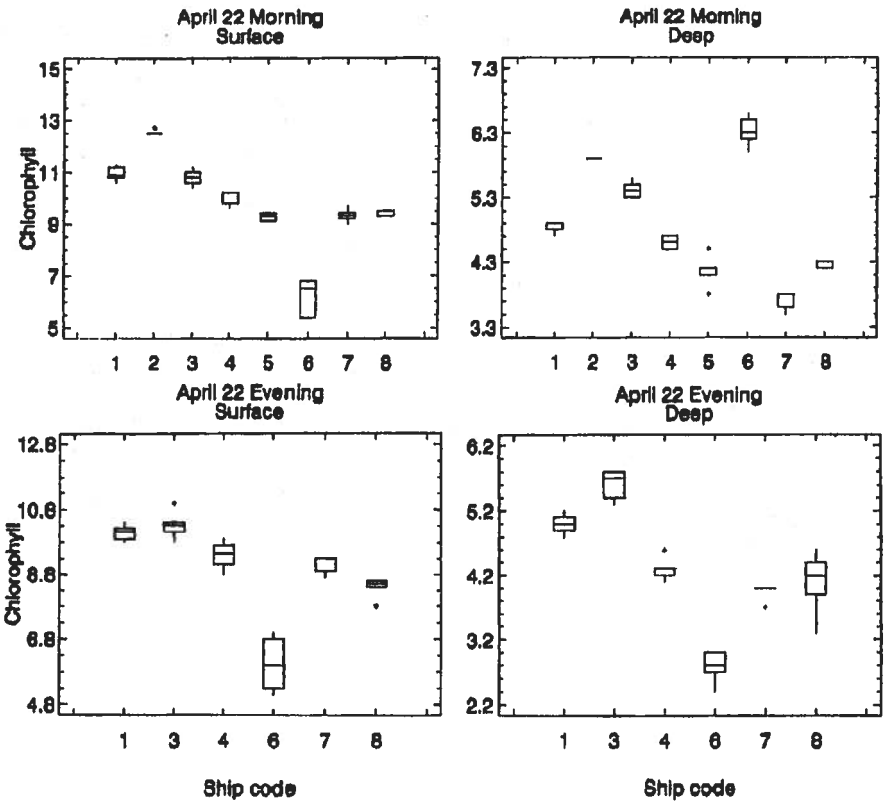



Fig. 1. Distribution of the chlorophyll *a* (mg $m^{-3}$) of the ships obtained on April 22. The horizontal lines represent the median, the boxes cover 50 % of the data (upper and lower quartiles), the vertical bars show the range, and deviating values are marked by asterisks.

The concentration of purified chlorophyll *a* in 90 % acetone was also measured by all ships. The coefficient of variation between the measurements of the different ships was 2.3 % (Table 3).

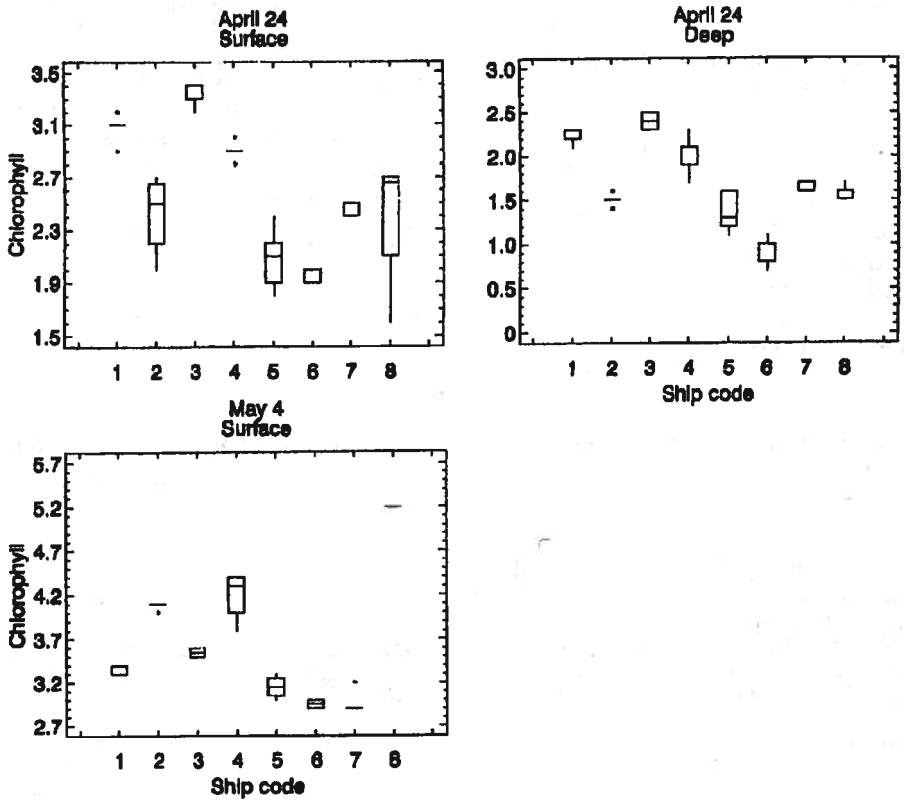



Fig. 2. Distribution of the chlorophyll *a* (mg $m^{-3}$) of the ships obtained on April 24 and May 4.. The horizontal lines represent the median, the boxes cover 50 % of the data (upper and lower quartiles), the vertical bars show the range, and deviating values are marked by asterisks.

Table 1. Statistical characteristics of the chlorophyll *a* results (mg $m^{-3}$). Summary of all ships.

| | April 22, morning | | April 22, evening | |
|---|---|---|---|---|
| | Surface | Deep | Surface | Deep |
| Sample size | 36 | 38 | 29 | 30 |
| Average | 10.04 | 4.93 | 8.87 | 4.28 |
| Median | 10.00 | 4.75 | 9.30 | 4.20 |
| Variance | 2.60 | 0.78 | 2.34 | 0.87 |
| Standard deviation | 1.00 | 0.88 | 1.53 | 0.93 |
| Standard error | 0.20 | 0.14 | 0.28 | 0.17 |
| | April 24 | | May 4 | |
| | Surface | Deep | Surface | |
| Sample size | 36 | 40 | 29 | |
| Average | 2.62 | 1.71 | 3.58 | |
| Median | 2.65 | 1.60 | 3.40 | |
| Variance | 0.25 | 0.23 | 0.35 | |
| Standard deviation | 0.50 | 0.478 | 0.59 | |
| Standard error | 0.08 | 0.075 | 0.11 | |

Table 2. Coefficients of variation (%) for the chlorophyll *a* subsamples of the different ships.

| Experiment | Ship code | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| April 22, morning, surface | 2.6 | 0.6 | 3.0 | 2.8 | 1.6 | 11.9 | 2.8 | 1.3 |
| April 22, morning, deep | 1.9 | 0.0 | 2.4 | 2.2 | 6.0 | 3.8 | 3.8 | 1.4 |
| April 22, evening, surface | 2.4 | - | 4.3 | 4.8 | - | 14.2 | 3.0 | 3.9 |
| April 22, evening, deep | 3.2 | - | 4.1 | 4.4 | - | 9.0 | 3.3 | 12.5 |
| April 24, surface | 3.6 | 12.8 | 2.4 | 2.4 | 11.5 | 3.0 | 2.4 | 22.5 |
| April 24, deep | 3.8 | 4.7 | 4.2 | 11.3 | 16.9 | 17.9 | 3.3 | 5.3 |
| May 4, surface | 1.6 | 1.1 | 2.0 | 6.4 | 4.1 | 2.4 | 4.5 | - |

Table 3. Chlorophyll *a* concentrations (mg $dm^{-3}$) in the purified extract measured by the participating ships.

| Ship code | Concentration | Diff. from the mean of all ships (%) |
|---|---|---|
| 1 | 0.87 | +0.6 |
| 2 | 0.83 | -4.0 |
| 3 | 0.86 | +0.6 |
| 4 | 0.88 | +1.7 |
| 5 | 0.77 | -11 |
| 6 | 0.92 | +6.4 |
| 7 | 0.87 | +0.06 |
| 8 | 0.88 | +1.7 |

### 3.2. Primary production capacity

According to the measurements of the production-irradiance ratio made by one ship, the saturation level for primary production was reached between the irradiance of 300-500 μmol $m^{-2}$ $s^{-1}$. The irradiance in most of the incubators was below this level (Fig. 3).

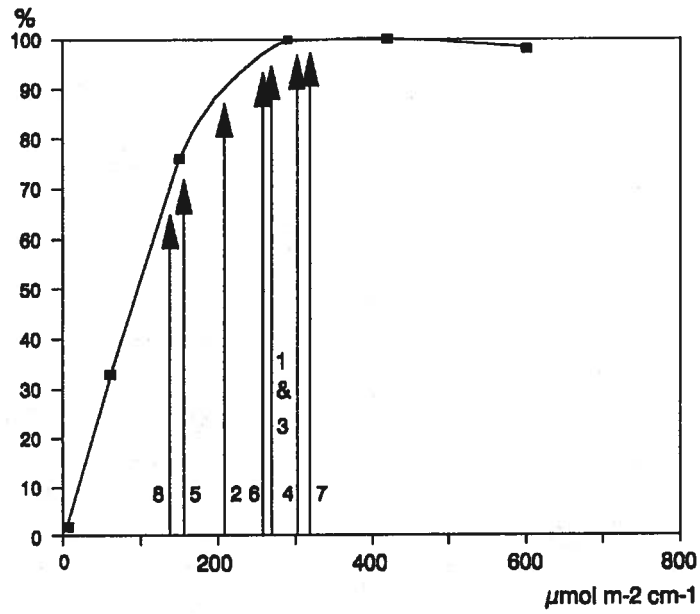



Fig. 3. Irradiances used in the incubators for primary production measurement as compared to the average irradiance-production curve obtained during PEX'86. Numbers refer to ship code.

The measured and reported activities of the $^{14}C$ solutions are presented in Table 4.

Table 4. Activities of the $^{14}C$ solutions (μCi $cm^{-3}$).

| Ship code | Measured | Reported by the users |
|---|---|---|
| 1 | 20.4 | 20.4 |
| 2 | 3.7 | ca. 4 |
| 3 | 8.6 | - |
| 4 | 17.2 | 9.1 |
| 5 | 22.7 | - |
| 6 | 31.9 | 25 |
| 7 | 10.4 | 10 |
| 8 | 32.1 | 40 |

The differences between the results reported by the ships were significant in all experiments. In general, the production values reported by ship no. 3 and 6 were above and for ship no. 5 below the mean of all ships, but this was not

always the case (Fig. 4). The coefficients of variation for the results of a single ship were in most cases <10 %. However, the variation in the results of ship no 2 was very high (Fig. 4) and therefore its results are excluded from the following calculations. The coefficients of variation for the means of all ships ranged between 25 and 27 % (Table 5). The 95 % confidence limit for the means of all ships was ±3 mgC $m^{-3}h^{-1}$ in the first intercalibration, when the production level was high. In the other two exercises the 95 % confidence limits were ±0.5 $mgCm^{-3}h^{-1}$.

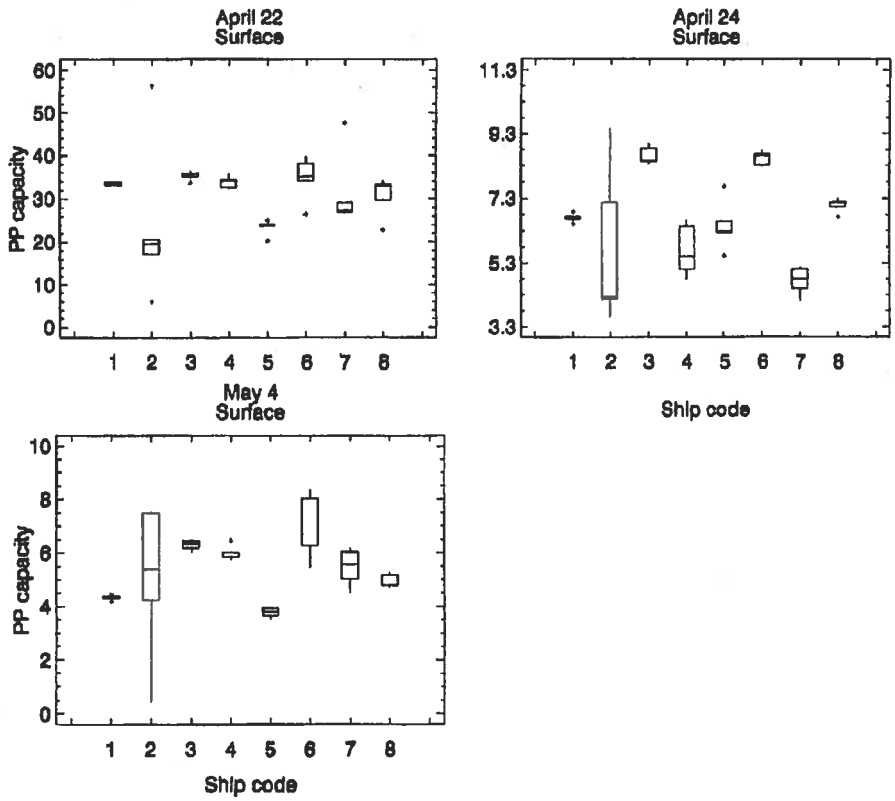



Fig. 4. Distribution of the primary production capacity results (mg C $m^{-3}$ $h^{-1}$) obtained by the ships on April 24 and May 4.. The horizontal lines represent the median, the boxes cover 50 % of the data (upper and lower quartiles), the vertical bars show the range, and deviating values are marked by asterisks.

Table 5. Statistical characteristics for the primary production samples (mgC $m^{-3}h^{-1}$). The results of ship no. 2 are excluded from the summary.

| | April 22 | April 24 | May 4 |
|---|---|---|---|
| Sample size | 35 | 35 | 35 |
| Average | 31.80 | 6.83 | 5.44 |
| Median | 33.36 | 6.72 | 5.43 |
| Geometric mean | 31.32 | 6.68 | 5.31 |
| Variance | 30.48 | 1.95 | 1.52 |
| Standard deviation | 5.52 | 1.40 | 1.23 |
| Standard error | 0.93 | 0.24 | 0.21 |

### 3.3. Phytoplankton

Four laboratories reported a complete list of species encountered in the sample. Altogether 53 phytoplankton taxa were identified in the sample, but only 15 of these were common for all the laboratories (Table 6).

Intercomparison counting results were reported by seven laboratories. The results are presented in Table 7 and Figs. 5 and 6.

Ship no. 7 reported the lowest cell numbers for all species except *G. catenata*. The reason for this was the different method used in concentrating the cells for counting. (Figs. 5 and 6).

None of the laboratories which had used the same method differed from each other in respect to all phytoplankton species. Ships no. 3 and 6 tended to have highest counts of *Achnanthes, Chaetoceros* and *Skeletonema* but not of other species. Nested analysis of variance was used for testing the relative importance of three different variation sources - differences between laboratories, between subsamples and between countings.

For all species except *G. catenata* the main source of variation was due to variability between ships - the samples were counted by different people. For *Chaetoceros wighamii, Skeletonema costatum, Thalassiosira baltica* and *T. levanderi* this was true at the 0.1 % risk level (Table 7).

The results for *G. catenata* were converse - most of the variation was caused by differences between repeated countings. This is explained by the sparse occurrence of the species in the sample. None of the ships had counted the suggested minimum number of cells. Generally less than 50 cells were counted instead of 200.

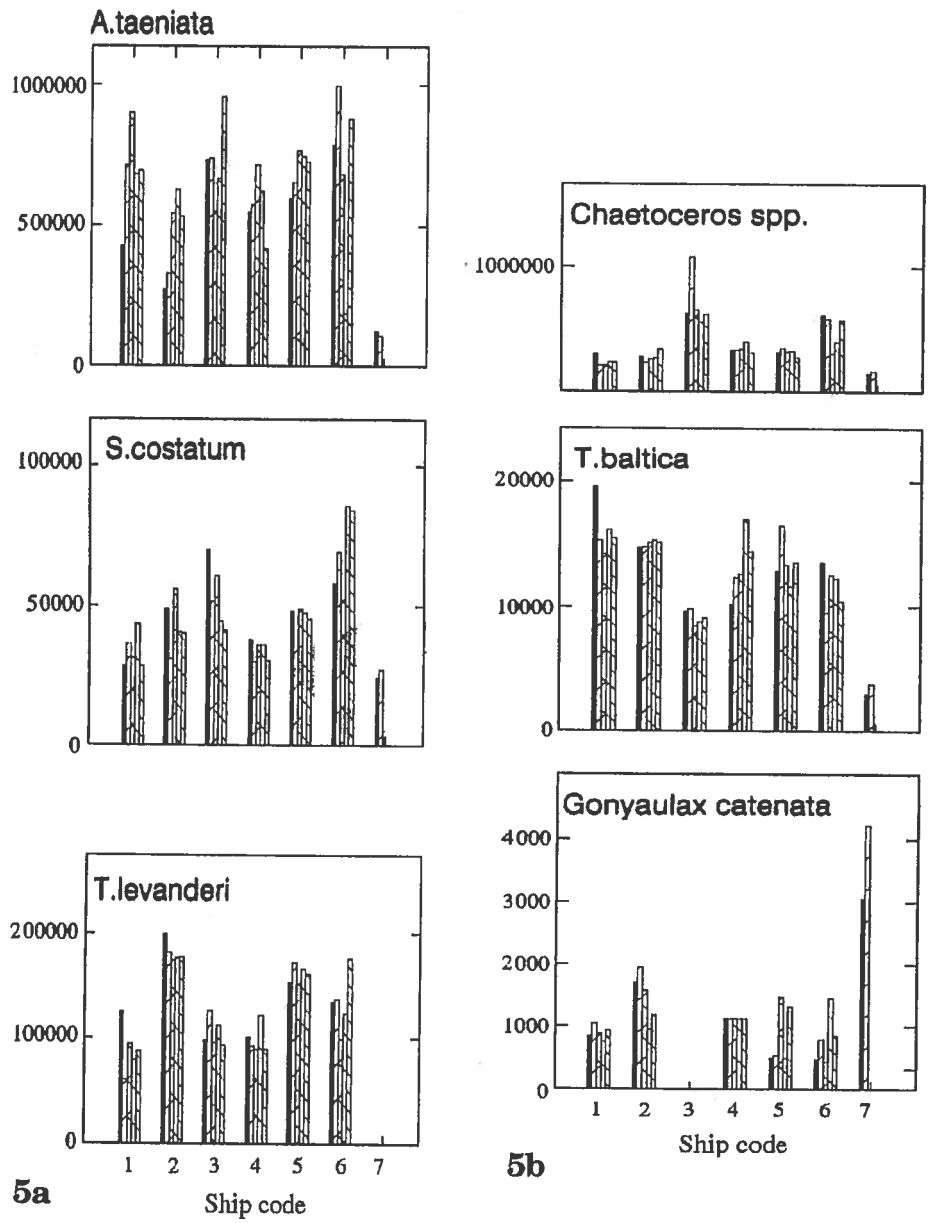
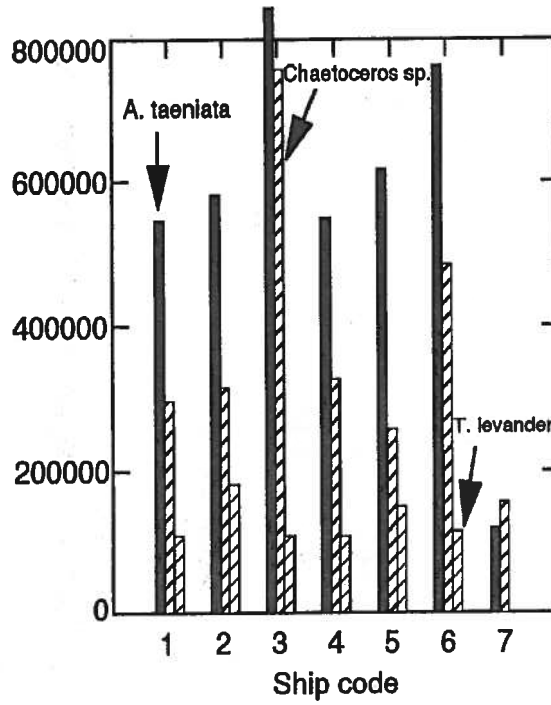



Fig. 5a and b. Results of the 5 parallel phytoplankton countings (cells $dm^{-3}$) of the same sample (samples 1-5).

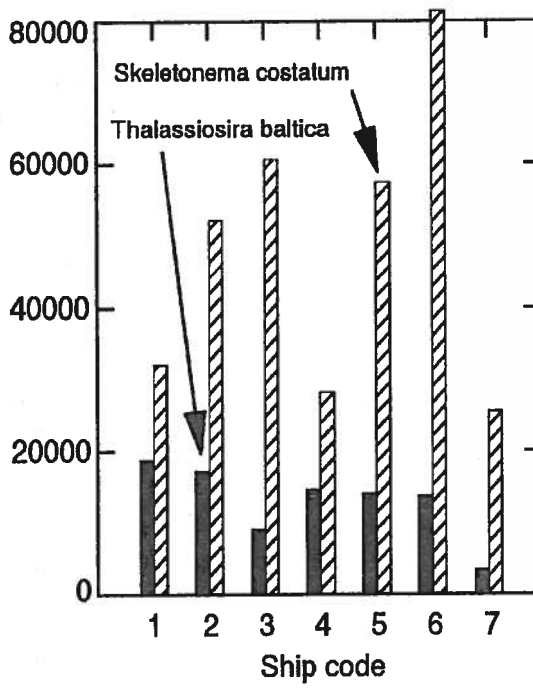
Table 6. The list of species encountered in the sample by four laboratories.

| Species | Laboratory number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| CYANOPHYCEAE | | | | |
| Coelosphaerium kuetzingianum | | | * | |
| Gomphosphaeria lacustris v.lac. | * | * | * | |
| Microcystis reinboldii | * | | | |
| Aphanizomenon flos-aquae | * | * | * | |
| Nodularia sp. | * | | | |
| CRYPTOPHYCEAE | | | | |
| Cryptomonas 6 µm | * | * | * | * |
| Cryptomonas 15 µm | | * | | |
| Katablepharis ovalis | * | | | |
| DINOPHYCEAE | | | | |
| Dinophysis acuminata | * | * | * | * |
| Dinophysis norvegica | | * | | |
| Amphidinium sp. 46 µm | * | | | |
| Gymnodinium westificii | | * | | |
| Gymnodinium sp. 20 µm | * | * | * | * |
| Gymnodinium sp. 29 µm | * | | | |
| Gymnodinium simplex | * | * | | |
| Katodinium rotunda | * | * | | |
| Glenodinium sp. 45 µm | * | | | |
| Gonyaulax catenata | * | * | * | |
| Peridinium sp. | | | * | |
| Protoperidinium bipes | * | | * | * |
| Protoperidinium granii | * | * | | |
| Ebria tripartita | * | * | * | * |
| PRYMNESIOPHYCEAE | | | | |
| Chrysochromulina sp. | * | * | | |
| CHRYSOPHYCEAE | | | | |
| Dinobryon bavaricum | * | | | |
| Pedinella tricostata | * | | | |
| EUSTIGMATOPHYCEAE | | | | |
| Nannochloropsis sp. | | * | | |
| DIATOMOPHYCEAE | | | | |
| Actinocyclus octonarius | * | | | |
| Chaetoceros borealis | | | * | |
| Chaetoceros ceratosporus | * | * | * | * |
| Chaetoceros holsaticus | * | * | * | * |
| Chaetoceros septentrionalis | | * | * | * |
| Chaetoceros subtilis | * | * | * | * |
| Chaetoceros wighamii | * | * | * | * |
| Chaetoceros socialis | * | * | * | * |
| Chaetoceros danicus | * | * | * | |
| Melosira arctica | * | * | * | * |
| Skeletonema costatum | * | * | * | * |

| Species | Laboratory number | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| DIATOMOPHYCEAE (contd.) | | | | |
| Thalassiosira baltica | * | * | * | * |
| Thalassiosira baltica 80 µm | | * | * | |
| Thalassiosira bramaputrae | * | * | * | * |
| Thalassiosira levanderi | * | * | * | * |
| Thalassiosira quillardii | * | | | |
| Thalassiosira pseudonana | * | | | |
| Achnanthes taeniata 20 µm × 30 µm | * | * | * | * |
| Achnanthes taeniata 20 µm × 6 µm | * | * | | |
| Navicula vanhoeffenii | * | | * | |
| Navicula sp. 29 mm | | * | | |
| Nitzschia longissima | * | * | | |
| Nitzschia frigida | | * | * | |
| Synedra tabulata | | * | | |
| EUGLENOPHYCEAE | | | | |
| Eutreptiella sp. | | * | * | * |
| PRASINOPHYCEAE | | | | |
| Pyramimonas grossi | * | | | |
| Pyramimonas orientalis | * | | | |
| Pyramimonas virgina | * | | | |
| Pyramimonas sp. | * | | * | * |
| CHLOROPHYCEAE | | | | |
| Oocystis spp. | * | * | | * |
| Planktonema lauterbornii | * | | | |
| unidentified flagellates | * | | | |
| Salpingoeca (calliacangtha) | * | | | |
| Mesodinium rubrum | * | * | * | |
| Dissodinium pseudolunula | | | | * |

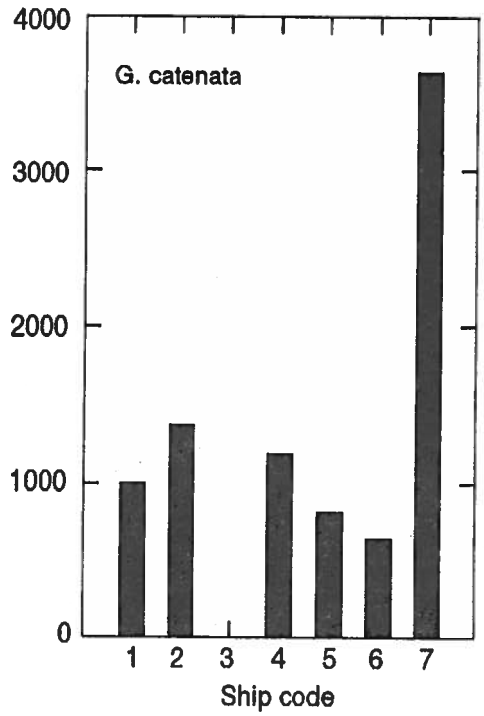



6a




6b

Figs. 6 a, b and c. Means of the counting results of the 5 parallel phytoplankton samples (cells $dm^{-3}$).




Figs. 6 a, b and c. Means of the counting results of the 5 parallel phytoplankton samples (cells $dm^{-3}$).

Table 7. Results of the nested analysis of variance of the phytoplankton species data.

| Species | Percentage of variance components associated with variance | |
|---|---|---|
| | a) between ships | b) within ships |
| Gonyaulax catenata | 32 | 68 |
| Achnanthes taeniata | 80 | 20 |
| Chaetoceros spp. | 71 | 29 |
| Skeletonema costatum | 71 | 29 |
| Thalassiosira baltica | 79 | 21 |
| Thalassiosira levanderi | 80 | 20 |

The counting error for most of the species was close to the theoretical estimate (ca. 13 %, Lund et al. 1958). When some clear mistakes were excluded the 95 % confidence limits for total means of the countings of different species were (mean = total mean of all parallel samples, n = 32):

| Species | mean | confidence limit |
|---|---|---|
| Gonyaulax catenata | 1062 | ±227 |
| Achnanthes taeniata | 631152 | ±73997 |
| Chaetoceros spp. | 405836 | ±73800 |
| Skeletonema costatum | 49427 | ±8367 |
| Thalassiosira baltica | 15600 | ±1034 |
| Thalassiosira levanderi | 127342 | ±12684 |

## 3.4 Mesozooplankton

The counting results were reported by 8 laboratories. As the number of counted subsamples varied between 1 and 5 and different splitters were used to produce subsamples of different size, no comparison of the variances between the subsamples was carried out. The analysis is restricted to comparison of the variances of the results of the different laboratories.

The results are shown in Fig. 7 and in Tables 9 and 10. Single, extremely high and low values regarded as mistakes are excluded from the calculation for Tables 8-10.

The 95 % confidence limits range from 10 to 34 % of the mean of all ships. (The extreme value of 73 % for *Centropages* C IV-V stages can be explained by the sparse occurrence of this species and is not included.)

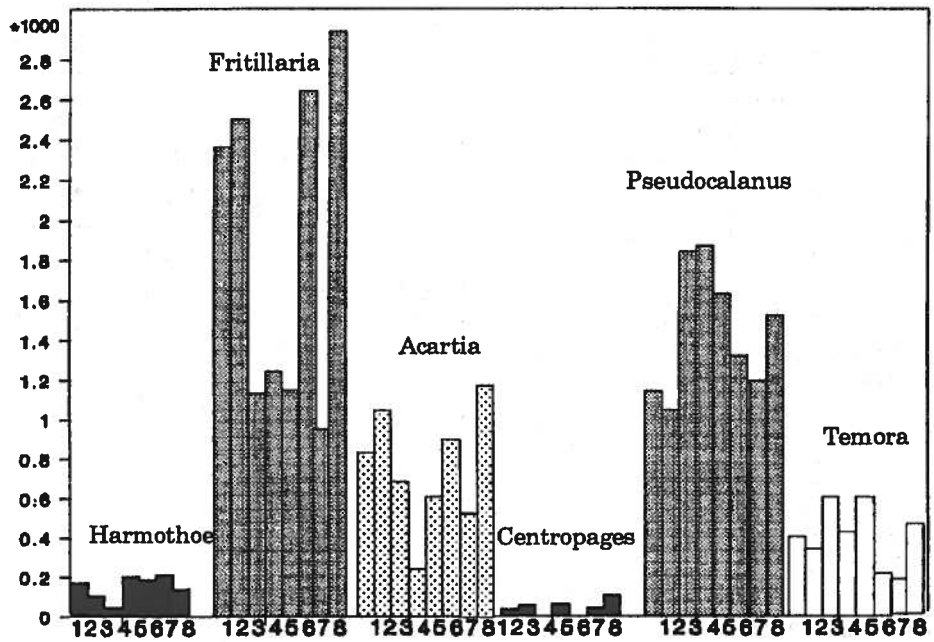



Fig. 7. Counting results (ind. $m^{-3}$) of the ships for the different mesozooplankton species.

Table 8. Mean (x), standard deviation (SD), coefficient of variation (CV %), number of counted subsamples (n) and part counted (1/x) of mesozooplankton intercalibration countings for copepods.

| | | | all stages | | | without nauplii | | | without nauplii and C I-III stages | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ship | n | 1/x | x | SD | CV % | x | SD | CV % | x | SD | CV % |
| **1. Acartia spp.** | | | | | | | | | | | |
| 1 | 1 | 8 | 10848 | - | - | 832 | - | - | 176 | - | - |
| 2 | 1 | 8 | 11592 | - | - | 1048 | 56 | 5 | 208 | 8 | 4 |
| 3 | 2 | 32 | 10592 | 672 | 6 | 688 | 112 | 16 | 288 | 32 | 11 |
| 4 | 2 | 32 | 544 | 32 | 6 | 240 | 16 | 7 | 192 | 0 | - |
| 5 | 2 | 64 | 8736 | 1056 | 12 | 608 | 32 | 5 | 128 | 0 | - |
| 6 | 4 | 64 | 10521 | 348 | 3 | 898 | 93 | 10 | 221 | 130 | 59 |
| 7 | 3 | 100 | 11200 | 490 | 4 | 500 | 141 | 28 | 67 | 94 | 140 |
| 8 | 2 | 43.5 | 15182 | 1958 | 13 | 1114 | 216 | 19 | 296 | 121 | 41 |
| **2. Temora longicornis** | | | | | | | | | | | |
| 1 | 1 | 8 | 424 | - | - | 408 | - | - | 408 | - | - |
| 2 | 1 | 8 | 344 | 32 | 9 | 344 | 32 | 9 | 332 | 28 | 8 |
| 3 | 2 | 32 | 672 | 0 | 0 | 608 | 32 | 5 | 496 | 48 | 10 |
| 4 | 2 | 32 | 1136 | 16 | 1 | 432 | 80 | 19 | 400 | 80 | 20 |
| 5 | 2 | 64 | 608 | 160 | 26 | 608 | 160 | 26 | 608 | 160 | 26 |
| 6 | 4 | 64 | 221 | 137 | 62 | 221 | 137 | 62 | 221 | 137 | 62 |
| 7 | 3 | 100 | 233 | 94 | 40 | 167 | 47 | 28 | 167 | 47 | 28 |
| 8 | 2 | 43.5 | 435 | 110 | 25 | 435 | 110 | 25 | 426 | 108 | 25 |
| **3. Pseudocalanus minutus elongatus** | | | | | | | | | | | |
| 1 | 1 | 8 | 5840 | - | - | 1144 | - | - | 1104 | - | - |
| 2 | 1 | 8 | 6072 | - | - | 1048 | 160 | 15 | 1012 | 140 | 14 |
| 3 | 2 | 32 | 7552 | 64 | 1 | 1840 | 48 | 3 | 1376 | 96 | 7 |
| 4 | 2 | 32 | 11568 | 272 | 2 | 1872 | 80 | 4 | 1376 | 96 | 7 |
| 5 | 2 | 64 | 4512 | 1312 | 29 | 1632 | 416 | 26 | 1504 | 416 | 28 |
| 6 | 4 | 64 | 7418 | 757 | 10 | 1323 | 118 | 9 | 1260 | 118 | 9 |
| 7 | 3 | 100 | 4367 | 772 | 18 | 1133 | 330 | 29 | 933 | 411 | 44 |
| 8 | 2 | 43.5 | 7787 | 218 | 3 | 1444 | 51 | 4 | 1427 | 51 | 4 |
| **4. Centropages hamatus** | | | C IV-V stages | | | | | | | | |
| 1 | 1 | 8 | 40 | - | - | | | | | | |
| 2 | 1 | 8 | 56 | 8 | 14 | | | | | | |
| 3 | 2 | 32 | 0 | - | - | | | | | | |
| 4 | 2 | 32 | 64 | 0 | 0 | | | | | | |
| 5 | 2 | 64 | 0 | - | - | | | | | | |
| 6 | 4 | 64 | 47 | 52 | 111 | | | | | | |
| 7 | 3 | 100 | 0 | - | - | | | | | | |
| 8 | 2 | 43.5 | 96 | 43 | 45 | | | | | | |
| **Species 1, 2, 3** | | | nauplii | | | copepodite stages I-III | | | | | |
| 1 | 1 | 8 | 14728 | - | - | 696 | - | - | | | |
| 2 | 1 | 8 | 15672 | - | - | 884 | 28 | 3 | | | |
| 3 | 2 | 32 | 15680 | 708 | 5 | 992 | 128 | 13 | | | |
| 4 | 2 | 32 | 10720 | 416 | 4 | 576 | 32 | 6 | | | |
| 5 | 2 | 64 | 11008 | 1984 | 18 | 608 | 32 | 5 | | | |
| 6 | 4 | 64 | 15719 | 720 | 5 | 740 | 82 | 11 | | | |
| 7 | 3 | 100 | 14000 | 1020 | 7 | 633 | 47 | 7 | | | |
| 8 | 2 | 43.5 | 20228 | 1653 | 8 | 861 | 133 | 16 | | | |

As it is sometimes difficult to identify the species of nauplii and young copepodite stages, these groups are analysed for all species together. For copepods three different classifications were made: 1. all stages together, 2. without nauplii, and 3. without nauplii and copepodite stages I-III. The coefficient of variation decreases when both nauplii and copepodite stages I-III are excluded. An exception is *Acartia*, probably because of the difficulties in differentiating between *A. longiremis* and *A. bifilosa* (Table 10). Generally, the results of ship no. 7 tend to be lower and those of ship no. 8 to be higher than the others, but this is not the case for every species. Also the results of ship no. 4 often show deviating values.

Table 9. Mean (x), standard deviation (SD), coefficient of variation (CV %), number of counted subsamples (n) and part counted (1/x) of mesozooplankton intercalibration countings for *Fritillaria borealis*, Polychaeta larvae and *Evadne nordmanni*.

| ship | n | 1/x | x | SD | CV % |
|---|---|---|---|---|---|
| **Fritillaria borealis** | | | | | |
| 1 | 1 | 8 | 2368 | - | - |
| 2 | 2 | 8 | 2504 | 80 | 3 |
| 3 | 2 | 32 | 1136 | 16 | 1 |
| 4 | 2 | 32 | 1248 | 128 | 10 |
| 5 | 2 | 64 | 1152 | 192 | 17 |
| 6 | 4 | 64 | 2646 | 336 | 13 |
| 7 | 3 | 100 | 900 | 94 | 10 |
| 8 | 5 | 43.5 | 2784 | 44 | 2 |
| **Polychaeta larvae** | | | | | |
| 1 | 1 | 8 | 176 | - | - |
| 2 | 2 | 8 | 108 | 84 | 78 |
| 3 | 2 | 32 | 48 | 16 | 33 |
| 4 | 2 | 32 | 208 | 48 | 23 |
| 5 | 2 | 64 | 192 | 64 | 33 |
| 6 | 4 | 64 | 221 | 105 | 48 |
| 7 | 3 | 100 | 133 | 47 | 35 |
| 8 | 5 | 43.5 | 0 | 0 | - |
| **Evadne nordmanni** | | | | | |
| 1 | 1 | 8 | 40 | - | - |
| 2 | 2 | 8 | 92 | 20 | 22 |
| 3 | 2 | 32 | 112 | 48 | 43 |
| 4 | 2 | 32 | 96 | 32 | 33 |
| 5 | 2 | 64 | 64 | 0 | 0 |
| 6 | 4 | 64 | 95 | 70 | 74 |
| 7 | 3 | 100 | 67 | 47 | 70 |
| 8 | 5 | 43.5 | 61 | 44 | 72 |

Table 10. Mean of all ships (x), standard deviation (SD), coefficient of variation (CV %), standard error (SE) and 95 % confidence limits (95 % CL, based on t-values after Student) for the counted species.

| species | mean | SD | CV % | SE | 95 % CL |
|---|---|---|---|---|---|
| **Acartia spp.** | | | | | |
| all stages | 10959 | 1246 | 11 | 471 | + 1153 |
| without nauplii | 803 | 197 | 25 | 74 | + 181 |
| without nauplii + C I-III | 214 | 52 | 24 | 19 | + |
| **Centropages hamatus** | | | | | |
| C IV-V | 38 | 33 | 87 | 12 | + 28 |
| **Temora longicornis** | | | | | |
| all stages | 427 | 152 | 36 | 57 | + 140 |
| without nauplii | 409 | 142 | 35 | 50 | + 119 |
| without nauplii + C I-III | 369 | 100 | 27 | 35 | + 83 |
| **Pseudocalanus minutus elongatus** | | | | | |
| all stages | 6484 | 1017 | 16 | 384 | + 940 |
| without nauplii | 1430 | 302 | 21 | 107 | + 253 |
| without nauplii + C I-III | 1282 | 158 | 12 | 56 | + 132 |
| all nauplii | 14761 | 2156 | 15 | 762 | + 1803 |
| all stages C I-III | 749 | 140 | 19 | 49 | + 117 |
| Fritillaria borealis | 1842 | 747 | 41 | 264 | + 625 |
| Polychaeta larvae | 160 | 51 | 32 | 19 | + 47 |
| Evadne nordmanni | 78 | 22 | 28 | 8 | + 19 |

## 4. DISCUSSION

Both chlorophyll *a* and primary production capacity analyses require several procedures which all contribute to the variation in the results.

According to the analysis of the purified chlorophyll *a* extract, the accuracy of the measuring instruments was good. The precision of the replicate measurement by the individual ships was usually good. The differences between the ships were, however, statistically significant. Since identical filters and extraction solvents were used, the most probable source for variation for the chlorophyll *a* results is the extraction procedure including homogenization of the sample. The variation within and between the sample sets was of the same order of magnitude as in previous international intercalibration exercises in the Baltic Sea (Larsson et al. 1978, Barinova et al. 1980, Helcom 1983b).

The variation that might have been caused by different $^{14}C$ activity determinations was eliminated, since all the $^{14}C$ activities were measured on board one ship. Some marked differences between the measured and reported activities of the $^{14}C$ batches indicate differences in the beta-counting methods. Preadjustment of the irradiance levels in the incubators also unified the results. Still, the irradiance used in most of the incubators was below the level recommended for the Baltic Monitoring Programme. The actual irradiance levels and production rates were not, however, correlated. In general, the precision was good; only the variation between the replicates for ship no. 2 was

unacceptably large. The variation between the laboratories was similar to that during the previous HELCOM intercalibration in Rønne (HELCOM 1983a) but, probably due to the more homogeneous procedure, clearly less than in the ICES intercomparison in Hirtshals (Anon. 1987).

According to the previous HELCOM intercalibration (HELCOM 1983b), the most important factor causing the differences between the phytoplankton counting results of the different laboratories is species identification. This was evident in this experiment, too. The number of species identified by different people varied remarkably.

The coefficients of variation of all the phytoplankton counting results remained considerably lower than those determined for natural samples during the HELCOM intercalibration in Rønne 1982; they were in the same range as for the culture samples in Rønne (HELCOM 1983b).

The variation found in the parallel countings of the same chamber was quite high, in some cases even higher than that between subsamples, indicating an inhomogeneous distribution of the cells in the chamber. All the species counted occurred in chains, and the cells were thus not randomly distributed. In addition, some reasons for the variation could be as follows:

- *Gonyaulax catenata* and *Skeletonema costatum* - the number of counted cells was in most cases less than 100;
- *Achnanthes taeniata* - the species was in the active growth phase, thus having a lot of dividing and just divided cells. Differenting between them was sometimes difficult. The cells also had a large size variation which made the identification even more difficult;
- *Chaetoceros* spp.- detection and differentiation of the cells was difficult due to the vertical orientation of the chains and their poor condition;
- *Thalassiosira baltica* - it would appear that in many cases *T. bramaputrae* have been included in these countings.

The differences in the mesozooplankton countings were in some cases caused by the identification problems. Especially the nauplii and the young development stages of copepods are difficult to associate with species. The different methods of splitting should have an impact on the variability. This is not, however, seen in the results. The subsamples which were delivered to the participants of the intercomparison experiment may not have contained exact equivalents, owing to possible splitting errors. Some of the differences can be explained by species specific reasons:

- For *Fritillaria borealis*, the high variation might be caused by aggregation of the animals, which makes it impossible to produce randomly distributed subsamples. Statistically insufficient amount of individuals were counted for *Centropages hamatus*. This is the case for *Evadne nordmanni* and Polychaeta larvae, too.
- For the copepods, the coefficient of variation decreases considerably when nauplii and C I-III stages are excluded. An exception is *Acartia*, which is probably caused by the problem of differentiating between *A. longiremis* and *A. bifilosa*.

The coefficients of variation for all comparable mesozooplankton species were considerably smaller than those obtained in the intercalibration workshop in Rønne (HELCOM 1983b).

## 5. CONCLUSIONS

The results of the purified chlorophyll *a* extract demonstrate the good accuracy of the measuring instruments. Both spectrophotometric and fluorometric methods gave comparable results. Homogenization of the filtered samples and extraction of chlorophyll *a* seem to be the procedures responsible for most of the differences.

The intercomparison of primary production capacity measurements indicated good laboratory procedures on board most of the ships, as evidenced by the small variation in the replicates. However, only a few incubators met the demands of the Baltic Monitoring Programme (HELCOM 1983a). The differences between the activities of the $^{14}C$ batches measured during the experiment and reported by the users indicate possible calibration errors of the beta-counters.

Fairly comparable phytoplankton counting results were achieved with the method used in the Baltic Sea Monitoring Programme when the species identification was uniform and a sufficient number of cells was counted. Intercalibration of species identification rather than counting methods are recommended at this stage of the monitoring programme.

For mesozooplankton when interpreaing the results of international projects like the Baltic Monitoring Programme, most attention should be given to adult copepods and older copepodite stages, since there are difficulties in determining the younger stages and nauplii at the species level. A sufficient number (500 individuals) of adults and later copepodite stages must be counted in order to reduce the variation.

**Acknowledgement**

The liquid scintillation counter and the scintillation cocktail for the $^{14}C$ determination were provided by Wallac Oy, Finland.

## REFERENCES

Anon., 1987: ICES $^{14}C$ primary production intercomparison exercise. Preliminary data report. - ICES CM 1987/L:27, 18 pp. (mimeogr.)

Barinova, S.P., Forsskåhl, M., Kukk, E., Melnikova, L., Melvasalo, T., Niemi, Å., Piirsoo, K. & Viljamaa, H., 1980: Phytoplankton. - In: Järvekulg, A., Kukk, E., Lassig, J., Melvasalo T., Niemi, Å. & Saava, A., Finnish-Soviet intercalibration of biological parameters used for monitoring the conditions of the Gulf of Finland. - Meri 8:1-78.

Dybern, B.I. & Hansen, H.-P., 1989: Baltic Sea Patchiness Experiment (PEX-86), Part I. General Report. - ICES, Cooperative Research Report No. 163:1-100.

HELCOM, 1983a: Guidelines for the Baltic Monitoring Programme for the second stage. - Baltic Sea Environment Proceedings 12:1-251.

- " - 1983b: Second biological intercalibration workshop. -Baltic Sea Environment Proceedings 9:1-95.

Larsson, U., Norling, L., Carlberg, S., Lööf, S. Tolstoy, A., von Bröckel, K., Elizarjeva, V., Kaiser, W., Lassig, J., Mäkinen, I. & Melvasalo, T., 1978: Intercalibration of methods for chlorophyll measurements in the Baltic Sea. - Merentutkimuslait. Julk./Havsforskningsinst. Skr. 243:63-76.

Lund, J.W.G., Kipling, C., LeCren, E.D., 1958: The inverted microscope method for estimating algal numbers and the statistical basis of estimation by counting. - Hydrobiologia 11:143-70.

Sournia, A. (ed.), 1978: Phytoplankton manual. - 337 pp. UNESCO, Paris.

Steeman Nielsen, E., 1952: The use of radioactive carbon ($^{14}C$) for measuring organic production in the sea. - J. Cons. int. Explor. Mer 18:117-140.

Utermöhl, H., 1958: Zur Vervollkommnung der quantitativen Phytoplankton-Methodik. - Mitt. int. Verein. theor. angew. Limnol. 9:1-38.

Finnish Marine Research 257 (1990):59-74

# PLUTONIUM ISOTOPE RATIOS IN BALTIC SEA SEDIMENTS

Per Östlund

IVL, Swedish Environmental Research Institute
P.O. Box 21060
S-100 31 Stockholm
Sweden

## ABSTRACT

Isotope ratios of plutonium ($^{238}Pu/^{239,240}Pu$) have been used to identify plutonium sources in Baltic Sea sediments. In 1988, sediment samples were collected from open-sea stations in the western Baltic Proper, south of Stockholm. The main Pu source is suggested to be global fallout from thermounuclear bomb tests. Global fallout, which was at a maximum in 1963-64, was found as subsurficial activity peaks. Pu with enhanced isotope activity ratios was found in the uppermost layers of the samples. Conceivable sources of this Pu are suggested. The total activities of $^{239,240}Pu$ ranged from 40 to 135 $Bq \cdot m^{-2}$.

Key words: Baltic Sea sediments, Pu distribution, Pu sources.

## 1. INTRODUCTION

Plutonium (Pu) is widely distributed over the Earth, mainly as a consequence of anthropogenic activities. The Pu isotope ratios of different sources are often specific, and it is therefore possible to distinguish between various sources, particularly between local and global ones. This is an advantage when assessing the short and long-term fate of the pollutants. In this paper total inventories of deposited Pu, as well as $^{238}Pu/^{239,240}Pu$ isotope activity ratios from Baltic Sea sediment samples, are presented and compared with literature data.

### 1.1 Global Pu sources

Before 1986, atmospheric fallout from tests of thermonuclear weapons and the burned-up satellite SNAP-9A were considered to be the sole Pu source in the Baltic area (Simola et al., 1979; Tuomainen et al., 1986). In 1986 the Chernobyl accident increased these amounts. Stratospheric thermonuclear weapon testing took place mainly during the 1950s and early '60s, and contributed to Pu-fallout throughout both hemispheres. There is a general latitudinal dependence, especially in the northern hemisphere, with maximum fallout in the mid-latitudes, and minima towards the equatorial and polar regions. According to the generalized fallout inventory of Hardy et al. (1973), about 50 $Bq\,m^{-2}$ of cumulative fallout Pu would be expected in the central Baltic Sea area (the Baltic Proper). This assumption, which was based on only a few soil samples, proved to be consistent with the sediment inventories of Simola et al. (1979) and Salo et al. (1986), where 20-90 $Bq \cdot m^{-2}$ were reported from open sea stations in the Baltic Proper.

The $^{238}Pu/^{239,240}Pu$ isotope activity ratio of weapons fallout is estimated to be 0.024. In 1964, the US navigational satellite SNAP-9A with a nuclear power source containing almost 100 % $^{238}Pu$ burned up at high altitude over the Indian Ocean. This Pu was widely distributed and altered the $^{238}Pu/^{239,240}Pu$ isotope activity ratio of the fallout in the northern hemisphere to 0.036 (Hardy et al. 1973; Harley, 1980).

The deposition of global fallout vs. time can be demonstrated by the quarterly deposition of $^{90}Sr$(strontium) measured in New York City (Fig. 1). The values recorded for $^{90}Sr$ can be taken as representative for $^{239,240}Pu$, since their relationship to Pu is fairly constant in fresh global fallout debris (Harley, 1980; Sholkovitz, 1983). Figure 1 can be compared with the quarterly activities of $^{137}Cs$ (cesium) measured in Leningrad surface air, better representing the fallout over the Baltic Area (Fig. 2). The almost perfect agreement in time of these two records suggests that there was a simultaneous distribution of global fallout. As can be seen from the figures, the fallout peaked in 1963.

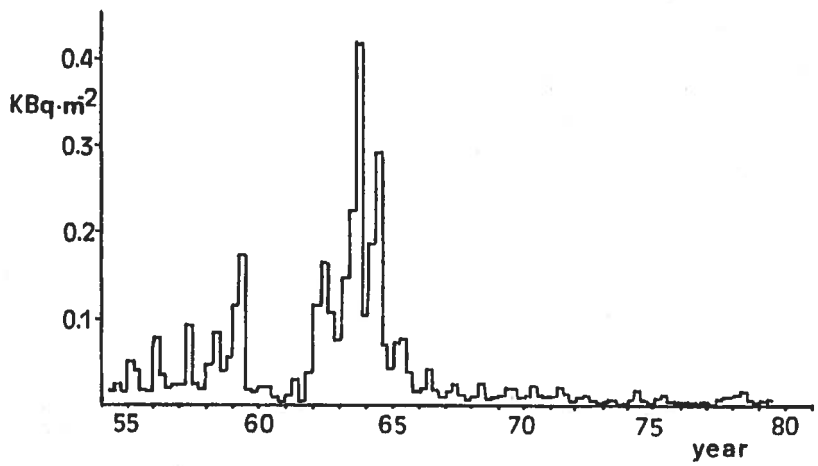



Fig. 1. Quarterly deposition of $^{90}Sr$ at New York city between 1954 and 1980. Redrawn from Environmental Measurement Laboratory (1980).

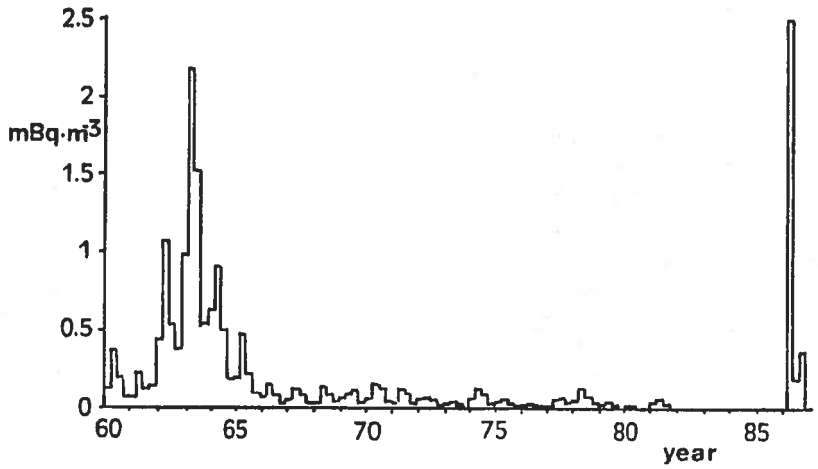



Fig. 2. Quarterly activities of $^{137}Cs$ in Leningrad surface air between 1960 and 1986. 1960-77 from Gritchenko et al. (1979); 1978-86 from Gritchenko, pers. com.

## 1.2 Regional plutonium sources

European reprocessing facilities for spent nuclear fuels discharge substantial amounts of transuranic elements into the sea. The most important nuclides in this context are $^{238}Pu$, $^{239}Pu$, $^{240}Pu$, $^{241}Pu$ and $^{241}Am$ (americium). By far, the largest amounts originate from the British Sellafield plant (formerly Windscale) and the French installation at Cap de la Hague. A number of smaller sources can also be identified, e.g. the Scottish reprocessing facility at Dounreay and the low-level waste disposal operations in the northeastern Atlantic Ocean (Needler and Templeton, 1981). Their contributions are, however, negligible on a larger scale. The $^{238}Pu/^{239,240}Pu$ ratio of the Sellafield Pu is larger than that of the global fallout and during the years 1978-1984, for example, was about 0.3 with only minor variations from year to year (BNFL, 1979-1984).

The distribution of Sellafield-derived Pu in the Atlantic Ocean water column is well documented. Most of it is deposited close to the discharge pipes, but a fraction is also transported both southwards in the Iris Sea, and northwards around the coast of Scotland and then south into the North Sea and northeast into the waters of Norway, Spitsbergen and Greenland (Livingston and Bowen, 1977; Murray & Kautsky, 1977; Murray et al., 1978, 1979; Livingston et al., 1982; Hallstadius et al., 1986). The $^{238}Pu/^{239,240}Pu$ ratios in the North Sea were found to be significantly larger (about 5 times larger) than those in areas where only global fallout Pu is present (Murray & Kautsky, 1977; Dunice et al., 1983; Duursma, pers. com.). Sellafield-Pu, detected as enhanced $^{238}Pu/^{239,240}Pu$ ratios, has also been reported in Kattegat surface water (Hallstadius et al., 1986). Plutonium has not been reported to enter the Baltic Sea from the North Sea.

## 1.3 Local sources

In april 1986 the Soviet nuclear power station at Chernobyl became the largest industrial source of radioactive material in the atmosphere so far registered, and large amounts of radioactive material were emitted and spread widely (Devell et al., 1986; IAEA, 1986; Levi, 1986). Chernobyl Pu, as well as other nuclides, have been found in soil, biota and sediments of the Baltic area (e.g. Ikäheimonen, 1988; Jaakkola et al., 1988; Rioseco et al., 1988). The $^{238}Pu/^{239,240}Pu$ isotope activity ratio of the Chernobyl fallout dust was estimated to be about 0.5 (Aarkrog, 1988).

## 1.4 Baltic Sea sediment as a fallout recipient

The fact that 98-99 % of all Pu in the Baltic Sea is found in the sediments implies that Pu is efficiently scavenged and removed from the watermass (Leskinen et al., 1986; Salo et al., 1986). What is more, with a sedimentation rate in the order of one millimeter per year and a large concentration of trace metals on particulate material in the Baltic Sea (3-9 and 8-290 times higher than in the North Sea and the NE Atlantic respectively, Brügman, 1986), a rapid rate of removal would be expected. A Pu additive, in chemical or physical form similar to that of global fallout, should therefore be found in sediments

shortly after emission and lying above of the global fallout. Furthermore, large areas of the Baltic Sea are depleted of oxygen and have stagnant bottom water, which results in almost no bioturbation and laminated sediments (Johnnson et al., 1990). The possibility of remobilization of Pu as a result of diagenesis has been adressed in several studies (e.g. Livingston & Bowen, 1979; Carpenter & Beasley, 1981; Beasley et al., 1982; Santschi et al., 1983; Malcolm et al., 1990). Interstitial water studies (Nelson & Lovett, 1981; Sholkovitz & Mann, 1984; Buesseler & Sholkovitz, 1987) have all suggested that there is little postdepositional mobilization of Pu. For these reasons, Baltic Sea sediments are eminently suitable for studies on time series of pollutants. Samples were collected from an area between the Swedish mainland and the island of Gotland (Fig. 3) in order to identify Pu from different sources.

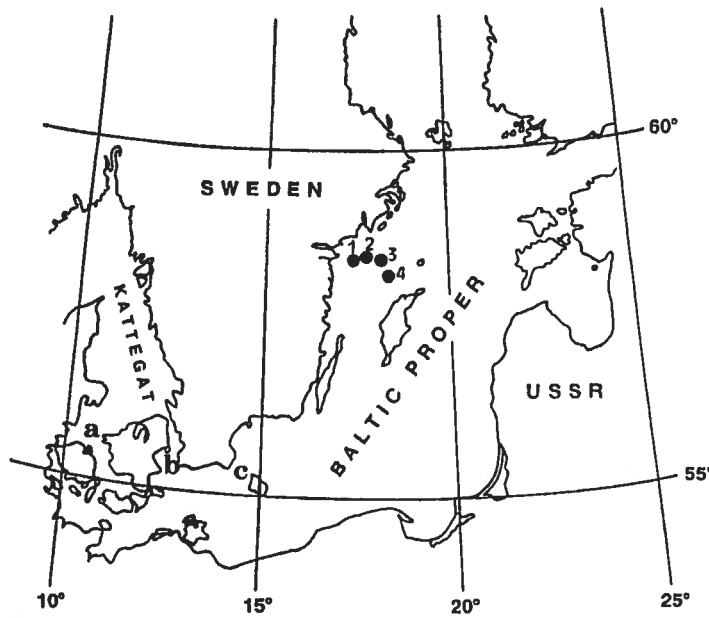



Fig. 3. The Baltic Sea area. Sampling stations indicated by numerals; the Danish Belts by "a"; Öresund by "b"; Bornholm Strait by "c".

## 2. MATERIALS AND METHODS

In 1988, sediment cores were sampled with plastic tubes (int. diam. 50 or 65 mm) fitted with pistons in order to avoid core-shortening. The samples were subsampled from box-cores. The cores were sliced into 1 cm sections, freeze-dried, and ground in an agate mortar to a homogeneous powder. Each core section was analyzed for Pu.

### 2.1 Plutonium analysis

Two to four g of each sample were spiked with $^{242}Pu$ and extracted with 5 M nitric acid (50 ml, 120°C, 2 h). Plutonium was recovered using the method described by Holm and Fukai (1977). A TTA-extraction step (1-(2-Thenoyl)-

3,3,3-trifluoroacetone) was also included. The $^{238,239,240}Pu$ activities were measured by alpha spectrometry after electro-deposition on stainless steel planchettes (Hallstadius, 1984). The $^{239}Pu$ and $^{240}Pu$ activities are reported as combined values due to their similar alpha-particle energies.

## 3. RESULTS

### 3.1 Station 1

One core was sampled from a box-core taken at a water depth of 63 m. The sediment was grey-reddish in colour with clear signs of bioturbation. Living species of *Macoma* were found. The LoI was about 7 % wt, and the grains were of the coarse silt size fraction and significantly coarser than those of the other stations (pers. com. Carman). Station 1 therefore represents a transport-bottom according to the classification of Håkanson & Jansson (1982). Plutonium values were fairly uniform down to about 4 cm (Fig. 4). The $^{238}Pu/^{239,240}Pu$ ratio, plotted in Fig. 4, varied only slightly and was about 0.04 and hence in agreement with reported global fallout ratios (SNAP-9A included). The accumulative $^{239,240}Pu$ activity was calculated as 40 $Bq \cdot m^{-2}$ (Table 1).

### 3.2 Station 2

Two cores were sampled from a box-core taken at a water depth of 75 m. The sediment was dark grey-black without signs of turbation. The grains were fine and of the silt fraction (pers. com. Carman). Station 2 represents an accumulation-bottom, according to the classification by Håkanson & Jansson (1982). Plutonium was measured down to about 7 cm and exhibited a well defined subsurface maxima that presumably reflected the fallout peak in 1963. Due to the atmospheric injection of $^{238}Pu$ from the SNAP-9A accident in 1964, the $^{238}Pu/^{239,240}Pu$ isotope ratio increased from about 0.02 to 0.04 in the 3-4 cm layer (Fig. 4). The $^{238}Pu/^{239,240}Pu$ isotope ratio in the 0-1 cm layer was about 0.07. Only the 0-1 cm layer of core B was measured, but there was almost total concordance with core A in this layer (Fig. 4). The accumulative $^{239,240}Pu$ activity was calculated as 136 $Bq \cdot m^{-2}$ (Table 1).

### 3.3 Station 3 and 4

One core was sampled at station 3 and two cores at station 4 from box-cores taken at water depths of 103 and 132 m respectively. The samples were very dark grey-black with an odour of hydrogen sulfide. The cores were also clearly laminated. The grains were fine and of the silt fraction (pers. com. Carman). These two stations represent oxygen depleted accumulation-bottoms (Håkanson & Jansson, 1982). The sharp Pu subsurface maxima reflect the 1963 fallout peak. The $^{238}Pu/^{239,240}Pu$ ratios, plotted in Fig. 4, varied only slightly around 0.04, except for the 0-1 cm layer where the ratios were enhanced: 0.064 in core 3; 0.118 in core 4A; 0.071 in core 4B. The accumulative $^{239,240}Pu$ activities were calculated as 72 $Bq \cdot m^{-2}$ (station 3) and 94 $Bq \cdot m^{-2}$ (average from core 4A and 4B), respectively (Table 1). The concordance between core 4A and 4B is almost total.

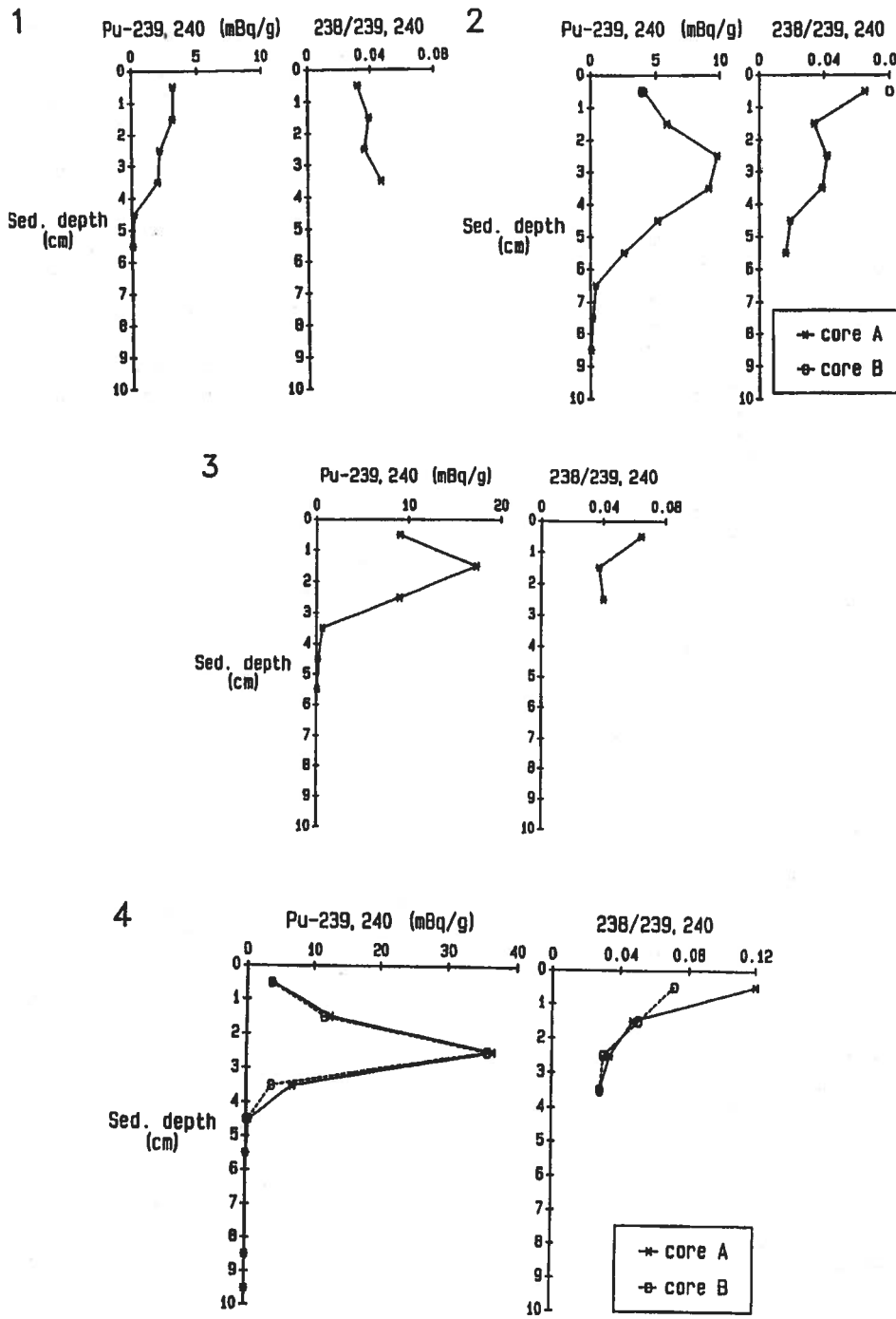



Fig. 4. Vertical sediment profiles of $^{239,240}Pu$ and $^{238}Pu/^{239,240}Pu$ ratios at open-sea stations from the Baltic Sea.

Table 1. Amounts of $^{239,240}Pu$ per unit area and $^{238}Pu/^{239,240}Pu$ ratios in sampled cores ± 1 σ of the radio essay. The integrated (total) activities are expressed as $mBq \cdot cm^{-2}$. $1 mBq \cdot cm^{-2} = 10\ Bq \cdot m^{-2}$.

**Station 1, water depth: 63 m**

| Sample depth (cm) | Dry matter (g)* | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 4.84 | 0.797±0.006 | 0.032±0.008 |
| 1-2 | 7.58 | 1.226±0.007 | 0.039±0.011 |
| 2-3 | 8.33 | 0.918±0.007 | 0.036±0.010 |
| 3-4 | 9.28 | 0.943±0.008 | 0.047±0.011 |
| 4-5 | 12.29 | 0.102±0.027 | - |
| 5-6 | 11.95 | 0.033±0.044 | - |
| Total activity: | | 4.02 ± 0.10 $mBq \cdot cm^{-2}$ | |

**Station 2A, water depth: 75 m**

| Sample depth (cm) | Dry matter (g)* | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 5.21 | 1.090±0.004 | 0.065±0.010 |
| 1-2 | 4.70 | 1.408±0.003 | 0.034±0.006 |
| 2-3 | 6.82 | 3.410±0.003 | 0.042±0.004 |
| 3-4 | 8.79 | 4.099±0.006 | 0.039±0.006 |
| 4-5 | 8.61 | 2.258±0.005 | 0.019±0.004 |
| 5-6 | 9.32 | 1.225±0.009 | 0.016±0.007 |
| 6-7 | 11.97 | 0.257±0.019 | - |
| 7-8 | 10.89 | 0.094±0.024 | - |
| 8-9 | 10.47 | 0.032±0.035 | - |
| Total activity: | | 13.64 ± 0.10 $mBq \cdot cm^{-2}$ | |

**Station 2B, water depth: 75 m**

| Sample depth (cm) | Dry matter (g)* | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 2.664 | 0.533±0.008 | 0.082±0.029 |

**Station 3, water depth: 103 m**

| Sample depth (cm) | Dry matter (g)* | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 2.60 | 1.211±0.004 | 0.064±0.012 |
| 1-2 | 3.32 | 2.933±0.003 | 0.037±0.005 |
| 2-3 | 5.92 | 2.747±0.006 | 0.040±0.008 |
| 3-4 | 6.04 | 0.219±0.032 | - |
| 4-5 | 6.84 | 0.068±0.033 | - |
| 5-6 | 7.92 | 0.038±0.039 | - |
| Total activity: | | 7.22 ± 0.12 $mBq \cdot cm^{-2}$ | |

**Station 4A, water depth: 132 m**

| Sample depth (cm) | Dry matter (g)** | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 3.65 | 0.436±0.002 | 0.118±0.016 |
| 1-2 | 3.28 | 1.245±0.002 | 0.047±0.006 |
| 2-3 | 5.26 | 5.808±0.002 | 0.034±0.003 |
| 3-4 | 10.42 | 2.193±0.004 | 0.028±0.005 |
| 4-5 | 12.26 | 0.129±0.016 | - |
| 7-8 | 20.00 | - | - |
| 8-9 | 20.27 | - | - |
| 9-10 | 24.10 | - | - |
| Total activity: | | 9.80 ± 0.03 $mBq \cdot cm^{-2}$ | |

**Station 4B, water depth: 132 m**

| Sample depth (cm) | Dry matter (g)** | $^{239,240}Pu$ $mBq \cdot cm^{-2}$ | $^{238}Pu/^{239,240}Pu$ |
|---|---|---|---|
| 0-1 | 3.04 | 0.365±0.002 | 0.071±0.017 |
| 1-2 | 3.08 | 1.099±0.001 | 0.050±0.006 |
| 2-3 | 5.69 | 6.170±0.001 | 0.030±0.002 |
| 3-4 | 9.93 | 1.209±0.015 | 0.028±0.007 |
| 4-5 | 12.54 | 0.117±0.017 | - |
| Total activity: | | 8.96 ± 0.04 $mBq \cdot cm^{-2}$ | |

- = not detected, * sample area: 19.63 $cm^2$, ** sample area: 33.18 $cm^2$

### 3.4 All stations

The cumulative $^{239,240}Pu$ activities were in the 40-136 $Bq \cdot m^{-2}$ range, which is of the same order of magnitude as reported by other scientists (Simola et al., 1979; Salo et al., 1986; Ikäheimonen et al., 1988; Saxén et al., 1989). The horizontal distribution was found to vary significantly, even between samples collected from similar bottom types. There was considerably less variation in the vertical distribution, and most of the deposited Pu was found in and above the 2-3 or 3-4 cm sections (Table 1).

## 4. DISCUSSION

Assuming that the Pu activity maxima represent 1963, then the mean annual increment of the 0-3 cm sediment layer is about 1 mm. The high water content of these sediments has been taken into account in this calculation. The sedimentation rate of the Baltic Sea varies considerably (0.05 - 2.0 $mm \cdot yr^{-1}$, Niemistö and Voipio, 1974), but the average value is estimated to about 0.1 $mm \cdot yr^{-1}$, (Ignatius et al., 1981). Of the four sampled stations, three represent accumulation bottoms. According to the study of Jonsson et al., (1990), at least station 3 and 4 are typical representatives of accumulation bottoms below the halocline. Jonsson et al., (1990) also estimated the distribution of this type of accumulation bottom, and suggested that it covers about one third of the total Baltic Proper area. The measured vertical distribution of Pu in the accumulation bottoms (station 3 and 4) is consistent with the results by Simola et al., (1979). Ilus et al., (1989) and Saxen et al., (1989), on the other hand, report a somewhat different vertical distribution with Pu maxima in the 5-10 cm section. However, if the vertical distribution suggested from this study is applicable, then almost all the Pu in one third of the Baltic Proper would be expected to be found in the top 3 to 4 cm layer.

The enhanced isotope ratios in the surface layers are tentatively explained by the Chernobyl accident. However, pre-Chernobyl measurements from Baltic Sea sediments with $^{238}Pu$ data are very sparsely reported in the literature. Not one profile sectioned into 1 cm, or less, intervals was found with corresponding isotope ratio data. Literature data are given in Table 2. Only surface layer data are included in this table. The term "surface layer" is discussed below.

After the Chernobyl accident great efforts were made to investigate the distribution of various Pu isotopes. Both enhanced and unchanged isotope ratios in comparison with global fallout ratios were reported from Finnish post-Chernobyl measurements (Table 2). Dahlgaard et al. (1988) found, in a survey of surface sediments (0-3 cm) in the Baltic Sea, that the contribution of Chernobyl was too small to be detected and hence had not affected the Pu ratios (the grounds for using 0-3 cm samples are discussed below). There is therefore evidence both for and against the accident having had an effect on the isotope ratios in Baltic sediments.

In this context it should be noted that enhanced isotope ratios in sediments were occasionally reported even before the Chernobyl accident, e.g. by Miettinen et al., (1975) and Risø, (1978 and 1979) (Table 2). It has been suggested that the isotope ratio in late global fallout had become enhanced, and has therefore altered the ratios measured in surface sediments (Nishiwaki, 1975).

The isotope ratios of bomb debris may differ considerably from one nuclear detonation to another, depending on the materials tested and the conditions. For example, the Pu isotope activity ratios of radioactive hot particles after the Soviet nuclear tests in 1961 and 1962 were observed to be relatively high (0.1-0.3), and the ratios of hot particles from Chinese tests in 1964-66 to be considerably lower (0.01-0.04) (Nishiwaki, 1975). However, in order to explain the enhanced ratios on the basis of altered composition of the global fallout, the latest fallout must have been highly enriched in $^{238}Pu$ according to the infinitesimal fallout after 1970 (see Figs. 1 and 2).

## 4.1 Some remarks related to methodology

Another possible explanation for the enhanced Pu isotope ratios, even before the Chernobyl accident, is that an undiscovered Pu source has been present. The possibility that Pu with relatively high $^{238}Pu/^{239,240}Pu$ ratio enters the Baltic from the North Sea should not yet be dismissed. Investigations of both Baltic Sea water and Baltic sediments resulting in conclusions contradicting this theory have been made (Aarkrog et al., 1981; Duniec et al., 1983; Duniec et al., 1985). However, some reservations about these investigations must be mentioned. It has been concluded from the Pu isotope ratio analysis of surface water from Öresund and the Bornholm Strait (Fig. 3) that Sellafield Pu does not enter the Baltic Sea (Duniec et al., 1983). Whether or not water-transported Pu enters the Baltic Sea remains an open question since North Sea water, because of its higher density primarily enters the Baltic Sea as bottom currents through the Danish Belts (Fig. 3). Since the theoretical residence time of water in the Baltic Sea is about 22 years (Fonselius, 1970), Duniec et al., (1983) analyzed surface water on its way out from the Baltic Sea. One can also speculate on the fact that ocean-water, besides continuous inflow, also enters the Baltic Sea as large intermittent breakthroughs governed by meteorological conditions over the Atlantic Ocean (Fonselius, 1969; Dickson, 1973). It is therefore possible that particle-reactive elements like Pu are transported by ocean water into the Baltic Sea, scavenged by the high density of particles in Baltic Sea water, and rapidly deposited without being detected in the water-mass. Major inflows are extremely variable in time, both annually and over longer periods, and are conspicuous by their irregular occurrence (Falkenmark & Mikulski, 1974). Inflows take place more frequently in fall and winter. However, Baltic water contains more particles during the spring and summer seasons, due to dominating anemobaric conditions (wind, air-pressure etc.), larger river-loadings and enhanced primary production in the water-mass. It is therefore suggested that, in order to detect North Sea Pu in the Baltic water phase, samples should be collected in timeseries over periods when ocean water breakthroughs could be expected. The timing for sampling of less particle-reactive elements, such as Cs (Assinder et al., 1985), which have been detected in Baltic water (e.g. Holm et al., 1986), is probably not as critical.

Based on measurements of sediment samples (0-3 cm sections), Aarkrog et al., (1981) have reported typical fallout ratios from the Danish Belts. Duniec et al., (1985) concluded from $^{241}Am/^{239,240}Pu$ activity ratio measurements on 0-3 cm sediment sections from the Baltic Sea that these ratios are close to values typical for global fallout, and hence not affected by effluent Pu with

different isotope ratios. In this study, almost all the deposited Pu was found in the 0-3 cm surface fraction of the sediments. A vertical $^{239,240}Pu$ distribution has also been reported by other scientists (Simola et al., 1979). The topmost 30 mm in a core from an area with a mean annual sedimentation rate of 1 mm would therefore contain the Pu deposited during the last 30 years. Addition of Pu from a new source with moderate total amounts of Pu, would most likely be so diluted as to be undetectable. This can be readily exemplified by the equation of Duniec et al. (1983):

$$x = (g - 0.036) / (0.170 - 0.036) \quad (1)$$

where x = the fraction of Pu originating from a new source
$g$ = the measured $^{238}Pu/^{239,240}Pu$ ratio
0.036 = the global fallout ratio (including SNAP-9A)
0.170 = the ratio of a new source (in this example corresponding to Kattegat ratios) (Duniec et al., 1983).

Table 2. Reported $^{238}Pu/^{239,240}Pu$ activity ratios in Baltic Sea surface sediments.

| Year | Position | Sample thickness (cm) | Ratio | Reference |
|---|---|---|---|---|
| Before the Chernobyl accident | | | | |
| 1973 | Gulf of Bothnia, open sea st. | 0-2 | 0.041[13] | Östlund, 1990 |
| 1974 | Tvärminne (59°50'N;23°15'E) | 0-1 | 0.071[4] | Miettinen, et al., 1975 |
| 1976 | Ringhals-1,3 | 0-3 | 0.037[2] | Risø-386, 1977 |
| 1977 | Ringhals-1,3 | 0-3 | 0.034[2] | - " - |
| 1978 | Ringhals-1 | 0-3 | 0.063 | Risø-403, 1978 |
| - " - | XV-1 (60°15'N; 27°15'E) | 0-25 | 0.028 | STL-A38, 1982 |
| - " - | Teili-1 (59°26'N; 21°32'E) | 0-20 | 0.034 | - " - |
| 1979 | LL-3a (60°04'N; 26°21'E) | 0-25 | 0.031 | - " - |
| - " - | EB-1 (61°04'N; 19°45'E) | 0-18 | 0.038 | - " - |
| - " - | C-VI (65°14'N; 23°33'E) | 0-12 | 0.039 | - " - |
| 1980 | Ringhals-2 | 0-3 | 0.071 | Risø-447, 1980 |
| - " - | Loviisa | 0-38 | 0.029[2] | STL-A38, 1982 |
| - " - | Olkiluoto | 0-25 | 0.037[5] | - " - |
| - " - | F-81 (57°19'N; 20°02'E) | 0-25 | 0.034 | - " - |
| - " - | LL-3a | 0-20 | 0.035 | - " - |
| - " - | EB-1 | 0-20 | 0.033 | - " - |
| - " - | XV-1 | 0-25 | 0.027 | - " - |
| - " - | Teili-1 | 0-20 | 0.038 | - " - |
| 1981 | EB-1 | 0-23 | 0.036 | STL-A40, 1982 |
| - " - | XV-1 | 0-25 | 0.027 | - " - |
| - " - | LL-3a | 0-20 | 0.033 | - " - |
| - " - | Teili-1 | 0-20 | 0.028 | - " - |
| - " - | F-81 | 0-20 | 0.063 | - " - |
| 1982 | C-VI | 0-20 | 0.056 | STL-A47, 1983 |
| - " - | EB-1 | 0-19 | 0.038 | - " - |
| - " - | XV-1 | 0-25 | 0.025 | - " - |
| - " - | LL-3a | 0-25 | 0.041 | - " - |
| - " - | Teili-1 | 0-20 | 0.038 | - " - |

Table 2. Condt.

| Year | Position | Sample thickness (cm) | Ratio | References |
|---|---|---|---|---|
| After the Chernobyl accident | | | | |
| 1986 | Teili-1 (June) | 0-1 | 0.081 | Ilus et al., 1987a |
| - " - | Teili-1 (October) | 0-1 | 0.124 | Ilus et al., 1987a |
| - " - | Loviisa-1,2,3,4,5,7,10,R1 | 0-5 | 0.039[8] | Ilus et al., 1987b |
| - " - | C-VI | 0-10 | 0.029 | Ikäheimonen et al., 1988 |
| - " - | EB-1 | 0-15 | 0.027 | - " - |
| - " - | XV-1 | 0-20 | 0.036 | - " - |
| - " - | LL-3a | 0-10 | 0.036 | - " - |
| - " - | BY-15 | 0-17 | 0.036 | - " - |
| - " - | 54°48'N; 19°19'E | 0-3 | 0.041 | Dahlgaard et al., 1988 |
| - " - | 55°17'N; 12°33'E | 0-3 | 0.048 | - " - |
| - " - | 55°34'N; 15°09'E | 0-3 | 0.043 | - " - |
| - " - | 56°05'N; 17°42'E | 0-3 | 0.013 | - " - |
| - " - | 57°00'N; 12°00'E | 0-3 | 0.054 | - " - |
| - " - | 58°00'N; 18°00'E | 0-3 | 0.063 | - " - |
| - " - | 58°45'N; 18°30'E | 0-3 | 0.050 | - " - |
| - " - | 58°53'N; 19°50'E | 0-3 | 0.024 | - " - |
| - " - | 60°10'N; 26°35'E | 0-3 | 0.045 | - " - |
| - " - | 60°13'N; 19°04'E | 0-3 | 0.019 | - " - |
| - " - | 61°04'N; 19°42'E | 0-3 | 0.040 | - " - |
| - " - | 62°00'N; 20°30'E | 0-3 | 0.028 | - " - |
| - " - | 64°05'N; 21°56'E | 0-3 | 0.033 | - " - |
| 1987 | C-VI | 0-5 | 0.031 | Ikäheimonen et al., 1988 |
| - " - | - " - | 0-15 | 0.032 | - " - |
| - " - | EB-1 | 0-5 | 0.047 | - " - |
| - " - | - " - | 0-20 | 0.068 | - " - |
| - " - | XV-1 | 0-5 | 0.061 | - " - |
| - " - | - " - | 0-20 | 0.038 | - " - |
| - " - | LL-3a | 0-5 | 0.045 | - " - |
| - " - | - " - | 0-20 | 0.043 | - " - |
| - " - | BY-15 | 0-5 | 0.035 | - " - |
| - " - | - " - | 0-20 | 0.036 | - " - |
| - " - | Olkiluoto-1,2,4,9 | 0-5 | 0.058[4] | Sjöblom et al., 1989 |
| - " - | Teili-1 | 0-1 | 0.125 | Ikäheimonen, 1988 |
| 1988 | - " - | 0-1 | 0.059 | Saxen et al., 1989 |
| - " - | - " - | 0-5 | 0.064 | - " - |
| - " - | C-VI | 0-5 | 0.029 | - " - |
| - " - | EB-1 | 0-5 | 0.039 | - " - |
| - " - | XV-1 | 0-5 | 0.017 | - " - |
| - " - | LL-3a | 0-5 | 0.044 | - " - |
| 1988 | Fig. 3, this paper | 0-1 | 0.072[6] | This study |

Multiple samples are indicated by superscribed numerals.

As an example we can assume the following: A sediment from the Baltic Proper is studied. The sediment has received effluent Pu during the period when the 0-1 cm layer was deposited. The total Pu activites are "1", "3" and "20" in the 0-1, 1-2 and 2-3 cm layers respectively, which are reasonable values according to the results of this study (e.g. see stations 2-4, Table 1).

The $^{238}Pu/^{239,240}Pu$ ratio in the 0-1 cm section is 0.080, and in the others 0.036. If these figures are applied to Eq. (1), this means that 33 % of the Pu in the 0-1 cm layer originates from the Kattegat ($x = (0.080 - 0.036)/(0.170-0.036)$; $x = 0.33$; 0.33/1 = 0.33). The same contribution measured in a 0-2 cm section corresponds to an 8 % addition (0.33/4 = 0.08) and in a 0-3 cm section to a 1.4 % addition (0.33/24 = 0.014). A 1.4 % addition of Kattegat Pu corresponds to a ratio of 0.038 (0.014 = ($g$ - 0.036)/(0.170 - 0.036); $g$ = 0.038). Conclusions should therefore not be made on the basis of 0-3 cm sections. This effect can be seen in Table 2, where the only significant deviations from the integrated fallout ratios were registered in 0-1 cm sections, even before the Chernobyl accident.

The ratios were also sporadically enhanced in 0-3 and 0-5 cm sections near the coast (Table 2), where high sedimentation rates offering enhanced vertical resolution, relative to that at open-sea stations, may be suspected. There is, of course, one analytical problem associated with the use of 1 cm sections (or possibly considerably less), namely the problem of collecting samples sufficiently large for alpha analysis. Apart from long counting times, the influence of contamination from other elements increases when very small samples are analyzed (i.e. overestimation of $^{238}Pu$ from $^{228}Th$). However, the contamination problem is easily overcome with modern separation techniques, and the sample size problem avoided by collecting multiple samples or by increasing the core volume.

## 5. CONCLUSIONS

It is difficult to form an unambiguous picture of the distribution of different Pu isotopes in Baltic Sea sediments, especially in open-sea areas, due to a lack of applicable data. There is obviously a general and serious methodological problem in collecting samples.

The major portion of the deposited Pu is to be found in the upper 3-4 cm of the sediment in one third of the Baltic Proper.

The $^{238}Pu/^{239,240}Pu$ ratios at subsurface activity maxima are typical of global fallout from thermonuclear weapons testing. However, the ratio close to the sediment surface is enhanced. Two possible sources of Pu comparatively rich in $^{238}Pu$ are suggested in the literature; late global fallout and Chernobyl fallout, while the possibility of a third is discussed in this paper; Pu in inflowing North Sea water. The latter is supported by the fact that enhanced ratios have also been reported before the Chernobyl accident.

Acknowledgement

This work was financially supported by SSI, the Swedish National Institute for Radiation Protection.

## 6. REFERENCES

Aarkrog, A. 1988: The radiological impact of the Chernobyl debris compared with that from nuclear weapons fallout. - J. Environ. Radioactivity 6:151-162.

- " - , Bötter-Jensen, L., Dahlgaard, H., Hansen, H., Lippert, J., Nielsen, S. P. & Nilsson, K. 1981: Environmental radioactivity in Denmark in 1980. - Risö National Laboratory. Risö-R-447.

Assinder, D.J., Kelly, M. & Aston, S.R. 1985: Tidal variations in dissolved and particulate phase radionuclide activities in the Esk estuary, England, and their distribution coefficients and particulate activity fractions. - J. Environ. Radioactivity 2:1-22.

Beasley, T. M., Carpenter, R. & Jennings, C.D. 1982: Plutonium, $^{241}Am$ and $^{137}Cs$ ratios, inventories and vertical profiles in Washington and Oregon continental shelf sediments. - Geochim. Cosmochim. Acta 46:1931-1946.

BNFL (1979, 1980, 1981, 1982, 1983, 1984) Annual report on radioactive discharges and monitoring of the environment, British Nuclear Fuels plc, Health and Safety Directorate.

Brügman, L. 1986: Particulate trace metals in waters of the Baltic Sea and parts of the adjacent NE Atlantic. - Beitr. Meersk. 55:3-18.

Buesseler, K.O. & Sholkovitz, E.R. 1987: The geochemistry of fallout plutonium in the North Atlantic: 1. A pore water study in shelf, slope, and deep-sea sediments. - Geochim. Cosmochim. Acta 51:2605-2622.

Carpenter, R. & Beasley, T.M. 1981: Plutonium and americium in anoxic marine sediments: Evidence against remobilization. - Geochim Cosmochim. Acta 45:1917-1931.

Dahlgaard, H., Aarkrog, A. & Nielsen, S.P. 1988: Chernobyl og "de Nordiske have" (Danish). - Paper presented at The 5th Nordic Radioecoly Seminar, Rättvik, Sweden, 22-26 August 1988.

Devell, L., Tovedal, H., Bergström, U., Appelgren, A., Chryssler, J. & Andersson, L. 1986: Initial observations of fallout from the reactor accident at Chernobyl. - Nature 321:192-193.

Dickson, R.R. 1973: The prediction of major Baltic inflows. - Dtsch. Hydrogr. Z. 26:97-105.

Duniec, S. Hallstadius, L. & Holm, E. 1983: A study of the transport of radionuclides in the sea by use of isotopic ratios. In: Proc. Symposium on the Behaviour of Long-Lived Radionuclides in the Marine Environment, La Spezia: 245-254.

- " - , Hallstadius, L., Holm, E., Rioseco, J., Guerrin, G. & Skwarzec, B. 1985: A radioecological investigation of the Baltic Sea. - In: Proc. 7th Meeting of the Nordic Society for Radiation Protection, Copenhagen, 1984.

Environmental Measurement Laboratory, USA 1980: EML Environmental Quarterly, EML-370 Appendix. p. A-3.

Falkenmark, M. & Mikulski, Z. 1974: Hydrology of the Baltic Sea. - Water balance of the Baltic Sea. A regional cooperation project of the Baltic countries. - International Hydrological Decade, Project document No. 1. Stockholm - Warszawa 1974, 51 p.

Fonselius, S.H. 1969: Hydrography of the Baltic deep basins III. Fishery Board of Sweden - Ser. Hydrogr. 23:1-97.

- " - 1970: Stagnant Sea. - Environment, 12(6):2-11.

Gritchenko, Z. G., Flegontov, V.M. & Suprunenko, A.N. 1979: Radioactive contamination of the environment. I. Radionuclide concentrations in ground air in the vicinity of Lenignrad for 1959-1977 (Russian). - Khlopin Radium Institute, PN-96, 44 p.

Håkanson, L. & Jansson, M. 1982: Lake sedimentology. - Springer-Verlag, 316 p.

Hallstadius, L. 1984: A method for the electrodeposition of actinides. - Nucl. Instrum. Method. Phys. Res. 223:266.

- " - , Aarkrog, A., Dahlgard, H., Holm, E., Boelskifte, S., Duniec, S. & Persson, B. 1986: Plutonium and americium in Arctic waters, the North Sea and Scottish and Irish coastal zones. - J. Environ. Radioactivity 4:11-30.

Hardy, E.P., Krey, P.W. & Volchok, H.L. 1973: Global inventory and distribution of fallout plutonium. - Nature 241:444-445.

Harley, J.H. 1980: Plutonium in the environment - A review. - J. Radiat. Res. 21:83-104.

Holm, E. & Fukai, R. 1977: Method for multi-element alpha-spectrometry of actinides and its application to environmental radioactivity studies. - Talanta 24:659-64.

- " - , Duniec, S., Hallstadius, L., Mattsson, S., Rioseco, J. & Samuelsson, C. 1986: Releases, distribution and pathways for radionuclides in the Baltic Sea. - In: Study of radioactive materials in the Baltic sea, Helsinki 24-28 Sept. 1984. IAEA-TECDOC-362:152-161 IAEA, Vienna.

IAEA, 1986. USSR state committe on the utilization of atomic energy. The accident at the Chernobyl nuclear power plant and its consequences. - Information compiled for the IAEA expert meeting, 25-29 Aug., 1986. IAEA, Vienna, draft I, 56 p.

Ignatius, H., Axberg, S., Niemistö, L. & Winterhalter, B. 1981: Quarternary geology of the Baltic Sea. In: A. Voipio (ed.), The Baltic sea: 54-104. - Elsevier Oceanography series 30. Amsterdam.

Ikäheimonen, T.K. 1988: Transuraner i omgivningen i Finland efter Tjernobyl-olyckan (Swedish). - Paper presented at the 5th Nordic Radioecoly Seminar, Rättvik, Sweden, 22-26 August 1988.

- " - , Ilus, E. & Saxén, R. 1988: Finnish studies on radioactivity in the Baltic Sea in 1987. - Supplement 8 to Annual Report STUK-A74. - Report STUK-A82:1-35. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

Ilus, E., Ikäheimonen, T.K., Saxén, R., Sjöblom, K.-L., Klemola, S. & Aaltonen, H. 1989: Review of the Finnish studies on the radioactive substances in the Baltic Sea in 1986-1988. Baltic Marine Environment Protection Commission-Helsinki Commission - 1989. "Three years observations of the levels of some radionuclides in the Baltic Sea after the Chernobyl Accident" - Seminar on radionuclides in the Baltic Sea, 29 May 1989, Rostock-Warnemünde, German Democratic Republic. - Baltic Sea Environ. Proceedings No. 31. Helsinki 1989:81-93.

- " - , Sjöblom, K.-L., Aaltonen, H., Klemola, S. & Arvela, H. 1987: Monitoring of radioactivity in the environs of Finnish nuclear power stations in 1986. - Supplement 12 to Annual Report STUK-A55. - Report STUK-A67:1-82. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

- " - , Sjöblom, K.-L., Saxén, R., Aaltonen, H. & Taipale, T.K. 1987: Finnish studies on radioactivity in the Baltic Sea after the Chernobyl accident in 1986. - Supplement 11 to Annual Report STUK-A55. - Report STUK-A66:1-35. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

Institute of Radiation Protection, 1982: Studies on environmental radioactivity in Finland 1980. - Annual report STL-A38:91-106. Helsinki.

- " - , 1982: Studies on environmental radioactivity in Finland 1981. - Annual report STL-A40:93-109. Helsinki

- " - , 1983: Studies on environmental radioactivity in Finland 1982. - Annual report STL-A47:93-113. Helsinki.

Jaakkola, T., Paatero, J. & Suutarinen, R. 1988: Upptag av plutonium, americium och curium i ren och älg (Swedish). - Paper presented at the 5th Nordic Radioecoly Seminar, Rättvik, Sweden, 22-26 August 1988.

Jonsson, P., Carman, R. & Wulff, F. 1990: Laminated sediments in the Baltic Sea. - Ambio 19(3):152-158.

Leskinen, S., Jaakkola, T. & Miettinen, J.K. 1986: Studies on behaviour of longlived actinides plutonium and americium in the Baltic Sea; effect of season, distribution coefficients in particulate matter and surface sediment. - In: Behaviour of long-lived radionuclides associated with deep-sea disposal of radioactive wastes. IAEA-TECDOC-368:61-72 IAEA, Vienna.

Levi, B. G. 1986: Soviets assess cause of Chernobyl accident. - Physics Today 39:17-20.

Livingston, H.D. & Bowen, V.T. 1977: Windscale effluent in the waters and sediments of the Minch. - Nature 279:586-588.

- " - & Bowen, V.T. 1979: Pu and 137Cs in coastal sediments. - Earth Planet Sci. Lett. 43:29-45.

- " - Bowen, V.T. & Kupferman, S.L. 1982: Radionuclides from Windscale discharges, I. Non-equilibrium tracer experiment in high latitude oceanography. - J. Mar. Res. 40:253-272.

Malcolm, S.J., Kershaw, P.J., Lovett, M.B. & Harvey, B.R. 1990: The interstitial water chemistry of $^{239,240}Pu$ and $^{241}Am$ in the sediments of the north-east Irish Sea. - Geochim. Cosmochim. Acta 54:29-35.

Miettinen, J.K., Jaakkola, T. & Järvinen, M. 1975: Plutonium isotopes in aquatic food chains in the Baltic sea. - In: Proc. Impacts of nuclear releases into the aquatic environment, Otaniemi, Finland, 1975:147-155. IAEA, Vienna.

Murray, C.N. & Kautsky, H. 1977: Plutonium and americium activities in the North Sea and German coastal regions. - Est. Coastal Mar. Sci. 5:319-328.

- " - , Kautsky, H., Hoppenheit, M. & Domain, M. 1978: Actinide activities in water entering the northern North Sea. - Nature 276:225-230.

- " - , Kautsky, H., & Eicke, H.F. 1979: Transfer of actinides from the English Channel into the southern North Sea. - Nature 278:617-620.

Needler, G.T. & Templeton, W.C. 1981: Radioactive waste: the need to calculate an oceanic capacity. - Oceanus 24:60-67.

Nelson, D.M. & Lovett, M.B. 1981: Measurements of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea. - In: Impacts of Radionuclide Releases into the Marine Environment. Proc. Symp.:105-108. IAEA, Vienna.

Niemistö, L. & Voipio, A. 1974: Studies on the recent sediments in the Gotland Deep. - Merentutkimuslait. Julk./Havsforskningsinst. Skr. 238:17-32.

Nishiwaki, Y., 1976: Discussion - In: Proc. Impacts of nuclear releases into the aquatic environment, Otaniemi, Finland, 1975:153, IAEA, Vienna.

Rioseco, J., Holm, E., & Samuelsson, C. 1988: Plutonium, americium och curiumisotoper från Tjernobyl fallout. (Swedish). - Paper presented at the 5th Nordic Radioecoloy Seminar, Rättvik, Sweden, 22-26 August 1988, 12 p.

Risø National Laboratory: Environmental radioactivity in Denmark 1977-1980. - Risø National Laboratory, Risø Report Nos. 386, 403, 447.

Salo, A., Tuomainen, K. & Voipio, A. 1986: Inventories of some long-lived radionuclides in the Baltic Sea. - The Science of the Total Environment 54:247-60.

Santschi, P.H., Li, Y.- H., Adler, D.M., Amdurer, M., Bell, J. & Nyffeler, U.R. 1983: The relative mobility of natural (Th, Pb, Po) and fallout (Pu, Am, Cs) nuclides in the coastal marine environment: Result from model ecosystems (MERL) and Narragansett Bay. - Geochim. Cosmochim. Acta 47:201-210.

Saxén, R. Ikäheimonen, T.K., & Ilus, E. 1989: Monitoring of radionuclides in the Baltic Sea in 1988. - Supplement 1 to Annual Report STUK-A89. - Report STUK-A90:1-24. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

Sholkovitz, E.R. 1983: The geochemistry of plutonium in fresh and marine water environments. - Earth-Science Reviews 19:95-161.

- " - & Mann, D.R. 1984: The pore water chemistry of $^{239,240}Pu$ and $^{137}Cs$ in sediments of Buzzards Bay, Massachusetts. - Geochim. Cosmochim. Acta 48:1107-1114.

Simola, K., Jaakkola, T., Miettinen, J.K., Niemistö, L. & Voipio, A. 1979: Vertical distribution of fallout plutonium in some sediment cores from the Baltic Sea. - Finnish Mar. Res. 246:125-134.

Sjöblom, K.-L., Klemola, S., Ilus, E., Arvela, H. & Blomqvist, L. 1989: Monitoring of radioactivity in the environs of Finnish nuclear power stations in 1987. - Supplement 5 to Annual Report STUK-A74. - Report STUK-A79. Finnish Centre for Radiation and Nuclear Safety, Helsinki.

Tuomainen, K., Ilus, E. & Taipale, T.K. 1986: Long-lived radionuclides in the sediments of the Gulf of Bothnia. - In: Proc. of the third Finnish-Swedish seminar on the Gulf of Bothnia, Pori, Finland, 20-21 August, 1984. - Publications of the Water Research Institute, National Board of Waters, Finland 68:91-95.

Östlund, P. 1990: Interrelations between plutonium and some transition elements in Gulf of Bothnian sediments. - Ambio (in press).

Merentutkimuslaitos
PL 33
00931 Helsinki

Havsforskningsinstitutet
PB 33
00931 Helsingfors

Finnish Institute of Marine Research
P.O.Box 33
SF-00931 Helsinki, Finland

ISSN 0357-1076
Helsinki 1990. Valtion painatuskeskus