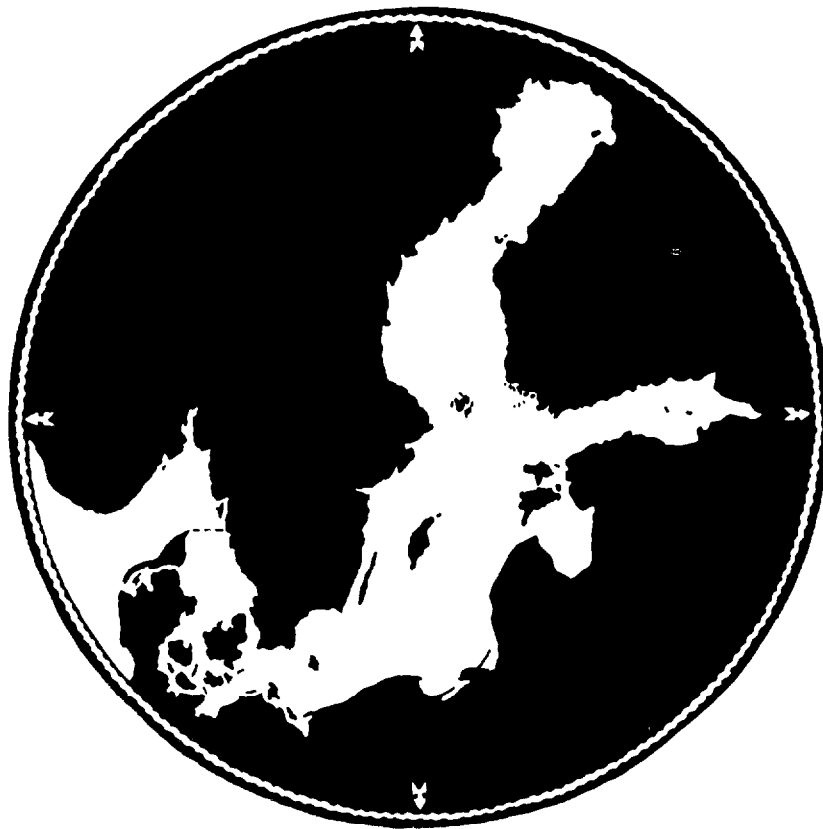


# BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 5 B

## ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980

PART A-1: OVERALL CONCLUSIONS  
PART A-2: SUMMARY OF RESULTS  
PART B: SCIENTIFIC MATERIAL



Editor: Terttu Melvasalo

Editorial Board: Janet Pawlak (Editorial Secretary),  
Klaus Grasshoff, Lars Thorell and  
Alla Tsiban

BALTIC' MARINE ENVIRONMENT PROTECTION COMMISSION  
-- HELSINKI COMMISSION --

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**The Overall Conclusions were approved by the Advisory  
Committee on Marine Pollution of the International  
Council for the Exploration of the Sea (ICES) on 11 October  
1980 and the Helsinki Commission at its Second  
Meeting on 16-19 February 1981**

Editor: Terttu Melvasalo

Editorial Board: Janet Pawlak (Editorial Secretary),  
Klaus Grasshoff, Lars Thorell and  
Alla Tsiban

BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION  
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# Preface

*This document was commissioned by the (then Interim) Helsinki Commission in November 1978 to review the existing data on the parameters, substances, and processes relevant to, and affected by, pollution in the Baltic Sea and to provide an assessment of the present state of pollution and its effects. The International Council for the Exploration Of the Sea (ICES) was requested to provide assistance in this work.*

*In order to carry out this task, a five-member Editorial Board was established by .a joint STWG/ICES ad hoc Group of Experts. The Editorial Board planned the execution of the work, enlisted the assistance Of about thirty scientists to prepare draft sections of the document, coordinated the extensive review process and finally compiled and edited the full document. Part A-1, Overall Conclusions of the full document was reviewed and approved by the joint STWG/ICES ad hoc Group Of Experts and ultimately by the Advisory Committee on Marine Pollution Of ICES and the Second Meeting of the Helsinki Commission.*

*The Overall Conclusions are based on scientific data contributed by experts on the condition of the Baltic Sea, which is presented in Part B Of the full document.*

*We would like to express OUR most sincere appreciation to the scientists who contributed the original drafts for Part B of the full document, Scientific Material used for the Assessment. We would also like to express*

our gratitude to Prof. G. Kullenberg, Prof. H. Velner, Prof. A. Voipio and Mr. H. Tambs-Lyche for their encouragement of this work, and also express our appreciation to the many other persons who have unselfishly given their valuable time to assist this project.

It is our sad duty to announce that, during the final stages of the completion of this project, heavy losses for Baltic marine research were incurred in the death of two scientists closely associated with this project. Professor Klaus Grasshoff, a member of the Editorial Board, died on 11 March 1981 and Professor Kaare Gundersen, contributor of the section on nitrogen, died on 24 January 1981.

We hope that the results of this project may assist in the preparation of further surveys on the assessment of pollution in the Baltic Sea.

Copenhagen, May 1981

Terttu Melvasalo  
Janet F. Pawlak

CONTRIBUTORS\* OF ORIGINAL DRAFTS FOR PART B OF THE DOCUMENT  
 "SCIENTIFIC MATERIAL USED FOR ASSESSMENT"

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In some cases contributions of several authors have been combined together into a joint section or chapter.

\*

Owing to the extensive editorial work conducted by the Editorial Board on the basis Of the review comments received, the contributors should not necessarily be considered to be responsible for all the opinions and conclusions presented in this document.

\*\*

Full addresses on page 425.

## OBITUARIES

Professor Kaare Gundersen

Professor Kaare Gundersen died 24 January 1981 after a short illness. Professor Gundersen was born in Oslo in 1922 and studied at the University of Copenhagen and then at the University of Gothenburg, where he earned his Ph.D. degree in 1962. He worked as a professor at the University of Hawaii and was appointed professor in marine microbiology at the University of Gothenburg in 1974. Professor Gundersen's main interest was the nitrogen cycle in the sea and he was responsible for the nitrogen chapter of this document. The death of Professor Gundersen is a heavy loss for Baltic marine research.

Professor Klaus Grasshoff

Professor Klaus Grasshoff, member of the Editorial Board, died on 11 March 1981 after a few months of illness. Klaus Grasshoff was born in 1932 in Swinemiinde. He graduated from the University of Würzburg. In 1961, he was named head of the Chemistry Working Group of the Institute of Marine Research at the University of Kiel. He was appointed director of the new Marine Chemistry Department of the Institute in 1971. He followed the traditions of Hermann Wattenberg and brought his department to a leading position in the Baltic research community. Professor Grasshoff's main interest was in the field of analytical techniques, especially automatic procedures and intercalibrations. He was the editor of the handbook "Methods of Sea Water Analyses" and author of many scientific publications. - Klaus was a well-known person not only in Baltic marine research but among oceanographers over the whole world. His enthusiasm and feeling for the main points of the scientific problems made him a valued and liked member of the Baltic oceanographic community. We all miss Klaus as a colleague and very good friend.

"A scientist's life should not be valued in years but what he has achieved during these years".

Stig Fonselius  
for the Editorial Board.

## A C K N O W L E D G E M E N T S

*On the basis Of the additional information and comments received by the Editorial Board on the First Draft of the documents essential work for compiling the Second Draft was done, in addition to the contributors, by many scientists. The principal reviewers were:*

Mr. S. Carlberg	National Board of Fisheries of Sweden
Mr. U. Ehlin	Swedish Meteorological and Hydrological Institute
Dr. R. Elmgren	University of Stockholm, Sweden
Dr. S. Fonselius	National Board of Fisheries of Sweden
Prof. K. Gundersen †	University of Gothenburg, Sweden
Dr. A. Jensen	Miljøstyrelsen, Denmark
Prof. H. Luther	University of Helsinki, Finland
Dr. P. Mälkki	Institute of Marine Research, Finland
Mr. A. Nielsen	Miljøstyrelsen, Denmark
Prof. Å. Niemi	University of Helsinki, Finland
Dr. L. Feutergårdh	Swedish Environment Protection Board
Dr. G. Sundström	Swedish Environment Protection Board
Mrs. H. Viljamaa	Helsinki City Water Laboratory, Finland
Prof. A. Voipio	Institute of Marine Research, Finland
Dr. I. Wallentinus	University of Stockholm, Sweden
Dr. F. Wulff	University of Stockholm, Sweden

*Furthermore, many scientists dealing with pollution problems Of the Baltic Sea in all the Baltic Sea States have expressed their views and supported the Editorial Board with several comments.*

*Mr. Jan Strömberg assisted the Editorial Secretary during the period May to July 1980.*

*Technical assistance on the drafts and typing was done by the Secretariat Of ICES, National Board Of Waters Of Finland, Mrs. Iia Järvi, Mrs. Paula Lamio, Mrs. Virpi Nieminen, Mrs. Sinikka Susi and Mrs. Sys Enevold.*

*The map Of the Baltic Sea was prepared under the direction Of Dr. Boris Winterhalter (Finland) and for the layout of the document and the map expertise Of Mrs. Gunhild Högman (Sweden) was used.*

*We wish to express our gratitude to all the persons mentioned above as well as to the Governments Of the Baltic Sea States for encouraging and supporting scientists from all the Baltic Sea States to cooperate in this project.*

# Background and history of the project

*This document "Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea" is compiled and edited by an Editorial Board established for this purpose by representatives of the Scientific Technological Working Group (STWG) of the (Interim) Helsinki Commission and the International Council for the Exploration of the Sea (ICES).*

*The Editorial Board carefully selected scientists who were requested to study the available data on the parameters and substances relevant to pollution in the Baltic marine environment, and to assess the effects of pollution on these parameters, on important processes, and on living organisms in the Baltic Sea. Approximately thirty scientists with experience in disciplines relevant to this work were invited to contribute to this project and draft preliminary sections. The expertise of individual members of the Baltic Marine Biologists was also invited.*

*To assist these scientists in their work, the Editorial Board prepared guidelines concerning the types of information it deemed necessary for an appropriate assessment.*

*In this first stage of the assessment, mainly the Baltic Sea Area (which means the open sea area according to the Helsinki Convention) should be covered. However, the assessment of coastal areas was preliminarily discussed wherever necessary.*

*As a general rule, contributors were asked to provide information on as many of the following topics as were*

relevant to their specific subject:

#### Methods

The accuracy and precision of the methods used in relation to the levels observed and the estimation of trends.

The comparability of data from different sources.

#### Gaps

Are the gaps, if any, due to a lack of applicable studies, or

Are the gaps due to a lack of adequate methodologies?

#### Trends

What are the levels, including statistical variances, the trends in these levels and their significance?

#### Sub-areas

What are the differences between various sub-areas of the Baltic Sea?

What is the influence of these differences on the overall picture of the marine environment?

What are the causes for differences between regions?

#### Inter-relationships

What are the inter-relationships between the parameter under discussion and other parameters or processes?

What is the influence of these parameters on the fate of pollutants, on living resources, and on important processes in the marine environment?

#### Input to the Baltic Sea

What are the sources and amounts, and mass balances, if possible?



### Human activities

What is the background level of the parameter or substance in the Baltic Sea?

What is the influence of human activities, both polluting activities and abatement measures, on each parameter?

To what extent should the input of pollutants be reduced in order to reach the background level in the Baltic Sea?

### Degree of pollution of the Baltic Sea

Should the Baltic Sea or some of its sub-areas be considered polluted and to what extent according to the information available?

Concerning the substance of this assessment work, we wished to distinguish this project from the earlier task requested of ICES which resulted in the document "Assessment of the Marine Environment of the Baltic Sea Area", which provided background information relevant to the development of an appropriate programme to monitor and assess the effects of pollution on the Baltic marine environment, especially on its living resources.

The project described here has been commissioned to review the existing data on the parameters, substances, and processes relevant to, and affected by, pollution in the Baltic Sea and to provide an assessment of the present state of pollution and its effects. By an "assessment" we mean an evaluation or judgement of the conditions and quality of the environment as well as the products of this environment, i.e., living organisms. Ideally, this work should function as a type of "baseline assessment" from which trends may hopefully be determined in subsequent assessments using data from the Baltic Monitoring Programme, which started in 1979.

Given that this work cannot cover everything concerning the Baltic marine environment, only the most important parameters relevant to the pollution level have been chosen. This choice has mainly been based on the parameters included in the Baltic Monitoring Programme. The information for this work has been taken from existing data in published form which is readily available.

Only some background information about the Baltic Sea was included to the document. This was partly due to the efforts to keep the documents as concise as possible. On the other hand, there is at least one publication covering this field entirely which has been written by a number of scientists from different Baltic Sea countries and will be easily available in the nearest future (Voipio (ed.), 1981).

The main information included in Part A, the overall conclusions, of the document was based on the scientific material provided by the scientists for the project and presented in Part B. Some additional information, which was considered relevant to the assessment but not covered by the above material, was taken up from recent reports prepared, e.g., on a bilateral basis (Belt Sea, Gulf of Bothnia, Gulf of Finland, Kattegat, The Sound). The history of the scientific information presented in Part B of the document is different for the different chapters. The chapters were worked up on the basis of the comments and additional information received using the expertise of a number of scientists from all the Baltic Sea states.

The material received for the document was more extensive than was expected and than could be used for the final document. Because a great deal of detailed scientific information was thus excluded, the contributors were encouraged to publish the entire primary material

OR parts of it in any appropriate series after the Commission has noted that the project has been completed.

The project arose from the decisions of the Interim Commission and its Scientific Technological Working Group. Some features of this background are described in the following.

The Interim Baltic Marine Environment Protection Commission (IC) (Helsinki Commission from 3.5.1980) decided at its meeting in November 1978 in Helsinki that the assessment of the state of the marine environment of the Baltic Sea Area on the basis of the compilation of results and other relevant information including data on coastal waters and input data should be prepared on a periodical basis.

In order to get the project started the meeting of Interim Commission in 1978 considered that, in view of the fact that the Baltic Monitoring Programme will have begun in 1979, it would be necessary to prepare an assessment of the known conditions of the Baltic marine environment as a basis for the evaluation of the Baltic Monitoring Programme. The meeting considered that such an assessment should utilize all relevant existing data, and should also make use of results from bilateral programmes in the Gulfs of Finland and Bothnia, and the Sound which were currently being conducted. It was suggested that such a detailed assessment should be carried out under the responsibility of the *Scientific-Technological Working Group (STWG)* of the Interim Commission, using the expertise of the international Baltic scientific community within the International Council for the Exploration of the Sea (ICES) and the Baltic Marine Biologists (BMB) and the assistance of the ICES Secretariat.

The Commission invited ICES to establish with it a joint *STWG/ICES ad hoc* Group of Experts, consisting of Baltic marine scientists with as wide a field of expertise as possible, covering the various disciplines and uses of the marine environment.

The *STWG/ICES ad hoc* Group of Experts met on 25 - 26 January 1979 in Tallinn under the chairmanship of Professor G. Kullenberg, Professor H. Velner and Professor A. Voipio.

At this meeting, the Group discussed a preliminary draft outline of the work and established an Editorial Board to co-ordinate the preparation of the assessment document. The Editorial Board, as determined consisted of Ms. Terttu Melvasalo (Editor, Finland), Dr. (Ms.) Janet Pawlak (Editorial Secretary), Professor Dr. Klaus Grasshoff (FRG), Mr. Lars Thorell (Sweden) and Dr. (Ms.) Alla Tsiban (USSR).

The Editorial Board developed and refined the draft outline of the assessment work, which was accepted by the Interim Commission at its sixth meeting in Helsinki in November 1979. The meeting requested the Editorial Board to continue its work with its existing membership.

The Scientific-Technological Working Group had recommended at its meeting in September 1979 that the document should be written in a clear, concise, precise and objective manner so that it would be understandable and useful to persons who will ultimately decide upon measures to be taken to protect the Baltic Sea.

The Seventh Meeting of the STWG in September 1980 decided to recommend to the Commission that, due to its scientific value, the final version of the Assessment document should be published after completion by the Editorial Board. However, the Meeting felt that the scientific material (Part B) and its summary (Part A-2) should be under responsibility of the Editorial Board, so that neither the contributors nor the STWG and ICES need to accept all the statements contained therein. It was decided that only the overall conclusions (Part A-1) should be considered in detail on the basis of the drafts and comments received. Following the decision by the STWG-7, the overall conclusions (Part A-1) were redrafted after the meeting of the Editorial Board and representatives of the STWG/ICES ad hoc Group of Experts and accepted by the ICES Advisory Committee on Marine Pollution with minor remarks.

Some members of the STWG/ICES ad hoc Group of Experts met in Helsinki on 1 to 2 December 1980. They also accepted the overall conclusions of the document but recommended some linguistic amendments, which were also acceptable to ICES.

The Document was presented to the Second Meeting of the Helsinki Commission on 16 - 19 February

1981. The Commission approved the overall conclusions (Part A-1) and noted the scientific value of the background material in Part B and its summary (Part A-2).

Additionally, the Commission recommended to the Governments of the Baltic Sea Countries to take into account the results of this assessment when taking measures towards the abatement of pollution in the Baltic Sea.

PART A

S u m m a r y   a n d   C o n c l u s i o n s

PART A-1

## O v e r a l l   C o n c l u s i o n s

The Overall Conclusions were approved by the Advisory Committee on Marine Pollution (ACMP) of ICES on 11 October 1980. At its meeting on 1 to 2 December 1980 members of the STWG/ICES *ad hoc* Group of Experts considered the Overall Conclusions as approved by the ACMP, and adopted them for submission to the Helsinki Commission with a few minor linguistic clarifications, which were also acceptable to ICES.

The Helsinki Commission approved the Overall Conclusions at its Second Meeting on 16 - 19 February, 1981.

# Overall conclusions

## Introduction

The Baltic Sea is one of the largest brackish water areas in the world. Its basic features are well known. Based on the present scientific knowledge, it can be concluded that since the beginning of this century environmental changes have been observed in the Baltic ecosystem, especially in the coastal waters. A number of the observed changes can be attributed to natural causes alone, while others are partly or solely caused by human activities.

The Baltic Sea is a complicated system of deep basins, bays, and gulfs. Its hydrographic and biological properties vary depending on what part we consider. The level and type of pollution may also vary from area to area. It has to be stressed that satisfactory and even good conditions may be found in certain areas. The least polluted water is found in the entrance area where the water exchange is efficient. Owing to these regional differences, the overall conclusions below will only concern the Baltic Sea in general.

The greatest concerns have so far been directed towards the levels and effects of chlorinated hydrocarbons, heavy metals, oil and nutrients. The decreased oxygen concentrations in the deep waters are also a source of concern. Apart from chlorinated hydrocarbons, the main pollution-caused effects have been demonstrated in local areas with clearly traceable pollution sources. However, because of the complicated interaction between



natural processes and human activities, many long-term effects on the Baltic Sea ecosystem may have been overlooked due to a lack of knowledge and means to detect and interpret the changes in detail. This implies that there is a great need to improve our knowledge about the present levels of known contaminants and their effects on the ecosystem.

Substances not yet recognised as contaminants may also exert an impact on the ecosystem. The response of the Baltic ecosystem may take place very slowly or in an unexpected manner, as was the case with PCBs. In order to avoid harmful and possibly irreversible effects on the ecosystem, it is necessary that countermeasures be taken at the earliest possible stage. To facilitate this, possible effects of the contaminants on the biota and the environment should be investigated and monitored in detail in future.

A description of the physical and biological characteristics of the Baltic Sea, as well as the known environmental levels of the pollutants, is given in Part B of this document. These overall conclusions summarize from Part B the changes which have been observed in the Baltic marine environment in this century according to whether such changes are

- due to natural causes alone,
- partly due to human activities, or
- due to human activities alone.

# Changes

## 2.1 Natural changes

The changes listed in this section are considered natural changes in the marine environment of the Baltic Sea. In order to be able to assess anthropogenically induced changes in the marine environment, and to be able to establish the causes and effects of such changes, it is necessary to have as good as possible a knowledge of the natural changes which are inevitably taking place in the environment.

The irregular intrusions of water of higher salinity into the deep basins of the Baltic Sea are primarily regulated by meteorological processes over Northern Europe. The frequency of these intrusions varies. In the Baltic Proper, a distinct layering of the water column is a clear feature. A distinction can be made between (a) the less saline surface water with a warm top layer during summer, (b) the deep water with higher salinity, separated by a pronounced thermo-halocline from the surface water, and (c) the bottom water with somewhat higher salinities. The bottom water may remain for long periods in the main deep basins. The temperature of the deep and bottom water is not influenced by seasonal changes.

Since the beginning of this century, an increase in the temperature and salinity in the deep and the bottom waters of the Baltic Sea has been observed. On average, the temperature has increased by  $0.6 - 2.7^{\circ}\text{C}$  and the salinity by  $0.8 - 1.7\text{‰}$ . In the surface layer, the sa-

linity has increased by 0.2 - 0.5‰ less than in the deep water. The depth of the primary halocline has been displaced slightly upwards by about 5 - 10 m in the Gotland Basin. The increase in salinity is reflected in a changed distribution of marine organisms in the Baltic Sea. Marine species are now found further north in the Baltic Sea than previously.

The deep water in the Baltic Proper is renewed by a more or less continuous inflow through the Danish Straits. In contrast, the bottom water is only renewed aperiodically by inflows of water with a high enough density to force the old bottom water out of place. After each renewal, the bottom water remains until an inflow of new water with higher density displaces it. During the period between inflows, the oxygen is continuously consumed by the oxidation of organic material in the surface sediments and organic material sinking from above, as well as respiration by organisms.

If the period between bottom water renewals is long enough, all the dissolved oxygen will be consumed and anoxic conditions will occur with subsequent formation of hydrogen sulfide. Such conditions can also occasionally reach parts of the deep water. A serious deterioration in the oxygen conditions of the bottom water is accompanied by a deterioration of the benthic community, followed by a disappearance of the benthic fauna if anoxic conditions develop and prevail. Anoxic conditions in the bottom water also cause, among other things, a rapid release of bound phosphorus from the sediment.

## 2.2 **Changes due to natural and/or anthropogenic causes**

For the changes covered in this section, doubt exists

as to whether they can be attributed to natural causes, anthropogenic influences or both. At present, it is not really possible to determine the amount of influence contributed by man to these changes.

The oxygen content of the bottom water and part of the deep water in the Baltic Proper has decreased during this century from 2 to 3 cm<sup>3</sup>/dm<sup>3</sup> to about zero. During inflows of new bottom water, the oxygen concentration in the bottom water may increase temporarily. Large areas near the bottom are occasionally covered by hydrogen sulfide-containing water. Decreased amounts of oxygen diminish, and the formation of hydrogen sulfide prevents, the existence of higher forms of life in the bottom areas.

The size of the bottom areas with reduced conditions for life varies from year to year. In 1975, the area was estimated to be about 100 000 km<sup>2</sup>, which is the maximum value so far observed. During periods of zero oxygen concentrations, the zoobenthos disappears, creating "benthic deserts". After an inflow of new bottom water occurs, a slow recolonization of the bottom fauna is observed. However, the new populations tend to have a decreased species diversity than had earlier been found in the area. A change in species composition has also been observed.

Since the 1950s, the phosphate concentrations have increased in the deep and bottom waters of the central basins of the Baltic Sea by about 100 - 300%. This increase in phosphate concentrations is related partly to the anoxic conditions, under which precipitated phosphate is released from the sediments, and partly to accumulation of biogenic phosphate due to stagnant conditions. In the Baltic Proper, an increase in the phosphate concentration in the surface layer has been

observed during the winter. This phosphate is mostly converted into organically bound phosphorus during the spring bloom of phytoplankton. The annual net input of phosphorus to the Baltic Sea from natural and anthropogenic sources is estimated at around 26 000 tonnes. This is as high as 6 -8% of the total content in the water body of the Baltic Sea.

It is not clear to what extent the changes in oxygen and phosphate concentrations in the Baltic Sea are due to long-term hydrographic changes and to what extent they are due to the nutrient load caused by man.

Owing to differences in the methods used to measure phytoplankton primary production, it is difficult to compare data in an attempt to determine trends. On the basis of the information available, it appears that primary production may have increased during the last two decades in some parts of the open Baltic Sea and it has clearly increased in coastal waters receiving discharges of large amounts of municipal waste water.

Different factors (e.g., phosphorus, nitrogen and light) act as limiting factors for primary production in the various sub-areas of the Baltic Sea. In many coastal areas, especially in the central and northern parts of the Baltic Sea and in the vicinity of population centers, changes in the species composition of phytoplankton have been observed along with an increase in primary production and an increase in the supply of organic material to the benthic community. In such areas, a change in the fish populations has also been observed. Eutrophication has been accompanied by a favouring of some fresh water species at the cost of other commercially more valuable species. Spawning grounds of the herring can also be destroyed.

It is difficult to distinguish between the effects of pollution, fishery and natural factors on fish stocks in the open Baltic Sea. Nonetheless, fish populations are known to be influenced by the changing salinity and by the oxygen conditions in the deep waters. This applies particularly to cod which spawns in the deep waters and has pelagic eggs. These require a salinity of at least 10‰ for buoyancy and are very vulnerable to low oxygen concentrations. In the Gotland Sea, large areas now show an oxygen content which is continuously too low. In the Bornholm Basin and the Gulf of Gdańsk this phenomenon occurs periodically. A sufficient recruitment is possible, however, in the southern part of the Baltic Proper and no permanent decrease in the Baltic cod stock has been noted.

### 2.3 **Changes caused by human activities**

Human activities have been responsible for the release into the environment of harmful or toxic synthetic organic chemicals (e.g., PCBs, DDT, chlorinated terpenes, PCTs) and organic wastes which are not natural in origin (e.g., lignin sulfonates), as well as for increasing the amounts of certain natural substances, e.g., nutrients, trace elements and hydrocarbons, in the marine environment.

The accumulation of the chlorinated hydrocarbons, DDT and PCBs, is considered to be an acute problem in the Baltic Sea. They have been shown to be present in all organisms investigated from the Baltic Sea. Due to the ban on the use of these substances in most of the Baltic Sea countries, a decrease in DDT has been revealed in the sediments and fish.

The major known effect of DDT in the Baltic Sea has been the decrease in egg shell thickness of birds feeding on fish and mussels. This has been observed for razorbills (*Alca torda*), guillemots (*Uria aalge*), black guillemots (*Cepphus grylle*), and white-tailed eagles (*Haliaeetus albicilla*). For the white-tailed eagle, a significant negative correlation has been found between reproductive success and levels of DDT and PCBs in the eggs.

PCBs have been widely used in industrial processes and products, but the sources of PCB pollution are often difficult to trace. Atmospheric fall-out has been recognised as a major source of PCB input to the Baltic Sea. The concentrations of PCB substances in fish in the Baltic Sea appear to be higher than those found in the North Sea. Regional differences within the Baltic Sea are difficult to interpret, since our knowledge of migration routes of the different populations or species of fish is limited. Very little is known about the metabolic and accumulation pathway of PCBs and other chlorinated hydrocarbons. No direct toxic effects of PCBs on fish or invertebrates have been documented. But the concentrations of PCBs are so high that, e.g., Danish and Swedish authorities have declared liver from cod caught in the Baltic Sea unsuitable for human consumption.

One serious effect which has been attributed to PCBs in the Baltic Sea has been on the reproduction of marine mammals, especially seals. Harbour seal (*Phoca vitulina*), ringed seal (*Pusa hispida*) and grey seal (*Halichoerus grypus*) populations in the Baltic Sea have declined rapidly in recent decades, partly due to decreased reproductive success. A large percentage (about 40%) of the female seals of reproductive age, especially those in the Gulf of Bothnia, have been

found to exhibit serious pathological changes in the uterus, which are believed to be caused by PCBs. The PCB levels in the relatively stable seal populations of the entrance area are significantly lower than in the populations of the Baltic Proper. It is possible that PCBs have been partly responsible for the decline in the populations of other mammals in the Baltic Sea area, namely otter (*Lutra lutra*) and porpoise (*Phocoena phocoena*).

Another indication of human activity is the presence of lignin sulfonates in Baltic Sea water. These compounds are introduced by the pulp and paper industry, in contrast to humic substances, which are naturally occurring compounds. Due to the lack of long data series, changes in the amount of these substances cannot be estimated at present.

The data available concerning the contribution by human activities to the heavy metal load does not cover the whole Baltic Sea. However, investigations of heavy metal concentrations in recent sediments in accumulation areas in the Baltic Sea show that the levels of zinc and lead have increased threefold and mercury and cadmium have increased more than tenfold over background levels in sediments, while other metals, e.g., nickel and chromium, do not appear to have increased over background concentrations, at least in open sea sediments.

Although a ban on mercury compounds used, for example, in the pulp and paper industry has resulted in some decreased mercury concentrations in fish from the northern Baltic Sea, there are still many coastal areas seriously contaminated by mercury.

Oil spills in the Baltic Sea have considerable local



effects, depending on the location of the spill and the time of the year. Coastal benthic communities and birds seem to be the most sensitive parts of the ecosystem to single oil spills. In sheltered coastal zones where currents and wave action are weak so that oil tends to accumulate, clear effects can be shown on benthic macrofauna and meiofauna, including reductions in the number of organisms and abnormal development of eggs. Changes in the pelagic system are generally short-term, whereas it may take several years for the benthic community to recover. Birds are particularly affected by oil spills, due to the coating of their feathers, and mass mortalities may occur even from relatively small amounts of oil spilled.

The discharge of nutrients, e.g., via domestic waste water, to certain coastal areas where there is a low rate of water exchange has caused an increase in the nutrient concentrations in those areas resulting in hypertrophication.

There are also other substances (e.g., radioactive isotopes, pesticides, by-products from the production of plastics, chemicals and pharmaceuticals) which are released through human activities. Some of these substances are likely to cause harmful effects in the Baltic marine environment.

Examples of substances recently detected in Baltic biota are polychlorinated terphenyls (PCTs), chlorinated terpenes, chlordanes and halogenated paraffins. These substances appear to be highly toxic and bio-accumulating, but further investigations are needed in order to clarify this issue.

## 2.4 Implications of the changes

Large natural changes have many implications for an environmental assessment. First, we cannot be sure where in a sequence of fluctuations we are observing the conditions until we have obtained a time series of observations long enough to cover what may appear to be the dominating natural periods of variability. For example, sedimentary records seem to indicate that anoxic conditions in the Baltic Sea have occurred in historical times. One difficulty is to ascertain to what extent human interference can amplify natural trends or trigger natural processes.

The temperature increase in the deep and bottom waters of the Baltic Sea implies an increased rate of oxidation of organic matter and thereby an increased rate of oxygen loss; it also means that less oxygen enters the Baltic Sea with the incoming water due to its higher temperature. The increase in salinity has created a change in the stratification in the deep and bottom waters which may have influenced the vertical mixing there. The mixing between the deep water and the surface layer water across the primary halocline layer is related to the stability across this layer which, however, does not appear to have changed significantly.

The phosphate accumulated in the bottom water during anoxic periods will partly be mixed into the surface layers in connection with bottom water renewals. Due to the increase in the phosphate in the surface water, primary production may increase. This, in turn, implies an increase in the supply of organic matter sinking down to the deep water, which results in an increased oxygen demand.

# Problem areas

## 3.1 Unresolved issues

In the overall conclusions given above, an attempt has been made to review the most widely accepted opinions regarding the factors responsible for the various changes observed in the conditions of the Baltic Sea. Even though the Baltic Sea is one of the most extensively studied sea areas, it is evident that there are several cases where different opinions regarding the causes for and the effects of these changes still exist. Some of these opinions involve different interpretations of the same or similar sets of experimental data. This clearly indicates that the knowledge of the dynamics of the Baltic ecosystem still needs considerable improvement.

One of the unresolved issues concerns the degree, causes and effects of eutrophication and its relation to the oxygen depletion in the deep basins.

Another unresolved issue concerns the nitrogen cycle in the Baltic Sea, which is very complicated and only poorly understood. Nitrogen compounds are important nutrients, which may have a major influence on primary production. Many questions still remain concerning the role and transformations of nitrogen in the Baltic Sea, e.g., reduction of nitrate to nitrogen gas when the oxygen concentration in the water is low, and ammonia originating from the bottom water which is nitrified to nitrate in water containing oxygen. Additionally, blue-green algae fix atmospheric nitrogen in the

sea surface. There are differing views on the limiting role of nitrogen compounds for primary production in the Baltic Sea and on the increase in nitrate concentrations in the surface layers of the Baltic Proper.

Other areas where generally accepted opinions have not been formulated include the long-term biological effects of accumulating harmful substances as well as their residence time in the marine environment. Furthermore, the identification of new potentially harmful substances needs special attention.

### **3.2 Areas requiring action**

The unresolved issues mentioned above cannot be resolved without extensive studies on the factors regulating the Baltic ecosystem. For instance, in order to resolve the problem of to what extent the primary production in the Baltic Sea has increased and to what extent this is beneficial or harmful, not only longer time series but also more frequent observations are needed.

The environmental contamination by various anthropogenic substances leads to a number of problems. The analytical methods used to determine these substances are not always accurate and precise enough to permit a reasonable trend analysis of the concentrations of these substances in the various compartments of the Baltic ecosystem. Additionally, the effects of these contaminants on the biota must be studied in detail. It should be stressed that the knowledge about potentially harmful substances in the Baltic Sea is far from complete;

Finally, it should be mentioned that additional information on land-based inputs of pollutants as well as

on the air-borne load is needed. Observations on the levels of contaminants are needed, both in relation to their input to the Baltic Sea and their concentrations in the various compartments of the Baltic ecosystem. Input from the land-based sources to the Baltic Sea could be controlled by the Baltic Sea States themselves. This is more difficult concerning a considerable part of the atmospheric input.

## Final remarks

Environmental protection measures are considered to have resulted in some positive changes in the Baltic ecosystem. A reduction in the DDT content in biota as well as a decrease in mercury concentrations in fish and other organisms has been found in the Baltic Sea as a result of a ban on the use of these substances in many countries.

The main changes demonstrated in the open Baltic Sea are the decrease in oxygen content in the deep waters and the effects of chlorinated hydrocarbons on Baltic biota.

Changes due to discharges of nutrients, e.g., phosphorus and nitrogen, have been demonstrated in coastal areas. An increase in the phosphorus content of the open Baltic Sea has been observed.

The levels of some heavy metals, e.g., mercury and cadmium, have increased in sediments, and this is considered to be caused by man. The presence of lignin sulfonates, waste products from pulp and paper industries, has been reported in the whole Baltic Sea.

It has been shown that in some areas even relatively small oil spills have had considerable effects on local bird populations and benthic communities.

The presence of new contaminants, e.g., PCTs and chlorinated terpenes, which are considered to be highly toxic and bioaccumulative, has been reported from some areas of the Baltic Sea. Their effects on the ecosystem is an open question which needs further investigation.

In recent years more sophisticated techniques have been developed which allow scientists to measure the effects of various contaminants on marine life. It is essential that these techniques be further developed and applied within research and monitoring programmes towards a better understanding of the Baltic ecosystem and man's impact on it.

PART A-2

S u m m a r y   o f   R e s u l t s



# Summary of results

This compilation of the present knowledge of the pollution of the Baltic Sea and its effects on biota is based on the detailed information given with references in PART B of the document.

A list of questions prepared by the Editorial Board was presented to the contributors and reviewers in order to help them draft the sections of the document. These questions, which were requested to be answered whenever possible, are presented in this section along with the answers which can be given at this time.

## 2.1 Methods

Questions:

- What are the accuracy and precision of the methods used in relation to the levels observed and the estimation of trends?
- What is the level of comparability of data from different sources?
- Are there gaps due to a lack of adequate methodologies?

As the assessment of the effects of pollution on the Baltic Sea environment should be based on all available data obtained from baseline studies, monitoring programmes and other research activities, it is essential to consider the reliability of the data. The results of this consideration are given below, for each of the parameters discussed in the document.

### 2.1.1 *Physical Parameters*

*Salinity.* Measurements have been comparable within a

range of  $\pm 0.05$  ‰ since about 1905 (Sec. 3.1.1).

*Temperature.* Measurements have been comparable within a range of  $\pm 0.05^{\circ}\text{C}$  for a number of decades (Sec. 3.1.1).

### 2.1.2 *Dissolved Gases*

*Oxygen.* Intercalibration exercises have shown that results from the different Baltic Sea countries are generally comparable. The accuracy cannot be exactly determined due to the difficulty of preparing standard samples with a precisely known oxygen content. The precision may be  $\pm 0.02 \text{ cm}^3/\text{dm}^3$ , expressed as the standard deviation for oxygen concentrations of less than  $2 \text{ cm}^3/\text{dm}^3$  water or  $\pm 0.04 \text{ cm}^3/\text{dm}^3$  for concentrations above  $2 \text{ cm}^3/\text{dm}^3$  (Sec. 4.1.1).

*Hydrogen sulfide.* Generally only one method is used in the Baltic Sea area to determine hydrogen sulfide, but this method has not been intercalibrated among the Baltic laboratories. Although the accuracy and precision of this method cannot be given, the technique is simple, sensitive and specific. Therefore, there is no reason to believe that the results from different countries would not be comparable (Sec. 4.1.1).

*Redox potential measurements.* Redox potential measurements have met criticism because of the undefined nature of the the participating chemical reactions. However, a good correlation has been found between the results of two different methods used to analyse sediment samples collected from 17 stations in the Baltic Proper and the Gulf of Bothnia (Sec. 4.2).

### 2.1.3 *Nutrients*

*Phosphorus.* The lower limit of detection of inorganic phosphorus is about  $0.01 \mu\text{mol}/\text{dm}^3$ . The relative standard

deviation at low levels ( $0.2 \mu\text{mol}/\text{dm}^3$ ) is about  $\pm 15\%$  and at high levels ( $2.8 \mu\text{mol}/\text{dm}^3$ ) about  $\pm 1\%$ . An intercalibration among all Baltic Sea countries has shown that the methods used for phosphate and total phosphorus analyses are sufficiently accurate and that data from different sources are comparable. The accuracy and precision of the analysis were  $\pm 0.05$  and  $0.03 \mu\text{mol}/\text{dm}^3$ , respectively, in the range  $0 - 2 \mu\text{mol}/\text{dm}^3$  (Sec. 5.1.2).

*Nitrogen.* The analysis of nitrogen compounds in sea water has long been hampered by methods of low specificity, sensitivity and reproducibility. Owing to the lack of reliable methods from earlier decades, no long-term trends can be determined at present (Sec. 5.2.1).

*Ammonium* analysis has been intercalibrated among the Baltic Sea States and a 30% relative error was obtained. The lower limit of detection is about  $0.05 \mu\text{mol}$  ammonium-N/ $\text{dm}^3$ . Problems are encountered in obtaining reproducible results with the method in use and contamination by ammonia from various sources easily occurs.

*Nitrate.* The analytical method generally used in the Baltic Sea laboratories has a good reproducibility with a lower limit of detection of about  $0.05 \mu\text{mol}$  nitrate-N/ $\text{dm}^3$ .

*Nitrite.* The analytical method is reliable, very sensitive and has a high precision. It permits the determination of as little as  $0.01 \mu\text{mol}/\text{dm}^3$ .

Urea has only recently been analysed in Baltic Sea water. A preferred and apparently reliable method is available.

*Dissolved organic nitrogen.* Methods for determining

total amino acids, individual amino acids, amino sugars and uronic acid are well developed and sufficiently precise.

*Particulate organic nitrogen.* This fraction has not been regularly analysed in the Baltic Sea.

*Total nitrogen.* An intercalibration of the method in general use in the Baltic Sea States has shown that the results cannot yet be considered reliable. Until a more accurate method has been discovered, it seems to be useless to analyse total nitrogen in sea water.

*Silicate.* The method generally used for measuring silicon as inorganic silicate is considered reliable. The relative accuracy is  $\pm 6\%$  or better, depending on the concentration level. Interfering substances for the analysis are hydrogen sulfide, fluoride and some trace metals in high concentrations. In addition a "salt" effect has to be accounted for (Sec. 5.3.1).

#### 2.1.4 Harmful Substances

*Trace elements.* Several methods are available to determine the concentrations of trace elements in the different compartments of the marine environment (Sec. 6.1.1).

For sea water, recent intercalibrations have shown a substantial improvement in the comparability of results among participating laboratories. Coefficients of variation (CV) for acidified samples were  $\pm 39\%$  for zinc,  $\pm 63\%$  for copper,  $\pm 77\%$  for cadmium, and  $\pm 101\%$  for lead. In another intercalibration, a coefficient of variation of  $\pm 82\%$  was obtained for mercury determinations. In addition to variations arising during analysis, substantial variations in results (due in part to contamination) can be caused by the use of different methods of sampling, sample preparation and storage.

For biological material, a recent intercalibration exercise has shown that the majority of participating laboratories can obtain comparable and accurate results for mercury (CV  $\pm$  12-25%), copper (CV  $\pm$  8%), and zinc (CV  $\pm$  7%). For cadmium and lead, however, few laboratories use methods capable of determining the low levels of these metals in fish muscle tissue.

Regarding sediments, no international intercalibrations have yet been held, but due to the relatively high levels of trace metals in sediments, a relatively good comparability of analytical results could be expected.

*Chlorinated hydrocarbons.* Very few laboratories are capable of carrying out reliable analyses of organochlorine compounds in sea water because the concentrations of these substances are close to the detection limit of the analytical method in use ( $10^{-12}$  g/dm<sup>3</sup>).

Additional reasons for discrepancies in results include contamination of the water sampler and/or glassware and the use of different methods (Sec. 6.2.1).

For biological materials, recent intercalibration exercises have shown that the coefficients of variation of results obtained for the DDT group were in the range  $\pm$ 38-44% and for PCBs the CVs were up to  $\pm$  50%. Moreover, in some cases incorrect identifications or quantifications were supplied, indicating that a few results reported in the literature might be tenuous at best.

There is no information about the comparability of results of analyses of chlorinated hydrocarbons in sediments, but it can be assumed that the reliability of the results should be higher than the reliability of results obtained from sea water analysis.

At present, no intercalibration exercises have been held on the analysis of the other organochlorine compounds mentioned in this report, i.e., PCTs, chlorinated terpenes and chlordanes compounds (Sec. 6.2.4).

*Humic substances and lignin sulfonates.* These substances are determined in water samples using a fluorimetric method. The accuracy of the method depends on the agreement between the fluorescence properties of the standards and those of the dissolved humic substances and lignin sulfonates in the water; the standards used seem to be representative for the Baltic Sea. The precision of the method is better than 5% for humic substances and better than 10% for lignin sulfonates (Sec. 6.3.2).

*Petroleum hydrocarbons (mineral oil).* The UV-fluorescence method is used in laboratories for routine measurements in many Baltic Sea countries. The results obtained by this method are in good agreement, even though different oil standards are used in different laboratories. The sensitivity is about  $1 \mu\text{g oil/dm}^3$ . Another method, infrared spectrophotometry, is used in some laboratories but tends to give falsely high values, at least for unfiltered water. This method is not as sensitive as the UV-fluorescence method and has a lower limit of detection of about  $50 \mu\text{g oil/dm}^3$ . Another method is gas chromatography which is applied by some laboratories, although rarely for routine analysis of water. The method is sensitive and gives good qualitative information on the nature of the hydrocarbons found in the samples.

#### 2.1.5 *Biological Parameters*

*Micro-organisms.* Two methods, Koch's plate method and the most probable number method, are in common use for determining the quantities of bacteria and yeasts in wa-

ter and sediment samples. Both methods permit comparison with results obtained in investigations over the past ten years.

Since 1970, a variety of modern methods has been available to measure the activity of bacteria, but none of these methods have been intercalibrated (Sec. 7.1.1).

*Phytoplankton.* The parameters primarily determined in pollution studies are (a) species composition, (b) standing stock (biomass), and (c) primary production. An intercalibration workshop on the agreed methods for measuring these parameters in the Baltic Sea has shown that there is no satisfactory comparability between the results from different laboratories at the present time (Sec. 7.2.2).

In species composition studies, species identification is a difficult task. Problems are particularly encountered in the identification and enumeration of nanoplankton, especially fragile flagellates which lose their structure due to the preservatives used on the sample. Although check lists have recently become available for uniform nomenclature, a unified list of species for the entire Baltic Sea is needed.

Regarding the determination of the number of individual species of phytoplankton, intercalibrations among Baltic laboratories have shown that more precise instructions for the counting procedures are needed than those recommended in the Guidelines for the Baltic Monitoring Programme for the first stage.

For the determination of phytoplankton standing stock (biomass), two methods are commonly in use, the calculation of total phytoplankton volume and the determination of chlorophyll a. The calculations of total phytoplankton volume are comparable from year to year when

the same method is used by the same planktologist, but results from different areas of the Baltic Sea are generally not comparable. Although there is agreement on the conversion factors to be used to obtain the appropriate carbon content for the cell volumes, some species show great differences in cell volume in different regions of the Baltic Sea. Chlorophyll a determinations have been used as an indicator of the primary production capacity of the phytoplankton. The precision and accuracy of the method for chlorophyll a analysis are adequate if the method recommended in the Guidelines for the Baltic Monitoring Programme are used. However, the estimation of phytoplankton biomass from chlorophyll a data is not reliable.

The measurement of primary production can be made *in situ* in the natural environment or in an incubator using constant light and temperature settings. Owing to its greater ease of use, the latter method has been recommended for the Baltic Monitoring Programme. The precision and accuracy of the method are mainly dependent upon the sampling time, temperature and light conditions, as well as on the concentration of the radioactive solution added to the samples. An intercalibration among Baltic laboratories has shown that there is no satisfactory comparability yet between the results from different laboratories. In addition, the degree of comparability of results using the new liquid scintillation method with those using the Geiger-Müller method is not clear. Finally, the low frequency of sampling agreed upon for the first stage of the Baltic Monitoring Programme is not intended to give the annual level of primary production in the different areas of the Baltic Sea, but rather to serve as a warning system.

*Zooplankton.* A recommended counting procedure, accepted by all Baltic Sea countries, has been developed that will



provide comparable data from most zooplankton investigations in the near future. An open question is the accurate estimation of biomass, but work is well under way so that reliable methods can be expected to be in use from 1980 for the whole Baltic Sea area. Methods are not yet available, however, for the quantitatively correct sampling of jellyfish (Sec. 7.3.3).

*Phytobenthos.* Although formerly, methodological difficulties limited studies of phytobenthos to qualitative and semi-quantitative descriptions, the development of diving techniques and diver-operated equipment has permitted quantitative sampling programmes to be carried out in recent years. In spite of the lack of quantitative trend information, older data from species and association studies can be used to detect changes in the ecosystem (Section 7.4.1).

*Macrozoobenthos.* There is general agreement on the methods to be used in the study of macrozoobenthos in the Baltic Sea. Intercalibration exercises have shown that for only some methods are the accuracy and precision adequate for a comparison of results from different laboratories. Several methodological problems still remain. Earlier results obtained in different laboratories cannot be considered comparable owing to the differences in the methods used (Section 7.5).

*Vertebrates.* The effects of pollutants on fish, birds and seals have mainly been studied in laboratory investigations. Owing to a lack of fundamental ecological information, there are no methods presently available to study the effects of pollutants on vertebrates in their natural environments (Sec. 7.6).

## 2.2 Gaps

Question:

- Are there any gaps due to a lack of applicable studies (other than those due to a lack of adequate methodologies)?

In order to conduct as complete as possible an assessment of the effects of pollution in the Baltic Sea, it was necessary to be able to obtain all relevant information. Thus, contributors were asked to identify any gaps in the information they needed which were due to a lack of applicable studies. The gaps due to a lack of adequate methodologies have been considered under Section 2.1, *Methods*.

Open questions were found, for instance, concerning the reasons for changes in the water balance and mass balance calculations. Too little is known about the atmospheric fallout to the open Baltic Sea and about the fate of pollutants discharged from land-based sources. To develop a reliable model for the Baltic Sea, more precise information is also needed about the water exchange between coastal waters and the open sea, as well as the residence time of the water. In addition, different biological processes in the sea water and at boundary levels are insufficiently known. Some of the open questions are connected with the nitrogen cycle in the Baltic Sea ecosystem.

Although agreed methodologies are available, there is still a lack of reliable up-to-date baseline data on trace metal concentrations in biota for most parts of the Baltic Sea. There is also a lack of information about the environmental impact of some potentially harmful or toxic substances identified in the Baltic waters. In many cases, interpretation of changes found in the Baltic Sea ecosystem is not possible due to the lack of

adequate studies on the effects of pollution. There are also some parameters which are considered to be important for the assessment of the effects of pollution which are not yet monitored regularly in the Baltic Sea. In addition, due to the lack of sufficient information on pollutant discharges and environmental processes, the levels of discharge of a substance cannot yet be related to its levels in the marine environment.

### 2.2.1 *Geological History Of the Baltic Sea*

Because of the great environmental changes happening during the evolutionary history of the Baltic Sea, there is an open question: Which trends calculated on the basis of data covering ten or some tens of years are in fact natural "noise" in the trends of some thousands of years and which have been caused or triggered by human activities? (Sec. 1.3).

There is still land upheaval in the northern part of the Baltic Sea. To what extent this phenomenon causes changes in the eustatic sea level remains open.

The inflow and outflow through the Danish Straits and the change in the mixing of different water masses make it difficult to give an exact value for the *residence time* of the water of the whole Baltic Sea. At present, residence times of 25 - 40 years are assumed for the Central Baltic deep water.

### 2.2.2 *Physical and Chemical Features*

The distribution of the *fresh water surplus*, the inflow through rivers, and the water balance between precipitation and evaporation are not even over the whole Baltic Sea. There is a lack of precise knowledge about the changes found in the fresh water surplus due to human activities or as a result of natural variations associated with meteorological circulation. More calculations

and the development of a reliable model are needed (Sec. 3.2.4).

Too little is known about the *atmospheric input* of substances to the Baltic Sea. This is due to the lack of reliable methods for sampling in open sea areas. In addition, methods for collecting representative atmospheric fallout material in general are not yet considered to be good enough. Many measurements from nearshore zones, however, point to the fact that the atmospheric input may be significant for some trace metals (Pb, Hg, Cd, Cu) and organochlorine compounds (e.g., PCBs) (Secs. 5.1.7, 6.1.5, 6.2.1).

On the basis of present knowledge, it is not possible to state with certainty to what extent human activities are responsible for the formation of *hydrogen sulfide* in Baltic deep basins in recent decades or to what extent it is a natural phenomenon caused mainly by hydrographic and meteorological large-scale changes during the present century. It has been suggested that these last-mentioned factors are the primary reasons for the stagnation and that the increased discharges of easily oxidizable organic matter and nutrients may be a secondary reason, which has accelerated hydrogen sulfide formation. Other scientists maintain that these latter are solely responsible (Sec. 4.1.6).

*Particulate organic nitrogen.* This fraction has not been regularly analysed in Baltic Sea water, although more detailed information on its distribution and abundance would be of considerable interest in assessing the pollution situation (Sec. 5.2.1).

It is not clear how much of the *nitrogen* reaching the sediments is returned to the water column (Sec. 5.2.3).

It is not known what mechanisms control the beginning and cessation of the *nitrification* process (Sec. 5.2.4).

The condition or mechanism triggering the extensive *blooms* of blue-green algae is not yet known. There is a hypothesis that nitrogen fixed by blue-green algae is mineralized and nitrified and that a comparable amount of nitrate is denitrified in the low-oxygen deep water and lost from the cycle. Investigations to verify this are under way (Sec. 5.2.5).

Due to a lack of long-term measurements on a routine basis in the Baltic Sea, it is not possible to decide if any changes in the *silicate concentration* in the water have occurred during the present century (Sec. 5.3.4).

There is a lack of reliable up-to-date baseline data on *trace metal concentrations* in sea water for most parts of the Baltic Sea. Although for some areas a considerable amount of data appears to be available, due to unsatisfactory methods they are not always reliable. Therefore, trends in heavy metal concentrations in sea water cannot be determined. On the basis of recently published data, some average values, or at least ranges, can be expressed for concentrations of some trace elements in the open Baltic Sea. However, for other elements (e.g., Bi, Se, Sb, Tl, V), no data for the open sea are available or they are so scarce that no general conclusions are possible (Sec. 6.1.2).

Data on *heavy metals in sediments* do not cover the whole Baltic Sea. The methods have not yet been unified or intercalibrated (Sec. 6.1.3).

Because of uncertainties regarding the accuracy of data on trace metals in sea water and due to a lack of reliable data from all sub-areas, only preliminary calcula-

tions for budgets are available. There is a lack of heavy metal input data for municipal and industrial discharges from most of the coastal areas of the Baltic Sea. There is also a lack of knowledge of the annual heavy metal deposition rates in sediments, which are needed for reliable mass balance calculations (Sec. 6.1.5).

There is a gap of unknown magnitude and significance concerning possible *organic contaminants* of the Baltic Sea and their ecological impact (Sec. 6.2).

We still lack sufficient knowledge about the *effects* of organochlorine compounds *on the physiological mechanisms* of marine biota. In addition, too little is known in manycases to be able to identify which substance (or substances) is causing a given reaction or effect observed in an organism (Sec. 6.2.1).

Although *DDT* has been in use in the Baltic Sea area for about 30 years and *PCBs* for a slightly longer period there are no data published about the total quantity of chlorinated hydrocarbons used during these years (Sec. 6.2.1).

There are few data available on *chlorinated hydrocarbon concentrations* in Baltic Sea water and no systematic investigations of chlorinated hydrocarbons in the bottom deposits of the Baltic Sea have been made (Sec. 6.2.2).

In addition, very little is known about possible interactions between organochlorines and other pollutants (Sec. 6.2.2).

A group of compounds structurally related to the PCBs, *polychlorinated terphenyls* (PCTs), has recently been reported to be present in biota from the Baltic Sea area. There is a need for more investigation on these substan-

ces as well as on *chlorinated terpenes* and *chlordanes* compounds, other toxic substances recently found in Baltic biota.

The average *humic* content of rivers discharging into the Baltic Sea is insufficiently known as also is the case for the annual *input of lignin sulfonates* from the wood-processing industry to the Baltic Proper (Sec. 6.3.4).

The knowledge of the effects of *oil* on organisms derives mainly from laboratory studies, the results of which are difficult to extrapolate to natural systems. More studies are needed to cover this gap (Sec. 6.4.5).

### 2.2.3 *Biological Parameters*

Investigations on the *microbiology* of the open Baltic Sea are rather few. Most of the studies have been done on the microbiology of the water and almost none on the sediments (Sec. 7.1).

Further information is needed on the role of *bacteria* in the *food chain*, including the relationship between bacteria and primary producers and the subsequent energy transmission to consumers (Sec. 7.1.6).

The knowledge of the *microbial decomposition of organic pollutants* is also far from sufficient. Information is needed on the types of micro-organisms which are able to degrade the various organic pollutants as well as on the intermediate and end products of this decomposition (Sec. 7.1.6).

For *phytoplankton* studies, a check list covering the whole Baltic Sea area is needed which indicates the dominant and typical species for the different regions and seasons (Sec. 7.2.1). There is very little reliable in-

formation on the possible effects of toxic substances on phytoplankton communities in their natural habitat (Sec. 7.2.3).

Despite the significance of *zooplankton* in the marine food chain, there is relatively little knowledge about zooplankton (Sec. 7.3). Not much work has been done on zooplankton in relation to pollution (Sec. 7.3.3) and there are few investigations on the concentrations of harmful substances in zooplankton (Sec. 7.3.4).

Concerning *phytobenthos*, due to the complexity and mosaic structure of this biota, much information is still needed before even the normal variations within this sub-system in the Baltic Sea can be fully understood and quantified (Sec. 7.4.1). Further information is also needed before calculations can be made on the influence of a moderate increase in the nutrient level on the overall benthic primary production (Sec. 7.4.2). Although some studies have been done on the concentrations of heavy metals in some macroalgae, further knowledge is needed to be able to establish the total ranges of concentrations in algae from truly unaffected areas and to estimate the effects of heavy metals in the algae as well as the importance of bioaccumulation (Sec. 7.4.2).

To assess the effects of pollution on the *vertebrate populations*, information is needed not only on the occurrence of pollutants in the environment and in the biota, but also on how the vertebrates are behaving in the unpolluted areas. This information is very sparse and there is a need to intensify research activities in this field (Sec. 7.6).

At present, good field data on the effects of harmful substances on fish do not exist (Sec. 7.6.1). Further information is needed concerning the actual effects of organochlorine compounds on marine vertebrates, especially marine mammals, in the Baltic Sea area (Sec. 7.6.5).



## 2.3 Trends

Question:

- What are the levels, including statistical variances, the trends in these levels and their significance?

This section describes those trends which have been able to be shown based on reliable time-series of data. For many parameters, however, no trends can be determined as the methodologies have not been sufficiently accurate and precise over a long enough time period to allow any trends to be revealed.

### 2.3.1 *Physical Parameters*

*Salinity and temperature.* Since the beginning of this century, there has been a trend towards a regionally different *increase in temperature* as well as *salinity* in the *deep water* of the Baltic Proper. The frequency and intensity of salt water inflows through the Danish Straits play a major role in increasing the salinity and density and, depending on the time of the year at which the inflow occurs, changing the temperature of the deep water. Thus, the actual size of the changes are somewhat different in the different sub-areas of the Baltic Sea. On average, the increase in the temperature of the deep water is about 0.6 - 2.7°C and the increase in the salinity is about 0.8 - 1.7‰. The average salinity in the Gulf of Bothnia has also increased. Long-term trends in the temperature of the surface water are difficult to detect. For salinity, however, the calculations show that the average *increase in the salinity of the surface water* has been 0.2 - 0.5‰ less than in the deep water (Sec. 3.1.4).

The average increase in salinity since the beginning of this century has caused some *reduction in the depths of the isohalines*. The mean increase in salinity has been

accompanied by an *increase in density*, which has been reported to have increased by  $1 \text{ g/dm}^3$  between 1900 and 1967 in the Northern Central Basin (Sec. 3.1.4).

There are some calculations showing that the *stability of the stratification* in the Gotland Deep water has increased from the beginning of the century up to the middle of the 1950s. However, on the basis of the recent results, this has been questioned (Sec. 3.1.4).

*Fresh water surplus and water balance.* The Baltic Sea has a *positive water balance*. On the basis of present calculations a mean annual value of  $438 \text{ km}^3/\text{yr}$ , with a standard deviation of  $52 \text{ km}^3/\text{yr}$ , has been given for the fresh water surplus. No clear trend can be observed over the past 50 years, indicating that the precipitation and evaporation more or less equal each other (Sec. 3.2.2).

It has been suggested that a slight increase in the mean stability in some layers in some parts of the Baltic Sea has been shown. However, there appear to be no safe indications of a long-term trend towards a smaller vertical mixing in the interior of the Baltic Sea (Sec. 3.2.5).

### 2.3.2 *Dissolved Gases*

Since the beginning of the present century, the *oxygen concentration* in the deep water in the Baltic Proper has *decreased* from around  $3 \text{ cm}^3/\text{dm}^3$  to around zero. This decrease has been shown in the different basins in the Baltic Proper between 1900 and the 1970s (Sec. 4.1.5). It has been suggested that this oxygen decrease has been caused by two large salt water inflows (Sec. 4.1.6).

Studies of sediment cores from the Baltic deep basins have shown that *hydrogen sulfide* formation has occurred in the Baltic Sea during former geological times, e.g., 5000 - 4000 B.C. In addition, it has been shown that

during 1600 - 1700 A.D. the hydrogen sulfide formation was more frequent than during the present time (Sec. 4.1.5). However, it is not possible to state with certainty whether human activities are responsible for the recurrent periods of hydrogen sulfide formation during this century or whether this is a natural phenomenon caused by hydrographic and meteorological large-scale changes (Sec. 4.1.6).

*Redox potential* studies of sediment cores have revealed several cycles from 1970 to 1750 A.D. In the Gotland Deep sediments, the redox values have ranged from -70 mV to -230 mV. However, at present it is difficult to say whether the general *decreasing trend* is caused by processes inside the sediments or whether it indicates any long-term trend in the hydrographic conditions. The results indicate that the recent great variations are not unique in the history of the Baltic Sea, but might rather reflect climate variations (Sec. 4.2).

### 2.3.3 *Nutrients*

*Increasing phosphate* concentrations have been observed for several years in the mixed winter surface layer of the Baltic Proper. The rate of increase was about 0.04  $\mu\text{mol}/\text{dm}^3$  per year from 1969 to 1978. In the Gulf of Bothnia, some studies show a declining trend from 1966 to 1977 in the total phosphorus concentration during the winter. No clear trend has been observed in the phosphate concentration in the surface water of the Gulf of Finland (Sec. 5.1.6).

A substantial accumulation of phosphate has also taken place in the deep water of the central Baltic basins in recent decades. This water is partially mixed into the surface water by hydrographic processes. Therefore, the surface water contains increasing amounts of phosphate. In the Gotland Deep at a depth of 100 m an *increase in*

*phosphate* concentrations from about 1  $\mu\text{mol}/\text{dm}^3$  in 1958 to over 2.5  $\mu\text{mol}/\text{dm}^3$  in 1978 has been observed. A long-term trend of *phosphate accumulation* in the deep water has also been observed in other central basins of the Baltic Sea. However, in the Bornholm and Gdańsk Deeps, the situation is not so clear although some increase is apparent since the 1960s. In the Gulf of Finland, no increase in the concentrations of inorganic or total phosphorus in the deep water has been observed from the 1920s to 1978. Similarly, no long-term trend of phosphate accumulation in the deep water of the Gulf of Bothnia has been observed (Sec. 5.1.6).

The increase in the phosphate content observed in the mixed winter surface layer of the Baltic Proper since 1968 correlates closely with an increase in salinity and, thus, with hydrographic processes (Sec. 5.1.6). At present, it is not possible to state with certainty whether the phosphate accumulation observed in the deep water of the central basins of the Baltic Sea is primarily due to natural causes or is a consequence of increasing pollution (Sec. 5.1.7).

A mass balance estimate of phosphorus in the Baltic Sea (excluding the Kattegat) shows an annual net supply of 26 000 t (Sec. 5.1.7).

On the basis of *nitrogen data* collected during the past 10 -15 years which can be considered reliable, there do not appear to be clear indications that an increasing degree of pollution of the Baltic Sea is reflected in the nitrogen picture of the Baltic Sea as a whole. An important conclusion to be drawn from this assessment is that the various biological processes in the nitrogen cycle which participate in the transformation of the diverse species of nitrogen seem to be in balance (Sec. 5.2.5).

Due to analytical difficulties, there is a lack of reliable data older than 10 - 15 years on total nitrogen and thus no long-term trends can be determined.

*Silicate* has been measured on a routine basis in the Baltic Sea only during the past decade. Therefore, it is not possible to determine whether any changes in the silicate concentrations in the water have occurred during the present century (Sec. 5.3.4).

#### 2.3.4 Harmful Substances

For *heavy metals in sea water*, there is still a lack of reliable recent baseline data. Therefore, general trends cannot be established (Sec. 6.1.2).

When comparing the *heavy metal concentrations in the sediments* from the earlier stages of the Baltic Sea with those observed in the most recent sediments from accumulation areas, three groups can be distinguished: (1) metals whose contents have remained nearly constant during the ages, e.g., nickel and chromium; (2) metals for which background levels have increased by a factor of 1.5 to 2, e.g., copper and cobalt, or by a factor of 3, e.g., zinc and lead; and (3) metals which have shown more than a tenfold increase over background concentrations, e.g., cadmium and mercury. Recent deposits in the central parts of the Baltic Sea show high mercury, cadmium and lead levels compared with oceanic deep sea sediments and mean levels in the earth's crust (Sec. 6.1.3).

At present, no clear information on trends in *heavy metal concentrations in organisms* is available (Sec. 6.1.4).

Reliable results for the determination of *organochlorine concentrations in Baltic Sea water* have not been available over a long enough time to permit the determination

of trends. Some information, however, indicates that the average ratio of PCBs to CDDT has increased in the past few years (Sec. 6.2.2).

Although no overall investigations of the concentrations of chlorinated hydrocarbons in the bottom deposits of the Baltic Sea have been made, one study has indicated that there is a significant difference between the concentrations of DDT and PCBs in surface sediments and those in the deeper layers of sediment. The concentration curves are closely related to the history of the application of these compounds in the Baltic countries (Sec. 6.2.2).

Trend studies on the concentrations of DDT and PCBs in Baltic biota have shown decreasing levels of DDT residues in various fish species, including cod, herring, sprat, garfish, and pike, since 1971. No change in PCB concentrations in these species of fish were found. Similarly, studies on guillemots have shown DDT levels decreasing since 1971, whereas no changes were evident in PCB concentrations (Sec. 6.2.2).

*Humic substances* and *lignin sulfonates* were measured in the Baltic Sea surface water and deep water from 1974 to 1977. No trends in the concentrations were observed during this period (Sec. 6.3.3).

No time-series studies of the concentrations of *petroleum hydrocarbons* in sea water or organisms have been conducted which are suitable for the determination of trends (cf. Sec. 6.4.3), whereas there is some evidence that petroleum hydrocarbons may be accumulating in recent sediments in certain areas of the Baltic Sea (Sec. 6.4.4).

#### 2.3.5 *Biological Parameters*

There are insufficient time-series data on the distribution, composition, and activity of *micro-organisms* to be able to determine trends (Sec. 7.1.6).

Because of the inability to compare older quantitative *phytoplankton* data with recent results, it is difficult to determine possible trends in the phytoplankton composition, distribution and standing stock during this century (Sec. 7.2.3).

It has been suggested that there is an increasing trend in the appearance of blooms of blue-green algae, but this has not been verified due to a lack of appropriate data (Sec. 7.2.3).

The *primary production* results from the years 1965-1980 are not easy to compare owing to the differences in the methods used. Nonetheless, in eutrophied coastal waters, the increasing eutrophication is clearly indicated by an increase in the primary production and the production capacity. Apart from local areas with clearly traceable pollution sources, no increase in phytoplankton standing stock or primary production is ascertainable at present because of the lack of comparable quantitative data from the past (Sec. 7.2.3).

Regarding *zooplankton*, some coastal areas have exhibited changes in species composition as a result of eutrophication. It is difficult to compare older and more recent data on zooplankton biomass, but it may be possible that there is a gradual increase in the zooplankton biomass in the Baltic Proper (Sec. 7.3.4 and Sec. 7.3.5).

Owing to a lack of quantitative sampling techniques until recent years, statistically significant trends in the biomass of *phytobenthos* on hard bottom substrates in the Baltic Sea over longer periods are not possible to obtain at present (Sec. 7.4.1). Nonetheless, changes in the dominance and composition of species in the phytobenthos have been shown in coastal areas subjected to heavy discharges of organic wastes or toxic substances (Sec. 7.4.4).

*Zoobenthos* is one of the few parameters which give exact information on changes on deep bottoms during this century. A general decrease in the oxygen content and the consequent deterioration of the macrozoobenthos was recorded in the mid-1950s in the southern Baltic Sea and the Gotland Deep and in the late 1960s and at the beginning of the 1970s in the northern parts of the central basin and in the Gulf of Finland. Although in the shallow parts of the open Baltic Sea, the biomass and abundance of macrofauna have shown greater stability, increasing trends with time have been found for macrozoobenthos abundance and biomass in several areas of the Baltic Sea. The increase occurring in open shallow areas has been explained by an increase in the phytoplankton primary production (Sec. 7.5.2). Also, decreases in macrozoobenthos abundance and biomass in areas receiving heavy discharges of organic or inorganic substances have been found in coastal areas around the Baltic Sea (Sec. 7.5.2 and Sec. 7.5.3).

A decrease in egg-shell thickness of some Baltic *birds* during this century has been reported, caused by high DDT and PCB body burdens in the birds (Sec. 7.6.2). A rapid decrease in *seal populations* during the last decades has been reported owing to reproductive failure, probably induced by high body burdens of organochlorines (Sec. 7.6.3).

## 2.4 Human activities

Questions:

- What is the background level of the parameter or substance in the Baltic Sea?
- What is the influence of human activities, both polluting activities and abatement measures, on each parameter?'



- To what extent should the input of pollutants be reduced in order to reach background levels in the Baltic Sea?

On the basis of the background document, the effects of human activities can be divided into two main categories: those for which man is solely responsible (e.g., the effects caused by synthetic organic chemicals) and those for which man is partially responsible but for which it is difficult to apportion the exact contribution of anthropogenic influences and natural causes (e.g., the decrease in oxygen content of the deep water with ultimate formation of hydrogen sulfide). The changes partly or wholly caused by human activities are described below.

At present, it is not possible to state with certainty to what extent human activities are responsible for the decrease in oxygen concentrations in the deep water and eventual *hydrogen sulfide* formation or to what extent these are natural phenomena caused by hydrographic and meteorological large-scale changes. During the last three decades, hydrogen sulfide has been formed occasionally in all of the main deep basins of the Baltic Proper. It has been suggested that hydrographic and meteorological large-scale changes have created stagnant or semi-stagnant conditions in the deep basins, resulting in the severe depletion of oxygen. The anthropogenic discharges of easily oxidizable organic matter and nutrients causing increased eutrophication of the surface water have been suggested as the second reason which has accelerated hydrogen sulfide formation (Sec. 4.1.6).

A mass balance estimate of the *phosphorus* in the Baltic Sea, excluding the Kattegat, has revealed an annual net supply of 26 000 tonnes, which is equivalent to the amount of phosphorus input from man-made wastes. However, at

present, it is not possible to state with certainty to what extent the phosphate accumulation observed in the deep water of the central basins of the Baltic Sea is due to natural causes and to what extent it is a consequence of pollution (Sec. 5.1.7).

The conclusion drawn from the studies on *nitrogen* is that all the biological processes in the nitrogen cycle, which participate in the transformation of the diverse species of nitrogen, seem to be in balance. It is difficult to assess whether the extensive blooms of blue-green algae, which contribute hundreds of thousands of tonnes of combined nitrogen to the Baltic Sea, are triggered by an imbalance in the nitrogen-phosphorus relationship (Sec. 5.2.5).

The relatively high *silicate* concentration in the Baltic Sea water is mainly due to the large runoff of river water. It has been shown that the silicate content of the Baltic Proper is mainly regulated by the silicate concentrations in Kattegat water and Gulf of Bothnia water. It has been suggested that the regulation of river runoff through the construction of power dams may have influenced the transport of silicon, especially in particulate form, to the Baltic Sea. The dams decrease the spring flood caused by the melting of the snow, so particulate silicon may settle in the dams and dissolved silicate may be co-precipitated with the settling material. Due to a lack of data from the first half of the century, no evidence can be found of a decreasing silicate concentration in the Baltic Sea (Sec. 5.3.4).

The presence of elevated concentrations of *heavy metals* in the sediments of the Baltic Sea has resulted from anthropogenic discharges. The concentrations of mercury and cadmium have been shown to have increased more than ten times over background levels. In addition, signi-

ificantly higher levels of lead, zinc, copper and chromium have been measured in the upper segments of sediment profiles. Compared with natural background data from the Baltic Sea, very high levels of mercury, cadmium and lead have been found (Sec. 6.1.3). After the ban on the use of mercurial compounds in the pulp and paper industry in the northern Baltic Sea countries, a decrease in mercury concentrations has been found.

The presence of the chlorinated hydrocarbons *DDT* and *PCBs* in organisms in the Baltic Sea is caused by man. Considerable amounts of DDT and PCBs have been found in the eggs of guillemots and in Baltic herring, salmon and seals. Among the known effects of these substances is the great increase in the number of sterile seals in the Baltic Sea, which has been proved to be caused by PCBs.

The most severe changes in the *coastal ecosystems* have been caused by sewage discharges. In many cases, low-production ecosystems have changed into hypertrophic. The consequence of these changes has been changes in the food chain, resulting in changes in fish species, with economically valuable fishes being replaced by species of low economic value.

The presence of *lignin sulfonates* in Baltic Sea water is caused by human activities alone, as these substances are waste products from sulfite pulp mills.

Waste water effluents from *industries* often have a toxic and inhibitory effect on the ecosystem in the vicinity of the outfall.

Severe effects of *oil spills* have been observed locally in pelagic, littoral and benthic ecosystems, although they have proved to be of short duration in the pelagic

system. On the other hand, effects on soft bottom fauna may remain for over two years after a major spill has occurred.

Chronic *oil pollution* near oil refineries and oil harbours causes clear changes in littoral and benthic fauna. It has been shown, however, that after totally disappearing, zoobenthos can partially recover after the construction of effective waste water treatment plants.

## 2.5 Sub-areas

Questions:

- What are the differences between the various sub-areas of the Baltic Sea?
- What is the influence of these differences on the overall picture of the marine environment?
- What are the causes for differences between regions?

In this section, the conditions in the eight main sub-areas of the Baltic Sea are considered. The areas are: the Kattegat, the Øresund, the Belt Sea, the Kiel Bight, the Baltic Proper, the Gulf of Riga, the Gulf of Finland and the Gulf of Bothnia.

There are many natural differences between the sub-areas of the Baltic Sea due to the fact that the annual productive period is about 9 - 10 months in the south but only 4 - 5 months in the north. In addition, ice covers the northern part of the Baltic Sea for about 5-6 months of the year, but sea ice occurs only occasionally in the southern and southwestern parts of the Baltic Sea.

An essential factor causing differences between the sub-areas is the different nutrient inputs. One of the

sources affecting production in the open Baltic Sea and in certain coastal areas is the upwelling of phosphorus-rich Baltic deep water.

In the sections below, a short description of the major characteristics is given. Although most of the basis for this material has been given in the background document, in some cases new information has been added.

### 2.5.1 *The Kattegat*

The conditions in the Kattegat have not been described in detail in the background document (Part B), so important facts concerning this area are given in this section.

The Kattegat is part of the Transition Area between the North Sea and the Baltic Sea. Because of its positive water balance (the fresh water input from rivers and precipitation exceeds the evaporation), the Baltic Sea discharges about 450 km<sup>3</sup> of water through the Kattegat annually. Because of its low density, this brackish water flows northwards as a surface water current, the Baltic current, in the Kattegat mostly along the Swedish coast.

From the main body of the Kattegat water, which is derived from the North Sea, water flows through the Øresund and the Belt Sea into the Baltic. As the Kattegat water has a higher density than the Baltic waters, the Kattegat water will enter the Baltic Sea as a deep water, thus replenishing the deep or bottom water of the Baltic.

The Kattegat water and the water of the Baltic current usually co-exist in the Kattegat. However, the proportions between the two water types and their flow directions vary largely depending upon the governing factors. Thus, under the influence of westerly winds and a low

air pressure over the Baltic Sea, the Kattegat water will flow into the Baltic. On the other hand, when the air pressure over the Baltic Sea is high, the Baltic current will extend through the Kattegat and into the Skagerrak. As a consequence, the Baltic current has to be regarded as a net transport of surface water out of the Baltic Sea rather than as an ever-present current.

In the Transition Area, a part of the outflowing Baltic water is mixed with Kattegat water, and thus water flowing into the Baltic consists roughly of  $1/3$  high saline Kattegat deep water and  $2/3$  Baltic Sea surface water. The mean salinity of the water thus entering the Baltic Sea is about  $17\text{‰}$  in contrast to a salinity of  $20 - 30\text{‰}$  in the northern Kattegat.

One important consequence of these hydrographic conditions is an oxygen minimum appearing in the Kattegat deep water every autumn. The minimum, which is most pronounced in the southern part, is a result of the speed and magnitude of the water exchange processes and the degradation of organic matter. Thus, the degree of this oxygen minimum and its geographic extent vary from year to year.

Land-based pollution enters the Kattegat not only from the surrounding countries, but also from the Baltic Sea itself by the Baltic current and to a far lesser extent from the North Sea by the Jutland current. The mean temperature in the surface water is relatively high and this leads to higher biological activity, and possibly also biochemical degradation, than in the Baltic Sea.

With the exception of the archipelago areas in the northeastern part of the Kattegat, there are no archipelagos in the Kattegat. Therefore, there is a rapid transport of pollutants from the coast to the open sea areas and also a good mixing of different water bodies in the area.

The important sources of land-based pollutants on the eastern coast of the Kattegat are not only municipal discharges, but also oil refineries, pulp and paper industries and petrochemical industries. This leads to a considerable load of oxygen-consuming organic substances as well as nutrients and other material. In certain parts of the easterncoastal areas, local eutrophication is a well-established fact, but there is no clear indication of eutrophication in the open sea area itself. On the western and southern coasts of the Kattegat, there are relatively few sources of pollution.

During recent years, local problems with low oxygen content (less than  $3\text{cm}^3/\text{dm}^3$ ) in the bottom water have been experienced in some bays on the east coast of the Kattegat. This has led to the absence of sport and commercial fish and a temporary, almost complete, destruction of the bottom fauna. As this has occurred in connection with the mass development of green algae (*Cladophora*) or phytoplankton (dinoflagellates, in particular), it was suspected to be caused by eutrophication. However, it cannot be regarded as a problem which is caused only by local factors. These local incidents must be viewed in the light of the general hydrographic situation with the low oxygen content in the bottom water during autumn periods, as described above.

Along the Swedish coastline, high concentrations of zinc are found in the sediments and the levels of mercury, dieldrin or PCBs are so high that there is a ban on the sale of local catches of certain fish species for human consumption.

#### 2.5.2 *The Øre sund*

Land-based pollution is considered to be the main reason for the following changes in the ecosystem of this area: An increase in nitrogen, phosphorus and organic compounds

in the sediments during the last decade, especially in the northern area; an increase in organic compounds in the sea water as well as in inorganic phosphorus during the 1970s; and changes in the species composition of bottom flora in coastal areas.

The following changes have been found without showing a connection with an increase in land-based pollution: Some fish diseases have been found (not only in polluted areas) which are possibly caused by micro-organisms; long-term changes in phytoplankton species composition have occurred, which might be partly caused by changes in nutrient levels or in the salinity of the water; and a long-term increase in the phytoplankton primary production, especially in the northern part of the area, has taken place from 1930 to 1970.

In addition, long-term studies (over about 50 years) have not revealed any changes caused by pollution in bottom fauna in the open water of the Øresund. The load of organic compounds has not been found to cause changes in the primary oxygen consumption in this area as a whole and no changes in the bottom flora in the open Øresund water have been revealed.

### 2.5.3 *The Belt Sea*

Recent studies of the Belt Sea have concluded that, with the exception of the fjords, the water exchange in the Belt Sea is large and intensive and, thus, no negative effects owing to the discharge of organic matter and nutrients can be observed in the open waters. However, in the vicinity of major discharges of such materials and in the innermost part of some of the bigger fjord systems, negative effects have been observed. Additionally, an increase in the phytoplankton production has been observed in the Great Belt and the Little Belt during this century.



#### 2.5.4 *Kiel Bight*

In spite of the relatively large water exchange, critical oxygen values are frequently observed in the deeper water layers (below 15m) in late summer, especially if there has been low cyclonic activities. In the case of a sudden shift from easterly to westerly winds, the oxygen-poor water reaches the surface along the southwestern shores, leading to significant fish kills. A slight trend toward increasing eutrophication has been observed.

The levels of trace metals in the water and the living organisms are not significantly higher than in the open sea. Only in minor parts of the fjords have higher trace metal levels been observed. The level of trace metals in fish is, on average, far below permissible values.

The level of petroleum hydrocarbons in the water is relatively low. Usually, fluctuating values of 10 - 20  $\mu\text{g}/\text{dm}^3$ , with maxima around 40 - 50  $\mu\text{g}/\text{dm}^3$ , have been reported. The petroleum hydrocarbons consist mainly of diesel oil and combustion products and possibly stem from ships. The amount of DDT in the water and fish has significantly decreased whereas the level of PCBs is constant, if not increasing. Increasing amounts of lindane have also been reported. In general, the major problem of the Kiel Bight with respect to pollution may be eutrophication and the resulting deficit in the oxygen balance.

#### 2.5.5 *Baltic Proper*

The Baltic Proper was formerly considered to be an oligotrophic sea, but there is a good deal of evidence that the conditions have changed to be more eutrophic. The reasons for this change are difficult to establish.

A slight oceanisation has occurred since the 1930s, when the salinity was unusually low. It is quite evident that both the salinity and the temperature in the deep water have increased since the beginning of the century. This increase in salinity can also be found in the surface water. The reasons for these increases are certainly climatological. We also know that the oxygen concentration of the deep water has decreased to almost zero and that hydrogen sulfide occasionally is found in the bottom water of the deep basins. This decrease in the oxygen concentration is probably caused by the diminished water exchange through the Danish Straits during this century and, therefore, associated with the increase in salinity. The decreased water exchange causes a longer residence time for the water in the Baltic Sea and, therefore, more stagnant conditions in the deep water.

It has also been observed that the phosphate concentrations in both the surface water and the deep water have increased since the measurements began after World War II. The increased phosphate in the deep water is partly due to accumulation in the water and partly to the dissolution of precipitated phosphate during anoxic conditions in the deep basins. Ammonia is also accumulated during these conditions.

The increased phosphate concentration in the surface water is certainly due partly to the transport of phosphate-rich water from the deep water through the halocline. It may also be partly due to increased discharges of waste water from industries and communities. There is clear evidence that coastal waters, especially in archipelagos around large cities, have become eutrophied through the discharge of easily oxidized organic matter and nutrients. Whether these nutrients reach the open sea and influence the conditions there is still an open question. Due to the increased nutri-

ent content of the surface water, the primary production seems to have increased in the whole Baltic Sea. It must, however, be stressed that this effect will occur regardless of the origin of the nutrients. The time series of reliable nitrate, nitrite and ammonia results are too short for an evaluation of changes in the conditions.

Blooms of blue-green algae were already observed during the 1930s. As there do not exist any long series of quantitative measurements, it cannot be demonstrated that the frequency of intensity of these blooms has increased.

The discharge of toxic substances, e.g., certain heavy metals and chlorinated hydrocarbons, has resulted in the accumulation of some of these substances in water, biota and sediments, due to the long turnover time of the water in the Baltic Sea. The concentrations of heavy metals are not regarded as serious in the open sea, but the chlorinated hydrocarbons have reached concentrations up to 10 times higher than in the sea areas outside the Baltic Sea.

The level of petroleum hydrocarbons in the water is generally low and the effects of oil on biota can only be detected in connection with oil spill accidents, when relatively large amounts of oil are discharged.

#### 2.5.6 *Gulf of Riga*

The Gulf of Riga is a shallow basin separated from the Baltic Proper by the Irben Strait, which has a sill depth of only about 10 m. Consequently, the stratification of the Gulf waters is limited and the exchange with the Baltic Proper poor. The main land-based pollution, including the urban and industrial waste waters from Riga, comes through the drainage of the Daugava River. Although the Gulf has a certain ability for self-purific-

ation from the organic pollutants, eutrophication processes are significant and in nearshore areas some oil and coliform pollution have been noted at times.

#### 2.5.7 *Gulf of Finland*

Land-based pollution is considered to be the main reason for the following changes in the ecosystem of this area. A long-term increase in the amounts of phosphorus and nitrogen in the upper layer of sea water during the ice-free winter period in the open sea has been found. Changes in the species composition and amounts of plankton, bottom fauna and bottom flora in nearshore areas as well as changes in the composition of fish species have been observed.

A decrease in oxygen concentrations in the 1960s and an increase in the 1970s in near-bottom water layers in the open sea areas have been found. This might be associated with the water movements caused by irregular intrusions of saline water through the Danish Straits. No long-term changes which could be considered to be caused by pollution have been found in the species composition of phytoplankton in the open sea areas.

The levels of heavy metals measured in sea water, organisms and sediments are not very high, although they are higher in nearshore areas than in the open sea. A slight decrease in the loads of phosphorus and organic substances has been found to result from the treatment of sewage. Input data are available for total nitrogen, total phosphorus and organic substances ( $BOD_7$ ) since 1977.

#### 2.5.8 **Gulf of Bothnia**

The Gulf of Bothnia consists of two sub-areas, the Bothnian Bay and the Bothnian Sea, which have quite

different hydrographic, chemical and ecological characteristics.

The Bothnian Bay receives the major part of the total fresh water input to the Baltic Sea. The overall salinity is very low and the ecosystem is dominated by fresh water species. The brown algae belt and the mussels, which dominate the benthic communities further south, are missing here. An effective precipitation of phosphate onto the bottom sediment due to the large river inputs of iron may be the explanation for the extremely high nitrogen to phosphorus ratios observed in this area. The overall productivity is very low due to the small amount of phosphate available in the water column.

The productivity is higher in the Bothnian Sea and the nitrogen to phosphorus ratio decreases markedly when the southward surface current of water from the Bothnian Bay is mixed with Baltic saline water with a higher phosphate content. The salinity is sufficiently high for many species characteristic of other Baltic Sea ecosystems to be maintained.

Both sub-areas receive large inputs of oxygen-demanding substances from wood processing industries.

The following changes have been observed. High metal concentrations have been noted in recent sediments in many nearshore areas. A slight increase in phytoplankton primary production in the northeastern part of the Bothnian Bay during the last few decades has been found. An increasing eutrophication in many coastal areas is evident.

A slight decrease in the oxygen concentration in the deep parts of the Bothnian Sea has been found during recent years. Increases in the phosphorus concentration and primary production have been revealed simul-

taneously. The reason might be owing to the the increase in salinity, i.e., oceanization.

There is no indication of eutrophication of the Bothnian Sea as a whole. A decrease in DDT concentrations in animals has been found during the 1970s. Input data are available since the 1970s and no long-term trends in phosphorus have been found in the open sea. The load of nitrogen has increased from municipal and industrial sources as well as from river discharges and non-point sources. The main source of discharge of land-based matter into the Gulf of Bothnia is rivers, which carry 80% of the total.

## 2.6 Inter-relationships

Questions:

- What is the interrelationship between the parameter under discussion and other parameters and processes?
- What is the influence of these parameters on the fate of pollutants, on living resources and on important processes in the marine environment?

A great deal of the information related to these questions has been presented in Sections 2.2 Gaps and 2.3 Trends. The most evident interrelationship which has been observed in the Baltic Sea during this century is the correlation between salinity and phosphorus. Additionally, the fluctuations in oxygen concentration, including the development of hydrogen sulfide in the deep water are shown to be associated with changes in salinity and phosphorus as well as in the amount of organic matter. Assuming that the water is in constant motion but that sampling for most of the parameters can be done only sporadically, we face the fact that the

present knowledge of the Baltic Sea ecosystem is not sufficient. For example, an association between heavy metals and organic matter has been revealed, but the knowledge of the fate of these substances in the Baltic Sea is insufficient.

## 2.7 Input to the Baltic Sea

Question:

- What are the sources and amounts of pollutants entering the Baltic Sea and their mass balances, if possible?

The International Council for the Exploration of the Sea (ICES) has collected information about the total input of pollutants to the Baltic Sea (1970, 1977). Information from the end of the 1960s and the beginning of the 1970s is available in these documents. This information includes data on municipal and industrial discharges, on the one hand, and on the direct and indirect loads, on the other hand. The information is mainly based on the results of a questionnaire survey and on estimates. Only a limited amount of data has been available for these reports.

More recent data exist for some sub-areas of the Baltic Sea. Data based mainly on statistics on inputs from waste water discharges, rivers (and some atmospheric deposition) have been published covering the Gulf of Bothnia, the Gulf of Finland and the Øresund (National Environment Protection Board, Sweden, and National Board of Waters, Finland, 1978 and 1979; Finnish-soviet Working Group on the Protection of the Gulf of Finland, 1979; Øresundskommissionen, 1980).

The desirability of a questionnaire survey covering the total load from all seven Baltic Sea countries has been discussed. In 1979, the Interim Helsinki Commission agreed that Finland should submit a detailed proposal on how to execute the project to obtain information on the total input of pollutants to the Baltic Sea. This proposal is under discussion in the Scientific-Technological Working Group (STWG) and the final decision will be made by the Commission.

In summary., the input information presently available covers mainly the amounts of phosphorus and organic matter carried by rivers or discharged in waste water from municipalities and industries. Only some information on nitrogen can be used.

There is a lack of data on the atmospheric input of substances to the Baltic Sea, especially to the open sea. There is also a great need for knowledge about vertical mixing of the water as well as about processes governing the transport of materials between the different water layers, and at the sediment-water interface and the water-atmosphere interface. Additionally, information is needed regarding the exchange between coastal waters and the open sea.

These types of information are needed for mass balance calculations and evaluations of the effects of discharges and atmospheric fallout, as well as for an understanding of the fate of pollutants in the ecosystem.

## 2.8 Degree of pollution

Question:

- Should the Baltic Sea or some of its sub-areas be considered polluted and to what extent, according to the information available?



Human activities have been responsible for the release into the environment of harmful or toxic synthetic organic chemicals (e.g., PCBs, DDT, chlorinated terpenes, PCTs) and organic wastes which are not natural in origin (e.g., lignin sulfonates), as well as for increasing the amounts of certain natural substances, e.g., nutrients, trace elements and hydrocarbons, in the marine environment.

The accumulation of the chlorinated hydrocarbons, DDT and PCBs, is considered to be an acute problem in the Baltic Sea. They have been shown to be present in all organisms investigated from the Baltic Sea. Due to the ban on the use of these substances in most of the Baltic Sea countries, a decrease in DDT has been revealed in the sediments and fish. The major known effect of DDT in the Baltic Sea has been the decrease in egg shell thickness of birds feeding on fish and mussels.

The concentrations of PCB residues in fish in the Baltic Sea appear to be higher than those found in fish from the North Sea. Regional differences within the Baltic Sea are difficult to interpret, since our knowledge of the migration routes of the different populations or species of fish is limited.

No direct toxic effects of PCBs on fish or invertebrates have been documented, but the concentrations of PCBs are so high that, e.g., Danish and Swedish authorities have declared liver from cod caught in the Baltic Sea unsuitable for human consumption. However, a serious effect which has been attributed to PCBs in the Baltic Sea has been on the reproduction of marine mammals, especially seals. Harbour seal (*Phoca vitulina*), ringed seal (*Pusa hispida*) and grey seal (*Halichoerus grypus*) populations in the Baltic Sea have

declined rapidly in recent decades, partly due to decreased reproductive success believed to be caused by PCBs.

Another indication of human activity is the presence of lignin sulfonates in Baltic Sea water. These compounds are waste products from the pulp and paper industry.

Although the contribution by human activities is not known, investigations of heavy metal concentrations in recent sediments in accumulation areas in the Baltic Sea show that the levels of zinc and lead have increased threefold and mercury and cadmium have increased more than tenfold over background levels in sediments.

Despite the fact that a ban on mercury compounds used, for example, in the pulp and paper industry has resulted in some decreased mercury concentrations in fish from the northern Baltic Sea, there are still many coastal areas seriously contaminated by mercury.

Oil spills in the Baltic Sea have considerable local effects, depending on the location of the spill and the time of the year. Coastal benthic communities and birds seem to be the most sensitive parts of the ecosystem to single oil spills. In sheltered coastal zones where currents and wave action are weak so that oil tends to accumulate, clear effects can be shown on benthic macrofauna and meiofauna. Changes in the pelagic system are generally short-term, whereas it may take several years for the benthic community to recover. Birds are particularly affected by oil spills and mass mortalities may occur even from relatively small amounts of oil spilled.

The discharge of nutrients, e.g., via domestic waste water, to certain coastal areas where there is a low rate of water exchange has caused an increase in the nutrient concentrations in those areas resulting in hypertrophication.

Finally, several new contaminants have recently been detected in Baltic biota, namely, polychlorinated terphenyls (PCTs), chlorinated terpenes, chlordanes and halogenated paraffins. These substances appear to be highly toxic and bioaccumulating.

PART B

S c i e n t i f i c   M a t e r i a l  
u s e d   f o r   t h e   A s s e s s m e n t

# Introduction and basic information about the Baltic Sea

## 1.1 Assessment

In this document, an attempt has been made to assess the effects of pollution on the natural resources of the Baltic Sea. By "assessment" is meant the process of evaluating the conditions and quality of the environment and its products, especially living organisms. Assessment should be a fairly continuous process using the data obtained from baseline studies, monitoring programmes, field studies, and research activities. In particular, monitoring (i.e., repeated observations of selected parameters or substances as part of a time series) should be an integral part of the assessment process.

In an ideal situation, to assess the effect of a pollutant on the marine environment, a pre-discharge assessment should be carried out to determine the baseline quality of the environment, followed by periodic monitoring of the discharge rates of the substance and its possible effects on the various parts of the ecosystem.

This ideal situation rarely exists and there are further complications due to the great complexity of the marine environment and its processes. For example, the levels of discharge of a substance cannot yet be related to its levels in the marine environment because we lack

- a) sufficient information on environmental processes which influence the distribution and concentration

of the substances, e.g., dispersion, degradation, bioaccumulation, removal to surfaces, etc.,

- b) sufficiently comprehensive, detailed and accurate input information, and
- c) knowledge of the number of years and rate of discharge of the substance which have resulted in its observed environmental levels.

Furthermore, concerning the possible effects of pollutants, it is difficult, *inter alia*,

- a) to distinguish between natural changes in the ecosystem and those induced by man's activities and discharges, and
- b) to relate effects on the ecosystem, especially biota, to levels of a substance in the environment.

These examples illustrate only some of the difficulties involved in attempting to assess the impact of pollutants on the marine environment.

In this document, it is intended to summarize the existing information concerning the level of pollutants in the Baltic environment, the processes which affect the distribution and fate of pollutants, and the processes and organisms which are or may be affected by pollutants. Where possible, it has been attempted to (a) evaluate the risks for different targets caused by different harmful substances, (b) identify trends of changes in the environment, and (c) assess the overall state of pollution in the Baltic Sea.

## 1.2 Pollution development

Generally, pollution is the consequence of population growth. Agriculture, forestry and industrial develop-

ment have increased with urban growth over the centuries. The Romans had sewage systems and water pollution problems in and around their big cities. The Inca cities had sanitary installations to control pollution. Water pollution from the medieval and post-medieval towns of Europe with their bad hygienic conditions successively included also wastes from small industrial establishments, e.g., textile factories, dye-works and slaughter-houses. The first signs of marine pollution arose from cities lying on the shores of enclosed parts of the sea. Examples of this from the Baltic Sea area are Stockholm and Copenhagen.

In early times, marine pollution was very local and mainly consisted of hypertrophication of the water. In the late 19th and early 20th centuries, the marine areas affected by pollution grew, especially in western and northwestern Europe where industrialization and intense agricultural fertilization began to produce more waste.



Photo: I. Viitasalo

When swimming and bathing in the sea became more frequent and popular, pathogenic bacteria and viruses began to cause problems. Eutrophication and hypertrophication also began to cause unpleasant effects in recipient sea water. The natural resources of the sea were not yet, however, threatened.

Since the middle of the present century, particularly after World War II, the marine environmental situation has deteriorated very rapidly in many parts of the world. The areas affected by pollution have grown,



especially along the coasts of the industrialized countries. Some more or less enclosed sea areas like the Mediterranean Sea, the Arabian (Persian) Gulf, the East China Sea and the Japanese "Inland Sea" have been increasingly affected by pollution. At the same time, the kinds of pollutants have drastically changed due to the tendency for industrial and agricultural wastes to contain more types of toxic matter which are increasingly dangerous to living resources. The situation in many coastal waters is now as bad as in some inland waters. Certain pollutants have spread widely, e.g. through the air, and have created "background contamination" in more or less the entire world ocean.

The Baltic Sea is especially vulnerable to pollution due to its hydrographic properties. Scientists became interested in this sea area a century ago. At present, a great number of local and regional organizations and institutions are concerned with the pollution problems in the Baltic Sea. In fact, the Baltic Sea is probably the most intensively investigated and studied sea area of the world. These activities have resulted in a general awareness among the public and politicians about the seriousness of the pollution problem. Additionally, comparatively far-reaching practical measures for pollution abatement have been taken, leading to a general reduction in the speed of deterioration, and in a few cases even to an improvement in the situation. The activities and measures taken in the Baltic Sea often form a model for similar efforts elsewhere.

### 1.3 **Geological history of the Baltic Sea**

The geological history of the Baltic Sea shows that in its present form it is a young sea. In spite of the fact that the general topographic outlines of the Baltic Sea were established long before the beginning of the Pleistocene glaciation, the changes in the Baltic

Sea area after the last ice age have been enormous. At the end of the Baltic Ice Lake period (about 10 000 years ago), saline water intruded into the Baltic Sea area resulting in a period with rather saline and cold water (Yoldia Sea) covering mainly the present Baltic Proper and the Gulf of Finland. By the end of the Yoldia Sea phase, the ice had vanished from Finland but was still present on the mainland of Sweden. The progressing uplift finally overtook the eustatic sea level rise, cutting the oceanic connection. As a result, the Baltic Sea basin, isolated from the ocean was changed into a fresh water lake, the Ancylus Lake (see Figure 1).

Because the land uplift was greater in the north than in the south, the sea floor of the Ancylus Lake tilted and finally a new contact with the ocean through the Danish Sound and Straits was established about 7 500 years ago. Paleontological evidence shows that the initial phase of the Littorina Sea thus formed was definitively more saline than present Baltic Sea water.

The evolutionary history of the Baltic Sea illustrates how difficult or even misleading it might be to draw detailed conclusions regarding the most recent trends. The trends found on the basis of time series consisting of data for ten, or some tens of years, might be only natural noise in the trends of some thousands of years resulting in drastic changes in the properties of the Baltic Sea, as referred to above. Furthermore, it must be kept in mind that the "dialogue" between land uplift and eustatic sea level changes has not finished. For instance, even today the land upheaval reaches the maximum rate of 10 mm/y at the Bothnian Bay

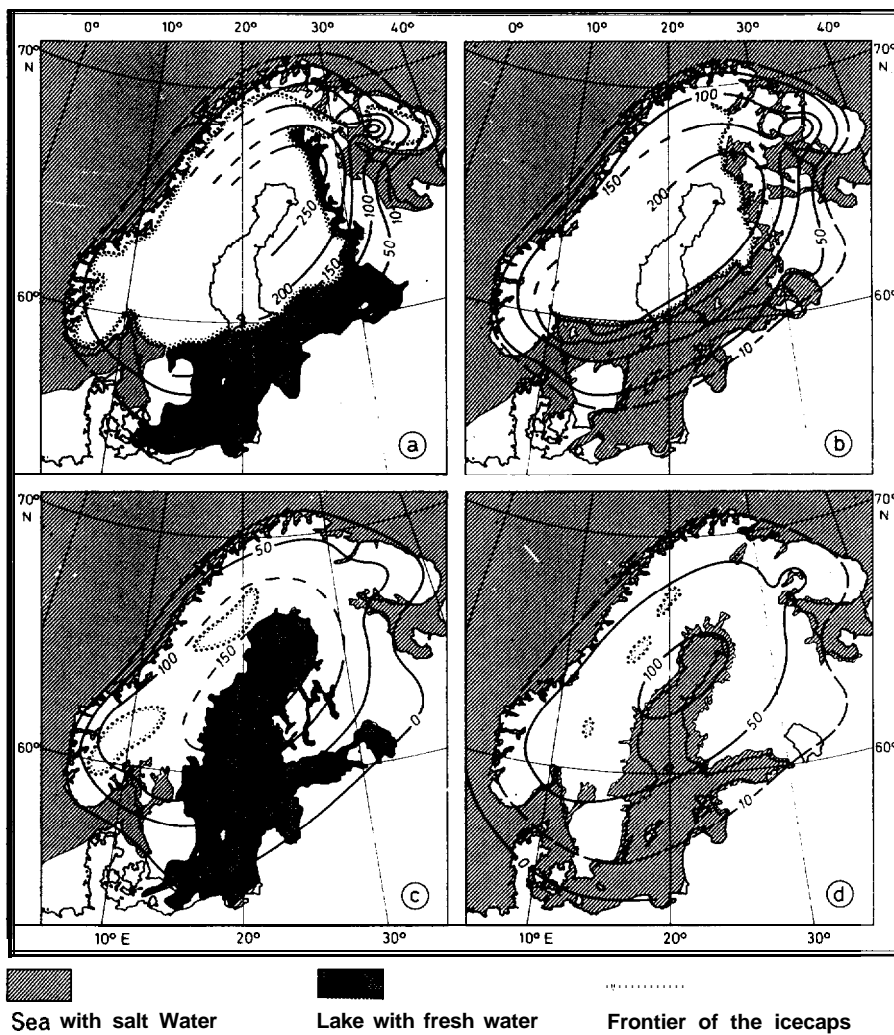


Figure 1. *The postglacial development of the Baltic Sea (from Sauramo, 1958).*

- (a) *Baltic Ice Sea* 12000 - 8000 B.C.  
 (b) *Yoldia Sea* 8000 - 7250 "  
 (c) *Ancylus Sea* 7250 - 2000 "  
 (d) *Littorina Sea* 2000 - 500 A.D.

#### 1.4 Major characteristics of the Baltic Sea

A schematic diagram of the bottom profile along a longitudinal section of the Baltic Sea is shown in Figure 2.

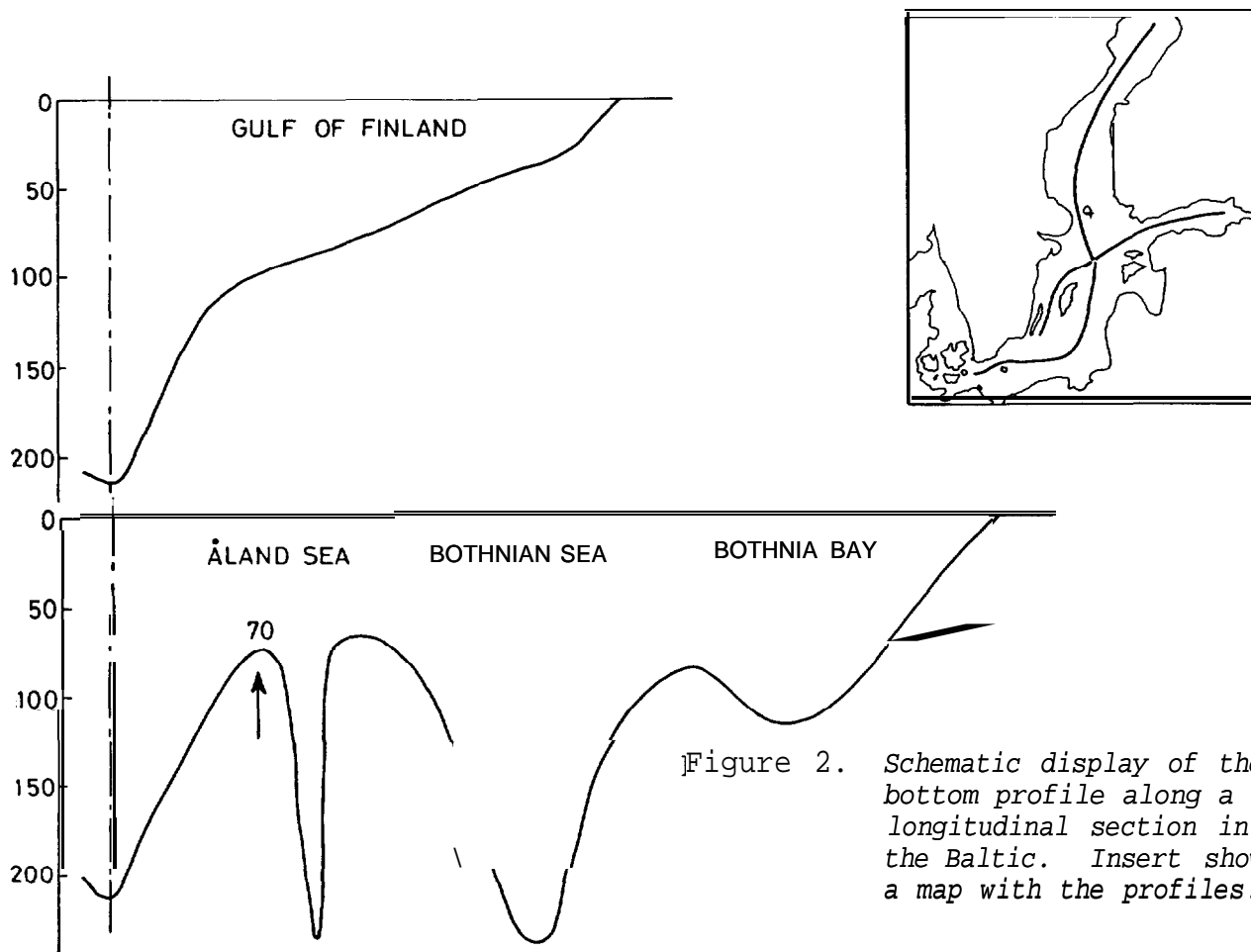
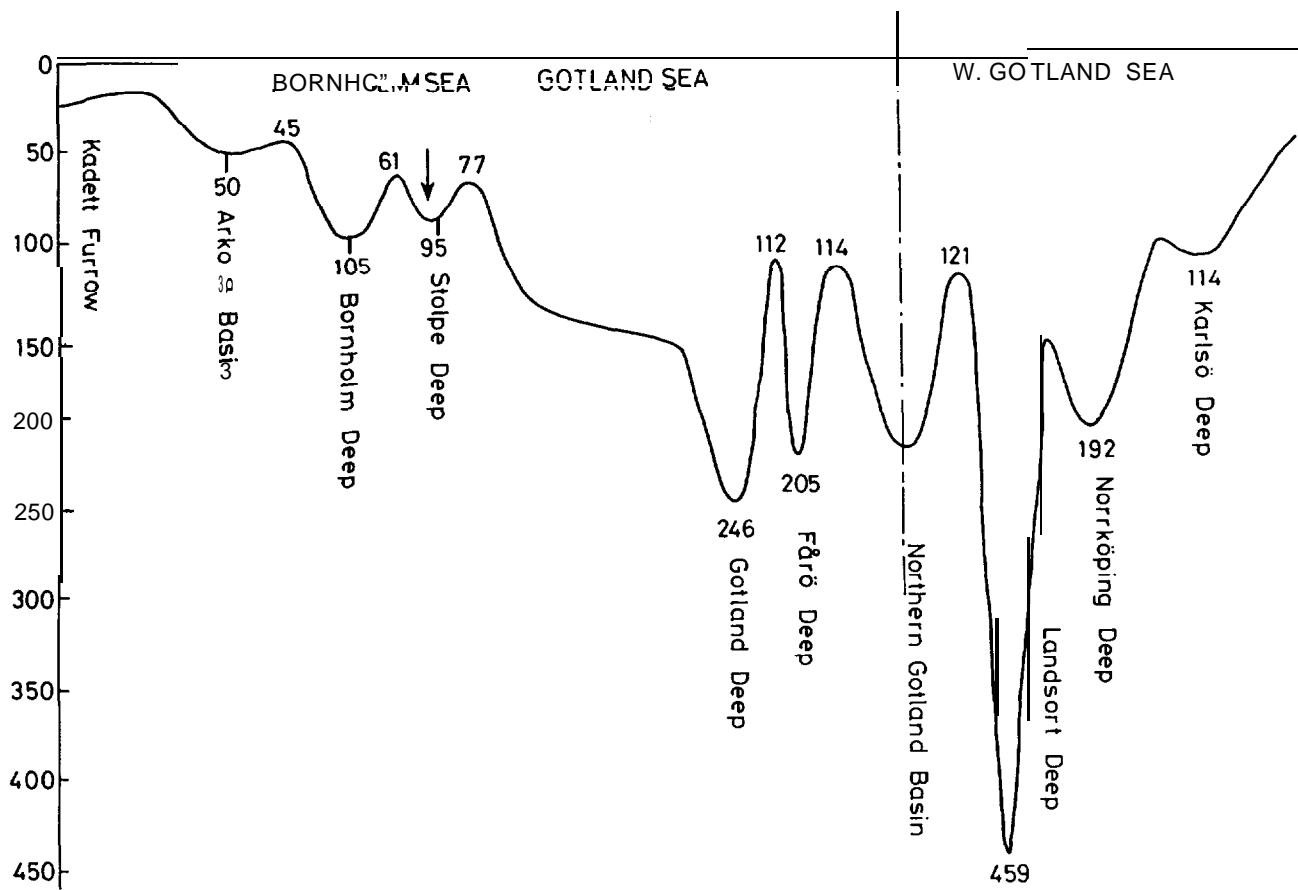


Figure 2. Schematic display of the bottom profile along a longitudinal section in the Baltic. Insert shows a map with the profiles.

The basic hydrographic features of the Baltic Sea are a result of the following three factors:

- i) The entrance to the Baltic Sea is narrow and shallow. The Baltic Sea may be regarded as a huge fjord with a stratified brackish water system.
- ii) The water balance of the Baltic Sea is positive, i.e., the sum of run-off and precipitation clearly exceeds the amount of evaporation.
- iii) The Baltic Sea is shallow, the average depth being only 55 m. However, its geomorphology is characterized by several more or less separated basins.

The fjord character and positive water balance result in the dominating feature of the Baltic Sea, namely the marked permanent salinity stratification. The interface between the upper ("outgoing") less saline water and the lower ("incoming") more saline water is called the halocline. Its depth varies not only regionally but also temporally and usually exists around 60 - 80 m in the northern Baltic Proper, rising in the southern Baltic Sea and in the Gulf of Finland.

The inflow of water with a salinity of 18 - 20‰ is by no means continuous. However, it is regular enough to keep the salinity conditions in the Baltic Sea relatively stable. Occasionally, there are intrusions of exceptionally large amounts of more saline water resulting in medium- or long-term trends in the level of salinity. These intrusions also contribute to the fine structure of the salinity and temperature distribution regulating the exchange of the bottom water and thereby the oxygen supply of deep basins (see Figures 3 and 4).

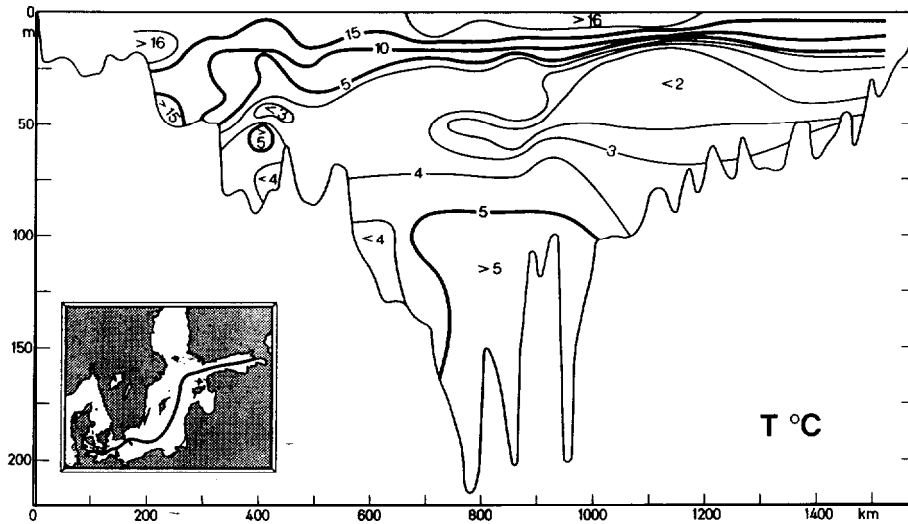


Figure 3. *Distribution of temperature along a longitudinal section in the Baltic Sea in August, 1969 (from Grasshoff, 1975).*

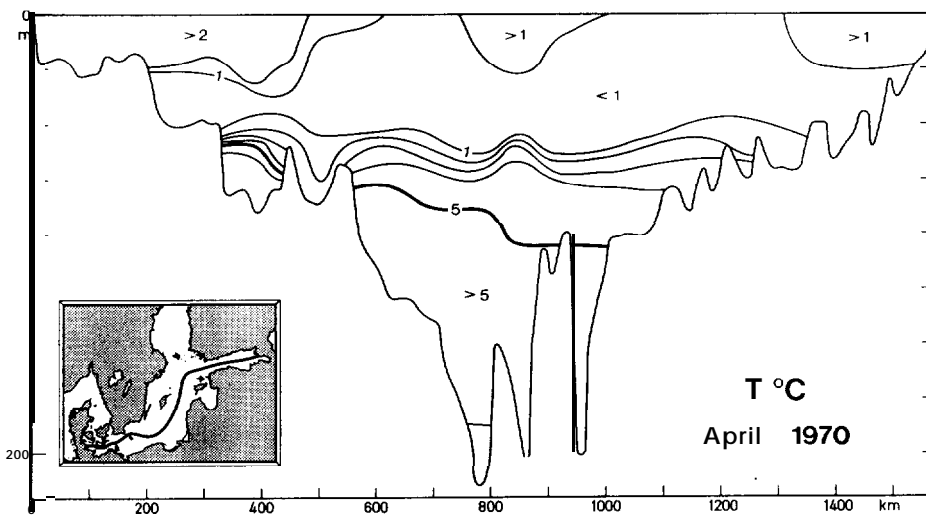


Figure 4. *Distribution of temperature along a longitudinal section in the Baltic Sea in April, 1970 (from Grasshoff, 1975).*

The factors controlling the water exchange between the Baltic Sea and the North Sea are associated with the meteorological situation in the North Atlantic region and the oceanographic conditions in the Kattegat area.

The fact that the outgoing and inflowing water masses partly mix outside the Danish Straits makes it difficult to give any exact value for the residence time in

the entire Baltic Sea. The estimates based on various approximations give values from about 25 to 40 years. However, the residence time in the various sub-areas and basins is often considerably shorter as a result of relatively good mixing conditions.

Within a geologically short period, the different marine and fresh water stages have resulted in a succession of ecosystems since the last glaciation. Mainly fresh water and marine organisms with a wide osmotic tolerance have been able to survive; the number of species is small. The location of the Baltic Sea in the northern high latitudes also affects the structure and function of the Baltic ecosystem.

There are large regional differences in surface salinity and chemical properties. The largest part of the Baltic Sea surface water belongs to the salinity range of 5-10‰ with the 10‰ -surface isohaline in the southern Belt Sea area and the 5‰ -surface isohaline in the Quark of the Gulf of Bothnia and in the inner part of the Gulf of Finland. The Baltic deep water below the permanent halocline has a salinity exceeding 10‰ ; this water reaches the Gulf of Finland, but there is no permanent salinity stratification in the Gulf of Bothnia (see Figure 5).

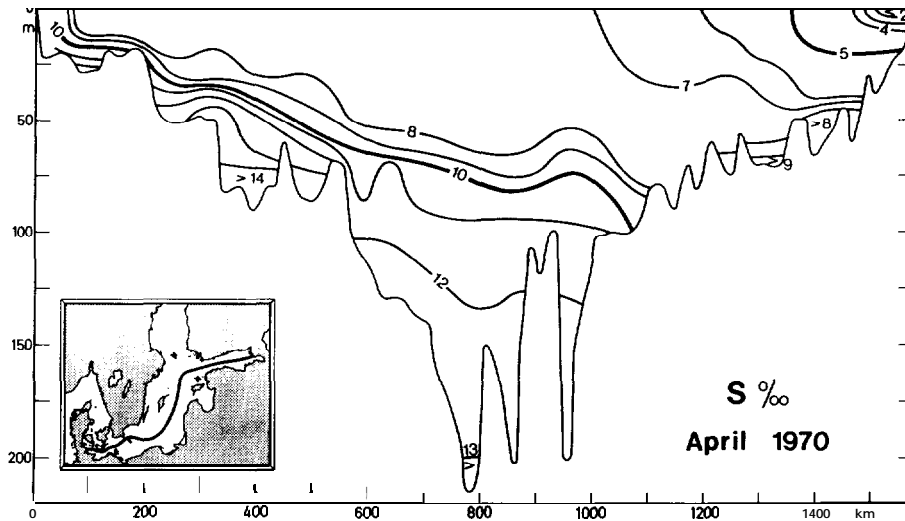


Figure 5. *Distribution Of salinity along a longitudinal section in the Baltic Sea in April, 1970 (from Grasshoff, 1975).*

The productive system of the Baltic Sea consists of the trophogenic layers of the pelagic system and the littoral system; the latter is of great importance in the northern part of the area because of the long and relatively shallow coast. The location of the Baltic Sea in high latitudes causes a pronounced maximum of light in summer. The productive period is about 9 - 10 months in the south but only 4 - 5 months in the north.

The duration of the ice cover is of decisive importance for the seasonal development of the vegetation and ecosystem functions and exhibits large year-to-year variations. In general, ice covers the northern part of the Baltic Sea for about 5-6 months, but sea ice sometimes occurs also in the southern and southwestern parts of the Baltic Sea (see Figure 6).



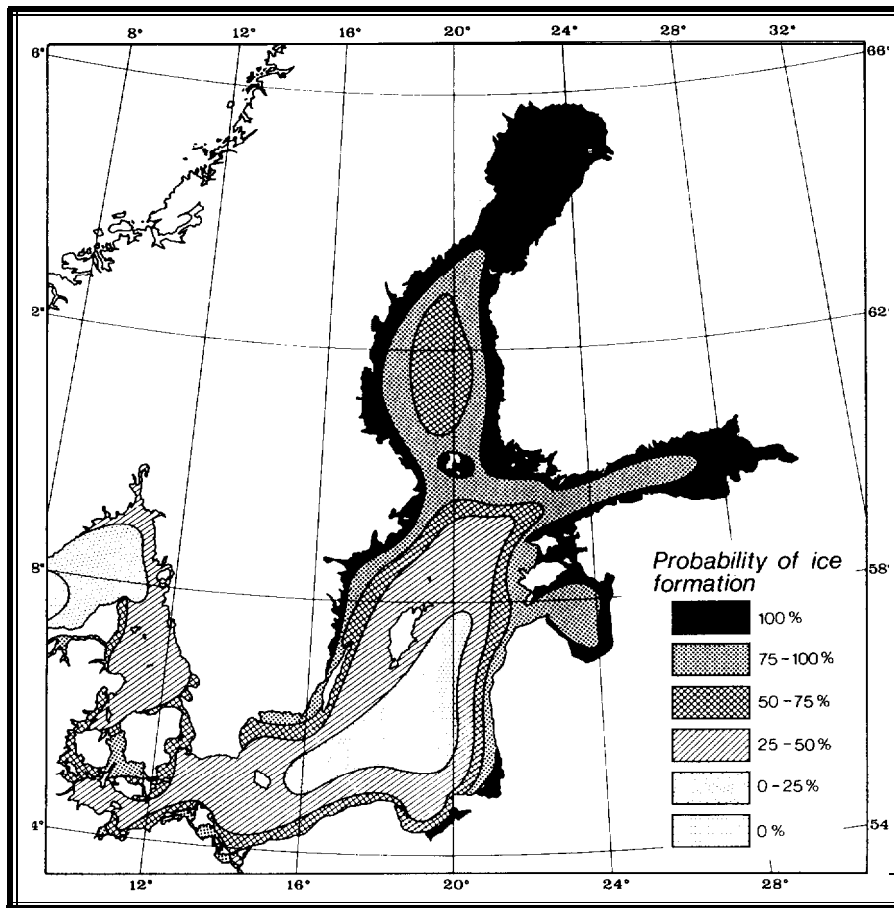


Figure 6. *The long-term frequency of maximal ice coverage in the Baltic Sea (from Palosuo, 1966).*

The nutrient level is another essential factor regulating production. The nutrient input to the productive systems comes from four sources: (1) natural erosion from land, (2) waste water discharges and fertilizer runoff, (3) dry and wet atmospheric fallout, and (4) the upwelling of phosphorus-rich Baltic deep water. The last source is absent in the Gulf of Bothnia, which, especially in the Bothnian Bay, has markedly lower nutrient levels than are found in the Baltic Proper.

More detailed information is available in recent publications (see e.g., Voipio (ed.), 1981).

## 1.5 Meteorological conditions

The area of the Baltic Sea forms climatologically an overpassing area where the marine influence of the Northern Atlantic is strong in the southern and western parts but diminishes towards the eastern and northern Baltic Sea, where continental-like climatic properties can be seen more clearly.

According to the general atmospheric circulation pattern of the Northern Hemisphere, the dominant air flows in northwestern Europe and over the Baltic Sea are from west or southwest. Particularly during the wintertime, however, the polar front activity and Northern Atlantic low generate cyclones which travel generally from west to east. This cyclonic activity is a very important factor regulating the weather and meteorological conditions over the North Sea, Scandinavia and the Baltic Sea, causing e.g. air pressure and wind field variations depending on the paths of the cyclones over northwestern Europe. Therefore, a high variability in meteorological conditions is characteristic of Scandinavia and the Baltic Sea area. Variations especially in wind and pressure fields are also of primary importance to oceanographic and water exchange conditions in the Baltic Sea.

For more details, a number of references are available (e.g., Defant, 1972; Liljequist, 1970).

# Baltic ecosystem

Although scientific research on the Baltic Sea began a century ago, there are few background data to permit the demonstration of concrete indices of change in the pelagic system of the open Baltic Sea. However, more exact information on changes in the deep bottom macro-fauna during this century is available and the increasing eutrophication in certain coastal waters around the Baltic Sea is a familiar phenomenon.

In general, the Baltic Sea is characterized by a low primary production, a slow mineralic cycling and poor water exchange. However, conditions vary from region to region. Some scientists are of the opinion that these conditions are being changed by long-term processes which can be summarized as eutrophication, oceanization and the accumulation of harmful substances in the ecosystem (Jansson, 1978). These phenomena are discussed below.

## 2.1 Environmental changes during this century

These can be divided into three groups:

1. The increase in the nutrient load from land causing eutrophication.
2. The increase in salinity, resulting from hydrographic changes, also called oceanization (Jansson, 1978; Leppäkoski, 1975b). An increase in temperature has also been observed.
3. The discharge of harmful substances into the ecosystem.

The increase in salinity (Granqvist, 1949; Segerstråle, 1965; Fonselius, 1969b; Matthäus, 1977a, 1979a) has caused changes in all areas, whereas the nutrient load is concentrated near pollution centres in coastal areas. This is also true for several harmful substances, although others have spread into the whole ecosystem of the Baltic Sea (Jensen et al., 1972a).

## 2.2 The influence of the nutrient load

The increased nutrient supply to the Baltic Sea during this century, especially from sewage discharges, has caused marked changes in many coastal ecosystems (Waern, 1973; Lehmusluoto and Pesonen, 1973; Rohde and Schulz, 1973; Eagge and Ilus, 1973; Anttila, 1973; Anger, 1975a, 1975b; Anttila et al., 1975; Melvasalo and Viljamaa, 1975; Wiktor and Plinski, 1975; Peussa and Ravanko, 1975; Lindgren, 1975; Andrušaitis and Marcinkeviča, 1978; Bagge, 1969; Leppäkoski, 1975a; Niemi, 1972; Alasaarela, 1979a). Low-production ecosystems have changed into eutrophic or hypertrophic ecosystems in the vicinity of the discharges. The major changes in the *most affected coastal ecosystems* are as follows.

The primary production of the pelagic system in the eutrophied coastal waters has increased to a great degree. A large part of the organic matter resulting from primary production sinks, causing oxygen depletion below the pycnocline and an increase in organic sediments. Animal communities favoured by oxygen-rich water vanish and the function and balance of the ecosystem may exhibit changes (Ackefors et al., 1978).

In weakly and moderately eutrophic coastal waters, the production of periphyton has greatly increased (Öre-

sundkommissionen, 1979). The abundant periphyton and sedimenting organic matter cover the aquatic plants, thus causing unfavourable conditions for seaweeds.

The large amounts of organic matter in the water have increased the turbidity in the most eutrophied coastal waters (Anger, 1975). This limits the euphotic layer to a narrow 1 - 2 m thick surface layer, thus restricting the productive zone to a thin border near the surface. Even in quite shallow coastal waters, the sub-photic layer encompasses rather large volumes (Niemi and Pesonen, 1974).

The composition of the biological community in the most affected coastal ecosystems has changed. The phytoplankton has changed to an *Oscillatoria agardhii*-assemblage or to other assemblages dominated by blue-green algae (Häyrén, 1921; Melvasalo and Viljamaa, 1975; Niemi, 1972b; Alasaarela, 1979b; Melin and Lindahl, 1973; Niemi, 1971). The distribution of large seaweeds, especially *Fucus vesiculosus*, has changed (Peussa and Ravanko, 1975; Lindgren, 1975; Pekkari, 1975). Saprobiic green algae (*Enteromorpha* spp.) have become dominant.

In the most affected coastal ecosystems, the benthic animal community has changed and the species diversity has apparently decreased (Luotamo, 1971; Leppäkoski, 1975a). Fish species not adapted to putting energy into fast swimming are favoured. Pike, perch and sea trout have been replaced by bream and roach, fishes of low economic value (Jansson, 1978; Anttila, 1973; Anttila et al., 1975).

Reed belts have invaded the archipelagos. Even in the outer archipelago zone, the reed belts have markedly increased (Luther, 1950; Wallentinus, 1975). Part of this increase in the central and northern areas of the

Baltic Sea is a result of newly exposed sediments owing to the uplift of the seabed.

Such changes are familiar in many coastal areas of the Baltic Sea. Because waste water discharges include large quantities of nutrients which in unaffected areas may be limiting for production, it is difficult to point out regulating elements for hypertrophication. Nitrogen and phosphorus (and perhaps micronutrients) play different roles in different parts of the Baltic Sea; the interaction between these elements is complex and may vary during different seasons (Melin and Lindahl, 1973; Horstmann, 1975; Malewicz, 1975; Sen Gupta, 1972a; Tarkiainen et al., 1974; Niemi, 1975, 1979). The eutrophic coastal waters in the Baltic Sea area are found near cities and estuaries, spreading far out from pollution centres.

Has the increased load of nutrients from land increased the trophic status of the open sea areas of the Baltic Sea? The Baltic surface water is fertilized not only from land runoff but also from the deep basins as a result of upwelling in particular areas in the Baltic Proper and the Gulf of Finland (Jansson, 1978; Niemi, 1975; Svansson, 1975; Sjöblom, 1967; Voipio, 1968; Hela, 1946). The trend toward decreasing oxygen concentrations below the permanent halocline during this century is associated at certain times with a considerable accumulation of inorganic phosphorus in anaerobic deep water layers (Fonselius, 1969b; Francke et al., 1977) .

Due to the upwelling of Baltic deep water rich in phosphorus, this important element for primary production is carried up into the productive surface layers in upwelling areas. Upwelling seems to be localized in certain areas of the Baltic, e.g., between Gotland and the Swedish mainland (Jansson, 1978; Svansson, 1975;

Jansson and Nyqvist, 1977) and in the Gulf of Finland (Sjöblom, 1967; Voipio, 1968; Niemi, 1975; Hela, 1946). The excess phosphorus (inorganic N:P ca. 3:11) in the Baltic deep water below the permanent halocline (Fonselius, 1969b; Shaffer, 1979) can result in an increase in the excess of phosphorus also in the Baltic surface water. Judging from all, this phosphorus surplus seems to be at least one of the essential factors causing heavy blue-green algal blooms in the Baltic Sea (Jansson, 1978; Niemi, 1979; Öström, 1976).

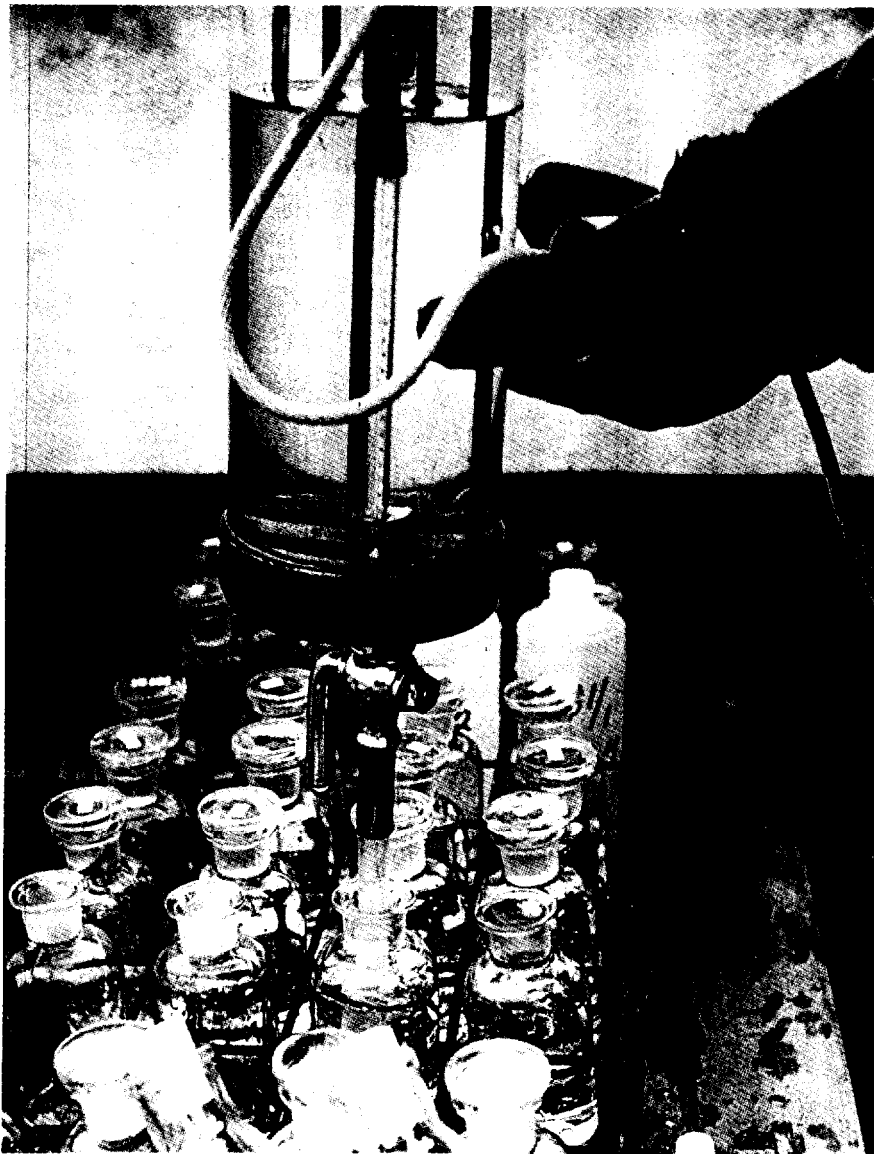


Photo: I. Viitasalo

The heterocystous phytoplankton species causing the blooms are favoured by a surplus of phosphorus but do not require inorganic nitrogen (Melin and Lindahl, 1973; Horstmann, 1975; Rinne and Tarkiainen, 1975). They are able to fix considerable amounts of molecular nitrogen (Hübel and Hübel, 1974, 1976a, 1976b; Rinne et al., 1978, 1980; Brattberg, 1977), thus creating the N:P ratio most effective for phytoplankton production (Niemi, 1979). These blooms make up an intermediate step in the food chain. They have an eutrophying influence on the Baltic surface water (Niemi, 1979; Öström, 1976).

The extensive blue-green algal blooms in the open sea have been considered as an index of the eutrophication of the Baltic Sea (Horstmann, 1975). However, phytoplankton blooms were already observed a century ago (Pouchet and de Guerne, 1885; Niemi, 1979) when the nutrient input from land was of minor importance compared with today. Unfortunately, there are only very few reliable quantitative data on these past blooms and blue-green algae production. It is difficult to determine whether the mass occurrences are caused by the increased upward transport of phosphate during the past decade or whether land-based sources of nutrients have a greater impact on such production in the open sea. The absence of detailed information about the water exchange between the coastal areas and the open sea restricts the possibility of quantifying the transport of land-based nutrients seawards. The archipelago areas function as effective filters of land-based nutrients. However, the occurrence of extraordinarily vigorous blooms of nitrogen-fixing blue-green algae in practically all areas of the Baltic Sea during the past decade seems to be evident.

The macrozoobenthic biomass above the permanent halocline has increased compared with biomass values half



a century ago (Jansson, 1978; Elmgren and Cederwall, 1979). This indicates an increased supply of sinking organic matter, which again seems to be associated with an increase in the primary production. Furthermore, in the outer archipelago zone a long distance from pollution sources, there is some information that the transparency of the water has decreased, the fishing nets have become much dirtier, and the bladderwrack is apparently more covered by epiphytes and periphyton than in the 1930s (Jansson, 1978; Kangas and Autio, 1980). This information implies an increase in the production in the open sea areas and possible increase in the trophic status of the Baltic Sea. An increased primary production in the coastal areas and an increased transport of organic matter toward the open sea deep basins (Jansson, 1972) will cause a more rapid consumption of oxygen and an accumulation of phosphorus in the Baltic deep basins. Due to upwelling, such water will again fertilize the productive surface layer. However, it is difficult to determine the extent of the influence of land-based nutrients upon these processes.

Because the Baltic deep water does not penetrate into the Gulf of Bothnia, the deep water phosphorus depots will not directly influence the production of organic matter in that area. However, the increased concentration of phosphorus in the Baltic Proper surface water, penetrating through the Archipelago Sea to the Bothnian Sea in late autumn, may influence the phosphorus concentration of the Gulf of Bothnia and, possibly, the primary production (Pietikäinen et al., 1978). Surface water from the Baltic Proper sinks during the winter into the Åland Sea (Palosuo, 1964).

Except in coastal areas, it is difficult to point out clear signs of change in the trophic status of the Gulf of Bothnia (Alasaarela, 1979a, 1979b; Meskus,

1976; Jokinen, 1978; Sevola, 1978; Isotalo and Häkikilä, 1978). Blue-green algal blooms occur in the southern Bothnian Sea. This is in conformity with the low N:P ratios occurring in that area (Niemi, 1979; Pietikäinen et al., 1978). The low production of organic matter in the Bothnian Bay (Meskus, 1976; Alasaarela, 1979; Lassig et al., 1978) was noted already early in the century (Buch, 1932; Välikangas, 1933). At present, the level of primary production in this area is still much lower in comparison with many other Baltic Sea areas (Lassig et al., 1978). Nonetheless, even here there are indications of an increase in benthic macrofauna biomass (Andersin et al., 1978b; Elmgren et al., in press).

In the Belt Sea area, some eutrophication of the surface waters has occurred during the last decades. Blue-green algal blooms are frequent in the Sound and the level of primary production is quite high (Oresundskommissionen, 1979; Edler, 1977, 1978; Gargas et al., 1975-77). However, Danish primary production and phytoplankton biomass studies do not show clear signs that the phytoplankton production in the Belt Sea and in the Baltic Proper is increasing (Gargas et al., 1978). Some effects of eutrophication may, however, be found at higher trophic levels (zooplankton, medusae, zoobenthos, pelagic fish).

The decreasing trend of the oxygen concentration in the deep basins of the Baltic Proper can be seen in the deterioration of the macrobenthic communities (Andersin et al., 1978a; Järvekülg, 1976; Zmudzinski, 1975). Since the turn of the century, these communities have fluctuated in accordance with the oxygen conditions. The fluctuations have been marked in the Bornholm Deep and the Central Basin. The decline in oxygen concentration has caused a deterioration in the bottom fauna below the permanent halocline over large deep areas in the Baltic Proper and the Gulf of Finland. Such

changes in the bottom fauna have not been observed in the Gulf of Bothnia, where the oxygen conditions have declined only slightly (Andersin et al., 1978a, b). In the Baltic Proper and the Gulf of Finland, some recovery of the macrofauna has occurred during the last few years (Andersin et al., 1979).

Numerous studies in eutrophic coastal areas around the Baltic Sea have shown a change in benthic macrofauna toward saprobic communities characterized by a changed species composition and a decrease in the species diversity (Anger, 1975; Bagge, 1969; Leppäkoski, 1975a; Oresundskommissionen, 1979; Varmon and Skog, 1980; Järvekülg, 1976; Tulkki, 1960, 1964).

### 2.3 The influence of the increase in salinity

There are some suggestions that an increase in the frequency of the intrusions of North Sea water has increased the deep water body of the Baltic Proper by about 350 km<sup>3</sup> and raised the centre of the primary halocline by about 5 - 6 m since the beginning of this century (Matthäus, 1979b). The 8‰ isohaline of the Gotland Deep appears to have been raised from its location at about 75 m depth in 1900 to the present 60 m level (Fonselius, 1969b; Matthäus, 1979b). The stability between surface and deep waters appears to have increased slowly during this century (Fonselius, 1969b); since the middle of the 1950s, however, the stability obviously seems to have diminished again (Voipio and Mälkki, 1972; Matthäus, 1973). In the northern Baltic Proper, the salinity of the deep water has increased by roughly 1‰ and the temperature by 1°C since the beginning of the century.

The distribution of species in the Baltic Sea is to a high degree regulated by the salinity. Fluctuations

in the salinity are thus mirrored in the species composition (Purasjoki, 1945b; Segerstråle, 1951, 1965). The recolonization of the Bornholm Basin after the great stagnation period in the late 1960s also showed clear features of oceanization in the species distribution and zoogeographic elements and feeding types (Leppäkoski, 1975b). Most of the Arctic relicts have been replaced by marine Atlantic-boreal and cosmopolitan species and the previous dominance of suspension feeders has been taken over by non-selective deposit feeders.

The large plankton animals, such as the jellyfish *Aurelia surita*, have extended further north into the Gulf of Bothnia and the Gulf of Finland (Lindqvist, 1962). The episodic occurrences of *Cyanea* in the northeastern Baltic Proper and the Gulf of Finland in autumn 1978 must be ascribed to the clear increase in salinity (Sarvala, pers.comm.). The abundant occurrence of cod in the Gulf of Finland is also associated with the inflow of saline water into the Gulf.

The influx of Kattegat water is regulated by meteorological processes over northern Europe (Hela, 1950). The influxes cause the deep water in the series of Baltic deep basins to move in pulses inwards and at times to rise by upwelling to the surface in certain areas, particularly between Gotland and the Swedish mainland and in the Gulf of Finland during favourable meteorological conditions. This causes a significant release of phosphorus to the trophogenic layer in such areas. The oceanization characterized by increased stability and strong pulse-like inflows and upwelling has increased the mobilization of phosphorus to the Baltic surface layer. Thus, changes in the trophic status of the sea area may also be influenced by the oceanization process.

## 2.4 The discharge of harmful substances

The harmful substances which have been most studied in the Baltic Sea are certain heavy metals, halogenated hydrocarbons and oil products (Jensen et al., 1972a). Some incomplete information is available on their inputs to the Baltic Sea.

Real concern over environmentally harmful substances arose when considerable amounts of DDT were found in the eggs of guillemots from the Baltic Sea area (Jensen et al., 1969a). Extensive investigations of DDT and PCB concentrations in Baltic marine animals revealed fairly high total DDT and PCB concentrations in herring, salmon and ringed, common and gray seals (Olsson et al., 1975). These concentrations were up to ten times higher than in North Sea populations. The white-tailed eagle from the archipelago of Stockholm showed a concentration of total DDT and PCBs 100 times higher than in populations from northern Sweden (Jensen et al., 1969a). DDT and PCB concentrations were found to be higher in the eastern Bornholm Basin than west of Bornholm. The concentrations decreased towards the north and the Gulf of Bothnia.

The concentrations of mercury in Baltic pike have shown locally high values (Ackefors, 1971). After the ban on the use of mercury compounds in the paper industry in Finland and Sweden, the levels of mercury have apparently decreased in the northern part of the Baltic Sea.

DDT concentrations have shown a decreasing trend in the 1970s (Linko et al., 1974; Voipio et al., 1977). PCBs are far more persistent and can be expected to remain concentrated in the higher trophic levels of the ecosystem for a long time. No decrease in PCB concentrations in the Baltic have yet been observed. The

great increase in the number of sterile seals in the Baltic Sea has now been proved to be caused by the presence of PCBs in those mammals (Olsson et al., 1975), which threatens the very survival of these animal species in the Baltic Sea.

The closed nature of the Baltic ecosystem, the long residence time of the water and the low temperature effectively slow down the decomposition processes of organic contaminants. This makes the Baltic Sea sensitive to harmful substances and a collector of substances from land runoff and atmosphere (Jansson, 1978). Probably a great share is accumulated in the sediments adsorbed to organic material. The same mechanism seems to work for heavy metals such as Hg, Pb, Zn, Cu, Cr, and Cd, which show a strong correlation with the amount of organic matter (Oden and Ekstedt, 1976b).

The oil spill risk in the Baltic Sea is considerable, and several spills of small to moderate size have already occurred, e.g., in 1969 in the Archipelago Sea, when 30 % of the resident bird population was killed (Leppäkoski, 1973), and in 1976 off Öland, when a very small spill led to the death of at least 30,000 *Clangula hyemalis* (Rodebrand, 1976). Effects lasting for several years were found on the fauna of the *Fucus* belt following a spill in the Stockholm archipelago in 1978 (Notini, 1978). The most thoroughly studied spill so far is the "Tsesis" spill of over 1 000 tonnes of medium grade fuel oil in the Askö area in 1977 (Linden et al., 1979; Kinemann et al., 1980). Severe effects were found, at least locally, in the pelagic, littoral and benthic ecosystems, but they proved to be of short duration in the pelagic system. After about one year, recovery was well under way in the littoral system, whereas in the soft-bottom communities not even the beginning of a recovery was found. The environmental conditions of the Baltic (low temperature, low turbulent

energy, low water exchange) are such that a large oil spill could become a real environmental disaster, with long consequences.

# Physical parameters

## 3.1 Temperature, salinity and density

### 3.1.1 *Vertical distribution of salinity and temperature*

The conditions in the Baltic Sea represent an outstanding example of the interaction between natural changes in the environment and man-induced changes. An understanding of the major hydrographic processes in the Baltic Sea is necessary for a proper assessment of the changes in and the stresses on the Baltic ecosystem which may be caused by man-induced (anthropogenic) factors.

Salinity measurements have been comparable within a range of  $\pm 0.05\text{‰}$  since about 1905 and measurements of temperature have also long been comparable within a range of  $\pm 0.05^{\circ}\text{C}$ .

One of the hydrographic characteristics of the Baltic Sea is the vertical and horizontal variation in temperature, salinity and density. River run-off gives rise to a permanent, relatively low-density surface layer which is poor in salt and is characterized by typical seasonal variations. Salt-rich Kattegat water flowing in through the Danish Belts and the Sound intrudes, due to its greater density, into the deeper layers. Haline stratification of most regions of the Baltic Sea persists throughout the year. Except for the inner parts of the Gulf of Finland and the Gulf of Bothnia, the surface and deep water are separated by a pronounced pycnocline consisting of a halocline, usually reinforced by a thermocline. This permanent



discontinuity layer is situated at a depth of 10-20 m in the Transition Area (Sound and Belt Sea), 35-40 m in the Arkona Basin and 65-70 m in the central Baltic. During the summer, a further distinct thermocline is formed in the Baltic Proper at a depth of 10-30 m. This separates the cold intermediate water formed during the winter season from the warm surface layer. The intensity of the permanent discontinuity layer declines from the Transition Area towards the central part of the Baltic Sea and is only weak inside the Gulf of Finland and the Gulf of Bothnia. In the Transition Area, haline stratification leads to the formation of the Belt Sea and Skagerrak fronts which shift in response to changes in meteorological and oceanological conditions.

### 3.1.2 *Horizontal distribution of salinity and temperature*

The horizontal distribution of the surface temperature is governed by the increasing climatic influence of the continent from west to east and the considerable north-south extent of the Baltic. Large parts of the Gulf of Finland and the Gulf of Bothnia are closed by ice every winter (see Figure 6), whereas the average winter temperatures are around 2°C in the Transition Area and the southern parts of the Baltic. Mean surface temperatures during August are 16-18°C in the Transition Area and the southern part of the Baltic Proper, about 16°C in the Gotland Sea, between 15 and 17°C in the Gulf of Finland, and 14-15°C in the Gulf of Bothnia (Lenz, 1971). The surface salinity decreases from about 30 ‰ in the Kattegat to 10‰ in the Arkona Basin, 6-8‰ in the Central Baltic, and from 6‰ to 0.5‰ in the Gulf of Finland and the Gulf of Bothnia (Bock, 1971a).

Although the salinity and density values of the deep water below the permanent discontinuity layer are greater, their horizontal distributions are similar

(see Table 1).

Table 1. *Approximate temperature, salinity and density in the deep water of the Baltic Sea (according to Lenz, 1971; and Bock, 1971a, 1971b)*

Sea area	T (°C)	S (‰)	Density (a,)
Kattegat	- *)	30 - 34	22 - 27
Belt Sea	- *)	12 - 30	10 - 24
Bornholm Basin	5 - 9	14 - 17	11 - 14
Gotland Basin	5 - 6	10 - 12	6 - 10
Gulf of Finland	1 - 4	5 - 8	4 - 7
Gulf of Bothnia	1 - 4	3 - 6	2 - 5

\*) pronounced annual fluctuations up to the near-bottom layers.

### 3.1.3 Short-term and seasonal variations

Short-term variations in temperature, salinity and density lasting from minutes to days are mainly caused by internal waves, inertial waves and seiches. Of the different regions of the Baltic, the Arkona Basin exhibits especially large variations in these parameters in space and time, particularly in summer. In the vertical direction, the fluctuations are greatest near the discontinuity layer.

Seasonal variations in the thermohaline conditions are among the most striking characteristics of the Baltic Sea (see Figures 7 and 8). Their effects on deeper layers vary from region to region depending on thermal convection, turbulence and advective exchange, and they govern the seasonal course of thermohaline stratification. Table 2 shows the mean seasonal variations in surface temperature and salinity.

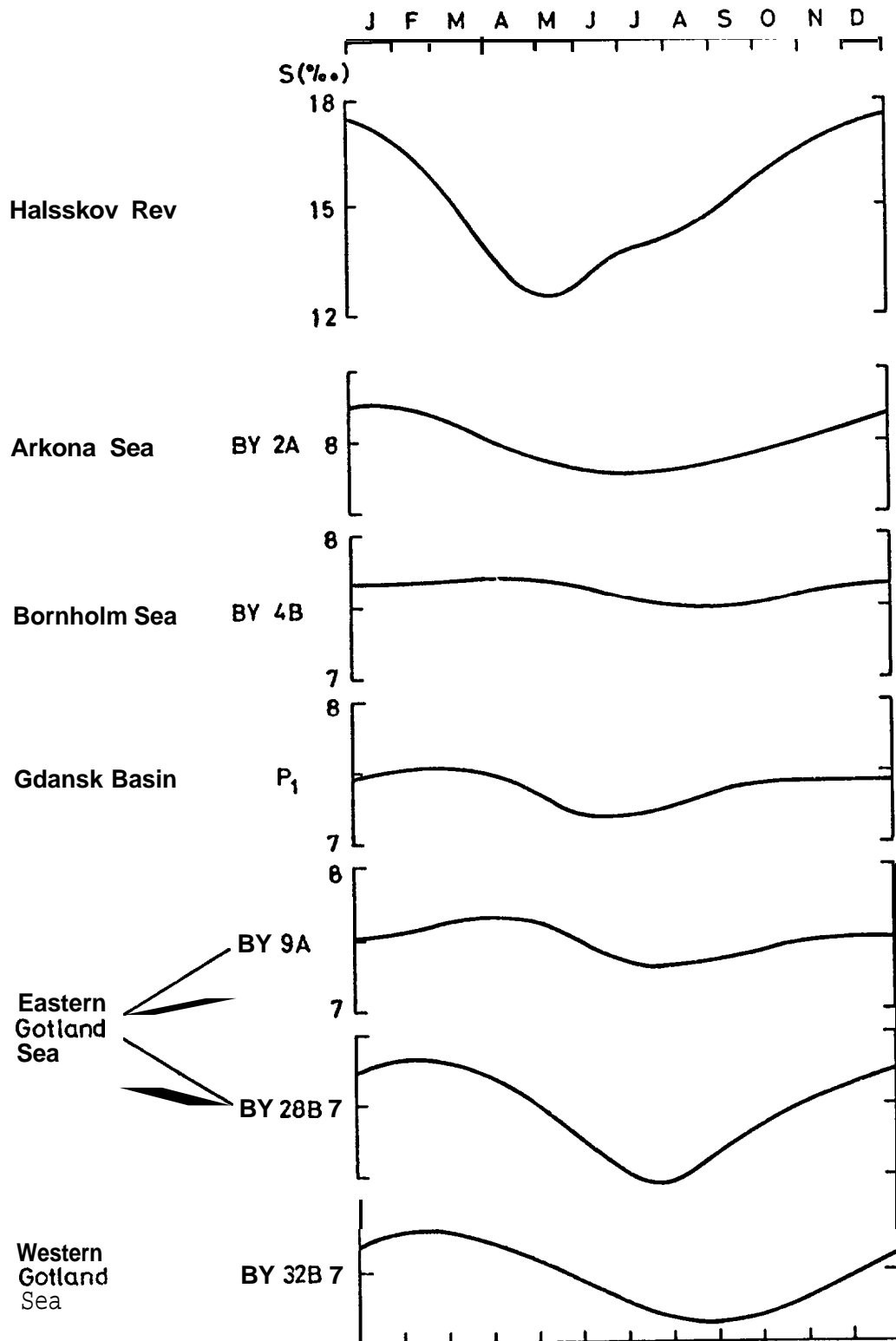


Figure 7. Mean seasonal variations of surface salinity in the Baltic Sea (from Matthäus, 1978c; and Miljøstyrelsen, 1976).

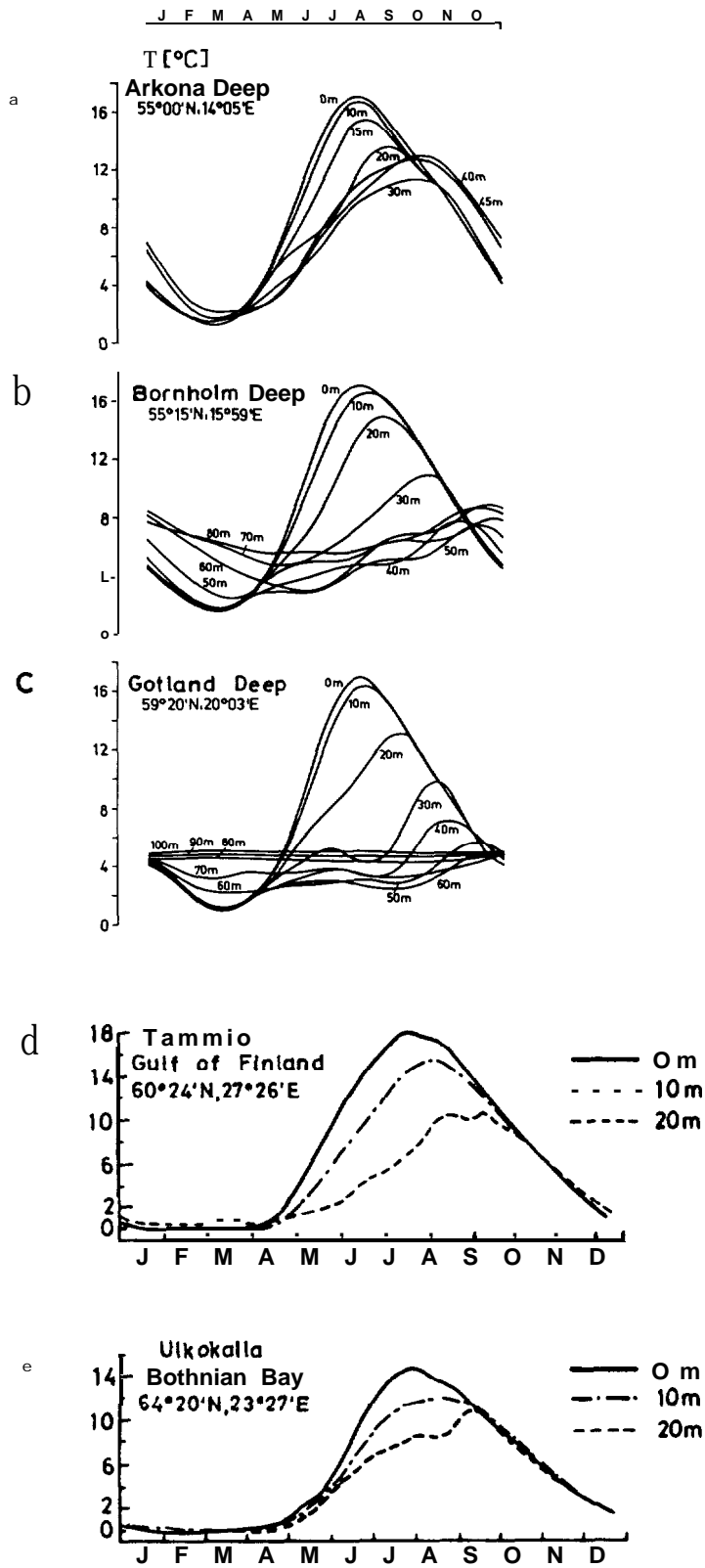


Figure 8. Mean seasonal variations of temperature in the Baltic Proper (a-e from Matthäus, 1977b; and d-e Launiainen and Koljonen).

Table 2. *Mean seasonal variations of surface temperature and salinity in the Baltic Sea (according to Dietrich, 1950, and Finnish observations in the Gulfs Of Finland and Bothnia).*

Sea area	AT ( $^{\circ}$ C)	$\Delta$ S ( $\text{‰}$ )
Kattegat	15 - 16	5 - 7
Belt Sea	15	3 - 4
Bornholm Basin	14 - 15	
Gotland Basin	14 - 16	0.5
Gulf of Finland	15 - 17	0.5 - 1
Gulf of Bothnia	15 - 17	0.5 - 1

Although the deep layers in the Transition Area and the Arkona Sea are also subject to pronounced seasonal variations, the deep water of the Baltic Proper shows only a very small, irregular annual course. Seasonal courses in temperature, salinity and density of the deep water reappear, although in less pronounced form, in the more northern parts, especially in the Gulf of Finland and the Gulf of Bothnia where stratification is less stable.

#### 3.1.4 *Long-term variations*

Periodic fluctuations lasting several years have been observed especially in connection with salinity. Dickson (1971) showed that the transport of salt-rich water from the Atlantic into the Kattegat has reached a peak every three or four years in the course of this century. Börngen(1978) found salinity fluctuations with a period of three years at the lightships "Lappegrund" and "Gedser Rev" (off Gedser). Such periodic fluctuations in the salinity of the deep water are also present in the central Baltic as a result of salt water inflows into the Baltic (see Figure 9).

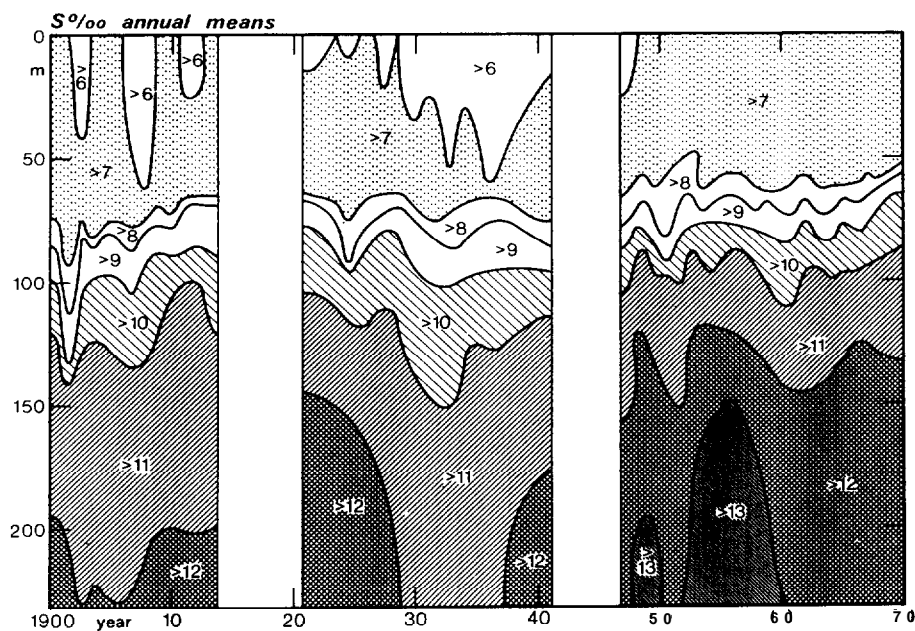


Figure 9. Annual means of salinity at the station in the Northern Gotland Sea (from *Fonselius, 1969a*).

The inflow of salt-rich water from the Kattegat results in the partial or complete renewal of the deep water in the different basins (see Figure 10). The frequency and intensity of these salt water inflows play a major role both in increasing the salinity and density, and, depending on the time of year at which the inflow occurs, changing the temperature of the deep water. The general trend shown by the deep water of the Baltic Proper since the beginning of this century is towards a regionally different average increase in temperature (about 0.6 to 2.7°C) (see Figure 11) and salinity (about 0.8-1.7‰) (see Figure 12). This increase in bottom water temperature of the Baltic Proper may be due to the intrusion of warmer water from the south associated with relatively low vertical thermal diffusion during stagnation periods. The average salinity in the Gulf of Bothnia has also risen (see Table 3).

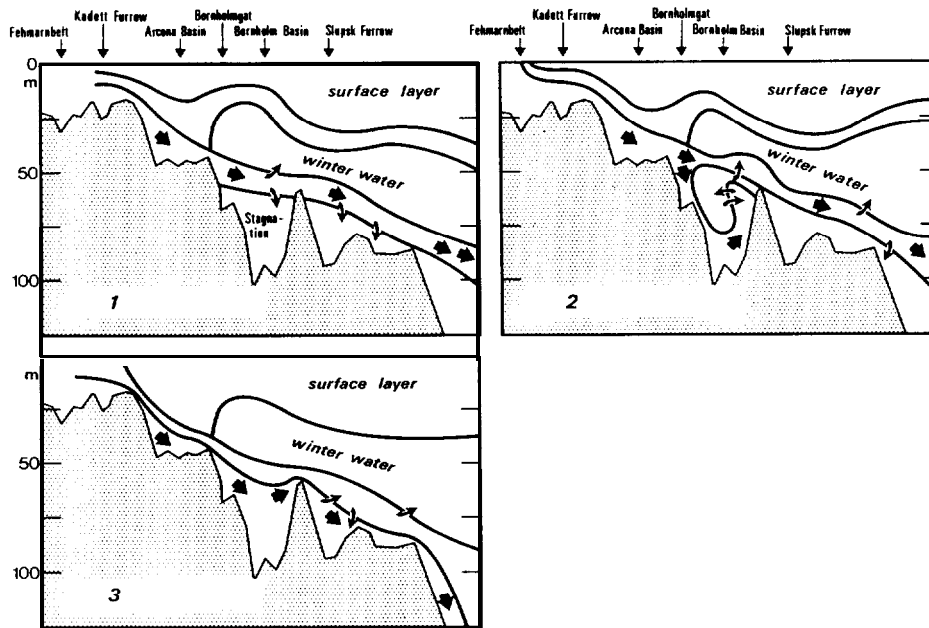


Figure 10. Schematic diagram of the different modes of salt water intrusion into the Baltic Proper:

- (1) regular inflow just below the primary halocline;
  - (2) occasional inflow of saline water, exchanging the Bornholm Deep water;
  - (3) rather infrequent occasional inflow of large amounts of saline water exchanging the Gotland Deep water
- (from Grasshoff, 1975).

Table 3. Mean increase in temperature and salinity in the deep water of the Baltic Sea.

Sea area	Period	Depth (m)	$\Delta T$ (°C)	$\Delta S$ (‰)	References
Bornholm Deep	1900-75	80	2.7	no trend	Matthäus (1979a)
Gotland Basin	1900-75	200	1.47	0.98	Matthäus (1979a)
Landsort Deep	1900-75	400	0.78	0.94	Matthäus (1979a)
Norrköping Deep	1900-75	150	0.84	1.04	Matthäus (1979a)
Gulf of Bothnia	since 1900	near bottom	slight incr.	$\approx 0.5$	Pietikäinen et al. (1978)

This overall increase has been accompanied by long periods during which both salinity and temperature have tended to decline as has, for example, been observed since 1952 in the deep water of the Baltic Proper (Matthäus, 1978a, 1978b).

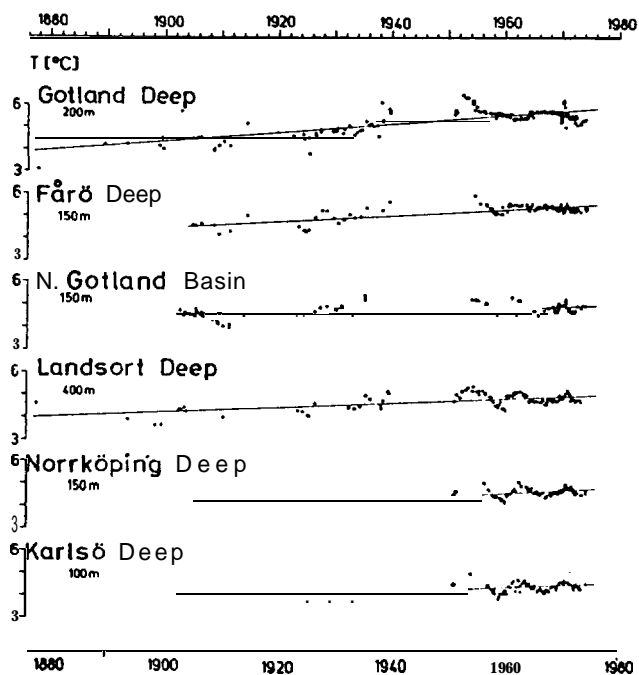


Figure 11. Long-term variations of temperature in the deep water of the Baltic Proper (from Matthäus, 1979a).



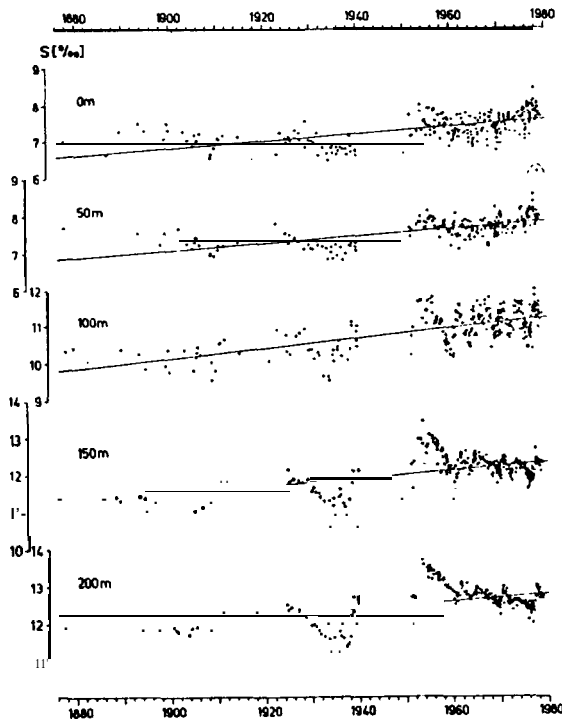


Figure 12. Long-term variations of salinity in the Gotland Deep (from Matthäus, 1979b).

Because the surface water is subject to substantial seasonal temperature variations, long-term trends in the temperature of the surface water of the open Baltic are difficult to detect. Long-term variations calculated hitherto have, therefore, been restricted to salinity (see Table 4). These show that the average increase in surface water salinity is about 0.2 - 0.5‰ less than in the deep water.

Table 4. Mean increase in salinity in the surface water of the Baltic Sea.

Sea area	Period	AS (‰)	References
<i>Baltic Proper</i>			
Gotland Basin	1900-75	0.50	Matthäus (1977a)
Landsort Deep	1900-75	0.59	Matthäus (1977a)
Norrköping Deep	1900-75	0.56	Matthäus (1977a)
<i>Gulf of Finland</i>	1962-78	0.5	Perttilä et al.(1979) Pietikäinen et al.(1978)
<i>Gulf of Bothnia</i>	since 1900	slight incr.	Pietikäinen et al.(1978)

According to studies by Matthäus (1979b), the average increase in salinity since the beginning of this century has reduced the depth of the isohalines. For example, in the Gotland Basin the 8‰ isohaline has risen by about 17 m and the 12‰ isohaline by about 52 m. In contrast, the primary halocline has risen by only 5 -6 m on average. This, however, means a redistribution of the volumes of the surface waters and the deep waters. It was estimated that the contact area between surface and deep waters has increased by about 4 500 km<sup>2</sup> and the volume of the deep water has increased by about 359 km<sup>3</sup> (Matthäus, 1979b).

The mean increase in salinity has been accompanied by an increase in density during the course of this century. Fonselius (1969b) reports that the density of the deep water in the Northern Central Basin increased by 1 g/dm<sup>3</sup> between 1900 and 1967.

The density of the water is closely related to the stability of the stratification. Fonselius (1969b) showed that in the Gotland Basin the stability in the region of the halocline has increased slowly during the course of this century. Since the middle of the 1950s, however, the stability between surface and deep waters and within the deep water obviously appears to have diminished again (Voipio and Mälkki, 1972; Matthäus, 1973).

## 3.2 Mixing, exchange and transport processes

### 3.2.1 General remarks

The understanding of the exchange and mixing in the Baltic are related to the following features:

- (1) The narrow and shallow connection to the world ocean.
- (2) The division of the Baltic into various basins separated by sills.
- (3) The positive water balance (400 - 500 km<sup>3</sup> of fresh water is added yearly).
- (4) The strong pulsations of exchange driven by the changing wind and air pressure fields.
- (5) Wind conditions over the Baltic.

The most shallow sills between the Baltic and the North Sea are located in the area between the Belt Sea and Sound, on one side, and the Arkona Basin on the other. The sill depth is 18 m in the Belt Sea and 8 m in the Sound. The sills reduce the inflow of salt water and leave the surface waters of the Baltic rather brackish. Extreme meteorological and hydrographic conditions do, however, occasionally permit bottom water with high salinity to pass the Darss sill. If the density is higher than that of the water which already occupies the deep basins, a replacement will take place.

Renewal of the bottom water under the present conditions has advantages and disadvantages. The immediate profit is the supply of oxygen, but the increase in the static stability as a result of the presence of dense bottom water prevents a new replacement for a considerable period of time.

#### *The path of inflowing deep water*

Inflows of water with intermediate salinity take place

more or less continuously, and this water forms the so-called active deep layer. The active deep layer is separated from the stagnant water in the deep basins by a halocline which is considerably weaker than the halocline between the active layer and the surface layer. The upper halocline is often called the 'primary' halocline and the deeper one is referred to as the 'secondary' halocline. The primary halocline is only found in sufficiently deep water and the secondary halocline may be absent. Figure 2 shows a schematic drawing illustrating the bottom profile along a longitudinal section in the Baltic Sea. Schematic diagrams of the water exchange between the Baltic and the North Sea are given in Figures 2 and 13.

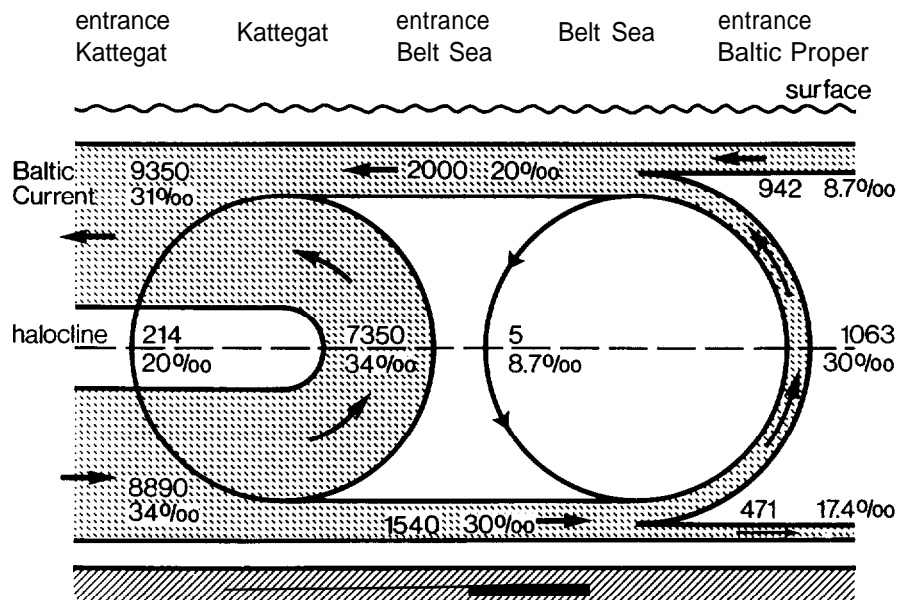


Figure 13. Schematic diagram of the water exchange between the Baltic and the North Sea (from Steenman-Nielsen, 1940, as modified by Grasshoff, 1975).

Bottom water from the Kattegat enters the Baltic Sea via the Great Belt and the Sound. In the Sound it penetrates without much reduction in salinity to an area northwest of Barsebäck where the deep channel ends. Further penetration into the Baltic is rendered very difficult because of the shallows between Copenhagen and Malmö (sill depth 8 metres). However, during situ-

ations with strong southgoing currents, it may pass the sill with somewhat reduced salinity (see Wyrтки (1954b) for a detailed description of the salinity in this area).

The bottom water penetrates more easily through the deeper Great Belt. The deeper sill (18 m) allows a quasi-continuous inflow of deep water, which under certain conditions attains salinities of up to 25‰ (Wyrтки, 1954b).

The inflowing water enters the Arkona Basin and follows the deepest passage, the Bornholm Channel north of Bornholm (46 m). (See Petrén and Walin (1976) for a discussion of this inflow and the associated salt flux.)

From the Bornholm Channel, the water passes the Bornholm Basin and flows through the Stolpe Channel (60 m) into a series of central basins. (See Pedersen (1977) and Rydberg (1976) for a description of the inflow through this area.)

The passage from the first of the central basins, the Gotland Basin, to the Gdańsk Deep is 88 m. To the north the sill depth is 140 m to the Fårö Deep, and further 115 m to the Northern Central Basin. The Landsort Deep marks the western end of the Northern Central Basin, reaching 457 m in depth. The Gulf of Finland is not separated from this basin.

South of the Landsort Deep (and west of Gotland) are the Norrköping and Karlsö Deeps, both having sill depths close to 100 m. The deep water cannot reach them directly from the Bornholm Basin since the sill depth between them and the Bornholm Basin is only 46 m. Thus, the deep water moves through a series of basins in a counter-clockwise direction, a movement

which is also supported by the coriolis force.

The access to the Gulf of Bothnia is through the Åland Sea. There are three sills, of 70, 65, and 100 m depth, respectively, to pass before the water is well into the Bothnian Sea. The first of these (70 m) was only discovered recently and is very narrow but nevertheless important (Fonselius, 1971). The Bothnian Bay is separated from the Bothnian Sea by a 25 m sill at Norra Kvarken.

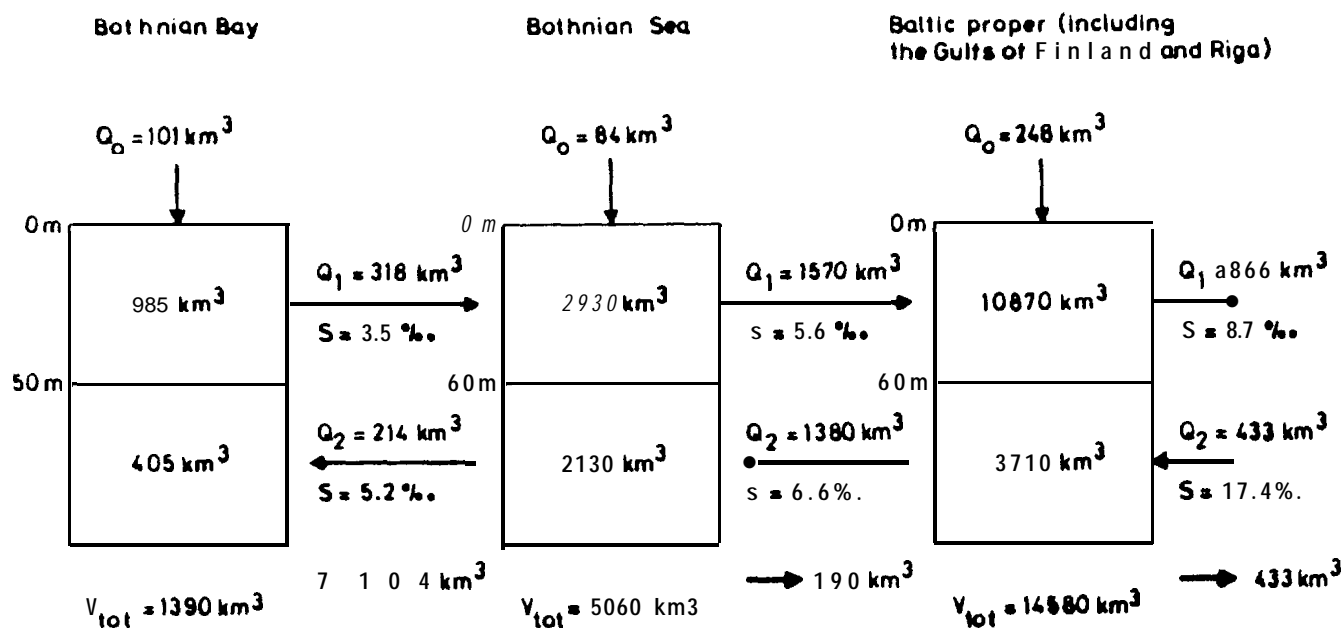
Water from 50 to 70 m depths in the Northern Central Basin flows into the Bothnian Sea as deep water during the summer, and continues as a warm and salt tongue northward along the Finnish coast. During the winter, surface water with a high oxygen content is forced from the Baltic Proper into the Åland Sea by strong winds, and it continues into the Bothnian Sea along the depth contours (Palosuo, 1973).

The bottom water in the Bothnian Bay stems from the surface layer of the Bothnian Sea (Palosuo, 1973). The stratification in the Bothnian Bay is so weak that the incoming water can penetrate to the bottom by convection during the fall and winter (Palosuo, 1964).

The passage time of the deep water from the Darss sill to the Gotland Basin normally takes 5-7 months (Kaleis, 1976).

### 3.2.2 *Fresh water surplus and water balance*

The water balance of the Baltic Sea is positive, i.e., the supply of fresh water to the Baltic from rivers,  $R$ , and precipitation,  $P$ , is greater than the evaporation,  $E$ , from the Baltic. See the box model in Figure 14.



V = Water volumes (according to Dahlin 1973,1977)  
 Q<sub>0</sub> = Inflow of river water (according to Mikulski 1972)  
 Q<sub>1</sub> = Volume of the outflowing water  
 Q<sub>2</sub> = Volume of the inflowing water  
 S = Salinity (according to Dahlin 1977)

Figure 14. Box mode2 Of the Baltic Sea showing the water volumes and the water balance (Nyqvist, Original figure).

The fresh water surplus, Q<sub>0</sub>, may be described by the following equation:

$$Q_0 = R + P - E$$

surplus = river runoff + precipitation - evaporation

and the following figures in km<sup>3</sup>/y:

Q <sub>0</sub>	R	P	E
469	435	243	209

The fresh water surplus of the Baltic Sea is about 2% of the volume of the Baltic itself. However, regional differences exist, as shown in Table 5.

Table 5. *The distribution of the fresh water surplus in the different regions of the Baltic.*

Sea area	Fresh water surplus* ) $Q_0$ km <sup>3</sup> /y	Surface area $A$ km <sup>2</sup> x 10 <sup>-3</sup>	Volume $V$ km <sup>3</sup> x 10 <sup>-3</sup>	$(Q_0/V) \times 100\%$
Bothnian Bay	103	36	1.5	7
Bothnian Sea	96	78	4.9	2
Gulf of Finland	131	29	1.1	11
Gulf of Riga	43	16	0.4	11
Baltic Proper	99	212	13.1	1
Belt Sea	7	21	0.3	7
Kattegat	28	22	0.5	5
Total	507	415	21.7	2

\*) From Brogmus (1952), except the Kattegat, which is based on results 1931-60.

The yearly variations in fresh water surplus, river runoff, precipitation and evaporation are shown in Figure 15. The fresh water surplus peaks in May-June and attains the lowest values in November-December.



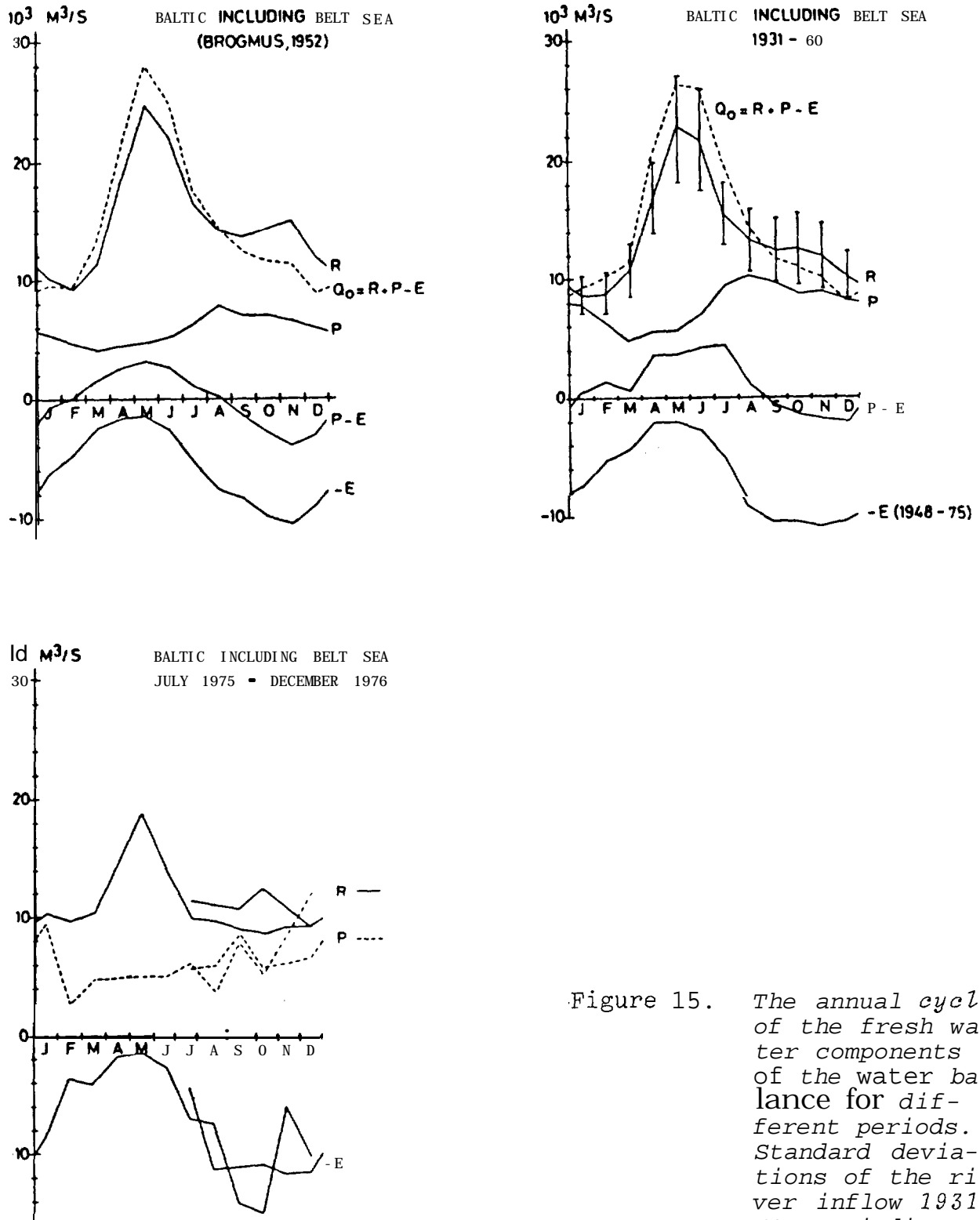


Figure 15. The annual cycle of the fresh water components of the water balance for different periods. Standard deviations of the river inflow 1931-60 are indicated.

Mikulski (1975) and Hupfer et al. (1979) have studied the river runoff in detail over the time period 1921-1970. Great variations appear from year to year, but no clear trend can be observed. This indicates that

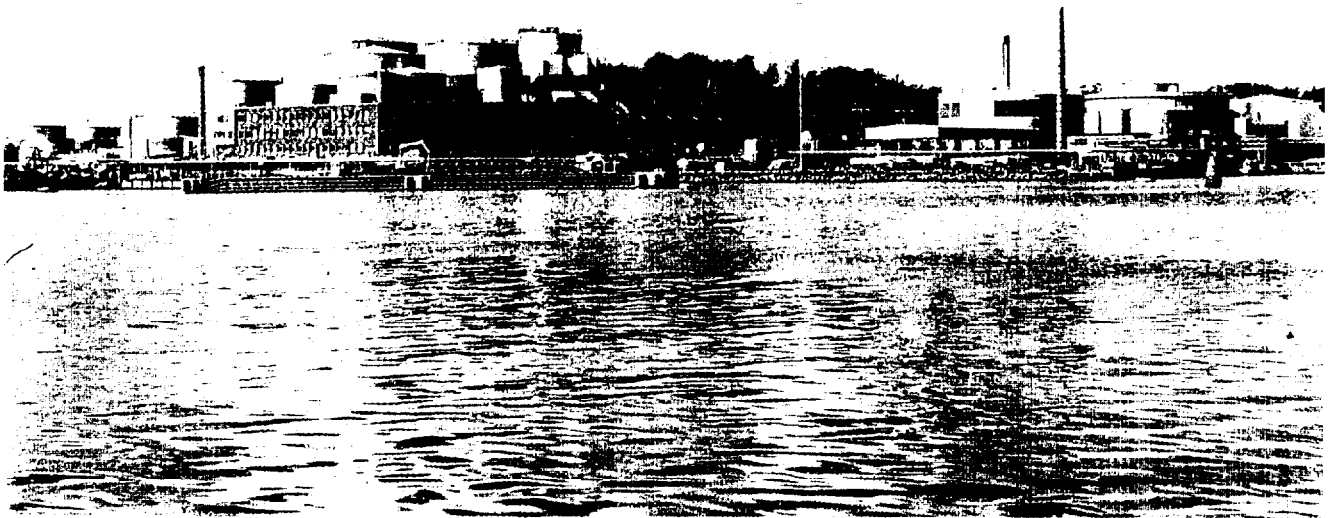


Photo: Tommie Ekström

The Baltic Sea is an important route for transport of energy



Photo: U. Duhren

"Oil spills in the Baltic Sea have considerable local effects, depending on the location of the spill and the time of the year."

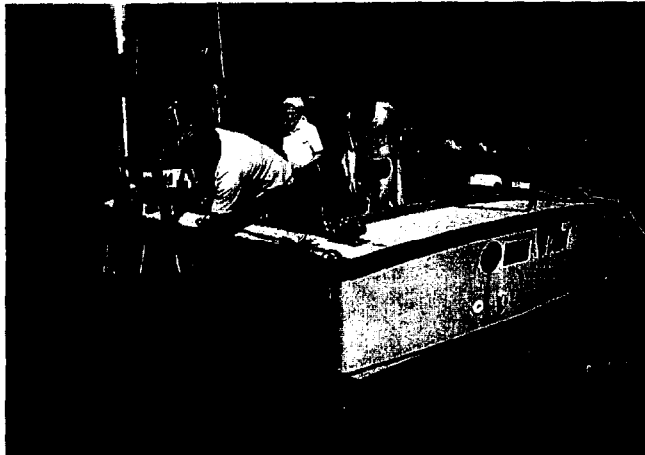


Photo: R. Varmo

Scientists using a gravity corer to obtain a sediment sample

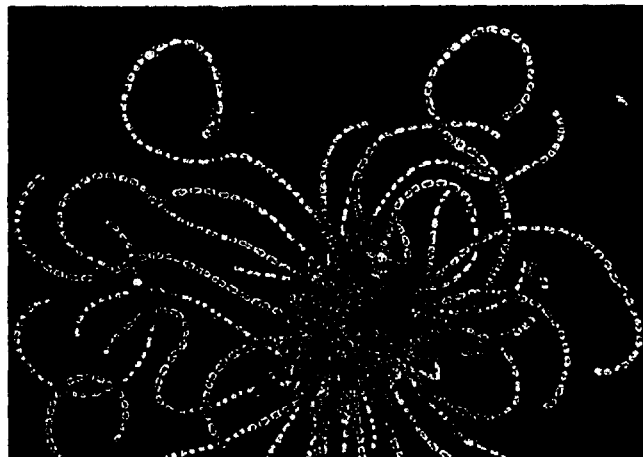


Photo: H. Viljamaa

Microscopic photo of a phytoplankton species (Anabaena sp.)



Photos: I. Rinne

Two stages of blue-green algal bloom in the open Baltic Proper

UNDERWATER PHOTOGRAPHS

Photos: Markku Porkka



Mussels (*Mytilus* sp.)  
covered by algae



Group of animals growing  
immobile on a stone,  
(*Balanus* sp.)



Rockweed (*Fucus*)



*Fucus* covered by epiphytic  
algae

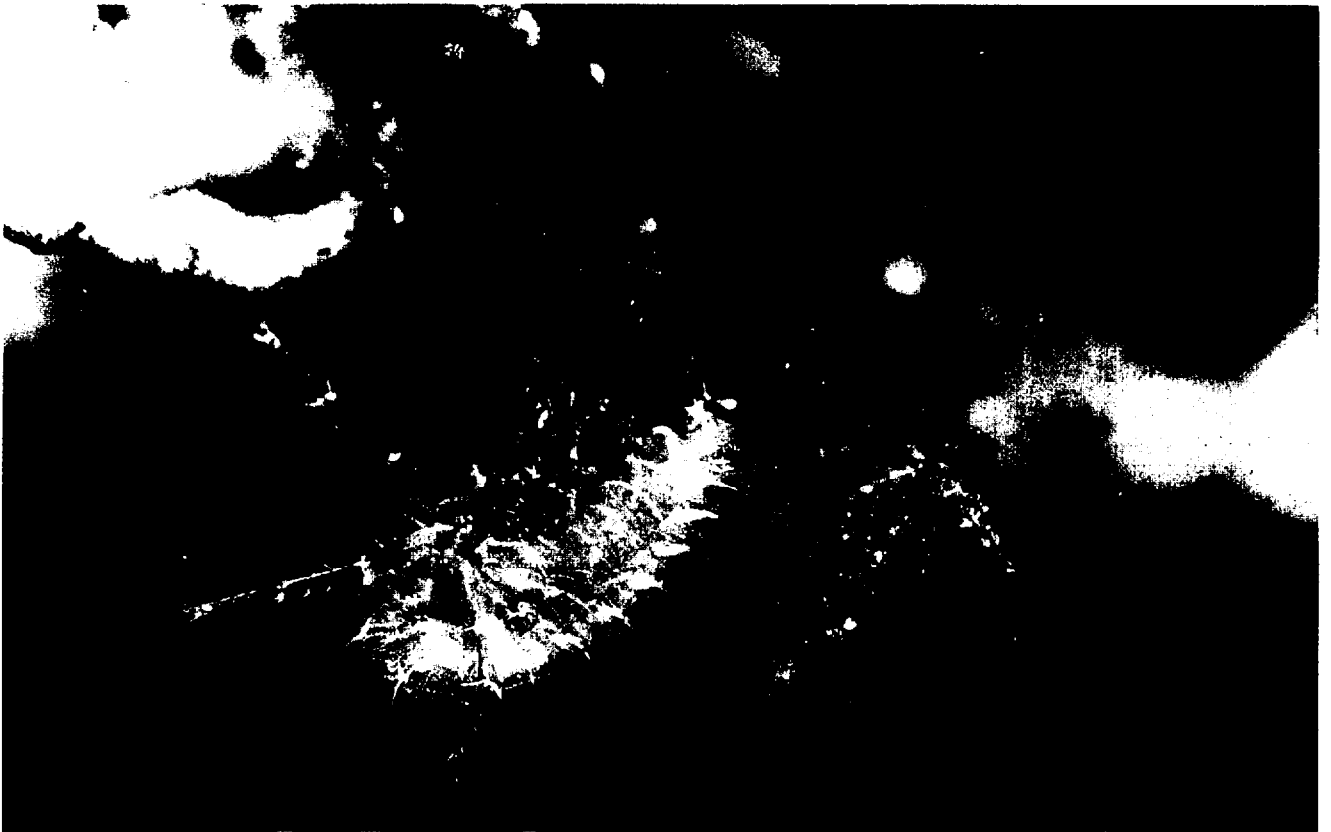


Photo: G. Aneer

As consumers of primary production the small amphipods play an important role in the Baltic Sea food chain



Photo: Ulf Aneer

Common goby is an example of the few species of fish living in the coastal areas of the Baltic Sea

the fresh water surplus has not changed during this century because the precipitation and the evaporation more or less equal each other. The mean annual value for fresh water surplus has been calculated to be  $438 \text{ km}^3/\text{y}$ , with a standard deviation of  $52 \text{ km}^3/\text{y}$ , for the interval 1921-1970.

The net outflow through the Danish Straits equals  $Q_0$  only if averages are taken over a very long time. The proper balance equation is:

$$Q = Q_0 - dV/dt$$

where  $Q$  is the net outflow through the Straits and  $dV/dt$  is the change of the volume of the Baltic with time. The storage change,  $dV/dt$ , is highly variable and results mainly from the changing fields of wind and air pressure over the Baltic and the North Sea. The maximum value observed is about  $400000 \text{ m}^3/\text{s}$ . The maximum observed volume difference between the lowest and the highest mean sea level in the Baltic Sea is of the same size as the annual fresh water surplus  $Q_0$ .

The annual cycle in the mean sea level over the northwest European shelf is also found in the Baltic Sea. The sea level is at a minimum in May and a maximum in October. The corresponding change in storage ( $dV/dt$ ) is about  $10^{11} \text{ m}^3$ .

Net inflow to the Baltic Sea takes place under the influence of westerly winds which press water into the Kattegat and away from the western Baltic. The difference in sea level thus created is followed by strong currents which depend only very little on local meteorological conditions. Net outflow is usually associated with calm weather or easterly winds. The outflows are less intensive and the situations last longer than the inflows.

We can summarise the exchange with the Kattegat through the Transition Area as follows: superimposed on an estuarine circulation with an outflow of brackish water in the top layer are meteorologically forced pulsations with a characteristic duration of 3 to 30 days. Their intensity is an order of magnitude higher than the estuarine mean flow. The presence of barotropic pulsations and the fact that the head loss through the Transition Area is mainly due to friction have so far prevented any complete and reliable theoretical modelling of the water exchange.

### 3.2.3 *Water exchange between the Baltic and the North Sea*

A brackish water body gives rise to a pressure gradient which on average is directed out of the estuary in the surface layer and the opposite in the deep layer. Accordingly, there is on average an outflow in the top layer and an inflow in the bottom layer. This flow system is here called the baroclinic circulation.

Superimposed on this circulation are the variations in the exchange caused primarily by wind and air pressure. The modelling of storm surges in the Baltic Sea shows that these variations can be treated independently of the baroclinic structure. This is known as the assumption of barotropic decoupling, and the variations in the exchange will be called barotropic exchange.

The water exchange, which is the combined effect of the baroclinic and the barotropic exchange, can be measured directly, but the high energy associated with the barotropic exchange makes it difficult to reveal the weaker baroclinic exchange. In the Belt Sea it has been found that the ratio of the standard deviation of the daily net exchange to the mean net flow is of the order of 8 - 10 (Jacobsen, 1979).

The barotropic part of the exchange can be determined from the volume fluctuations of the basin, i.e., from measurements of the sea level. The baroclinic circulation can be inferred partly from the salinity distribution by means of Knudsen's hydrographical theorem (Knudsen, 1900).

According to definition, barotropic exchange is equal to the fluctuations in volume,  $dV/dt$ :

$$Q = Q_0 - dV/dt$$

Net flow                      Fresh water                      Volume variation

As the most energetic oscillations of the volume take place in the interval from a few days to a few months, the basic data for an investigation of the variation in volume should not be averaged over a time much longer than one day. Lisitzin (1967) proposed that the annual sum of increases from day to day in mean sea level for the entire Baltic Sea amounts to 480 cm or 1 754 km<sup>3</sup>, using mean values from 1931 - 1960. This amounts to an outflow of 2 000 km<sup>3</sup>/y and an inflow of 1 500 km<sup>3</sup>/y, if  $Q_0$  is taken as constant for simplicity.

Direct measurements during 1976 with automatic recording instruments in the Belt Sea gave a sum total out- and inflow of 3 450 km<sup>3</sup> (Jacobsen, 1979), which is in good agreement with the findings of Lisitzin.

It can be concluded that the barotropic outflow in the Transition Area is about 2 000 km<sup>3</sup>/y, the inflow being smaller by the amount of  $Q_0$  (400 - 500 km<sup>3</sup>/y). A similar study of the barotropic exchange between the Baltic Proper and the Gulf of Bothnia was carried out in the Åland Sea (Ambjörn, 1978). The monthly sum of inflow and outflow amounted to 200 - 250 km<sup>3</sup>, which is almost as much as the flow through the Sound and the Belts.



Based on mean salinities and  $Q_0$ , Kullenberg (1967) calculated the half-time of a conservative substance which is assumed to have a uniform concentration in the Baltic. The half residence time found was 24 years. The weak mixing through the primary halocline will modify the result, but it is useful as an order of magnitude estimate.

*Horizontal two-dimensional mean circulation*

The horizontal current circulation is weak and cyclonic (counterclockwise) in the Baltic Proper as well as in the Gulf of Finland and the Gulf of Bothnia. There is one gyre in the Bothnian Sea and one in the Bothnian Bay. The mean velocities are of the order of a few cm/s in the surface layer and about 1 cm/s in the deep water (Palmén, 1930). The inflowing deep water is forced into cyclonic motion both by the coriolis force and by the flow route determined by the deep basins and the locations of the sills. Accordingly, the mean salinity and temperature are higher at the east coast than at the west coast.

*Two-dimensional horizontal time-dependent circulation*

*Tidal motion* in the Baltic Sea is very weak, of the order of 1 cm/s. It is an order of magnitude higher in the Kattegat, but the tidal wave is reduced through the Transition Area by friction in the shallow waters. *Inertia2 oscillations* occur often in the Baltic. The period is about 14 hours.

*Seiches* (free oscillations) occur in the Baltic at various frequencies, depending on the oscillating system (western Baltic - Gulf of Finland, western Baltic - Gulf of Bothnia). An often observed oscillation with a 50 -60 hour period has recently been described as the basic eigenoscillation of the Baltic (Krauss, 1974).

*Forced oscillations* are produced by quasi-periodic variations in wind and air pressure. The associated variations in sea level are of the order of 1 metre in the northern and southern Baltic, but generally much less in the central Baltic. Oscillations with about a 5-day periodicity have often been observed and have been explained by a series of passing low pressure systems (Magaard and Krauss, 1966; Prival'skiy, 1968).

#### 3.2.4 *The possible effect of man*

Soskin(1963) and Fonselius (1969b) were of the opinion that a decrease in the fresh water surplus results in an increase in the static stability. They found a close correlation between decreasing river runoff and increasing salinity in the deep water during this century (see also Kaleis,1976). An opposite conclusion was, however, reached by Welander (1974), based on a theoretical model.

Some of the driving forces can be altered by human activities. The mean river runoff can be changed by making alterations in the course of the rivers, and the amplitude of the annual cycle of the river runoff can become smaller due to the regulation of river flow in order to optimise the production of hydroelectric power. The volume variations can also be affected if additional frictional losses are introduced in the entrance area to the Baltic Sea. Pedersen (1978) expected a reduction of a few percent in the volume variations after the construction of a proposed bridge across the Great Belt, and a subsequent reduction of 0.2 - 0.4‰ in the salinity of the upper and the deep water layers within the Baltic.

The following effects can be expected to take place:

- (1) A decrease in the fresh water surplus will raise the salinity in the surface and deep waters.
- (2) An increased friction in the entrance area to the Baltic Sea will lower the salinity in both layers.

A changed fresh water surplus can be the result of natural variations or of human activities. If it is the result of natural variations, there is a coupling to evaporation/precipitation over the Baltic Sea and the catchment area of the Baltic, which in turn is governed by meteorological circulation. Thus, the barotropic exchange is also influenced. But the fresh water supply could be lowered considerably by taking water from the large rivers without any change in the other forcing functions. The resulting salinity and static stability is not expected to be the same in these two cases. It is not felt that additional safe conclusions can as yet be drawn about the response of the Baltic Sea to a change in the driving forces. A convincing model which has been verified for short- and long-period oscillations is still lacking.

### 3.2.5 *Vertical and horizontal mixing in the Baltic Sea*

#### *Vertical mixing*

The turbulent mixing in the sea is far more important than the molecular mixing. While the latter depends on the inherent properties of the water, turbulent mixing is a phenomenon which results from the averaging of non-linear terms in the small scale motion. The coefficient of turbulent mixing is accordingly not a material constant, but has been found to depend on several parameters, in particular the stratification, the current shear and the boundary stresses.

The variation of salinity with depth in the top layer is small during summer and almost nil in the winter time. This is accomplished by wind-generated mixing and thermohaline convection during the autumn and early winter. During the spring and summer, a thermocline is developed over most of the Baltic Sea at depths between 15 and 20 m. This thermocline, which can be very strong, suppresses the mixing in the surface layer during this part of the year.

The convective mixing caused by cooling of the surface during the winter reaches the top of the primary halocline, but cannot cross it. A small winter thermocline can develop when the surface is cooled further, and the water above this thermocline is normally cooled to its freezing point, slightly less than  $0^{\circ}\text{C}$ . The layer between the winter thermocline and the primary halocline stays homothermal during the rest of the winter. When heating begins in spring, the summer thermocline develops so rapidly that the lowest part of the surface layer is not heated by thermal convection at all. This winter water stays on top of the primary halocline, and a corresponding temperature minimum can be found in most areas of the Baltic Sea, usually between 40 and 60 m.

The mixing coefficients are in general lower in the Arkona Basin than in the Gotland Basin; this is ascribed to a smaller wind fetch. According to the theoretical relationships between wind force, wind fetch and wave heights, the maximum wave height which can develop in the Baltic is about 9 m. Calculations by Hela (1966) for the northern Baltic Sea are within the same range as the results of Matthäus (1977c).

Kullenberg (1977) has investigated the vertical mixing on smaller time scales by the method of injected tra-

cers. The coefficients found in the thermocline or the halocline layer at depths between 25 and 55 metres in the Arkona and Bornholm Basins were in the range  $0.2 - 0.01 \text{ cm}^2/\text{s}$  at the respective levels. These values are in good agreement with the mean values found by Matthäus (1977c) at corresponding levels. Kullenberg argued that the total mixing in the interior of the Baltic Sea is of the same order as the intense mixing in the coastal boundary layer. It can be concluded that there are no safe indications of a long-term trend towards a smaller vertical mixing in the Baltic Sea. Fluctuations can, however, be large.

#### *Horizontal mixing*

Horizontal mixing has been studied in a limited number of experiments by means of tracers and drifters. The horizontal diffusion velocities are an order of magnitude smaller than in the oceanic surface layer.

Understanding and modelling of horizontal transport and mixing is essential to the development of realistic predictive models for the distribution of floating, dissolved and dispersed materials, e.g., oil.

# Dissolved gases

## 4.1 Oxygen and hydrogen sulphide in the deep water

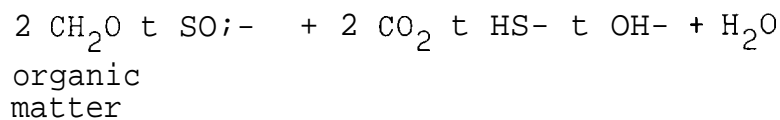
### 4.1.1 *Properties and analytical methods*

Oxygen and hydrogen sulfide are gases which dissolve in water. Oxygen dissolves physically according to Henry's law. The oxygen of the atmosphere is in equilibrium with the dissolved oxygen in the surface water of the seas and oceans and the surface water is therefore normally saturated with oxygen.

Generally, dissolved oxygen is analyzed titrimetrically using the old Winkler method (Winkler, 1888) or modifications thereof (see Fonselius, 1966a; Fonselius and Carlberg, 1972; Grasshoff, 1976a). In only a few cases have results using oxygen sensors been reported from the Baltic Sea area and therefore these methods and their results will not be discussed here. The accuracy and precision of the Winkler method are difficult to establish. The accuracy cannot be exactly determined due to the difficulty of preparing standard samples with a precisely known oxygen content. The precision may be  $\pm 0.02 \text{ cm}^3/\text{dm}^3$ , expressed as the standard deviation for oxygen concentrations of less than  $2 \text{ cm}^3/\text{dm}^3$  water, or  $\pm 0.04 \text{ cm}^3/\text{dm}^3$  for oxygen concentrations above  $2 \text{ cm}^3/\text{dm}^3$ . Intercalibration among five laboratories from the Baltic Sea - North Sea area resulted in a standard deviation of  $\pm 0.03 \text{ cm}^3/\text{dm}^3$  (Fonselius, 1966a, 1966b). Intercalibration exercises have shown that results from different Baltic Sea countries generally are comparable (Fonselius, 1966a, 1966b).

Hydrogen sulfide is formed in deep water at the sediment surface and dissolves physically and chemically

in the water forming sulfide ions. In sea water, mainly  $\text{HS}^-$  ions are formed. The solubility of hydrogen sulfide ( $437 \text{ cm}^3/\text{dm}^3$  in distilled water at  $0^\circ\text{C}$ ) is therefore much greater than that of oxygen ( $7 - 11 \text{ cm}^3/\text{dm}^3$  according to temperature and salinity). The ionization of hydrogen sulfide regulates its solubility. Hydrogen sulfide is an extremely poisonous gas and therefore no higher life can exist in sulfide-containing water. Hydrogen sulfide formation in natural waters is a bacterial process in which sulfate ions are reduced to sulfide. The oxygen of the sulfate ions is used for oxidation of dead organic matter to carbon dioxide and water:



Because sulfate is one of the major ions in sea water, large amounts of hydrogen sulfide may be formed in the water.

Hydrogen sulfide is generally analyzed spectrophotometrically in the Baltic Sea area, using the Methylene Blue method (Fonselius, 1976a). The method has not been intercalibrated among the Baltic Sea countries and, therefore, the accuracy and precision of the method cannot be given. The technique is, however, methodically simple, sensitive and specific and there is no reason to believe that results from different countries would not be comparable.

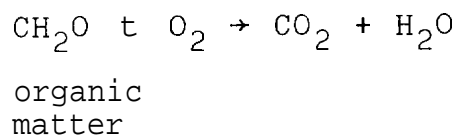
#### 4.1.2 Dissolution and vertical distribution of oxygen

The following processes may influence the oxygen concentration in the water:

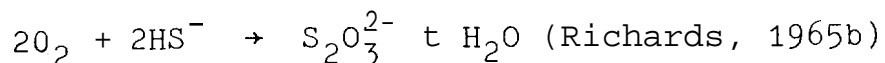
- a) *Physical processes.* Changes in water temperature and salinity change the solubility of oxygen, increasing it with decreasing temperature and sali-

nity, and vice versa. Oxygen is transported by horizontal and vertical water movements, e.g., bottom currents, thermohaline convection and turbulent diffusion. Ice conditions may also influence the transport of oxygen through the sea surface.

- b) *Biological processes.* The respiration of organisms consumes dissolved oxygen and the carbon dioxide assimilation of green plants produces oxygen in the photic zone of the sea. The most important oxidation process in natural waters is the biochemical oxidation of organic carbon to carbon dioxide carried out by bacteria:



- c) *Chemical processes.* Oxidation-reduction processes in the water may consume oxygen. For example, the reaction between dissolved oxygen and sulfide ions in the boundary layer between oxygen- and hydrogen sulfide-containing water decreases the oxygen content (and also the sulfide content) of the water:



During the winter, the oxygen concentration of the surface water increases due to the increasing solubility of oxygen in water with decreasing temperatures (see Figure 16). The thermohaline convection which takes place during the winter transports oxygen-saturated water downward when the thermocline disappears. In this way, oxygen-saturated water is mixed down to the permanent halocline of the Baltic Sea. When the



thermocline is again formed during the summer, the surface water becomes warmer and the oxygen solubility decreases. Therefore, we may find higher oxygen concentrations in the cold winter water below the thermocline during the summer than in the warm surface water (Matthäus, 1978d).

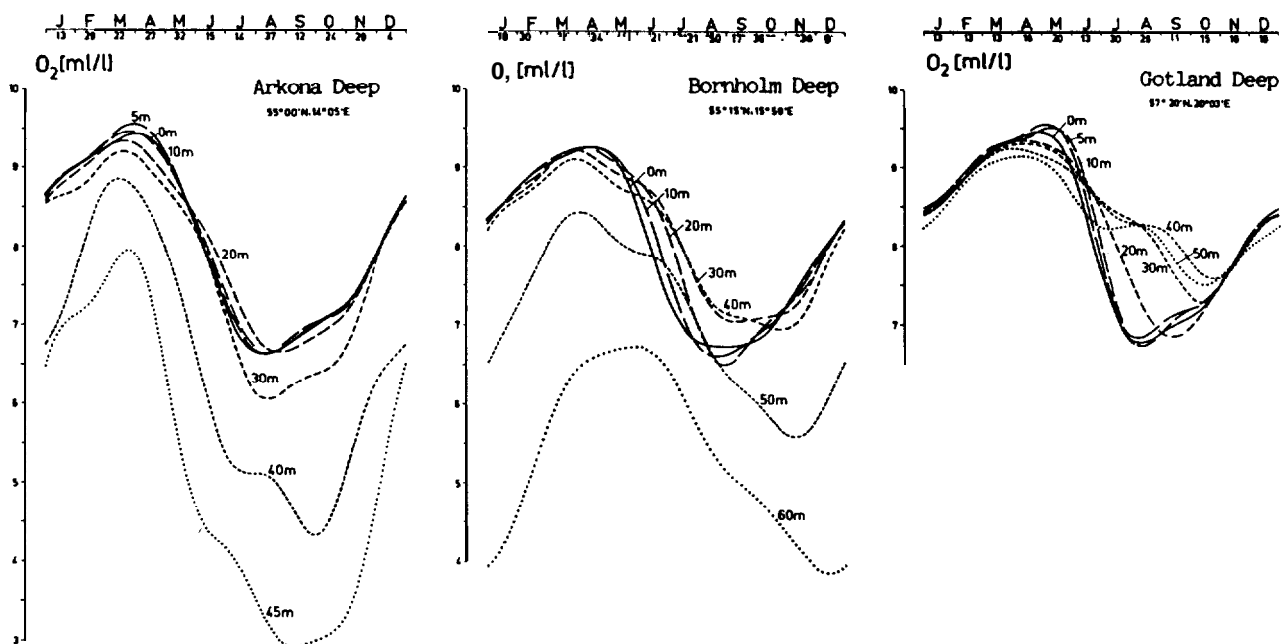


Figure 16. Mean seasonal variations of oxygen concentrations in the Baltic Proper (from Matthäus, 1978d).

Below the halocline the oxygen concentration decreases rapidly downward, reaching values close to or at zero near the bottom of the deep basins of the Baltic Proper. This water has lost most of its oxygen during the long transport below the halocline from the Belt Sea to the deeper parts of the Baltic Sea (see Figure 17). Such transport, for example, to the Gotland Deep and the Landsort Deep may take 6-12 months (Fonselius, 1962), during which time oxygen is consumed by the oxidation of dead organic matter sinking

down through the water. As water exchange through the halocline is restricted, the oxygen lost through the oxidation of organic matter cannot be fully replaced.

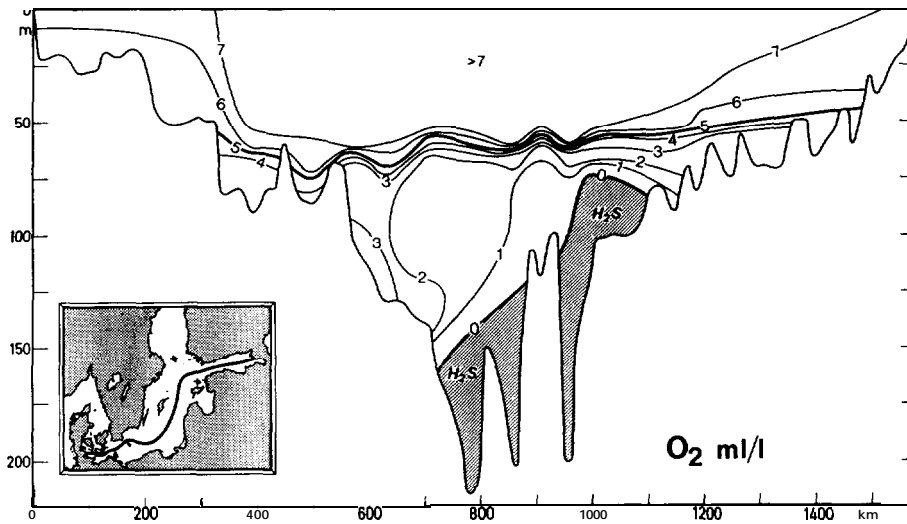


Figure 17. *Distribution of dissolved oxygen along a longitudinal section in the Baltic Sea in August, 1969 (from Grasshoff, 1975).*

Figure 18 shows the normal distribution of dissolved oxygen at a Baltic deep station during the winter and summer. The oxygen concentration below the halocline is barely influenced by seasonal variations in the surface water. The only effective changes are caused by the consumption of oxygen due to the decomposition of organic matter or by inflows of new water along the bottom of the Baltic Sea from the Kattegat and turbulent diffusion which slowly dilutes the water in the stagnant basins thereby reducing the salinity. This new water may have either a higher or a lower oxygen concentration than the stagnant water in the basin. If hydrogen sulfide has been formed in the water, it will react with the oxygen.

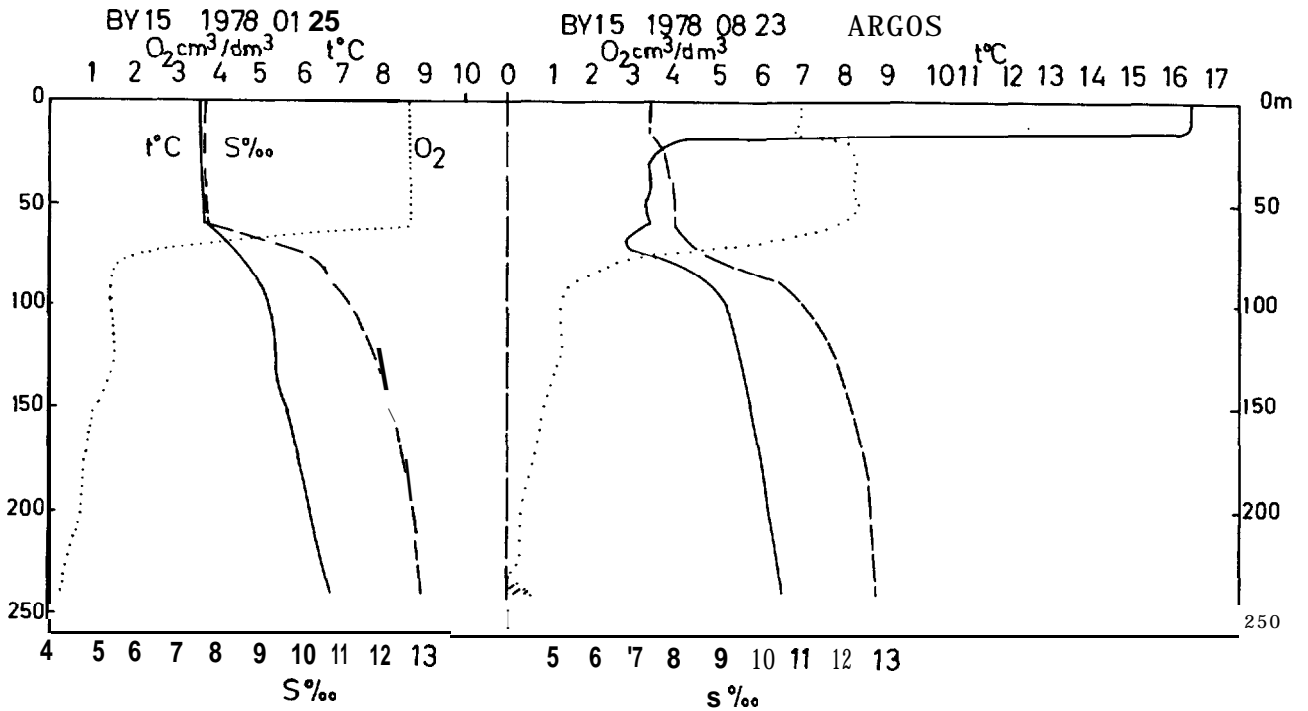


Figure 18. The vertical distribution of temperature, salinity and dissolved oxygen in the Gotland Deep (BY 15) in January and August 1978. R.V. Argos. (Fonselius, original figure).

Generally, the oxidation of organic matter occurs faster than the supplying of oxygen through turbulent diffusion and, therefore, this latter effect is difficult to detect. Thus, the inflow of new water along the bottom is the only visible phenomenon in stagnant basins. These changes can be followed by studying changes in the temperature, salinity, oxygen, hydrogen sulfide and nutrient concentrations in the water. The oxygen variations are the most spectacular, especially if stagnant conditions have led to hydrogen sulfide formation.

#### 4.1.3 Oxygen and hydrogen sulfide variations

The following figures show examples of the oxygen variations at some representative stations in the different main deep basins of the Baltic Proper. Figure 19 shows the variations at 80-90 m in the Bornholm Basin, measured at station BY 5 (the Bornholm Deep) from 1958 to 1979. It can be seen that at least 16 inflows of new water with high oxygen content have occurred during this time. There are at least three periods with hydrogen sulfide formation in the bottom water. From the diagram it can also be seen that most water renewals occur during the winter, but they may occasionally happen during other seasons.

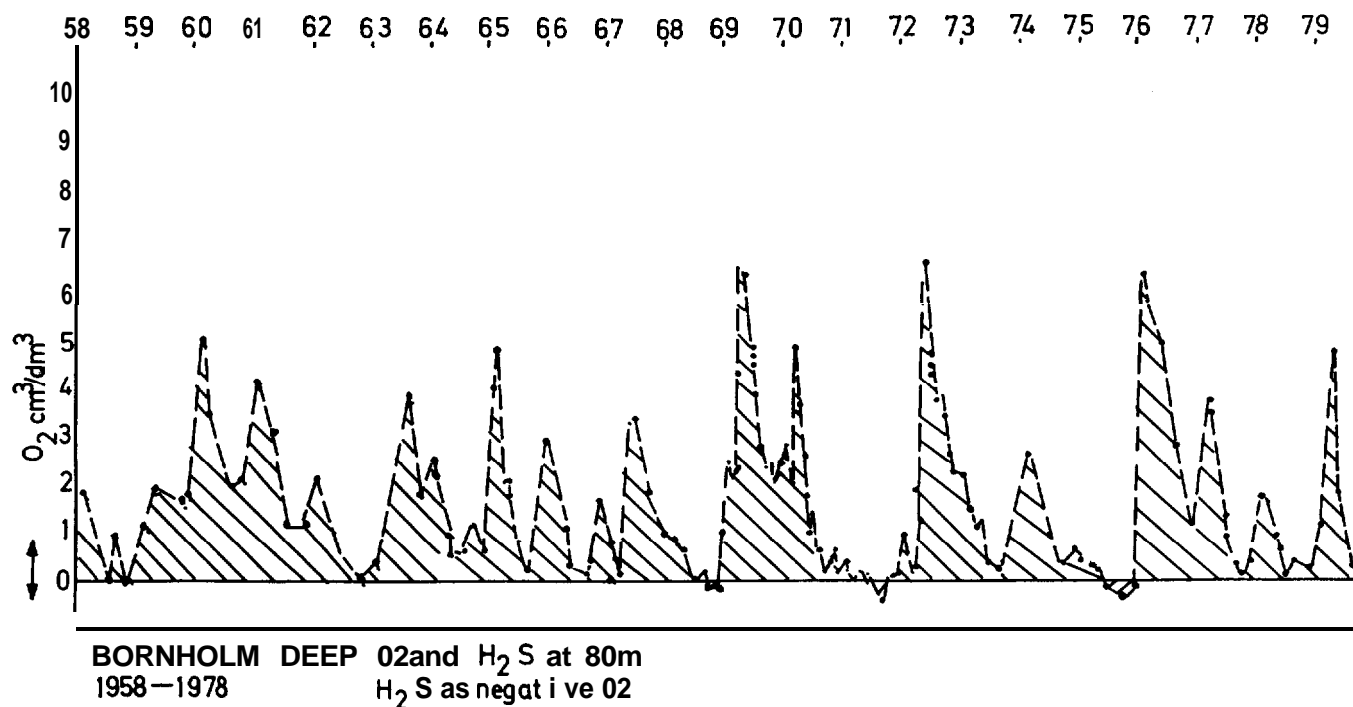


Figure 19. Oxygen and hydrogen sulfide variations in the Bornholm Basin (BY 5) at 80 m from 1958 to 1979 (Fonselius, original figure).

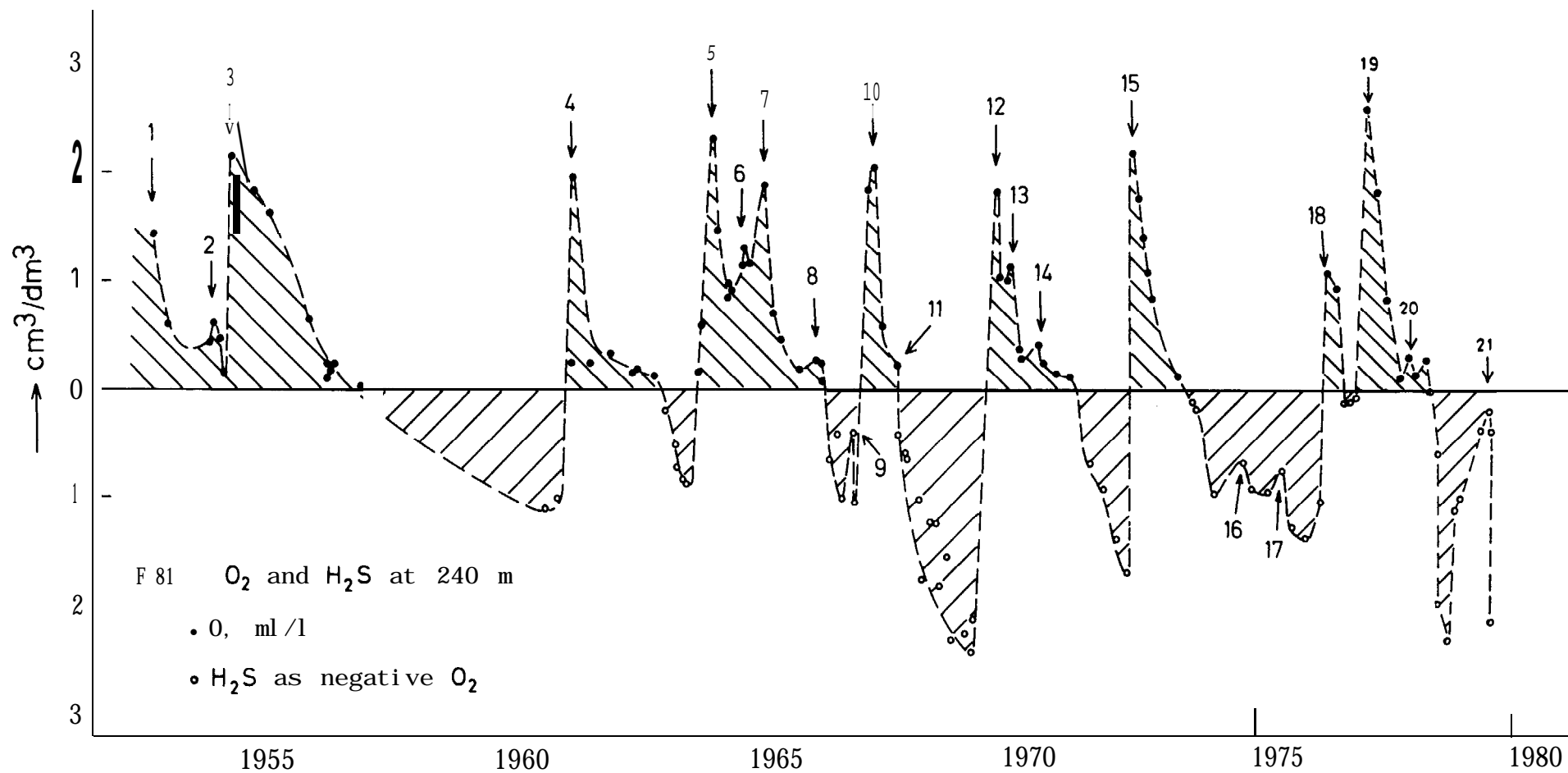


Figure 20. Oxygen and hydrogen sulfide variations in the eastern Gotland basin (BY 15) at 240 m from 1954 to 1979 (Fonselius, original figure).

Figure 20 shows the oxygen and hydrogen sulfide variations from 1954 to 1979 in the eastern Gotland Basin measured at station BY 15 (the Gotland Deep) at 240 m. The hydrogen sulfide values are, as in the previous figure, expressed as negative oxygen. ("Negative oxygen" is the amount of oxygen equal to the amount of  $\text{H}_2\text{S}$  produced through reduction of  $\text{SO}_4^{2-}$ . The sulfate ion contains 4 atoms of oxygen which are used for the bacterial oxidation of organic matter and one atom of sulfur which is reduced from  $\text{S}^{6+}$  to  $\text{S}^{2-}$ . Multiplication of the  $\text{H}_2\text{S}$  value expressed in  $\text{cm}^3/\text{dm}^3$  by 2 gives the "Negative  $\text{O}_2$ ".) Since 1957 there have been eight stagnation periods with hydrogen sulfide formation. The Gotland Deep is representative of conditions in the eastern Baltic Sea. Other deep stations with hydrogen sulfide formation in this area are the Gdańsk Deep and the Fårö Deep, which are located in separate small basins belonging to the large eastern Gotland Basin. From the figure, it can be seen that at least 21 water inflows (marked with numbers and arrows) have occurred during this period. The inflows until 1970 have been described and discussed in more detail by Fonselius and Rattanasen (1970).

The northern Central Basin is represented by stations BY 28 and BY 31. Figure 21 shows the variations at 150 m at BY 28. Here a period with very poor oxygen conditions can be distinguished between 1968 and 1975. In 1976 the conditions improved considerably, but in 1979 hydrogen sulfide was again found at 150 m depth. The conditions in the Landsort Deep (BY 31) are shown in Figure 22. This is the deepest point in the Baltic Sea and the values are from 440 m depth. Here also the pattern can be seen for very poor oxygen conditions between 1968 and 1976 followed by improved conditions. No hydrogen sulfide was, however, found in

1979 as on the previous station. It is also easy to see that the conditions have deteriorated since 1953 when the series was started. The improvement since 1976 has not brought back the high oxygen levels which were found during the 1950s. Hydrographically, the Gulf of Finland belongs to this basin. However, hydrogen sulfide has only been observed there on a few occasions, e.g., in 1970 when water from the eastern Gotland Basin was forced into the northern Central Basin and pushed westwards to the Landsort Deep and eastwards to the Gulf of Finland in front of the new water entering the deep areas of the whole Baltic Proper.

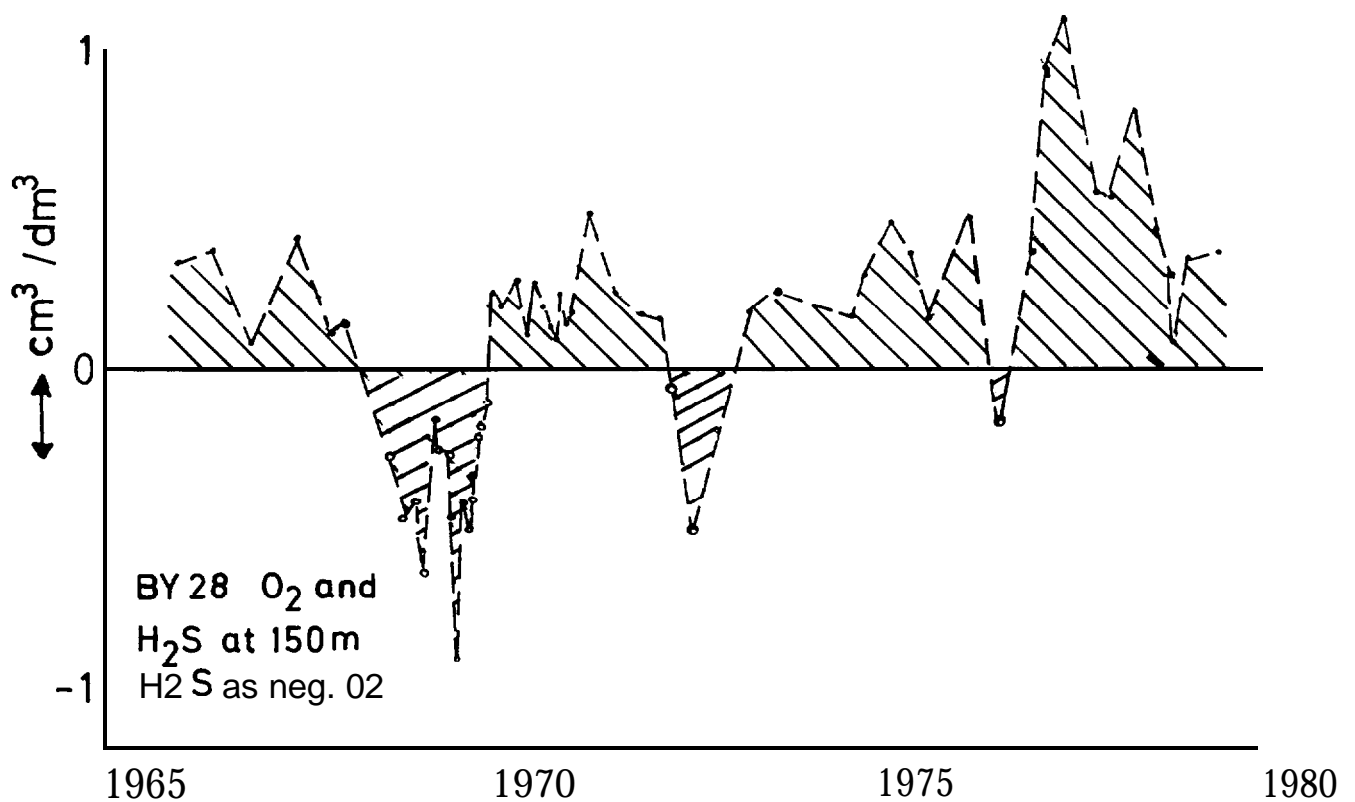


Figure 21. Oxygen and hydrogen sulfide variations in the northern Central Basin (BY 28) at 150 m from 1965 to 1979 (Fonselius, original figure).

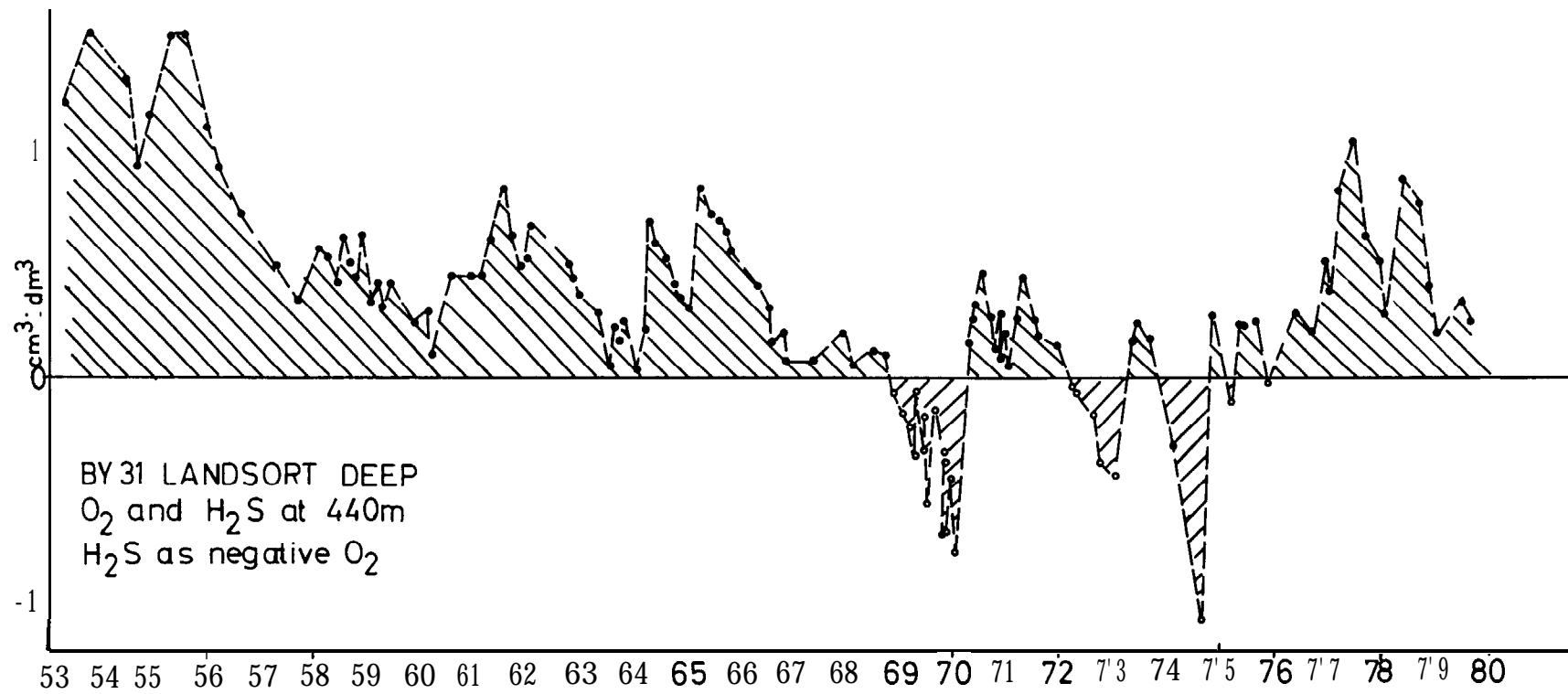


Figure 22. Oxygen and hydrogen sulfide variations in the Landsort Deep (BY 31) at 440 m from 1954 to 1979.  $H_2S$  expressed as negative oxygen. (Fonselius, original figure).



#### 4.1.4 *Water renewals*

The reason for the alternations described between oxygen and hydrogen sulfide in the deep basins is that when occasionally water with high density enters the Baltic Sea through the Belts, this water streams along the bottom following the deepest connections between the different basins. When one basin has been filled up to the sill connecting it with the next basin, the water begins to flow into this next basin. Depending on the amount of inflowing water and its density, the water may fill only some of the first basins or it may go through the whole Baltic Proper filling all deep basins with new water. The old water with lower density is pushed out of the basin and forced further into the Baltic Sea in front of the new water. If a basin happens to contain water with a higher density than the new water, the inflowing water may continue over this basin at intermediate levels. During the inflow, the new water is continuously diluted with Baltic water (Fonselius, 1974). The new water may remain for several years in the deep basins (Fonselius, 1969a), during which time the oxygen content decreases and hydrogen sulfide may eventually be formed when all oxygen has been exhausted. This stagnant water is slowly diluted with new water, partly due to turbulent diffusion and partly due to horizontal mixing through small inflows of water. When the density of the stagnant water in the basin has decreased so much that new water can displace it, it is forced out of the basin and partly mixed with the water above and partly pushed further into the Baltic, as described earlier. When, e.g., in 1969 - 1970 the stagnant water was renewed in the whole Baltic Proper, the old hydrogen sulfide-containing water from the eastern Gotland Basin was forced into the Gulf of Finland and the western Gotland Basin (Fonselius, 1970).

The bottom topography of the Baltic Sea prevents the exchange of deep water between the Baltic Proper and the Gulf of Bothnia. In the Baltic Proper, the deep water cannot continue from the western Gotland Basin southward, due to the shallow banks south and southeast of Gotland. Because almost no deep water with high density can enter the Gulf of Bothnia, the stratification there is rather weak and stagnant conditions cannot develop. Figure 23 shows the areas contaminated by hydrogen sulfide in the Baltic Proper during the years 1963 - 1979.

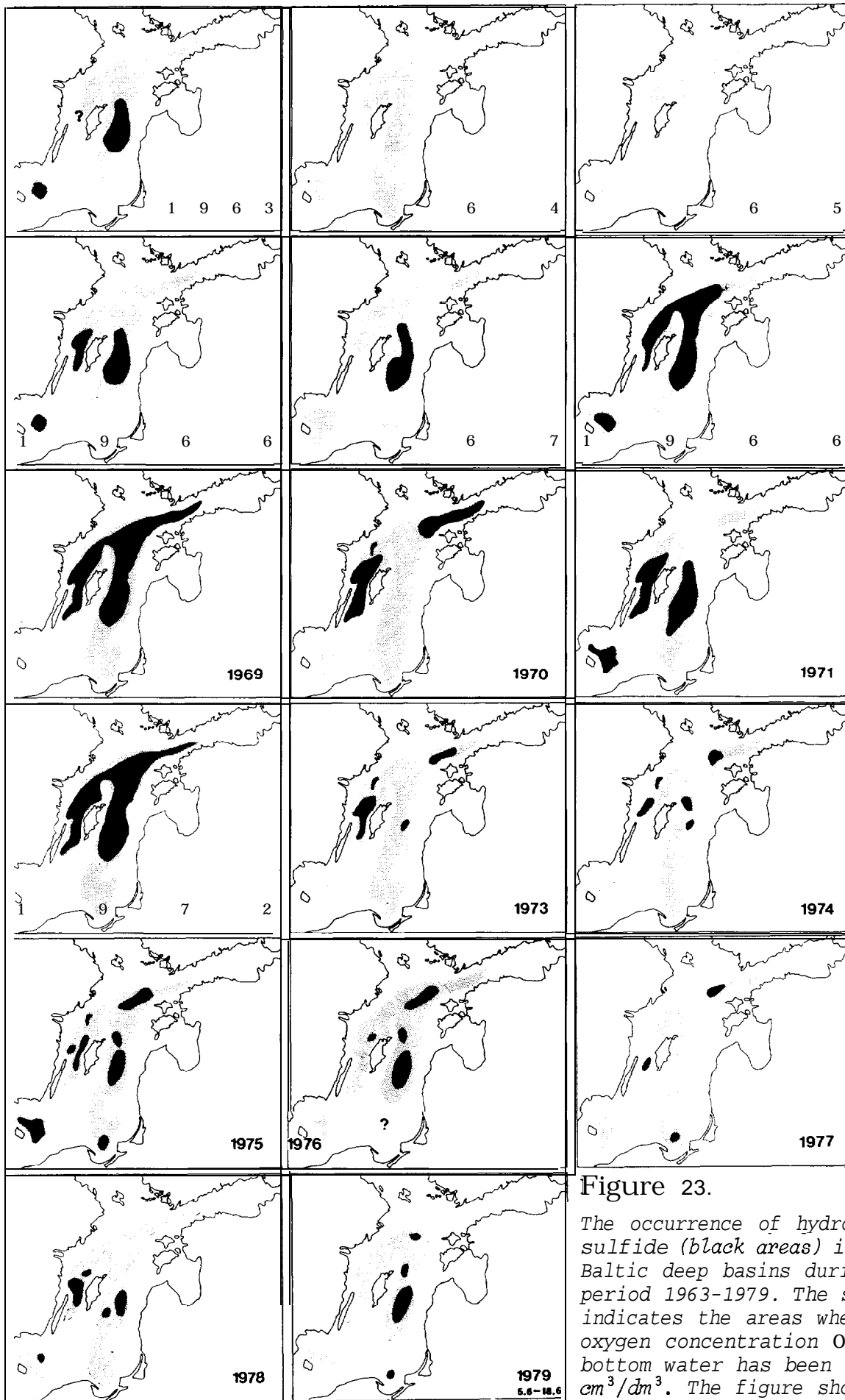


Figure 23.

The occurrence of hydrogen sulfide (black areas) in the Baltic deep basins during the period 1963-1979. The shading indicates the areas where the oxygen concentration of the bottom water has been below  $2 \text{ cm}^3/\text{dm}^3$ . The figure shows the most unfavourable conditions for each year. (Andersin et al., 1979).

#### 4.1.5 Long-term variations

It has been shown (Fonselius, 1969a) that, since the beginning of the present century, the oxygen concentration in the deep water in the Baltic Proper has decreased from around  $3 \text{ cm}^3/\text{dm}^3$  to around zero. Figure 24 shows this development in the Baltic Sea deeps from 1900 to 1978. This decrease has been studied more closely by Matthäus (1978e, 1979a). Matthäus (1978e) has statistically calculated the decrease from 1900 to 1975 and from 1952 to 1974 at some of the deep stations. The results are shown in a simplified form in Table 6.

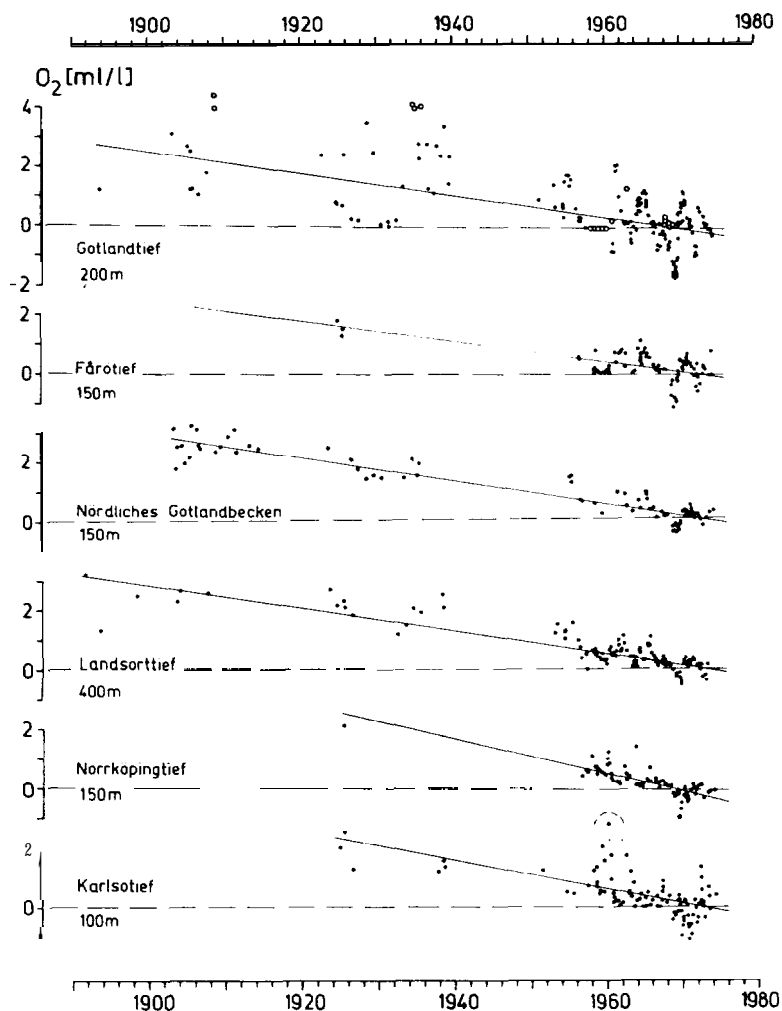


Figure 24. Long-term variations in oxygen concentrations in the deep water of the Baltic Proper (from Matthäus, 1979a).

Table 6. *Decrease in Oxygen Concentrations at Stations in Some Baltic Basins*

Basin and station	Depth (m)	$\Delta O_2$ (cm <sup>3</sup> /dm <sup>3</sup> )	
		1900-1975	1952-1974
Arkona Basin	45	- 0.76	
Bornholm Basin	80	- 2.33	- 0.75
Gdańsk Basin	100	- 2.02	- 1.18
Eastern Gotland Basin			
BY 9	100	- 2.43	
BY 15	100	- 3.33	- 1.13
	150	- 3.05	- 0.95
	200	- 2.69	- 1.44
BY 20	100	- 3.51	- 1.03
	150	- 2.54	- 0.42
Northern Central Basin			
BY 28	100	- 3.27	- 1.44
	150	- 2.99	- 1.36
BY 31	100	- 3.08	- 1.28
	150	- 3.10	- 1.25
	200	- 2.93	- 1.31
	300	- 3.06	- 1.31
	400	- 2.87	- 1.19
Western Gotland Basin			
BY 32	100	- 4.06	
	150	- 4.37	
BY 38	100	- 3.66	- 1.68

Matthäus' calculations also include hydrogen sulfide as negative oxygen (Fonselius, 1969a).

Hydrogen sulfide formation is known to have occurred in the Baltic Sea during former geological times, e.g., between the Anclylus and Littorina Sea periods around 5000 - 4000 BC. During 1600 - 1700 AD, the hydrogen sulfide formation was more frequent than during the

present time. These conclusions have been drawn from studies of sediment cores from the Baltic deep basins (Hallberg, 1974; Ignatius et al., 1971; Niemistö and Voipio, 1974) (see also section 4.2).

#### 4.1.6 *Discussion*

As has been shown here, during the last three decades hydrogen sulfide has been formed occasionally in all the main deep basins of the Baltic Proper. The oxygen decrease from the beginning of the century has most probably been caused by two large salt water inflows, which caused stagnant or semi-stagnant conditions in the deep basins for long periods (Fonselius and Rattanasen, 1970). The first inflow occurred sometime during World War I and led to continuously decreasing oxygen concentrations in the bottom water of the Gotland Deep during the 1920s. In 1931, hydrogen sulfide was found in the bottom water. The water was renewed in 1932 (Kalle, 1943). The second large inflow occurred in 1951 (Wyrтки, 1954b), and it led to hydrogen sulfide formation in 1957 (Fonselius, 1962).

It seems to be very difficult for the Baltic Sea to recover from this last large salt water inflow. The reason for this may be due to increasing discharges of wastes from communities and industries in the countries around the Baltic Sea. A "vicious circle" of hydrogen sulfide and oxygen periods may have been created (Fonselius, 1969b). These problems have also been discussed by Engström and Fonselius (1974), Grasshoff (1974) and Nehring and Brüggmann (1976). It is at present not possible to state with certainty if human activities are responsible for the present hydrogen sulfide formation or if it is a purely natural phenomenon caused by hydrographic and meteorological large scale changes during the present century. It has been suggested that these last-mentioned factors are the primary reasons for the stagnation and that increased discharges of easily oxidizable organic matter and nutrients and the increasing eutrophication

of the surface water due to this, may be a secondary reason, which has accelerated hydrogen sulfide formation (Fonselius, 1969b; Matthäus, 1978e).

Further information is needed on the development of anoxic conditions in coastal waters, the causes and effects of such anoxic conditions.

#### 4.1.7 Coastal waters

Oxygen depletion and anoxic conditions occur at several places in coastal waters due to the discharging of oxygen-consuming wastes from communities and industries. These conditions will hardly influence the conditions in the open Baltic Sea. A full description of the coastal problems cannot be included in a general assessment of the Baltic Sea without enlarging the description enormously. The material is very large and varying due to different conditions and problems in different areas. Most of the material is written in internal reports and in the language of the country concerned. The coastal areas are inside territorial waters and it is difficult to get access to the material. References from some Baltic Sea countries are available, e.g., Schulz, 1968; Berner et al., 1973; Nehring and Francke, 1974; Francke et al., 1977; Isotalo and Häkkilä, 1976; Svansson, 1966; Cronholm, 1965; Landner et al., 1971; Schaffer, 1979 .

## 4.2 Redox processes in sediments

The seabed of the Baltic Sea consists of several different bottom types, ranging from hard rocky bottoms to very soft sediments. About 50% of the bottom area is covered by soft sediments. These sediments are very interesting with regard to redox processes.

A soft bottom is characterized by a high content of fine-grained mineral particles mixed with a high content of organic matter. Most of the sedimented organic matter in the Baltic Sea is of planktonic origin (Jansson, 1974).

Micro-organisms are responsible for most of the chemical changes in the sediments. Bacteria produce energy by degrading organic matter down to inorganic compounds such as carbon dioxide, water, phosphate and ammonium. Thus, organic matter is one of the main factors influencing redox processes in the sediments. Other important factors are temperature, oxygen and light.

The result of redox processes in sediments can be separated into two pathways. The oxygen concentration determines whether oxidizing or reducing conditions prevail.

Under oxidizing conditions, the surface sediment (a few centimetres deep) accumulates metals deriving from deeper reduced zones in the sediment or from the degradation of organic matter. The metals are precipitated mainly as oxides, hydroxides and phosphates, which means that phosphate is also accumulated in an oxidized sediment. The phosphate originates partly from the degradation of organic matter and partly from dissolved phosphate minerals in the reduced deeper parts of the sediment.

In a reduced sediment, there is in most cases no hindrance for reduced transportable metal ions to pass the sediment-water interface and reach the water mass. Some of the metals, especially iron, are however precipitated as monosulfides due to bacterial sulfate reduction producing hydrogen sulfite. Certain other metals are not trapped as sulfides, probably due to chelating mechanisms which allow a further transport to the water mass.



Phosphate is released from the sediments during a re-ox-turnover from oxidizing to reducing conditions, e.g., when oxygen is depleted from the water mass above. The intensity of the phosphate release is dependent on the amount of degraded organic matter available as a carbon source for sulfate-reducing bacteria which dominate the mineralization processes under anoxic conditions. The sediment surface layer active in the exchange of phosphate is rarely more than 5 cm thick in the Baltic Sea (Holm, 1978c).

Nitrogen is released from the sediments under both oxidizing and reducing conditions. As nitrogen is mainly coupled to organic matter, the exchange is dependent on the primary production and sedimentation rates. The release of nitrogen from the sediments is governed by the activity of bacteria (Engvall, 1978, 1980). Under reducing conditions, the activity of sulfate-reducing bacteria at the sediment-water interface is dependent on the available organic matter (both its quantity and quality) and the temperature (B&gander,

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The reducing processes in the sediments are delayed in areas within the photic zone because light influences algal oxygen production. Small basins with shallow depths can keep an oxidized surface sediment despite a heavy load of organic matter. However, the deep basin sediments in the Baltic Sea are strongly influenced by the halocline which obstructs oxygen diffusion to the bottom water. Therefore, the area of reduced sediments may increase below the halocline, thus increasing the release of phosphate and creating the possibility of increased production of organic matter.

Mortimer (1939, 1941) found that when iron occurs in the oxidized form, phosphorus is bound to iron compounds, whereas phosphorus is released when iron is

reduced. It has been assumed that the recent rise in the phosphorus level in the Baltic Sea has partly resulted from the release of phosphorus from an increasing area of anoxic sedimentary conditions (Fonselius, 1962). However, some phosphorus (up to 1 mg P per gram of dry sediment) is trapped in the sediment also under reducing conditions (e.g., Niemistö and Voipio, 1974).

Redox potential measurements have met criticism because of the undefined nature of the participating chemical reactions. Bågander and Niemistö(1978) found, however, a good correlation between the results of two separate methods used for sediment samples collected from 17 stations in the Baltic Proper and the Gulf of Bothnia.

Nonetheless, great difficulties are caused by two factors. Firstly, the sediment bed of the Baltic Sea is by no means horizontally homogeneous even in the larger basins. Secondly, the vertical stratification has such a fine structure that it is often practically impossible to collect samples representing one thin single layer. Real samples usually consist of several (micro) layers. The redox value measured is very sensitive to the presence or absence of the peripheral layer included in the samples.

Redox potential measurements are probably quite unimportant in studying the state of the water column. In sediment studies, however, they often yield a useful parameter giving information on the conditions prevailing during deposition. Hallberg (1974) suggested that the copper-to-zinc ratio in the Gotland Deep sediment should reflect redox conditions in the water during deposition.

An interesting question in the Baltic Sea has been

whether it is possible to discern the remains of stagnation conditions of the Baltic Sea in the past by studying redox potentials in dated sediment cores. Several cycles in the redox potential during the time period from 1970 to 1750 A.D. have been found (Ignatius et al., 1971; Niemistö and Voipio, 1974). The redox values recorded ranged from -70mV to -230mV in the Gotland Deep sediments. It is very difficult to say whether the general decreasing trend is caused by processes inside the sediments or whether it indicates any long-term trend in the hydrographic conditions. However, the maxima and minima evidently reflect hydrographic situations and/or production-degradation conditions during deposition. They show that the recent great variations are not unique in the history of the Baltic Sea but might rather reflect climatic variations, as suggested by Niemistö and Voipio (1974) and Hallberg (1974).

# Nutrients

Nutrients are elements functionally involved in the life processes of organisms. In chemical oceanography the term has been applied almost exclusively to phosphorus, nitrogen and silicon. Strictly speaking, most of the major elements of sea water are nutrient elements. So are also a large number of trace metals. Phosphorus, nitrogen and silicon occur in sea water in low concentrations and may therefore limit the primary production of phytoplankton. The major elements of sea water are present in large amounts and the concentrations are hardly influenced by phytoplankton growth (Spencer, 19'75).

## 5.1 Phosphorus

### 5.1.1 *Definition: Chemical speciation*

The most important phosphorus compounds in sea water are orthophosphates, commonly called inorganic or reactive phosphates, and a variety of organic phosphorus compounds which are generally not further differentiated. The latter are united under the term "organic phosphorus" and calculated as the difference between the total phosphorus and the inorganic phosphate.

### 5.1.2 *Properties and analytical methods*

The analysis of inorganic phosphate is based on the reaction of its ions with an acidified molybdate reagent to yield a phosphomolybdate complex. This complex can easily be reduced to molybdenum blue (Koroleff, 1976). The intensity of this colour is proportional to the phosphate concentration and can

be measured spectrophotometrically. Besides orthophosphate, low quantities of labile bound esters of phosphorus acids also form molybdenum blue. Therefore, the types of phosphorus determined by this method are called "reactive phosphate".

Organic phosphorus compounds can be converted into phosphate by different oxidation methods (Koroleff, 1972; Brüggmann and Wilde, 1975).

The lower limit of detection of inorganic phosphorus is about  $0.01 \mu\text{mol}/\text{dm}^3$  (Koroleff, 1976). The relative standard deviation at low levels ( $0.2 \mu\text{mol}/\text{dm}^3$ ) is about  $\pm 15\%$  and at high levels ( $2.8 \mu\text{mol}/\text{dm}^3$ ) about  $\pm 2\%$  (Koroleff, 1976).

It was shown at the Baltic Intercalibration Workshop, held in 1977 at Kiel with the participation of all countries surrounding the Baltic Sea, that the methods used for phosphate and total phosphorus analysis in the Baltic Sea States are sufficiently accurate and that data from different sources are comparable (Anon., 1977). The accuracy and precision of the analysis are  $\pm 0.05$  and  $0.03 \mu\text{mol}/\text{dm}^3$ , respectively, in the range  $0 - 2 \mu\text{mol}/\text{dm}^3$ .

### 5.1.3 General distribution

Phosphate distribution in the Baltic Sea is mainly governed by hydrographic conditions and biological processes, although long-term trends are also apparent. In winter, when primary production is limited by the low light intensity, phosphate is accumulated in the surface layer and reaches concentrations of  $0.2 - 0.4 \mu\text{mol}/\text{dm}^3$ \*) in the Baltic Proper. Higher values are

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\*)  $\mu\text{mole} = 31 \times 10^{-6} \text{ g phosphorus}$

found in the Belt Sea ( $0.5 - 0.7 \mu\text{mol}/\text{dm}^3$ ) and the Kattegat ( $0.4 - 0.6 \mu\text{mol}/\text{dm}^3$ ). The phosphate content in the surface layer of the Gulf of Finland in winter appears to be greater than in the Baltic Proper and is about  $0.5 - 0.7 \mu\text{mol}/\text{dm}^3$  (e.g., Nehring and Francke, 1976; Perttilä et al., 1980a), whereas values of only  $0.1 - 0.3 \mu\text{mol}/\text{dm}^3$  are reached in the Gulf of Bothnia (Voipio, 1976; cf. Fonselius, 1979). The lowest phosphate content is observed in the Bothnian Bay. The reason is probably in the precipitation of phosphate by trivalent iron, which is discharged in relatively high concentrations by rivers in this area (Voipio, 1969a).

In the oxic deep water of the central basins of the Baltic Sea, the phosphate concentrations are between  $2 - 3 \mu\text{mol}/\text{dm}^3$ , increasing to over  $6 \mu\text{mol}/\text{dm}^3$  under anoxic conditions. Phosphate concentrations are lower in the deep water of the Gulf of Bothnia and the Gulf of Finland and in the relatively shallow western sub-areas of the Baltic Sea, where restricted water exchange regularly occurs. Phosphate concentrations are found between  $0.5$  and  $1.0 \mu\text{mol}/\text{dm}^3$  in the Kattegat and the Gulf of Bothnia,  $1 - 2 \mu\text{mol}/\text{dm}^3$  in the Gulf of Finland and the Arkona Sea and can rise to  $2 - 3 \mu\text{mol}/\text{dm}^3$ , especially in late summer in the deep water of the Belt Sea. Figure 25 shows an example of dissolved inorganic phosphate concentrations in a longitudinal section of the Baltic Sea.

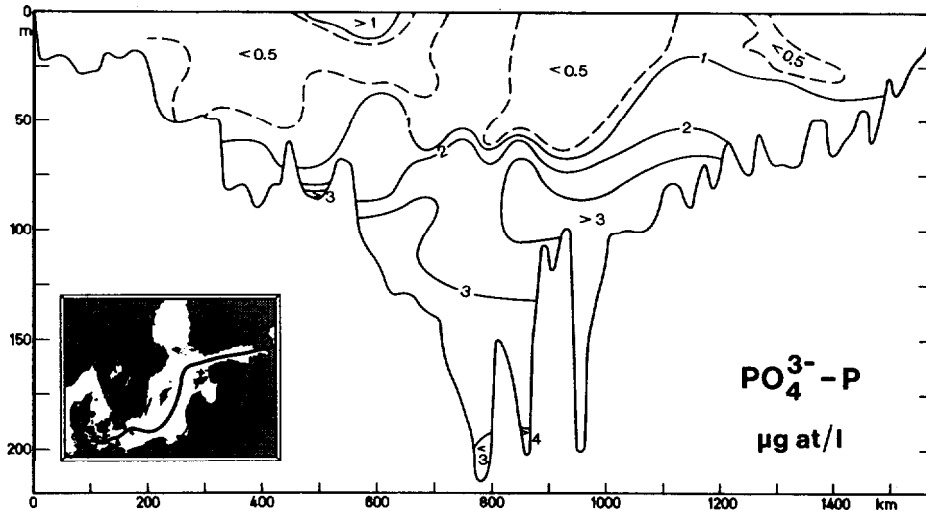


Figure 25. *Longitudinal section of the Baltic Sea showing dissolved inorganic phosphate concentrations in August 1969 (from Grasshoff, 1975).*

The levels of total phosphorus were about 0.15, 0.25 and 0.35  $\mu\text{mol}/\text{dm}^3$  in surface water samples collected from the Bothnian Bay, the Bothnian Sea and the Gulf of Finland, respectively, in July - August during the years 1966 - 1975. The last-mentioned value corresponds rather closely to the level in the Baltic Proper in late summer. In the deep layers, the total phosphorus concentration is only slightly higher than the phosphate concentration.

In the surface waters of the Baltic Proper, the concentration of organic phosphorus is about 0.3  $\mu\text{mol}/\text{dm}^3$  (Jurkovskij et al., 1976; Nehring and Brüggmann, 1977; Perttilä and Tervo, 1979). Beneath the halocline, the concentration decreases to about half the surface value and can drop to zero under anoxic conditions. Similar vertical distributions have been observed in the Kattegat and the Gulf of Finland (cf. Perttilä et al., 1980a). In the Gulf of Bothnia, the organic phosphorus concentration is lower and lies between 0.15 and 0.2  $\mu\text{mol}/\text{dm}^3$  (Perttilä and Tervo, 1979; Pietikäinen et al., 1978).

The phosphorus concentrations in areas affected by effluents from major urban and industrial centres can be substantially higher. In coastal waters and estuaries strongly influenced by river discharges, considerably higher values are also frequently observed.

#### 5.1.4 *Seasonal and long-term variations*

Nutrients are consumed during the spring development of the phytoplankton. Depending on the meteorological conditions and the stratification of the water column, this process starts at the beginning of March in the Belt Sea, reaching the Arkona Sea and the Gdańsk Basin at the end of March and the Bornholm Sea in the first half of April, and finally the Gotland Basin and the Gulfs of Bothnia and Finland at the end of April and the beginning of May (Kaiser and Schulz, 1976). Since vertical exchange is greatly restricted by the halocline and, during the warm season, by the thermocline, the phosphate concentrations of the surface layer decline to below  $0.1 \mu\text{mol}/\text{dm}^3$ , with values in the Baltic Proper often reaching the limit of analytical detection.

The thermocline is destroyed during the autumn as a result of cooling and increased turbulent mixing. Consequently, nutrients can enter the surface layer again but can no longer be fully utilized in photosynthesis due to the declining light intensity. The phosphate content gradually approaches the winter level as the season proceeds.

The deep water<sup>\*)</sup> of the Baltic Proper is dominated by episodic changes which are closely related to the inflow of highly saline water across the Darss Sill. During the periods of stagnation, which are especially

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\*) Deep water is here defined as the water mass below the halocline.



characteristic for the deep water of the Bornholm and Gdańsk Basins as well as for the eastern, northern and western Gotland Basins and often last for several years, considerable quantities of phosphate are accumulated below the halocline as a result of the biochemical destruction of organic matter. Under anoxic conditions (see Chapter 4), precipitated phosphate is also released from the bottom. According to Holm (1978a), during the stagnation period in 1975, about  $1.7 \text{ g P/m}^2$  was exchanged in the Bornholm Basin. The chemical reduction of iron phosphate plays an important role in this connection (see Figure 26) (Koroleff, 1968; Fonselius, 1968, 1969b; Holm, 1978b; Holm and

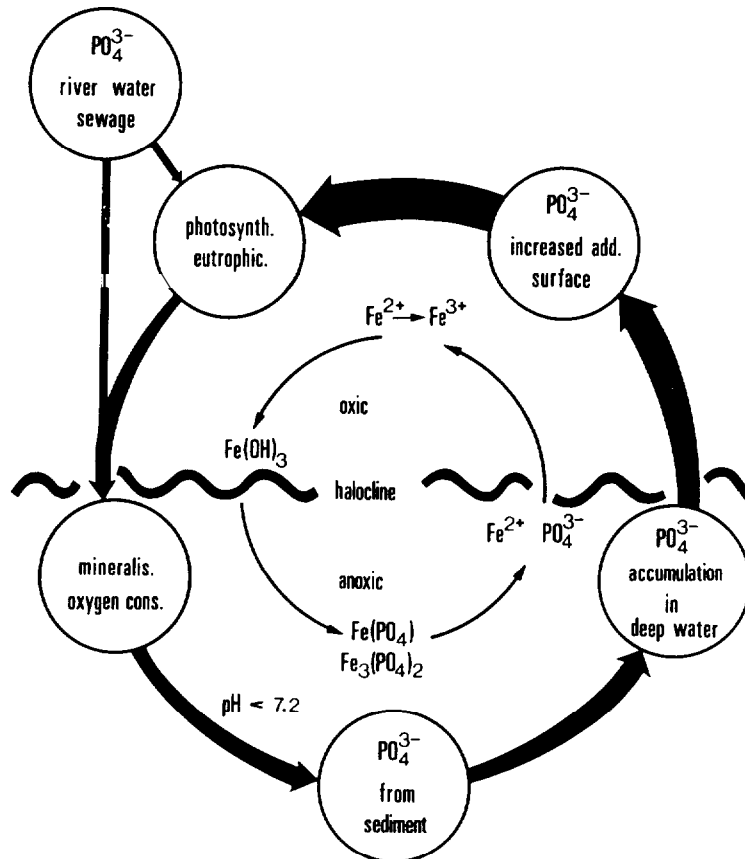


Figure 26. Schematic diagram of the cycling of phosphorus between the aerobic and anaerobic regimes in the Baltic Sea (from Grasshoff, 1975).

Lindström, 1978). Other important factors are the composition of the sediments and the pH value, as well as the depth in which the sediments are deposited (Holm, 1978a, 1978b).

Under anoxic conditions, the phosphate concentration increases to over  $6 \mu\text{mol}/\text{dm}^3$ . In the near-bottom water layer of the Gotland Deep, this increase correlates closely with the decrease in oxygen (Matthäus, 1973) and the increase in hydrogen sulfide (Gieskes and Grasshoff, 1969). Increasing phosphate concentrations are also correlated with decreasing pH values (Fonselius, 1967, 1969b).

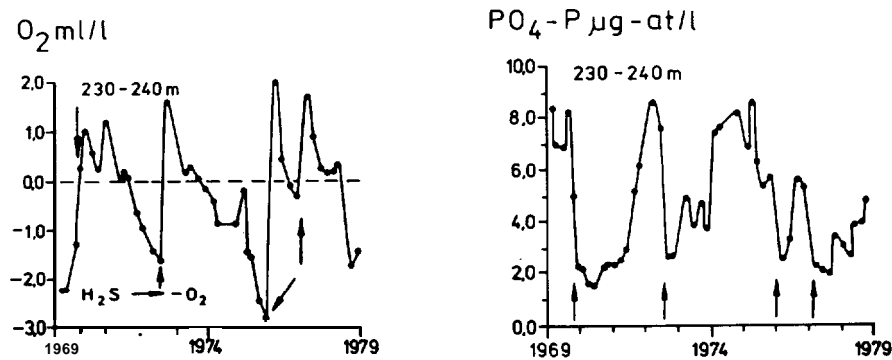


Figure 27. Changes in oxygen (left) and phosphate (right) concentrations in the bottom water layer of the Gotland Deep. (Hydrogen sulfide is expressed as negative oxygen equivalents. The beginning of the water renewal is marked by arrows.) (Nehring, original figure).

Inflows of highly saline water which lead to advective renewal of the bottom water layers in the Baltic Sea partly reactivate the phosphate resources accumulated in the deeps and transport them into the euphotic layer. Due to the return to oxic conditions, however, some of the phosphate is precipitated as iron phosphate and returns to the bottom. Figure 27 shows the changes in the phosphate concentration as conditions alternate between oxic and anoxic.

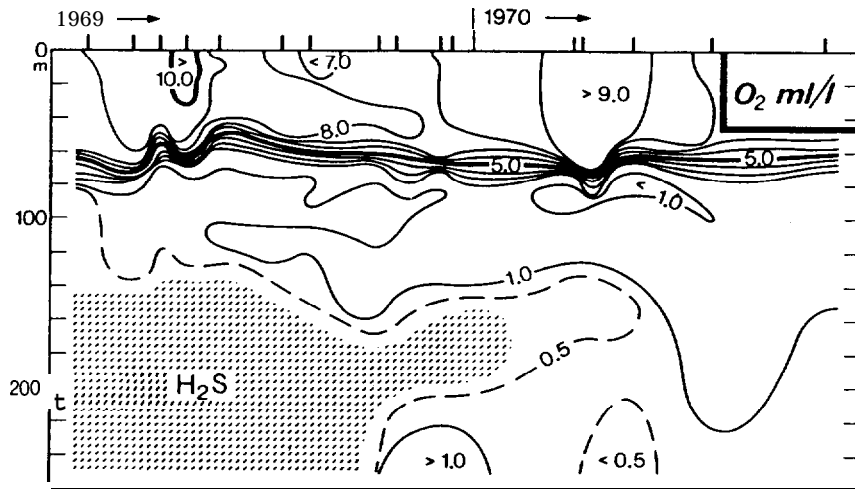


Figure 28. Medium-term variations in the oxygen concentrations in the Gotland Deep from January 1969 to November 1970 (from Nehring and Francke, 1971).

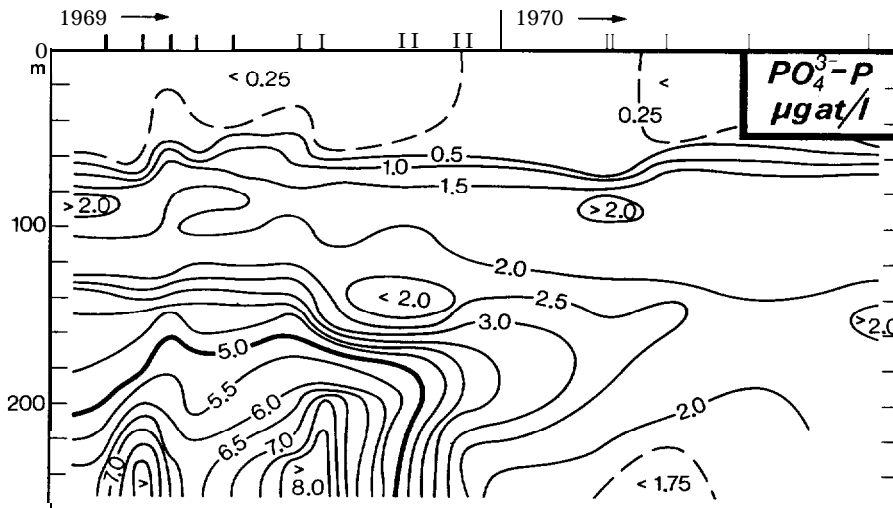


Figure 29. Variations in the dissolved phosphate concentrations in the Gotland Deep from January 1969 to November 1970 (from Nehring and Francke, 1971).

In Figures 28 and 29 the relationship can be seen between the variations in the oxygen concentrations and the dissolved phosphate concentrations in the Gotland Deep in 1969 and part of 1970.

### 5.1.5 Relationships with other nutrients and elements

The atomic ratio between inorganic nitrogen ( $\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ ) and phosphate phosphorus or between nitrate nitrogen and phosphate phosphorus, which corresponds to the composition of marine organisms, is about N:P = 16:1 in the oceans (Fleming, 1940). In the Baltic Sea it is characterized by substantial variations in space and time (Nehring et al., 1969; Gieskes and Grasshoff, 1971; Sen Gupta, 1973; Fonselius, 1976c). On occasions there is a higher ratio as, for example, in the Bothnian Bay (Fonselius, 1979). Usually, however, the ratio is lower. In the mixed winter surface layer of the central Baltic, the atomic ratio of nitrate to phosphate is about 6 to 7:1, whereas the ratio of nitrate, nitrite and ammonia to phosphate is 7 to 8:1 (Nehring, 1980). In the Belt Sea and the Gulf of Finland, it is higher but does not reach the oceanic ratio.

In the deep water, the inorganic nitrogen to phosphate ratio is about 2 to 4:1, decreasing under anoxic conditions to 1:1 and below (Nehring, 1974; Fonselius, 1976c). Only ammonia is stable under anoxic conditions. As previously mentioned, phosphate is released from the bottom under such conditions.

In contrast, the relation between phosphate and silicate is linear (Fonselius, 1969b, 1977; Gieskes and Grasshoff, 1971), thus indicating that they are mineralized from the organic matter at a constant ratio. Under anoxic conditions, however, the release of phosphate from the bottom may cause deviations.

As a result of chemical reactions associated with the changes from anoxic to oxic conditions in the deep water, there is no constant relation in the Baltic Sea between the Apparent Oxygen Utilization (AOU) and the phosphate concentration (Gieskes and Grasshoff,

1971). Above the intermittently anoxic layer, a ratio of AOU:P = 378:1 has been found (Sen Gupta, 1973), which is greater than the ratio of 276:1 observed in the oceans (Richards, 1965b).

The composition of the organic matter in the Baltic Sea differs considerably from the atomic ratio found in the oceans, which on average is C : N : P = 106 : 16 : 1 (Fleming, 1940). A mean ratio of roughly C : N : P = 2000 : 80 : 1 has been found in unfiltered Baltic Sea water samples (Perttilä and Tervo, 1979). The large surplus of organic carbon and nitrogen is attributed to humic substances (Sen Gupta, 1973), which are poor in phosphorus. The C : N : P ratio in the Baltic Sea differs in space and time and is probably affected by plankton development. There are, however, few differences between the chemical composition of Baltic plankton and that of oceanic organisms (Sen Gupta and Koroleff, 1973; Voipio, 1973a, 1973b).

#### 5.1.6 *Trends in the phosphorus content*

Increasing phosphate concentrations have been observed for several years in the mixed winter surface layer of the Baltic Proper (Fonselius, 1976b; Nehring, 1979; Jurkovskij, 1980). This increase is especially pronounced in the southern part of the eastern Gotland Basin, but has also been observed in the Arkona, Bornholm and Gdańsk Basins. The mean phosphate content of the mixed winter surface layer has shown a significant increase since 1969, as can be seen from Figure 30 for the eastern Gotland Basin. Taking this basin and the Arkona, Bornholm and Gdańsk Basins into account, the rate of increase was about 0.04  $\mu\text{mol}/\text{dm}^3$  per year from 1969 to 1978 (Nehring, 1979).

In the Gulf of Bothnia, in contrast, some studies appear to show a declining trend from 1966 to 1977 (Pitkänen, 1978), if the total phosphorus concentration is used as a basis. No clear trend has been observed in the phosphate concentration in the surface layer of the Gulf of Finland (Perttilä et al., 1980a).

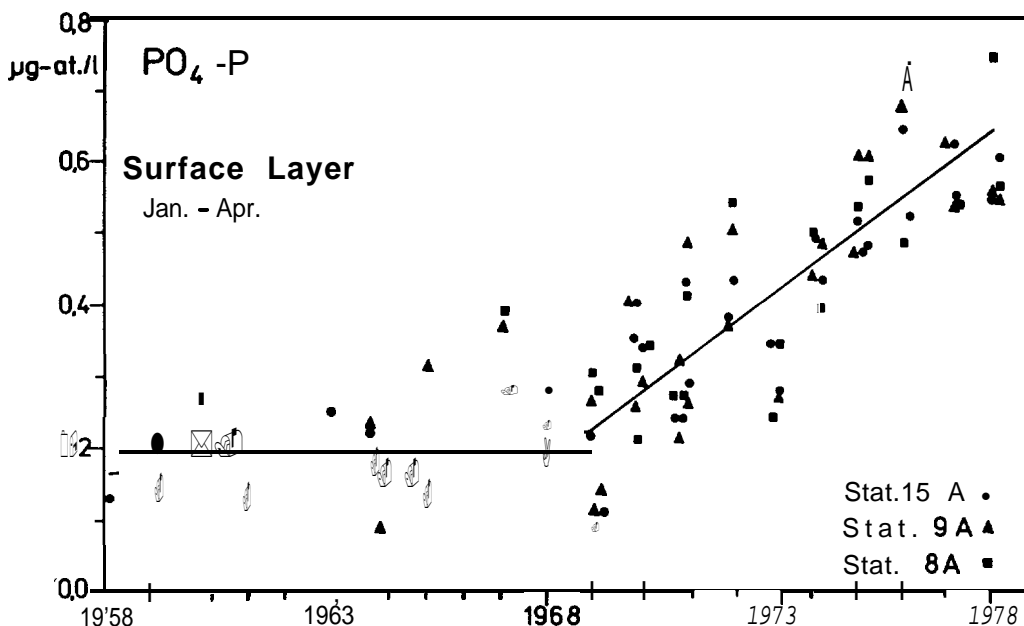


Figure 30. Distribution of *mean phosphate concentrations in the mixed winter surface layer of the eastern Gotland Basin from 1958 to 1978 (from Nehring, 1979).*

The increase in the phosphate content observed in the mixed winter surface layer of the Baltic Proper from 1969 to 1978 correlated closely with an increase in salinity (see Figure 31; cf. Nehring, 1979). Mixed Kattegat water generally intruded to a greater extent into the intermediate layers of the Baltic Sea during this period. The intensification of the vertical exchange induced an upward mass transport which resulted in an increased nutrient and salt flow into the surface layer of the Baltic Sea.

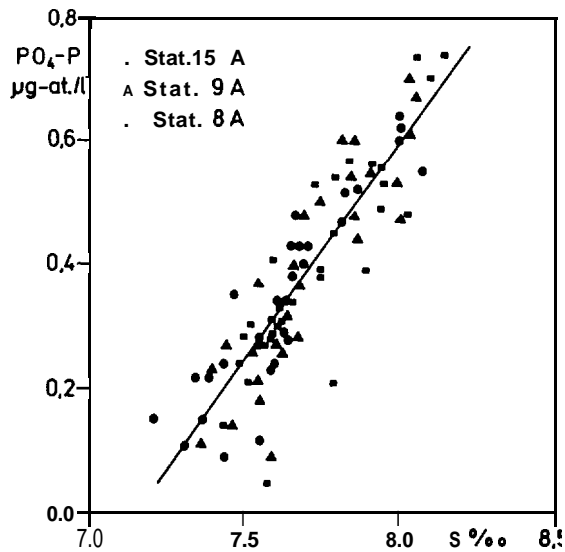


Figure 31. Mean concentrations of phosphate versus salinity in the mixed winter surface layer in the eastern Gotland Sea from 1964 - 1968 (from Nehring, 1979).

In this connection, it must be noted that a substantial accumulation of phosphate has taken place in the deep water of the central Baltic basins in recent decades, and that this water is partially mixed into the surface layer by hydrographic processes. Therefore, the surface water contains increasing amounts of phosphate. The phosphate content at a depth of 100 m in the Gotland Deep rose from about  $1 \mu\text{mol}/\text{dm}^3$  in 1958 to over  $2.5 \mu\text{mol}/\text{dm}^3$  in 1978 (Nehring, 1979). This increase, which on the whole is linear, as shown in Figure 32, is subject to superimposed variations associated with the stagnation and renewal of the deep water. Due to the alternation of anoxic and oxic conditions, these variations are much more intense in the near-bottom water layers (see Figure 33) and mask the long-term trend of phosphate accumulation.

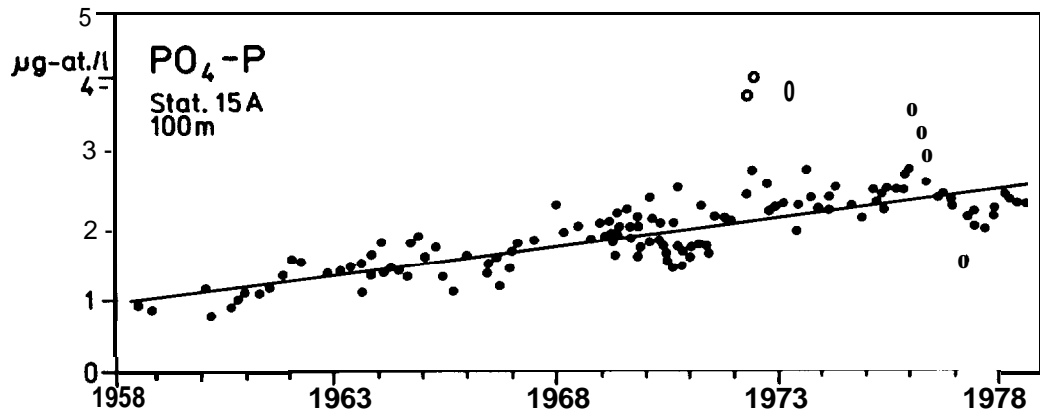


Figure 32. Increase in mean phosphate concentrations at a depth of 100 m in the Gotland Deep from 1958 to 1978 (from Nehring, 1979).

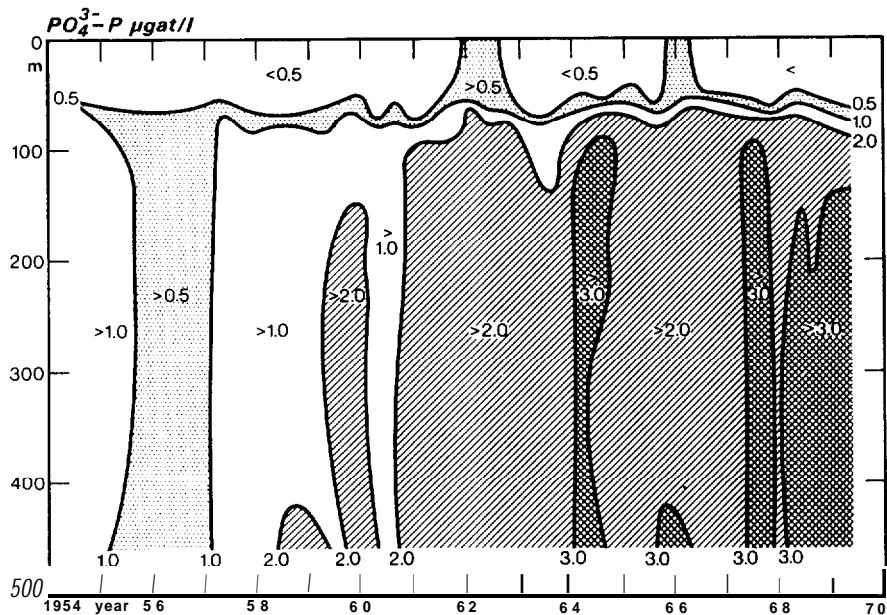


Figure 33. Isopleth diagram of phosphate concentrations in the Landsort Deep from 1954 - 1970 (from Fonselius, 1969a).

Phosphate accumulation in the deep water has also been observed at other stations in the Gotland Basin (Fonselius, 1969b). In one case, the phosphate content rose from about  $1 \mu\text{mol}/\text{dm}^3$  to  $3-4 \mu\text{mol}/\text{dm}^3$  in the course of 10 - 15 years. Concerning long-term fluctuations in the Bornholm and Gdańsk Deeps, the situation is not so clear. The increase in the mean con-



centration of phosphates in the Gotland Deep (see Figure 32) is in good agreement with the increase observed in the Bornholm and the Gdańsk Deeps, beginning in the early 1960s (see Figure 34), but linearity is not so clear and periodic fluctuations are most distinguishable.

On the other hand, there is some information which indicates that the concentrations of inorganic and total phosphorus have not increased in the Gulf of Finland (cf. Pertillä et al., 1980a; Pitkänen and Malin, 1980). Information also indicates that no long-term phosphate accumulation has been observed in the deep water of the Gulf of Bothnia (Pietikäinen et al., 1978).

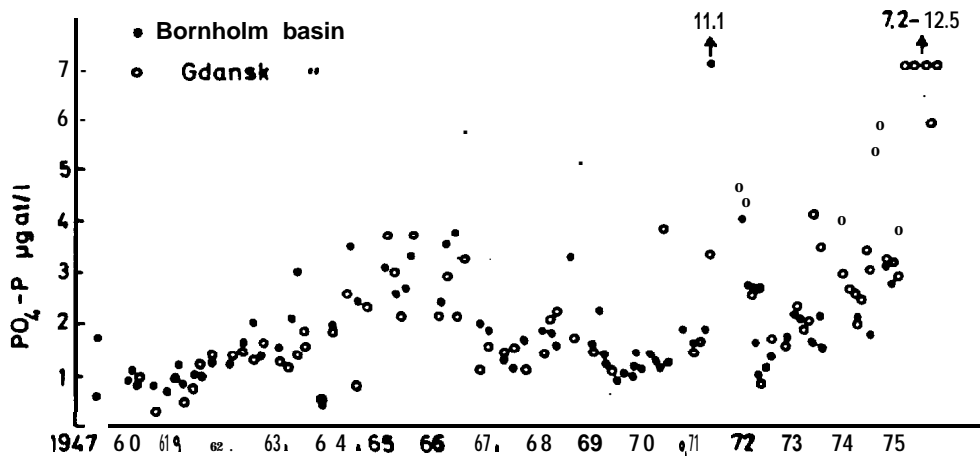


Figure 34. Long-term fluctuations of mean phosphate concentrations in the deep water of the Bornholm Deep (70 m - bottom) and the Gdańsk Deep (80 m - bottom) during 1947 - 1976 (from Majewski et al., 1976).

As with phosphate phosphorus, the total phosphorus concentration also shows in many cases a clearly increasing trend. From the pollution point of view, the 'situation in the surface layer is very important. The first report regarding the increase in the total phosphorus concentration in the surface water of the Gotland Deep was produced by Fonselius (1976b). Later,

Perttilä et al. (1980b) have shown a statistically very significant increase in the total phosphorus content in the northern Baltic Proper, while no clear trend has been observed in the Gulf of Finland and the Gulf of Bothnia (Perttilä et al., 1980a, 1980b; Pietikäinen et al., 1978; Pitkänen and Malin, 1980), excluding a slight decreasing trend from 1966 - 1977 in the samples collected in the wintertime from the Gulf of Bothnia (Pitkänen, 1978).

#### 5.1.7 *Input and mass balance*

At present it is not possible to say with certainty whether the accumulation of phosphate observed in the deep water of the central basins is mainly due to natural causes or is a consequence of increasing pollution. According to studies undertaken by ICES (1977), roughly 33 000 t of phosphorus are discharged via domestic and industrial wastes every year into the Baltic<sup>\*</sup>). This input is either direct or discharged by rivers. Deliberate dumping activities of industrial wastes and sewage sludge played no significant role from 1967 to 1979. The river input was calculated for the second half of 1975 and for 1976 from the total phosphorus concentration and the mean water discharge of the rivers flowing into the Baltic (Voipio and Tervo, 1977, 1979) in connection with the IHP/IHD project. The calculated values were 21 000<sup>\*\*</sup>) and 31 000 t/y, respectively.

Ship-generated wastes such as garbage and sewage also contribute to the pollution. However, no reliable estimates are available.

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\*) The following particulars for the mass balance of phosphorus refer to the Baltic excluding the Kattegat.

\*\*\*) The value for the second half of 1975 has been doubled.

The contribution by atmospheric fallout of phosphorus into the Baltic Sea is uncertain. Although wet deposition is slight on average, too little importance appears to have been attached in the past to dry deposition. It is estimated that the atmospheric input to the Baltic Sea is roughly 9 000 t/y (Nehring and Wilde, 1979). The amount of phosphorus transferred to the atmosphere by aerosols is probably slight and can be ignored in a mass balance.

The annual deposition of phosphorus in the sediments of the Baltic Sea is estimated at about 22 000 t (Voio-  
pio and Niemistö, 1979). In regions with temporary anoxic conditions in the deep water, on average roughly 7 000 t is released from the bottom per year (Holm, 1978a).

Inflow through the Danish Straits brings 4 000 t (Voio-  
pio, 1969a) to 10 000 t (Fonselius, 1969b) of phosphorus into the Baltic Sea every year, while 10 000 t or 11 000 t are removed with the outflowing water.

Currently, about 800 000 t of fish are caught annually in the Baltic Sea (Anon., 1978a). The phosphorus content of fresh fish depends on the species, age and condition (fat content) of the fish. A mean value of 0.5 % can be used for calculations (Schober, 1979), so that fisheries remove about 4 000 t of phosphorus from the Baltic Sea annually.

An earlier mass balance estimate for phosphorus showed that the net input to the Baltic Sea was between 15 500 and 44 000 t/y (ICES, 1977). This balance is supplemented on the basis of new knowledge in Table 7 (see also Figure 35). Where different figures were available, the less favourable figure was used.

Table 7. *Mass balance of phosphorus in the Baltic Sea*

Input	Phosphorus (t/y)
Domestic and industrial wastes	33 000
Dumping	0
Atmospheric fallout	g 000
Danish Straits	10 000
Natural river input	3 000
Ship-generated wastes	?
Release from sediments	7 000
Sum	62 000
output	Phosphorus (t/y)
Danish Straits	10 000
Sedimentation	22 000
Fisheries	4 000
Aerosols	0
Sum	36 000
Net supply	26 000

The figures quoted above are in some cases very uncertain. However, the calculated net supply is rather too low than too high. This value nearly corresponds to the input by domestic and industrial wastes, thus indicating one important reason for the increasing phosphate accumulation in the deep water of the central Baltic basins.

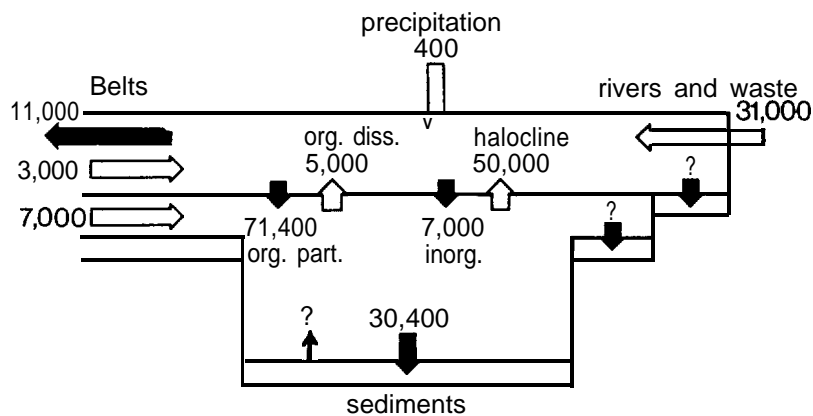


Figure 35. *Phosphorus balance of the Baltic Proper under aerobic conditions (in tonnes P per year) (from Grasshoff, 1975).*

The phosphate resources in the deep water of the Baltic Proper have been estimated at 300 000 - 400 000 t (Dybern, 1972). The annual net input of 26 000 t is about 6 - 8 % of this amount.

#### 5.1.8 Summary

- Current methods of analyzing phosphate and total phosphorus have the required accuracy. Data from different sources are comparable.
- In contrast to the surface layer where seasonal changes predominate as a result of plankton development, phosphate concentrations below the haloclines are related to the inflow of highly saline water over the Darss Sill. In the winter surface layer of the Baltic Proper, the phosphate concentration increases to 0.2 - 0.4  $\mu\text{mol}/\text{dm}^3$  and reaches 0.7  $\mu\text{mol}/\text{dm}^3$  in the western Baltic and the Gulf of Finland and 0.1 - 0.2  $\mu\text{mol}/\text{dm}^3$  in the Gulf of Bothnia. During the summer, the phosphate concentration can decline to the limit of analytical detection.
- Phosphate concentrations in the deep water lie between 0.5 and 4  $\mu\text{mol}/\text{dm}^3$ . Under anoxic conditions, values exceeding 6  $\mu\text{mol}/\text{dm}^3$  can occur.

- The organic phosphorus concentration is 0.15 - 0.3  $\mu\text{mol}/\text{dm}^3$  in the surface layer and declines with increasing depth.
- The phosphate concentrations in the surface layer and in the deep water of the central Baltic follow long-term trends. In the mixed winter surface layer, phosphate has increased at a mean annual rate of 0.04  $\mu\text{mol}/\text{dm}^3$  between 1969 and 1978. The increase in phosphate correlates closely with the increase in salinity and thus with hydrographic processes.
- The total phosphorus concentrations in surface water have also shown a clearly increasing trend in the Baltic Proper.
- A substantial accumulation of phosphorus has been taking place in the deep water since the 1950s. In the course of 10 - 20 years, the phosphate concentration rose from about 1  $\mu\text{mol}/\text{dm}^3$  to 2.5 - 4  $\mu\text{mol}/\text{dm}^3$ .
- A mass balance estimate of the phosphorus in the Baltic Sea (excluding the Kattegat) revealed an annual net supply of 26 000 t resulting mainly from man-made wastes.
- At present it is not possible to state with certainty whether the phosphate accumulation observed in the deep water of the central basins of the Baltic Sea is due primarily to natural causes or is a consequence of pollution.

## 5.2 Nitrogen

In quantitative terms, nitrogen is not one of the major components of sea water, but because of its significance for life in the sea, it is one of the important elements. Nitrogen occurs in a wide variety

of chemical combinations, organic and inorganic, and may exist in either reduced form (as in ammonium and in most organic substances) or in an oxidized state (as in nitrate and nitrite).

The most abundant form of nitrogen in the sea is nitrogen gas, which is chemically inert under normal conditions, but can be utilized as a nutrient by a small group of blue-green algae and micro-organisms. Sea water is in equilibrium with the atmosphere with respect to nitrogen gas and its solubility is determined entirely by physical factors. All other forms of nitrogen are dissolved or suspended in sea water in small quantities and the abundance, distribution, and chemical composition of each individual compound, as well as their transformations, are primarily determined by the biological activity of marine organisms.

#### 5.2.1 *Analytical chemistry of nitrogen in the sea*

The analysis of nitrogen compounds in sea water has long been hampered by methods of low specificity, sensitivity, and reproducibility. Of early methods, only the sensitive diazo reaction method for nitrite and the Kjeldahl method for particulate organic nitrogen are still in use. The lack of confidence in older data is unfortunate since it restricts our possibilities to determine long-term trends to detect possible adverse effects of human activities. We shall here mainly discuss the analysis of nitrogen compounds which are regularly monitored in the Baltic Sea and which were subject to evaluation during the 1977 Baltic Intercalibration Workshop in Kiel, FRG (see Anon., 1977).

a. *Inorganic nitrogen*

Ammonium is present in the Baltic, Sea in variable concentrations and rarely exceeds  $1.5 \mu\text{mol}/\text{dm}^3$ . The most reliable method for its determination is a variant of the Richards and Kletsch (1964) indophenol method described by Koroleff (in Carlberg, 1972). However, as samples are easily contaminated with ammonia from various sources, and as the method also requires a good deal of practice to yield reproducible results, data obtained by different laboratories (or by different analysts) are not always comparable. As much as 30 % relative error was obtained during the Kiel Workshop. The lower limit of detection is about  $0.05 \mu\text{moles ammonium-N}/\text{dm}^3$ .

Nitrate is the most abundant form of inorganic nitrogen except in surface waters during the productive period. In the Baltic Sea, its concentration rarely exceeds  $10 \mu\text{mol}/\text{dm}^3$ . Nitrate is analyzed as nitrite after reduction in a cadmium-mercury (or cadmium-copper) column (Wood et al., 1967). The method has good reproducibility with a lower limit of detection of about  $0.05 \mu\text{moles nitrate-N}/\text{dm}^3$ .

Nitrite occurs in small concentrations ( $0.02 - 0.5 \mu\text{mol}/\text{dm}^3$ ) in the Baltic Sea and is an important indicator of certain biological activities. A reliable and very sensitive method is the old Griess reaction adapted for sea water by Bendschneider and Robinson (1952). The same reaction is used for nitrate after its reduction to nitrite. The method has a high precision and permits the determination of as little as  $0.01 \mu\text{mol}/\text{dm}^3$ .

b. *Organic nitrogen*

Urea has only recently been investigated in the Baltic Sea and is interesting because of its biological origin and potential importance as a plant nutrient



when the inorganic forms of nitrogen have been exhausted. The concentration range of urea is similar to that of ammonium. A preferred and apparently reliable method is a modification of the Newell et al. (1967) diacetylmonoxim method worked out by Koroleff (in Grasshoff, 1976b).

*Dissolved organic nitrogen.* The total fraction of dissolved organic nitrogen can be determined by subtraction from total nitrogen (see below) or by UV-oxidation according to Armstrong et al. (1966). In addition to urea (Valderrama, 1979), amino acids, and a variety of other natural products, this fraction contains lignin and humic substances (Nyquist, 1979a) and probably the bulk of other nitrogen-containing pollutants in the Baltic Sea. Methods for determining total amino acids, individual amino acids, amino sugars and uronic acid are well developed and sufficiently precise.

*Particulate organic nitrogen,* the bulk of which consists of living and dead plankton organisms and detritus of various origins, is usually determined by the Kjeldahl method or by automated CHN-analysis after filtration through glass or membrane filters. As with the dissolved organic nitrogen, the particulate fraction has not been analyzed regularly in the Baltic Sea, but more detailed information on its distribution and abundance would be of considerable interest in assessing the pollution situation.

### c. *Total nitrogen*

In the determination of total nitrogen, it has become the practice to use the wet oxidation method with persulfate as an oxidant (Koroleff, 1969). However, the Intercalibration Workshop in Kiel found that results

obtained by this method showed too much variation between parallels and between laboratories for the method to be considered reliable. Total nitrogen (together with total phosphorus) has been determined on a regular basis by some groups monitoring the Baltic Sea. An examination of their data from vertical profiles, different areas, and through annual cycles does not show any meaningful trends. Until a safer method has been found, it seems a waste of time to carry out total nitrogen analysis.

For details of the methods referred to above, see the manuals edited by Carlberg (1972), Strickland and Parsons (1972), and Grasshoff (1976).

#### 5.2.2 *Previous reviews and important reports*

A comprehensive study of the chemistry of nitrogen in the Baltic Sea was made by Sen Gupta in 1973. In the report, Sen Gupta discusses much of the earlier work done on nitrogen and phosphorus and has listed a number of useful references. Aspects of the nitrogen status of the Baltic Sea have also been discussed by Grasshoff (1975) and, most recently, by Fonselius (1978) in relation to the productivity in the Baltic Sea.

The present report is based mainly on data from the extensive Hydrographical Reports from the Baltic Sea published biannually by the Swedish Fisheries Board, Gothenburg, Sweden. Time has not permitted the comparison of these sets of data with hydrographic data collected by other national groups.

#### 5.2.3 *Distribution Of nitrogen in the Baltic Sea*

In addition to the effects of physical processes, the distribution of the various forms of nitrogen and their transformations are more specifically controlled

by such factors as light, dissolved oxygen, and the availability of energy-rich organic matter.

a. *Vertical and seasonal distribution*

Since many of the biological nitrogen-transforming processes take place within well-defined strata in the water column, it is practical to discuss the vertical distribution of nitrogen in terms of horizontal zones (see Figure 36).

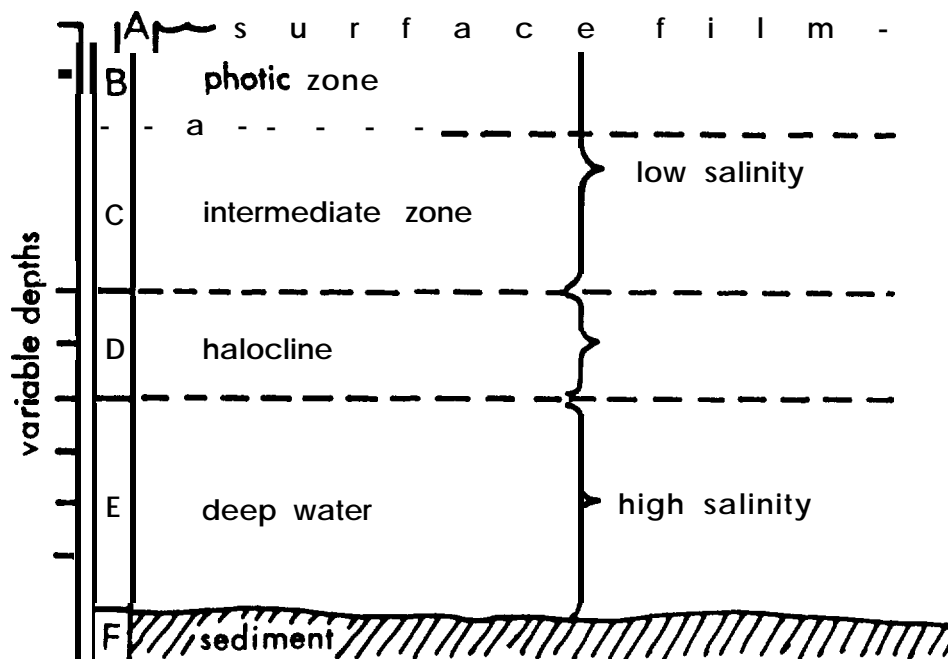


Figure 36. *Biological and physical zonation of the water column of the Baltic Sea (Gundersen, original figure).*

Zone A is the surface film through which gases like molecular nitrogen and oxygen are exchanged between the atmosphere and the water. No investigations seem to have been carried out on the properties of the surface film in the Baltic Sea although this important interface plays a significant role. Frequently, large

areas of the Baltic Sea are covered with dust and debris, oil slicks, and other floating matter and seasonally also with blankets of coniferous and other pollen, and remains from algal blooms. It can be predicted that zone A from time to time will contain significant amounts of particulate nitrogen-containing matter as well as nitrogen-containing fat-like materials (lipoproteins, amines, etc.).

Zone B is the photic zone in which photosynthetic processes in planktonic algae, benthic algae, seagrasses, etc. take place. The depth of this zone in the Baltic Sea is variable with season and the distance from land, but in general the zone extends to 10 - 20 m below the surface. The photic zone is always well oxygenated and sometimes supersaturated due to the rapid heating of the surface water in the spring and early summer, but also due to photosynthetic oxygen production. The distribution of nitrogen in the photic zone is to a large extent controlled by light, temperature, and mixing processes, and, therefore, undergoes distinct seasonal variations. Figure 37 shows the appearance and disappearance of nitrate and nitrite in the three major parts of the Baltic Sea during the period 1974 - 1978. Within one and the same region (Baltic Proper, Bothnian Sea, Bothnian Bay), the patterns are nearly identical with only small quantitative differences.

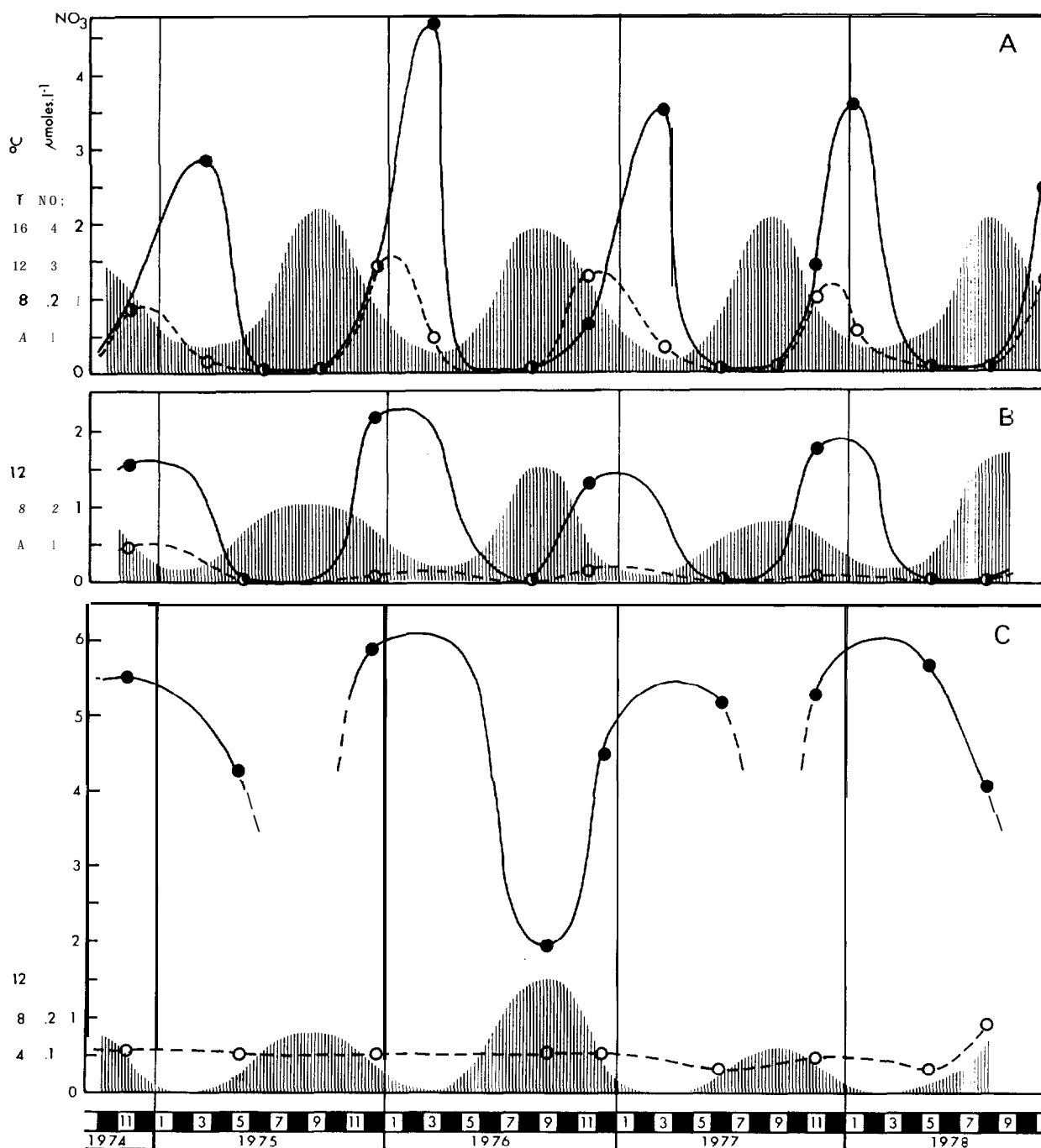


Figure 37. Temporal changes in temperature (hatched areas), nitrate (full-drawn lines), and nitrite (broken lines) in the photic zone (0-20 m) from 1974-1978. (A) Baltic Proper, station BY 9 (Klaipeda); (B) Bothnian Sea, station MS 8; (C) Bothnian Bay, station F 8. (Gundersen, original figure).

Remarks: The low number of observations (stations) in B and C, and particularly the lack of observations in late winter, makes the positioning of the peaks and the estimation of true peak heights uncertain. The maximum concentrations of nitrate and nitrite, especially in the Bothnian Sea (B), presumably are a good deal higher than the figure shows. This is indicated by the considerably higher concentrations of nitrate (but not of nitrite) in November-December compared with those in the Baltic Proper (A) during these months.

The concentrations of both of these nutrients increase rapidly in the late fall. They appear simultaneously in the water but, whereas the nitrite reaches its maximum concentration by mid-winter and then falls off, the nitrate concentration continues to increase and peaks shortly before the spring bloom in March. These events are repeated with striking regularity year after year (see also Sen Gupta, 1973, and Fonselius, 1978).

The sudden vernal outburst of phytoplankton production taking place in March - May at the different latitudes results in a rapid and complete exhaustion of the inorganic nitrogen. From May through September the concentration of nitrate and nitrite is near zero. The nitrogen is now contained in particulate organic form in the planktonic and other organisms which make up the food web of the upper waters. As no more nitrate is formed during the summer months, the sustenance of primary production is dependent on the recycling of nitrogen via ammonium, urea, and perhaps amino acids.

The concentration of ammonium in the photic zone during the summer is variable and usually below 0.3 - 0.4  $\mu\text{mol}/\text{dm}^3$ . Accumulations of as much as 0.5 - 1.0  $\mu\text{mol}/\text{dm}^3$  are occasionally observed. Urea also occurs in amounts similar to those of ammonium. Valderrama (1979) reported urea concentrations from 0.37 - 0.42  $\mu\text{mol}/\text{dm}^3$  in the summer and from 0.25 - 0.30  $\mu\text{mol}/\text{dm}^3$  in the winter in the Baltic Proper. The fluctuations in urea concentration correlate with fluctuations in zooplankton abundance. Closer to land (Bay of Finland and Hanö Bay), somewhat higher concentrations (**0.40** - 0.50  $\mu\text{mol}/\text{dm}^3$ ) were interpreted as effects of agricultural runoff from land.

Zone C is also characterized by low salinity water but is below the limit of photosynthetic production. Typical for this zone, which extends down to the halocline, are regenerative processes in which organically bound nitrogen (particulate and dissolved) is continuously being mineralized with the formation of ammonium. That such processes occur is also evident from the oxygen distribution which usually shows some undersaturation during the productive season. The seasonal fluctuations of nitrate and nitrite, which were evident in zone B, are also seen in zone C. From October to March, zones B and C are well mixed due to cooling of the surface water, instability and thermohaline convection. Zone C may extend as far down as 70 m during certain years.

Zone D is identical with the halocline and is the transition zone between the low salinity upper water and the higher salinity deeper water of the Baltic Sea. The halocline region is extremely stably stratified, thus considerable vertical fluctuations due to internal waves can occur, but turbulence and hence mixing, if it occurs, are very intermittent. This zone appears to be a zone of high biological activity, which is reflected in a variety of biological and chemical observations. Its depth is usually positioned within the interval 40 to **80** metres, with **50** to **70** metres as the most frequent position.

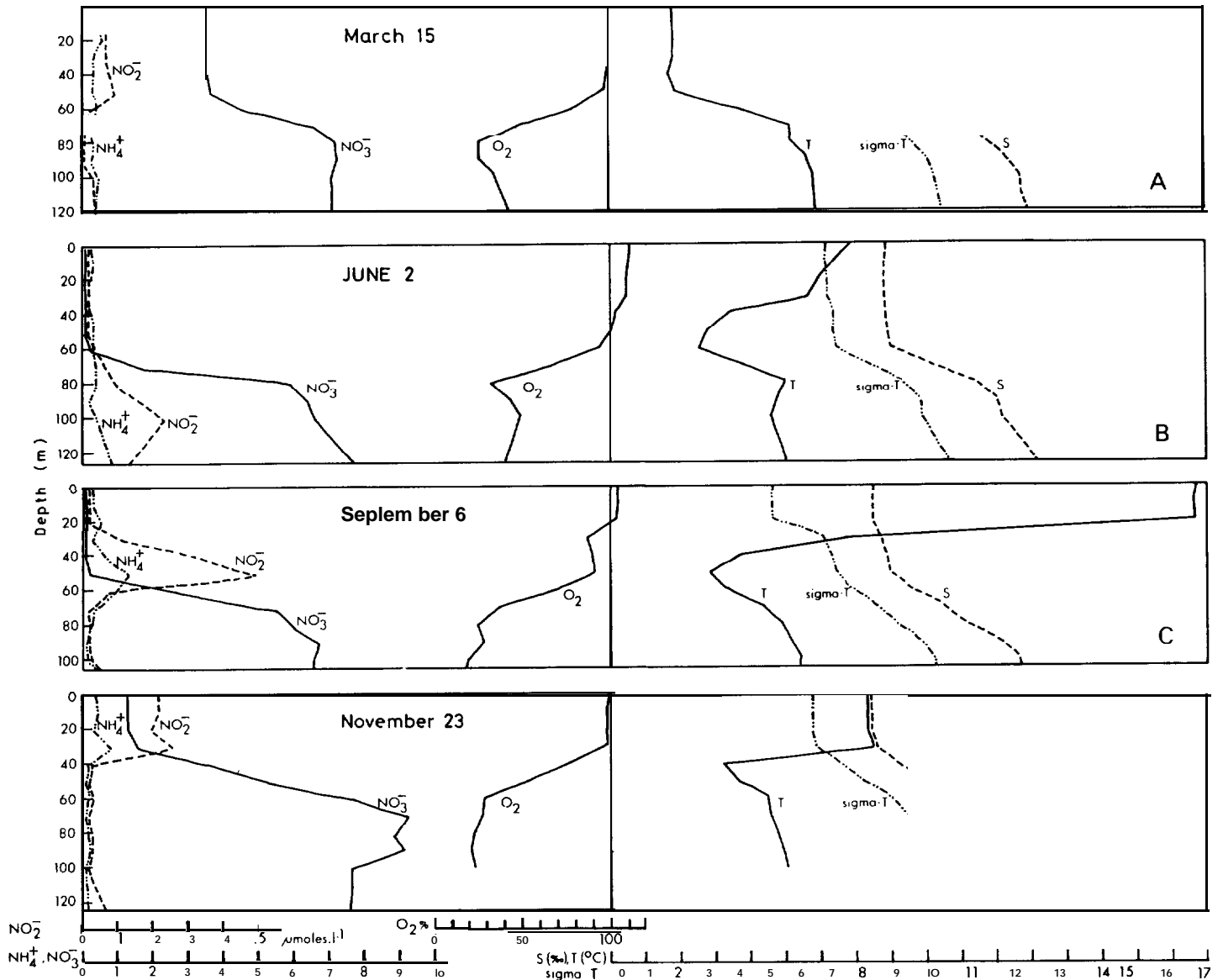


Figure 38. Seasonal structure of the water column, Station BY 9 (Klaipeda) (Gundersen, original figure).

Characteristic for this zone is the rapidly decreasing concentration of dissolved oxygen and the rapidly increasing concentration of nitrate. Another recurring event in zone D is the distinct maxima of ammonium and nitrite which build up in late August and September. At the same time, the nitrate concentration increases rapidly with depth. These events are seen in Figures 38 and 39 and are evidence of bacterial decomposition (ammonification) and nitrification.



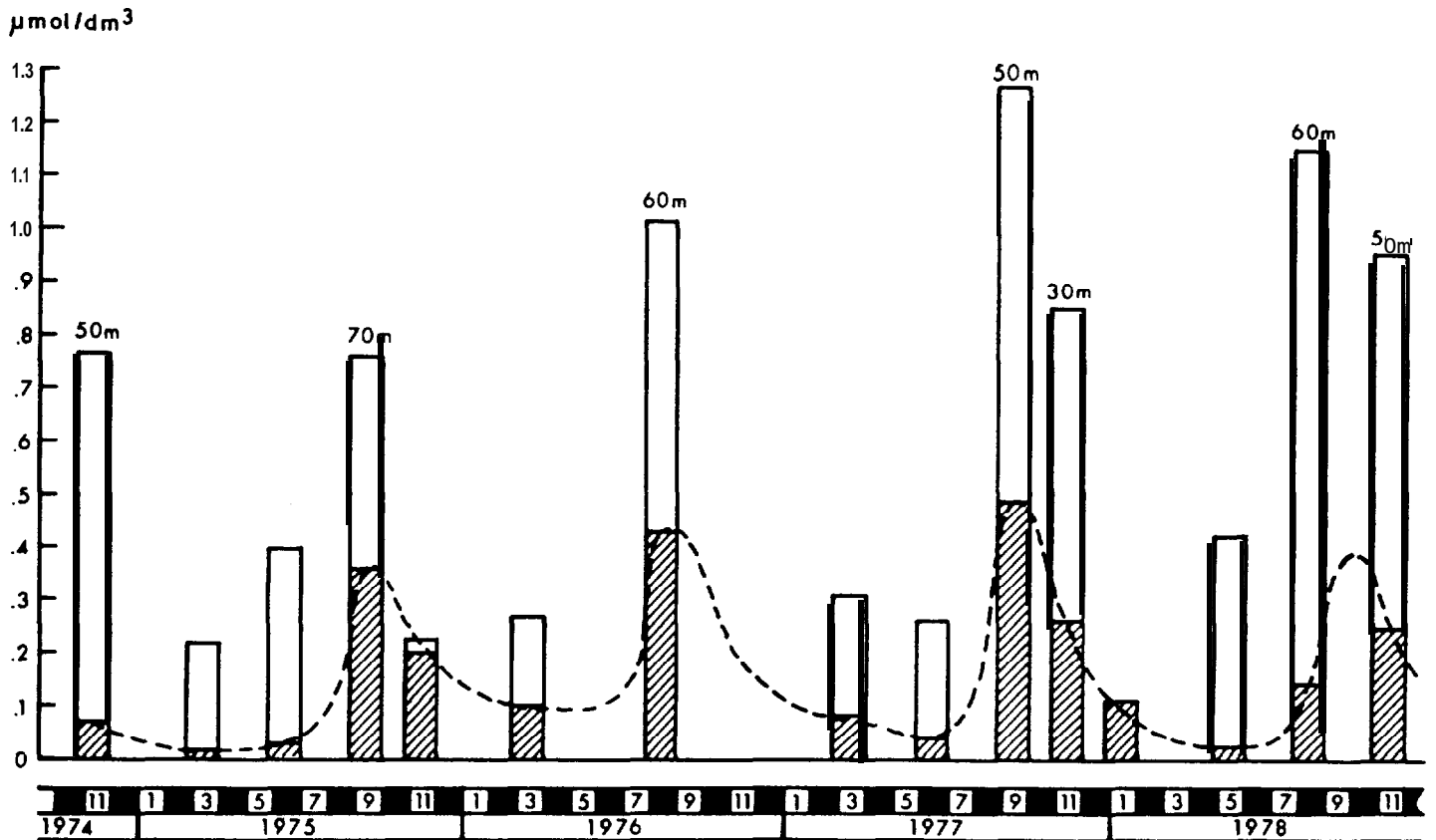


Figure 39. Annual cycles of ammonium and nitrite in the halocline region (zone D) in the Baltic Proper 1974-78, exemplified by station BY 9 (Klaipeda). Entire column, ammonium; hatched portion, nitrite. The water depth at the maximum is indicated above the column. The broken-line curve emphasizes the regularity of the nitrite maximum. (Gundersen, original figure).

The formation of ammonia and its subsequent oxidation to nitrate via nitrite proceeds throughout the winter. With increasing instability of the upper water column and the resultant thermohaline convection, these nutrients become evenly distributed within the entire low-salinity water column.

Zone E consists of the high salinity deep water of the Baltic Sea, which generally has a low content of oxygen and a high concentration of nitrate. The low oxygen content is a result of continuous consumption by bacteria which decompose and mineralize particulate and dissolved organic material supplied from above. As the oxygen nears exhaustion, which is a common event in the most productive parts of the Baltic Sea and particularly in the basins and deeps (see Chapter 4), nitrate respiration in certain anaerobic bacteria begins and results in the production of nitrogen gas and possibly ammonium. This process may also result in the accumulation of small amounts of nitrous oxide (see Figure 40), an intermediate metabolite in denitrification (Rönner and Gundersen, 1978).

The excess of dissolved nitrogen gas in the oxygen-poor deep water is difficult to measure precisely but can be calculated from a model of organic decomposition proposed by Richards (1965a). This model relates oxygen consumption with the oxidation of oceanic plankton material containing a relative atomic carbon, nitrogen, and phosphorus ratio of 106:16:1 and the formation of carbon dioxide, nitrate and phosphate. The elemental composition of mixed plankton from the Baltic Sea has been shown by Voipio (1969b) to be on average 104:20:1. Therefore, the model (with small modifications) is probably also valid for the Baltic Sea. When applied to the oxygen-nitrate concentration distribution in zone E, a substantial nitrate deficit (anomaly) is disclosed (see Figure 40), which in some cases may be close to  $40 \mu\text{mol}/\text{dm}^3$  of nitrate. This corresponds to a supersaturation of nitrogen gas of about 3%, which actually is lost from the combined nitrogen pool of the Baltic Sea. When all the oxygen and nitrate have been used up in the deep water, further decomposition will occur at the expense of sul-

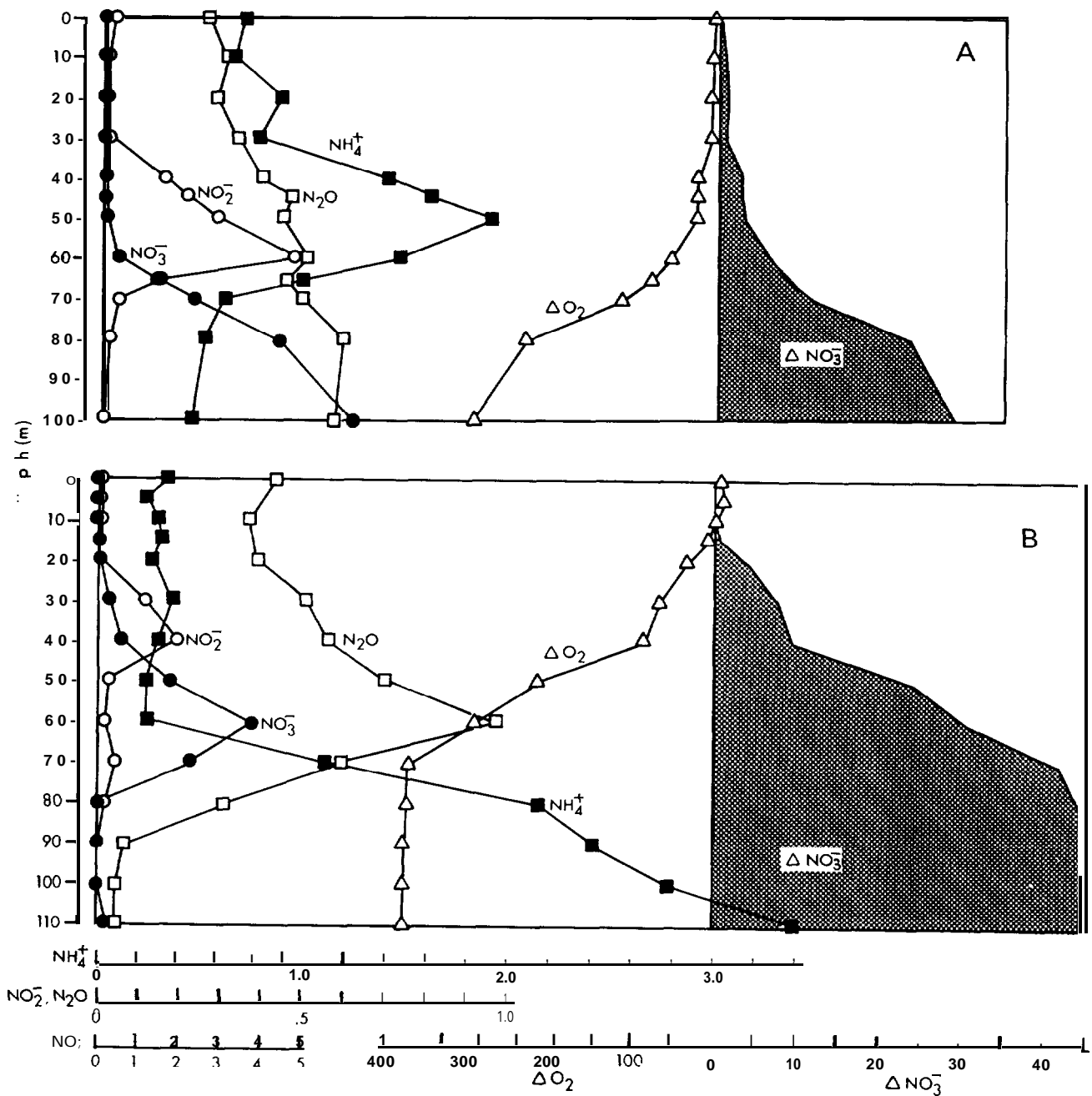


Figure 40. Vertical distribution of ammonium, nitrite, nitrate and nitrous oxide ( $\text{N}_2\text{O}$ ) as well as the oxygen deficit ( $\Delta\text{O}_2$ ) and the computed nitrate anomaly ( $\Delta\text{NO}_3^-$ , shaded area), on two stations in the Baltic Proper: (A) Station BY 9 (Klaipeda), September 6, 1977, and (B) Station BY 38 (Karlsö Deep), September 1, 1977. Concentrations in  $\mu\text{mol}/\text{dm}^3$ , except nitrous oxide which is  $\mu\text{g}/\text{dm}^3$ . (Gundersen, original figure).

fate by anaerobic sulfate-reducing bacteria and lead to the formation of sulfide (Chapter 4). Under the reducing conditions which now prevail, ammonium, sometimes in large amounts, will accumulate in the deep water (see Figure 40, part B).

*Zone F.* This is the sediment in which particulate nitrogen accumulates and decomposes, and, depending on the conditions, may be further metabolised. If the bottom water is oxic, then the upper 1 - 10 cm of the sediment may also be oxic. Due to the particulate nature and higher content of organic matter, sediments are biologically much more active than the water. Mineralization processes proceed rapidly and lead to the formation of ammonium which is rapidly nitrified with the formation of nitrate. Some of the nitrate diffuses up into the bottom water and may eventually be carried to the photic zone through convection and diffusive mixing (in shallow water) or upwelling. Some of the nitrate diffuses downwards into anoxic layers of the sediment and is usually denitrified. If the sediment surface is within the photic zone, as is the case in estuaries and near land, benthic micro- and macroalgae may efficiently absorb the ammonium and nitrate produced in the sediments. In sediments under anoxic bottom water, the ammonium is not nitrified and, therefore, accumulates in the interstitial water and in the bottom water. It is doubtful whether all the nitrogen reaching the sediments is returned to the water. Engvall (1978) considers the soft bottom sediments, particularly the anoxic ones, of the Baltic Sea to be sinks for nitrogen.

#### b. *Regional distribution*

The vertical zonation and seasonal trends in the nitrogen distribution described above form a general pattern which applies to the entire Baltic water system. However, certain quantitative differences exist between the Baltic Proper (including the Bay of Fin-

land and the Arkona region), the Bothnian Sea, and the Bothnian Bay (see Figures 41 and 42).

Some striking differences are seen in Figure 37 with respect to the seasonal distribution of nitrate and nitrite in the photic zone (zone B). In the Bothnian Sea both maxima are much lower than in the Baltic Proper, with the nitrate concentration almost half and nitrite almost non-existent. However, as in the Baltic Proper, the summer values are low indicating efficient assimilation by the phytoplankton. In the Bothnian Bay, on the other hand, there are high concentrations of nitrate throughout the water column and the surface water never seems to become exhausted in nitrate, as is the case in all other regions.

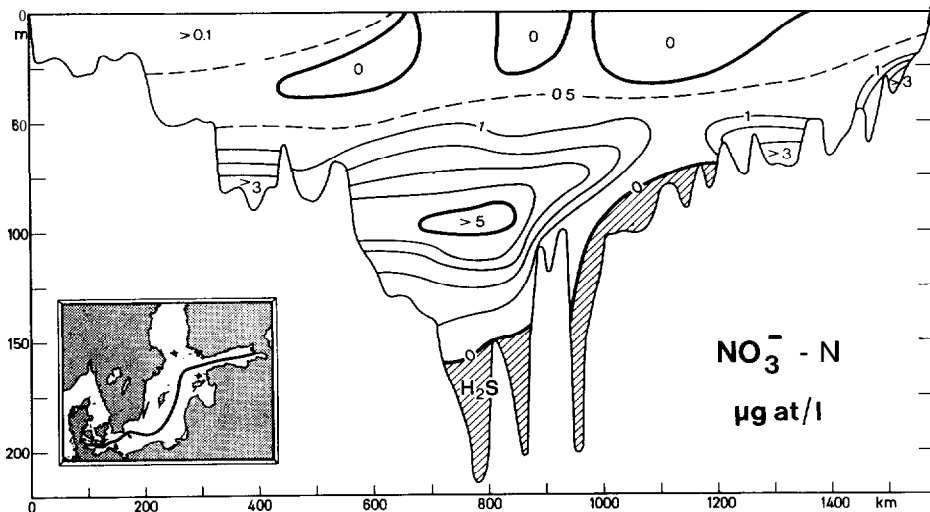


Figure 41. *Longitudinal section of the Baltic Sea showing the nitrate distribution in June 1969 (from Crasshoff, 1975).*

Unfortunately, the frequency of observations in the Bothnian Bay is too low to permit definite conclusions regarding seasonal changes. However, it seems safe to draw the conclusion that primary production is not limited by nitrogen but rather possibly by phosphorus (Ackefors et al., 1978) or that some unknown factor controls primary production in the Bothnian Bay. In spite of a permanent near-saturation situation with regard to oxygen in the Bothnian Bay, the concentration of ammonium is surprisingly high (frequently more than  $1 \mu\text{mol}/\text{dm}^3$ ) all year round.

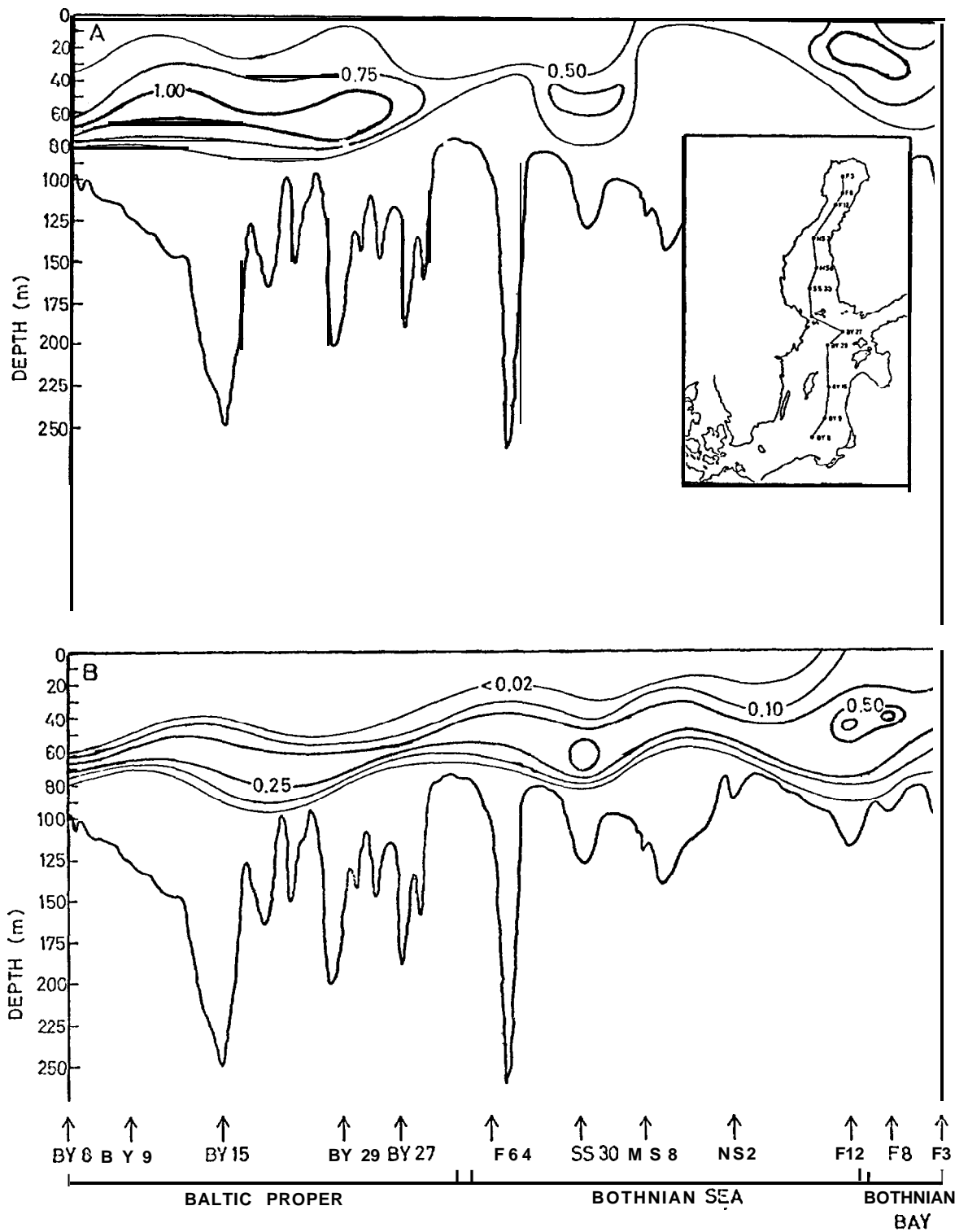


Figure 42. Distribution of ammonium (A) and nitrite (B) along a south-north transect of the entire Baltic Sea in late August 1976. Isopleth concentrations are in  $\mu\text{mol}/\text{dm}^3$ . (Gundersen, original figure).

The August - September nitrite maximum seen in zone D in the Baltic Proper can also be seen in the Bothnian Sea and the Bothnian Bay. The deep water (which has a much lower salinity than in the Baltic Proper) is well-oxygenated all year round and no nitrate anomalies, and therefore no denitrification, seem to occur.

#### 5.2.4 *The nitrogen cycle in the Baltic Sea*

##### a. *Assimilation of inorganic nitrogen*

The fairly large amounts of inorganic nitrogen, particularly nitrate but also some nitrite and ammonium, which have built up in the photic zone during the winter months control the size of the primary production during the spring bloom. An additional supply exists below the photic zone (zone C) which by physical processes is also made available to the phytoplankton during the few weeks of intensive primary production in the early spring. The mechanism of stripping the entire upper water layer of plant nutrients is fairly efficient.

If we take 4  $\mu$ moles of total inorganic nitrogen per litre as a typical mean value in the upper 50 m of the offshore water column at the onset of the spring bloom, and are using Voipio's (1969b) figures of 104:20 for the carbon:nitrogen ratio (see section 5.2.3(a)) as a measure of phytoplankton assimilation and final composition, it can be calculated that during the spring bloom about 12.5 g of carbon and 2.8 g of nitrogen are converted into phytoplankton biomass per square metre of sea surface. In an actual measurement of primary production in the Askö area during the 1975 spring bloom, Sjöberg and Wilmot (1977) found that 15.6 g of carbon was produced per square metre. From the decrease in nitrate in the water, they calculated that 2.74 g of nitrogen was transferred into biomass. This agreement is satisfactory.

Since the annual primary production in the Baltic Proper is roughly  $100 \text{ g C/m}^2$  (Ackefors et al., 1978), the production occurring during the rest of the productive season, roughly  $87.5 \text{ g C/m}^2$ , would require about  $70 \text{ } \mu\text{moles}$  of nitrogen per litre of water in the 20 metre deep photic zone. As no more nitrate is produced in the photic zone until October, phytoplankton production is entirely dependent on recycled nitrogen and on urea excreted by the zooplankton as well as on nitrogenous material brought down to the sea surface by rain or particulate precipitation or up by upwelling. If we assume that the productive season is 200 days in addition to the spring bloom, it can be calculated that as much as  $0.35 \text{ } \mu\text{moles}$  of inorganic nitrogen per litre per day will have to be supplied by recycling, etc., to support a production of  $100 \text{ g C/m}^2$ . This seems fully possible as mineralization rates in the sea are high; e.g., Gunnerson (1963) found that in Santa Monica Bay  $0.5 - 2 \text{ } \mu\text{moles}$  of ammonium-N/ $\text{dm}^3/\text{day}$  were produced from a continuous supply of about  $10 \text{ } \mu\text{g}$  organic nitrogen per litre. Similar mineralization rates were recently obtained in the Kattegat by Selmer (personal communication).

A fall bloom, usually much smaller than the spring bloom, is made possible in October while the light climate is still favorable and when nutrients, produced in zone D, begin to mix into the surface waters.

b. *Nitrogen fixation*

In late summer (July - August) another kind of plankton bloom occurs in the Baltic Sea, i.e., the short-lasting, but intensive, bloom of nitrogen-fixing blue-green algae. The input of combined nitrogen to the Baltic Sea from these organisms has been estimated by Lindahl et al. (1977) to be about  $0.6 \text{ g N/m}^2/\text{y}$  (equivalent to 150 000 tonnes for the entire Baltic Proper),



based on investigations in 1976 in the Askö area. Rinne et al. (1977, 1980) carried out studies in the northern Baltic Proper, the Gulf of Finland and the Gulf of Bothnia in 1974 - 1979. They estimated the amount of nitrogen fixed by blue-green algae to be 100 000 tonnes per year, i.e., almost the same level as the nitrogen input from land. Preliminary results of open sea studies in the Gulf of Bothnia in 1978 showed that in the southern Bothnian Sea the level of nitrogen-fixation was markedly lower than in the Gulf of Finland. In the northern area of the Gulf of Bothnia, which is characterized by a high inorganic nitrogen to phosphorus ratio, blooms of heterocystic blue-green algae and nitrogen-fixation were almost absent.

If we use the figure of  $0.6 \text{ g N/m}^2/\text{y}$  from Lindahl et al. and assume that it represents an overall average for the Baltic Sea (except the Bothnian Sea and the Bothnian Bay, for which no nitrogen-fixation data seem to exist), then the photic zone (20 m) receives an extra  $2.14 \text{ } \mu\text{moles}$  of combined nitrogen per litre during the late summer. Considering that only  $4 \text{ } \mu\text{mol/dm}^3$  of inorganic nitrogen was available at the onset of the productive season, the input from nitrogen-fixation is substantial.

### *c. Mineralization*

Mineralization (sometimes called regeneration) is the process by which organic matter is returned to its smallest inorganic building blocks (carbon dioxide, ammonium, phosphate, etc.) by bacterial action. Mineralization rates are highest when oxygen is available; mineralization will still occur under anoxic conditions, but less efficiently.

In the Baltic Sea, mineralization activity can be demonstrated at all depths and during all seasons. The rates are controlled by the water temperature, the

availability of oxygen, and the amount and composition of the organic material present.

d. *Nitrification*

The oxidation of ammonium to nitrate via nitrite is carried out by chemoautotrophic bacteria which derive energy from the process. As was shown in the previous section, nitrification in the Baltic Sea is restricted to zone D and is typically seasonal. The process is closely linked to the increase in mineralization rate which occurs in late August and September and continues throughout the winter. After the thermohaline convection has occurred, the nitrifying bacteria probably continue to nitrify, not only within the confines of zone D but throughout the entire upper water column. However, their activities cease in late winter or early spring when the ammonium is nearly exhausted and the phytoplankton bloom begins. It is not known what mechanisms control the onset and cessation of the nitrification process, but the onset could conceivably be triggered by the sudden increase in ammonium as the massive blue-green algal bloom in August dies off and the dead cells rapidly sink through the water column and accumulate in the well-developed pycnocline which occurs at that time of the year.

As long as there is sufficient oxygen present, and whenever ammonium is available, nitrification probably occurs throughout the year in the deep water (zone F) and in the upper part of the sediments. Nitrification has been shown to occur at oxygen levels as low as 10 % of saturation (Gundersen, 1966).

e. *Denitrification*

Denitrification is a respiratory process in which certain bacteria, in the near-absence of oxygen but in the presence of nitrate, are capable of producing

energy for biosynthesis and growth. When such conditions prevail, the nitrate is reduced to nitrogen gas with nitrite and nitrous oxide as intermediates. Depending on various environmental factors (pH, concentration and kind of organic material, and concentration of nitrate), one or more of the intermediate metabolites may accumulate in the water. Some investigators claim that ammonium may be an end product in an alternate pathway of denitrification (Tiedje et al., 1979), but conclusive evidence for this in marine systems is lacking.

Conditions for denitrification in the Baltic Sea are favorable in the nitrate-rich, oxygen-poor deeper water (zone E). As described above, the nitrate anomaly frequently found in the Baltic Proper (but not in the Bothnian Sea or Bothnian Bay) is evidence of denitrification (see Figure 40). If sufficient organic material is present in the water, the nitrate may be quantitatively reduced to nitrogen gas. This occurs simultaneously with the disappearance of the last traces of oxygen. The nitrous oxide found in the Baltic (Rönner and Gundersen, 1978) has a distribution similar to the distribution of nitrate and is undoubtedly a product of denitrifying activity. Traces of nitrite which sometimes are found within the nitrate anomaly presumably have the same origin. Due to the low temperatures in the deeper water, denitrification rates are low and the nitrate anomalies build up over several years. Thus, they are seasonal to a lesser extent than the ammonium-nitrite maxima found in the halocline region in the fall.

A schematic diagram showing an estimated overall mass balance of nitrogen in the Baltic Proper is given in Figure 43.

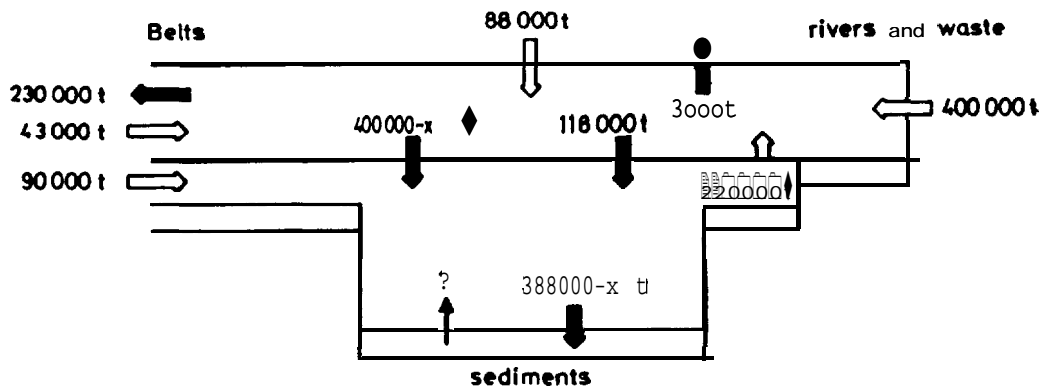


Figure 43. *Nitrogen balance of the Baltic Proper.*  
(Grasshoff, original figure).

### 5.2.5 Conclusions

Judging from data which can be considered reliable, and which has been collected during the past 10 - 15 years, there do not appear to be clear indications that an increasing degree of pollution of the Baltic is reflected in the nitrogen picture of the Baltic Sea as a whole. The most important conclusion to be drawn from this study is that all the various biological processes in the nitrogen cycle which participate in the transformation of the diverse species of nitrogen seem to be in balance. It is difficult to assess whether the extensive blooms of blue-green algae, which contribute hundreds of thousands of tonnes of combined nitrogen to the Baltic Sea in late summer, are triggered by an imbalance in the nitrogen-phosphorus relationship. (This is a complex and poorly understood "anomaly" in the Baltic Sea.) However, since there is no evidence for a build-up of organic or inorganic nitrogen in any of the horizontal zones of the water, it is conceivable that the amount of nitrogen fixed by the blue-green algae is mineralized and nitrified and that a comparable amount of nitrate is denitrified in the low-oxygen deep water and lost from the cycle. Investigations are under way to veri-

fy this hypothesis. Another possibility is that large amounts of nitrogen are buried in the sediments.

One observation which cannot as yet be explained satisfactorily is the accumulation of large amounts of inorganic nitrogen (ammonium and nitrate) in the Bothnian Bay. Given that the water column is well oxygenated throughout the year, one could expect the ammonium concentration to be much lower, at least seasonally.

A detailed investigation into the nitrogen situation and related parameters in the Bothnian Bay is warranted. It is also important to continue to monitor all the currently monitored nitrogen species and to attempt to improve the analytical techniques, particularly for total and dissolved organic nitrogen. It is also desirable to expand the spectrum of analysis of anthropogenic organic nitrogen compounds of potential harm to the biota of the Baltic Sea.

## 5.3 Silicate

### 5.3.1 *Properties and analytical methods*

Silicon is found in sea water in particulate form and in solution. Particulate silicon is contained in, e.g., mineral particles, shells and extracellular structures of diatoms and other silicious organisms. In solution, silicon most probably exists mainly as silicic acid,  $\text{Si}(\text{OH})_4$ , which dissociates in water. The solubility system of silicon is very complex and hereafter the term "silicate" will be used for all dissolved forms of silicic acid and its ions which react under the analytical method used. The solubility of silicate is around  $1800 \mu\text{mol}/\text{dm}^3$  and sea water is

very much under-saturated in respect to silicate. The highest values, around  $140 \mu\text{mol}/\text{dm}^3$ , are found in Pacific deep water. The average concentration in sea water is around  $36 \mu\text{mol}/\text{dm}^3$ . The surface water of oceans and the water in shallow seas have much lower concentrations, often close to zero. Semi-enclosed seas with a positive water balance, e.g., the Baltic Sea, often have relatively high surface concentrations of silicate. In the deep water of such basins, silicate is accumulated and the values may be 10 - 100 times higher there than in the surface water.

In contrast to phosphorus and nitrogen, silicon is an essential nutrient only for diatoms and some other species, e.g., radiolaria. It can, therefore, only act as a production-limiting factor for these species. Silicon is probably recirculated several times through the life cycle of such organisms during a season (Koroleff, 1976).

Silicon in sea water is normally analyzed using spectrophotometric methods. Silicic acid reacts with molybdate in acid solution forming a yellow complex which can be reduced to a blue colour by, e.g., ascorbic acid (Koroleff, 1976). Such methods give only the inorganic "reactive silicate" (Strickland and Parsons, 1965). Total and organic silicon may be oxidized to inorganic form by use of, e.g., peroxydisulfate and then analyzed for inorganic silicate as above (Koroleff, 1976).

The relative accuracy at low levels ( $4.5 \mu\text{mol}/\text{dm}^3$ ) is about  $\pm 4\%$ , at medium levels ( $45 \mu\text{mol}/\text{dm}^3$ ) about  $\pm 2.5\%$  and at high levels ( $150 \mu\text{mol}/\text{dm}^3$ ) about  $\pm 6\%$  (Koroleff and Palmork, 1972). Hydrogen sulfide interferes with the analysis at sulfide levels above  $5 \text{ mg}/\text{dm}^3$ . Other interfering substances are fluoride and some trace metals in high concentrations. There is also a "salt"

effect which has to be accounted for (Koroleff, 1976).

### 5.3.2 *Conditions in the Baltic Sea*

The relatively high silicate concentration in Baltic Sea water is mainly due to the large runoff of river water (Voipio, 1961). Voipio found that most of the silicate was carried to the Gulf of Bothnia in water from Swedish and Finnish rivers. In addition, Fonselius (1969b) has shown that the silicate content of the Baltic Proper is mainly regulated by the silicate concentrations in Kattegat water and Gulf of Bothnia water.

The accumulation of silicate in the deep water is also reflected by the positive correlation between the salinity and the silicate concentration in the water in the Gulf of Finland. The upwelling saline water seems to be more important as a silicate source than the river water, as shown by Voipio (1961) and Niemi (1975). The levels of silicate in the Gulf of Finland are somewhat similar to those in the northern Baltic Proper.

Because silicate is a nutrient for diatoms and other organisms requiring silicate for their shells or skeletons, the silicate concentration of the surface water shows seasonal variations according to the production of silicious organisms. Due to the relatively high concentrations found in the Baltic surface water, silicate does not act as a production-limiting factor for silicious organisms. Silicate values close to zero are not found in the Baltic Sea area except for the Kattegat, where values below the analytical detection limit may occasionally be found (see Figure 44). There is often a linear relationship between the concentrations of phosphate and silicate in Baltic Sea water, indicating that both nutrients accumulate

proportionally in the deep water. In deep basins containing hydrogen sulfide, the phosphate concentration, however, increases more than the silicate concentration, due to the dissolution of precipitated iron phosphate under reducing conditions (Fonselius, 1960b).

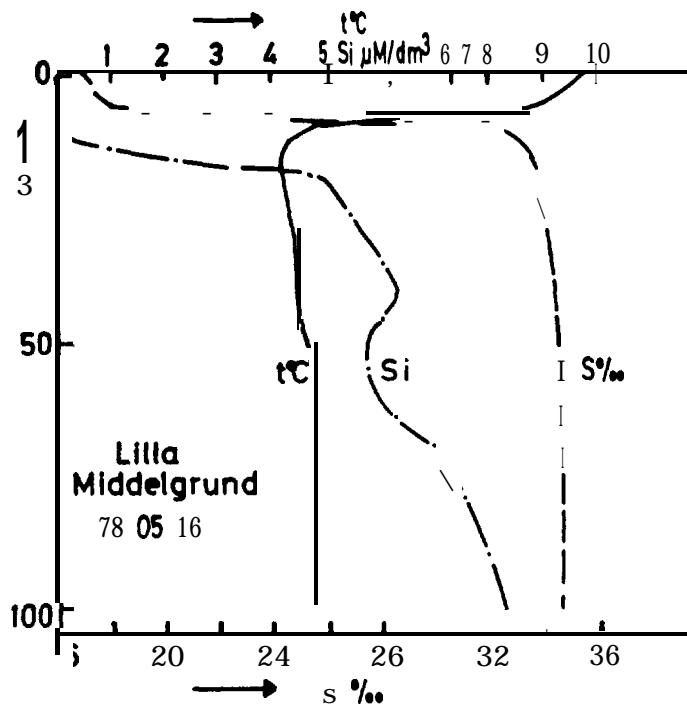


Figure 44. The distribution of salinity, temperature and silicate on station "Lilla Middelgrund" in the Kattegat. (Fonselius, original figure).

### 5.3.3 Regional distribution

In the Kattegat area, the silicate concentration during the winter is around 9 - 12  $\mu\text{mol}/\text{dm}^3$  from the surface down to the bottom, but during the summer the surface values may reach zero concentration due to diatom blooms (see Figure 44). In the southern Baltic Proper, the surface values may vary between 3 and 15  $\mu\text{mol}/\text{dm}^3$ , depending on the season. The deep water may exhibit values up to 80  $\mu\text{mol}/\text{dm}^3$ .



Figure 45 shows an example of the silicate distribution at the station BY 15 (the Gotland Deep) in the eastern Gotland Basin. The seasonal variations in the surface water may extend from around 5 to 20  $\mu\text{mol}/\text{dm}^3$ . During stagnant conditions the bottom values may even exceed 100  $\mu\text{mol}/\text{dm}^3$ .

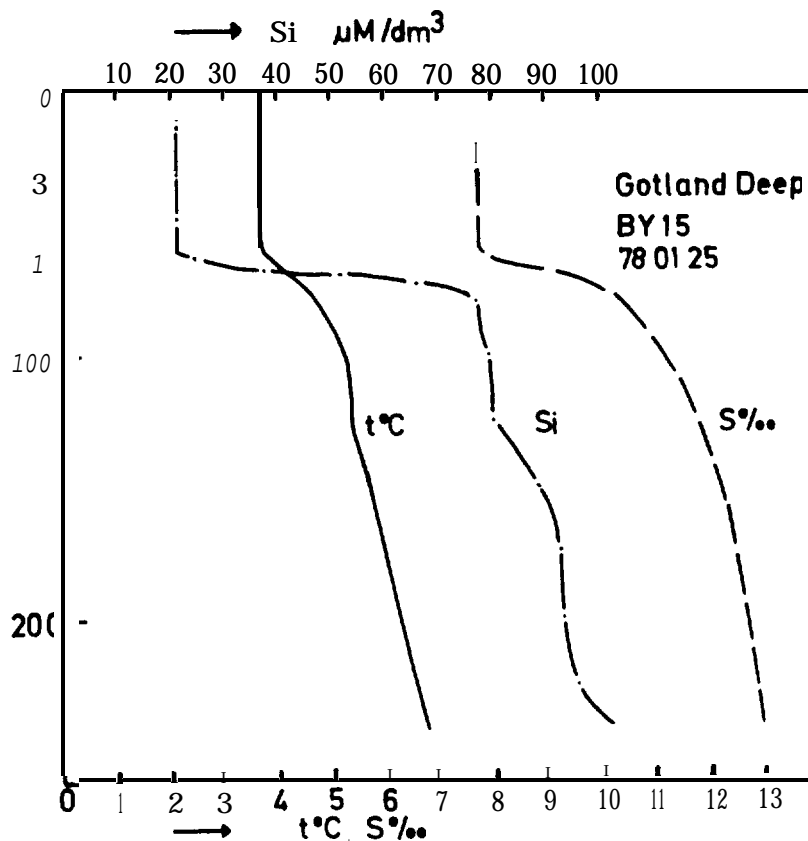


Figure 45. The distribution of salinity, temperature and silicate on the station BY 15 in the eastern Gotland Basin. (Fonselius, original figure).

The conditions in the northern Central Basin are shown in Figure 46, which is from station BY 31 (the Landsort Deep). In this figure we can see the effect of diatom production in the surface layer. The silicate values there are 7  $\mu\text{mol}/\text{dm}^3$ , while in the old winter

water with low temperatures they are around  $20 \mu\text{mol}/\text{dm}^3$ . Below the permanent halocline, the silicate values increase to  $70 \mu\text{mol}/\text{dm}^3$ .

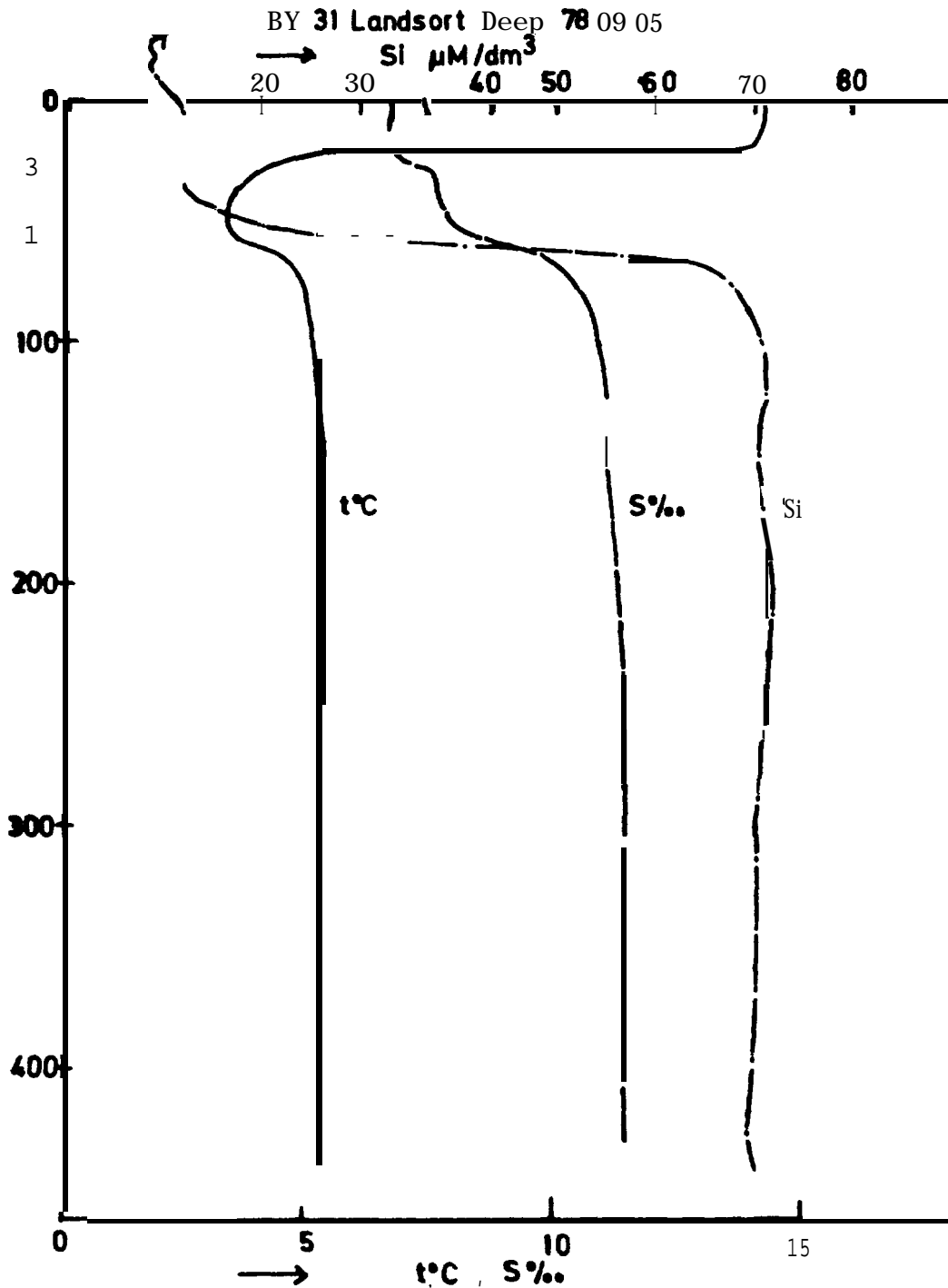


Figure 46. The distribution of salinity, temperature and silicate on the station BY 31 in the northern Central Basin. (Fonselius, original figure).

In the western Gotland Basin we find still higher concentrations of silicate, as shown in Figure 47. This figure is from the station BY 38 (the Karlsö Deep). The measurements were made in January 1978 and, therefore, no effects of diatom production can be seen. In the surface water the silicate concentration is  $30 \mu\text{mol}/\text{dm}^3$ , and in the deep water it exceeds  $90 \mu\text{mol}/\text{dm}^3$ . Below 100 m the water is stagnant and may soon contain hydrogen sulfide. Therefore, silicate is accumulated in this water.

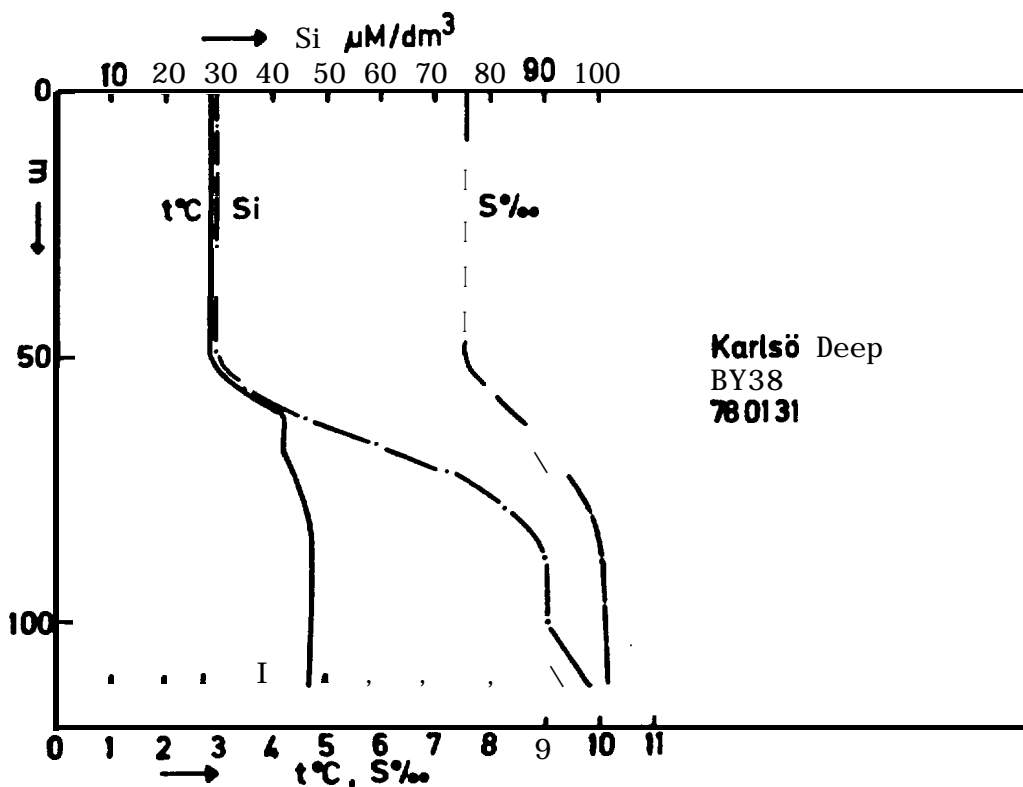


Figure 47. The distribution of salinity, temperature and silicate on the station BY 38 in the western Gotland Basin. (Fonselius, original figure).

The Gulf of Bothnia is not a stagnant basin due to the weak horizontal stratification of the water. Therefore, we do not find the large differences between the silicate concentrations in the surface water and those in the deep water which we find in the

Baltic Proper. Figure 48 shows an example of the silicate distribution in the Bothnian Sea at the station F 24 (the Ulvö Deep).

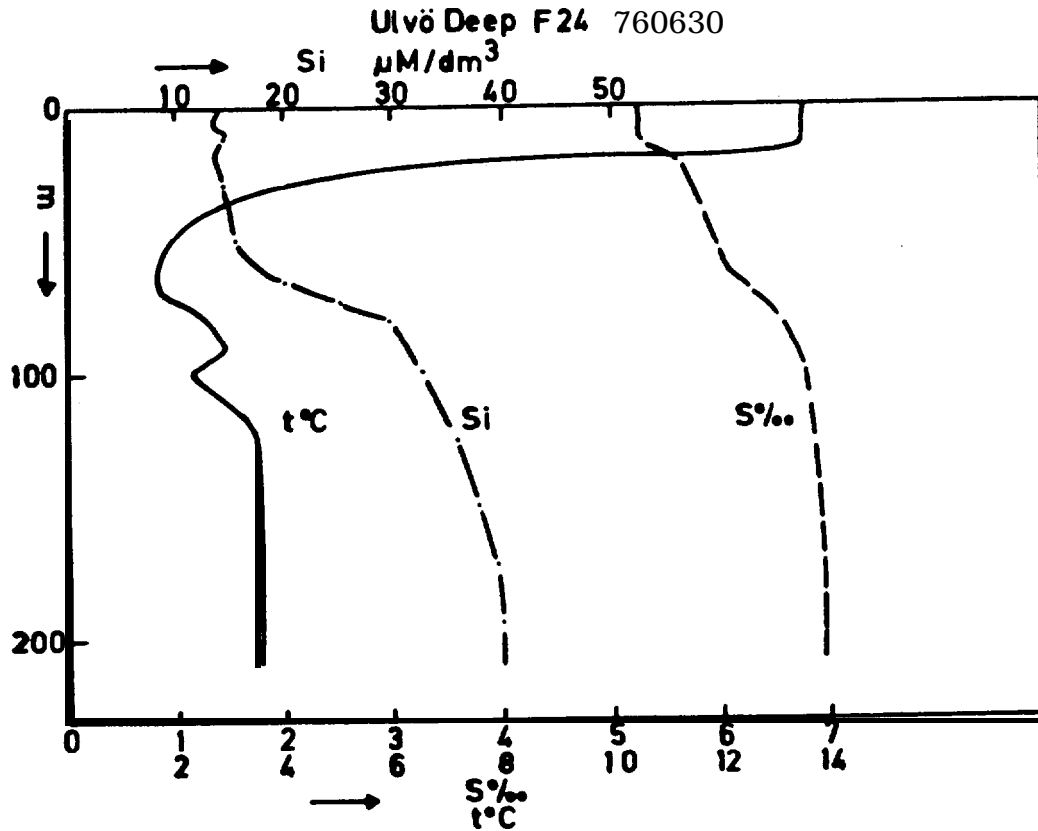


Figure 48. *The distribution of salinity, temperature and silicate on the station F 24 in the Bothnian Sea. (Fonselius, original figure).*

The silicate concentration below the halocline is somewhat higher than in the surface water because the deep water is not renewed annually and there is a slight accumulation of silicate in the deep water. In the Bothnian Bay, the winter convection extends down to the bottom and, therefore, the silicate concentration is almost the same from surface to bottom (see Figure 49). Here we also find the highest surface values,  $30 \mu\text{mol}/\text{dm}^3$ , due to the large river input of silicate.

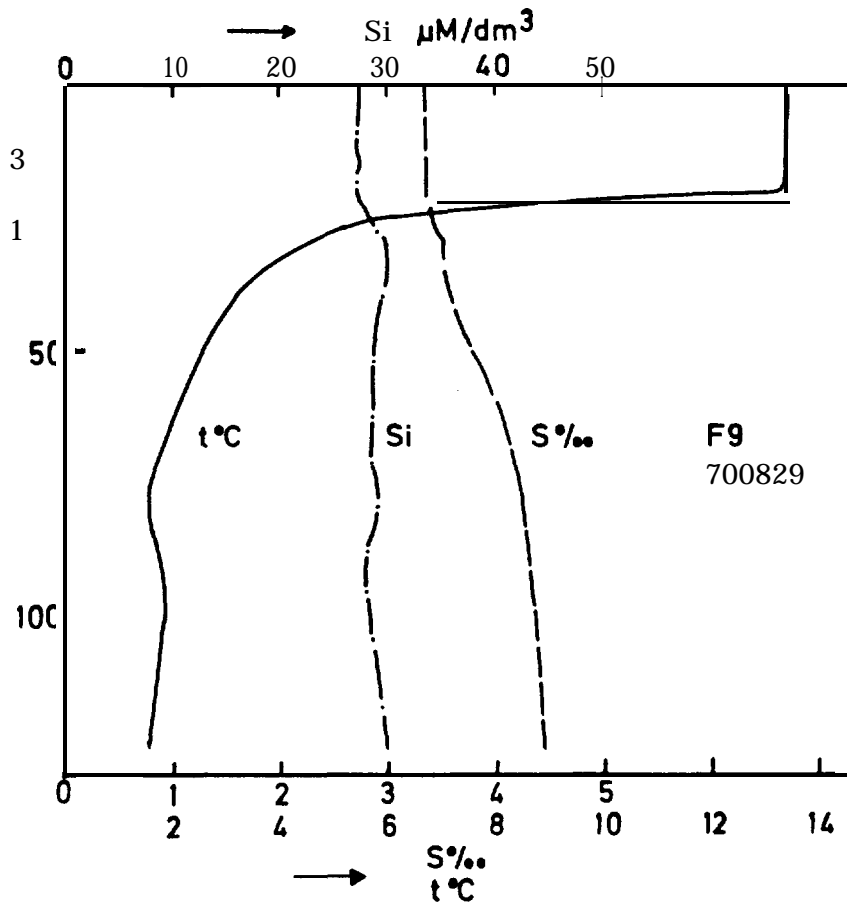


Figure 49. The distribution of salinity, temperature and silicate at the station F 9 in the Bothnian Bay. (Fonselius, original figure).

Figure 50 shows the distribution of silicate along a longitudinal section through the Baltic Sea.

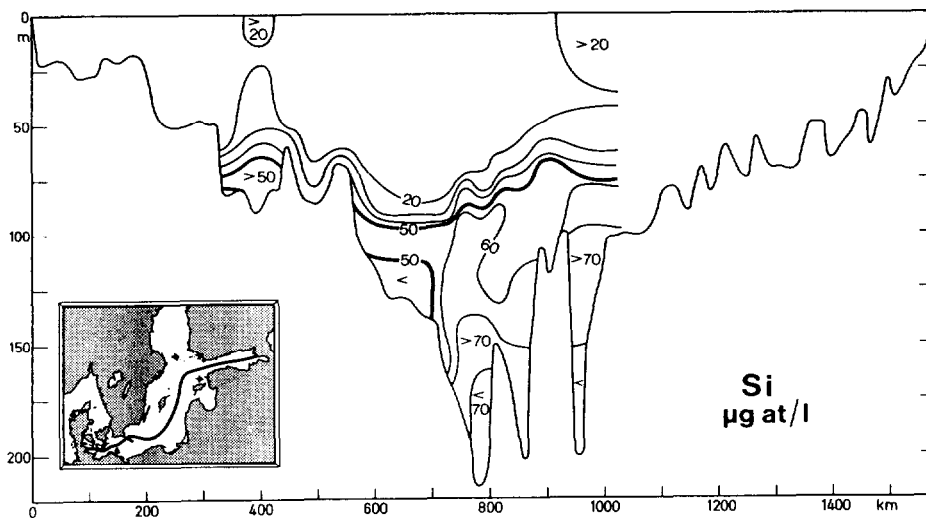


Figure 50. Distribution of silicate along a longitudinal section through the Baltic Sea in April 1970 (from Grasshoff, 1975).

#### 5.3.4 *Discussion*

Silicon has been measured on a routine basis in the Baltic Sea only during the last decade. Therefore, it is not possible to determine whether any changes in the silicate concentration in the water have occurred during the present century. The regulation of river runoff through the construction of power dams may have influenced the transport of silicon, especially in particulate form, to the Baltic Sea. Such dams decrease the spring flood caused by the melting of the snow cover, so particulate silicon may settle in these dams and dissolved silicate may be co-precipitated with the settling material. There is, however, no evidence of a decreasing silicate concentration in the Baltic Sea, owing to the lack of data from the first half of the century.

# Harmful substances

## 6.1 Trace elements

Trace elements of environmental significance include highly toxic elements such as mercury (Hg) and cadmium (Cd) and less toxic elements such as arsenic (As), antimony (Sb), bismuth (Bi), thallium (Tl) and nickel (Ni), and elements which are essential for living organisms below their respective critical levels but display progressively toxic actions above these thresholds, for example, copper (Cu), zinc (Zn), selenium (Se), vanadium (V), and cobalt (Co).

### 6.1.1 *Methods*

For the analysis of trace elements in samples from the Baltic Sea, widespread use is made of atomic absorption spectroscopy techniques, especially in the flameless mode using a graphite tube furnace for direct measurements in water (Cr), following an extraction step (Zn, Cu, Cd, Fe, Mn, Pb, Co, Ni, etc.) or in the reduction-aeration ("cold vapor" (Hg)) or hydride generation mode (e.g., Hg, As, Se), respectively. The second most common method is anodic stripping voltammetry because of its low detection limits, low price and its potentialities for speciation studies (Zn, Cd, Pb, Cu). In addition, neutron activation analysis (Hg), gas chromatography (methyl-Hg), X-ray fluorescence analysis and spectrophotometric methods are in use.

Employing suitable enrichment operations, the above-mentioned techniques are capable of determining common levels of trace elements in the different compartments of the marine environment. For example, the results of the 1978 intercalibration exercise on the analysis

of trace elements in sea water (Bewers et al., 1981) show a substantial improvement in the agreement among laboratories compared with previous intercalibrations of this type (see Table 8). However, substantial variations in results (due in part to contamination) can be caused by the use of different methods of sampling, sample preparation and storage. The actual magnitude of these variations still needs to be determined.

Table 8. *Coefficients of variation resulting from intercalibration exercises on trace metal analyses in sea water 1974 - 1978 ( $\pm$  %)*

Zn	Cd	Pb	Cu	Hg	References
		>500	-	-	Anon., 1974a
62	100	132	63	-	Jones, 1977
47	160	201	151	-	
44	46	48	42	38	Anon., 1977
				82	Olafsson, 1978
39	77	101	63	-	(1) Bewers et al., 1981
41	42	54	75	-	(2) Bewers et al., 1981

(1) stored acidified

(2) stored deep-frozen

For biological material, the 1978 - 1979 intercalibration exercise (Topping, 1979) showed that the majority of participating laboratories now obtain accurate and comparable results for mercury, copper and zinc, but for lead and cadmium few laboratories use methods capable of determining the low levels of these metals in fish muscle tissue (see Table 9). Thus, great caution must be used in interpreting the results reported here for cadmium and lead in biota. For sediments, no international intercalibrations have yet been held, but due to the relatively high levels of trace metals in sediments a relatively good comparability of analytical results could be expected.



Table 9. *Coefficients of variation (CV) resulting from intercalibration exercises for trace metal analyses in biological tissues (from Topping, in press)*

Zn	Cd	Pb	cu	Hg	As
7%	0.005 - 0.99 <sup>1)</sup>	0.018 - 7.5 <sup>1)</sup>	8% 12	- 25%	10% <sup>2)</sup>

1) Range in mg/kg as CV cannot be given because of the large variations

2) Calculated for 8 out of 16 laboratories

### 6.1.2 Water

The amount of data for trace metal concentrations in Baltic Sea water appears to be considerable (see Table 10). But because a large proportion of these values were obtained by unsatisfactory methods or stem from coastal areas, only a limited number can be considered representative of the open Baltic Sea. There is still a lack of reliable recent baseline data for most parts. Therefore, general trends cannot be established. Investigations on particulate trace metal concentrations have been carried out only sporadically (Weigel, 1976). First estimates reflect that this fraction must be taken into consideration when calculating budgets for the Baltic Sea (Pb, Hg). Speciation studies have shown that the relatively high content of dissolved organic matter in the Baltic Sea reduces the fraction of free or labile-bound heavy metals, which are potentially harmful to organisms, to about 20% (e.g., Cu, Hg) or 50% (Pb, Zn) of the total amounts (Brügmann, 1979b). The proportion of free or labile-bound heavy metals in the Baltic Sea is reduced by organic and inorganic complexation, adsorption and absorption on particulate matter, and coagulation with colloids. Labile heavy metal concentrations in the Baltic Sea may be effectively maintained at relatively low levels by such processes (Brügmann, 1979c).

Table 10. *Heavy metals in water ( $\mu\text{g}/\text{dm}^3$ )*

Region	Hg <sup>*)</sup>	Cd	Pb	cu	Zn	Ni
Kattegat, Øresund, Belts, Kiel Bight <sup>1)</sup>	1- 79	0.04-6	0.3 -27	0.8-52	3- 53	1 -4
Western Baltic <sup>2)</sup>	4- 76	0.01-2	0.1 - 3	1 -22	2- 82	-
Bornholm Basin <sup>3)</sup>	4- 208	0.02-1.2	0.2 - 3	1.2-24	2- 53	-
Gdańsk Bight <sup>4)</sup>	50-1200	0.04-0.4	0.2 - 0.9	0.3-10	2- 20	-
Southern Central Baltic <sup>5)</sup>	15- 95	0.02-0.5	0.04- 1.3	0.4- 3	2- 15	0.4-2
Eastern Gotland Basin <sup>6)</sup>	-	0.02-0.5	0.2 - 6	0.3- 7	2- 49	-
Western Gotland Basin <sup>7)</sup>	-	0.04-0.15	0.3 - 0.5	-	2- 6	1 -2
Landsort Deep <sup>8)</sup>		0.06-1.6	0.5 - 2	0.8- 5	1- 14	-
Gulf of Finland <sup>9)</sup>	-	0.02-1.5	0.3 - 3	0.6-10	2-120	-
Northern Central Baltic <sup>10)</sup>	-	0.04-0.07	0.3 - 0.4	-	3- 7	-

\*)  $\mu\text{g}/\text{dm}^3$

#### Reference list

- 1) Pedersen and Larsen, 1977; Schmidt, 1976; Sen Gupta, 1972b; Brüggmann, 1977; Gustavsson and Notter, 1977; Hägerhäll, 1973; Kremling et al., 1979; Morozov et al., 1974; Nordenberg, 1972; Magnusson and Westerlund, 1980.
- 2) Brüggmann, 1977, 1979a; Kremling, 1972; Morozov et al., 1974; Pedersen and Larsen, 1977; Schmidt, 1976; Sen Gupta, 1972b; Magnusson and Westerlund, 1980; Schmidt, in press.
- 3) Bojanowski, 1973; Brüggmann, 1977, 1979a; Kremling, 1972, 1973, 1978; Ott, 1978; Sen Gupta, 1972b; Magnusson and Westerlund, 1980.
- 4) Bojanowski, 1973; Brzezińska, 1978; Trzosińska et al., 1975.
- 5) Bojanowski, 1973; Brüggmann, 1979a; Brzezińska, 1978; Danielsson and Westerlund, 1978; Kremling, 1972; Schmidt and Zehle, 1979; Magnusson and Westerlund, 1980.
- 6) Brüggmann, 1977; Kremling, 1972, 1973; Sen Gupta, 1972b; Magnusson and Westerlund, 1980.
- 7) Brüggmann, 1977; Gustavsson and Notter, 1977; Magnusson and Westerlund, 1980.
- 8) Brüggmann, 1977; Gustavsson and Notter, 1977; Magnusson and Westerlund, 1980.
- 9) Brüggmann, 1977; Morozov et al., 1974; Sen Gupta, 1972b.
- 10) Brüggmann, 1977.

Considering the data published to date (see Table 10), the total concentrations seem to range from 1 - 7  $\mu\text{g}/\text{dm}^3$  for zinc, 0.3 - 3  $\mu\text{g}/\text{dm}^3$  for copper, 0.01 - 0.15  $\mu\text{g}/\text{dm}^3$  for cadmium, 0.4 - 2  $\mu\text{g}/\text{dm}^3$  for nickel and 4 - 80  $\text{ng}/\text{dm}^3$  for mercury in the central parts of the Baltic Sea. More recent studies confirm that levels at the lower end of these ranges are the most reliable (Magnusson and Westerlund, 1980). There are no universally accepted recent data for lead, but for offshore regions concentrations lower than 0.2  $\mu\text{g}/\text{dm}^3$  can be assumed. Values of about 10  $\mu\text{g}/\text{dm}^3$  have been reported for molybdenum (Kremling, 1978) and between 0.03 and 0.7  $\mu\text{g}/\text{dm}^3$  for cobalt (Gustavsson and Notter, 1977; Morozov et al., 1974; Sen Gupta, 1972b). For chromium, concentrations  $< 1 \mu\text{g}/\text{dm}^3$  seem to be likely (Anon., 1977; Gustavsson and Notter, 1977). Arsenic concentrations are reported in the range  $\sim 0.5 - 7 \mu\text{g}/\text{dm}^3$ . For other elements (e.g., Bi, Se, Sb, Tl, V), no data for the open Baltic Sea are available or they are so scarce that no general conclusions are possible. The trace metal data taken from Table 10 may just as likely be under-estimated due to incomplete extraction of organically associated fractions as over-estimated by contamination.

### 6.1.3 *Sediments*

Deposited organic and inorganic matter reflects the development history of a sea, including the impact of man. Therefore, sediment cores may be a good indicator of metal loads in deposition areas when combined with estimation of the sedimentation rate by suitable radiometric techniques.

Although the methods used for metal analysis in sediment samples have not yet been intercalibrated, better agreement is found among published data (see Table 11) than in the case of water because the measurements do not need to be carried out near the detection limit and contamination risks are reduced.

Table 11. Heavy metals in sediments (mg/kg dry weight)

Region	Core, cm	Hg <sup>*)</sup>	Cd	Pb	cu	Zn	Cr	Ni	co
Kattegat, Øresund, Belts <sup>1)</sup>	2, 20	14-6500		2 -201	2-160	6- 100		2- 14	1- 7
Kiel Bight <sup>2)</sup>	122		0.2 -1.9	17 - 82	35-71	110- 340		60-920	8-26
Mecklenburg Bight <sup>3)</sup>	5, 430	15- 94	0.4 -2.0	20 - 64	9-35	66- 150	57 - 93	32- 55	3-28
Arkona Basin <sup>4)</sup>	450	12- 86	0.3 -2.9	13 - 47	20-28	48- 130	47 - 68	37- 55	3-13
Bornholm Basin <sup>5)</sup>	34, 280		0.5 -2.2	3 -105	1-71	6- 270	2 - 71	34- 88	4-10
Gdańsk Bight <sup>6)</sup>	surface	50- 610	0.2 -7.4	2.8- 84	1-46	8- 307	0.5- 28	11- 94	7-22
Southern Central Baltic <sup>7)</sup>	10	10- 190	0.4 -6.3	30 -130	20-75	83- 434	25 - 40	27- 52	13-17
Gotland Deep <sup>8)</sup>	46				25-214	41- 639			
Northern Central Baltic <sup>9)</sup>	15	10- 680	0.05-5.6	10 -100	7-64	46- 477	11 - 50	10- 47	2-36
Gulf of Bothnia <sup>10)</sup>	4	2 800	4.1	67	33	129	-	70	25
Baltic nearshore <sup>11)</sup>	20	20-5000	<0.01-8.1	2 -400	1-283	12-2090	-	1- 17	
Baltic offshore <sup>12)</sup>	20	20-1250	(0.01-2.1	3 - 52	5-21	10- 225		3- 24	-
Baltic <sup>13)</sup>	5	-			10-72	10- 268	19 -252	10- 60	-

\*) µg/kg      \*\*) only labile organic associated fractions

Reference list below

1) Anon., 1978c; Olausson, 1975<sup>\*\*) ;</sup>  
Pedersen and Larsen, 1977.

2) Erlenkeuser et al., 1974.

3) Brüggemann et al., in press; Rudolph, 1965.

4) Brüggemann et al., in press.

5) Anon., 1978c; Suess and Erlenkeuser,  
1975; Madsen and Larsen, 1974.

6) Andrulowicz et al., 1979.

7) Niemistö and Tervo, 1978a.

8) Hallberg, 1974

9) Niemistö and Tervo, 1978b.

10) Hallberg, 1979.

11) Olausson et al., 1977. \*)

12) Olausson et al., 1977. \*)

13) Emelvanov, 1976.

The available pool of data does not cover the whole Baltic Sea. Baseline investigations including all representative parts of the Baltic Sea, and thus permitting characterization of the present situation, have not yet been carried out. However, somewhat better knowledge exists of some coastal areas influenced directly by pollution.

When comparing the heavy metal concentrations in the earlier stages of the Baltic Sea to those observed in the most recent sediments from accumulation areas, there are three different groups. The first group consists of metals whose contents have been nearly constant during the ages. Nickel and chromium are included in this group. In the second group, which includes copper and cobalt, background levels have increased by a factor of 1.5 to 2. Zinc and lead have increased by a factor of about 3, while cadmium and mercury - the third group - show today more than a tenfold increase in concentration compared with the background level (Niemistö and Voipio, 1979). Recent deposits in the central parts of the Baltic Sea show high mercury, cadmium and lead levels (see Table 11) compared with oceanic deep sea sediments and mean levels in the earth's crust.

#### 6.1.4 *Organisms*

As can be seen from Table 12, the data on trace metal concentrations in organisms from the Baltic Sea cover a broad range. The obvious differences reflect in most cases local or regional variations caused by pollution. But, as the results of intercalibration exercises show, the determination of low lead and cadmium concentrations in organisms is still a difficult analytical problem (Topping, 1979, in press). For these elements, the reported amount includes some uncertainties caused by contamination and other problems associated with measurement near the detection limit.

Table 12. *Heavy metals in organisms (mg/kg wet weight)*

Species	Hg <sup>*)</sup>	Cd <sup>*)</sup>	Pb	cu	Zn
<i>Fish</i>					
Cod <sup>1)</sup>	20-880	2- 50	0.03 -1.3	0.08- 2.4	1.2- 9.2
Herring, sprat <sup>2)</sup>	4- 90	2-200	0.01 -1.4	0.30- 1.9	3.4- 32
Flounder, plaice <sup>3)</sup>	10-450	2-100	0.02 -0.26	0.10- 0.89	3.5- 11.3
<i>Mussels</i> <sup>4)</sup>	4-300	130-560	0.16 -1.56	1.0 -16	16 -110
<i>Macrophyta</i> <sup>5)</sup>	1-183	210-500	(0.002-5	0.1 - 5	3 - 65

\*)  $\mu\text{g}/\text{kg}$

Reference list below

- 1) Anon., 1978b; ICES, 1977; Ohlin and Vaz, 1978.
- 2) Anon., 1978b; ICES, 1977.
- 3) Anon., 1978b; ICES, 1977; Ohlin and Vaz, 1978.
- 4) Anon., 1978b; ICES, 1977; Ohlin and Vaz, 1978; Stoepler et al., 1977.
- 5) Anon., 1978b; Bojanowski, 1973; Hägerhäll, 1973.

As expected, for all organisms investigated the lowest trace metal concentrations were found in organisms from open Baltic waters, with maxima in nearshore regions (e.g., Swedish archipelagos, the Øresund, Gulf of Finland, Gdańsk Bay, Bothnian Bay). Compared with data from the North Atlantic, the trace metal levels are not significantly higher. For vertebrates, most authors have reported significant positive correlations between age (length, weight) and the cadmium or mercury burdens in the total bodies and/or at special accumulating sites (e.g., kidneys for cadmium, muscle for mercury).

Due to the greater availability of representative samples of the organisms listed in Table 12 than of other organisms (e.g., sea birds, seals, macrophytes, benthic fauna), these have been analysed relatively often. Data on the lowest organisms in the food chain (phyto- and zooplankton) are scarce because contamination risks due to unsuitable sampling devices are high, the collected material does not as a rule consist of only one defined plankton species and is accompanied by other organic and/or inorganic particles of natural or anthropogenic origin.

The biological availability of trace elements to marine organisms depends on a number of factors, including the speciation of the metal and the salinity and concentration of particulate matter in the water. For cadmium, for example, 95 % of the soluble cadmium is bound in chlorocomplexes at a salinity of 35‰, whereas less than half of the soluble cadmium is bound at salinities below 5‰ (Møhlenberg, 1980). For this and several other metals (zinc, lead, iron), there appears to be a greater bio-availability in brackish waters than in marine waters (Phillips, 1977, 1978).

#### 6.1.5 *Budgets and Balances*

Owing to uncertainties regarding the accuracy of data concerning trace metal concentrations in sea water (Pb, Cd, Hg) and a lack of reliable data from all sub-areas of the Baltic Sea, any calculation of budgets and estimation of elemental residence times in the water column (related to annual total input or output values) should be considered preliminary and will therefore not be given here. However, initial figures on published trace metal inputs will be summarized (see Table 13). They should be regarded as reflecting the current situation to within approximately one order of magnitude.

Table 13. *Heavy metal inputs to the Baltic Sea*

Metal	Total <sup>1)</sup> inputs 10 <sup>3</sup> t/y	Atmospheric deposition mg/m <sup>2</sup> /y
Hg	0.029 <sup>2)</sup>	
Cd	0.21 <sup>4)</sup> , 0.25 <sup>5)</sup>	0.14 - 0.25 <sup>4)</sup> , 0.2 - 0.3 <sup>5)</sup>
Pb	4.3 <sup>4)</sup> , 6.2 <sup>5)</sup>	5.2 - 10.1 <sup>4)</sup> , 8.2 - 12.1 <sup>5)</sup>
cu	4.5 <sup>4)</sup> , 7.8 <sup>5)</sup> , 8.5 <sup>6)</sup>	1.2 - 1.5 <sup>4)</sup> , 1.8 <sup>5)</sup>
Zn	15.5 <sup>4)</sup> , 18.9 <sup>5)</sup>	9.3 - 17.0 <sup>4)</sup> , 16 - 20.9 <sup>5)</sup>
Cr	0.9 <sup>5)</sup>	0.55)
Ni	2.1 <sup>4)</sup> , 2.2 <sup>5)</sup> , 5.1 <sup>6)</sup>	0.75)

1) Sums of river inflow and atmospheric fall-out

2) Somer, 1977

4) Hovmand, 1979

5) Hansen et al., 1976, atmospheric deposition data from Hovmand (1975)

6) Emelyanov, 1976

The main routes of trace metal inputs to the Baltic Sea are river inflow and atmospheric fall-out. For lead, mercury, cadmium, and copper the main source (about 50 - 80 %) is fall-out, while the main load of chromium, nickel and zinc (53 - 83 %) seems to come with river inflow (Brzezińska and Garbalewski, 1978; Hansen et al., 1976). Municipal sewage contributes considerably less to the total metal load (1 - 6 %). Industrial discharges affect the trace metal balances significantly in limited regions (e.g., Øresund, Hanö Bight, Kalmar Sound, Gdańsk Bight, Bothnian Bay).

If there would be a state of equilibrium, the total inputs (rivers, fall-out, municipal, industrial) would be balanced by the sum of the amounts of trace metals deposited at the bottom, exported to the North Sea and possibly also contained in aerosols leaving the surface (Cattell and Scott, 1978). With regard to these different components, the existing data on river inflow and atmospheric fall-



out can be used for first estimates. For municipal and industrial discharges, available values are rather limited (Engwall, 1972; Thorell, 1975, 1977; Haverinen and Vuoristo, 1978; Vuoristo, 1980). The influence of technological improvements in industrial processes and additional waste water treatment plants necessitates periodic re-assessment of values published in the past. The calculation of the trace metal export is a difficult problem and the aerosol-forming parts are probably of lesser importance.

In most cases it is possible to estimate the annual local accumulation rate of sediment components quite accurately using  $^{210}\text{Pb}$ . Various estimates of long-term regional mean accumulation rates based on geological data vary within a factor of two. These regional estimates agree with local  $^{210}\text{Pb}$ -based determinations. It would thus be possible to calculate reasonable annual regional accumulation rates of heavy metals in sediments as soon as the numerous unpublished values on heavy metal concentrations have been collected.

## 6.2 Organic substances

The number of organic chemicals known to man at the present time exceeds one million compounds. A wide range of these substances occurs in animals and plants and in natural products (GESAMP, 1976). A small proportion of the total amount of organic chemicals is produced by man in large quantities, but most of these chemicals, if released into the sea, might be hazardous to the environment. A small percentage of man-made chemicals persists in the oceans and this has led man to consider the well-being of the marine ecosystems.

Organic compounds are classified as pollutants for different reasons, either because they are toxic and very often non-biodegradable or because they rapidly consume the dissolved oxygen of the water. Organic substances

which degrade very slowly in the natural environment can be a serious threat to the ecosystem. They may accumulate in the food chain and their concentrations may increase with each link of the chain.

Despite the potentially very large number of organic pollutants which are likely to enter the Baltic *Sea* in domestic sewage and industrial effluents, and from rivers, precipitation, ships, accidental spills and discharges, or as a result of past and present dumping, the number of organic substances actually measured on a scale sufficiently large for an overall assessment is rather small. These substances are:

- (a) mineral oil (petroleum hydrocarbons),
- (b) chlorinated hydrocarbon-type pesticides (DDT, toxaphene, chlordane),
- (c) polychlorinated biphenyls (PCBs) and related compounds.

These substances, especially in the case of mineral oil, consist of many individual chemical components. In addition, there may be many more, chemically different organic substances with potentially harmful effects present in the Baltic Sea, such as phthalate ester plasticizers (Ehrhardt and Derenbach 1980) and low-molecular weight halogenated hydrocarbons (Jernelöv et al., 1972), both of which can be determined in sea water, as well as substances which have not yet been detected in sea water (e.g., components of pulp mill effluents, non-halogenated hydrocarbon pesticides, degradation products of contaminants).

Thus, at present it is difficult to assess the overall degree of pollution of the Baltic Sea by organic substances, because any estimation of the relative hazard to the ecosystem of the small number of frequently measured organic substances must be regarded as no more than an educated guess.

Once in the sea, organochlorine compounds may be concentrated either in surface films or by marine organisms. Some, adsorbed onto particulate material, will be carried to the seabed and a certain amount will remain dissolved in the sea water at a very low concentration. Some of the organochlorine pesticides, particularly DDT, are known to be distributed on a world-wide basis. The residence time in the environment generally seems to be in the order of years.

To date, organic marine chemists have mainly studied mineral oil (petroleum hydrocarbons) and chlorinated hydrocarbons in the environment. This is due to the large amounts of these substances introduced into or transported across the Baltic Sea, their known toxicities, the obvious ecological impact of large scale oil contamination (which is an ever present threat), and the relative ease with which these substances can be analysed. A gas chromatograph equipped with a flame ionization detector is ideally suited for hydrocarbon trace analysis, while a gas chromatograph furnished with an electron capture detector is excellent for the detection and measurement of chlorinated hydrocarbons. However, despite these recent advances in analytical instrumentation, marine organic trace analysis remains a formidable challenge. It is important to recognize that a gap of unknown magnitude and significance exists concerning possible organic contaminants of the Baltic Sea and their ecological impact.

This gap, which is not unique to the situation in the Baltic but exists in every ocean environment, may be closed by a careful search for organic trace constituents of sea water. In this search, difficulties are encountered less with the methods of analysis, which have been developed to a fairly high degree of sophistication, e.g., computerized gas chromatography - mass spectrometry, than with the very low concentrations of organic sub-

stances whether indigenous or man-made in sea water. Successful attempts have been made to overcome this problem (Ahnoff and Josefsson, 1974; Osterroht, 1974; Ehrhardt, 1978), which should lead to a broader understanding of marine organic chemistry in general and the degree of pollution of the Baltic Sea in particular.

### 6.2.1 DDT and PCB residues

#### *DDT and its metabolites*

The term DDT is generally understood throughout the world and refers to 1,1-bis-(4-chlorophenyl)-2,2,2-trichloroethane. It is the prototype of the broad-action, persistent insecticides. It is stable under most environmental conditions and resistant to complete breakdown by the enzymes present in micro-organisms and higher organisms. Some of its metabolites, notably DDE (1,1-bis-(4-chlorophenyl)-2,2-dichloroethene), have a stability equal to or greater than that of the parent compound.

The metabolism of p,p'-DDT begins in the aliphatic part of the molecule and usually proceeds by two pathways, as shown in Figure 51.

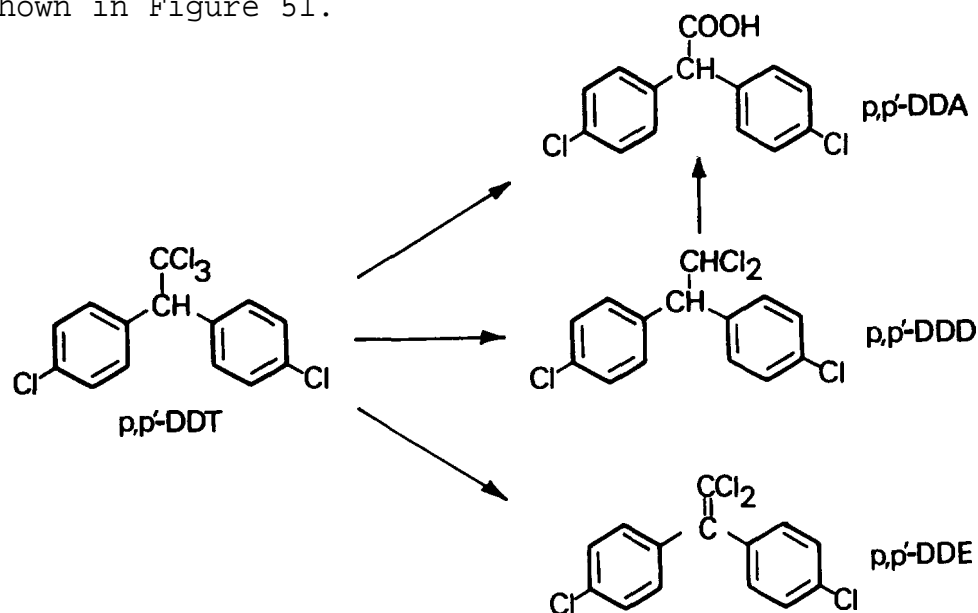


Figure 51. *The major metabolic pathways of DDT (Sundström, original figure).*

It has been found that organochlorine pesticides affect the transmission of impulses in the central nervous system and also affect calcium deposition in birds' eggs. Their acute toxicity to marine organisms is now fairly well documented (WHO, 1979). Crustacea are particularly sensitive; DDT concentrations as low as 3  $\mu\text{g}/\text{dm}^3$  in water have been documented to be lethal to shrimp, although fish can tolerate higher concentrations.

*PCBs and related compounds*

Polychlorinated biphenyl compounds (PCBs) form a class of chlorinated hydrocarbons. They are manufactured commercially by the progressive chlorination of biphenyl in the presence of a suitable catalyst. The chlorination of biphenyl can lead to the replacement of 1 to 10 hydrogen atoms by chlorine (see Figure 52).

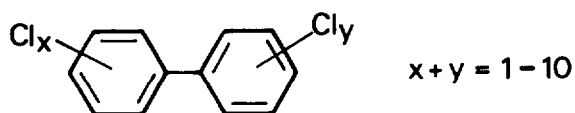


Figure 52. *The general chemical structure of PCBs.*

It has been calculated that 210 different biphenyl compounds of different chlorine content are theoretically possible, but in practice some of them are not obtainable by direct chlorination.

There is a variety of different PCB formulations, depending upon the degree of chlorination of the biphenyl molecule; the greater the degree of chlorination, the higher the viscosity. PCBs have a wide range of industrial uses, particularly in the electrical industry. However, this usage has now been restricted in a number of countries.

Much of what has been written on organochlorine pesticides will also apply to PCBs. They are just as widespread in the marine environment and their persistence and concentration in marine biota exceeds that of DDT. The mode of action of PCBs is not well understood but may be similar to that of organochlorine insecticides. The acute toxicity of PCBs is generally lower than that of organochlorine pesticides. There is some evidence, however, that they have a high chronic toxicity, but this may also be attributable to impurities in certain formulations. In some areas quite high levels of PCBs have been reported in fish and in the livers of sea birds, but the extent of damage to these organisms is not yet clear (WHO, 1976).

#### *Analytical methods*

Individual organic pollutants are not easily distinguishable against the background of naturally occurring components of the sample. Chlorine-containing organic compounds, such as DDT and its derivatives and PCBs, give clear, marked responses on an electron capture detector (ECD) upon analysis by gas chromatography (GC). That is why the vast majority of laboratories use the ECD for analytical work.

The detection limit of DDT and PCBs when using the ECD ranges from  $10^{-9}$  to  $10^{-12}$  g. DDT and PCB compounds are found in appreciable concentrations in many marine organisms, especially in those with a high lipid content and those at the top of the food chain, where the concentration level of chlorinated residues exceeds  $10^{-6}$  g/g fresh tissue. Concentrations of organochlorine compounds in oceanic water are close to the normally accepted detectable level, i.e.,  $10^{-12}$  g/dm<sup>3</sup>. As a consequence, there are very few laboratories in the world capable of carrying out reliable analyses of chlorinated hydrocarbons in sea water (Goldberg, 1976). Results of international intercalibration exercises and workshops

confirm this conclusion. During the Baltic Intercalibration Workshop in Kiel (Anon., 1977), the variations between determinations of chlorinated hydrocarbons in sea water spread over a wide range: PCBs 0.8 - 33 ng/dm<sup>3</sup>, DDT 0.1 - 9.4 ng/dm<sup>3</sup>. Discrepancies between the estimated values were recognized to be due to contamination of the water sampler and/or glassware, and the use of different methods. The conclusion which may be drawn from the experience so far is that most results of water analyses are not yet reliable.

One major problem concerning analyses of water samples has to be stressed and that is to define the sample as to content of suspended matter, and find the true amount of organochlorines dissolved in the water. This knowledge might increase the possibility to predict the biological availability of organochlorines.

In biological material the concentrations of chlorinated hydrocarbons are much higher, and analyses of them are more common. In particular, data are available for fish, shellfish, birds, and mammals. There have been a few intercalibrations on the analysis of chlorinated hydrocarbons in biological material in which Baltic laboratories have taken part (Baltic Sea Expert Meeting, 1974; ICES, 1977; Holden, 1980). The most recent intercalibration in which Baltic laboratories took part was the third intercalibration exercise on organochlorines sponsored by ICES (Holden, 1980). The coefficients of variation of the results obtained for the DDT group were in the range 38 - 44%, and for PCBs up to 50 %. Several laboratories supplied incorrect identification and quantification. The conclusion which can be drawn in view of this experience is that the results obtained so far by the Baltic laboratories are mainly similar, i.e., most of them should agree within  $\pm 50\%$ , but a few of them might be tenuous at best.

There is no overall view about the comparability of analyses of chlorinated hydrocarbons in sediments or particulate matter. But as the levels of chlorinated hydrocarbons in these matrices are within the range of those in organisms, it may be assumed that the reliability of the results should be higher than the reliability of results obtained from analysis of sea water. Nevertheless, separate intercalibrations on sediments should be carried out.

#### *Input of DDT and PCBs to the Baltic Sea*

In the Baltic Sea area, DDT has been in use for about 30 years and PCBs for a slightly longer period. Still, there are no data published about the total quantity of chlorinated hydrocarbons used during these years. It is well known that during application, a certain percentage of these compounds is inevitably lost and eventually reaches the sea along various routes.

Investigations of these routes have been almost totally neglected and there are only a few papers on the atmospheric fallout of chlorinated hydrocarbons (Södergren, 1972; Andrulowicz et al., 1977). These studies are not devoted to the Baltic Sea as a whole, but deal instead with certain coastal zones of the Baltic. However, in view of the lack of additional data, they might be considered as typical for the Baltic Sea as a whole.

Studies carried out along the southern coast of Sweden in the years 1969 - 1971 (Södergren, 1972) gave a range of atmospheric deposition from 0.14 ng/m<sup>2</sup>/h to 2.3 ng/m<sup>2</sup>/h for DDE and DDT. Considerable regional differences were noticed, i.e., a fivefold increase in the occurrence of DDE and DDT was observed along the section from Malmö to Kristianstad.

According to calculations based on results obtained at the Gdynia and Hel stations on the Polish coast from



1974 to 1976, dry fallout is the major deposition route of chlorinated pesticides into the sea (Andrulewicz et al., 1977). However, considerable local differences were observed between Gdynia and Hel. The average values for these stations were 60.9 and 32.4 ng/m<sup>2</sup>/h, respectively. Some differences were also found due to the method of collection used. The dry fallout sampled using a water collector gave results for chlorinated hydrocarbons ranging from 10.7 to 87.5 ng/m<sup>2</sup>/h.

The  $\Sigma$  DDT concentrations in wet precipitation collected monthly in the coastal zone of the Gulf of Gdańsk varied widely, from 0.6 ng/dm<sup>3</sup> to 21.8 ng/dm<sup>3</sup>. A certain seasonality was observed, i.e., there was a tendency for the highest concentrations to appear during March and April, while the lowest concentrations occurred during August and September.

The routes of entry of PCBs to the marine environment are still under investigation. Analysis of sewage sludge has revealed that most sewage contains PCBs. The atmosphere has been also suggested as an important transport route of PCBs to the oceans (WHO, 1976). Results obtained by Södergren for PCBs in dry fallout were in the range from 1 ng/m<sup>2</sup>/h to 15 ng/m<sup>2</sup>/h. The only information about river input of PCBs to the Baltic Sea area is available for the Göta river in Sweden, where values from 0.2 to 1.2 ng/dm<sup>3</sup> were found (Ahnoff and Josefsson, 1975).

Under the Helsinki Convention, the Baltic Sea countries have radically restricted or even eliminated the use of DDT and PCBs. Table 14 contains information on the actual application of those substances according to the Scientific-Technological Working Group of the Helsinki Commission (STWG, 1979).

Table 14. *Use of the DDT and PCB groups of substances in Baltic Sea countries in 1979*

	DDT and its derivatives	PCBs
Denmark	Negligible use; total ban expected	No production; use under restriction since 1976
Finland	Use abolished from Jan., 1977	No production; no import since 1979; a special study on amounts used under way
German Democratic Republic	Total ban since 1971	No production; 85% of use in closed systems
Federal Republic of Germany	Total ban since 1977	2000 tonnes low-chlorinated and 4000 tonnes high-chlorinated PCBs produced; 2000 tonnes of both processed annually; losses 25 g/PCBs tonne produced
Poland	Total ban since 1976	Negligible production; use in mining industry; since 1972 total ban on discharging into inland and Gulf of Gdańsk waters
Sweden	Total ban as pesticide from 1975; negligible use for medical purposes	No production; 1500-2000 tonnes in present use (capacitors) plus some amounts very hard to estimate
Union of Soviet Socialist Republics	Total ban since 1974	Total ban of use since 1971

Although there are few data on the actual impact of the restrictions on the use of DDT and PCBs, some data have been published showing a remarkable decrease in DDT levels in river water from Poland (Taylor and Bogacka, 1977). However, no decrease in  $\Sigma$  DDT in sea water has so far been observed (Andrulewicz et al., 1977; Andrulewicz and Samp, 1978; Nielsen, 1979).

## 6.2.2 Levels of organochlorine compounds

## Water

There are few analytical data available on chlorinated hydrocarbon concentrations in Baltic Sea water (Stadler and Ziebarth, 1976; Stadler, 1977a, 1977b; Osterroht, 1977; Andrulowicz et al., 1977). Multiyear observations (1974 - 1980) were carried out in Poland (Andrulowicz et al., 1977; Andrulowicz and Samp, 1978), but the most recent data (from 1978 - 1980) have not yet been published. Table 15, taken from a publication by Andrulowicz and Samp (1978), summarizes concentration data for different areas of the Baltic Sea.

Table 15<sup>\*)</sup> Comparison of analytical data on chlorinated hydrocarbon levels in water in the Baltic Sea area

Authors	Study area	Concentrations (ng/dm <sup>3</sup> )					PCBs
		DDT	DDE	DDD	ΣDDT		
Ahnoff and Josefsson, 1975	Göta River (surface layer)						0.3- 1.2
Osterroht, 1977	Baltic (Hanö Bay)	0.1 - 0.2	0.5 - 5.2	-			0.3- 3.0
Stadler and Ziebarth, 1976	Western Baltic (surface layer)	0.1 - 0.3	-	0.8 - 3.4	-		1.1- 5.9
Andrulowicz et al., 1977	Gdańsk Basin	0.03-4.22	0.03-3.00	0.02-1.1	0.08-6.85		0.1-10.2
Andrulowicz and Samp, 1978	Gdynia-EOSEX-77	-			1.1 - 4.7		1.5-28.1

<sup>\*)</sup> reproduced from Andrulowicz and Samp (1978).

Additional information is presented in Table 16, reproduced from a publication by Brüggmann and Luckas (1978).

Table 16<sup>\*)</sup>. PCBs and DDT in Baltic Sea water

Sea Area	Date of Sampling (1976)	PCBs (ng/dm <sup>3</sup> )	pp'-DDT/ pp'-DDE (ng/dm <sup>3</sup> )
1. Lübecker Bight	24.03	1.6	0.6
	06.08	6.1	0.8
2. Fehmarn Belt	06.08	138.8	2.3
3. Mecklenburger Bight	28.01	6.1	2.6
	18.02	2.1	0.6
	07.08	18.9	0.6
4. Kadetrinne	07.08	11.5	0.5
5. Arkona Basin	21.02		0.4
	26.03	1.8	0.3
	27.03	0.7	0.3
	08.08	8.6	0.8
	08.08	7.6	0.7
6. Bornholmsgat	08.08	6.6	0.7
7. Bornholm Basin	29.03	0.9	0.2
	09.08	1.6	0.2
	10.08	3.8	0.4
	10.08	5.5	0.8
8. Gdańsk Deep	07.04	5.9	0.4
	11.08	8.1	0.4
9. Southeast Gotland	10.04	0.3	0.2
10. Gotland Basin	20.02		0.4
	12.08	1.4	0.5
	13.08	2.7	0.2
	13.08	3.0	0.3
11. Western Gotland	15.08	2.9	0.4
12. Fårö Deep	08.04	2.3	0.3
	14.06	4.0	0.4
13. Landsort Deep	15.08	9.1	0.8
Concentration range		0.3-138.8	0.2-2.6
Mean value 1)		5.0	0.63
Standard deviation 1)		4.2	0.56
Relative standard deviation 1) (%)		84	89

1) Omitting PCB value of station No. 2

\*) reproduced from Brüggemann and Luckas (1978)

The geographical distribution of  $\Sigma$  DDT in the sub-surface layers of the Gdańsk Basin shows that  $\Sigma$  DDT concentrations decrease slightly from the land to the open sea (Andrulewicz and Samp, 1978). At the same time,  $\Sigma$  DDT concentrations were often higher in the open Baltic Sea than in the Gdańsk Basin. The same effect was observed for PCBs.

The percentages of the different components of the total DDT content calculated for 1974-1976 were: DDT 45%, DDE 31%, and DDD 24%. Since the ban was imposed on the use of DDT, the equilibrium among the individual components of total DDT has begun to shift towards a preponderance of the DDE metabolite. The results of current analyses (1977-1980) show that DDE has become the dominant component of  $\Sigma$  DDT and that DDD values have decreased to barely detectable levels. The average ratio of  $\frac{\text{PCB}}{\Sigma \text{ DDT}}$  has increased from 1.45 to 3.24 during the research period.

#### *Sediments*

No systematic investigations of chlorinated hydrocarbons in the bottom deposits of the Baltic Sea have been made.

At present, results obtained in Finland, the Federal Republic of Germany, Poland and Sweden are available (Oden and Ekstedt, 1976; Niemistij and Tervo, 1978a; Andrulewicz et al., 1979; Osterroht and Smetacek, 1979; Voipio and Niemistö, 1979). The data are compared in Table 17. It was found that chlorinated hydrocarbons are strongly associated with organic carbon, so their geographical distribution in surface sediments matches the geographical distribution of organic carbon (Andrulewicz et al., 1979).

Table 17. Comparison of analytical data on chlorinated hydrocarbons in surface Baltic Sea sediments

Authors/Area	$\Sigma$ DDT (ng/g)	PCBs (ng/g)
Oden and Ekstedt, 1976		
1) Near the BOSEX area		175
2) Gotland Deep	8-50	950
Niemistij and Tervo, 1978a		
1) BOSEX area	29	106
2) Gotland Deep	22	31
Osterroht and Smetacek, 1979		
Kiel Bight	(DDE+DDT) 2.2	9.6
Andrulewicz et al., 1979		
sediments from coastal stations of the Polish sector		
1) sands	7	43
2) muds	18	204

Voipio and Niemistij (1979) indicated a significant difference between the concentrations of chlorinated hydrocarbons in surface sediments and those in the deeper layers of sediment (see Figure 53). The concentration curves are closely related to the history of the application of these compounds in the Baltic countries.

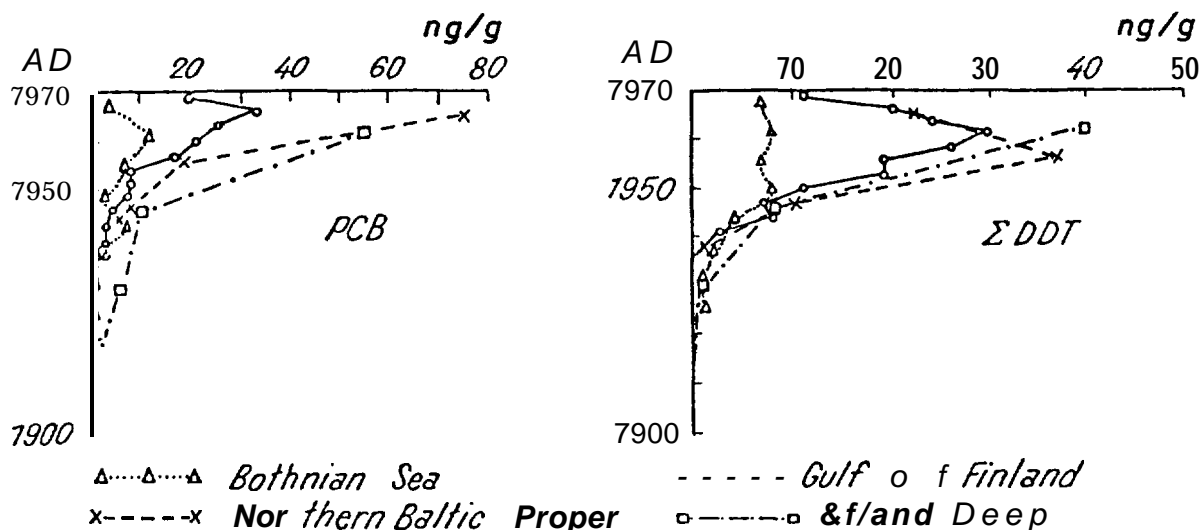


Figure 53. Vertical distribution of PCBs and  $\Sigma$  DDT in sediment cores from four Baltic Sea stations. Concentrations are in ng/g. (from Voipio and Niemistij, 1979).

### *Organisms*

DDT and PCB residues are associated with the lipid fraction of marine organisms. The particular level in any single organism or group of organisms depends upon the degree of exposure, i.e., the levels of these pollutants in the water in which the organisms live and in the food they consume.

Plankton samples from both the open sea (Brügmann and Luckas, 1978; Jensen et al., 1972c) and locally polluted archipelago areas (Jensen et al., 1972c; Linko et al., 1974b, 1979) have been analysed. Zooplankton caught near the coast of Finland have exhibited total DDT concentrations on a wet weight basis ranging from 0.6 - 15 µg/kg and on a fat weight basis from 30 - 85 µg/kg (Miettinen and Hattula, 1978). PCB levels in the range of 0.1 - 4.8 mg/kg dry tissue (Brügmann and Luckas, 1978) and 3.1 - 340 mg/kg fat weight have been estimated (Jensen et al., 1972c; Linko et al., 1974b, 1979). The latter value, however, was obtained from a locally polluted area (Linko et al., 1979). When collecting plankton samples, the risk of contamination from boat bottom paint containing PCBs must be pointed out (Jensen et al., 1972c).

During the Baltic Baseline Study in 1974/1975 (ICES, 1977), two countries sampled and analysed the shellfish *Mytilus edulis*, *Macoma baltica* and *Mesidothea entomon*. The results are presented in Table 18. This table also includes the results of analyses of *Crangon crangon* which were obtained at the same time at the Institute of Meteorology and Water Management in Poland.

Table 18. Chlorinated hydrocarbon concentrations in selected benthic organisms in 1974/1975

Organism	DDT	DDE	DDD	Σ DDT	PCBs
	(µg/kg wet weight)				
<i>Mytilus edulis</i>	6-52	6- 9	7-85	11-132	32-139
<i>Macoma baltica</i>	T*-38	7-21	8-76	22-112	20- 98
<i>Mesidothea entomon</i>	T*-92	3-68	T*-98	8-480	60-130
<i>Crangon crangon</i>	10-18	8-27	30-45	48-115	40- 98

T\* - traces

Most studies on the levels of organochlorines have been made using samples of fish muscle. Some representative values for several species are given in Table 19.

Mean levels of DDT residues in different catches of herring (*Clupea harengus*) have been reported in muscle ranging from 2.1 - 86 mg/kg (fat weight), corresponding to 0.07 - 3.2 mg/kg (fresh weight) (see Figure 54 for examples of some values from the southern Baltic Sea). Values for PCB residues in the same samples were 4.2 - 41 mg/kg (fat weight) and 0.15 - 1.5 mg/kg (fresh weight) (Jensen et al., 1972a; Linko et al., 1974a; Luckas et al., 1980a, 1980b).



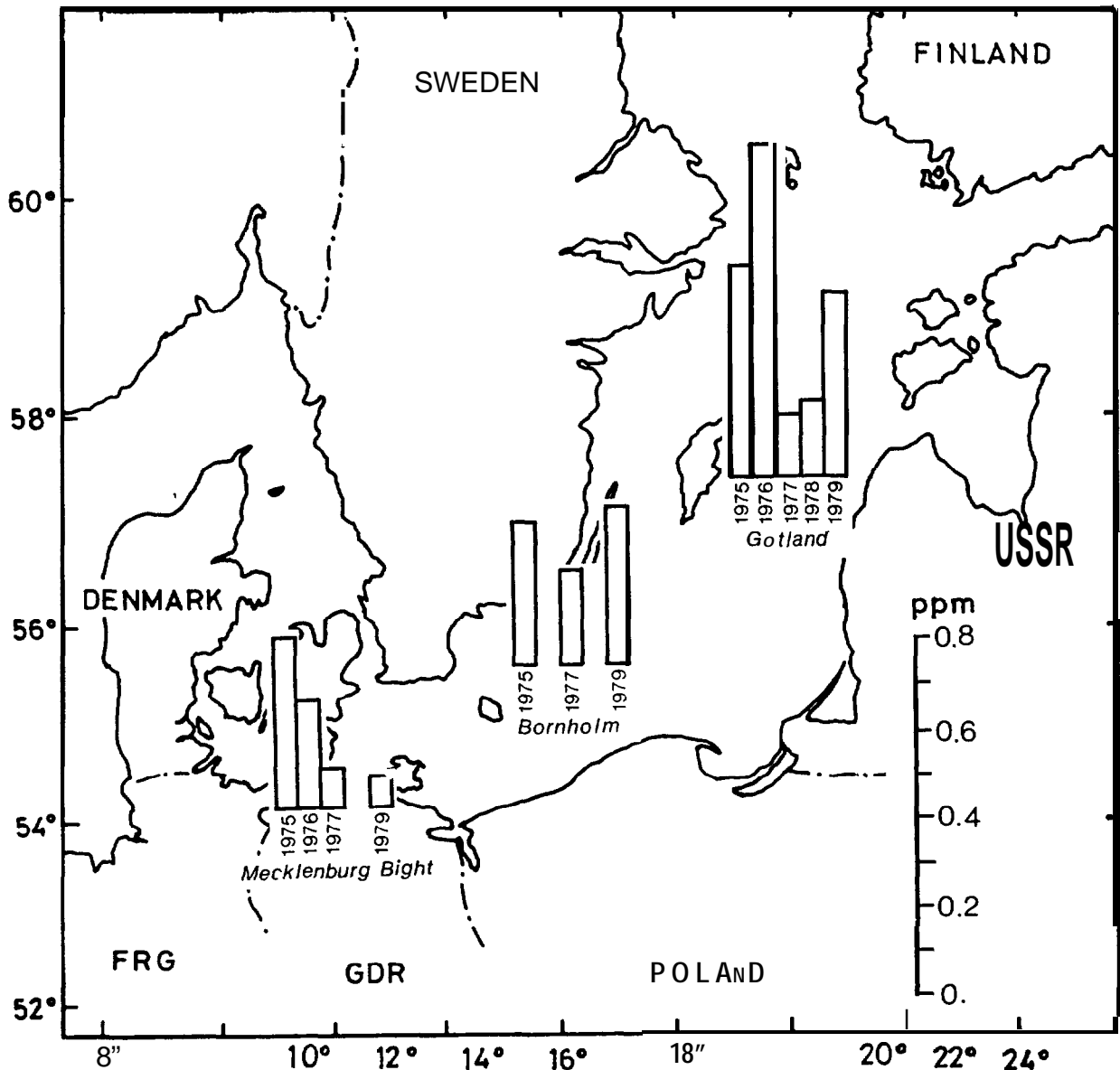


Figure 54. Total DDT concentrations in herring (muscle tissue) from the central and southern Baltic Sea (Figure prepared by Ehrhardt using data from Luckas et al., 1980a).

Several authors have reported levels in cod (*Gadus morhua*), with most of the data for cod liver. The mean DDT and PCB concentrations in extractable fat of livers ranged from 19 to 64 mg/kg and 4.1 to 32 mg/kg (fat weight), respectively, in various catches. Corresponding figures on a wet (fresh) weight basis were 1.2 - 18 mg/kg and 1.9 - 15 mg/kg (Jensen et al., 1972a; Luckas et al., 1980a, 1980b). Mean levels of DDT residues in cod muscle from various catches were in the range of 0.023 - 0.25 mg/kg (fresh tissue) and 4.4 - 40 mg/kg (extractable fat), while PCB concentrations in cod muscle were 0.016 - 0.39 mg/kg (fresh tissue) and 1.9 - 35 mg/kg (extractable fat) (Jensen et al., 1972a).

Table 19. Mean concentrations of PCBs and  $\Sigma$  DDT (on a fresh weight basis) as well as PCB/CDDT ratios in fish from the Baltic Sea (from Luckas et al., 1980a)

Year	Mecklenburger Bay				Bornholm Basin				Gotland Basin			
	Number of Samples	PCB mg/kg	$\Sigma$ DDT mg/kg	$\frac{\text{PCB}}{\Sigma \text{ DDT}}$	Number of Samples	PCB mg/kg	$\Sigma$ DDT mg/kg	$\frac{\text{PCB}}{\Sigma \text{ DDT}}$	Number of Samples	PCB mg/kg	$\Sigma$ DDT mg/kg	$\frac{\text{PCB}}{\Sigma \text{ DDT}}$
<u>HERRING</u> <sup>1)</sup>												
1975	30	0.61	0.38	1.6	50	0.33	0.32	1.0	90	0.55	0.47	1.2
1976	30	0.44	0.24	1.8				-	20	0.65	0.47	0.9
1977	25	0.28	0.09	3.1	5	0.32	0.21	1.5	30	0.23	0.14	1.6
1978								-	95	0.26	0.17	1.5
1979	20	0.36	0.07	5.1	10	0.95	0.35	2.7	40	1.12	0.41	2.7
<u>SPRAT</u> <sup>2)</sup>												
1975	15	0.53	0.35	1.5				-	35	0.58	0.69	0.8
1976	20	0.56	0.17	3.3	-	-	-	-	25	0.69	0.44	1.6
1977								-	5	0.62	0.36	1.7
1978	20	0.49	0.15	3.3	5	0.40	0.26	1.5	44	0.26	0.15	1.7
<u>GARPIKE</u> <sup>1)</sup>												
	Rügen Area											
1976	21	0.58	0.47	1.2								
1977	20	0.59	0.21	2.8								
1978	27	0.29	0.13	2.2								

1) muscle filets

2) ungutted fish without head

Other fish species investigated, including sprat (*Sprattus sprattus*) and garfish (*Bellone bellone*), have much the same levels in fresh muscle as herring (Jensen et al., 1972a; Luckas et al., 1980b), while flounder (*Platichthys flesus*), plaice (*Pleuronectes platessa*) (Jensen et al., 1972a) and pike (*Esox lucius*) (Linko et al., 1974a; Olsson and Jensen, 1975; Jensen et al., 1977) have levels in fresh tissue much the same as those in cod muscle. Salmon (*Salmosalar*), being a fat fish, has concentrations of DDT and PCB residues in fresh muscle ranging from 0.5 to 7.2 mg/kg and 0.4 to 2.7 mg/kg, respectively.

An important question is whether the levels of organochlorines found in fish are a result of a simple bioaccumulation (concentrating of a compound in a species as compared to the environment) or of a biomagnification (increase in levels through the food chain caused by food intake) and if the levels represent a steady state concentration - water to fish - or a lifelong accumulation. Jensen et al. (1972a) found increasing levels of DDT and PCB residues in Baltic Sea herring with increasing age. They concluded that not only is the age or exposure time important, but also the migration route within a heterogeneous environment. Olsson and Jensen (1975), studying sub-populations of the stationary pike, found no correlation between DDT and PCB levels in extractable fat and the weight of the fish. Nor did they find any differences in levels between females and males.

Luckas et al. (1978) and Schneider and Osterroht (1977) found increasing levels of DDT and PCBs in fresh cod liver with increasing length of the cod. Simultaneously, the lipid content of the liver increased. As an explanation, Schneider and Osterroht suggested that with increased fish length, the size of the prey increased and, thus, the trophic level of the prey will be elevated when the predator grows. They believed that a biomagnification might explain the variance. In a later work,

Schneider (1978) studied the food chain in Kiel Bay but found no correlation between PCB concentrations and trophic levels. Thus, he agreed with Scura and Theilacker (1977) who concluded that the levels found in fish are a result of the partitioning of organochlorines between sea or lake water and the various lipids in the organism. The rapid seasonal variations in PCB levels found in perch from a Swedish lake (Olsson et al., 1978) and in perch from the Baltic coast (Edgren et al., unpublished), with twice as high levels during late spring and early summer compared with other periods of the year, also indicate a partitioning between water and the lipids of the organism.

Thus, as a general rule, the concentrations of organochlorine compounds in the extractable fat of fish are much the same independent of species. On a fresh tissue basis the variance among species is mostly due to different concentrations of lipids. However, there appear to be some differences in concentrations between fish species even on the basis of extractable fat. The stationary species young, yellow eel (*Anguilla anguilla*) and pike (*Esox lucius*) from the same localities were sampled simultaneously from several areas along the Swedish coast (Jensen et al., 1977). The levels of DDT and PCB residues in the extractable fat of eel did not exceed 4.6 mg/kg, while corresponding levels in pike never fell below 5.3 mg/kg but ranged up to 28 mg/kg. Thus, there are obviously some differences between species in the partitioning of water:lipids of organisms.

In contrast, organochlorine levels in Baltic Sea birds and mammals are a result of true biomagnification. Thus, the levels in extractable fat (not always in fresh tissue) in these animals reflect the levels in their prey. Birds feeding on marine invertebrates generally have levels of both DDT and PCB residues below 20 mg/kg in extractable fat (Olsson et al., 1973; Olsson, unpub-

lished; Odsjö and Olsson, 1976; Figge et al., 1976). Birds feeding on fatty fishes such as herring and sprat show levels above 100 mg/kg in extractable fat (Olsson et al., 1973; Falandysz, 1980; Jensen et al., 1972b; Andersson et al., 1974; Figge et al., 1976), while birds feeding on lean fishes such as the young of perch, roach, three-spined stickleback, etc., generally show intermediate levels (Figge et al., 1976; Olsson et al., 1973; Lemmetyinen et al., 1977; Falandysz, 1980). Finally, the top predators (white-tailed eagle and eagle-owl) also contain the highest concentrations of organochlorine residues. Levels up to about 10 000 mg/kg have been found in these birds. All specimens analysed were found dead (Jensen et al., 1969b; Odsjö, 1973).

When studying the levels of organochlorines in birds, the age and sex of the birds have to be considered. The females of arctic terns show lower levels than the males and this is probably caused by the release of large amounts of fat through the egg-laying process of the female (Lemmetyinen and Rantamäki, unpublished). During growth, the levels in the young terns seem to decrease, at least if the nesting area is less polluted than the wintering and migrating areas (Jensen et al., 1972b; Lemmetyinen and Rantamäki, unpublished). However, this occurs also in guillemot fledglings where the adults stay all year round within the nesting area (Olsson, unpublished). Levels found in adult birds are to a large extent representative of the wintering area and the migration route of the birds and only partly representative of the nesting areas, especially at the beginning of the nesting period (Jensen et al., 1972b; Lemmetyinen and Rantamäki, unpublished).

Baltic marine mammals feeding on fish have considerable levels of both DDT and PCB residues. In adult ringed seals (*Phoca hispida*), common seals (*Phoca vitulina*), and grey seals (*Halichoerus grypus*), the levels are generally about 100 mg/kg in the extractable fat of blubber

(Olsson et al., 1974; Helle et al., 1976a; Clausen, 1978). The same is also true for the common porpoise (*Phocoena phocoena*) (Harms et al., 1977/1978; Otterlind, 1976). In otter (*Lutra lutra*) living in coastal areas, the PCB levels are also of the same magnitude (Sandegren et al., 1979). The levels of organochlorines increase with age in adult seal males but not in females (Helle et al., 1976b).

#### *Regional differences in contaminant levels*

Several authors have reported regional differences in the levels of DDT and PCB residues. In plankton, local influences have been recorded outside Stockholm, Turku and in the Mecklenburger Bay (Brügmann and Luckas, 1978; Jensen et al., 1972c; Linko et al., 1979). In plankton samples from these areas, the levels of PCBs are higher compared with samples collected from the open sea. Also in fish (pike) from the archipelagos of Turku and Stockholm, the PCB levels decrease towards the open sea (Linko et al., 1974a; Olsson and Jensen, 1975; Verta et al., 1979), whereas DDT levels appear to increase. The livers in cod from the Kiel fjord were more polluted by PCBs than livers in cod from the Kiel Bay (Schneider and Osterroht, 1977). The livers in cod from the Mecklenburger Bay showed lower PCB levels than those from the open Baltic Proper east of Bornholm (Luckas et al., 1978). This is in contradiction to the PCB levels in plankton samples from comparable areas (Brügmann and Luckas, 1978) but in accordance with studies on herring (Jensen et al., 1972a; Jensen et al., 1977) showing higher PCB and DDT levels east of Bornholm than west. The lowest levels in herring for both DDT and PCB residues were recorded in the Kattegat and the highest in the Baltic Proper east of Bornholm (Jensen et al., 1972a). East of Bornholm the DDT levels decreased to the north and the lowest levels were found in the Gulf of Bothnia, whereas PCB levels were much the same from south to north (Jensen et al., 1972a). These

regional differences in DDT and PCB concentrations in herring have been confirmed by investigations on herring-feeding seals (Olsson, 1977).

The pollution pattern of pelagic herring and seals differs from that of benthic fish species such as eel and pike (Jensen et al., 1977). The highest levels of PCBs in benthic fish were found in the northern part of the Skagerrak and in the Øresund. Furthermore, neither eel nor pike showed any obvious increase in DDT levels in the southern part of the Baltic Proper east of Bornholm, as was found with herring. In fact, even if small variations in levels between different areas were found, no general regional changes such as the herring display could be found among benthic fish species. One possible explanation is that the benthic fish species analysed live in relatively shallow water which is part of the surface waters above the halocline, while herring during feeding periods meet an environmental influence from both the surface water and the bottom water below the halocline. Such areas are especially developed in the deep basin regions in the Baltic Proper. This indicates a quantitative difference in the DDT and PCB contamination between surface and bottom waters.

It is obvious that there is a need for good knowledge concerning the migration routes of the fish species to be analysed in any monitoring programme.

#### *Trends in contaminant levels*

Trend studies concerning levels of DDT and PCBs in Baltic biota have been carried out mainly on fish but also on birds. The main problem in these studies is to select species and populations for annual collection in such a way that the samples will be comparable from year to year. This is a major problem particularly for migrating fish species. So far no trend studies on Baltic Sea stationary fish populations are known.

However, several authors have found decreasing levels of DDT residues in various fish species. Thus, Luckas et al. (1980a, 1980b) have found decreasing DDT concentrations in the southern Baltic Sea in cod liver, herring, sprat and garfish during the period 1971 - 1977. The PCB levels were more or less constant. Schneider (1978) found constant PCB levels but decreasing DDT levels in the livers of cod collected in 1974 and 1977 in the Kiel Bay. Also Paasivirta et al. (1976) have detected a significant decrease in DDT in annually collected herring samples from the Baltic Sea during the period 1973 - 1975. Similar observations have been made by Nielsen (1979) and Chodyniecki (1979).

Compared with earlier results in the Turku archipelago (Olsson and Jensen, 1975), Verta et al. (1979) found a decrease in the DDT concentrations in pike muscle, whereas a decrease in PCB levels was not evident.

The herring- and sprat-feeding bird guillemot stays all year within the Baltic area (Helle et al., 1976b). This makes the bird valuable as a monitoring organism. Eggs have been collected annually since 1968 and analysed for DDT and PCB residues. The maximum DDT levels were found in 1969 - 1970 and since then a successive decrease has continued until 1975 (Olsson, 1978a). The PCB levels have not decreased during the same period.

Based on the information now available, it appears that DDT levels are decreasing in Baltic biota, while PCB levels have remained nearly constant.

#### *Influence on levels from other pollutants*

Little is known about interactions between organochlorines and other pollutants. However, two interactions should be mentioned since both might give alterations in the concentrations of DDT and PCBs in biota.



First, it is a well-known fact that a temperature increase causes an increased metabolic rate in fish. Laboratory studies have shown that the uptake of organochlorines in brackish water fish increases at increased temperatures (Edgren et al., 1979). The levels of DDT and PCB residues were also higher in perch collected outside a power plant in the heated water recipient than in the adjacent area where the intake of cooling water took place (Edgren et al., unpublished).

Secondly, since organochlorines, such as DDT and PCB residues, are bioaccumulating substances, the density of the biomass influences the concentrations in the biomass. The larger the biomass, the lower the organochlorine concentration per gramme of biomass at a given discharge (Olsson et al., 1975).

### 6.2.3 *Budget*

It would be valuable to construct a model of the flow of halogenated hydrocarbons in the Baltic ecosystem and to determine the budget of these compounds in the Baltic Sea. There is no literature published on this subject as far as pesticides are concerned and there are not enough analytical data to calculate the budget properly.

In 1978 Kihlström and Berglund published a paper estimating the amounts of polychlorinated biphenyls in the biomass of the Baltic Sea. They concluded that the main source of PCBs in the Baltic Sea seems to be atmospheric fallout and, according to the very few data available, this amounts to approximately 6 000 kg per year. There seems to be between 2 000 and 3 000 kg of PCBs accumulated in organisms, 100 kg of which is contained in fish. 30% to 60% of this amount is removed annually in the commercial catch of fish. The paper indicates that the amounts of PCBs in the Baltic Sea might be increasing.

On the basis of data which were adopted by Kihlström and Berglund, i.e., a total biomass of fish of  $1.8 \times 10^9$  kg and a total biomass of macrofauna of  $28 \times 10^9$  kg, and assuming that the concentrations of  $\Sigma$  DDT in fish in general might be as high as 50  $\mu\text{g}/\text{kg}$  and in macrofauna 10  $\mu\text{g}/\text{kg}$ , we obtain values of 90 kg of  $\Sigma$  DDT accumulated in fish and 280 kg of  $\Sigma$  DDT in macrofauna. Considering that the concentration of  $\Sigma$  DDT in Baltic water is about 0.7  $\text{ng}/\text{dm}^3$ , it is estimated that about  $15 \times 10^3$  kg of  $\Sigma$  DDT are present in Baltic sea water.

A complete budget, however, must also take into account the amounts of organochlorines in the sediments of the Baltic Sea and the processes of sedimentation and resuspension of these substances. This information is generally not available.

#### 6.2.4 Other organochlorine compounds

##### *Polychlorinated terphenyls (PCTs)*

A group of compounds structurally related to PCBs is the polychlorinated terphenyls (PCTs). The amounts used and the use pattern of PCTs are not very well known, but investigations in Japan, USA and western Europe have shown that PCTs are present in environmental samples from several locations as well as in man (Japan).

PCTs have recently been reported to be present in biota from the Baltic Sea area. Using an analytical method based on perchlorination of purified fat samples, three white-tailed eagles (*Haliaeetus albicilla*) were shown to contain 2.8, 3.9 and 17.2 mg PCT/kg fat. Likewise, three grey seals (*Halichoerus grypus*) contained 0.50, 0.66 and 1.0 mg PCT/kg fat. These levels correspond to about 1% of the total PCB levels in the samples (Renberg et al., 1978).

PCTs were also detected in two samples of black-headed gulls (*Larus ridibundus*) from the Baltic south coast (Falandysh, 1980). The pectoral muscle of the birds contained 13 and 1.5 mg PCT/kg extractable fat and the liver and adipose tissue of the first sample contained 21 and 1.9 mg PCT/kg, respectively.

#### *Chlorinated terpenes (toxaphene) and chlordane compounds*

At present, chlorinated terpenes are the chlorinated pesticides most extensively used in the world. The world production and use is today larger than that of DDT ever was. Due to analytical difficulties, their occurrence and distribution in the ecosystem are poorly understood.

Recently, chlorinated terpenes and chlordane compounds were found in Baltic biota (Jansson et al., 1979). The levels in extractable fat of herring were comparable to or even higher than the PCB and DDT levels in the same sample. It appears that these compounds do not bio-magnify like PCBs and DDT since the levels were approximately the same in the predators, the guillemot and the seal, as in their prey, the herring. Because the chlorinated terpenes are extremely toxic to fish, the contamination of the Baltic Sea by these substances should be carefully followed in the future.

## 6.3 **Lignin sulphonates and humic substances**

### 6.3.1 *Introduction*

Humic substances are naturally occurring dark-coloured polyphenolic compounds. The chemical structure of humic substances in fresh and coastal waters is far from well-known, but many observations indicate that biologically and abiotically modified lignin is an important constituent. In the Baltic Sea, a considerable fraction of the water soluble humic substances (i.e., fulvic acids) is

probably of terrigenous origin, although some types of humic substances can also be formed from cellular products of aquatic organisms.

Lignin sulfonates found in the Baltic Sea are exclusively waste products from sulfite pulp mills. The high polarity of the sulfonic acid groups makes the lignin macromolecule water soluble which in turn leads to a wide geographical dispersal. Kraft lignins, formed during sulfite pulping, are poorly soluble in water and therefore will only be found in localized areas.

Because the absorption of humic substances increases toward shorter wavelengths (cf. Jerlov, 1976; Nyquist, 1979b), the presence of humic substances results in decreased light transmittance in the blue part of the visible spectrum. Therefore, the transmittance maximum of the Baltic Sea water is displaced to a longer wavelength (555 nm; cf. Højerslev, 1974) compared with open ocean waters (475 nm). Lignin sulfonates absorb predominantly in the ultra-violet range and will not influence the transmittance of daylight; however, colored products in the sulfite wastes influence some areas.

Ultra-violet (UV) measurements have been used for a long time to determine the yellow substances ("Gelbstoff") in the Baltic Sea. This "Gelbstoff" consists mainly of fulvic acids. The UV measurements show that the light absorption properties of Baltic water increase when the salinity decreases, indicating an input of yellow substances via river discharges. Absorption data have been used to characterize water masses and to study mixing processes (cf. Jerlov, 1955). Fluorescence measurements were previously applied. However, there has been a lack of reliable standards for the conversion of absorbance or fluorescence readings to fulvic acid concentrations. UV measurements of lignin sulfonates can

only be used close to sulfite waste water outlets because of the much lower sensitivity and specificity of these measurements compared to fluorimetric determinations.

### 6.3.2 *Methods*

Humic substances and lignin sulfonates are determined simultaneously in water samples by a fluorimetric method. The method, including theory and procedure, is described by Nyquist (1979b). Briefly, the method utilizes the differences in fluorescence emission maxima of humic substances and lignin sulfonates. By measuring the fluorescence intensity at different wavelengths, the concentrations can be calculated (cf. Almgren et al., 1975). At the wavelengths used (excitation at 313 nm; emission at 365 to 430 nm), interference from other fluorescent substances is as a rule negligible. However, reliable standard substances for lignin sulfonates and humic substances are needed. The accuracy of the method depends on the agreement between the fluorescence properties of the standards and the dissolved humic substances and lignin sulfonates in the Baltic Sea. The standards used seem to be representative for the Baltic. The precision of the method is better than 5% for humic substances and 10% for lignin sulfonates.

### 6.3.3 *Mean concentrations in various sub-areas of the Baltic Sea*

Humic substances and lignin sulfonates were determined in the Baltic Sea from 1974 to 1977. The concentrations in the sub-areas of the Baltic Sea (cf. Nyquist, 1979b) were calculated as shown in Table 20.

Table 20. *Concentrations of humic substances and lignin sulfonates in several sub-areas of the Baltic Sea*

Sub-area	Depth (m)	Number of sampling occasions	Concentration (mg/dm <sup>3</sup> )	
			Humic substances	Lignin sulfonates
Baltic Proper	0	4	1.27 ± 0.11	0.35 ± 0.03
	100	4	1.13 ± 0.11	0.29 ± 0.04
Bothnian Sea	0	5	1.62 ± 0.03	0.30 ± 0.02
	100	5	1.51 ± 0.07	0.31 ± 0.02
Bothnian Bay	0	7		
	80	6	2.63 ± 0.16 2.35 ± 0.16	0.18 ± 0.03 0.18 ± 0.03

The humic concentrations in the surface water layer were significantly higher (confidence level = 95%) than those in the bottom water in the Baltic Proper and the Bothnian Bay (10% higher). The lignin sulfonate concentrations in the Baltic Proper were 20% higher in the surface water than in the bottom water. Otherwise, there were no significant differences between the surface and bottom concentrations. No trends in the concentrations were observed over the sampling period.

#### 6.3.4 *Inputs to the Baltic Sea*

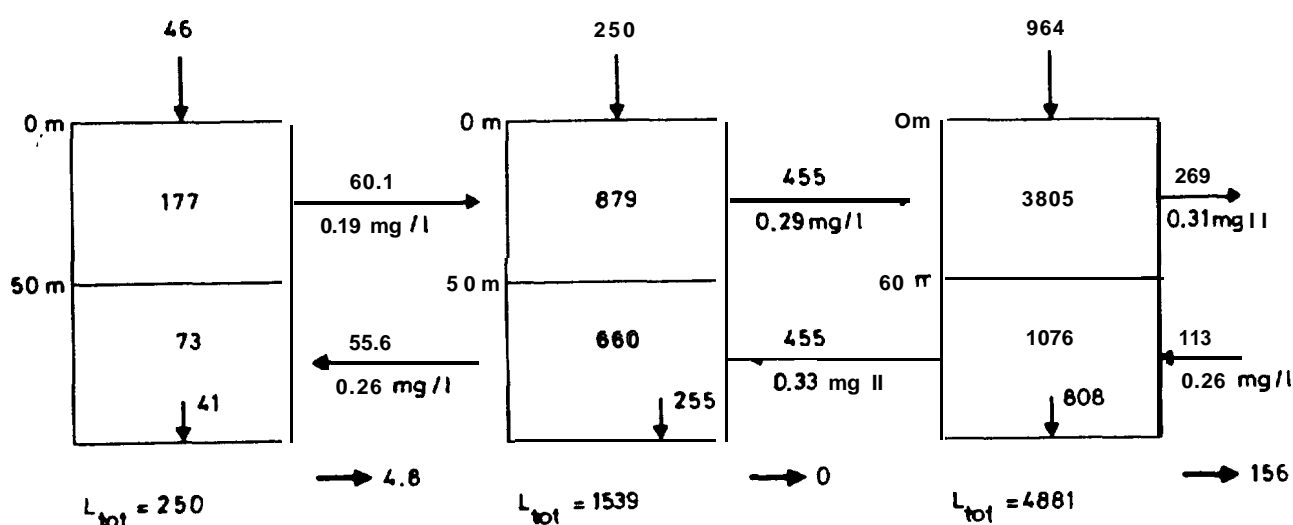
The input of humic substances to the Baltic Sea is controlled by the local conditions (type of vegetation, water drainage, etc.), the time of the year and the discharge rates of the rivers. The average humic content of rivers discharging into the Baltic Sea is insufficiently known, but from available data the mean humic concentration of rivers discharging into the Gulf of Bothnia is approximately 10 mg/dm<sup>3</sup> and into the Baltic Proper 5 mg/dm<sup>3</sup>. The amount of humic substances removed by estuarine mixing was estimated to be 50% (Nyquist, 1979a; cf. Sholkovitz et al., 1978). The removal mechanisms can be flocculation, adsorption onto particles and precipitation when the negatively charged humic colloids are neutralized by sea water cations. The humic fractions

of high molecular weight are especially affected by these processes. Humic substances and lignin sulfonates are fairly stable against oxidation, although in the surface water UV light may decompose part of the humic substances.

Based on Swedish and Finnish data, the annual input of lignin sulfonates from the wood processing industry to the Bothnian Sea is approximately  $250 \times 10^6$  kg and to the Bothnian Bay  $50 \times 10^6$  kg. The input to the Baltic Proper is insufficiently known.

### 6.3.5 Mass balance

Box models showing the balances of water (see Figure 14), humic substances and lignin sulfonates are given in Figures 55 and 56. Knudsen's relations have been used to calculate the water exchange. At small differences between the salinities of the outgoing and inflowing water, these calculations have a large uncertainty and can only be used to estimate the order of magnitude of the transports. The exchange between the top and bottom water layers is not considered in the figures.

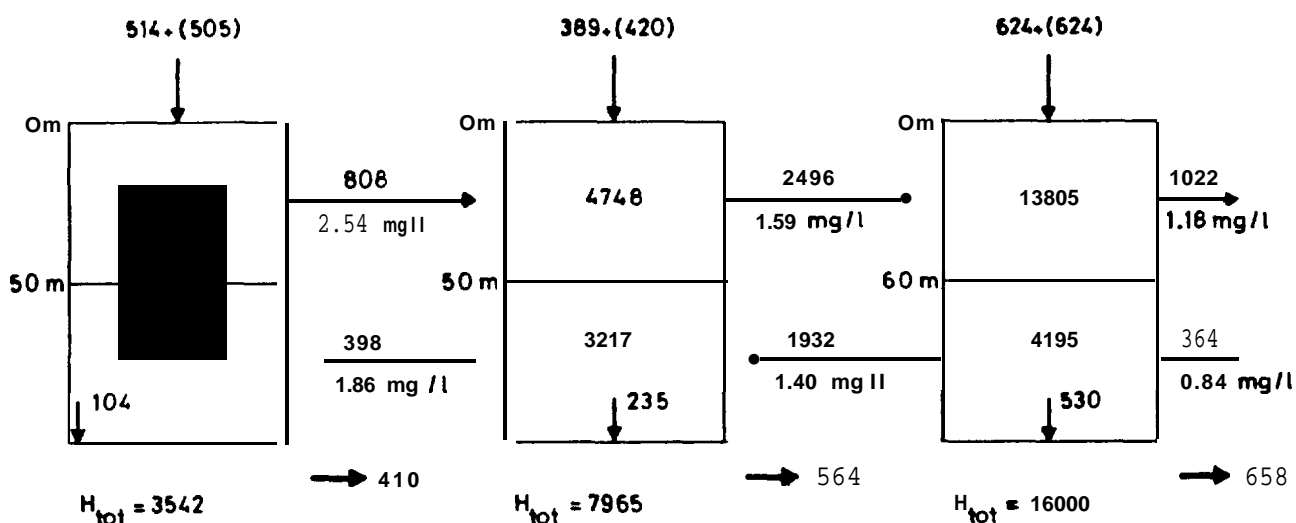


$L_{tot}$  = total amount of dissolved lignin sulfonates

↓ annual river discharge      ↓ annual removal  
 → annual outflow              ← annual inflow

Figure 55. Box model of the Baltic Sea showing the balance of lignin sulfonates (1000 tonnes). (Nyquist, original figure).

Assuming a steady state, the input of humic substances or lignin sulfonates should equal the output. A positive difference implies removal, mainly to the sediments. As a result of this removal, the half-lives of humic substances and lignin sulfonates in the Baltic Sea were estimated to be 23 and 4 years, respectively. The values in Figures 55 and 56 yield a mean concentration of dissolved carbon as humic substances and lignin sulfonates of  $0.70 \text{ mg C/dm}^3$  in the Baltic Sea. Measurements of dissolved organic carbon showed an average concentration of  $5 \text{ mg C/dm}^3$  (Fonselius, 1972). Thus, the measured humic substances and lignin sulfonates account for about 15% of the dissolved organic carbon in the Baltic Sea.



$H_{tot}$  = total amount of dissolved humic substances

→ annual net flow      ↓ annual      → annual outflow  
    river discharge  
    ↓ annual removal      ← annual inflow

Figure 56. Box model of the Baltic Sea showing the balance of humic substances (1000 tonnes). The amount of humic substances removed at the river mouths is given in parentheses at the river input. (Nyquist, original figure).



### 6.3.6 *Effects on the Baltic ecosystem*

The effect of humic substances on the Baltic Sea is above all a decreased light transmittance in the blue wavelength range of the visible spectrum. As humic substances are resistant to microbiological decomposition (Jackson, 1975), the influence on the oxygen concentration is negligible. Humic substances are able to bind a wide range of divalent and trivalent metal ions and to form complexes with a variety of non-humic organic compounds; there is evidence that various metals in sea water are to a large extent bound to humic substances. Furthermore, there are grounds to believe that humic substances in coastal waters stimulate the growth of phytoplankton (cf. Jackson, 1975).

Pure lignin sulfonates are non-toxic, resistant to decomposition and absorb light predominantly in the ultraviolet region of the spectrum. Therefore, the ecological effect of lignin sulfonates on the Baltic Sea is in general small, but in limited areas the influence can be significant. Lignin sulfonates can be used as fluorescent tracers for the determination of the spread and dispersion of waste water discharges from sulfite pulp mills. Because the flow pattern of lignin sulfonates is similar to that of other compounds in the waste water, e.g., toxic substances and inorganic nutrients of ecological significance, it can be used to study the dispersion of these substances. Fluorimetric measurements of lignin sulfonates can also be useful in studies of water exchange processes.

## **6.4 Petroleum hydrocarbons**

Oil is understood to include crude oils and refined products but not petrochemicals. Crude oil is composed of a complex mixture of different organic compounds that were built up by natural processes millions of years ago. The original organic material (dead plants and

animals) was transformed by geochemical processes into new organic compounds consisting mainly of hydrocarbons (>75%) (Posthuma, 1977). Compounds containing oxygen, nitrogen and sulfur also occur in crude oil, although of minor importance. Trace metals, e.g., Ni, V, Fe, Zn, Cu and U, are even less abundant. Crude oils from different parts of the world differ in chemical composition and physical characteristics.

Four main groups of hydrocarbons are found in crude oil (Posthuma, 1977), as follows:

- (a) Normal and branched alkanes (paraffins of aliphatic compounds). These constitute the largest fraction of crude oil, fuel oil and refined products;
- (b) Cycloalkanes (naphthenes or alicyclic compounds);
- (c) Aromatic compounds;
- (d) Olefins. Not usually present in crude oil, but occur in refined products.

The boiling point and water solubility characteristics are different for each group.

#### 6.4.1 *The fate of oil in the marine environment*

Pollution by crude oil arises from tanker accidents, deballasting operations and tank washings, natural seepages and losses from offshore drilling and production. Fuel oil and other refined products are also released into the sea. In addition, oil refineries and untreated municipal and industrial wastes contribute many types of refined and partly weathered oils. The amount of oil deposited from the atmosphere is less well understood, but it does contribute to the total input (GESAMP, 1977). The total annual input of oil to the Baltic Sea is estimated to be around 50 000 - 100 000 tonnes per year.

A variety of simultaneous physico-chemical processes (weathering) govern the distribution and fate of oil

immediately after an oil discharge or spill. Figure 57 shows the most important processes influencing the dispersion and modification, of oil and the relative time scales involved.

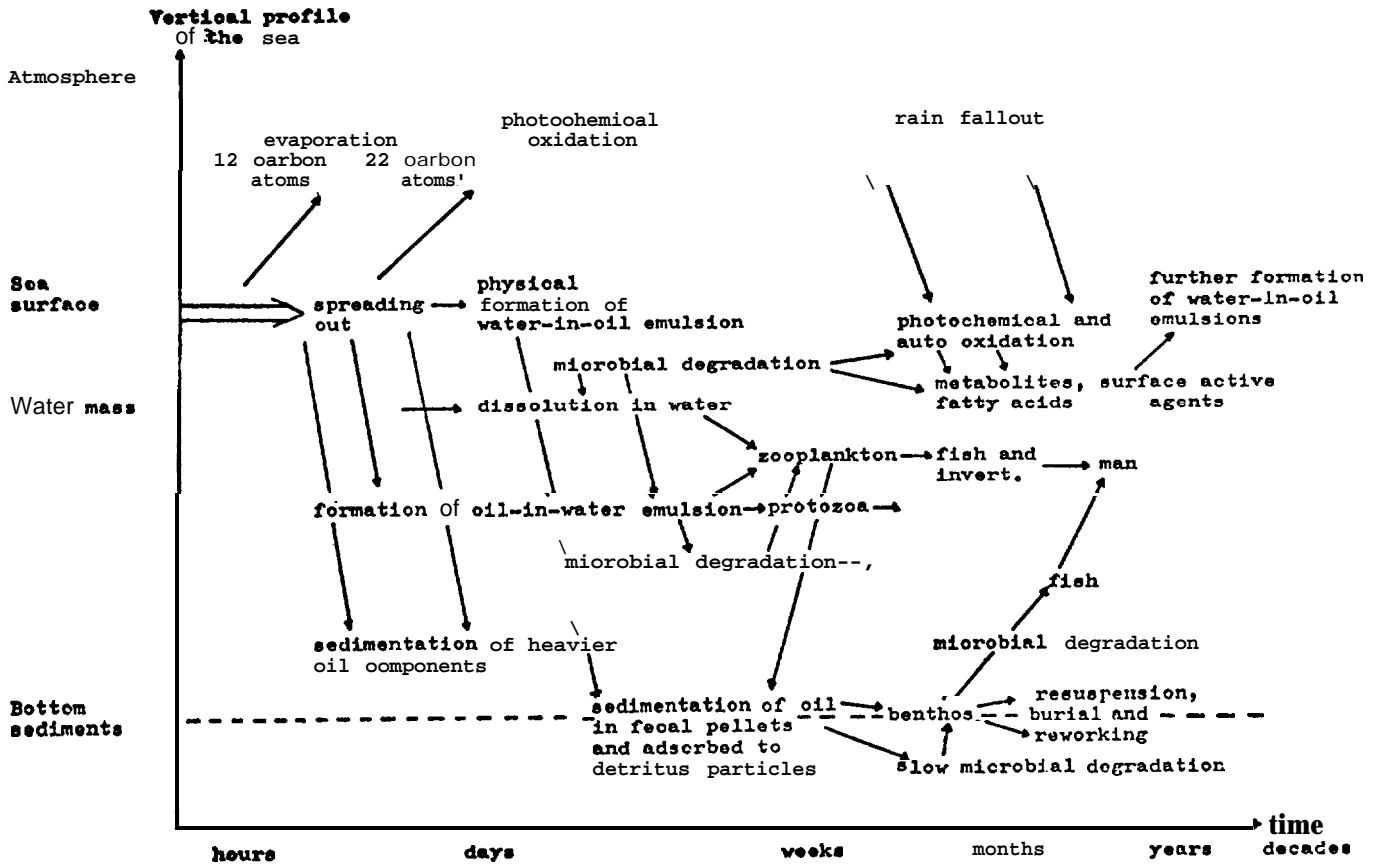


Figure 57. Diagrammatic summary of the fate of oil (modified from GESAMP, 1977).

The following processes redistribute, transform or remove the oil (GESAMP, 1977; Anon., 1978d): spreading (both on the water surface and in the sediments), evaporation, aerosol formation, dissolution in the water, photo-chemical oxidation and microbial degradation (Gibbs, 1977). For microbial degradation, see Section 7.1. Many of these processes occur simultaneously.

Spreading on the surface is initially the dominating process, and the rate is dependent on the thickness of the oil layer. The viscosity plays only a minor role. The evaporation rate depends upon the vapour pressure of the different components and, thus, on the temperature at the water surface, and is also affected by wind, waves and currents. Evaporation will remove about 30-50% of the crude oil from the surface if it is not combatted by dispersants. Components with a boiling point below about 250 - 260°C (up to 12 carbon atoms) will normally evaporate in less than about 24 hours (GESAMP, 1977) and become part of the atmospheric load.

The dissolution of oil in the water progresses continuously, but is a much slower process than evaporation. Because it is dependent on the surface area of the oil slick, this process is most pronounced when a dispersion of oil-in-water is formed.

While evaporation and dissolution redistribute the oil, photochemical oxidation and bacterial degradation transform it. The photochemical oxidation of hydrocarbons is dependent upon ultra-violet (UV) irradiation and will therefore only occur in the upper surface layers. The aromatic hydrocarbons absorb UV radiation with high efficiency and are mainly transformed into hydrogen peroxides. Alkanes are much less efficient in absorbing UV radiation and are only to a small extent transformed by this process. The result is possibly a polymerization of the hydrocarbons that can promote or inhibit their solubility.

Photochemical oxidation must be regarded as a very slow process for eliminating oil. Laboratory studies have shown that the rate of speed of the process increases considerably if UV radiation of shorter wavelengths than those in sunlight is employed.

Under the influence of wind and waves (turbulent energy), the oil can be emulsified into either a stable water-in-oil emulsion (80% water) or an oil-in-water emulsion. Oil-in-water emulsions can adsorb onto inorganic and organic particles with subsequent sedimentation, while a water-in-oil emulsion (sometimes known as chocolate mousse) transforms over time to pelagic tar that floats on the water (GESAMP, 1977).

#### 6.4.2 *Analytical Methodology*

Analytical methodology includes the sampling, isolation, separation and analysis of individual or groups of hydrocarbons (e.g., aromatics) in sea water, sediments and organisms.

When taking samples, it is imperative (a) to avoid contamination from any source, (b) to store the samples deep frozen only, so as to prevent any alteration, and (c) to ensure that samples are representative.

The next step is the extraction of the fractions containing the petroleum hydrocarbons from the sediment, sea water or biological material, followed by the separation procedures (e.g., extraction steps) and quantitative measurements, most of which are independent of the different sample types. The organic solvents used in the extraction must be of extreme purity.

Non-hydrocarbons in the initial extract are removed by column or thin-layer chromatography, which also fractionates the hydrocarbons. Further fractionation into alkanes, naphthenes and aromatics can be achieved by

gradient elution involving increasing concentrations of benzene in a pentane/benzene solvent mixture (GESAMP, 1977).

A number of methods are in use for the determination of crude oil, individual hydrocarbons, hydrocarbon fractions, etc. The methods most commonly used in the Baltic countries (Anon., 1977) are gas-liquid chromatography for qualitative information, IR-spectrophotometry and UV-fluorescence. The quantitative measurement of oil concentrations usually follows the principles of the analytical procedure recommended by Unesco (1976, 1977).

- 1) Infrared spectrophotometry: Absorption of infrared (IR) radiation at specific wavelengths to measure concentrations of fossil hydrocarbons. It has at least two drawbacks: (a) the method is not very sensitive (lower limit of detection  $50 \mu\text{g oil/dm}^3$  of water (Carlberg, 1977)), and (b) the method cannot distinguish between recent biogenic and fossil hydrocarbons (Bocard et al., 1977). This is of importance for unfiltered water samples, where the method may give unrealistically high values.
- 2) UV-fluorescence: The fluorescence values of the extracts are compared with those of standard oils in known concentrations. There are certain difficulties involved in this method, too. The reporting of results in crude oil equivalents is based on the assumption that the hydrocarbon mixtures extracted contain fluorescent aromatic hydrocarbons in roughly the same proportion as for crude oils. However, some investigations (Bouchertall and Ehrhardt, 1979) indicate that a substantial contribution to the hydrocarbon mixture consists of high boiling paraffins. These are not detected by the fluorescence method, and a high paraffin content in the extracts will result in the calculation of oil concentrations which are too low. Abundant, naturally occurring

terpene hydrocarbons absorb UV radiation and can therefore also bias the measurements. Some data show, however, an overwhelming contribution to fluorescent material by fossil hydrocarbons (Bouchertall and Ehrhardt, 1979; Ahnoff and Eklund, 1979).

At the intercalibration workshop in Kiel in 1977 (Anon., 1977), it was decided that UV-fluorescence should be used, at least in open waters, in future Baltic Sea studies. The method permits the determination of a spectrum of fluorescent aromatic hydrocarbons of petroleum origin but with an undefined error, because of the problem of selecting the right standard for the calibration of spectrofluorimeters.

Considering the fact that different oil standards have been used by different laboratories (Iranian crude, Russian crude, Kuwait crude and Ekofisk crude oils), the Overall agreement of results by the fluorescence method seems satisfactory. Quantitative data (UV-method) based on calibration with Kuwait and Ekofisk crude oils did not differ by more than 15% (Anon., 1977).

When methods are used to determine particular components of oil or specific features (e.g., fluorescence) of oil, the results presented as "total oil" or "oil fractions" can be misleading as oil is subjected to processes of degradation and differentiation within the aquatic environment.

#### 6.4.3 *Water*

Bearing in mind the limitations of the methods and the difficulties in comparing results using different methods, in the Baltic Proper oil concentrations (IR-method) in 84% of 275 samples were below  $50 \mu\text{g}/\text{dm}^3$  (detection limit), 13% were in the  $50 - 100 \mu\text{g}/\text{dm}^3$  range and only 2% were higher than this. In the Katte-

gat-Skagerrak area, 74.4% of 125 samples were found to contain oil below  $50 \mu\text{g}/\text{dm}^3$ , 21.7% were in the 50 - 100  $\mu\text{g}/\text{dm}^3$  range and 3.9% were above (Carlberg, 1977).

A statistical analysis of the data, taking into account the different number of samples (275 *vs.* 125), showed that there was no statistical difference between the results from these two sea areas.

Swedish inshore waters have been found to contain oil (UV-method) of concentrations from 7 - 20  $\mu\text{g}/\text{dm}^3$  above the pycnocline and 3 - 7  $\mu\text{g}/\text{dm}^3$  below (Anon., 1974). In the open Baltic Sea, concentrations were found to range from 0.3 - 8.3  $\mu\text{g}/\text{dm}^3$  (Ahnoff and Johnson, 1976). In the Bothnian Bay the values were lowest, averaging 0.3  $\mu\text{g}/\text{dm}^3$ , and in the Baltic Proper they averaged 1.8  $\mu\text{g}/\text{dm}^3$  (Dahlmann et al., 1979). Figure 58 shows concentrations of oil in the water column at 6 - 30 m water depths.



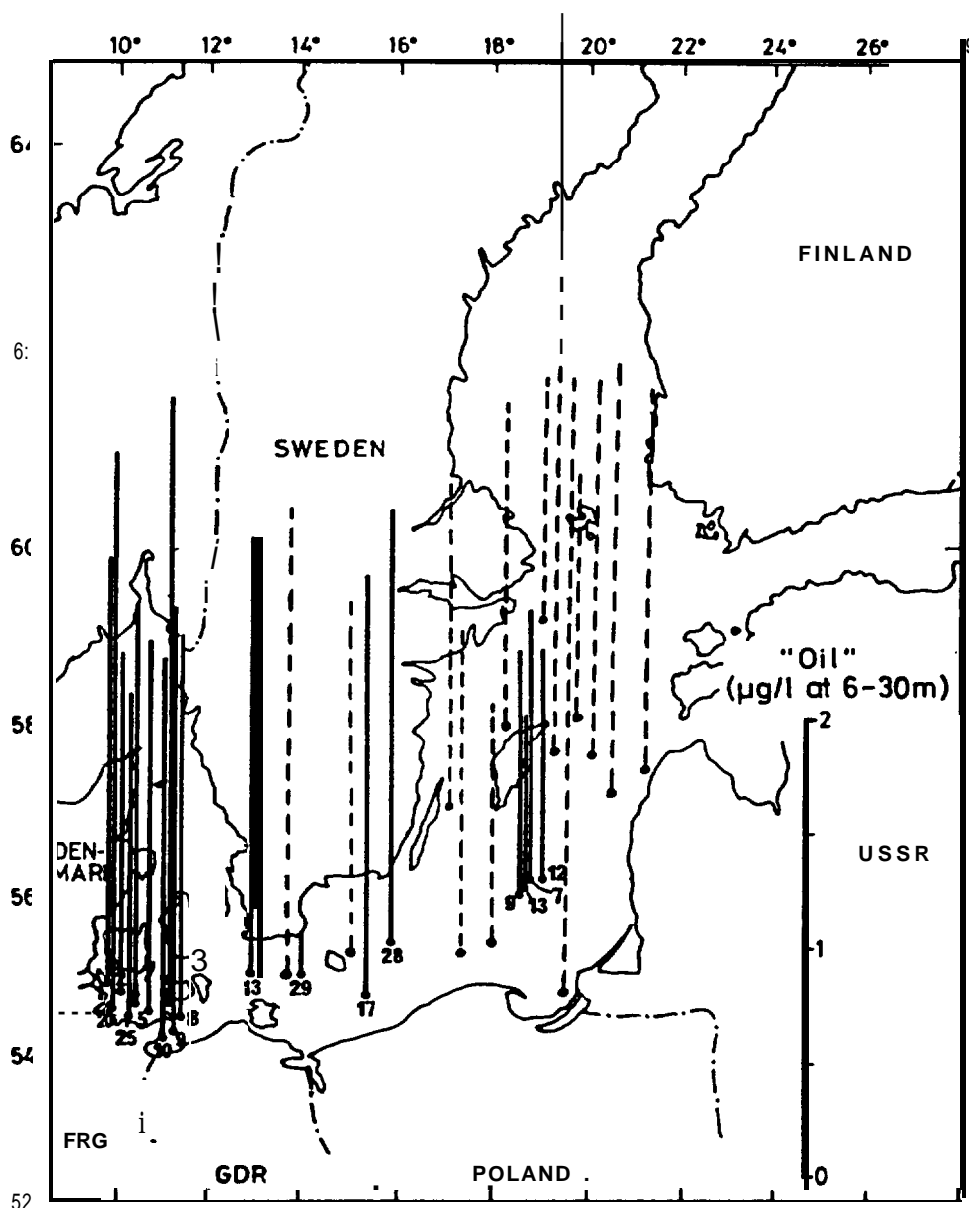


Figure 58. Oil concentrations in different parts of the Baltic at water depths of 6 - 30 m. (unbroken bar-values from Dahlmann et al., 1979; broken bar-values from Ahnoff et al., 1977).

No general tendency is apparent in the data to indicate areas or depth horizons in the water column with exceptionally high concentrations of oil. Oil concentrations in the surface film range from 33 - 717  $\mu\text{g}/\text{m}^2$  with an average of 215  $\mu\text{g}/\text{m}^2$  (Dahlmann et al., 1979).

#### 6.4.4 *Sediments*

Although not much research has been done concerning oil pollution in sediments in the Baltic Sea, in 1972 - 1977 a study was carried out using several different analytical methods (Rudling, 1976). The following is mainly from this project.

The type of sediments, environmental conditions and location near urbanized areas all affect the concentration levels of oil in sediments. Sediments with low paraffin-naphthenic concentrations (8 - 16 mg/kg dry weight) were from clay-sand bottoms or from sub-surface samples from soft bottom sediments (silt-clay). All surface sediments with high paraffin-naphthenic concentrations (>160 mg/kg d.w.) were either from heavily polluted urbanized areas or from areas where stagnant and consequently reduced conditions prevail.

Analysis of the aromatic fraction in the sediments showed that the aromatic content was in general 10-25% of the hydrocarbon concentration in the paraffin-naphthenic fraction. There was a higher content of aromatics in anoxic sediments.

Values of petroleum hydrocarbons from the areas studied were: 40 - 400 mg/kg d.w. near urbanized areas, often with a higher content in deeper core layers of these sediments, 2 - 20 mg/kg d.w. in the archipelagos of the east coast of Sweden and in the Baltic Sea, and 20 - 50 mg/kg d.w. in the archipelagos of the west coast from Gothenburg to Strömstad. Compared with the "natural background" concentration, which is < 1-2 mg/kg d.w., all soft bottom sediments contained increased amounts of petroleum hydrocarbons. The amounts are continuously accumulating due to the very low degradability of petroleum hydrocarbons in the sediments (Blumer and Sass, 1972).

The results from sediment analyses should be treated carefully because of the analytical problems in distinguishing between recent biogenic hydrocarbons and petroleum hydrocarbons.

#### 6.4.5 Effects

Crude oils of different origins vary widely in physical properties and chemical composition, and the toxicity of crude oils and different fractions thereof depends on the physico-chemical characteristics of the different component hydrocarbons. There is agreement (Cowell, 1976) that the toxicity increases along the series:

paraffins → naphthenes → olefins → aromatics  
 crude oil → refined products (higher aromatic content).

Within each series of hydrocarbons, the smaller molecules are more toxic than the larger ones. An increased number of methyl groups also increases the toxicity. In addition, low boiling point compounds are more toxic than high boiling point compounds.

The polyaromatic hydrocarbons (PAH) are the most persistent in the water and sediment phases and are the most toxic of the petroleum hydrocarbons. At least some of these are known to be carcinogenic (e.g., 3,5-benzpyrene and 1,2-benz-anthracene). n-Paraffins and, to a lesser degree, naphthenic compounds degrade at a faster rate than PAH once the oil is dispersed in the sea (Rudling, 1976).

#### *Micro-organisms*

Micro-organisms are capable of degrading oil by biological oxidation. Their action will be most important several days after the input, see Figure 57.

The rate of degradation by micro-organisms is dependent on environmental factors (temperature, salinity, oxygen and nutrients) and on the chemical composition

of the crude oils, because of their different persistence, solubility and toxicity. Molecular configuration seems to be the most important factor influencing the degradation processes. Alkanes are attacked more readily by micro-organisms than either naphthenic or aromatic compounds, and the most water soluble compounds are degraded more easily than less soluble compounds. Toxic compounds in crude oil, e.g., phenols and cyclohexane, can inhibit microbial activity.

Microbial degradation occurs at the oil-water interface. Thin oil films are degraded more easily than thick films, and oil-in-water emulsions (small oil droplets spread out in the water phase) are degraded at a faster rate than water-in-oil emulsions, which are degradable only to a slight degree by microbial activity, mainly because nutrient and oxygen concentrations decrease rapidly (Wade and Quinn, 1975; Levy and Walton, 1976). No single species of organisms is able to degrade all the hydrocarbons in crude oil, and some compounds can only be degraded if many species are present at the same time.

Degradation of crude oils in sediments is the least studied process and is only known in rough features. The rate of degradation varies widely with the type of oil and the local conditions. In sediments in more or less stagnant basins with bad oxygen conditions, the degradation process is very slow, owing to a rapid depletion of oxygen as well as a lack of photochemical oxidation and nutrients. Oils have been known to persist in sediments for several years without any sign of degradation (Blumer and Sass, 1972), and it has been shown that petroleum hydrocarbons are accumulating in Baltic sediments in certain areas (Rudling, 1976).

### *Organisms*

The lethal and sub-lethal effects of crude oil on organisms and their cellular functions are related to at least six important parameters: (1) the concentrations to which the organisms are exposed, (2) the chemical composition and characteristics of the crude oils or fractions thereof, (3) the length of exposure time, (4) the concentration of petroleum hydrocarbons in the tissues, (5) the biological half-life of the hydrocarbons, and (6) whether juvenile or adult forms of the organisms are involved.

The uptake of petroleum hydrocarbons takes place by absorption through the gills and other external surfaces (Fossato and Canzonier, 1976; Stegemann and Teal, 1973) and by assimilation of oil-contaminated food (Jensen and Zink Nielsen, 1976). In contact with the oil, uptake is a relatively rapid process. Initial elimination rates of petroleum hydrocarbons, provided the organisms are transplanted to clean water, are high; but 1 - 10% of the total uptake is eliminated only very slowly, if at all, and constitutes mainly aromatic compounds (PAH) stored in the lipid tissue.

The initial toxic effects of crude oil include a decreased activity level, a decreased muscle control and changed behavior (Linden, 1975, 1976b). These effects are considered to be acute narcotic effects because they result from an influence on the nervous system. The effects can be reversed if the hydrocarbons are eliminated before any damage to the nervous system occurs.

Sub-lethal or chronic effects occur when the petroleum hydrocarbons, especially the aromatic fraction, are not detoxified by the normal detoxification systems and/or when they are degraded to more toxic compounds, e.g., epoxides (Corner et al., 1973), with the possible consequence of carcinogenic effects due to changes in the genetic system.

Our knowledge of effects on organisms derives mainly from laboratory studies, the results of which are difficult to extrapolate to natural systems. Most studies have been concerned with the lethal levels of crude oil for different organisms and the sub-lethal levels affecting food intake, growth, reproduction, development, behavior and chemical communication. Larvae and juveniles are more sensitive than adults.

*Acartia* and *Oithona* spp. are common genera of zooplankton in the Baltic Sea. After 3 - 4 days immersion in sea water containing  $10 \mu\text{g oil/dm}^3$ , the juveniles died, whereas a longer exposure time was needed to kill adults (GESAMP, 1977). Amphipods show reduced fecundity and copulation and increased abortion of eggs and larvae from the brood chamber when exposed to sub-lethal concentrations of crude oil at levels down to about  $10 \mu\text{l/dm}^3$  (Linden, 1976a, 1976b; Ganning, 1970).

In the concentration range 0.05 - 1 ppm of crude oil (calculated as added amount rather than concentration), herring larvae showed abnormal swimming behavior, tissue injuries, abnormal development and increased death rate within 2 - 5 days (Linden, 1975). Figure 59 shows normal herring larvae (a) and abnormal larvae (b) after being exposed to crude oil.

Papillomatous tumors found in Baltic eels have been associated with deposits containing fuel oil (Batelle-Northwest, 1976).

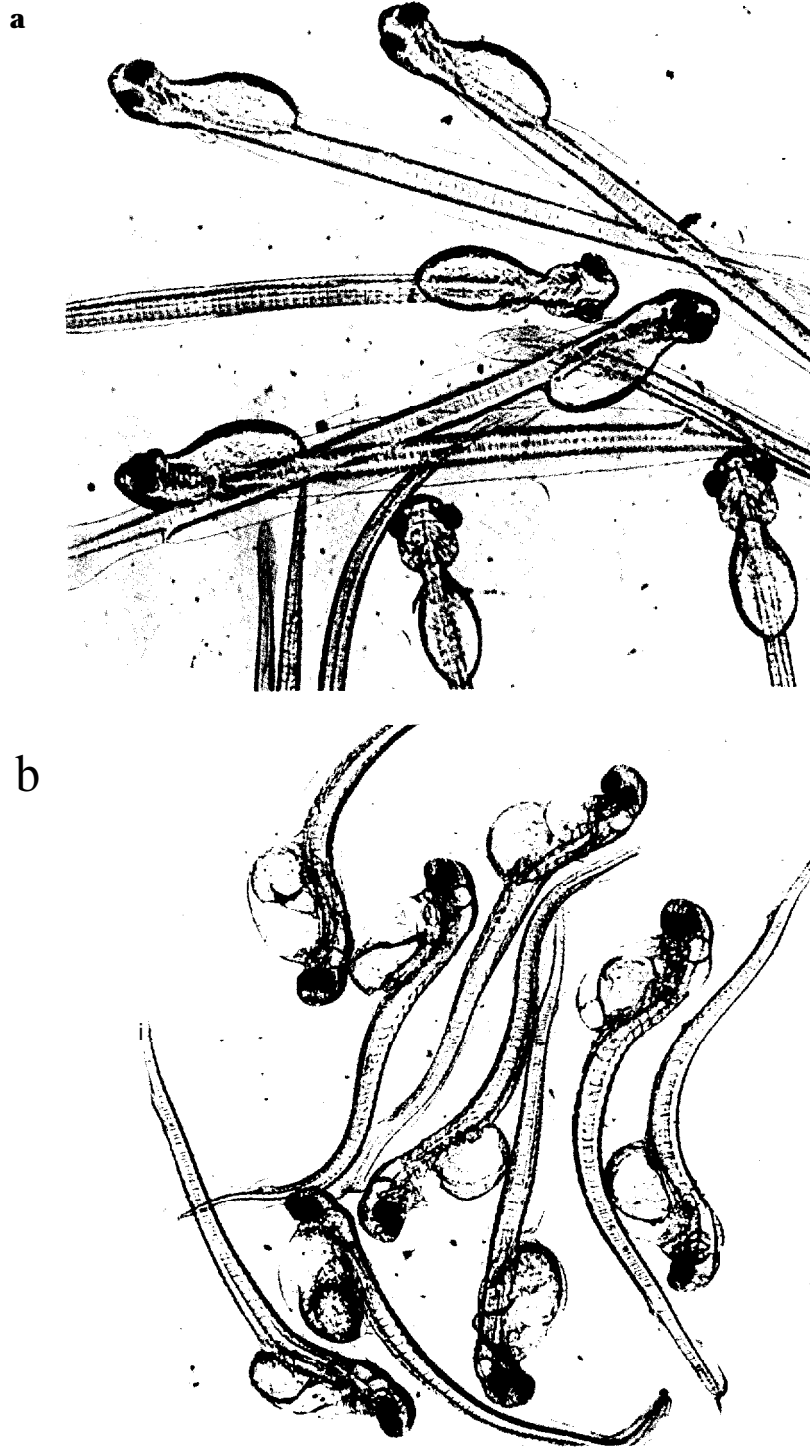


Figure 59. (a) *Normal* larvae developed from eggs exposed to natural brackish water.  
 (b) Larvae developed from eggs exposed to a mixture of BP 1100x and crude oil (2.5 ppm). The bodies are curved and the part anterior to the yolk sac is enlarged.  
 (from Lindén, 1976a).

Birds are always badly affected by oil pollution. In contact with oil, the feathers lose their insulation effect and the birds die due to temperature loss. Several studies of oil pollution and bird disasters exist (e.g., Joensen, 1973; Joensen and Hansen, 1977). Up to 30 000 birds (*Clangula hyemalis*) were killed at Öland as a result of a small oil spill. The effect is not correlated with the amount of oil.

Seals have been shown to be affected by oil pollution in other parts of the world (Geraci and Smith, 1976; Davis and Anderson, 1976), but not in the Baltic Sea. The effects are mainly reduced growth, eye injuries and liver diseases.

#### *Ecosystems*

In the open sea, no long-lasting impacts on or disturbances to the biological systems have been observed due to an oil spill, because of the weathering processes at the sea surface, the dilution capacity of the water masses, and the regenerative ability of the biological systems.

In inshore areas, however, oil discharges have been shown to seriously harm the ecosystem. Lethal effects on both invertebrates and vertebrates with subsequent severe long-lasting effects have been found, especially on the benthic organisms.

For example, continuous chronic discharges of oil (150 - 300 mg/d) from a refinery plant changed the benthic systems completely in an area off the southwest coast of Finland. After installation of a waste-water treatment plant, only partial recovery had occurred within two years (Leppäkoski and Lindström, 1978). In 1969, about 30% of the resident population of eider ducks (*Somateria mollissima*) was killed by a small oil spill in the Archipelago Sea (Leppäkoski, 1973). Long-lasting effects



on the fauna in the *Fucus* belt following an oil spill were observed in the Stockholm archipelago (Notini, 1978).

A detailed study of the effects of the "Tsesis" accident (Linden et al., 1979; Elmgren et al., in press) showed that the spilling of over 1000 tonnes of medium grade fuel oil in the Swedish archipelago of Södertälje clearly affected both macro- and meiofauna. Oil reached the sediment within about a week after the spill and, at the most affected station, the dominant macrobenthic animal, the crustaceans (amphipods) *Pontoporeia* spp., and most groups within the meiofauna (especially the ostracods) were greatly reduced. The few remaining gravid female *Pontoporeia* showed an increased proportion of abnormally developing eggs after the spill. The bivalve *Maeoma baltica* and the priapulid worm *Halicryptus* showed no significant mortality after the spill, but at least the *Maeoma* were heavily contaminated by oil over an area of tens of km<sup>2</sup>. No recovery of the affected components of the benthic community was found within the first year of the study. The "Tsesis" spill study thus indicates that the most persistent damage following an oil spill may well be that to the benthic communities.

#### 6. 4. 6 *Conclusions*

Inshore highly productive areas, benthic communities, and birds seem to be the most sensitive to oil pollution due to single oil spills, with heavy mortalities and long-term deleterious effects as a result. These inshore areas and benthic communities are characteristically very productive in the summer season and are essential for a rich fish fauna.

No effects have yet been shown due to chronic oil pollution in the pelagic systems in the Baltic Sea.

For benthic fauna (both infauna and epifauna), long-term chronic and sub-lethal effects have been demonstrated both due to single oil spills and to continuous discharges of oil with subsequent very slow recoveries of the biological systems in inshore areas.

In the deep sea sediments of the Baltic Sea, no studies on the effect of chronic oil pollution on benthos have been carried out. It should be stressed, however, that accumulation of petroleum hydrocarbons occurs in the sediments in some areas. At present, the amount of petroleum hydrocarbons is 20 times the background concentration in some of the most polluted sediments. The long-term and constant release of persistent aromatic hydrocarbons from the sediments could possibly cause serious sub-lethal effects on the benthos.

Chronic oil pollution and sub-lethal effects on organisms, e.g., reduced fecundity, must be considered an effect of serious ecological significance. Subtle changes of essential biological functions in important species in the marine food chain can be extremely difficult to observe in the field. In such a situation, effects can be disguised by natural fluctuations within and between species. However, they may affect the stability of the ecosystem and lead to long-term changes in faunal composition.

The use of dispersants, including the so-called "non-toxic" second and third generation dispersants, in combating oil on the sea surface will only increase the number of organisms exposed to a higher concentration of dispersed oil with subsequent increased lethal and sub-lethal effects. The use of dispersants also increases the amount of unweathered oil that will reach the sediments. The mixture of crude oil and dispersants is also more toxic than crude oil alone.

## 6.5 Cooling water

Although not a harmful substance in itself, cooling water discharges can cause changes in the composition of the biological communities and the functions of the ecosystem within the locally affected waters. In general, bioactivity increases at all levels of the ecosystem, from production, through metabolism, to degradation of organic material.

In the summer, the direct effects of heat are mainly restricted to the surface layers of the waters. In the winter, however, the plume dives deeply in brackish waters, affecting a larger area of deep water and sea bottom. The second main property of the discharge, the kinetic energy of the plume, is of short duration but may initiate large effects, especially in archipelago areas.

There are reasons to assume that a number of other effects have a considerably larger radius of action than the direct influence of heat. Particular attention should be paid to the combined effect of heat and different types of polluting substances, such as heavy metals, radioactive waste products, biocides and excess nutrients, the incorporation of which in biological material is stimulated by heat. Heat is thus conserved by its effects, which have a considerably longer duration in the water than the heat itself.

A related problem is that of the reinforcement of negative effects. The fact that lethal doses and critical exposure times to different toxic substances have a tendency to decrease at increased temperature is, for various reasons, difficult to demonstrate in the field. Negative influences on the vital functions of organisms must be assumed to exist in the ecosystem long before directly lethal levels are reached.

The interpretation of, and the balance between, negative and positive effects depends on a series of factors, for which man's conception of the environment is usually decisive. Having that in mind, the following summary of effects can be presented.

In temperate and arctic waters, temperature usually acts as a limiting factor for the production of organic material as well as for the rate of mineralization. An increased production of organic matter in the early stages of eutrophication as well as an increased decomposition rate of surplus organic matter in overloaded waters, stimulated by the supply of heat and oxygen, can be regarded as positive. This is also valid for a reduction in the length of time between rich year classes of fish and an increased availability of fish attracted by the warm effluents, as well as for the increased water temperature for recreational purposes.

The stabilization of thermal stratification in stagnant waters and losses of oxygen are not desirable. Increased incorporation and conservation of toxic substances in biota and an increased production of undesirable organisms, e.g., fish parasites, are decidedly negative, as also is the increased mortality of organisms due to their entrainment in cooling water systems. There is a risk for a deterioration in water quality for municipal, industrial and recreational purposes. Negative effects can also arise by changing migration routes, habitats, spawning sites, etc., for economically important fish species.

#### *Effects on the macrozoobenthos*

The effects of cooling water on the macrozoobenthos depend on the behaviour of the discharge, which varies with the season.

In the summer, the direct effect of the heat is mainly restricted to the upper littoral areas of the coast. After a relatively short time, the kinetic energy of the plume diminishes and the transport of heat is taken over by water movements in the recipient.

The overall effect is an increased production particularly of green algae and other organisms belonging to this belt. Disfavoured are organisms depending on uncovered hard bottoms or *Fucus* plants as a substrate, e.g., the filter-feeding blue mussel *Mytilus edulis*. In a locally affected bay on the Swedish east coast, populations of *Macoma baltica* and *Gammarus* species were eliminated. The gastropods, which initially respond positively to the increased temperature, disappear after some years probably as an effect of an intensified development of fish parasites, especially *Diplostomum*. *Corophium volutator* and chironomic species are presently the dominant species of macrozoobenthos in this area.

In the winter, the discharge plume dives deep in brackish waters. The heat floats out over the bottom and covers a relatively large area compared with the situation in summer. This has an obvious negative effect on the macrozoobenthos in these areas. The abundance and frequency of many species decline, e.g., *Mytilus edulis*, *Macoma baltica*, *Mesidothea entomon*, *Gammarus* spp. and to a certain degree *Pontoporeia affinis*. One possible explanation is that this is caused by the addition of heat during a period when the organisms are adapted to low temperatures. This means an increased activity and metabolism during a period when the availability of food is restricted, especially in exposed coastal bottom areas. The relatively limited effect on the *Pontoporeia* population, observed from spring to autumn, might depend on active migrations to and from the affected areas.

# Biological parameters

## 7.1 Micro-organisms

This field of study considers bacteria, fungi and viruses. With the exception of a small group of photo- and chemo-autotrophic bacteria, micro-organisms are heterotrophic, using organic substances as their source of basic nutrition. The degree of pollution greatly influences the microfloral composition of both the water and the sediments. The concentration of organic pollutants influences the species diversity and population size of bacteria. Micro-organisms rapidly adapt themselves to the appearance of new ecological factors of both natural and anthropogenic origin and thus serve as indicators of pollution. Recognized indicators of the presence of domestic (faecal) wastes include, for example, coliform, *Streptococcus* and *Clostridium*. Faecal waste frequently contains pathogenic micro-organisms from these three groups.

Through their adaptation and metabolic activities, bacteria and fungi play an essential role in the accumulation, transformation and decomposition of all organic matter and, consequently, in the purification of the water. They also form an important link in the production processes.

Under normal conditions almost all naturally occurring organic material can be catabolised. The final decomposition products are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and a few inorganic salts. The nutrient cycle is maintained through this mineralization process. If the load of pollutants is substantially increased, however, the mineralization processes are disrupted and the microfloral composition changes, resulting in the dominance of normally less common anaerobic species.

Bacteria, having a short generation period, often only a few hours, and being able to utilize very low nutrient concentrations, occupy a prominent position in the food chain. The generation time for a specific organism is a particularly important ecological parameter, giving an insight into the catabolic activity of the microflora in a water body under the prevailing environmental conditions.

The bacterial production in the water and the sediments strongly influences the development of the primary consumers and has a correspondingly great influence on the energy flow in the ecosystem.

Pollutants also influence the presence of parasitic micro-organisms on both marine plants and animals. A study of micro-organisms can therefore reflect changes that occur in the ecosystem.

Despite the significance of micro-organisms in the marine environment, both as indicators of pollution and decomposers of organic matter, and their role in the food chain, there is relatively little knowledge about the microflora of the Baltic Proper. The main attention has been paid to investigations of microbial processes in bays, archipelagos and separate areas in the southwestern Baltic Sea.

#### 7.1.1 *Methods*

Both conventional as well as recently developed methods (see Schlieper, 1968; Rodina, 1972; Rheinheimer, 1977; Maciejowska, 1981) have been used for microbiological investigations in the Baltic Sea.

Koch's plate method has for a long time served as the method for the determination of the numbers of heterotrophic bacteria and yeasts, faecal indicators (coliforms, *Streptococci*) and certain physiological groups (uric acid decomposers, starch, fat, chitin, and cellulose decom-

posers). The introduction of membrane filters and nutrient pad sets has considerably enhanced the validity of this method. In all cases, the development of colony-forming units is counted (Schlieper, 1968; Väättänen, 1977).

The most probable number method (MPN) also has a wide area of application. This is a dilution technique used to determine the quantity of bacteria and yeasts in the water and sediment samples. It can be used for the determination of total heterotrophs, for faecal indicators, or for counting members of any of the physiological groups (protein, urea, or oil decomposers, sulfur oxidizers, nitrifiers, etc.) (Schlieper, 1968). Both methods permit comparison with previous investigations and therefore allow continuity of the microbiological records in the water over the past ten years.

Determinations of the total bacterial numbers have recently been made easier by the use of the fluorescence microscope (Zimmermann and Meyer-Reil, 1974). By being able to differentiate different morphological forms and size classes, an analysis of the microflora is possible and the exact bacterial biomass can be determined. In calculating the biomass, the fungi may also be included.

Since 1970, a variety of modern methods has been employed to record the microbiological activity in the Baltic Sea. These methods include microautoradiography (Hoppe, 1977), the use of labelled carbon in investigations of heterotrophic activity (Williams and Askew, 1968; Gocke, 1977), monitoring the growth of micro-organisms on suspended membrane filters (Kunicka-Goldfinger, 1972; Meyer-Reil, 1975), etc.

Particularly important is a reliable sampling technique that can be used under sterile conditions (Schlieper, 1968). Water samples can be collected from depths down to 200 m in the Baltic Sea using sterilized glass bottles



with the ZoBell water sampler. For greater depths, Neoprene balls or plastic bags, according to the volume required, are recommended. Sediment samples can be obtained with the careful use of a clean grab (van Veen grab) or a box corer. The material for investigation should be taken from the middle of the sample using sterile utensils. A completely satisfactory sediment sampling technique for microbiological investigations has not yet been devised.

#### 7.1.2 *The Micro-organisms of the Baltic Sea and their Distribution*

The microflora of the Baltic Sea is distinctive because of the dominance of halophilic es'cuarine bacteria. This microflora achieves an optimum development in salinities from 10 - 25 ‰ and is inhibited by both fresh water and normal 35 ‰ sea water. In their biochemical and to a large extent also in their morphological qualities, the micro-organisms of the Baltic Sea correspond to micro-organisms found in other water bodies with similar nutrient conditions. The bacteria include the mobile rod forms together with small numbers of other morphological types as, for example, those to be found in the North Sea.

In the Baltic Proper, this distribution applies to the genera *Micrococcus*, *Flavobacterium*, *Arthrobacterium*, *Pseudomonas*, *Bacillus*, *Mycobacterium* and others (see Figure 60). The most widespread taxonomic groups among these are the micro-organisms belonging to the *Pseudomonas* and *Micrococcus* genera. In the western area of the Baltic Sea, however, larger numbers of *Agrobacterium* species with characteristic star and caterpillar-shaped aggregates may develop temporarily (Ahrens, 1969).

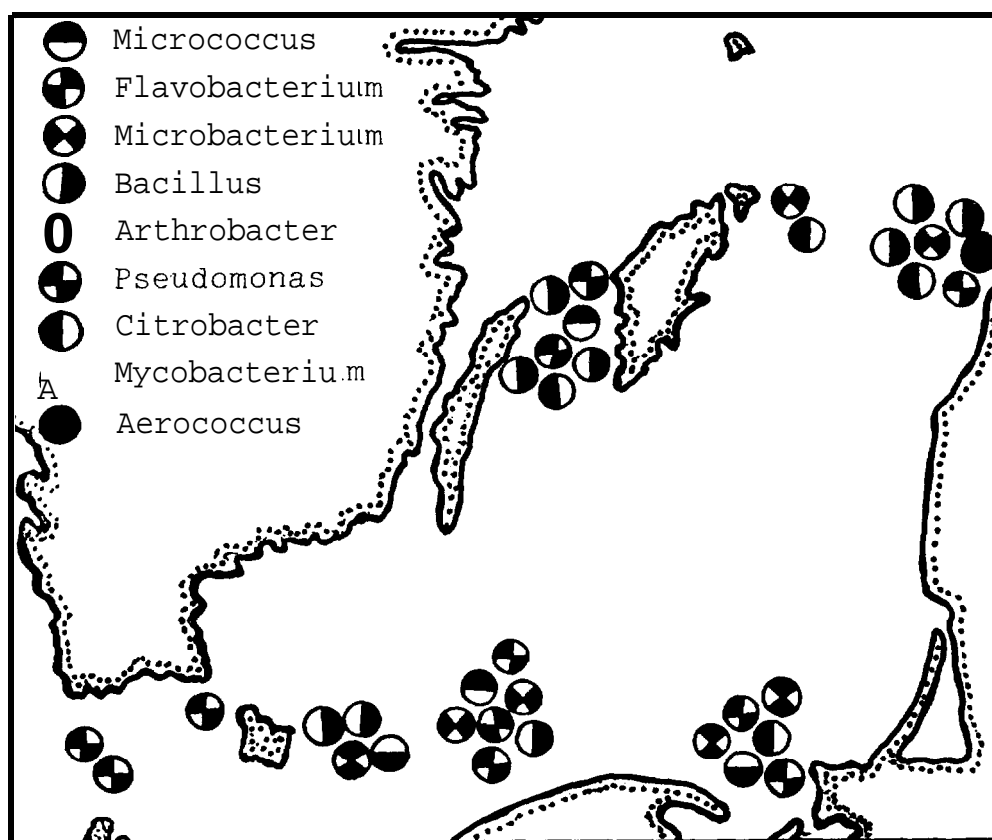


Figure 60. *The distribution of the taxonomic groups of micro-organisms in the Baltic Sea in summer 1976 (Tsiban et al., 19801).*

In addition to the halophilic forms, there are also a lesser number of osmophilic forms which do not require sodium chloride for their development, adjusting their osmotic values to that of the surrounding water. This applies to the soil and sewage bacteria, which also have the advantage that they can live for a prolonged period in low-nutrient Baltic Sea water.

Concerning fungi, the halophilic, brackish water forms do not play an important role. Most fungi possess a high salinity tolerance, greater than that of water bacteria, enabling many species found in the Baltic Sea to occur also in fresh water ponds and even in other sea areas. Lower fungi belonging to the orders Chytridiales and Saprolegniales are particularly well-represented. Among them are a large number of parasites, mostly of plankton and benthic organisms. Other fungi include the yeasts and the lignin-digesting *Ascomycetes* and *Deuteromycetes* (Hoppe, 1971; Schneider, 1969, 1977; Norkrans, 1966).

Similarly, viruses occur throughout the Baltic Sea. Autochthonous forms include bacteriophages, cyanophages, and other viruses, which attack eukaryotic algae and animals. Domestic and agricultural wastes also carry viruses capable of causing disease in humans and domestic animals, and other viruses including bacteriophages of non-pathogenic sewage bacteria.

The pattern of distribution of micro-organisms in the Baltic Sea is characterized by a concentration along the coastline, especially in bays and fjords. The highest concentrations can be found in heavily polluted areas, such as harbours, river mouths and the sites of waste discharge. The ecological and physiological groups represented here are quite different from those in the less polluted areas. The use of fluorescence microscopy allows a determination of the total and heterotrophic bacterial count for a section of the polluted inner Kiel Fjord and the relatively clean Kiel Bay (see Table 21 and Figure 61). The results show that the decline in heterotrophs in many cases is greater than the decline in total bacterial numbers.

Table 21. *Physiological groups of the colony-forming bacteria (average) of the Kiel Bight (1973-1975), as determined by macro-autoradiography in % of the total heterotrophic population (after Hoppe, 1977).*

<sup>14</sup> C-substrate	Kiel Fjord		Kiel Bight	
	water	sediment	water	sediment
Glucose	100	100	100	100
Fructose	93	100	100	
Xylose	77	91	74	81
Galactose	41	66	40	59
Saccharose	95	100	91	88
Lactose	71	75	68	73
Maltose	86		79	-
Glucosamine	90	-	-	-
Soluble starch	95	100	99	100
Sodium acetate	94	90	93	82
Glycerol	83	-	93	-
Glycolic acid	34	30	31	13
Uric acid	28	23	29	33
Aspartic acid	97	-	97	-
Fat	18	37	25	41
Phenol	21	66	14	24
DDT	11	1	3	3
Riboflavin	34	40	23	44

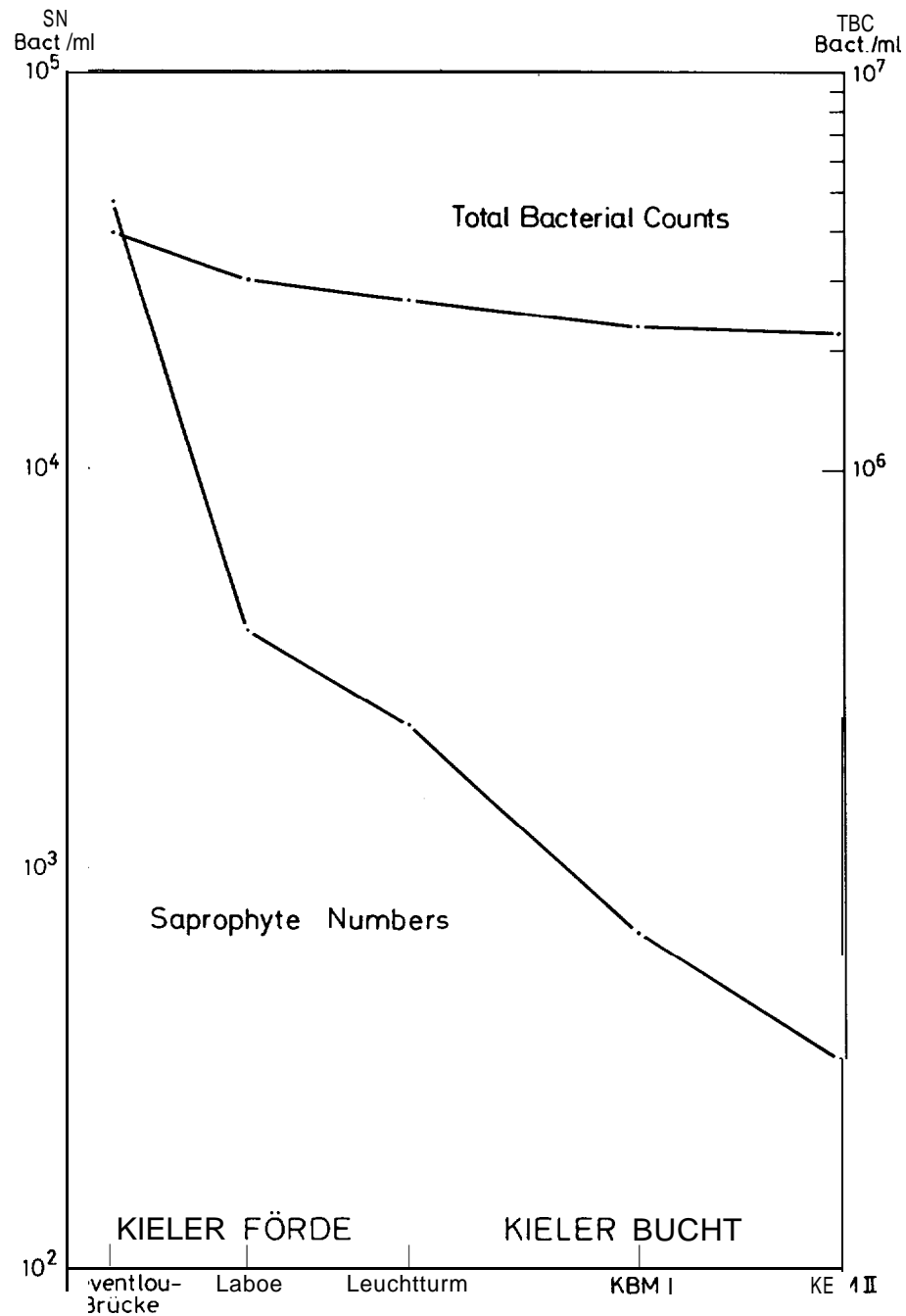


Figure 61. Total bacterial counts and heterotroph (*saprophyte*) numbers on a section from the polluted Kiel Fjord to the rather clean central Kiel Bight (after Zimmermann, 1977).

The heterotrophic bacteria actively break down proteins, carbohydrates and fats (see Table 22). In the presence of such substrates, they multiply rapidly; but after consumption of the substrate the population

rapidly declines. The heterotroph numbers give, therefore, important hints as to the degree of pollution by readily metabolizable organic pollutants.

Table 22. *Biochemical activity of the micro-organisms of the Baltic Proper (1976) in % of the total heterotroph population (after Tsiban et al., 1980).*

Biochemical activity	% of the total heterotroph population
Digestion of gelatin	39
Formation of ammonia	59
Hydrolysis of starch	4
Decomposition of glucose	20
Decomposition of maltose	61
Decomposition of saccharose	33
Decomposition of lactose	37
Decomposition of glycerol	33
Decomposition of mannitol	30
Assimilation of mineral nitrogen	100
Catalytic activity	78
Dehydrogenase activity	59

The total bacterial numbers in the Baltic Sea ranges between several hundred thousand and many millions per  $\text{cm}^3$  of water (see Figures 62 and 63). The best developed microcoenoses are found in the Southern Baltic Sea in the areas of the Bornholm and Arkona Deeps and partly in the Central Baltic Sea. A decrease in the numbers of the microbial population (of 5 - 10 fold) is observed northwards in the Baltic Sea. The numbers of heterotrophs are variable (see Figure 64). Their numbers in brackish water is between less than one hundred to several hundred thousand per  $\text{cm}^3$  water (Rheinheimer, 1977; Tsiban, 1980; Väättänen, 1976; Zute and Marcinkevics, 1974).

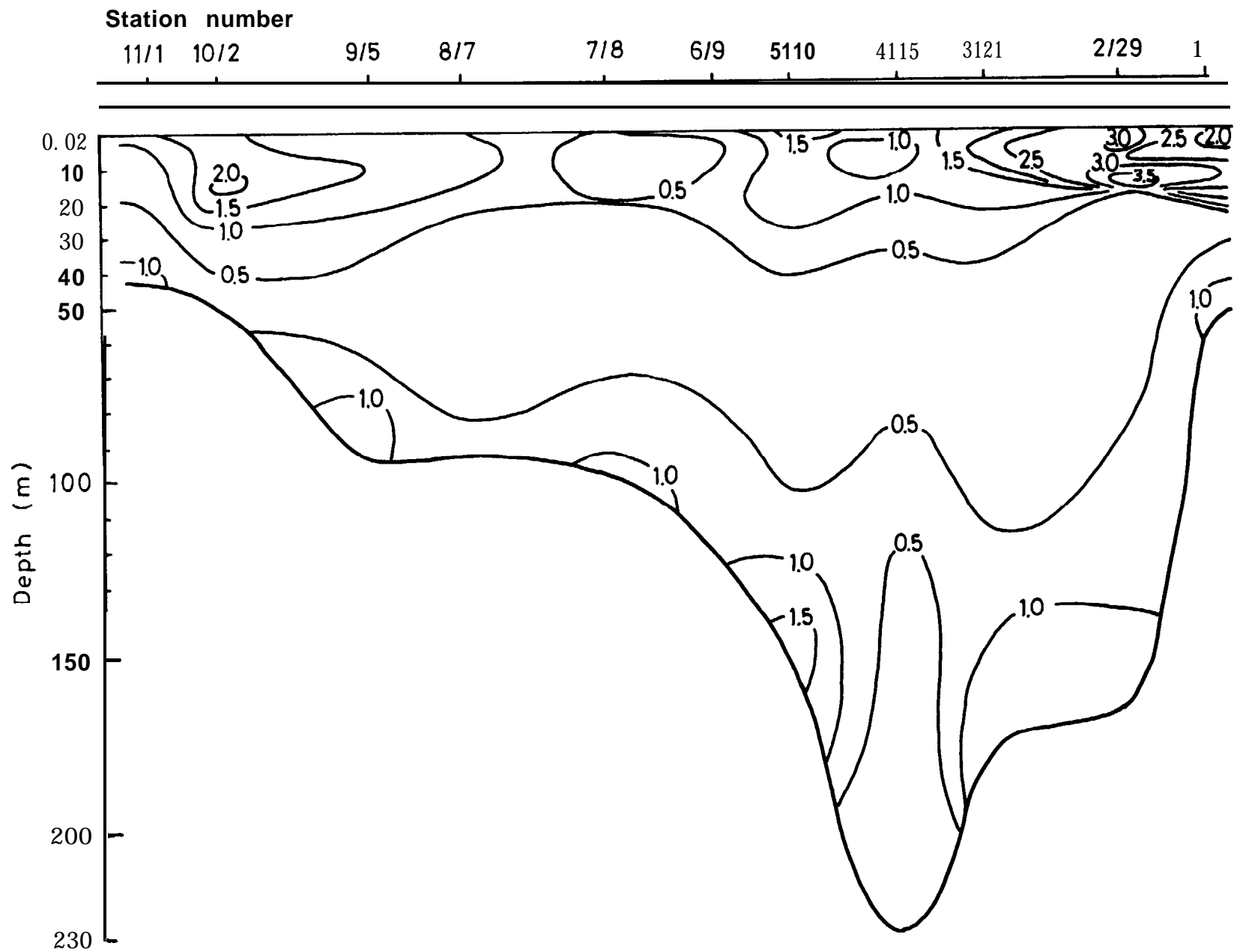


Figure 62. *The total number of bacteria (mil. col/ml) in the Baltic Sea, July 1979, (Tsiban, original figure).*

Corresponding to the decreasing salinity of the Baltic Sea going from west to east and from south to north, there are changes in bacterial populations. First, there is an increase in the brackish water forms, which gradually outnumber the true marine bacteria. Secondly, at salinities below about 8‰, the number of halotolerant fresh water forms gradually increases (Rheinheimer, 1968, 1971). There are surprisingly few parts of the Baltic Sea where bacteria of fresh water origin grow. They are represented in the Kiel and Lübeck Bights by usually less than 5% of the brackish water forms and exceed this figure only seldom in harbour areas and fjords. At river mouths and sewage inlets, most fresh water and sewage bacteria die out, being quickly replaced by halophilic brackish water forms.

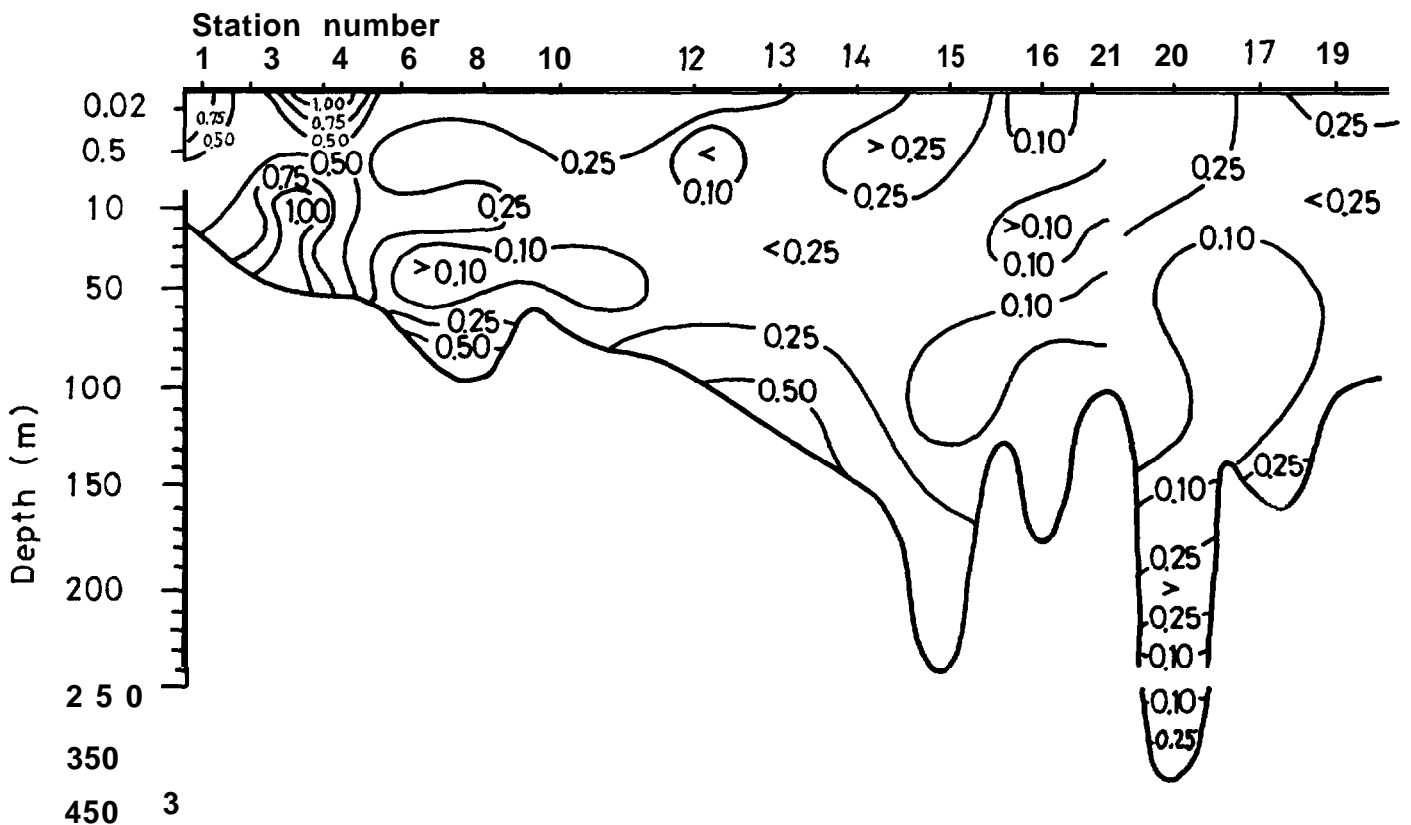


Figure 63. The total number of bacteria (mil. col/ml) in the Baltic Sea, March 1978 (Tsiban, original figure).



In contrast to the situation in the western Baltic Sea, the saline tolerant fresh water bacteria found in the Gdańsk Bight and the Gotland Basin represent between 20 and 90% of the total heterotrophic bacteria present.

The vertical distribution shows relatively high values in the upper 25 metres of the water column, as compared to the lower layers. The maximum numbers can often be found in the upper 5 metres, although it is not uncommon that it occurs between 10 and 25 metres, especially in the presence of a thermocline or halocline, for example, during the summer in the Belt Sea or the Kattegat (Rheinheimer, 1980). Below 25 metres, there is usually a marked decrease in numbers (Saava, 1980; Väätänen, 1976). However, just above the sea bottom there is again often an increased concentration.

The dimensions of the micro-organisms in open water areas vary in the following ranges: for rods, length 1.0 - 11.0  $\mu\text{m}$ , diameter 0.3 - 1.5  $\mu\text{m}$ ; for mycobacteria, 1.0 - 5.0  $\mu\text{m}$  and 0.4 - 1.5  $\mu\text{m}$ , respectively; for cocci, diameter 0.5 - 1.5  $\mu\text{m}$ . In the Kiel Bight, there is a remarkably high proportion of very small-celled bacteria. The short rod bacterium with a diameter of less than 0.4  $\mu\text{m}$  represents 70% of the total bacterial number (Zimmermann, 1977). The average cell volume amounts to 0.06  $\mu\text{m}^3$ .

The bacterial biomass in the Kiel Bight varied between 1.5 and 25.0  $\text{mg C/m}^3$  during monthly investigations from January 1974 to March 1975 (Zimmermann, 1977). In the central and eastern Baltic Sea, Dawson and Gocke (1978) recorded 0.9 - 6.9  $\text{mg C/m}^3$  in the summer of 1976. The data obtained by Tsiban (1980) are presented in Figures 65 and 66. There are relatively few detritus-attached bacteria in the Baltic Sea, the proportion ranging between 1 and 23% of the total bacterial numbers. The

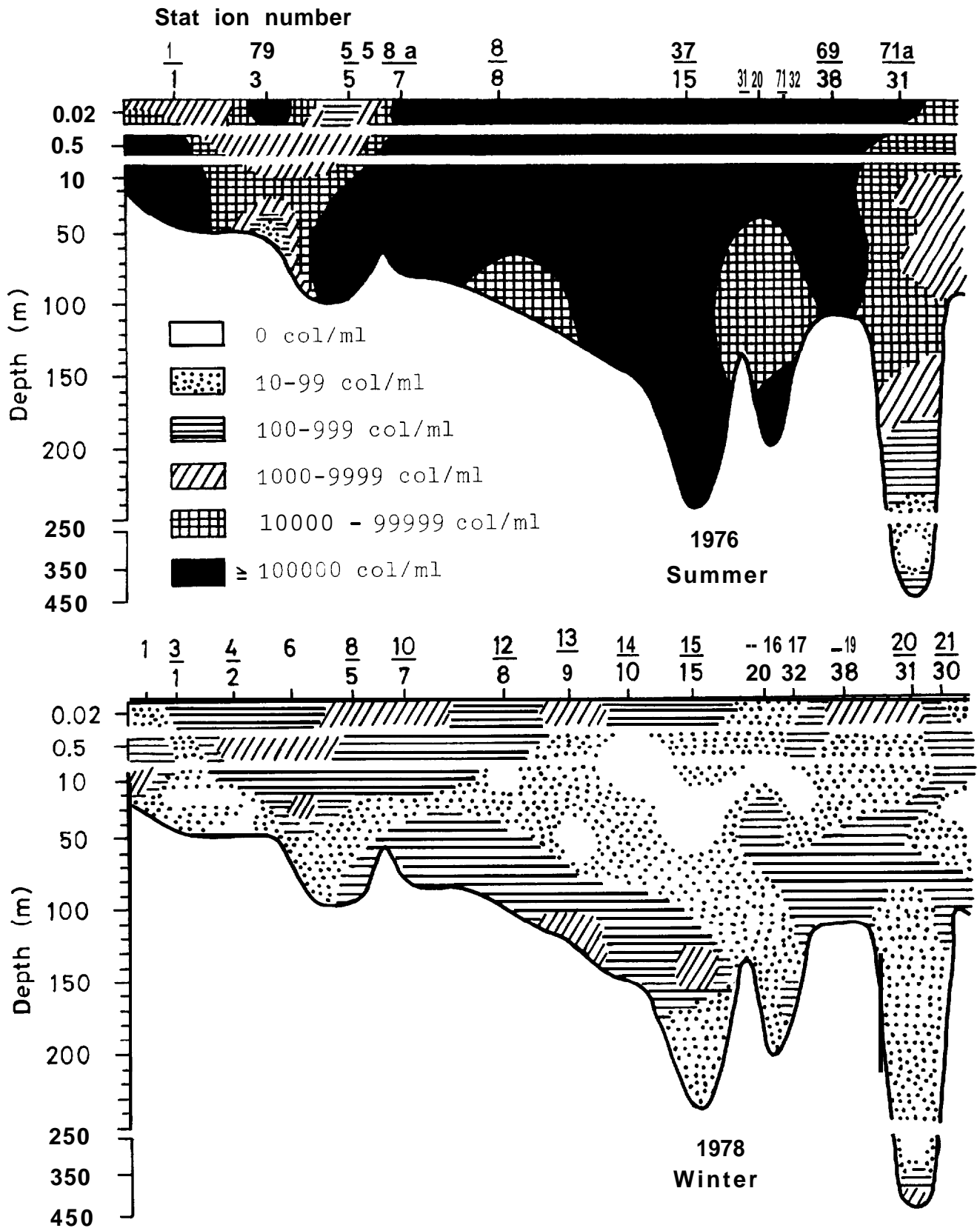


Figure 64. The heterotroph numbers in the Baltic Sea. (Tsiban, original figure).

average values for five stations in the Kiel Bight are 2.8 - 3.8% for surface water and 3.7 - 8.1% for the sea bottom (Zimmermann, 1977). During decomposition of plankton blooms, however, there can be a temporary increase of attached bacteria as has been repeatedly observed in the southern and central Baltic Sea.

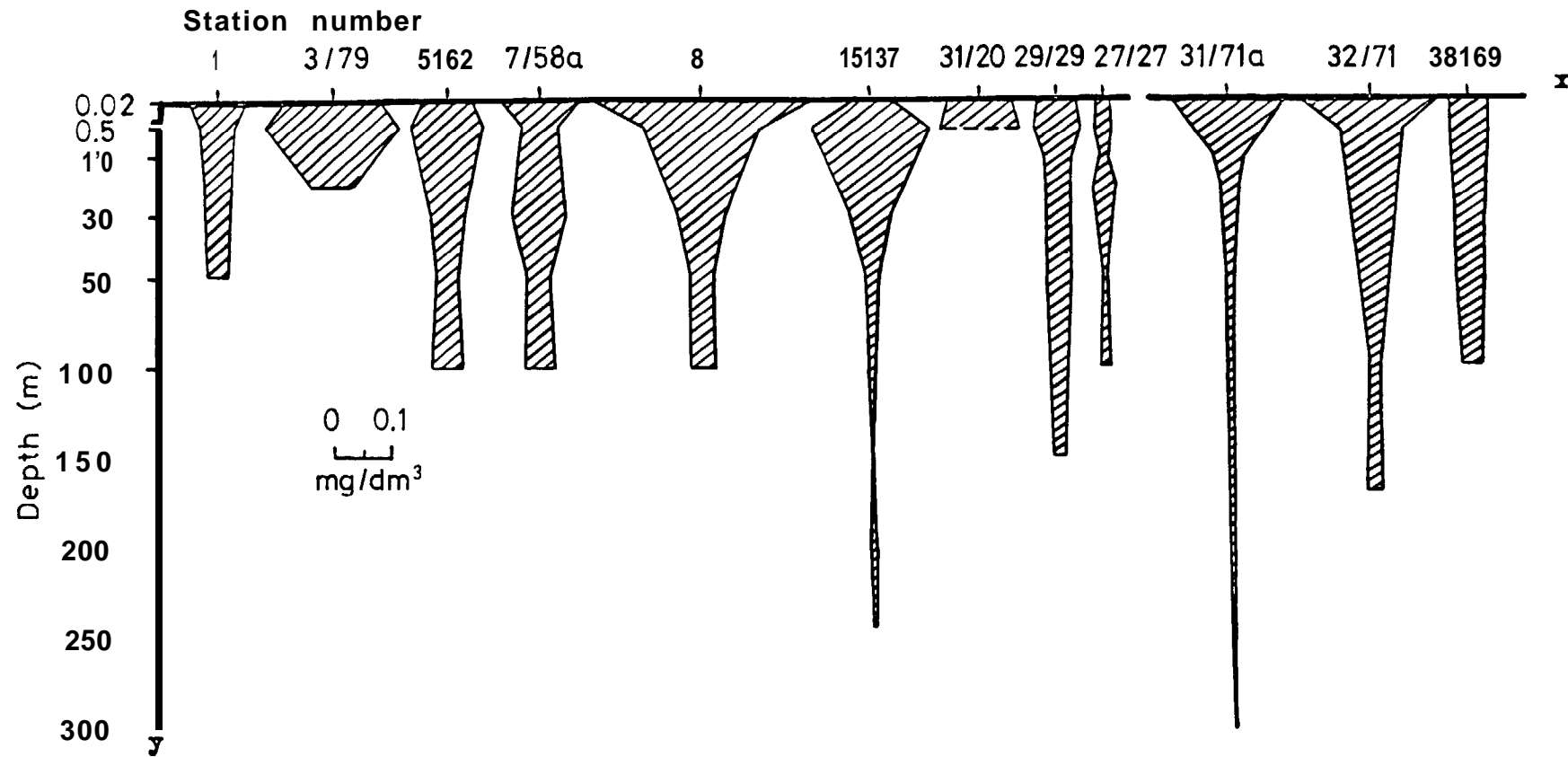


Figure 65. Distribution of bacteria2 biomass (mg/dm<sup>3</sup>) through a Baltic Sea transect in June 1976 (Tsiban, original figure).

Annual investigations in the western and northern Baltic Sea have established that there is a distinct seasonal pattern of total bacterial and heterotroph numbers. In all cases, the total bacterial count was higher in the summer than in the winter (see Figures 62-64). There is, however, a large difference between the pattern observed in the Gulf of Finland and that in the Kiel Bight. The heterotroph count in the Kiel Bight has, as a rule, a peak in the spring and a second peak in late summer or autumn (see Figure 67).

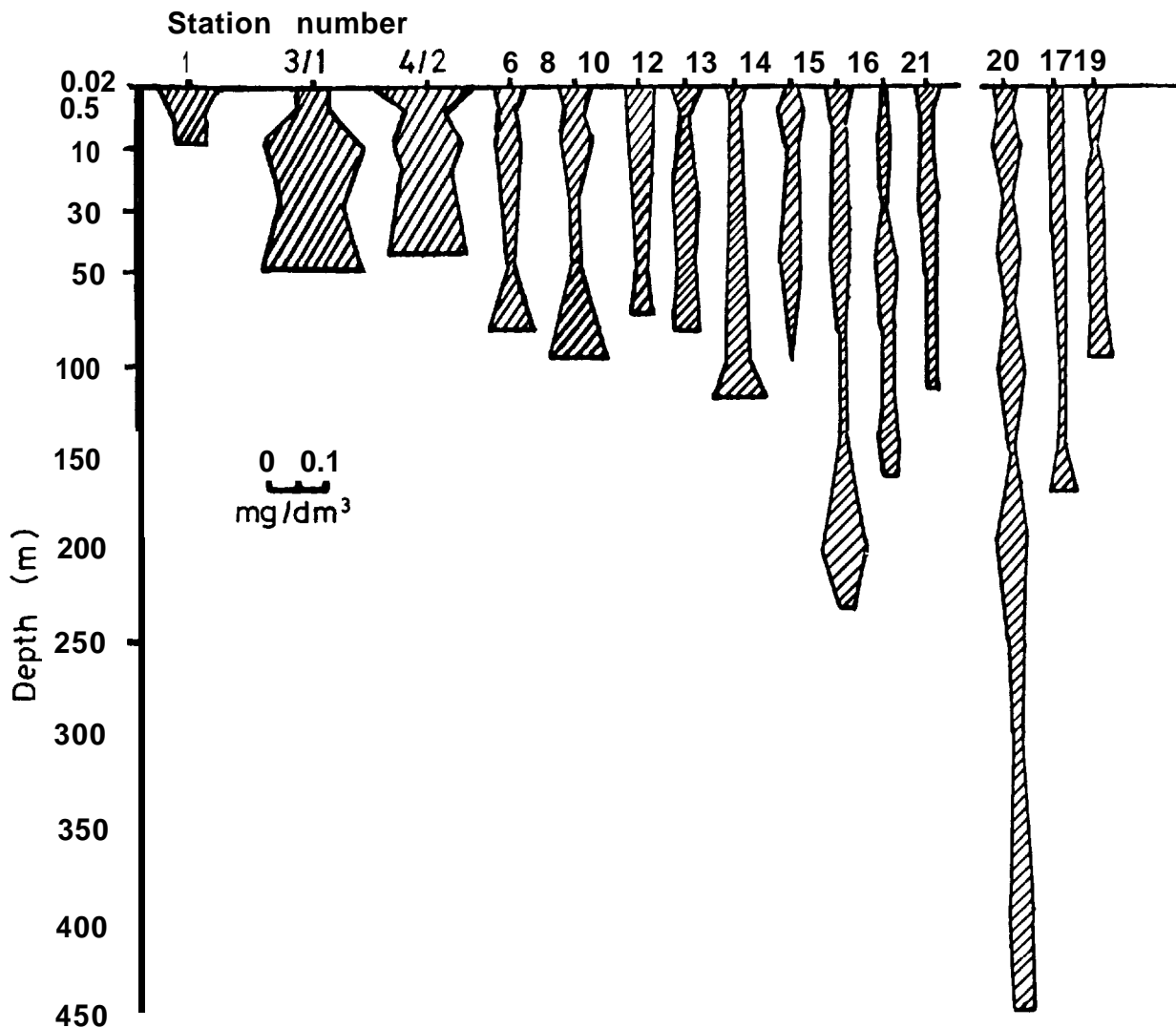


Figure 66. The distribution of the biomass of microorganisms along the central axial section of the Baltic Sea in winter (Tsiban, original figure).

The total bacterial count in the upper zone of the sediment (0 - 1 cm) ranges between many hundred million to a few hundred billion per  $\text{cm}^3$  of moist sediment. Seasonal differences here are dependent on phytoplankton production (Weise and Rheinheimer, 1979).

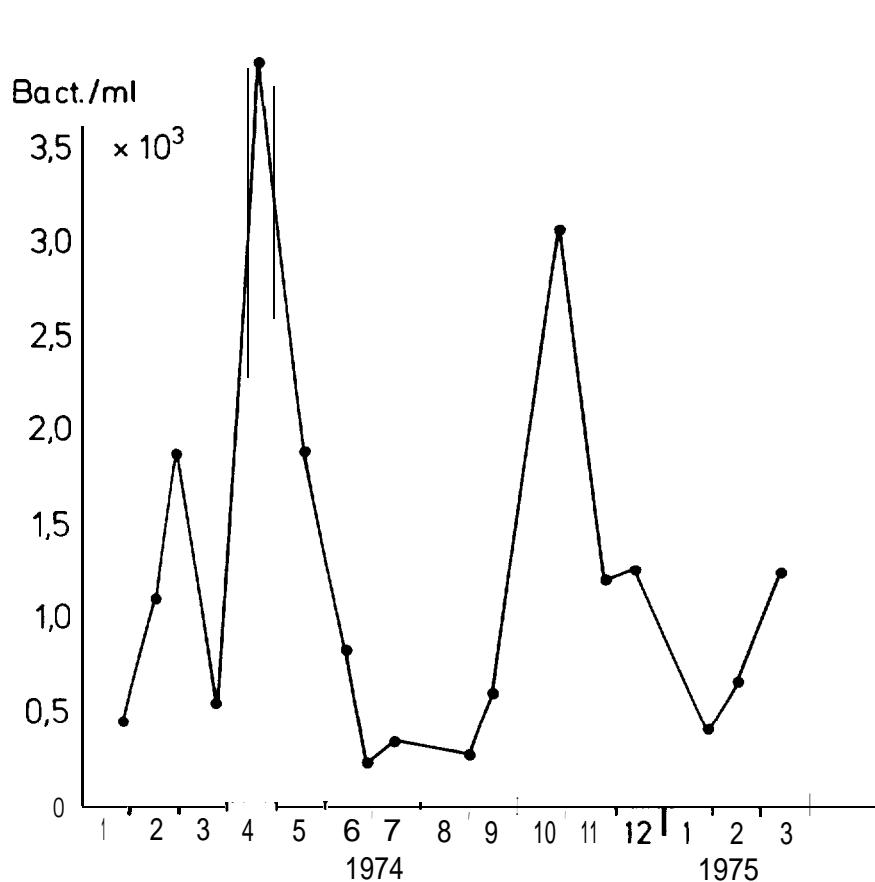


Figure 67. Annual cycle of heterotroph numbers in the central Kiel Bight. (Rheinheimer, original figure).

### 7.1.3 Inter-relationships between micro-organisms and plants and animals

The annual cycle of heterotrophic bacteria is related to phytoplankton development. The highest heterotroph count is always recorded after the phytoplankton have reached the peak of their productivity, i.e., either in spring or in summer when the plankton begins to die out. Meyer-Reil (1977), working in the Kiel Bight

area, reported a production rate of 9-57 g bacterial carbon per m<sup>2</sup> per year. That is about 15-30% of the primary productivity rate for the area.

A portion of the products of primary production are released by aquatic plants in the form of exudates which can serve as easily digestible nourishment for heterotrophic organisms. Larsson and Hagström (1979) found that exudates in the northern Baltic Sea are completely used up by bacteria. Of the yearly production rate of 110 g C/m<sup>3</sup>, 45% is exuded and subsequently metabolised by bacteria. The bacterial net production is 29 g C/m<sup>3</sup> or about 25% of the phytoplankton production. According to Iturriaga and Hoppe (1977), in the Kiel Bight region 2-21% of the products of primary production are exuded. The rate of uptake of these exudates ranges from 8 to 17.5% per hour. The investigation of an annual cycle by Wolter (1980) in 1978-1979 demonstrated exudation values ranging from 0 to 15.6% of the products of primary production and an uptake rate of 0 - 88.7% of these exudates within 24 hours by bacteria. The incorporation of exudates by bacteria begins in the spring after initiation of phytoplankton development and follows the seasonal fluctuations displayed by the primary producers. When the single algal cell reaches its stationary growth phase, the exudation process increases significantly, finally resulting in the destruction of the cell. At this stage, the bacterial growth on the algal cell increases rapidly and is followed by intensified grazing action of ciliates and rotifers.

Algae which are surrounded by a mucus sheath have a limited but highly specific microflora which are largely nourished by the mucus polysaccharides. As a result of investigations in the Schlei (western Baltic Sea), Rieper (1976) found that a partially symbiotic or mutualistic relationship exists between the mucus

bacteria and their host cells (*Microcystis aeruginosa*). Plankton and benthic algae, which do not possess mucus sheaths, show, at least during the end phase of growth, a bacterial covering rich in species.

Bacteria feed mainly on exudates and nutrients released from dead cells, which are primarily composed of proteins, amino acids, carbohydrates and organic acids. In the case of a cyanobacteria, *Nodularia* for example, an epiphytic flora can develop under the mucus sheath, directly on the cell surface. Young and actively growing cyanobacterial cultures are often free from epiphytes. Heterotrophic micro-organisms are particularly abundant on the surface of degenerating cells associated with phytoplankton blooms and on the older thalli of benthic algae. The resulting micro-organism cover is composed of a thick mass of bacteria together with fungi. Solid portions of dead cells can also be used as nourishment, encouraging a diverse covering of microflora. Bacteria-consuming ciliates and rotifers are not uncommon. As plankton feeders avoid directly feeding on some bloom-forming phytoplankton species (e.g., *Cyanophytes*), heterotrophic micro-organisms hold an accordingly important position in the food chain.

A considerable portion of the epiphytic bacteria sediments with the dead algae cells and so contribute to the detritus. This represents an important nutritional factor for the benthic fauna. Bacteria and, to a lesser extent, fungi play an important role in the nourishment of mobile and sessile animals which live on the sea bottom and in the sediment. Such organisms include members of the macrofauna (worms, mussels, gastropods, etc.) and to an even greater extent the meiofauna.

The role of the heterotrophic micro-organisms in the food chain is greatly influenced by the degree of eutrophic-



ation, which, if high, results in the development of a massive algal growth and subsequent bacterial and fungal development. There is usually also a parallel change in the composition of the heterotrophic microflora. The mass development of certain algae can exert a limiting effect on the action of the bacteria. Rieper (1976) showed that an isolated species of *Chlorella* from the western Baltic Sea caused a marked inhibition of *Escherichia coli*. This, however, was achieved by *Chlorella* only subsequent to its exponential growth phase, suggesting that the inhibitory substances may be the product of autolytic or decomposition processes, where they may similarly be able to control the development of another bacterium.

Bacteria, fungi and viruses attack the various plants and animals of the Baltic Sea. Facultative and obligate parasites belonging to the lower group of fungi are widely distributed (Sparrow, 1960; Schneider, 1977). These attack numerous planktonic and benthic organisms, yet epizootics of such activity are seldom observed. A myxomycete, *Labyrinthula coenocystis*, which lives as a parasite in higher algae and seagrass is also widespread. In the Baltic Sea area, diseases of *Zostera marina* are traced to *Labyrinthula* (Renn, 1936). Fish are also attacked by various fungi. *Ichthyosporidium hoferi*, the cause of rupture disease, is the only example known at present. Under bacterial diseases of fish, *Vibrio anguillarum* should be mentioned. This disease occurs in the southern and western Baltic Sea, especially during warm summers, causing high mortality rates in eel populations (Schäperclaus, 1954). Common virus-caused fish diseases include lymphocystis in flounders and soles, the cauliflower disease of eels, and fish pox. It is possible that an increase in the load of pollutants weakens the resistance of many higher organisms to attack by these disease-causing micro-organisms.

#### 7.1.4 *The role of micro-organisms in purification*

Bacteria and fungi play an important role in the purification of water. They are able to catabolise both solid as well as dissolved forms of organic compounds. Under suitable conditions, which must include adequate availability of oxygen, they can achieve complete mineralisation of most organic pollutants. As a rule, proteins, sugars, carbohydrates and some alcohols and organic acids (e.g., acetic acid) are relatively rapidly broken down. The cyclic hydrocarbons and their derivatives, fats, waxes, cellulose and lignin are very slowly and often only incompletely decomposed.

During the decomposition process, the microbial population changes. For instance, after a release of domestic sewage, the proteolytic bacteria often temporarily increase, followed by fat and cellulose decomposers. The presence of specific pollutants such as urea and its derivatives, uric acid, hydrocarbons, phenols, chlorinated organic compounds, etc., often results in an increase in those organisms that can use these substances as a carbon source.

The ability of micro-organisms to use the various organic compounds is very variable. Several specialized bacteria can use a particular combination as a sole source of carbon, while others can metabolise certain compounds only under co-oxidation with amino acids, sugars, etc. Compounds in solution may be absorbed directly by the appropriate micro-organisms, while insoluble compounds such as cellulose and lignin are utilized only after degradation by exoenzymes. The use of  $^{14}\text{C}$  or  $^3\text{H}$  autoradiography shows the uptake pattern of the labelled substances in cells. Investigations by Hoppe (1977) in the Limfjord and the Kiel Bight showed that, for example, almost all heterotrophic bacteria are able to assimilate glucose, however only 0 - 25% were able to incorporate DDT.

The average values from the 1973-1975 investigations in the water and sediments in the Kiel Bight are presented in Table 21. With the help of the MPN method, the portion of the urea decomposing bacteria represent, according to Steinmann (1976), in the Kiel Harbour water between 0.02 and 62.5% and in the less polluted outer part of the Kiel Fjord at Laboe between 0.01 and 21.6% of the total heterotrophic count.

By using the MPN method, Tsiban et al. (1980) found in the central and southern Baltic Sea oil decomposers in the order of 10 - 10000 cells per  $\text{cm}^3$  of water in the summer and 10 - 100 cells per  $\text{cm}^3$  in the winter. These numbers represent about 1 - 10% of the total heterotrophs present. The number of benzopyrene-oxidizing micro-organisms fell in a similar range, whereas PCB-decomposing micro-organisms were present at only about one-tenth of these values (see Figures 68 and 69).

Xylene-oxidizing bacteria were found in some areas of the Baltic Sea. They were more numerous in the central Baltic Sea, where their mean number amounted to tens of cells per  $\text{cm}^3$ . In the southern Baltic Sea, the recoveries varied between 0 and 1000 (on an average 10) cells per  $\text{cm}^3$ . These represent about 0.1% of the heterotrophs.

Lipolytic microflora was observed at all stations in the central Baltic Sea. The numbers ranged in the order between 100 and 10000 cells per  $\text{cm}^3$ . In the southern Baltic Sea, their number varied between tens and hundreds per  $\text{cm}^3$ .

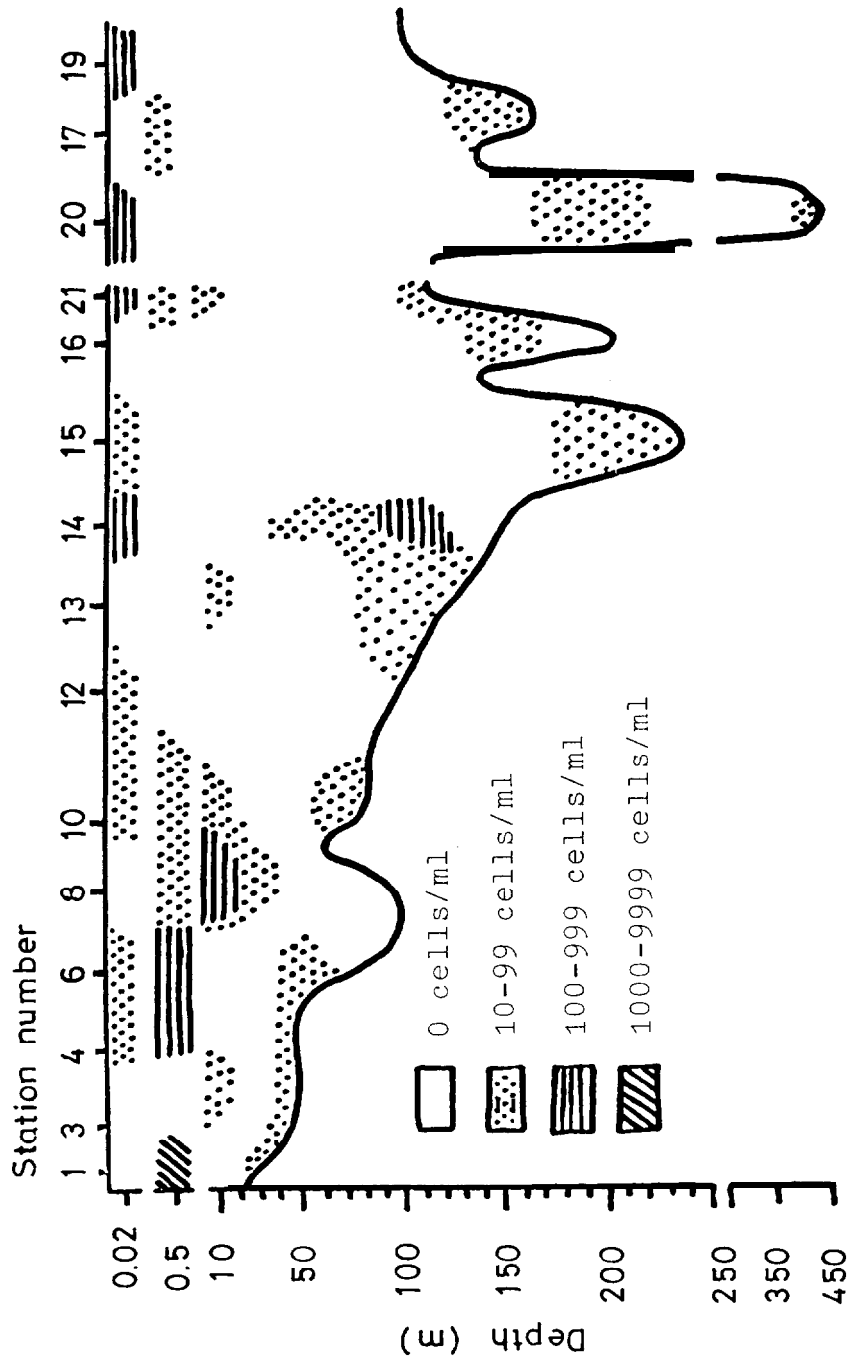


Figure 68. Vertical distribution of *bens(a)pyrene-oxidizing* micro-organisms through a Baltic Sea transect, March 1978 (Tsiban, original figure).

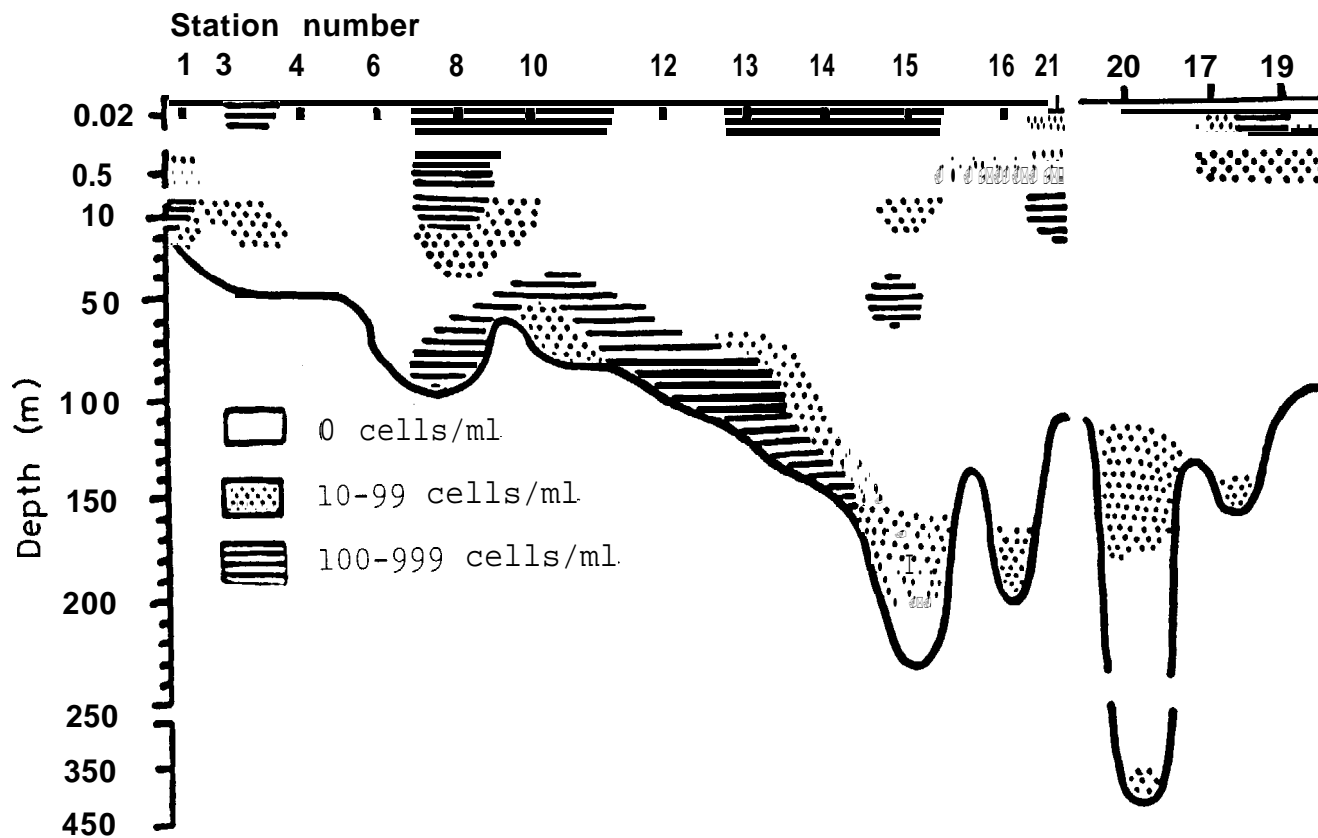


Figure 69. Vertical distribution of PCB-oxidizing micro-organisms through a Baltic Sea transect, March 1978. (Tsiban, original figure).

Gocke (1977) and Dawson and Gocke (1978) determined the rate of uptake for the different substances at the Kiel Bight station and in the Bornholm Basin, the Gdańsk Bight and the Gotland Basin. For the latter three areas, the average uptake of free amino acids over the whole water column has been investigated, with the following results:

	Depth (m)	Concentration ( $\mu\text{g}/\text{dm}^3$ )	Gross uptake ( $\mu\text{g}/\text{dm}^3/\text{day}$ )	Net uptake ( $\mu\text{g}/\text{dm}^3/\text{day}$ )
Bornholm Basin	87	28.3	7.6	5.9
Gdańsk Bight	100	28.2	9.3	7.0
Gotland Basin	240	21.2	4.2	3.2

Annual cycles in the turn-over times for glucose, aspartate, acetate and a mixture of amino acids in the Kiel Bight have been investigated (Gocke, 1977). As illustrated in Table 23, the turn-over times for these substances are clearly shorter in the April-to-October period than in the winter. The activity of cellulose-degrading bacteria is at a maximum during the autumn months, according to measurements in the Kiel Fjord, the Gdańsk Bight and the Gulf of Finland (Lehnberg, 1972; Maciejowska, 1969; Väätänen, 1976).

Figure 70 shows seasonal variations in the uptake of carbon by bacteria in the northern Baltic Sea, near Askö, Sweden.

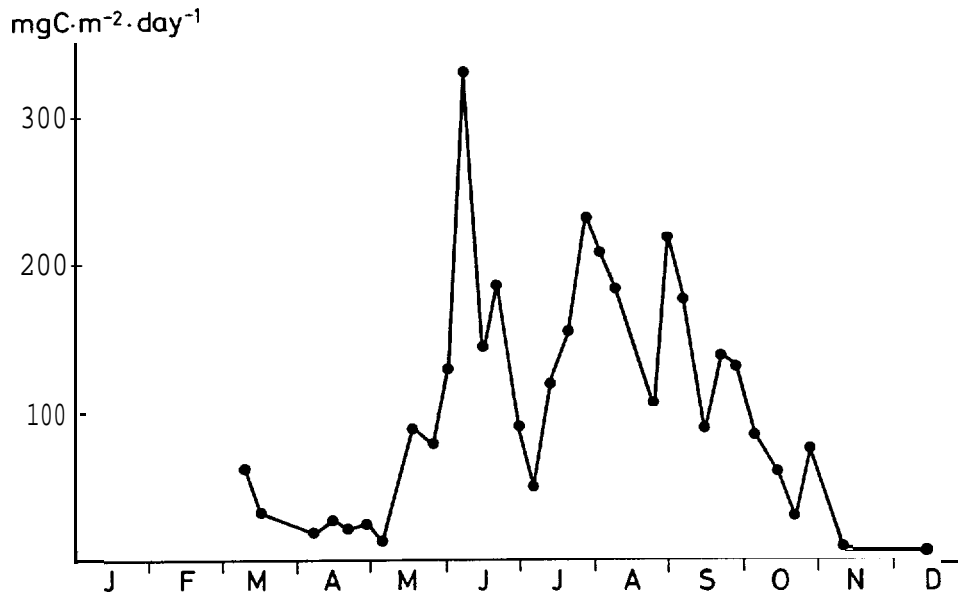


Figure 70. *Seasonal variations in carbon uptake by bacteria in the northern Baltic Sea near Askö, Sweden (after Larsson and Hagström, 1979).*

The microbial decomposition of mineral oil (ship fuel) in water samples from the Gdańsk Bight was investigated by Maciejowska and Rakowska (1973). They established that the breakdown process was most effective when the oil was present at very low concentrations. In Baltic Sea water at 20°C, the percentage decomposition after 4 weeks was 32 - 61% for an initial concentration of 0.5 g oil/dm<sup>3</sup> and only 28 - 40% for a 2.5 g oil/dm<sup>3</sup> concentration. After 8 weeks, the percentage decomposition values were, respectively, 44 - 73% and 41 - 70%. The decomposition of oil is a very slow process, especially at winter temperatures. The same pattern is observed for phenols, the main microbial decomposition occurring during the warmer season when the water temperatures are above 10°C (Iturriaga and Rheinheimer, 1972).

Microbial decomposition of organic matter, being an oxidation process, requires the presence of sufficient oxygen. Heavy organic pollution can lead to a complete loss of available molecular oxygen.

Table 23. *Turnover times (h) of an amino acid mixture in relation to water temperature observed in the relatively polluted Kiel Fjord at 2 m depth and in the rather clean central Kiel Bight at 10 m depth (after Gocke, 1977).*

Date	Kiel Fjord		Kiel Bight	
	°C	h	°C	h
28. 4. 1974	3.7	32.5	3.0	101.0
21. 3.	4.4	10.0	4.4	238.0
18. 4.	8.6	3.1	6.8	33.5
16. 5.	10.9	2.5	8.7	56.9
11. 6.	12.8	3.6	12.3	24.3
11. 7.	16.7	5.1	15.5	12.0
29. 8.	17.7	2.9	17.5	18.6
12. 9.	15.5	4.6	15.7	26.5
24.10.	10.5	2.7	10.4	16.6
21.11.	7.5	28.3	7.5	47.0
10.12.	6.5	22.2	6.5	119.0
23. 1. 1975	5.3	25.6	5.1	47.6
12. 2.	3.6	12.4	3.7	103.0
10. 3.	5.5	23.8	3.3	22.7

In regions with insufficient oxygen, as for example is often the case in deep water or in some sediments, denitrification first occurs and then sulfur reduction, whereby bacteria reduce sulfates to hydrogen sulfide. This process involves the obligate anaerobic heterotroph *Desulfovibrio desulfuricans*, which is associated with the further sulfate reducer *Desulfotomaculum nitrificans*. Besides the absence of oxygen, the other prerequisite for bacterial sulfate reduction is the presence of sulfate and an organic substance. This combination of factors is found in nutrient-rich muddy sediments.



Microbiological investigations concerning sulfur reduction have been conducted in the Limfjord (Jørgensen, 1977), in the Kiel Bight (Bansemir and Rheinheimer, 1974) and in the Gotland Deep (Seppänen and Voipio, 1971). In all cases, the numbers of sulfur reducing bacteria are many times higher in the sediments than in the water column, therefore, sulfate reduction occurs mainly in the sediments.

Proteolysis involves the breaking down of the sulfide-containing amino acids cystine, cysteine and methionine, resulting in the release of hydrogen sulfide. Because the content of these amino acids in the water and in the sediments is usually low, the proteolytically produced hydrogen sulfide is also low. In the border area between oxygen- and hydrogen sulfide-containing water, hydrogen sulfide can be oxidized by Thiobacillae. This can also occur on the surface of the sediments by the action of filaments of sulfate bacteria (*Beggiatoa*, *Thiobacillus*). The extent of this sulfur oxidation is, however, only locally important.

Disturbances of the purification processes are not only caused by a lack of oxygen, but also by the direct effects of toxic materials from industrial wastes and sewage effluents discharged into the affected water bodies. They can, if at a sufficiently high concentration, inhibit micro-organisms involved in the purification processes and ultimately kill them. Heavy metal compounds, cyanides and organic toxins can have this effect.

Metallic mercury and mercury ions have a lower toxicity to humans and other animals than organic mercury compounds. The latter can originate from bacterial methylation processes. Organic mercury compounds, being fat soluble, are able to penetrate the human nerv-

ous system. The mercury-resistant bacteria which are able to break down the methylated mercuric compounds function against the enrichment of dangerous organic mercuric compounds (Spangler et al., 1973).

#### 7.1.5 *Pathogenic micro-organisms in polluted waters*

Through the release of domestic sewage, many places in the Baltic Sea have populations of human pathogenic bacteria, fungi and viruses. The bacteriocidal action of the sea and brackish water inhibits their growth and finally may cause the death of such organisms (ZoBell, 1946). In spite of this, however, the various pathogenic agents can survive for varying periods in the prevailing conditions. Pathogenic intestinal bacteria, especially *Salmonella typhi* and *S. paratyphi* which cause typhus diseases, are found relatively frequently in polluted coastal waters. Intestinal disease-causing organisms are similarly distributed. Numerous other pathogenic micro-organisms are found in the immediate vicinity of sewage outlets. The survival time is usually greater in the sediments than in the water column. Solid organic particles, resulting from poorly treated sewage, are particularly dangerous when released into the sea, especially if they are of man or animal food origin. These particles can sustain pathogenic micro-organisms for a long time and may stimulate the propagation of intestinal bacteria. Spores of pathogenic Clostridia which cause gas gangrene (*Cl. perfringens*, *Cl. novyi* and *Cl. septicum*) can be concentrated in the sediments (Bonde, 1967) and this is also true for *Cl. botulinum*.

Occasionally infections are caused by halophilic *Vibrio* species which do not originate from sewage, e.g., *Vibrio alginolyticus* which causes a middle ear infection (Graevenitz and Carrington, 1973).

Pathogenic micro-organisms are found associated with mussels and other filter-feeding animals. These micro-organisms can be concentrated in mussels and pose a health hazard for human consumption.

Pathogenic micro-organisms are also present in the sand of recreational beaches. In addition to bacteria and viruses, fungi are found which cause skin diseases. Such dermatophytes are mostly grouped with the Fungi Imperfecti of the genus *Trichophyton*.

#### 7.1.6 *Conclusions*

Certain information is available on the distribution, composition and activity of microflora in the water and sediments in the Baltic Sea which permits interpretations on the level of pollution. The majority of the data pertains to the western and central Baltic Sea, while data for the northern area, in particular the Gulf of Bothnia, are largely non-existent. Some information on conditions ten years ago is available for a few coastal areas, but these data are insufficient for satisfactory comparisons to be made.

Recent intensive investigations concerning the inter-relationship between heterotrophic micro-organisms and other organisms have led to an expanded knowledge of the important role of bacteria in the food chain. Using well-developed tracer techniques for determining the transmittance of organic materials by micro-organisms, the relationship between bacteria and primary producers and the subsequent energy transmission to consumers, will become more apparent in the not too distant future.

However, our knowledge of the microbial decomposition of organic pollutants is far from sufficient. We know that the greater proportion of decomposition is accom-

plished by bacteria and a lesser part by fungi and that effective micro-organisms exist throughout the Baltic Sea in the water and the uppermost zone of the sediments. Very little is known about the decomposition processes or the intermediate products of decomposition. The difficulties of such investigations lie in the fact that the work is time-consuming and a close cooperation between microbiologists and chemists is necessary.

The organic pollutants associated with disease etiology are largely restricted to the heavily populated coastal areas. These problems, which restrict the recreational usage of the shoreline, are most intense at sewage discharge points, in harbours and river mouths. In recent years, attempts have been made in the western Baltic Sea to improve the hygiene of such areas by using new sewage treatment devices. Satisfactory water quality can be achieved only by the construction of appropriate sewage treatment facilities in the entire Baltic Sea area. Simultaneously, observations for any signs of disruption to the purification processes must be undertaken.

A uniform procedure for routine investigations of the quantity of faecal indicators (at least total coliforms and faecal coliforms) together with heterotroph counts (colony-forming units) in brackish water and fresh water should be conducted. The latter should be regarded as being ultimately a component of the oceans in spite of being far from the coastline.

## 7.2 Phytoplankton

Phytoplankton is the name given to floating plant communities made up of microscopic algae. Predominant among the phytoplankton species to be found in the Baltic Sea are diatoms, dinoflagellates, and blue-green

algae. Recent studies show that nanoplankton (1 - 20  $\mu\text{m}$ ) may temporarily be very abundant and contribute an essential share of the primary production (Hällfors and Niemi, 1981). It must be emphasized that phytoplankton as primary producers play an extremely important role in the ecology of the sea. This holds true not only for the pelagic environment, but also for the majority of zoobenthos communities, especially for those below the euphotic zone where phytobenthos is absent (Jansson, 1978).

#### 7.2.1 *Present knowledge on phytoplankton in the Baltic Sea*

Comprehensive studies on phytoplankton in the open Baltic Sea were performed already at the turn of the century by Levander (CIEM, 1914; Levander and Purasjoki, 1947), and later on by Riikoja (1925, 1928, 1929, 1931), Hessle and Vallin (1934), Rothe (1941) and others. However, those results do not give a reliable basis for quantitative comparisons with recent data. One example of a very detailed study of phytoplankton occurrence and biomass on the species level in the outer Kiel Bight is found in the work of Lohmann (1908).

Lists of literature on the Baltic Sea phytoplankton community structure and its seasonal succession are compiled in Willén (1962) and Niemi (1973, 1975). Checklists for Baltic phytoplankton are available only for the northern parts of the Baltic Sea (Hällfors, 1979). There are many environmental factors which regulate phytoplankton growth in the Baltic Sea. The basic factors are nutrients and light. Temperature governs the rate of mobilization of nutrients by biodegradation and algal growth; like salinity, it exercises a great influence on the growth conditions of most species, thus regulating the regional and seasonal species composition of the Baltic Sea phytoplankton community.

Turbulence and water stratification are further factors affecting phytoplankton growth. The increasing irradiation in the spring, combined with the development of stability in the water column, is the decisive factor triggering the spring algal bloom in the open waters of the Baltic Sea (Niemi, 1975; Kaiser and Schulz, 1978). This positive effect of the development of water stratification is reversed in the summer as the thermocline separates the impoverished euphotic zone of the pelagic area from the nutrient supply below. Temporary turbulence, but especially the upwelling of nutrient-rich water, may locally replenish the nutrient supply in the impoverished surface layers, as is the case in the autumn and winter in the whole Baltic Sea. Upwelling phenomena have been observed particularly along the northern coast of the Gulf of Finland (Voipio, 1968) and along the Swedish coast in the Baltic Proper (Jansson, 1978). Jansson has drawn attention to the importance of the upwelling phosphorus-rich water masses as the initial sites for vigorous blue-green algal blooms fixing molecular nitrogen (Jansson, 1978; Niemi, 1979).

Three factors are mainly responsible for the regional differences in the distribution and productivity of phytoplankton in the Baltic Sea: salinity, nutrient level and the annual cycle of physical factors.

The decreasing salinity from south to north exerts a strong effect on the species composition (Välikangas, 1933; Zenkevitch, 1963; Hällfors and Niemi, 1981). Many euryhaline species, abundant in the Kattegat and the Belt Sea area, cannot thrive in the central and northern Baltic Sea. On the other hand, the blue-green algae *Aphanizomenon flos-aquae* and *Nodularia spumigena*, noted for their mass development in the summer in most parts of the Baltic Sea, are adapted to lower salinities (ca. 3 - 12 ‰) than are usually found in the Belt Sea. In late summer, they may be observed

in outflowing Baltic Sea surface water in regions as remote as the Skagerrak.

In the northern Baltic Proper, the Gulf of Finland and the Bothnian Sea, the vernal bloom is made up of marine cold-water diatoms and dinoflagellates. But in the summer during the thermal stratification, the fresh water element is marked (Nikolaev, 1957; Niemi, 1973, 1975; Hällfors and Niemi, 1981). In the Bothnian Bay, the vernal phytoplankton consists chiefly of euryhaline marine cold-water diatoms and *Gonyaulax catenata*, but in the summer the fresh water element is dominant (Niemi and Ray, 1977; Alasaarela, 1979a, 1979b; Hällfors and Niemi, 1981). The phytoplankton of the Bothnian Bay differs by having a more dominant fresh water element than that in the Bothnian Sea, the Gulf of Finland and the northern and central Baltic Proper. In these latter sub-areas, the phytoplankton composition is generally quite similar.

Regarding nutrients, inshore areas usually provide a higher level of nutrient supply to the phytoplankton than offshore regions because of a closer contact in shallow coastal waters to the sea bottom, shore and fresh water outflow. An additional nutrient source is the inflowing North Sea water. Through vertical mixing and local upwelling, this inflow increases the nutrient stock of the surface layer in the southwestern Baltic Sea (e.g., Edler, 1977, 1978).

The annual cycles of the environmental factors, irradiation, turbulence and water stratification, determine the time of the onset and the duration of the growth period. In particular, the onset of the vernal bloom and the temporal development of the autumnal diatom blooms are determined by a stratification preventing the turbulence from reaching the critical depth for phytoplankton growth (Sverdrup, 1953; Niemi, 1975; Niemi and Ray, 1977; Kaiser and Schulz, 1978). Thus, year-to-year variations in meteorologically induced hydrogra-

phic conditions will markedly influence the seasonal succession and production of Baltic Sea phytoplankton. The change in factors with latitude is responsible for considerable differences between the southern and northern parts of the Baltic Sea, especially in the length of the growing period.

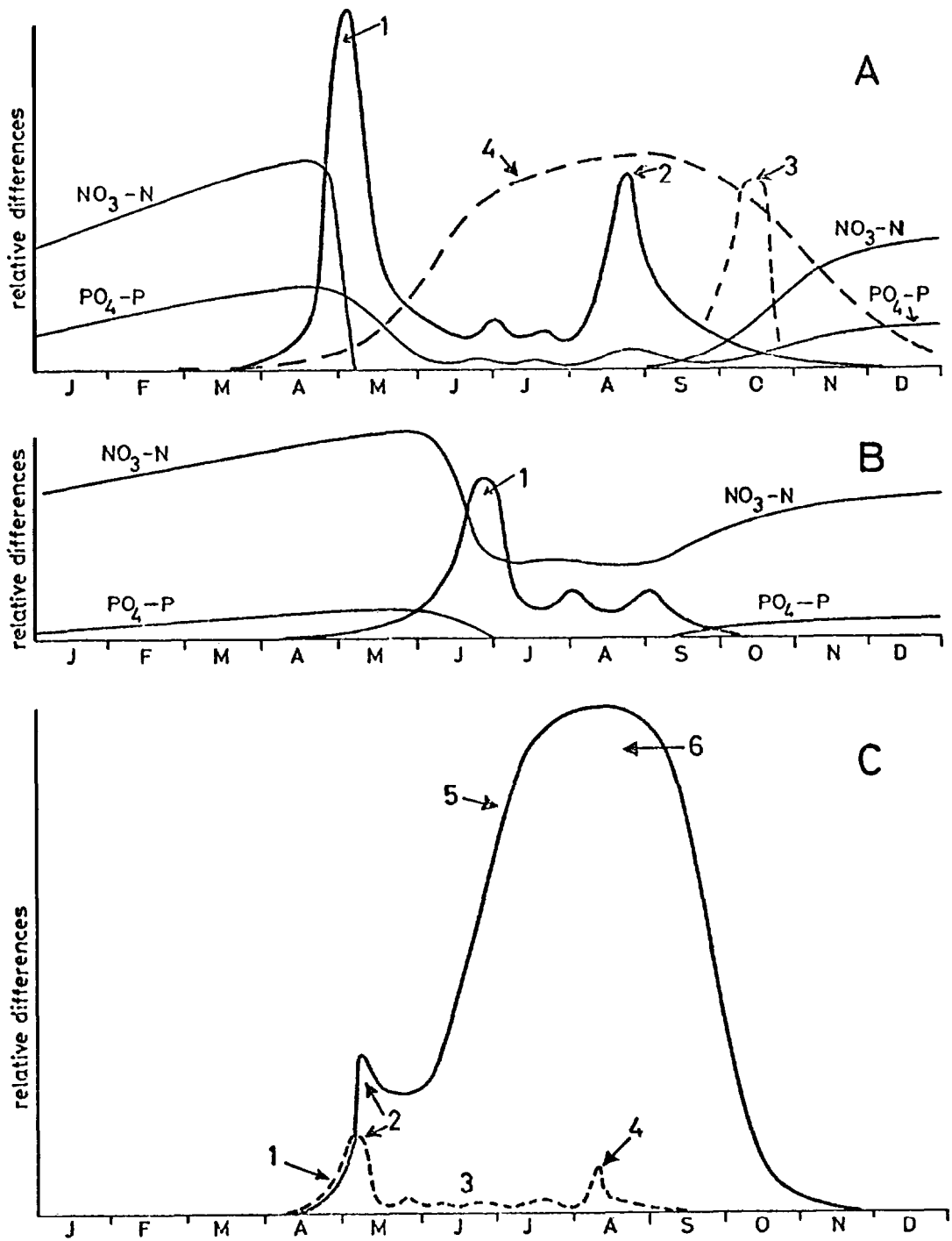
Grazing by herbivorous zooplankton is another factor controlling phytoplankton standing stock and exerting an influence on the species level of the community. The time lag between a phytoplankton bloom and the subsequent peak of planktonic herbivores is important, as it determines the direction of energy flow through the ecosystem. A short time lag means that most of the energy fixed by primary producers flows directly into the pelagic food chain, while with a long time lag a large portion of the phytoplankton sinks down to the bottom to serve as food for benthic organisms. This latter case is true for the vernal maximum in the central and northern Baltic Sea. The vernal bloom, when no grazers occur, brings an essential part of the annual energy input to the benthic system (Jansson, 1978). The unsuitability of blue-green algae as food for grazers (e.g., Nauwerch, 1965) also seems to favour the blue-green algal mass production in summer and autumn.

The occurrence of vigorous blue-green algal blooms in the open sea areas seems to be chiefly controlled by a surplus of phosphorus; blooms emerge particularly in upwelling areas (Jansson, 1978). The high inorganic N:P ratio in the northern parts of the Gulf of Bothnia seems to be the factor preventing blue-green algal blooms there (Niemi, 1979; Rinne et al., 1979, 1980).

Figure 71 depicts the annual cycle of phytoplankton standing stock and primary production in relation to environmental factors and the abundance of grazers in the shallow southwestern Baltic Sea. In the Belt Sea area, a pronounced vernal bloom of diatoms is followed



by a number of smaller blooms of dinoflagellates and diatoms in the summer (Smetacek, 1975). These are caused by irregular nutrient inputs to the euphotic zone through advection, increased turbulence through currents, or upwelling. In the Øresund, Edler (1976) has described a widely fluctuating seasonal cycle of planktonic algal production.



A=Northern Baltic Proper, Gulf of Finland and Bothnian Sea  
 1) Vernal bloom, marine cold water diatoms and *Gonyaulax catenata*  
 2) Blue-green algae blooms  
 3) Centric diatoms  
 4) Grazers

B=Bothnian Bay  
 1) Vernal diatom bloom

C=Northern part of the Baltic Sea  
 1) Phytoplankton biomass in undisturbed coastal waters  
 2) Vernal bloom  
 3) Summerminimum  
 4) Blue-green algae blooms  
 5) Phytoplankton biomass in eutrophied coastal waters  
 6) *Oscillatoria agardhii* community

Figure 71. The annual cycles of inorganic nutrients, standing stocks of phytoplankton and zooplankton in different areas of the Baltic Sea (Niemi, original figure).

In the Baltic Proper, the Gulf of Finland and the Bothnian Sea, the seasonal phytoplankton cycle is more regular than in the southwestern Baltic Sea. A generalized diagram (see Figure 72) shows the annual cycle of phytoplankton standing stock, nutrients and the abundance of grazers. The duration of the vernal diatom-*Gonyaulax* bloom seems to be regulated by the depletion of nitrate-nitrogen in the euphotic zone (Niemi, 1975; Hobro et al., 1975). The blue-green algal bloom (*Aphanizomenon f. Zos-aquae*, *Nodularia spumigena*, *Anabaena lemmermannii*) is controlled by a good supply of phosphorus combined with favourable hydrographic conditions (cf. Horstman, 1975, 1979; Niemi, 1972b, 1975, 1979; Öström, 1976; Rinne et al., 1978, 1979, 1980). An autumnal bloom of great centric diatoms (*Coscinodiscus granii*, *Thalassiosira baltica*) is chiefly regulated by the occurrence of fair weather, i.e., a good supply of irradiation and stability in the water column preventing turbulence below the critical depth for phytoplankton production (Niemi and Ray, 1977; Hällfors and Niemi, 1981). These three phytoplankton maxima seem to develop independently of grazing. On the contrary, during the summer minimum stage characterized by nanoplankton, particularly small flagellates, grazing is a regulating factor for phytoplankton production (Jansson, 1978).

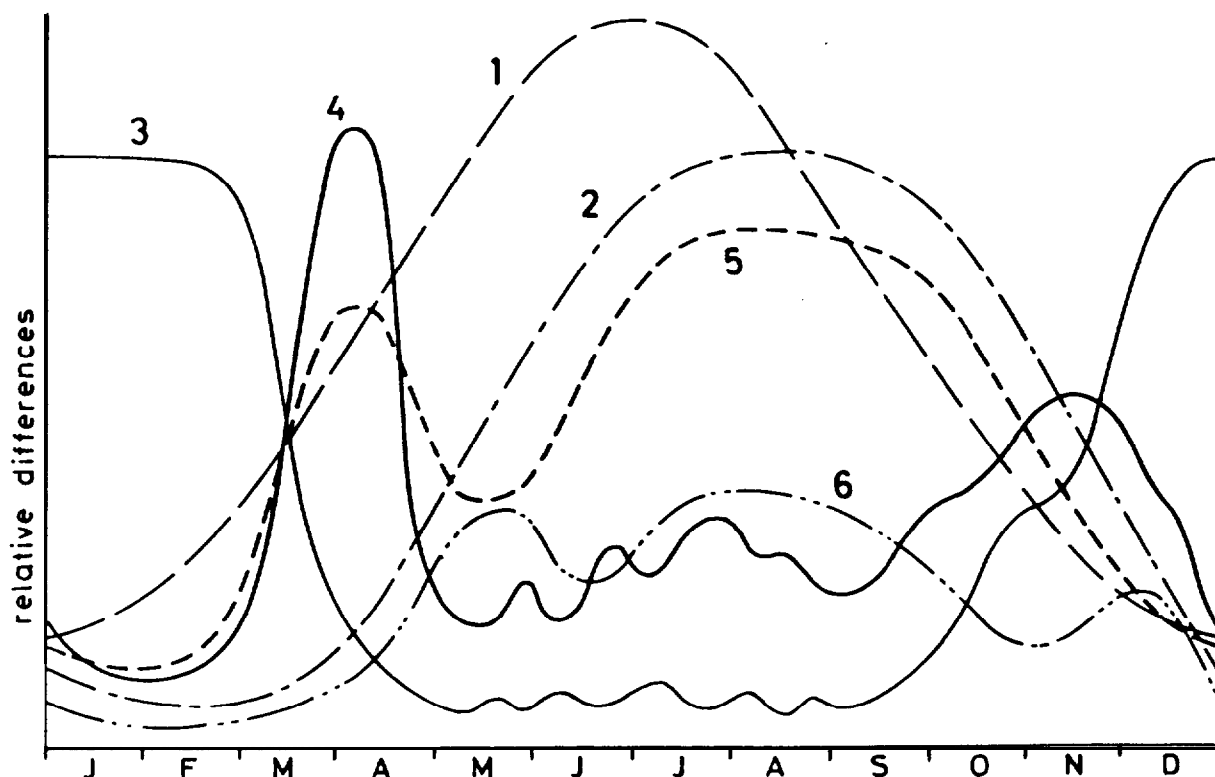


Figure 72. Schematic presentation of the annual cycle of irradiation (1), water temperature (2), inorganic nutrients (3), phytoplankton standing stock (4), primary production (5) and standing stock of grazing zooplankton (6) within the euphotic zone as typical of the western Baltic Sea. (Lenz, original figure).

In the Bothnian Bay, the phytoplankton maximum is moved toward summer, a feature of high latitudes (Lassig and Niemi, 1974, 1975, 1976; Alasaarela, 1979a, 1979b). Marked vernal or autumnal blooms are less discernable. As already mentioned, blue-green algae blooms do not occur.

In the Baltic Proper, the Gulf of Finland and the southern Bothnian Sea, the predominant feature in the summer is a mass development of *Nodularia spumigena* and *Aphanizomenon flos-aquae*. Owing to their ability to fix molecular nitrogen, they are able to thrive in the surface layer despite its general impoverishment of inorganic nitrogen during the summer stratification period (e.g., Niemi, 1976, 1979).

After the gradual breakdown of the thermocline in the autumn and the mixing of nutrients from below into the surface layer, an autumnal bloom of phytoplankton may occur. But this is much less pronounced than the spring bloom (Niemi and Ray, 1977). In the southwestern Baltic Sea, it is caused by dinoflagellates followed by diatoms (Smetacek, 1975), in the northern Baltic Sea by marine centric diatoms (Niemi and Ray, 1977).

Because the investigations on primary production in the Baltic Sea have recently been intensified, there are many values based on  $^{14}\text{C}$  measurements in different parts of the Baltic Sea (see Table 24; cf. Lassig et al., 1978). However, due to the lack of unified methods, the values are not quite comparable. All values are based on *in situ* measurements.

Table 24. *Estimations of primary production (g C/m<sup>2</sup>/yr) in different regions of the Baltic Sea*

Region	Primary Production (g C/m <sup>2</sup> /yr)	Source
Kattegat, central part	97 (mean W-3-1960)	Steemann Nielsen (1964)
Kattegat, central part	>100	Miljøstyrelsen (1980)
Great Belt	85 (mean 1953-1957)	Steemann Nielsen (1964)
Øresund, Svinbaden	77 (1972), 183 (1973)	Edler (1978)
Ven	70 (1972), 148 (1973)	
Kalkgrundet	75 (1972), 73 (1973)	
Kiel Bight	158 (1973)	von Bodungen (1975)
Arkona Sea	64 (mean 1966-1973) 65 (mean 1967-1972) 95 (1975)	Renk et al. (1974) Schulz and Kaiser (1974) Schulz et al. (1978)
Han6 Bight	154*(1973), 178*(1974) 194*(1975), 194*(1976)	Ackefors and Lindahl (1979)
Bornholm Sea	121 (1974) 77 (1975)	Ackefors and Lindahl (1975) Schulz et al. (1978)
Gdańsk Deep	118 69	Renk (1974) Renk et al. (1975)
Gdańsk Bight	104	Renk (1974)
Eastern Gotland Sea	134*(1973), 170*(1974) 141*(1975), 128*(1976)	Ackefors and Lindahl (1979)
Gulf of Finland, Kopparnäs	105 (mean 1975-1976)	Lassig et al. (1978)
Tvärminne	103 (mean 1972-1975)	Lassig et al. (1978)
Off Helsinki	53 (mean 1968-1975) 69 (mean 1976-1979)	Pesonen (1980) Pesonen (1980)
Åland Sea	138*(1973), 99*(1975) 96*(1976)	Ackefors et al. (1978)
Bothnian Sea, Kaskinen	57 (mean 1972-1974)	Lassig et al. (1978)
Norrbyckär	104*(1973), 103*(1974)	Ackefors et al. (1978)
Bothnian Bay, Luleå	13*(1976)	Ackefors et al. (1978)
Ulkokalla	18 (mean 1973-1975)	Lassig et al. (1978)
Central part of northern Bothnian Bay	20 (mean 1976-1977)	Alasaarela (1979)
Ulkokrunnit	21 (mean 1968-1972)	Alasaarela (1979)
Off Kemi	15 (1979)	Alasaarela (1979)

\*

Values corrected for liquid scintillation counting by a factor of 1.47. (It is not clear to what extent the correction factor 1.47 as indicated by Ackefors et al. (1978) and Ackefors and Lindahl (1979) should also be applied to the older data.)

As is to be expected from the different environmental conditions, the Kattegat, the Belt Sea area and the southwestern Baltic Sea are more productive than the northern parts of the Baltic Sea. However, a number of observation points are situated in shallow inshore areas and are therefore not representative of the less productive off-shore regions (cf. Miljøstyrelsen, 1980). The yearly variation is in most cases surprisingly low. Records of the annual level of primary production in different sub-areas show levels  $> 100$  g carbon per  $m^2$  per year in the above-mentioned outer areas. The level in the central and northern Baltic Proper and the Gulf of Finland is about  $100$  g C/ $m^2$ /y. The primary production levels in the Bothnian Sea and particularly in the Bothnian Bay are markedly lower, about  $60$  and  $20$  g C/ $m^2$ /y, respectively. This decreasing level seems to be connected with the decreasing level of phosphorus progressing northward (Baltic Proper ca.  $15$  g total phosphorus per  $m^3$ , Gulf of Finland ca.  $20$  g/ $m^3$ , Bothnian Sea ca.  $10$  g/ $m^3$  and Bothnian Bay ca.  $5$  g/ $m^3$ ) and with the progressively shorter growing period (Lassig et al., 1978; Niemi, 1979).

#### 7.2.2 *Methods used in phytoplankton research*

The analysis of species composition, the determination of the standing stock and the measurement of primary production are all parameters suitable for pollution studies. They have been adopted as part of the Baltic monitoring programme. The procedures adopted as obligatory in the programme, to ensure intercomparability of the results, are based on recommendations of the Baltic Marine Biologists (BMB Publ. Nos. 1, 2 and 5). However, the results of the intercalibration of methods for phytoplankton species and biomass determinations in Stralsund in 1979 among Baltic laboratories showed that there is no satisfactory comparability yet between the results from different laboratories (Edler, 1980). Much

standardization work remains. This is also true for primary production measurements (Nielsen, 1980).

*Species analysis.* Species identification is quite a difficult task and considerable experience is necessary to obtain reliable results. Problems are particularly encountered in the identification and enumeration of nanoplankton (1 - 20  $\mu\text{m}$ ), i.e., fragile flagellates, because of their difficult taxonomy, unknown ecology and the difficulties encountered in preservation (e.g., Thomsen, 1978). Occasionally, when the standing stock of phytoplankton is small, the share of nanoplankton may be marked, e.g., the groups *Cryptophyceae*, *Chrysophyceae*, *Prymnesiophyceae* and *Prasinophyceae* (Hällfors and Niemi, 1981).

*Determination of standing stock (biomass).* Two methods are commonly in use, the calculation of total phytoplankton volume and the determination of chlorophyll a. The cell volume can be converted into carbon content by means of conventional conversion factors (Smetacek, 1975; BMB Publ. 5). The total sum of cell carbon has the advantage of allowing direct comparison with production measurements of carbon. Although tedious and time-consuming, this method yields valuable information on the ecological role played by certain single species within the phytoplankton community. The precision of the method depends largely on the experience of the planktologist and the reliability of the conversion factors used, the latter being a matter of general agreement corresponding to the current stage of research.

Chlorophyll a has been used as a biomass index for algae. The method itself poses few problems, although discussions on improvements are in progress. It has the advantage of easy applicability combined with high precision. However, in shallow areas with many sediment particles stirred up from the bottom, there is a



danger that so-called detrital chlorophyll, consisting of degradation products of chlorophyll, will be measured together with the chlorophyll of living cells, thus leading to an over-estimation of the latter. The value of chlorophyll a does not give an exact correspondence to the biomass (e.g., Tolstoy, 1977), nor to the carbon content, but more to the production capacity of the phytoplankton. The chlorophyll concentration has been used to mirror areas of different productivity (e.g., Renk, 1973, 1974; Lassig and Niemi, 1973, 1975).

*Measurement of primary production.* The  $^{14}\text{C}$  method, whereby  $\text{NaH}^{14}\text{CO}_3$  is added to photosynthesizing algae for a particular incubation period, includes several sources of error. First, the duration of the incubation period is critical because the assimilated  $^{14}\text{C}$  is recycled through respiration and excretion. During longer incubations bacteria will interfere with the  $^{14}\text{C}$  assimilation. Moreover, the diurnal rhythm of algal metabolism will make the interpretation of results difficult.

The *in situ* exposure of algae enclosed in bottles in their environmental conditions is generally regarded to be the best method. However, on research vessels there is no time for long *in situ* incubations, so simulated *in situ* or incubator experiments must be performed. It has been agreed to use the constant light incubator method for the Baltic monitoring programme during the first stage. The values obtained do not represent the production *in situ* and include considerable sources of error. However, the method introduced by Gargas (1975) enables an approximate estimation of primary production under natural conditions by means of an incubator. Despite accessible BMB recommendations on methods for primary production measurements (Gargas, 1975), no agreement has been attained among Baltic scientists, so the primary production results published (see Table 24) are not quite comparable.

One example of the inexpediency of comparing old data with new data is found in Edler's (1978) work on phytoplankton production in the Øresund. Methods employed earlier, which gave the value of about 30 g C/m<sup>2</sup>/y, reported by Steemann Nielsen (1937), cannot be compared directly with recent results which are often twice as high. Also, the calculations made by Buch (1948, 1952) on primary production in the northern Baltic Proper gave values too low when compared with recent measurements.

In recent primary production measurements, a considerable error emerges when the sampling intervals are too widely spaced to cover the short-term dynamics of phytoplankton production. A short vigorous bloom may be missed. Moreover, the change to use *in situ* incubation means that the weather on the day of measurement, whether sunny or rainy, will influence the estimates of annual production. These problems have been discussed by Wulff (1979).

One of the greatest methodological problems is to get representative samples. Advection and patchiness are related factors making the interpretation of production measurements difficult. Advection plays a specially important role in narrow straits and in the Belt Sea area, as indicated by rapid changes in salinity. The same is true in coastal and archipelago waters, where complex movements of water masses from the open sea and from estuaries may occur (Niemi, 1973). Moreover, the natural variations in environmental conditions influencing the phytoplankton production make the study of regulating factors very difficult. A long-term observation programme with monthly sampling intervals in winter and biweekly intervals during the growth period could possibly provide the best compromise between maximum information gain and the effort invested in coping with all the problems mentioned. However, occasional fluctuations will not be observed. As Krey

et al. (1978) have shown in the Kiel Bight, the phytoplankton standing stock data scatter within approximately one order of magnitude. Also Voipio and Seppänen (1968) found great fluctuations in primary production between subsequent days in the open Baltic Proper, although there were no observed differences in environmental conditions. The infrequent sampling agreed upon for the first stage of the Baltic monitoring programme is aimed at providing only a warning system, and not giving the annual levels of primary production in different Baltic Sea areas.

### 7.2.3 *Present knowledge of the effects of pollution on phytoplankton and primary production*

Because of the inability to compare older quantitative phytoplankton data with recent results, it is difficult to determine possible trends in the phytoplankton composition, distribution and standing stock during this century. Comprehensive studies on phytoplankton in the open Baltic Sea were made already at the turn of the century. When comparing these phytoplankton data with modern results, it is difficult to find any changes in the Baltic Proper, the Gulf of Finland and the Gulf of Bothnia. The vigorous blue-green algal blooms (*Aphanizomenon*, *Nodularia*, *Anabaena*) have often been cited as indicators of increasing eutrophication. However, already in 1885, blooms appeared in the open sea (Pouchet and de Guerne, 1885). Possibly these blooms are phenomena belonging to the natural dynamics of the Baltic Sea ecosystem with a low inorganic N:P ratio (Niemi, 1979). However, the increased nutrient load from land and particularly the oceanization processes increasing the phosphorus concentration (Nehring, 1979) probably have favoured the development of blue-green algal blooms (Jansson, 1978). Poisonous effects from Baltic Sea blue-green algal blooms have not been observed, although the same species have in other areas caused detrimental effects on, for instance, cattle and ducks drinking the water.

Our position is much better as regards the general effects of eutrophication caused by the increased input of nutrients to the ecosystem near land. The resulting increase in primary production and in the standing stock of algae is already easily observable in the vicinity of larger ports, especially when they are situated at the end of narrow fjords, e.g., the Kiel Bight (Lenz, 1977), Stockholm (Melin and Lindahl, 1973), Helsinki (Melvasalo and Viljamaa, 1975), and Oulu (Alasaarela, 1979). Typical for such areas in the central and northern parts of the Baltic Sea is the change of the phytoplankton summer minimum stage from a low production to an *Oscillatoria agardhii* community causing a high production (Melvasalo, 1971; Melvasalo et al., 1975; Niemi, 1972b). The phytoplankton composition changes and is characterized by *O. agardhii*, *Anabaenopsis elenkinii*, *Microcystis reinboldii*, *Oblea rotunda*, etc., of which the first two mentioned do not occur in undisturbed coastal waters.

The primary production results from the years 1965 - 1980 are not easy to compare owing to the differences in and the development of measuring methods (cf. Lassig et al., 1978). In eutrophied coastal waters, however, the increasing eutrophication is clearly indicated by an increase in the primary production and the production capacity (Lehmusluoto and Pesonen, 1973; Alasaarela, 1979). Apart from local areas with clearly traceable pollution sources, no increase in phytoplankton standing stock or primary production is ascertainable at present because of the lack of comparable quantitative data from the past.

There is very little reliable information (e.g., Niemi, 1972a) on the possible effects of toxic substances on phytoplankton communities in their natural habitat, since the results obtained in laboratory experiments investigating the toxic influences of oil, heavy metals, etc., on single species can only be applied with strong reservations to the multi-species communities in the

sea. With the exception of serious pollution caused by tanker oil spills or in the vicinity of toxic discharges in high concentrations, where doses are lethal to phytoplankton cells, little reliable information is available on the possible effects of sub-lethal concentrations on phytoplankton communities in their natural habitat.

The reliability of future investigations into any pollution effects will largely depend on a careful consideration of all methodological drawbacks and the biotic and abiotic environmental influences on the results obtained.

### 7.3 Zooplankton

The zooplankton of the Baltic Sea encompasses a large variety of organisms. The word plankton sets the limits to those animals which live freely in the water and which, because of limited powers of locomotion, drift more or less passively along with the main water movements. Furthermore, the term zooplankton is split into two terms, namely "holoplankton", by which we mean organisms that spend their entire life cycle as plankton, and "meroplankton", by which we mean organisms which spend only part of their life history in a planktonic phase. The latter term mostly refers to larval or developmental stages of species belonging to the benthic fauna. Although fish eggs and fish larvae are "zooplankton" in the true sense of the word, they are generally classified separately as "ichthyoplankton".

The zooplankton of the Baltic Sea contains such extremes as the smallest of the protozoans ( $< 10 \mu\text{m}$ ) and the large medusae with a diameter of 40 - 50 cm. Zooplankton is often divided into different size-groups (see e.g., Sieburth et al., 1978) according to the following scheme:

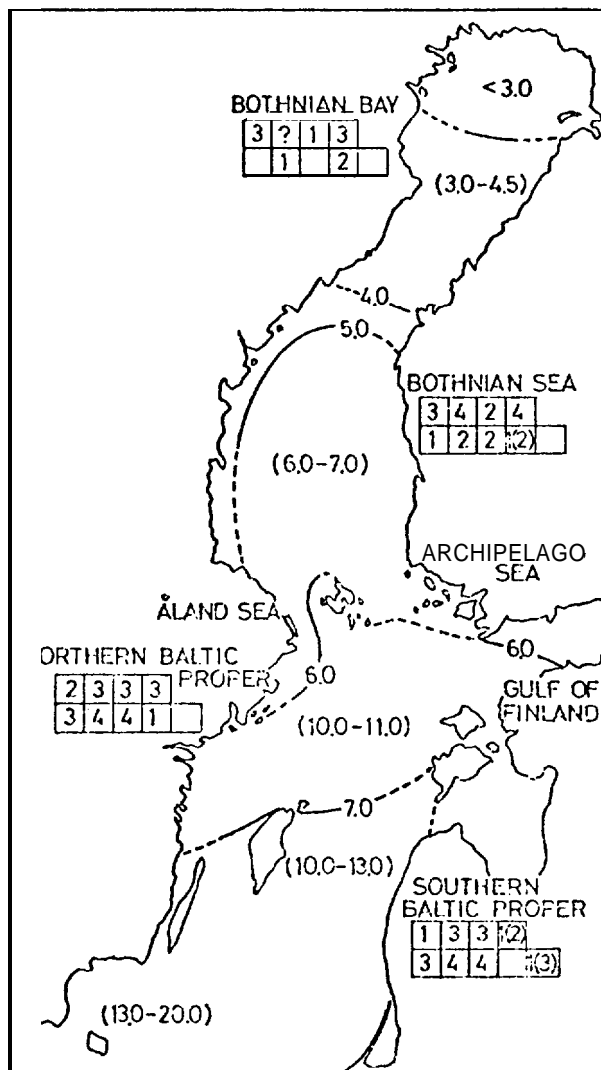
- Nanozooplankton ( 2 - 20  $\mu\text{m}$ )
- Microzooplankton ( 20 - 200  $\mu\text{m}$ )
- Mesozooplankton (0.2 - 20 mm)
- Macrozooplankton ( 2 - 20 cm)
- Megazooplankton 0 20 cm)

In terms of applied research, comparatively few studies have involved zooplankton. Despite its significance in the marine food chains, both as a regulator of phytoplankton primary production and as a food item for a variety of organisms at higher trophic levels, there is relatively little knowledge about zooplankton. One explanation for the situation could be that the zooplankton, with very few exceptions, is invisible to the human eye. It is, therefore, not thought of as an indicator of problems that would call for immediate action, like the mass occurrence of algae, shellfish poisoning, poor fish densities or sterile birds or mammals. Such reasoning is, however, deceiving. On the contrary, it is here, at the beginning of the food chain, that the accumulation and the transfer of substances start. Because of the large diversity of zooplankton organisms, this transfer of substances from one trophic level to another can take place along many paths within the food chain, a fact that is of prime importance in the spreading of pollutants.

#### 7.3.1 *The zooplankton of the Baltic Sea*

Of the zooplankton, the mesozooplankton and microzooplankton have been the best-studied fractions in the Baltic Sea since the last decades of the 19th century (e.g., CIEM, 1903-1909, 1910, 1914; Sokolova, 1927; Hessle and Vallin, 1934; Levander and Purasjoki, 1947; Halme, 1937, 1958). A list of the literature on the earlier zooplankton studies in the Baltic Sea can be found in, e.g., Ackefors (1969).

Because of the exceptional hydrographic conditions in the Baltic Sea, the planktonic fauna is different from that in adjacent areas, such as the Skagerrak or the North Sea. The brackish and stratified water masses form a demanding environment for the organisms and the total number of species is relatively low. The number of specimens, however, is well within the same magnitude as that in, e.g., the Skagerrak. The qualitative composition of the planktonic fauna differs gradually from the southern parts towards the most eastern and northern areas of the Baltic Sea. In the southern Baltic Sea there is a preponderance of marine species which gradually decreases towards the north, where instead the presence of fresh water species becomes more obvious (see Figure 73). There is also a distinct vertical zonation whereby the halocline constitutes the border between those species which prefer the colder and saltier water and those which live in the water masses with lower salinity and more pronounced seasonal variations. Coastal areas obviously have reasons for fewer representatives from the deep-water fauna. Instead, these areas have a greater proportion of fresh water species and species which can respond to the greater environmental variations in the coastal zone.



a	b	c	d
e	f	g	h
			i

Key to species

Species:

- a) *Limmocalanus grimaldii*
- b) *Acartia bifolosa*
- c) *Acartia longiremis*
- d) *Eurytemora* sp.
- e) *Centropages hamatus*
- f) *Pseudocalanus m. elongatus*
- g) *Temora longicornis*
- h) *Cyclops* sp.
- i) *Oithona similis*

Population density:

- 1) occasional specimens
- 2) low
- 3) medium
- 4) high

The approximate surface and bottom salinity is indicated in parentheses.

Figure 73. The occurrence of different copepods off the coast in the Baltic Sea (from Ackefors, 1969).

### 7.3.2 Factors influencing zooplankton

Despite the fact that our knowledge of the influence that pollution may have on zooplankton is quite poor at present, some general remarks can be made. Directly, the zooplankton can be affected both mechanically, phy-



siologically and genetically. Indirectly, changes in the surrounding fauna and flora may cause alterations within the zooplankton community.

Additionally, in eutrophied water, the effects of increased amounts of bacteria, epizoids and parasites on zooplankton should be taken into consideration. In the most eutrophied areas, the mass occurrence of phytoplankton algae may act as a mechanical nuisance for zooplankton species. In addition, heavy blooms of some algae, especially in their senescent phases, are often toxic and unsuitable as food for zooplankton.

An example of the mechanical effects on zooplankton is the damage to the appendages caused by passing through a power plant cooling system. This, together with intense predation by filtering barnacles in the tubes, is probably the major hazard to zooplankton from this type of installation (Sellei et al., 1979). Another mechanical damage that has become apparent is the problem of oil droplets sticking to vital appendages of the zooplankton (Johansson, 1979). A related problem is that of oil dispersants, which have been shown to cause a breakdown of the protective layer on the exoskeleton of copepods. As a result, the oil can pass through the exoskeleton and, once inside the animal, it can enter the natural lipid metabolism and cause harm to the organism (Gyllenberg and Lundqvist, 1976).

The effects of pollution through physiological processes are many. The most fundamental physiological aspect is the salinity of the environment. Although this itself is not a pollutant, many physiologically harmful processes are worsened by the stress arising from a change in salinity. An activity or construction that could cause only the slightest change of salinity in this brackish environment would have a very obvious impact on the composition of the fauna. The tolerance limits for many species are very narrow in this respect.

The oxygen concentration is another important parameter that affects zooplankton. It has been shown that zooplankton survives fairly well even at very low oxygen concentrations (Ackefors, 1969; Hernroth and Ackefors, 1979). However, the oxygen depletion which often occurs below the halocline is fatal to the resting stages of zooplankton on the bottom of the sea (e.g., Purasjoki, 1958). If the situation has evolved so far as to cause hydrogen sulfide production, no zooplankton will survive. The situation seems to be somewhat different for ichthyoplankton. Fish eggs which are planktonic, e.g., cod eggs, seem to be very vulnerable to low oxygen concentrations. Since these eggs require a salinity of 10 ‰ or more to be buoyant and since such salinities generally are restricted to the water layers below the halocline, it is obvious that the frequent occasions of low oxygen concentrations in the deeper parts of the Baltic Sea can represent a serious threat to the recruitment of certain fish species (Bagge, pers. comm.).

There are many abnormal physiological processes which are caused by the ingestion of harmful organic or inorganic substances. Oil and oil products have been shown to cause increased death rates of zooplankton (Mironov, 1970), narcotic effects on zooplankton (Johansson, 1979), and abnormal development of fish larvae (Linden, 1978a; Mironov, 1970). Heavy metals have been shown to cause increased mortality, decreased hatching frequency and abnormal development of cod larvae (Swedmark and Granmo, 1979). There are, however, also examples of zooplankton ingesting what is generally thought of as harmful substances without showing any symptom of damage or malfunction. One such example is that copepods can ingest oil droplets, letting them pass through the gut and excreting them attached to fecal pellets (Polak et al., 1978; Johansson, 1979). Generally speaking, however, harmful substances seem to affect zooplankton in a similar way to their effects on other types of biota and the level of damage done is related to the type of substance and its concentration.

Genetic or physiological changes that affect the reproduction of the organisms can also be an effect of pollution. It has been shown that very low oxygen concentrations can cause malformed polychaete larvae (Ackefors, 1969) and a change in the amount of food available can alter the reproduction pattern of, e.g., cladocerans.

### 7.3.3 Available methods for the detection of pollution

Summarizing the comments made by a number of scientists in connection with this assessment work, there is almost unanimous agreement that for zooplankton, the effects of pollution are best detected by changes in the qualitative composition of the fauna and to some extent also by biomass changes. The zooplankton can also be used for local pollution surveys by analyzing the chemical content of harmful substances. However, if high levels of a substance are found in a sample of zooplankton, it can be hard to trace the source, especially in areas with good water exchange.

As stated earlier, not much work has been done on zooplankton in relation to pollution, but this is not due to a lack of refined analysis. The pelagic system is so dynamic, so quickly responsive to environmental changes, that isolated or short-term sampling may cause serious errors if generalizations are made. A further difficulty connected with analysis of pollution-caused effects in the pelagic system is the very fact that these small organisms are moving. It is difficult or impossible to have a continuous observation of single specimens or even patches of organisms. It is thus obvious that the studies of zooplankton *versus* pollution are more oriented towards large-scale observations rather than locally restricted effects.

The methodological problems of sampling, sub-sampling, counting and biomass estimation have received increasing

attention in recent years. As a result, a standardized procedure has been developed that in the future will provide comparable data from most zooplankton investigations in the Baltic Sea. This has been accomplished mainly through the co-operative work within the Baltic Marine Biologists (Dybern et al., 1976; BMB Publ. No. 6, 1979). The gear and methods of analysis adopted are well tested and are comparable with those used by other major marine science organizations. There is still one gap in the methods available, however, and that is for sampling scyphomedusae (jellyfish) in a quantitatively correct way. But, apart from this, there is no reason to blame the poor effort in pollution-oriented zooplankton research on a lack of methods.

#### 7.3.4 *Present knowledge of pollution-caused effects*

Today clear evidence of pollution-caused effects on zooplankton has been demonstrated only in restricted areas (river mouths, larger harbours and near population centers). There are examples of changes that have occurred over a long time-span (e.g., an increase in biomass), but the causes for this are thought to be indirect (e.g., increased primary production) rather than direct.

Regarding the composition of the fauna, it is obvious that there has been a reaction to the slight increase in salinity that has taken place during this century (e.g., Mankowski, 1962). Two brackish water copepod species, *Eurytemora* sp. and *Limnocalanus macrurus* are much less abundant today in the Baltic Proper than they were at the beginning of the century. Instead, the euryhaline species *Temora longicornis* and *Pseudocalanus m. elongatus* have increased in number (Hessle and Vallin, 1934; Ackefors, 1969; Hernroth and Ackefors, 1979). In the Gdańsk Bay, it has been found that the chaetognath *Sagitta elegans baltica* has disappeared due to decreasing oxygen concentrations (Różańska, 1978).

Reduced oxygen concentrations in other deeper regions are also responsible for increasing difficulties for pelagic fish eggs (e.g., cod eggs in the Bornholm Deep) to develop normally.

Another effect on the qualitative composition of the planktonic fauna results from eutrophication in coastal areas. In the Helsinki area (Välikangas, 1926; Viljamaa, 1972; Eerola, 1979), in Himmerfjärden (Swedish east coast) (Askö Laboratory, 1979), and in the Gdańsk area (Róžańska, 1978), increased primary production levels have been observed. The zooplankton communities in these areas have responded in a similar way, by a shift in the dominance of species. All three areas show a pronounced increase in rotifers, cladocerans and cyclopoid copepods, and it is known that certain protozoans, rotifers and cladocerans are good indicators of eutrophication. Therefore, the role of microzooplankton is very important in this respect. Generally speaking, most scientists state that a shift in species composition is the best tool for discerning changes in the aquatic environment. In certain cases the indices of community structure, e.g., diversity index, may also prove useful in pollution-related studies (Melvasalo et al., 1975).

Regarding the biomass of zooplankton in the Baltic Sea, it is difficult to compare older and more recent data since the gear and methods have changed through the years. Today we know the accuracy of our gear (Unesco, 1968), but few tests have been made with older equipment. Nevertheless, long series of biomass data from scientists in Poland (Mankowski, 1978; Żmudziński, 1978) and the German Democratic Republic (Arndt and Stein, 1973) show an increase in biomass in the Baltic Proper. This increase has been especially obvious in the past twenty years and is most pronounced in the southern parts of the Baltic Sea. This increase has taken place without any major changes in the relative abundance of species. The cause of this

development is thought to be an increase in primary production over the whole area and a secondary effect should be a greater abundance and fat content of pelagic fish (Strzyzewska, 1978).

Other long-term investigations performed in the past ten years have not, however, shown such an increase (Hernroth and Ackefors, 1979; Niemi, 1980). But this is not to say that there has not been an increased production of phyto- and zooplankton. Fishery biologists have evidence of a higher fat content in sprat (Elwertowski et al., 1974). There has also been an increase in the amount of fish landed over the past twenty years, but it is questionable whether this is a result of eutrophication of the Baltic Sea or merely due to increased efforts and a change in fishing techniques and/or fishing areas (Otterlind, pers. comm.).

There have been few investigations on the concentrations of harmful substances in zooplankton. The general practice has been to go a step further in the food chain, i.e., to fish, when looking for accumulation of toxic substances. Few investigations have actually pointed to any great accumulation of such substances in zooplankton. PCBs, for instance, have been found in the same concentrations as in herring and the DDT levels have been relatively low in those investigations that have been made (Linko et al., 1979; Miettinen and Hattula, 1978). This does not mean that the role of zooplankton in transferring harmful substances is unimportant, it merely indicates that the bioaccumulation of some harmful substances within zooplankton may be on a rather small scale, partly due to their short life span.

### 7.3.5 *Summary*

The reactions of zooplankton to pollution in the Baltic Sea are at present relatively poorly investigated on a

large scale. However, the use of zooplankton studies in monitoring local and regional pollution has proved to be a very useful tool in many cases. There are some coastal areas that have had a change in species composition due to eutrophication. It is also possible that we are witnessing a gradual increase in zooplankton biomass in the Baltic Proper, which may be traced to an increased primary production of phytoplankton. In the Baltic Sea, some studies have dealt with the concentration and accumulation of some harmful substances such as polychlorinated biphenyls, DDT and some heavy metals, but the significance of different amounts of pollutants discharged into the Baltic for the organisms at different trophic levels and in different parts of the Baltic Sea still needs to be clarified.

#### 7.4 **Phytobenthos**

Benthos, the life confined to the bottom substrate or attached to it, includes both the littoral benthos (consisting of plants as well as animals, also called the "phytal zone") and below it the profundal benthos inhabited by animals only. Although the littoral benthos forms an ecosystem containing both plants and animals, a more conventional subdivision is followed here by a separate treatment of animals (zoobenthos) and plants (phytobenthos).

According to the Baltic Marine Biologists, the phytobenthos is defined as the communities of benthic plants, either attached or torn off, and the associated animals (Dybern et al., 1976); for methodological reasons it also includes the *Mytilus* belt on deeper hard bottoms.

The composition of the phytobenthic communities in the Baltic Sea and the Kattegat is greatly influenced by several environmental factors, including pollution.

The most important factors creating regional differences are the decreasing salinity moving northwards in the Baltic Sea and the different geomorphological structures of the coastal areas. The main features are described for the different sub-areas below. Local differences are dependent on the two factors mentioned above as well as on such major abiotic factors as the nutrient conditions in the water and light transmission.

The hard bottom communities are dominated by green, brown and red macroalgal species and by the common blue mussel, *Mytilus edulis*. Reeds, submersed phanerogams, charophytes and microalgae are the most important plants on soft substrates, but they are often mixed with loose-lying macroalgae.

The composition of the communities in the upper zones of the phytobenthos is highly dependent on the season, above all for the hard bottom communities. In addition to the normal seasonal fluctuations, there are often differences between years caused by factors such as mild or severe winters, different degrees of ice cover, changes in the water level, etc., which influence the organisms in different ways and must be taken into consideration when comparing data.

The status of the phytobenthic communities is of much public concern and many people associate pollution with drastic changes along the shores. Even if the negative changes within the phytobenthos do not always have an impact on the whole Baltic ecosystem, they can develop into nuisances such as drifting, decomposing algal mats, algae clogging fishing nets, landlocking of bays by increasing reed beds, etc.

#### 7.4.1 *Feasibility of using phytobenthos for pollution studies*

Quantitative investigations of the soft substrate inhabiting phytobenthic communities started early. Already



during the first part of this century the seagrass communities, above all of *Zostera marina*, were intensely studied in Denmark (Ostenfeld, 1908; Petersen, 1913; Petersen and Jensen, 1911) and in Poland (Bursa et al., 1939).

The study of the hard bottom communities was long limited to qualitative and semi-quantitative descriptions because of methodological difficulties. With the development of diving techniques and equipment operated by divers (e.g., Bursa et al., 1939; Dybern et al., 1976; Gislén, 1930; Kangas, 1972; Lundälv, 1971; Waern, 1952) the quantitative, as well as the qualitative, knowledge has increased immensely. However, due to the complexity and mosaic structure of this biota, much information is still needed before even the normal variations within this sub-system in the Baltic Sea can be fully understood and quantified.

Statistically significant trends or differences in biomasses of the hard bottom communities over longer periods in the Baltic Sea are thus not yet possible to obtain. The many recent quantitative sampling programmes, based on either stratified random sampling or permanent stations or transects (e.g., Fagerholm, 1975, 1978; Hällfors, 1976; Hällfors et al., 1975; Jansson and Kautsky, 1977; Jerling and Lindhe, 1977; Kangas, 1976; Kornfeldt, 1979b; Lappalainen et al., 1977; Lindgren 1978; Luther et al., 1975; Ravanko, 1972b; Rönnerberg, 1975; Skult, 1977; Trei, 1976; Wulff et al., 1977) will, however, offer great possibilities for future assessments, provided this biota is taken into consideration in the different monitoring programmes now starting in the Baltic Sea.

In spite of the lack of quantitative trend information, old data from species and association studies conducted along the Baltic Sea and Kattegat coasts can be used to

detect changes with time as well as with changes in environmental factors. Much information can be obtained by studying the species composition, the disappearance or invasion of indicator species, the shift in dominance due to changes in competitive strength, or the upward transfer of different belts due to deteriorating light conditions. Recorded changes of this type in the different sub-areas are described below. For the assessment of pollution in coastal waters along the Gulf of Finland, Häyrén (1921, 1933, 1937, 1944) developed a saprobic system for brackish water, based on plant associations, ranging from the most polluted polysaprobic state to the unpolluted katharobic state. This system has recently been extended further (Hällfors et al., 1976).

When comparing old descriptions with new ones, some difficulties arise because of the confusion in taxonomic classifications (cf, e.g., Pankow, 1971; Ray, 1974; Waern, 1952; Wallentinus, 1979a). This is especially true for green algae. However, if the data are interpreted with caution, this problem can be overcome in most cases.

Studies of changes in composition and dominance have mostly been restricted to a specific substrate, such as hard bottoms. However, the whole character of an area can change through the deposit of large quantities of sediments, for instance, by drastically increasing discharges or land runoff through rivers, and thus the previous hard substrate becomes covered with soft matter. This has implications for all types of biota, involving also changes in spawning areas for fish, as well as utilization of areas for recreational purposes.

In the assessment of the pollution of the Baltic Sea, the phytobenthic communities are not only of interest for studying the changes in the distribution pattern. Much information can also be obtained by chemical analyses of the dominant species, by measuring productivity, and by

determining uptake and release rates of different substances under different conditions. The stationary life forms of the plants and many of the dominant animals in this biota make them especially suitable to act as integrators of the water conditions over time in a specific area. Various phytobenthic organisms, above all the bladderwrack *Fucus vesiculosus* and the common blue mussel *Mytilus edulis*, have been widely used for studies of uptake rates, which are then used for estimating discharges of nutrients, heavy metals, radioactive isotopes, oil and chlorinated hydrocarbons along the Baltic Sea and Kattegat coasts.

#### 7.4.2 Nutrients

Nutrient uptake by macroalgae has been used to estimate the nutrient load in several areas, especially since macroalgae are stationary and can integrate the load over that specific area.

Long-term influences, reflected by increasing average contents of nutrients in algae with time, have been shown from the Øresund area (von Wachenfeldt, 1975a). There both phosphorus and nitrogen stored in *Fucus* plants reached higher levels in recent samples than in specimens from the beginning of the century. Through decomposition of the plants, these greater storages might enhance the recirculation of nutrients (von Wachenfeldt,

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Regional differences have been reported showing lower average nutrient contents in plants from the southern Baltic Sea (Blekinge, Sweden) than in those from the Øresund area (von Wachenfeldt, 1975a).

Geographical differences in nutrient content of phytobenthos have been recorded for various parts of the Baltic Sea (Feldner, 1976; Norin and Waern, 1973; Wallentinus, 1979a, 1979b). The highest values of phosphorus,

nitrogen and chlorophyll (which is significantly correlated with the nitrogen level) (Wallentinus, 1976a, 1979a, 1979b) occur in algae sampled close to sewage discharge outfalls or river mouths carrying land runoff. The nutrient concentrations in phytobenthos also vary highly with season, with maxima during the winter and early spring, coinciding with the higher nutrient concentrations in the water (Feldner, 1976; Jacobi, 1954; Kornfeldt, 1979a; Wallentinus, 1979b). Extremely high nitrogen to phosphorus ratios have been measured in green algae from an inner archipelago area during late spring, which reflected land runoff from a fertilized agricultural area, while at the same time the algae from the outer archipelago showed comparatively higher availability of phosphorus (Wallentinus, 1979b). Both high ammonium concentrations in the water and extremely high N:P ratios in algae have been shown to reduce the algal productivity, while moderately increased concentrations of nitrogen favour algal growth (Feldner, 1976; Kautsky, 1979; Norin and Waern, 1973; von Wachenfeldt, 1978; Wallentinus, 1976a, 1979b).

Nutrient analyses of rooted aquatic plants might be less useful for studying the direct influence of discharges (e.g., Wallentinus, 1975), since by root uptake, the plants also strongly mirror the conditions in the sediments. On the other hand, they can contribute to the recirculation of already deposited nutrients, either by leakage of nutrients from the living plants (e.g., McRoy et al., 1972) or by decomposition.

Nutrient-induced changes in the phytobenthos are briefly described below for the different sub-areas of the Baltic Sea. Influences on specific macroalgae and phanero-gams and the possibilities to use them as indicator species in the Baltic Sea have recently been described (see, e.g., Hällfors et al., 1976; Lindgren, 1975, 1978; Ray, 1974; Wallentinus, 1979a, 1979b).

Generally, nutrient enrichment causes a shift in dominance towards green and blue-green algal species (primarily of the genera *Enteromorpha*, *Blidingia*, *Ulva*, *Cladophora*, *Phormidium*, *Spirulina*) over *Fucus* and red algal communities (cf. also Bokn, 1979b). There are also increases in drifting algal communities, composed of both green and brown algae, and more intense epiphytic growth on *Fucus* plants. Furthermore, the extension of the algal belts to somewhat deeper areas is reduced due to deteriorating light conditions (cf. Söderström, 1976), thus enhancing the importance of the *Mytilus* belt in areas where the salinity is not too low.

More information is needed, however, before calculations can be made on the influence of a moderate increase in the nutrient level on the overall benthic primary production.

#### 7.4.3 *Effects of harmful substances on phytobenthos*

##### *Heavy metals*

Long-term increases in the concentrations of heavy metals such as lead and cadmium have been recorded in algae from the Øresund (von Wachenfeldt, 1975a). Hägerhäll (1973) also showed that, besides normal seasonal fluctuations in less affected areas, industrial outlets in the Øresund were responsible for concentrations of Cd, Cr, Cu, Ni and Pb more than 100 times their normal levels in macroalgae, but that the maximum concentrations in the algae were found at some distance from the outlet. He considered that this distribution was probably caused by a reduced toxicity or availability of the metals resulting from the effect of organic chelators in domestic sewage. This is in agreement with the finding that soil-extract chelates copper and reduces its toxicity, as shown for instance for the brown alga *Ectocarpus* (Morris and Russell, 1973). This alga has increased in the Øresund, while other species may have disappeared from the area because of their

higher sensitivity to heavy metals or because of synergistic effects (von Wachenfeldt, 1975a).

Results of heavy metal analyses in some macroalgae have been published for various areas of the Baltic Proper (Grimås, 1979; Mattson et al., 1980; Schelin, 1976, 1977). Algae growing in industrialized areas show higher than normal accumulations of particularly Cd, Cu, Ni, Pb and Zn. However, further knowledge is still needed to be able to establish the total ranges of values in algae from truly unaffected areas and to estimate the effects of the heavy metals on the algae as well as the importance of bioaccumulation. Furthermore, since algae from rather unpolluted areas also have a high enrichment of heavy metals compared with the concentrations in the water (Grimås, 1979; Schelin, 1976), high amounts of the metals are kept circulating within the biota.

*Mytilus edulis* is one of the most commonly used invertebrates to study heavy metal pollution. Mussels from areas affected by industrial effluents have been shown to accumulate Cd, Cu, Ni, Pb and Zn (Birklund, 1979; Phillips, 1977). The uptake of heavy metals has been found to be higher in unaffected areas in the Baltic Sea compared with similar areas in the Kattegat and Skagerrak. This has been considered to be due either to the effect of lower salinities or to different concentrations of heavy metals in the phytoplankton in the areas studied (Phillips, 1977).

Even though the reasons for higher concentrations of heavy metals in Baltic mussels are not clarified, they are a matter of concern considering the total high biomasses of the *Mytilus* population in the Baltic.

In the Bothnian Bay (Rönnskär), the snail *Lumnea* has been used as an indicator species, and decreasing concentrations of heavy metals with distance from the

discharge were found (Lithner, 1974).

Laboratory studies have also shown that the effects of heavy metals on different Baltic invertebrates are more harmful at low salinities and high temperatures (Bengtsson, 1977; Theede et al., 1979). These conditions are typical especially of phytobenthic communities in inner archipelago areas.

#### *Radioactive discharges and cooling water effluents*

Increases of radioactive products by more than tenfold have been measured in *Fucus* plants since the start of the nuclear power station at Barsebäck on the Øresund; marked increases of  $^{60}\text{Co}$  were found both there and outside Ringhals in the Kattegat (Holm et al., 1979; Mattson, 1980). The same authors also measured the accumulation of trans-uranium elements in *Fucus* from the Swedish west coast.

In the Baltic Proper, higher accumulations of radioactive isotopes were found in algae and other aquatic plants, mainly phytobenthic species, than in invertebrates or fish outside the nuclear power station at Oskarshamn (Grimås, 1979). It was also noted that deposited products in the sediments were being recirculated into plants and animals and thus were transferred through the food chain.

Different macroalgal species showed large variations in their uptake of several radioactive isotopes in a study along the Polish coast (Bojanowski and Pempkowiak, 1977). *Fucus* could concentrate  $^{90}\text{Sr}$  100 - 195 times and brown and red algae had concentrated  $^{137}\text{Cs}$  28 - 265 times, while the values for green algae were lower. Generally, the sum did not exceed 6% of the natural radioactivity. Analyses of plants from some Swedish coastal areas (Agne-dal, 1965; Grimås, 1974; Schelin, 1976) were considered to be more representative of atmospheric fallout than discharges from nuclear power stations.

Changes in the community structure showing increased growth of green algae, primarily the genus *Enteromorpha* but also *Cladophora* and loose-lying algae, have been noticed in cooling water discharge areas (Andersson and Karås, 1979; Grimås and Neumann, 1979; Ilus and Keskitalo, 1979; Nyqvist, 1979). The common reed *Phragmites* increased in importance, while *Fucus*, some other macroalgae and submersed phanerogams declined, probably associated with both competition from green algae and shading and turbulence (Andersson and Karås, 1979). Cooling water effluents also caused diminishing populations of lymneid snails and gammarids in the affected inner areas, while, e.g., chironomids and the crustacean *Corophium* increased (Grimås and Neumann, 1979; Ilus and Keskitalo, 1979; Stenbäck, 1979a, 1979b). In the Kiel Bight, on the other hand, the fauna was generally little affected by cooling water effluents, but a positive influence from increased turbulence could be noticed on *Mytilus* and *Balanus* (Möller, 1978b).

The effects of higher temperatures on the uptake rates of different toxic substances should not be neglected when discussing the effects of cooling water effluents at both the species and the ecosystem levels.

#### *Oil pollution*

The oil spills occurring in the Baltic Sea during the 1970s have triggered several studies on the effects of the oil on the phytobenthic sub-system. Generally, the littoral and sub-littoral hard-bottom communities seem to have recovered to a great extent after some severe changes during the acute phase. After one or a few years, the impact on the system as such is comparatively small and most plant and animal populations have re-established themselves (Kautsky, 1979; Linden et al., 1979; Notini, 1976a, 1976b, 1978, 1979, 1980; Notini et al., 1980; Pelkonen and Tulkki, 1972; Ravanko, 1972a). Likewise, small, chronic oil spills seem to



have had little influence on the overall structure of these communities (Mattson et al., 1980).

However, several effects have been observed on the different organism groups during the acute phase of a spill and the effects on the organisms are multiplied when oil and detergents are used together. Most Baltic macroalgae react with depressed photosynthesis when covered with oil (Ganning and Billing, 1974; Guterstam, 1979; Notini, 1976b; Schramm, 1972) and dead *Fucus* plants can be found in heavily oil-polluted areas (Pelkonen and Tulkki, 1972). In surviving algae, the fertility has been reported to be little affected (Ravanko, 1972a), and algae can even be found growing on old oil patches after the low molecular weight toxic components have vaporized (Notini et al., 1980; Ravanko, 1972a). Furthermore, sub-lethal effects on *Fucus* plants decrease comparatively quickly when conditions improve, at least if the oil has not been emulsified with detergents (Ganning and Billing, 1974; Kautsky, 1979). To sum up, the macroalgal vegetation seems to be little influenced by oil spills.

One of the most widely used indicators in detecting the level of oil pollution is the common blue mussel. Although some mussels, particularly small ones, may die as a result of an oil spill, most of the more or less sessile mussels survive the acute phase of a spill (Kautsky, 1979; Lindén et al., 1979; Notini, 1978, 1979; Notini et al., 1980; Pelkonen and Tulkki, 1972). The uptake of hydrocarbons by *Mytilus* is, however, both rapid and large, and elevated concentrations of oil can be found persisting even a year after a spill in heavily oil-polluted areas (Boehm et al., 1979; Lindén et al., 1979; Notini, 1980; Notini et al., 1980; Pelkonen and Tulkki, 1972). The levels are high even rather far out in areas with chronic oil-pollution (Birklund, 1979; Mattson et al., 1980; Rudling, 1976).

In the acute phase of an oil spill, the phytobenthic crustacean populations are often drastically affected and many animals die or disappear. Within a year there is a high degree of recovery, especially for the gammarids, due both to immigration from unaffected areas and to breeding of surviving specimens (Kautsky, 1979; Lindén et al., 1979; Notini, 1976b, 1978, 1980; Notini and Hagström, 1974; Pelkonen and Tulkki, 1972).

The high toxicity of fresh oil and of oil plus detergents to Baltic crustaceans, as well as the sub-lethal effects of low level concentrations of oil, have been observed in many laboratory studies (Lindén, 1976a, 1976b; Notini, 1976b; Notini and Hagström, 1974; Pelkonen and Tulkki, 1972; Zbytniewski et al., 1978; Zmudziński, 1975). Old weathered oil and small, chronic discharges of oil, on the other hand, seem to have little effect on the crustaceans (Mattson et al., 1980; Notini et al., 1980).

Even though many components in the phytobenthos have recovered in the investigations reported to date, the long-term effects of really large oil spills covering vast areas in the Baltic Sea are not known. The recruitment of new populations from unaffected areas is then more difficult and the sub-lethal effects on breeding and production might be more important.

#### *Chlorinated hydrocarbons*

Low concentrations of PCBs were found in *Fucus* and phytobenthic invertebrates from non-industrialized areas in the Baltic Proper and a Danish firth, while *Mytilus* from an industrialized area contained much higher levels (BIOKON, 1976; Helminen et al., 1973; Jensen et al., 1969a; Olsson et al., 1973; Rudling, 1976).

Low concentrations of DDT have been measured in *Mytilus* from the Swedish coast (Jensen et al., 1969a). The crab *Careinus* from a polluted Danish firth also had

rather low levels of DDT (BIOKON, 1976). On the other hand, *Mytilus* from the Polish coast was reported to contain somewhat higher DDT concentrations (Zmudziński, 1975).

Estimates of PCBs bound in the total populations of mussels and benthic invertebrates in the Baltic Proper were of the same order of magnitude as for the total fish population of that area (Kihlström and Berglund, 1978). Even higher values for mussels could be calculated if the dry weight values of Olsson et al. (1973) and Kautsky and Wallentinus (in press) are used, reaching 1.6 tonnes of PCBs for the total Baltic Proper.

#### 7.4.4 Sub-areas

##### *The coastal areas of the Kattegat*

Compared with the North Atlantic, the Kattegat area has a reduced but still highly diverse flora and fauna (BIOKON, 1976; van Braun, 1969; Kornfeldt, 1979b; Lindgren, 1965, 1973; Lundgren and Larsson, 1979; Mathiesen and Mathiesen, 1976; Mathiesen et al., 1972; Muus, 1967; Rasmussen, 1973; Rosenberg, 1977; Waern, 1964, 1965). The changing character of the shoreline, from the rocky archipelago south of Gothenburg to the predominantly sandy and open coasts along Halland and eastern Jutland, however, influence the composition of the phytobenthos and in many Danish firths and bays extensive communities of phanerogams are dominant.

Several coastal areas near densely populated or industrial centers, such as around Gothenburg and in the Danish firths, have experienced changes in species composition, mainly due to nutrient enrichment. Many macroalgae, including fucoids and charophytes, have disappeared (Lindgren, 1965, 1973; Mathiesen and Mathiesen, 1976; Mathiesen et al., 1972; Mathiesen, 1979) and in many cases extensive growth of attached or loose-

lying green algae has become pronounced. However, the more open and less land-influenced area of Laholmsbukten has also recently been subjected to a nuisance growth of the green alga *Cladophora glomerata* (Fleisher et al., 1978; Nyqvist and Persson, 1976; von Wachenfeldt, 1978), which is most likely caused by nutrients and reduced water circulation. The amount of algae thrown ashore is roughly estimated to correspond to a potential growth area of 2.5 - 3 km<sup>2</sup>, but less than half of that area was found along the bay using remote sensing techniques, and algae were considered to be transported there from the north before they died (Nyqvist and Persson, 1976). This nuisance growth shows that changes in the phytobenthos can be both rapid and large.

#### *The coastal areas of the Øresund*

The algal vegetation along the coasts of the Øresund was studied already before the start of this century and this made it possible to draw conclusions about long-term changes in the vegetation (von Wachenfeldt, 1975a). The human impact has caused the vegetation to pass through several phases. Examples can be seen in the enhanced growth of the green alga *Ulva* in the 1910s and 1920s, but during the 1960s this alga almost disappeared because of the increased levels of heavy metals (see Hägerhäll, 1973). Other green algae (e.g., *Enteromorpha*) and brown algae (*Ectocarpus* and *Pilayella*) have recently increased in several areas up to the nuisance level and are drifting ashore in fermenting mats. In some areas, *Fucus* plants have become covered by thick layers of blue-green and brown algae which later decay (Kristiansen, 1978).

This area probably provides one of the best examples of how man-induced changes can be monitored in the phytobenthos, both by a shift in the dominance and composition of species as well as by chemical analyses for nutrient concentrations. Comparatively little is

known, however, about the faunal part of the phyto-benthos (Dahl, 1948; Hagerman, 1966) and how animals are affected by pollution.

*The coastal areas of the Western Baltic Sea*

The composition of the phytobenthos in these areas is mainly affected by large fluctuations in salinity and by the scarcity of rocks in the predominantly sandy areas. Firths and bays often show pollution-induced changes.

In the Kiel Bight area, the influence of geomorphological structures on the composition of the algal vegetation has been described in many papers by Schwenke (e.g., 1964, 1969, 1974) and both the flora and the fauna are rather well-known (e.g., Anger, 1975a, 1975b, 1977; Gründel, 1976; Gulliksen, 1975; Hoffman, 1952; Homuth, 1975; Lüthje, 1978). Only scattered information seems to be available from the rest of the German coast and the Danish coast (Hoffman, 1952; Muus, 1967; Olsen, 1945; Pankow et al., 1971, 1967).

Studies of pollution-induced changes have been conducted mainly close to the bay Kieler Förde, where the organisms are influenced by discharges of both nutrients and toxic substances (Anger, 1975a, 1975b; Feldner, 1976; Theede et al., in press).

An increase in production of up to 65% was measured for *Fucus* plants in field experiments in sheltered areas close to sewage outlets at Kieler Förde compared with more distant areas (Feldner, 1976), but this effect was superimposed by negative effects on production at more exposed areas. Thus, hydrographic conditions modify the effects of pollution in this area. Laboratory experiments showed a growth increase of up to 100% for *Enteromorpha* in water from the same localities. In eel grass communities in the same area (Anger, 1975a, 1975b), the mean macrofauna biomass increased

about sixfold and the abundance about sevenfold from the outer to the innermost polluted area, while the number of species decreased slightly. The mussel beds had an abundance about three times higher and a slightly higher biomass, but a decreased number of species.

*The southern and eastern coasts of the Baltic Proper*

The salinity is stable in these areas and the main decisive factor is the open and sandy coasts, which favour the development of communities dominated by phanerogams and loose-lying macroalgae (Bursa, 1939, 1947; Kornas et al., 1960; Künzenbach, 1955/56; Overbeck, 1965; Trei, 1976, 1978; Wojtusiak et al., 1939, 1950, 1952). The inner bays are bordered with large reed beds (Krisch, 1978; Lindner, 1978) and have soft-bottom communities dominated by charophytes, loose-lying macroalgae and phanerogams (Hoppe and Pankow, 1968).

Filamentous green and brown algae have been found to be typical of the uppermost level in a polluted harbour area in Poland (Biernacka, 1968).

In studies of the fauna in the polluted waters around Tallinn, Järvekülg (1970) pointed out that one of the major factors affecting the low numbers of animals preferring hard bottoms was the lack of a suitable substrate in the area, and that species such as *Mytilus*, *Balanus*, *Electra* and many others could occur even in the moderately polluted area.

*The Swedish coast of the Baltic Proper*

Wide archipelago areas with many rocky islands are typical for long parts of this coastline. This provides excellent conditions for the development of hard-bottom communities. Thus, this area together with the Finnish Archipelago Sea, the Åland Sea and the western part of the Gulf of Finland are quantitatively the most important ones for the *Fucus* community. The in-

ner archipelagos have extensive reed beds.

During the past decades many investigations have been conducted (e.g., Anger, 1975a, 1975b; BMB, 1978; Berg, 1973; Haage, 1975, 1976; Wallentinus, 1976a, 1976b, 1979a, 1979b; Jansson and Kautsky, 1977; Jerling and Lindhe, 1977; Kautsky, 1974; Levring, 1940; Lundegårdh-Ericson, 1972; Lundgren and Larsson, 1979; Norin and Waern, 1973), but the general lack of old data does not permit a determination of changes in a long-term perspective. Nutrient-enriched areas close to sewage discharges and river mouths show the characteristic dominance of green algae, although the biomasses often are low (Norin and Waern, 1973; Wallentinus, 1976a, 1976b, 1979a, 1979b). *Fucus* and other algae have disappeared with increasing pollution (Björklund, 1979; Pekkari, 1973) or near cooling water discharges. The decrease in the number of species of brown and red algae, typical of many inner archipelago areas less influenced by nutrient enrichment, can often be attributed to seasonal fluctuations of salinity, but also to reduced light conditions (Björklund, 1979; Pekkari, 1973; Wallentinus, 1976a, 1976b, 1979a, 1979b).

*The coasts of the Gulf of Finland and the Archipelago Sea*

These areas also have the very rocky, jagged coastlines which favour the development of hard-bottom communities, but extensive reed beds are found in the inner archipelago areas. In the inner part of the Gulf of Finland, the low salinity, however, reduces the possibility for many marine organisms to survive. Even in the outer western part, salinity changes can induce shifts in abundances, such as the mass occurrence of *Mytilus* in some areas (Mathiesen and Mathiesen, 1976).

The Finnish coast is probably the best-studied area regarding qualitative and quantitative determinations of

the phytobenthic flora and fauna (e.g., Hällfors et al., 1975; Lappalainen et al., 1977; Lindgren, 1978; Luther, 1950; Luther et al., 1975; Ravanko, 1968, 1972b; Segerstråle, 1928, 1944; Skult, 1977; Tulkki, 1960).

The studies of the saprobic systems on the shores around Helsinki were started by Häyrén (e.g., 1921, 1933, 1944, 1947) and the shores were reinvestigated in the 1960s and 1970s (Hällfors et al., 1976; Lindgren, 1978; Ray, 1974). In the 1960s it was found that the size of the polluted areas near Helsinki had generally increased since the 1930s, but that the most polluted areas were not expanding to the same extent because of better sewage treatment (Ray, 1974). A quantitative saprobic index system based on plants was later developed (Hällfors et al., 1976; Lindgren, 1978) and the state of pollution for about 350 km of coastline was described. The same tendencies as in the 1960s could be found, namely the areas of heavy pollution had decreased, while the less polluted areas had increased in size and spread seawards. In the archipelago outside Helsinki, Lindgren (1975, 1978) noted both quantitative and qualitative effects on the algal vegetation on stations rather far from the city. The phytobenthic macrofaunal composition also showed a gradual change along the gradient (Skult, 1977).

Around Tvärminne, industrialized areas are locally affected by pollution (Kautsky, 1979) and an increased growth of the nutrient-favoured green alga *Enteromorpha* was found even after a reduction in the amount of nutrients discharged. Generally, this archipelago has been considered to be little influenced by pollution outside the bay of Pojoviken (Hällfors et al., 1975; Lappalainen et al., 1977; Luther et al., 1975). However, during the past decade, the growth of epiphytic algae on *Fucus vesiculosus* has increased at an average from about 5 to 20%, measured as dry weight (Kangas



and Autio, 1980). The epiphytes both reduce the light for the *Fucus* and enlarge the mechanical stress caused by water movements. This increase in epiphytes is thought to be responsible for the substantial decline in *Fucus* biomass observed in the archipelagos in southern Finland. Increased deposits of sediments and algal cover on the rocks might also contribute to the decline.

The inner part of the Turku archipelago has shown decreases in the extension of the *Fucus* belts since the 1950s, as well as a disappearance of other algal species, while the growth of *Enteromorpha* has increased (Peussa and Ravanko, 1975). Animals typical of the phytobenthic communities, such as *Balanus*, *Mytilus* and *Electra*, are almost totally lacking in the inner area close to Turku (Tulkki, 1964), mainly because of the heavy deposits of sediments on the bottom.

#### *The Coasts of the Åland Sea and the Bothnian Sea*

The phytobenthic communities in the Åland archipelago are very similar to those in the Baltic Proper (Fagerholm, 1975, 1978; Mathiesen, 1974; Rönnerberg, 1975; Waern, 1952, 1965), while in the Bothnian Sea the somewhat decreased salinity reduces the quantitative importance of many marine species, above all *Fucus* and *Mytilus*. Apart from the thorough investigation by Waern (1952) on the macroalgae, very little is known about the phytobenthos in the Bothnian Sea (Waern, 1952, 1965; Ericson, 1977).

In the southern part of the Bothnian Sea, nutrient enrichment has been found to favour the growth of several algae, including *Fucus vesiculosus*, but the typical dominance of green algae could also be found (Norin and Waern, 1973; Pekkari, 1973). Man-induced effects on the composition of the phytobenthic communities have also been recorded in locally restricted areas (Fagerholm, 1975, 1978; Rönnerberg, 1975).

### *The Coasts of the Bothnian Bay*

This area is characterized by low salinity and by comparatively low levels of nutrients and light transmission. Much of the shoreline, including in the archipelagos, is rather sandy and shallow or rich in boulders. The low salinity precludes the development of such quantitatively important phytobenthic communities as the *Fucus* and *Mytilus* belts, and the fauna and flora consist to a large extent of fresh water species. The hard-bottom communities are rather sparsely developed, while the soft-bottom phytobenthos is more diverse (Hällfors, 1976; Kangas, 1976; Pekkari, 1965; Valtonen, 1977; Wulff et al., 1977). The composition of and production in the phytobenthos are, however, totally unknown for large areas.

There are almost no studies on the effects of pollution on the phytobenthos. Pekkari (1973) noted a positive influence of domestic sewage on the quality and quantity of the bottom vegetation, which even permitted the growth of otherwise absent *Fucus vesiculosus*. A local influence of dredging on the vegetation in the Luleå archipelago has been described (Wulff et al., 1977), and the use of snails for indicating heavy metals was mentioned above (Lithner, 1974). Much more effort has to be made before anything can be said about pollution effects on these very particular phytobenthic communities.

#### 7.4.5 *Conclusions*

The stationary mode of life of the phytobenthic organisms makes them especially suitable for integrating pollution effects over space and time.

The phytobenthos provides many organisms which, by their high uptake and accumulation of both nutrients and harmful substances, can indicate pollution.

Qualitative and quantitative changes in dominance, composition and extension of the belts can be useful in mo-

monitoring pollution, but additional background knowledge is needed.

Some organisms, such as the brown alga *Fucus vesiculosus* and the blue mussel *Mytilus edulis*, can, because of their high total biomasses, bind considerable amounts of pollutants.

Consideration has to be given to the interactions within the whole Baltic ecosystem when studying the pollution effects on sub-systems such as the phytobenthos.

## 7.5 Zoobenthos

Zoobenthos, as defined here, includes the animals living on the bottom of the Baltic Sea. It encompasses a variety of animal types, such as oligochaetous and polychaetous worms, mussels, and crustaceans, which inhabit the surface of the bottom and some few centimetres of the uppermost layer of sediment. The species are of marine, fresh water, or brackish water origin.

The main natural factors affecting the composition of the zoobenthos are salinity, oxygen content, temperature, character of the bottom substrate, turbulence, and available food. The species composition, abundance, biomass, distribution, and diversity of the zoobenthos reflect the average situation of the overlying water mass.

The macrobenthic animals are rather long living and stationary and they are, therefore, suitable indicators of general environmental conditions. The diversity and biomass of the Baltic Sea macrozoobenthos are generally the largest in the south and the smallest in the north and east. The consequences of eutrophication on the zoobenthos are known; there are several

cases where altered relationships between species and changes in distribution, density and biomass of bottom fauna have been recorded (e.g., Anger, 1975a, 1975b; Leppäkoski, 1975a).

The zoobenthos can be divided according to the size of the animals, using the sieve mesh size needed to retain them. In the Baltic Sea area, macrofauna is generally defined (Dybern et al., 1976) as the animals retained on a 1 mm mesh sieve, whereas meiofauna passes the 1 mm sieve but is retained by a 40  $\mu$ m sieve, thus comprising virtually all of the microscopic metazooans.

Macrofauna samples are normally taken with the van Veen grab, sieved through 1.0 mm mesh, sometimes complemented with a 0.5 mm mesh, and preserved in formalin. Intercalibrations of the methods (Ankar, 1976; Ankar et al., 1978, 1980; Andersin et al., 1980; and the Interim Helsinki Commission Intercalibration Workshop, Stralsund, August 1979) have been very useful in disclosing most methodological differences. However, some unsolved problems still remain.

### 7.5.1 Open sea

At present, the major factor regulating macrozoobenthos below the permanent halocline (50 - 80 m) is the oxygen content, which has become critical for the macrofauna in the deepest parts of the southern and central Baltic Sea. In the Gulf of Bothnia, the oxygen content has not been significantly reduced. The studies published earlier this century on the macrozoobenthos of the Baltic Sea indicate, however, that no part of the Baltic Sea was entirely devoid of macrofauna at that time.

In the Arkona Basin, oxygen conditions have normally been satisfactory and macrozoobenthos is very diverse and abundant. Earlier this century, the macrozoobenthos communities in the southern Baltic Sea areas were dominated by the mussels. The highest values of the benthic macrofauna have been recorded in the Kiel Bight (over 600 g/m<sup>2</sup>, wet weight (Arntz, 1971)). Andersin et al. (1978a) reported an average wet weight biomass of about 200 g/m<sup>2</sup>, an abundance of about 2 000 ind./m<sup>2</sup>, and a predominance of polychaetes. More than 40 species were found there.

Drastic changes in the salinity and oxygen content are typical of the deepest parts of the Bornholm Basin and the Gulf of Gdańsk. The periods of azoic state alter with the recolonizations (Tulkki, 1965; Leppäkoski, 1969, 1971, 1975a, 1975b; Schulz, 1973; Zmudziński, 1977; Andersin et al., 1978a). First reports of the deterioration of the macrozoobenthos were given by Demel and Mankowski (1951), when the deepest parts of the Bornholm Basin were found devoid of macrofauna. The great change of macrozoobenthos in the southern Baltic Sea took place in the middle of the 1950s after the inflow of saline water in 1951 and a subsequent stagnation period. Data from 1954 showed bottoms devoid of macrofauna in the Gotland Deep and in the area between Gotland and Öland (Sjöblom, 1955). In the northern parts of the Central Basin, macrofauna was still found at that

time. A general decrease in the oxygen content and the consequent deterioration of the macrozoobenthos was recorded in the deepest parts of the central Gulf of Finland in the late 1960s and at the beginning of the 1970s (Andersin et al., 1978a).

In the early years of the 1970s, vast areas below the halocline were depopulated. The bottom "deserts" were largest in 1975, covering about 100 000 km<sup>2</sup> (Zmudziński, 1977). However, Andersin et al. (1979) found that in the northern deep parts, a recolonization of bottom fauna occurred. Similar observations were made in 1978 and 1979 in the Gdańsk Deep (Inst. of Marine Res., Helsinki, unpubl. data) and in the Gotland Deep, where monotonous macrofauna had recolonized some areas. The more diverse bottom fauna found earlier in those areas had not developed.

The macrozoobenthos of the two parts of the Gulf of Bothnia differ very much from each other. In the Bothnian Sea, the dominance of a few crustacean species is typical and the total number of species is low (1 - 6 species per haul, Elmgren, Rosenberg et al., in press). The macrozoobenthos biomass has been reported to be about 10 - 60 g/m<sup>2</sup> (wet weight) and the abundance around 3 000 - 5 000 ind./m<sup>2</sup>, while in the Bothnian Bay the biomass has been as low as about 1 g/m<sup>2</sup> and the abundance from around 200 to 500 ind./m<sup>2</sup> (Andersin et al., 1977; Elmgren, Rosenberg et al., in press).

In the shallow parts of the open Baltic Sea, the biomass and abundance of the macrofauna show greater stability (Elmgren and Cederwall, 1979). However, oscillations have been recorded, for instance, in the Gulf of Finland (Segerstråle, 1969) and in the Bothnian Sea, where Andersin et al. (1978c) found a cycle of 6 - 7 years in the abundance of the amphipod *Pontoporeia affinis*, the dominant macrofauna species. Trends showing increases with time of the macrozoobenthos abundance

and biomass have been found in several areas of the Baltic Sea. Arntz and Brunswig (1976) have reported elevated quantities of bottom fauna in the Kiel Bay. Near Gotland and Öland the biomass of macrofauna increased about four times and the abundance about seven times, but the increase in abundance may be greatly affected by methodological differences since the 1920s (Cederwall and Elmgren, in press). In the Gulf of Bothnia, elevated figures of the abundance of macrofauna were also found (Elmgren, Rosenberg et al., in press). The increase was statistically highly significant. In the Bothnian Sea, Andersin et al. (1978b) found an increase in the abundance of the predominating species. This increase in the quantity of the macrozoobenthos inhabiting open shallow areas can only be explained by postulating a considerable increase in the phytoplankton primary production (Elmgren and Cederwall, 1979; Cederwall and Elmgren, in press).

#### 7.5.2 *Coastal waters*

The faunal response to organic pollution in coastal waters is generally the following: the macrofauna is poorly developed or even absent close to the waste water outfall, followed by a maximum of high abundance and biomass of a few species farther away from the outfall and a sudden decrease of these values still farther away (see Figure 74).

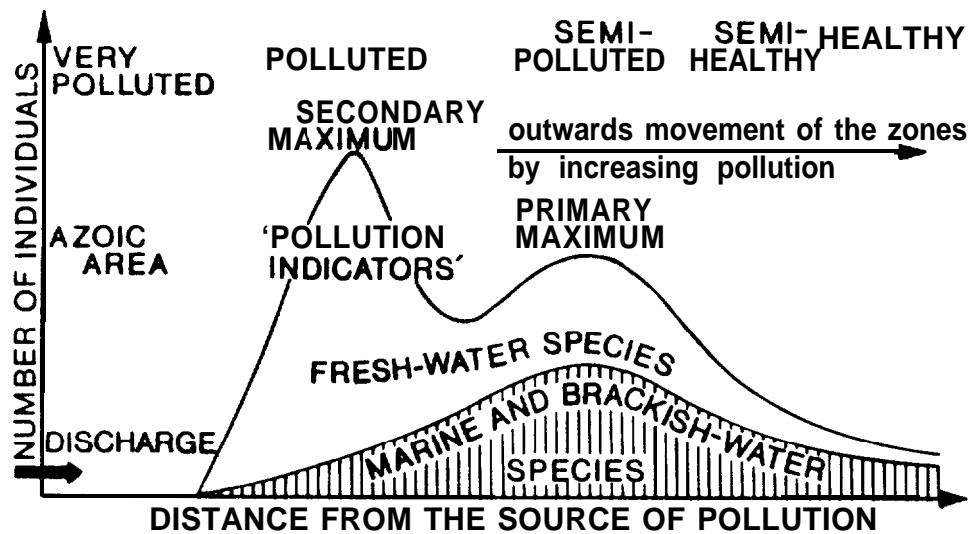


Figure 74. The general response of benthic fauna to organic pollution in coastal waters (Leppäkoski, 1979).

Bottom animals can be grouped according to their capability to tolerate or even benefit from a polluted environment (Leppäkoski, 1975a; Järvekülg, 1976). On the basis of the occurrence, abundance, and biomass of such indicator species, the degree of pollution can be evaluated. In most studies, the organically polluted areas have been divided into 3 - 5 zones depending on local conditions.

In order to illustrate the state of macrozoobenthos in polluted Baltic Sea coastal waters, examples from some localities can be mentioned.

A special bottom community dominated by polychaetes was found to inhabit polluted coastal localities on both sides of the Øresund. Four zones were identified. Signs of pollution were observed at a distance of a



few kilometres from the outlets (Henriksson, 1968, 1969).

In the Kiel Bight, three groups of indicator species were defined (Anger, 1975a, 1975b):

1. *Capitella* zone, 50 - 100 m from the outfall
2. *Pygospio* zone, 200 - 300 m from the outfall
3. *Bathyporeia* zone, over 700 m from the outfall.

The polychaetes *Capitella* and *Pygospio* indicated pollution when they occurred in masses, whereas *Bathyporeia* is an amphipod living only on unpolluted bottoms.

Off Tallinn, a succession of five zones of pollution has been described by Järvekülg (1979). He summarized the development of eutrophication of the Estonian coast as follows:

Area	Years	Increase of biomass during study period		Increase factor
Haapsalu Bay	1962-1975	from 120	to 140 g/m <sup>2</sup>	1.2
Pärnu Bay	1960-1976	53	73	1.4
Tallinn Bay	1963-1975	120	250	2.1
Matsalu Bay	1962-1975	10	62	6.0

A doubling of macrobenthic biomass was also observed as a result of increased loading off the city of Turku in the Archipelago Sea (Juuti and Leppäkoski, 1976). There a partial improvement in benthic communities during the long-term study was observed.

In the sea area off Helsinki, the pollution as assessed by macrozoobenthos studies showed a clear development since the beginning of the 1960s. The successive polluted zones moved some five kilometres seawards in about ten years (Laakso, 1965; Varmo and Skog, in press).

A great number of polluted coastal areas have been studied in Sweden during the past few years (Landner et al., 1977). In most areas, a restricted heavily polluted zone devoid of macrofauna occurred, extending from less than one square kilometre to a few square kilometres. Outside this zone, a transition zone normally was indicated by a few tolerant species. The third zone, characterized by the mass occurrence of opportunistic species, was followed by the healthy area.

Effluents from industries often have a toxic and inhibitory effect on zoobenthos. In the recipient areas of effluents from many metal industries, an azoic zone is a common phenomenon, as shown in the Bothnian Bay (Lithner and Samberg, 1976) and the Gulf of Finland (Luotamo and Luotamo, 1977). For example, outside the city of Pori an azoic area of 8 km<sup>2</sup> occurs, caused by discharges from a local titanium dioxide factory (Häkkiälä and Isotalo, 1978).

Chronic oil pollution near oil refineries and oil harbours causes clear changes in littoral and benthic fauna, e.g., a decreased number of species and density of specimens, total disappearance of macrozoobenthos and changes in faunal composition (cf. Leppäkoski and Lindström, 1978). There it was also shown that zoobenthos partially recovered after the construction of effective purification plants.

Monitoring studies after an accidental oil spill off the Swedish coast showed severe immediate local damage as well as drastic effects of a long-term nature in the benthic ecosystem (Lindén et al., 1979). After an accident in the winter of 1979, oil drifted into the southwestern archipelago of Finland. Elevated concentrations of oil were observed still a half-year later in blue mussels in this area (Pfister, 1980).

### 7.5.3 *Summary*

Macrozoobenthos is a widely used parameter when monitoring the long-term fluctuations in the state of the Baltic Sea. In the open sea regions, deterioration of the macrozoobenthos in vast areas below the halocline has been found since the 1950s. The largest area of dead bottom occurred in the middle 1970s. From the year 1977, signs of recovery of the zoobenthos have been observed. The immediate reason for these alterations is the fluctuation of oxygen concentrations in the deep water, which may be at least partly due to eutrophication. Many reports indicate elevated levels of biomass in the shallow open sea areas. These observations, together with the hydrographic and primary production data, support the opinion that eutrophication is a widespread phenomenon, which has led to higher macrobenthic biomasses above the halocline, but also to the virtual disappearance of macrofauna from the deeper parts of the Baltic Sea.

A decrease in macrozoobenthos due to heavy organic and inorganic pollution has been found in many coastal areas around the Baltic Sea. Biostimulation by organic pollution has also been widely documented. It is, however, difficult to estimate the net effect of pollution, namely, whether the biostimulation in some areas compensates for the adverse effects in the very polluted areas.

Heavy metals, oil, chlorinated hydrocarbons and cooling water effluents in the aquatic environment also have certain effects on the benthic fauna; this is discussed in Chapter 6.

## 7.6 Vertebrates

Whether and to what degree pollution has affected the vertebrate biota in the Baltic Sea is a fairly difficult question to answer. We need not only knowledge of the occurrence of the pollutants in the environment and in the various biota, but also how the vertebrate populations are functioning in an unpolluted area. This information on fundamental ecological facts is frequently very sparse. The necessity of intensified research in the field and not the least in the laboratory must be stressed.

Four main types of pollution may be distinguished: (a) "ordinary" pollution by municipal and industrial sewage and waste at the coasts, (b) heat pollution by warm cooling water from power plants, (c) oil pollution at the coasts as well as at sea, and (d) the occurrence of harmful substances, often widespread, partly air-borne and accumulating in the biota.

### 7.6.1 *Effects on fish*

#### *Pollution by sewage and waste*

Pollution by municipal and industrial sewage and waste is mainly noted close to the coasts and is most pronounced where and when the water exchange is restricted. The environment is influenced by eutrophication, sedimentation and by substances leading to avoidance reactions of the fish. Other chemicals may be harmful to fish although not immediately affecting their behaviour.

The impact of these types of pollution is most easily recognized on the stocks of fresh water fish which live in coastal and estuarine waters. Marine fish, particularly pelagic species like herring and other migrating fish, are less affected by coastal sewage and waste. Changes in stock size and migrations resulting from na-

tural conditions and variations in fishing activity may sometimes conceal pollution effects.

It may also be difficult to separate the influences of eutrophying substances from those of more or less harmful substances on fish stocks. The former frequently have a positive effect on fresh water fish. The influence of obstacles in the water courses (power plants, etc.) may be difficult to separate from those of pollution, e.g., in the case of the eel stock.

Wastes from wood-processing industries (factories for pulp, paper, etc.) are very frequent and important sources of pollution, particularly at the Finnish and northern Swedish coasts of the Baltic Sea. Locally, these industries and other chemical industries have negatively affected the fish fauna. The sea bottoms outside the factories are often covered by fibre masses, barking refuse, lime mud, etc., or affected by chemicals leading to a reduction in the amount of food organisms for the fish, either directly or indirectly by creating an oxygen deficit, and result in immediate avoidance reactions by the fish.

Spawning areas of the herring and other fish have been destroyed in the same way at a great many sites along the coasts of the Gulfs of Bothnia and Finland. The local occurrence and abundance of the fish species have changed in various respects. However, it is at present not really possible to identify any definite damage to the total Baltic herring stock.

Stock assessments in recent years (Anon., 1979a) indicate that the Gulf of Bothnia including the Åland Sea still has a rich herring stock giving an increasing yield. Although the cod stock here is relatively small compared with that of the Baltic Proper, it is at present (1980) exceptionally rich for these latitudes.

Indications of a more general eutrophication of a larger water area have been reported from the Mecklenburger Bight in the southwestern Baltic Sea (Berner and Rohde, 1973; Berner et al., 1973). A reduction in the oxygen content in the high salinity bottom water flowing in from the Belt Sea led during the summer-autumn seasons in the latter part of the 1960s to an alteration in the fisheries for cod and autumn-spawning herring. In the summer-autumn period these fish regularly moved over to the eastern water areas having better oxygen conditions.

In the northern and central parts of the Øresund, the oxygen level in the bottom water was also reduced during the 1960s, simultaneously with a decrease in the yield of the bottom-living fish species (Bagge, 1971). It is not confirmed, however, that this was purely an effect of pollution. Variations in the water exchange (e.g., as to season) might have been involved - a possibility also to be considered in the case of the Mecklenburger Bight. The reduction in the silver eel catches in the Øresund was, however, interpreted as a consequence of pollution in the Baltic water area (Bagge, 1971).

In the archipelago outside Helsinki on the northern coast of the Gulf of Finland, the occurrence of the herring has been modified in connection with increasing levels of pollution from Helsinki and its surroundings.

Since about 1950, the abundance of fish has decreased, particularly to the west of the city (the coastal current is directed westwards). Furthermore, the inner boundary for the regular occurrence of herring and sprat has been displaced against the open sea, as a consequence of eutrophication by pollution. On the other hand, the catch per herring trap still in use has increased during the period mentioned (Sjöblom et al., 1979; Lehtonen and Hildén, in press).

According to a Finnish report (Lehtonen and Hildén, in press) on the effects of pollution near the coast of the Gulf of Finland, the eutrophication there has been followed by a decline in the stocks of burbot (*Lota lota*), whitefish (*Coregonus* sp.), ide (*Leuciscus idus*) and pike (*Esox lucius*), while most Cyprinids and ruff (*Aeeringa cernua*) have increased. Like the herring, flounder (*Platichthys flesus*), sculpins (*Cottidae*) and eelpout (*Zoarees viviparus*) avoid the most polluted areas.

Probably the development is similar along the Swedish coasts and at the estuaries of the large rivers in the eastern and southern Baltic Sea, although no studies seem to be reported. An increase noted for the pike-perch (*Lucioperca lucioperca*) in the inner parts of the Stockholm archipelago and in Bråviken during the past decades is interpreted to be a result of better feeding conditions due to eutrophication. If excessive, however, the latter can be detrimental, as observed in the Helsinki area. A slight eutrophication here favored the pike-perch and bream (*Abramis brama*) stocks (Lehtonen and Hildén, in press).

In polluted coastal waters, a spoiled flavour of the fish has been noted, for instance, in the Finnish archipelagos (Lehtonen and Hildén, in press) and occasionally in the innermost part of the Stockholm archipelago. Gears, such as take-nets for silver eel, have sometimes been reported to be covered with some sort of vegetable slime and drifting small algae negatively affecting the yield.

#### *Heat pollution*

Outside energy generating power plants, heat pollution by cooling water will occur locally. Studies at a nuclear power plant have shown an influence on the fish populations. The temperature increase has favoured the growth

and survival of fry of perch (*Perca fluviatilis*) and roach (*Rutilus rutilus*), and an increased number of adult specimens of silver bream (*Blicca bjoerkna*), rudd, and pike has been shown. However, the number has decreased for perch, ruff, ide and sea scorpion (*Taurulus bubalis*) (Neuman, 1979a). During the winter and early spring, herring are attracted to the heated water and the spawning there is earlier than in the surrounding areas (Neuman, 1979b). These changes seem to be at least partly due to an alteration in food availability for the fish fauna (Karås, 1979).

Outside the power plant, a higher frequency of eye parasites - digena trematodes - was found in perch and roach compared to in fish from surrounding areas with natural temperatures (Stenbäck, 1979). A possible explanation is that the high temperatures cause a longer vegetation period and a longer period for the cercarie production of the intermediate host, a snail.

The increased temperatures have also been found to result in higher levels of DDT and PCB residues in fish living outside power plants (Edgren et al., in preparation).

### *Oil pollution*

The impact of the numerous oil spills and pollution from oil industries upon the fish population within the Baltic Sea environment has been studied on a restricted scale only. The main opinion, based partly on laboratory investigations, is that oil spills will cause avoidance reactions, the development of disturbances in early larval stages of the fish, and sub-lethal effects.

In 1977, an accident south of Stockholm resulted in the spilling of about 1 000 tonnes of fuel oil in an archipelago area. The local fish fauna was studied as to the following parameters: avoidance reaction among pelagic fish, spawning success of the herring, and uptake of oil



in fish tissues (Nellbring et al., 1979; Lindén et al., 1979).

No avoidance reaction among herring could be detected. However, significantly lower hatching success as well as a lower frequency of spawning sites was found in the polluted area. No oil contamination of pelagic herring samples was found, but the benthic flounder feeding on *Maeoma baltica* showed a high concentration of oil. It is important to continue this kind of investigation in the future.

Inshore highly productive areas and benthic communities are the most sensitive to oil spills and continuous oil discharges (Linden et al., 1979). These systems are very important for the production of fish food. A long-term continuous discharge may have greater direct effects on the fish and indirectly through the action of oil on fish food.

#### *Harmful substances*

At present, good field data on the effects of harmful substances on Baltic fish do not exist, although there are several laboratory results indicating the possible effects of metals (Bengtsson, 1974; Bengtsson et al., 1975) and of DDT and PCBs (Johansson et al., 1970; Haux and Larsson, 1979). Toxaphene, recently found in Baltic biota, is known to be extremely toxic to fish. It is very important to conduct further research on the effects of these and other harmful substances on fish.

Skeletal deformations in fish may possibly be a non-specific response to environmental pollution. Measurements on frequencies of deformities of this type have been suggested as one possible way of monitoring marine pollution (Bengtsson, 1979). Two other techniques proposed as biological monitoring methods are worth mentioning. One is studies of the balance of blood plas-

ma electrolytes (Haux and Larsson, 1979) and the other is a test of neuromotor response to environmental pollution (Lindhahl and Schwanbom, 1971; Olofsson, 1977).

Metals have been shown to induce certain infectious diseases caused by bacteria or viruses. The multifactorial complexes caused by *Vibrio* species (skin diseases) and the viral condition lymphocystis (also a skin disease) have been studied in particular (Jensen et al., 1978; Larsen and Jensen, 1978; Möller, 1978a; Pippy and Hare, 1979).

Whether or not metals in the natural environment will induce disease is a question of the ability of fish to avoid metals in certain concentrations, the reaction of bacteria and viruses to changing environments, and the nutritional condition of the fish (Möller, 1978a). Copper concentrations of about 30 - 60 ppb have been shown to induce "Vibriosis". The effect increases with decreasing salinity (Olafson et al., 1975). Avoidance reactions to copper have been shown to occur at concentrations about ten times lower than the incipient lethal levels (Katz, 1975).

### 7.6.2 Effects on birds

#### *Oil pollution*

Smaller oil spills occur frequently and aquatic birds are very sensitive to this type of pollution. There are, however, apparently very few data published concerning the impact on the Baltic bird populations, although a lot of data have been reported on the number of birds killed in various oil accidents.

Along the Polish coast, the number of aquatic birds killed by oil spills has been counted annually from 1970 to 1975 (Górski et al., 1976; Górski et al., 1977). For the period 1970-1974, a total of 3 900 birds were found dead, most of them during the winter. For the second period, 1974-1975, a total of 670 birds were found dead, most of them during March and April. The main species were long-tailed duck (*Clangula hyemalis*), velvet scoter (*Melanitta fusca*) and common scoter (*Melanitta nigra*).

A summary of the environmental effects of oil spills in Swedish waters during the past decade has been published recently (Thorell et al., 1979). Six different accidents were studied, none of them occurring during the vegetation period. The accident having the most serious effects upon sea birds occurred outside Oland in February 1976 (Wennergren et al., 1976). At least 33 000 long-tailed ducks were killed, but probably up to 60 000 may have died. Other birds, such as black guillemot (*Cephus grylle*) and guillemot (*Uria aalge*) were also found dead. The total amount of oil polluting the water at this time was very small - estimated at only about 10 tonnes.

In comparison, about 2 000 tonnes of oil polluted the southern coast of Sweden in December 1973 without any apparent harm to the local bird population. Several factors will of course determine the effects of an oil

spill, e.g., the concentration of birds, the season and the quantity and quality of the oil. The serious accident outside Oland mainly affected a species in its wintering area and the real effects on the population are unknown since its breeding areas are far outside the Baltic Sea environment.

#### *Harmful substances*

Although mercury was noted to have a very serious influence on the terrestrial bird fauna in the 1950s and 1960s, it seems to have only locally affected the Baltic Sea aquatic bird fauna. High mercury levels have been found in white-tailed eagles (*Haliaeetus albicilla*) outside Stockholm (Helander, 1975) and probably caused death to some individuals. However, no general impact of mercury on the Baltic bird fauna has been detected.

Recently, lead as an environmental pollutant in birds has been considered. Intoxication caused by lead apparently occurs in Baltic Sea birds, although the data do not separate the investigated material into marine and fresh water populations (Frank and Borg, 1979; Clausen and Wolstrup, 1979). Thus, it is still a question whether lead might possibly pose a threat to Baltic Sea bird populations or just to fresh water bird populations in the vicinity of the Baltic Sea.

It is a well-known fact that one of the major pollutants in the Baltic Sea - the DDT group - causes a serious decrease in egg-shell thickness among many birds. For that reason, some species are presently close to extinction in different parts of the world. Within the Baltic area, some populations have been investigated as to their reproduction or as to changes in their egg-shell thickness.

Razorbill (*Alca torda*) has been investigated in the archipelago outside Stockholm (Andersson et al., 1974). The

shellthickness of eggs collected during the 1970s was compared with that of eggs collected during the 19th century and at the beginning of the 20th century. Furthermore, the concentrations of mercury, DDT and PCB residues were determined in eggs and the production of young was studied and compared with the situation in other parts of the distribution area. A significant, 10 - 20% decrease in egg-shell thickness was found. However, no change in the reproduction rate could be detected. A decrease in egg-shell thickness of the same magnitude has also been found in guillemot and black guillemot (Odsjö and Johnels, 1972).

The white-tailed eagle has also shown a decrease in egg-shell thickness during this century, by about 15% (Helander, 1975; Odsjö and Johnels, 1972; Andersson and Hickey, 1974). Unpublished results on residue levels in eggs and the breeding success from more than 50 breedings or breeding attempts within the Swedish white-tailed eagle population demonstrate a significant negative correlation between reproductive success and levels of DDT and PCBs in the eggs (Helander et al., in preparation). No such correlation was found for mercury.

A study of DDT and PCB residues in eggs of nesting arctic terns (*Sterna paradisaea*) and of hooded crows (*Corvus cornix*) (Lemmetynen et al., 1977) in the archipelago of southwestern Finland did not show any developmental defects nor a decrease in the reproduction rate. However, the levels of DDT and PCBs in arctic terns were approximately 1/10 of those mentioned for white-tailed eagles.

### 7.6.3 *Effects on Mammals*

Within the Baltic Sea environment there are at present six species of marine mammals of special interest regarding pollution. All of them are suspected to be threatened by harmful substances. The different species are discussed below.

### *Seals*

In the Baltic Proper, the grey seal (*Halichoerus grypus*) and the harbour seal (*Phoca vitulina*) populations have decreased rapidly during the last decades. In the Gulf of Bothnia, the ringed seal (*Pusa hispida*) and grey seal populations have suffered in the same way. In the Kattegat, the grey seals have been rare for a very long time, while the harbour seal populations in both Denmark and Sweden show a more stable stock.

In all waters mentioned, there are today protection and hunting regulations. However, only in the Kattegat - Skagerrak area does this appear to have had a positive influence on the populations of the harbour seal (Almkvist, 1980; Härkönen and Oskarsson, 1980). Along the southern coasts of the Baltic Proper only have some few individuals been reported during the last decades (Holm Joensen and Bøgebjerg Hansen, 1978; Drescher, 1978; Gill, 1978). Various reasons can be given for the rapid decline of the populations, e.g., hunting and disturbances. However, the presence of persistent chemicals is probably the most important factor influencing the reproduction.

It has been stated that the reproduction rate of the ringed seal is very much reduced. At present, only about 25% of the females of reproductive age in the Bothnian Bay are annually pregnant (Helle, 1975, 1978). A normal figure is 60 - 90%. Investigations on the same population show that reproducing females have lower levels of DDT and PCBs than non-reproducing females (Helle et al., 1976). Furthermore, about 40% of the ringed seal females of reproductive age have been found to exhibit grave pathological changes in the uterine tract, implying that the uterus horns are closed by stenosis (Helle et al., 1976). Approximately the same frequency has been found among grey seals from the Baltic area (Olsson, 1978). Unpublished data indicate a further increasing percentage of stenosis and a de-

creasing reproductive rate in the ringed seals of the Gulf of Bothnia during the past three years (Helle, personal communication).

PCBs are believed to cause the reproductive failure, since laboratory investigations on mink have shown a distinct decrease in reproductive rate at residue levels comparable to those found in Baltic seals and in the seal diet (Kihlström et al., 1976). The investigations failed to show any interaction between DDT and reproduction in mink. The PCB levels in the relatively stable harbour seal populations of the Kattegat - Skagerrak area are significantly lower than the levels in the other two species (Olsson et al., 1974).

An attempt to envisage what influence a contaminant-caused reproductive failure will have upon the Baltic seal populations has been published (Olsson, 1977). The model presented displays the impact of a contaminant not only on females of reproductive age, but also on juvenile animals. The presence of non-reproducing females within a population hides the real effects upon the stock.

#### *Mink (Mustela vison)*

There are no data available on the status of the mink population in the Baltic Sea environment. Levels of PCBs in minks from laboratory investigations (Kihlström et al., 1976) where the females failed to reproduce are of the same magnitude as can be found in field-collected minks (Olsson, unpublished). There is reason to believe that this species might be threatened, at least in some areas.

#### *Otter (Lutra lutra)*

Several reports on the decreasing otter population along the coasts have been published (Heidemann, 1974, 1976; Erlinge, 1972; Erlinge and Nilsson, 1976, 1978; Heggberget and Myrberget, 1979). For this species also various

explanations can be given, including hunting, destruction of habitats, and pollution.

In order to study the difference in levels of contaminants between a stable or increasing otter population in the coastal part of Norway and the decreasing Swedish population, chemical analyses were carried out on tissue samples from the two populations (Sandegren et al., 1979). The levels of mercury, DDT and PCB residues were determined. Of special interest in this context were the levels found in the animals collected along the Swedish coast, which is one of the areas where the decline of the otter population has occurred very rapidly (Erlinge and Nilsson, 1978).

The mercury levels observed were the same in both the Swedish and Norwegian otter populations, but considerably higher PCB levels were found in the Swedish animals (Sandegren et al., 1979). The PCB levels in coastal otters were higher than levels in minks causing reproductive failure (Kihlström et al., 1976). Regarding the close relationship between mink and otter and the fact that Swedish otters have notably few pups (Sandegren et al., 1979), it seems probable that PCBs are at least partly responsible for the otter decline.

#### *Porpoise (Phocoena phocoena)*

The Baltic porpoise population has decreased drastically during the past decades. An identical trend is observed in the southern area of the North Sea. A review of the population status and possible explanations for its decline has been given (Otterlind, 1976). In this paper, the probable impact of environmental pollution has been stressed. Based on analytical figures concerning DDT and PCB levels, it was stated that the PCB load of the porpoises might threaten them in a way similar to the situation with seals.



The very small number of porpoises observed in the Baltic Sea area during the last two years might be mainly stragglers from the North Sea. The Baltic stock is, as a matter of fact, very close to extermination.

#### 7.6.4 *Effects on man*

So far there are no data showing any direct effect of PCB pollution on man. However, indirectly PCBs have caused some harm to the human community. The reports showing high levels of PCBs and DDT in Baltic Sea fish caused a market resistance to fish in Sweden at the beginning of the 1970s. So did reports on relatively high levels of mercury in polluted coastal areas in the 1960s. Furthermore, the high levels of DDT and PCBs found in cod livers have resulted in a ban on the sale of Baltic cod liver on the market. The black-listing of cod liver is valid not only for the Gulf of Bothnia and the Baltic Proper but also for the archipelago outside Gothenburg. Liver from burbot (*Lota lota*) outside Stockholm is also black listed (Anon., 1979b).

It can thus be stated that PCB and DDT pollution and mercury pollution in the 1960s have had an economic influence on the fish market in certain Baltic Sea countries. It should also be stressed that if the general rules in Sweden (Anon., 1979c) and in the USA (Anon., 1979d) for the highest acceptable levels of PCBs in fish were true also for salmon, Swedish salmon fishing would be in the risk zone of being stopped. At present, salmon is excluded from the general Swedish rule.

#### 7.6.5 *Action needed for the protection of biota and for intensified research*

The main pollution problems related to vertebrate biota in the Baltic Sea are no doubt caused by harmful substances. Although basic knowledge is limited, the account

presented above is serious, particularly concerning marine mammals. The situation is obviously very critical for the porpoise and otter populations of the whole Baltic Sea area, and also for all three seal species inside the Danish Belts and the Øresund.

There are strong indications that the sharp decline of these populations in recent decades can be ascribed primarily to the effects of harmful chemicals in the marine environment. The PCBs have a prominent position. However, substances other than well-known substances (like DDT and PCBs) in the Baltic Sea may have a role in this development. Recently observed high levels of chlorinated terpenes and chlordane components have called attention to this situation.

It is quite clear that a continued reduction in the populations of marine mammals, and in the long run probably of additional bird stocks and possibly also of fish stocks, will happen in the absence of more rigorous regulations on the use of harmful substances. One difficulty is that air-borne pollution from other areas shows no apparent signs of decrease so far. Effective international measures are urgently needed.

In this connection, the very great importance must be stressed of devising programmes to monitor the development of some major stocks of Baltic fish, birds and mammals. It is not sufficient to rely upon studies of the levels of harmful substances only.

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