MARINE CHEMISTRY

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HISTORY AND EVOLUTION OF MARINE CHEMISTRY

Oceanography as a science is concerned with the oceans and the processes that occur in them. It embraces a range of scientific disciplines including marine biology, geography, geology, physics and chemistry and is to a great extent interdisciplinary. Chemistry occupies a central position in oceanography. Indeed, in e.g. the field of physical oceanography, the knowledge of the water masses of the oceans and their origins, is largely based on measurements of chemical parameters, such as salinity and oxygen content. Determinations of the essential micro-nutrients, like nitrogen and phosphorus, are of great value to marine biologists concerned with the fertility of the sea, while measurements of heavy metals and pesticides are essential in ecotoxicology. Chemical studies are also of importance to geologists, e.g. by providing clues to the modes of formation of the mysterious manganese nodules which grow on the ocean floor. As a matter of fact, prior to world War II, chemical measurements in the ocean were made largely as aids to programs designed by physical, biological and geological oceanographers, while fundamental chemical studies were scarce. Since then, however, marine chemistry as a field of its own has witnessed a dramatic growth.

The scientific base of marine chemistry dates back to the epic voyage of the *Challenger* in 1873-76. The tremendous amount of data, collected by this expedition, took 19 years to synthesize and has resulted in a 50-volume report. As far as chemistry is concerned, the carbon dioxide contents of water samples, collected at depths down to 1,500 m, were measured at sea. Seventy-seven samples of water were also taken back to the laboratory where they were analyzed for major ions. These analyses, more than a century ago, were models of accuracy and compare well with recent values; they suggested that, within narrow limits, the ratios of the concentrations of the major ions in the sea are constant. The occurrence of dissolved oxygen attracted attention before the middle of the nineteenth century, but it was not until Winkler developed a simple method for its determination in 1888, that routine studies of the oxygen distribution in the sea were made.

It was soon realized that changes in the oxygen contents of water out of contact with the atmosphere were intimately related to the biological processes of photosynthesis and respiration occurring in them. These processes also influence the dissolved carbon dioxide content of the waters. Unlike the other atmospheric gases, carbon dioxide reacts with water. The problem of the carbon dioxide equilibria in sea water is a difficult one, but it was largely solved between 1915 and 1933. It had been realized for a long time by analogy with land-plants that marine plants and phytoplankton would require the micronutrient elements nitrogen and phosphorus for their growth. However, it was not until the development of rapid photometric methods of analysis for nitrate and phosphate in 1920-27 that it was possible to explore the close relationship between the fertility of sea water and its content of these micronutrients in detail. Analyses for these nutrients were included in biochemical programmes in the pioneering cruises between 1925 and 1927 of the *Meteor* to the South Atlantic and the *Discovery II* to the Southern Ocean. Data obtained on these voyages has done much to elucidate the movements of the water masses in these oceans and to demonstrate that the high fertility found in certain regions is associated with upwelling. More recently, in 1952, the development of the carbon-14 method of determining primary productivity has given a fresh impetus to the study of the fertility of sea water.

Hence, the history of marine chemistry shows that new developments have often coincided with the introduction of new techniques in analytical chemistry. The last few years have been particularly productive in analytical chemistry, so that impressive new progress in marine chemistry is to be expected soon. New highly sensitive physico-chemical methods of analysis have been developed lately, allowing the quantitative determination of organic and inorganic compounds which could not be assessed before in seawater in view of their low concentration levels. In fact, the main problem with these new ultrasensitive techniques is rather in avoiding contamination during sampling and in the analysis step. Also, several techniques have recently been developed for the analysis on an individual basis of particles, which are so important in the marine fluxes. Already, the tedium of analyzing the large numbers of samples collected on research cruises has been reduced by the adoption of automatic methods of nutrient analysis. The next logical step is the *in situ* estimation of chemical parameters. Electrode systems are available for the *in situ* measurement of e.g. pH, the partial pressures of oxygen and carbon dioxide and fluoride ion activity, but several other sensors are being developed now, e.g. to measure the sulphide concentration in sediments *in situ*.

In the meantime, marine chemistry has evolved from a discipline in which originally the concentration, properties and distribution of seawater components were only described, to an interdisciplinary approach concerned with the basic dynamic interactions in the ocean. Indeed, the ocean is not merely a chemical system; it is a phenomenon in a box, and the interaction of the ocean with its boundaries is of utmost importance. Modern marine chemistry is almost entirely interface chemistry. Three fundamental interaction types can be discerned:

- ocean/atmosphere interactions, related to the massive transfer of material between the sea and the air, both in gaseous and particulate form, both to the sea and into the air. Indeed, in addition to enormous amounts of energy, 85% of the water vapour that ultimately results in precipitation passes through the air-sea interface, while 300 l of vital oxygen is released per m^2 of ocean surface in the spring and absorbed in the fall, and most of the anthropogenic excess of CO_2 is taken up through this interface. More surprisingly, the oceans are the major source of atmospheric particulate matter on earth, since, through the process of the breaking of gas bubbles (on the average, 1-10 gas bubbles burst per s and cm^2 on the sea surface), one billion tonnes of seasalt particles are injected annually into the marine atmosphere; these can be remain airborne over long distances and act as cloud condensation nuclei, while their chemistry is intriguingly complex. On the other hand, the atmospheric input of particulate matter to the sea amounts globally also to several 100 million tonnes. Exactly a century ago, the presence of atmospherically transported eolian dust had already been noted in sediments off the coast of Africa and Australia, but interest in aerosol deposition to the sea rose considerably when Sahara dust was clearly demonstrated in the Caribbean Sea in 1967. Recently, it has been shown that 50 % or more of the total input of cadmium and lead to the North Sea is by deposition of aerosol particles.

- ocean/lithosphere interactions involves mass transfer processes between water and the ocean bottom or particles suspended in water, and the role of the oceans in the global sedimentary cycles. Most substances that enter the ocean ultimately end up in the sediments, but on their way, they participate in a variety of complex chemical and biological cycles. Even after deposition, interactions continue: sediments do not lie passively on the seabed. While deep-sea animals disturb the sediments as they forage for food and bottom currents result in erosion and resuspension, chemical reactions occur between the mineral grains and the overlying seawater and these reactions continue after burial of the sediment, as seawater becomes trapped as interstitial water. Nowadays, deep sea sediments are the focus of intense research, e.g. with the aim to understand on a global scale the fluxes of carbon and associated biogenic elements to the ocean floor. At the borderline between biology and chemistry is the now popular study of faecal pellets, which are responsible for more than 90 % of the downward flux of material, and of "marine snow", the organic aggregates that are rapidly formed, altered and destroyed in the water column. Major global research programs, like the Joint Global Ocean Flux Study, have been launched to tackle such problems of global significance. The marine chemistry in these fields is, of course, intimately linked with sedimentology and geology.

- ocean/biosphere interactions deal with the effect that marine organisms have on the water composition and with the effect of water composition changes due to man-made pollution on the organisms. The possibility that life processes in the ocean waters might govern in part their composition would have appeared strange to the pioneer marine chemists. Yet the relationship between the extent of photosynthesis and the levels of CO_2 and oxygen in surface waters, established in 1912, directed marine chemists to search and find other substances that might be involved in plant growth and consequently have their marine concentrations affected. As will be discussed below, the reverse process, the effect that pollutant have on the ecology in the marine environment, is a research topic of particularly high priority at present.

Indeed there is a clear awareness now of the potential threat to the sea caused by man's activities, in particular its role as the eventual receptacle for toxic wastes.

PRESENT TRENDS AND FUTURE

After inspection of the relevant recent literature in top-level scientific journals, the funding of giant research projects and the tasks given to scientific subcommittees in important international ocean science bodies, I am inclined to conclude that four fields are presently of paramount importance in marine chemistry, that they have contributed largely to the excitement and advance of the field over the last years and that they are to stay around during the near future:

(1) trace elements and pesticides in estuarine and coastal waters,

(2) nitrogen, phosphorus and organic carbon biogeochemistry,

(3) ocean paleochemistry in the context of "global change", and

(4) oceanic hydrothermal chemistry.

Let us consider each of these subfields in some detail.

(1) Trace Elements and Pesticides in Estuarine and Coastal Waters

The sea is becoming increasingly polluted as a result of man's activities, either incidentally, or as a direct result of its use for the disposal of waste products. Many of these may be toxic to some forms of marine life even at very low concentration levels (e.g. heavy metals and chlorine-containing pesticides). It is frequently argued that since the volume of the oceans is very large, dilution, and perhaps bacterial degradation, will soon render any pollutant innocuous. While this line of reasoning is in part true, it fails to take account of the damage which may occur before the pollutant is dispersed in the oceans, or through its concentration by the biota. Indeed, many toxic chemicals are concentrated as they pass through the various stages of the marine food chain to such an extent that there may be some hazard in eating sea-foods from certain areas. Moreover, harmful levels of pollution are frequently reached in bodies of water which have only limited exchange with the sea, e.g. estuaries and coastal waters.

Driven by research about pollutants, marine chemistry is now internationally increasingly turning towards the land/sea boundary. The study areas encompass brackish regions of rivers, through the estuaries themselves, into fringing wetlands, and finally onto the contiguous areas of shelf waters. This area until recently had generally not enjoyed the same attention as more open ocean areas, but the Belgian marine chemistry research has always concentrated largely on coastal and estuarine waters, for obvious geographical reasons. The attention on heavy metals in this context is well deserved because of their toxicity at low levels, their potential amplification in the food chain, and their role in redox processes and nutrient cycling. Considerable emphasis is being placed on quantifying the fluxes of trace elements within and through the coastal zone. E.g. much research is now devoted to the atmospheric input fluxes of trace elements, because it is found that in marine areas surrounded by highly industrialized countries like the North Sea, a very significant fraction of the total heavy metal load can be supplied by wet and dry deposition of atmospheric aerosols. Amongst the frontier fields of analytical chemistry which have advanced most lately are analysis techniques providing improved speciation capability. Speciation techniques, which allow the determination not only of an element concentration but also of its chemical form, are a hot topic nowadays, not only in analytical chemistry in general but also in marine chemistry. E.g. techniques have been developed to assess specifically organic tin compounds; concerns over the toxicity of tin compounds, particularly tributyltin used in antifouling paints, have heightened interest in this element. Such techniques have contributed to our knowledge of processes which remove and cycle trace elements in estuaries and coastal seas.

(2) Nitrogen, Phosphorus and Organic Carbon Biogeochemistry

The introduction of sewage, with its high content of organic matter and nitrogen and phosphorus compounds, into water produces two chemical effects, in addition to microbiological problems. Bacterial oxidation of its organic content may cause the oxygen content of the water to decrease to such a low level that it will not support life. In extreme instances the oxygen may be completely exhausted and formation of toxic hydrogen sulphide will then occur. The other threat comes from micronutrient elements, e.g. phosphorus, mostly from detergents present in domestic waste waters, and nitrogen which comes from agriculture land run-off and atmospheric sources as well. These elements encourage the explosive proliferation of plankton in the waters (eutrophication). The rapid decay of these organisms at the end of the bloom further decreases the oxygen content of the water and may render it toxic. Hence, pollution by sewage and effluents can produce rapid and far reaching effects. Thus, the waters at the centre of the Baltic Sea, which 25 years ago were oxygenated practically from top to bottom, now contain hydrogen sulphide in only the upper 75 m. Deoxygenation of water by sewage could be largely prevented by discharging sewage and organic industrial wastes only after purification by the normal process of screening and bacterial digestion of organic matter. However, such methods of treatment would not remove the nutrients which cause eutrophication, and, moreover, more subtle forms of eutrophication have been discovered lately.

Indeed, in addition to these "classical" aspects, the importance of this field has accelerated recently because of the discovery of much larger pools of analytically resistant dissolved organic carbon, anomalies in so-called "new production", and the potential role of atmospheric iron as a micro-nutrient for marine productivity. In this context, recent controversies are on the nature of organic matter in the sea, and on the amount of it. Fundamental is the knowledge of nutrient sources, and again atmospheric supplies are important, e.g. for required micro-nutrients such as iron.

(3) Ocean Paleochemistry

This subfield implies deriving information on the situation of the ocean in ancient times on the basis of chemical records; it is now enjoying immense attention because of issues that relate to the predicted change of the global climate in the near future, which has been termed "global change". This term is somewhat of a misnomer. While its intention is that of modern change by man, the earth in modern geologic (Quaternary) times has already undergone large global changes brought on by recent glacial epochs. The intention of quaternary ocean paleochemistry is to learn about the future of the earth by studying the past, e.g. the reaction of the oceans to increased atmospheric carbon dioxide levels.

Changes in the past have been evidenced in detail largely by mass spectrometric isotope measurement resulting in precise records in ancient times of the sea-salinity and temperature. Mass spectrometry is now also the tool of choice for the most sensitive and precise measurement of radio-isotopic tracers such as carbon-14 and thorium-230, best suited for the Quaternary. Changes in ocean chemistry, atmospheric carbon dioxide and carbonate preservation point to the role that the quaternary ocean has played in affecting large atmospheric changes of radiatively important carbon based gases. This includes records in the Southern Ocean of its role as a large biological pump, the parallel chemical records of which are found in the long Antarctic ice cores also obtained during the past few years. Studying these ice cores as a function of depth does indeed give a record of the composition of snow up to 200,000 years ago, and this reflects natural atmospheric global changes in the past. Detailed insight has also been gained into the history of chemical sedimentation, particularly using sediment cores from enclosed basins such as the Mediterranean and Black Sea.

(4) Oceanic Hydrothermal Chemistry

The discovery in 1977 of luxuriant benthic colonies clustered around hydrothermal vents at a depth of 2,500 m along the East Pacific Rise was a tremendous surprise to marine biologists, since normally deep sea life is extremely scarce. The geological setting of this discovery has now been established: the hydrothermal fluid pouring from fissures and crevices in the sea floor is the result of deep circulation of seawater within fractured rocks reacting with hot basalts. This primary hydrothermal fluid is anoxic, highly acid and rich in sulphides. This basis of life in the area is chemosynthesis rather than photosynthesis.

Nowadays, oceanic hydrothermal chemistry is still a field with an accelerating surge of importance for chemical oceanography, because of the intriguing chemistry of these fluids, and because the influx of hydrothermal fluids along mid-oceanic ridge or subduction areas is as important a source for many elements as riverine and groundwater inputs.

Advances in this field include the rapid exploitation of geophysical imaging which, in three dimensions, allow subsurface mapping along whole ridges, including the magma chamber. The characteristics of both the fluid and plume chemistry appear to be unique. The temporal stability of fluid compositions in several east Pacific hydrothermal fields over a number of years is strong evidence for a thermodynamic control on the chemistry of major elements and it is supported by thermodynamic models.

PAST AND PRESENT ROLE OF BELGIAN RESEARCHERS IN MARINE CHEMISTRY

In spite of its short coastline, Belgium has a strong tradition in oceanographic research. This is related to specific financing from the Ministry of Science Policy (DPWB) in the framework of the R&D Program on the North Sea, leading to the creation of the Management Unit of the Mathematical Model for the North Sea and Scheldt Estuary (BMM), the Concerted Action Oceanology (1976-81) and, more recently, the Interuniversity Concerted Research Action North Sea (1982-1990). Roughly speaking, Flemish researchers have focused on marine biology, while physical oceanography and modelling are clearly more prominent in the French speaking part of Belgium. For marine chemistry, the point of gravity was originally also in Wallonia, at the University of Liège (ULg) and the French-speaking Free University of Brussels (ULB), or at least these were the institutions which produced international scientific publications in this field prior to 1978. During the latest Concerted Action, the recent Global Change project and Eurotrac program from DPWB, significant financing for marine chemistry has also gone to the Flemish institutions. Also specific research tasks for the account of the Ministry of Health and especially BMM have been carried out by Flemish researchers. It is fair to state that now marine chemistry is carried out equally in the North and South parts of Belgium.

A computerized literature search through Chemical Abstracts for the period 1971-1991, has revealed a total of nearly 200 publication on marine chemistry by Belgian institutions. For the periods 71-74, 75-78, 79-82, 83-86 and 87-91, the publications by institutions in Wallonia (ULB, Ulg and to a minor extent the French speaking Catholic

University of Louvain (UCL)) amounted to 7, 18, 17, 24 and 17, and those by Flemish institutions (University of Antwerp (UA), Flemish Free University of Brussels (VUB), University of Ghent (UG), Ostend Marine Fisheries Research Station (RSZV) and Mol Nuclear Research Centre (SCK)) amounted to 0, 2, 16, 29 and 38, respectively. For the period 87-91, we could trace back 14 publications in the field of marine chemistry by UA, 13 by VUB, 9 by ULg, 7 by UG, 6 by ULB, 2 by RSZV and BMM and 1 by UCL and SCK. It must be borne in mind that not too much weight can be given to the above numerical data on publications: some articles are, of course, much more valuable and innovative than others, and in some subfields, it is more common and easy to publish frequently than in others. It seems that in this field, the scientists with the strongest international reputation are still Prof. R. Wollast (ULB), mostly for his work on the geochemistry of silica, aluminium and trace metals in the marine environment, and Prof. em. A. Distèche (ULg) for research on the carbon dioxide and carbonate chemistry.

The topics on which Belgian marine chemistry researchers have published most heavily over the last 20 years are: ecotoxicology for heavy metals and pesticides in marine organisms (22 publications), optimization of analytical methods for marine samples (21), heavy metals in marine aerosols (19), heavy metals and pesticides in the Scheldt and North Sea (18), biogeochemical cycles of nitrogen and phosphorus (14), carbonate and carbon dioxide chemistry (9), manganese nodules (8) and radioactivity in the marine environment (7).

Although it is possible that the results of a literature search do not give a very complete and reliable picture, it is the only tool I have available to try and discuss in somewhat more detail the marine chemistry work of the Belgian institutions over the last two decades. Only research teams with at least 3 papers on marine chemistry in this period will be considered. It will be seen that a significant fraction of the present Belgian marine chemistry research concerns the four topics of high priority, discussed above.

- ULB: The team around R. Wollast has studied intensively the biogeochemistry of aluminium and silicon in the sea and in interstitial waters, as well as carbonates and nitrates and, more recently, cobalt and nickel. G. Billen and co-workers have specialized on the biogeochemical cycle of nitrate and organic carbon, and the microbiological aspects involved. Both groups have put much emphasis on the North Sea and Scheldt. J. Jedwab has first focused on the geochemistry of natural and pollution particles and manganese nodules in the deep sea, and, more recently, on geothermal vents on the ocean floor.

- ULg: Already 20 years ago, A. Distèche and co-workers in the Oceanography Laboratory of ULg were very active in research concerning carbonate equilibria in seawater and carbon dioxide fluxes, while G. Gillain in the Analytical Chemistry Laboratory was developing seawater sampling techniques and highly sensitive analysis methods for heavy metals using anodic stripping voltammetry. Additional topics studied recently in these two institutes are concerned with the ecotoxicology of heavy metals and the practical industrial applications of manganese nodules.
- UA: In the Micro- and Trace Analysis Centre of UIA, the team with R. Van Grieken has been working, mostly over the last 10 years, on methodological problems in the application to marine samples of X-ray fluorescence analysis and single particle analysis using electron and laser microprobes, on the effects on seawater chemistry of titanium dioxide and alkaline aluminium waste dumping, and on single particle analysis and heavy metal determinations in suspensions, sediments and aerosols, both from the North Sea on from remote marine environments.
- VUB: In the Analytical Chemistry Section, W. Baeyens and co-workers have studied trace elements in the Scheldt and North Sea and in North Sea aerosols and rain water and have put special emphasis on mercury in the environment. In the same laboratory, F. Dehairs has focused on the biogeochemistry of barium, especially in Southern Ocean waters. In the Ecology Laboratory, C. Joiris and co-authors have studied PCB's and other organochlorine compounds in the North Sea.
- UG: In the Marine Biology section of the Zoology Institute, C. Heip and co-workers have investigated the ecotoxicity of various heavy metals to marine organisms, especially nematodes. In the Institute for Nuclear Sciences, R. Dams has carried out studies on the determination of mercury in the Scheldt, and W. Maenhaut has applied proton-induced X-ray emission analyses to remote marine aerosols.
- RSZV: Most research in this institute related to various heavy metals and organo-chlorine compounds in sediments and in various organisms in the North Sea.
- BMM: In addition to several management and quality status reports, BMM has issued marine chemistry articles concerning nitrate and cadmium.
- SCK: This centre has worked on radioactive compounds in water and sediments and mostly in algae.