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CHEMICAL TRACERS FOR STUDYING WATER MASSES AND PHYSICAL PROCESSES IN THE SEA

Proceedings of a Nordic Symposium
in Reykjavík, August 29 – September 1, 1984

Edited by
Unnsteinn Stefánsson

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Preface

A great deal of water has found its way into the oceans since the days when Martin Knudsen developed his precision method for chlorinity based on a Mohr-titration and Björn Helland-Hansen introduced the T, S diagram, which has since then so well served physical oceanographers. Aside from this, physical oceanographers have not, until recently, made much use of chemistry in their research. This can largely be ascribed to the fact that suitable methods were not available, except for simple techniques mainly based on preformed nutrients, reactive silicate or the relationship between oxygen (or nutrients) and density. As is well known, these routine methods have been extensively used by some oceanographers in the past and are still used for estimating or quantifying water mass composition. In recent decades marine chemistry has developed at an accelerated rate, and today chemical oceanographers have at their disposal precise and powerful analytical techniques which they can use, not only to investigate chemical properties, chemical processes and chemical speciation of major, minor and trace constituents in the sea, but also to provide information useful for other oceanographic disciplines.

The idea to hold a symposium devoted to the topic of "Chemical tracers for studying water masses and physical processes in the sea" evolved from discussions which took place in early 1983 at a Nordic meeting on the marine science cooperation in future between Nordic countries and the role of chemistry in that context. The very first draft of a proposal was developed in consultation with Professor Gunnar Kullenberg, University of Copenhagen. The proposal was submitted to the Nordisk Kollegium for Fysisk Oceanografi whose members decided to support it.

The objectives of the Symposium were to promote and stimulate inter-disciplinary cooperation in marine research, in particular between physical and chemical oceanographers of the Nordic countries. In light of this, the main emphasis in the programme was placed on the application of chemical methods, especially tracers, for studying the distribution and movement of water masses and physical processes, as well as physical tracer methods and studies of the water mass characteristics of a few specific oceanographic regions. To achieve this goal, marine scientists from the Nordic countries and in addition a few international experts on trace elements and chemical oceanographical tracer techniques, were invited to participate and present papers on original work as well as review papers. Furthermore, a few contributions from other research areas were included, viz. marine biology, marine geology and sea ice studies.

The Symposium was organized by the University of Iceland in cooperation with the Marine Research Institute, Reykjavík and the Nordisk Kollegium for Fysisk Oceanografi. It was held at the University of Iceland in Reykjavík August 29 – September 1, 1984. The organizing committee consisted of Unnsteinn Stefánsson (chairman), University of Iceland; Svend Aage Malmberg, Marine Research Institute, Reykjavík; and Jón Ólafsson, Marine Research Institute, Reykjavík.

Abstracts of papers presented at the Symposium were included in the preliminary programme distributed to participants prior to the meeting. The participants (listed in Appendix I) presented 26 papers, 21 of which are printed in this volume, either in extenso or as extended abstracts. All of the papers here published have been subjected to a review process.

Thanks are due to Nordisk Kollegium for Fysisk Oceanografi, Fiskimálasjóður, Reykjavík and Nordiska Forskarkurser for financial support which made the Symposium possible, and to the director of the Marine Research Institute, Reykjavík, Jakob Jakobsson, for the generous offer to print the proceedings in the Institute's publication. The editor wishes to express his thanks to the reviewers whose critical remarks have benefited the papers of this volume, and to the authors for their cooperation. Finally, the staff of Prentsmiðja Hafnarfjarðar hf., in particular the chief printer, Mr. Albert Thorsteinsson, are to be commended for their patience, efficiency and ready collaboration.

Unnsteinn Stefánsson

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Sources of chemical differences in sea water

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In spite of the fact that the seas are thin layers on the globe (a mean depth of 4 km can be compared with an average radius of 6367 km) and subjected to considerable wind stress and heating, there are numerous concentration gradients in the oceans. The sources of these gradients may be steady state processes with or without a seasonal pulse or transients. This paper is intented to be an overview of the sources of chemical differences in the seas.

CONTAMINANTS

Different pollutants produced by man are probably the most useful sources of chemical differences for tracing water masses and mixing processes. A data collection of C-14 (half-life 5730 ± 40 a) carbon dioxide in the atmosphere and ocean surface water by Nydal et al. (1980) shows the pulse in the beginning of the 1960s due to testing of heavy nuclear devices by USA and USSR. The decrease after 1963 is due to exchange of $^{14}CO_2$ in the air for $^{12}CO_2$ in the ocean. The decrease would correspond to a half-life of 7 years for $^{14}CO_2$ in the air rather than 10 years, if the tropospheric content had not been affected by Chinese and French tests. In spite of the variations of C-14 in the ocean surface the depth profiles indicate down-mixing of the surface water. (See treatments by Östlund and Stuiver 1980, and Quay and Stuiver 1980).

Our results for the Spitsbergen area are shown in Figure 1. The author's samples from the Ymer expedition in 1980 were analyzed by Ingrid Olsson at the University of Uppsala. In July 1957 Fonselius and Östlund (1959) sampled the Barents Sea and measured C-14. Their results, which are included in Figure 1, showed that without the extensive bomb testing the measurements would give practically no information about the vertical advection. The results of Stuiver

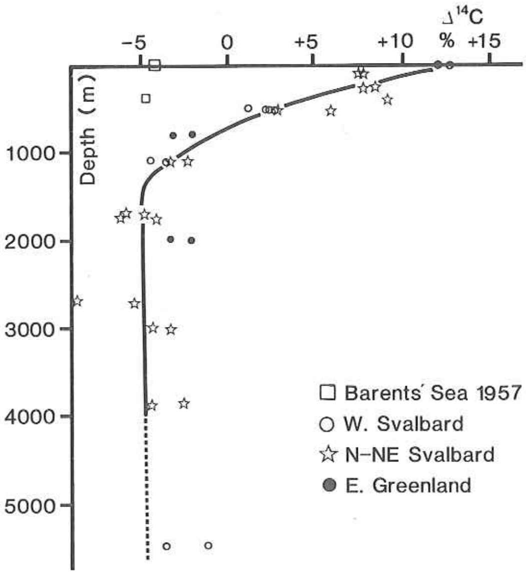

Fig. 1. Carbon-14 measurements by Dyrssen and Olsson for the Spitsbergen (Svalbard) area, and by Fonselius and Östlund (1959) for the Barents Sea. (From Dyrssen 1982).

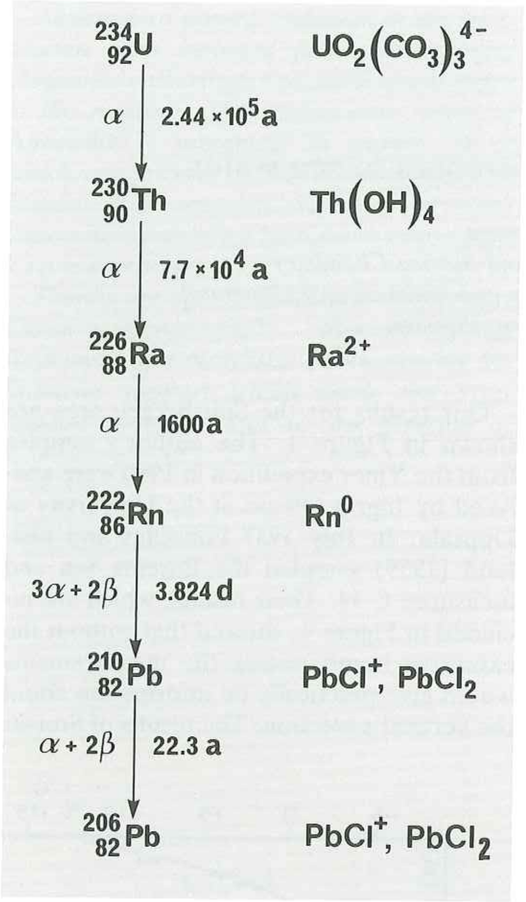

Fig. 2. Part of the decay series of uranium-238 showing the principal species.

and Östlund (1980) for the northernmost stations in the Geochemical Ocean Sections (GEOSECS) Atlantic Track 1972–73 (74°56′N and 1°7′W in the Greenland Sea) gave a mean value of −5.11 ± 0.38% between 820 and 3552 m which agrees with our results. The results indicate that the contamination of the Spitsbergen area between 1972 and 1980 was mostly due to inflowing water from the North Atlantic, which had a higher Δ^{14}C in 1972 (around +15%).

The contamination of the Arctic surface water by HTO (the half-life of H-3 is 12.35 a) from bomb tests has been determined by Östlund (1980). The contamination of deeper water in the Greenland and Norwegian Seas made it possible for Östlund and Fine (1979) to trace the deep water formation in the Atlantic Ocean.

Radioactive contaminants from Sellafield effluents into the Irish Sea have proven to be useful tracers of the penetration of North Atlantic water into the North Sea and the Arctic Ocean. Aarkrog and Livingston have treated this point source of radioactivity in this volume. Some results for the Greenland waters have been reported in Nature (Aarkrog et al. 1980).

Figure 2 shows part of the main decay series of uranium with the principal chemical forms in seawater. Uranium(VI) in the form of the negatively charged tricarbonate complex is not easily removed. Thorium in the form of an uncharged hydroxo complex is rapidly removed with descending particulate matter. Radium behaves much in the same way as barium although the source is quite different. Lead is also removed with particulate matter. Thorium in the sediments generates radium and radon; an excess of radon can be observed if the bottom water is not quickly mixed in. In an NSF proposal Smethie has suggested measurements of radium and radon in surface waters. The loss of radon is used to calculate the gas exchange rate across the air-sea

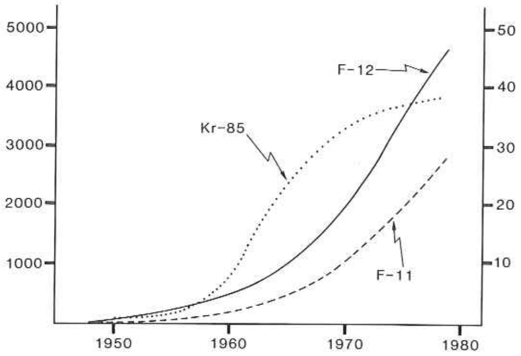

Fig. 3. Atmospheric time history of krypton-85 (dpm m^{-3}) and freons (10^7 moles in the atmosphere, left scale). (From a Transient Tracers in the Ocean (TTO) proposal by W. M. Smethie.)

interface. Smethie has treated another radioactive inert gas, krypton-85 (half-life 10.26 a), in this volume.

The atmospheric histories of krypton-85, freon-11 (CCl_3F, bp = 23.82), freon-12 (CCl_2F_2, bp = −29.79) are known (see Fig. 3). The ratio between the freon concentrations is shown in Figure 4. The variation of this ratio allows dating of water masses that have been in contact with the atmosphere.

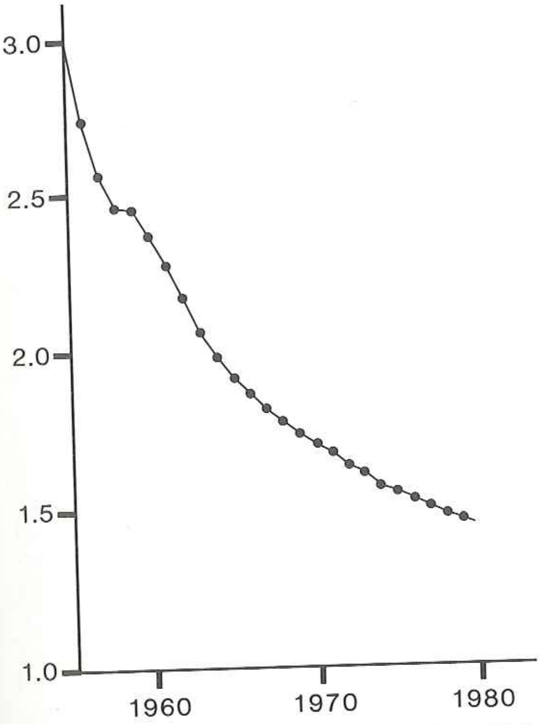

Fig. 4. Time history of the atmospheric freon-12/11 ratio. (From Fig. 3.)

Bullister and Weiss (1983) found different depth profiles for the two freons in the Greenland and Norwegian Seas. The conclusion from the data is deep convective mixing in the Greenland Sea and lateral mixing between the two seas below 1500 m.

Other halocarbons have been treated in the thesis of Fogelqvist (1984). Bromoform is formed from organic substances in sea water upon chlorination. In fresh water with low concentrations of bromide chloroform will be the main halocarbon. Bromoform is also generated from coastal algae belts. This permits tracing of waters flowing around Spitsbergen. Results from the Ymer expedition have been published (Dyrssen 1982; Fogelqvist 1984) and were discussed at a meeting in Göteborg (Carmack and Rudels 1983). The estimated annual global release of carbon tetrachloride and tetrachloro ethylene are shown in Figure 5 and a comparison with carbon-14 data is made in

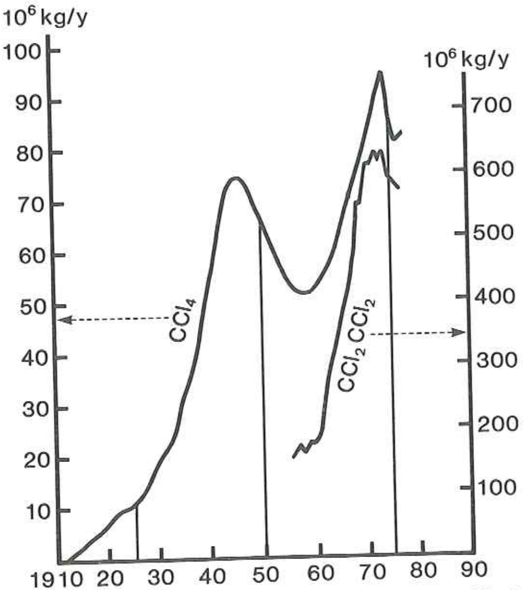

Fig. 5. Annual global release of carbon tetrachloride (left-hand scale) and tetrachloro ethylene (right-hand scale). (From Dyrssen 1982).

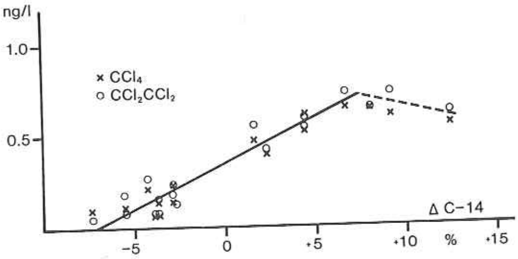

Fig. 6. Comparison between the depth profiles of carbon tetrachloride, tetrachloro ethylene and carbon-14. (From Dyrssen 1982).

Figure 6. The lack of agreement in layers above 400 m is probably due to different sources. Contamination of sea water with carbon tetrachloride and tetrachloroethylene will mainly occur in the industrial belt between 30° and 60°N.

BIOGENIC PRODUCTS

Photosynthesis and subsequent digestion of photosynthetic particles leads to many chemical differences in the oceans Dissolved organic compounds with limited half-lives are formed as exudates by the production of phytoplankton. The photosynthetic production in the oceans is mainly limited by the supply of nitrate from intermediate waters. The reason is probably that some nitrogen is lost in the decay of proteins. Figure 7 illustrates that proteins are decomposed to ammonia by enzymatic processes involving peptides, amino acids and urea as intermediates. In the bacterial transfer of ammonia to nitrate some nitrogen is lost as gaseous dinitrogen and dinitrogen oxide. This loss has to be compensated for on a global scale by nitrogen fixation. Reduction of nitrate to ammonia mainly occurs by photosynthetic production of proteins, but in limited areas reduction also occurs in anoxic waters. Thereby nitrogen can be lost in gaseous forms.

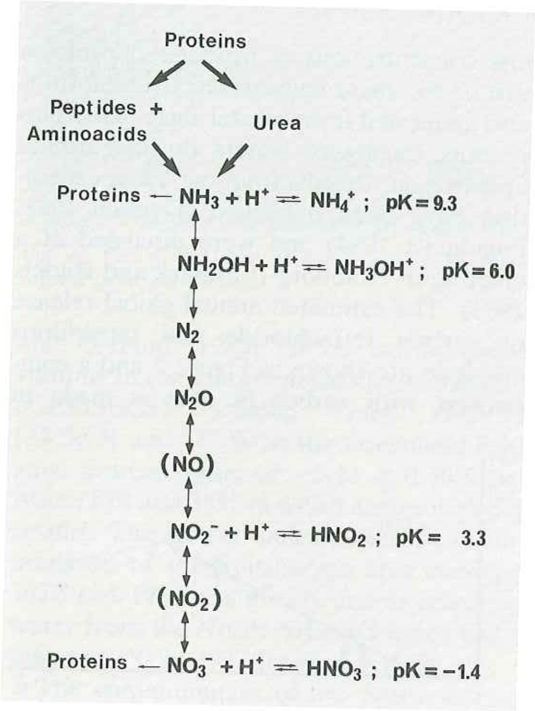

Fig. 7. Nitrogen species in the transfers upon production and decomposition of proteins (intermediates: peptides, amino acids and urea).

$$mCO_2 + nNO_3^- + pSO_4^{2-} + qSiO_2 + rCa^{2+} + MHPO_4 \xrightarrow{+\,H_2O}$$
$$(CH_2O)_s\,(CH_2)_t\,(NHCH_2CO)_u\,(NHCH_2CS)_v -$$
$$(SiO_2)_x(CaCO_3)_y(CHPO_4M)$$
$$+\ z\,O_2 + a\,OH^-$$

Fig. 8. Plankton formation stoichiometry including soft parts (carbohydrates, fats and proteins) and hard parts (silica and carbonate).

The stoichiometry of the formation of plankton including zooplankton with hard parts in the form of silica and calcium carbonate is shown in Figure 8. Many chemical shifts (Fig. 9) that occur upon the production and decomposition of plankton can be measured (Dyrssen 1977) and the GEOSECS data include nitrate, phosphate, silica and oxygen as well as alkalinity and total inorganic carbonate. About 10% of the amino acids in the proteins contain sulphur groups which are formed from sulphate. The influence on the sulphate concentration from this process is, however, not possible to determine.

$$m = s + t + 2u + 2v + 1 + y, \quad n = u + v,$$
$$p = v, \quad q = x, \quad r = y, \quad z = s + 1.5\,t + 3.5\,u +$$
$$+\ 5.5\,v + 1 \text{ and } a = n + 2\,p - 2\,r - 1$$

Fig. 9. Chemical shifts upon plankton formation (cf. Fig. 8).

The composition of the particulate matter produced in the euphotic surface layer is somewhat different from the composition of the particles that reach intermediate waters and the continental shelves. Most ocean waters below 200 m have a nitrate to phosphate ratio close to 15, but in deep Baffin Bay the ratio is 9.6 (Jones et al. 1984). Overviews of oxygen, phosphate and silica reveal marked oxygen minima and phosphate maxima in the intermediate water around 500 m within the tropics. On a world-wide basis one can see that the decay processes mostly influence the following regions: Eastern Atlantic and Pacific, Weddell and Bering Seas, Arabian Sea and Bay of Bengal. Subarctic waters are rather low in phosphate while high values of oxygen are found in arctic and antarctic waters. This is of course due to sinking of cold water. Thus both lateral and vertical gradients are set up. For oxygen at 500 m the lateral gradients are in the order of 600:100 or 550:50 (μM:μM) and for phosphate 1:3 (μM:μM).

Qualitatively the decay of particulate matter in the regeneration zone follows the stoichiometry in Figure 8 which can be seen from the depth profiles in Hawaiian waters (Dyrssen 1977). However, the stoichiometry varies with the depth and the carbonate from the hard parts is released after most of the soft parts have decayed.

The main sources of dissolved silica within the ocean are the Antarctic waters and the Bering Sea. The flow of Pacific water through the Arctic Ocean can be traced with Bering Strait silica. Sediment investigations show that practically no silica is stored in the sediments. Measurements at Soviet ice camps by Rusanov (1975) show that the water layers above 200 m in the Arctic Ocean are not well mixed and that inflowing water over the sill at Bering Strait with a depth of 40 to 60 m sinks. This gives rise to the well-known intermediate silica maxima. An increase of the silica concentration in the East Greenland outflow could also be seen in the data from the Ymer expedition. A silica budget for the Arctic Ocean (Anderson et al. 1983) demonstrates that the Bering Strait water is advected towards the east and thus silica is transported from the Pacific to the North Atlantic via the Canadian sounds and the Baffin Bay.

Inflows over sills occur also in the Black Sea, the Baltic Sea and fjords. In principle the inflows are pulses of heavy water that are sandwiched at different depths below the sill. If the water below the sill is stagnant, the sulphidic part of the sulphide (mainly in the form of H_2S and HS^-) will react with the inflowing oxygen. Thereby various oxidation products are formed (sulphur, thiosulphate, sulphite and sulphate) which can be determined. In the Black Sea Östlund (1974) tried to determine the strata by measurement of carbon-14. After studies of Byfjorden (Dyrssen and Svensson 1982) we have concentrated our efforts on the Norwegian fjord Framvaren. In this case we could see two sources of organic matter, one originating from phytoplankton and the other from leaves. In Iceland Einarsson and Stefánsson (1983) have studied sulphidic bottom water in Lake Miklavatn. Stig Fonselius has treated the Baltic Sea in this volume.

OTHER DIFFERENCES

In order to explain the chemical differences in the oceans we need mixing models as well as the source histories and knowledge of the biogeochemical processes that influence different substances.

Meteoric water has low values of $\delta^{18}O$ while no isotope separation occurs upon formation of sea ice. Thus it is possible to distinguish the dilution of seawater by river water from that by sea ice melt water. Rusanov's samples from the Central Arctic Ocean were measured by Vetstein and Malynk at Kiev (1974). Their slope of $\delta^{18}O$ against salinity is different from the slope obtained by Tan et al. (1983) in the East Greenland current. This calls for further investigations including the Bering Sea and the runoff from the glaciers on East Greenland.

Sea water that reacts with hot basalt may loose its magnesium and sulphate. In fact these processes may occur on such a large scale thaty they balance the river inputs (McDuff and Morel, 1980). Sea water that has reacted with hot basalt in rift areas should therefore have low values of magnesium and sulphate to chlorinity ratios. However, it would be expected that these chemical differences would soon not be discernible due to mixing processes. The differences found by Almgren et al. (1977) are probably due to analytical difficulties. It seems as rift water is preferably traced by determinations of helium-3 (Edmond et al. 1982).

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