A biologist's search for chemical solutions to physical problems

Torleiv Brattegard
Department of Marine Biology, University of Bergen
N-5065 Blomsterdalen
Norway

ABSTRACT

The selection and the potential use of certain chemical compounds as tracers and water mass markers are discussed from an ecological point of view. Organic compounds that can be used as a finger print for a water mass are most likely to be found among amino-acids, sterols, odd-chain n-alkanes and vitamins. More extensive use of nutrient data is recommended, notably the use of preformed nutrients which by definition are conservative properties of a water mass. Cooperation between physical, chemical and biological oceanographers is encouraged.

In recent years physical oceanographers are becoming increasingly aware of the potential which certain tracers may have for studying ocean circulation and physical processes in the sea. The application of tracers is not, however, restricted to one discipline of marine research. Often the same tracer may yield information not only important to physical oceanographers but to marine biologists and chemists as well. In this communication attention will be called from an ecological point of view to the possible use of compounds originating from organisms as finger prints for different water masses where conventional methods may fail. It is not, however, the intention to present an extensive treatment of the subject. Instead, it will be attempted to arouse interest and to stimulate inter-disciplinary cooperation by mentioning specific examples.

I will start by referring to three examples of problems which cannot be solved without knowledge of the water masses and how they behave in fjords and coastal areas.

The Korsfjord system on the west coast of Norway consists of two arms, the outer one running WSW to the sea, and the inner running SSE to connect with the relatively open fjord system of outer Hardanger, and some smaller branch fjords on the northern and the eastern sides. Matthews and Sands (1973) and Bakke and Sands (1977) have published results from hydrographical studies in the fjord in 1968–1977. Several events indicated extensive flushing, but the amount of flushing could not be estimated from the data (temperature, salinity, oxygen) since the conservative properties of the Korsfjorden basin were similar to the incoming oceanic water. What kind of additional data would help to solve this problem?

Recent studies of animal life close to the bottom have revealed large populations of the mysid crustacean *Boreomysis tridens* in depressions on the shelf and in deep fjords from the Kristiansund area and northwards at depths from about 330 to 520 m. This

12

species is known from the NE Atlantic where it occurs as a bathypelagic form in depths from 1000 to 3000 m. *Boreomysis tridens* does not perform vertical migration to the upper layers, but a sufficient number of individuals has nevertheless been transported from south of the Wyville-Thomson Ridge across the Norwegian shelf and dumped into some deep basins where it has established isolated populations. How did it happen?

Many of the fjords of western Norway are quite deep, the deepest reaching to 1300 m. The sill depth of most of the larger fjords is about 200 m. The temperature of the deep water is 6–7° and the salinity 35.0–35.25. Despite the uniform environment the fjords differ in having different assemblages of animals in the deep. Some have a large proportion of southern species (warm water) while others are dominated by species with a more northern type of distribution (cool or cold water). How can this phenomenon be explained?

A main problem for biologists is that seemingly identical water masses contain different assemblages of organisms. Frequently, knowledge of temperature, salinity and oxygen is not sufficient to identify the origin or nature of a water mass. This leads to the question: Is it possible to identify chemical compounds that can be used as markers from the multitude of compounds that pass through an organism or from those that are either synthesized or decomposed by organisms?

ECOLOGICAL BACKGROUND

Krebs (1972) defines ecology as the scientific study of the interactions that determine the distribution and abundance of organisms. Without organisms — no ecology. For studies of macro-organisms the basic ecological unit is a population of a specific species. Measures used to study the population are number of individuals per unit volume or unit area, but the number of individuals are often represented by their biomass such as dry weight (DW), ash-free dry weight (AFDW), organic carbon, organic nitrogen and chlorophyll *a*. The organisms can be treated as part of a food-web, as part of a community or as part of the environment. The basic problem is to determine the causes of distribution and abundance of organisms. These are often interconnected. Variables that affect the distribution of a species may also affect its abundance.

Some additional points should be stressed. The basis of the food pyramid is formed by the phytoplankton in the sun-lit layers. The conditions for starting, maintaining and ending the season of primary production in these layers are very important to understand. The place an organism has in a food-web is of great importance for its distribution. The plant-eaters are restricted to the near-surface layers, the carnivores can live at all depths, and the detritus-feeders are most abundant in the deeper parts. The net biomass or energy transfer descends to the sea floor. This means that the food-web stretches vertically through the water column. The rate of passive sinking and the rate and magnitude of active biological transport seem to be inversely correlated to stratification. Also, plankton diversity seems to be correlated to stratification in the same way.

It has for a long time been clear that each kind of water mass contains an assemblage of organisms characteristically different from that of other water masses. According to van der Spoel and Heyman (1983) this means that specific types of growth, reproduction, food specialization, feeding methods and even social behaviour all have a characteristic distribution in different water masses.

Primary water masses show a greater endemic diversity than secondary water masses (formed by inter-mixing of primary water masses), which tend to have relatively

few species of their own. The transition zone from one water mass to another can form a barrier to dispersal. If it acts as a barrier for many species it can be called a zoogeographic barrier. There is also a great difference between the communities in the upper and lower part of the pelagic realm — the first type changes strongly with the seasons while the second type is fairly stable. The changing or unstable communities of the upper layers are of two types: 1) species composition changing due to mixing and migration, and 2) species composition mainly changing due to pronounced breeding cycles of local species following a certain pattern of succession. The first type is typical of secondary surface water masses, the second is typical of primary surface waters of the high latitudes.

CHEMICAL TRACERS ORIGINATING FROM ORGANISMS

Chemical markers and tracers have been used to study structures and processes in biological systems ranging from sub-cellular systems via organs and individual organisms to the increasingly more complex systems of populations, communities and ecosystems.

Radio-isotopes have played an important role in such investigations, e.g. for studies of uptake and release of inorganic and organic compounds, growth processes and transfer of organic matter within a food-chain or food-web. Furthermore, the use of various radio-isotopes for studying physical processes in the sea is well established. But chemical substances originating from organisms may also have potential as tracers of water masses.

Organic compounds

Organisms are a source of particulate and dissolved matter. The particulate matter consists of inorganic substances and organic matter (POM). Parts of the inorganic matter will eventually go into solution. The POM will eventually be broken down and partly be turned into dissolved organic matter (DOM) and partly into dissolved inorganic matter.

The division between particulate and dissolved organic carbon (POC and DOC) is usually made on the arbitrary basis of filter pore size. For analytical purposes the distinction is between what can and cannot either be seen or filtered. Everything larger than about 0.45 μm (earlier 1 μm) is usually considered to be particulate. Since we are looking for compounds that can be sampled, identified and quantified in a relatively simple way, we can neglect the complex particulate organic matter in the following discussion.

The presence of dissolved organic substances in sea water is due to the release of metabolites from living organisms and to the decomposition of dead organisms. How much dissolved organic matter is present in the ocean?

From a summary of values in the literature, Williams (1975) reported that in less than 100 m depth dissolved organic carbon (DOC) values range from 0.6 to 2.0 mg C/l while deep-water values range from 0.4 to 1.5 mg C/l. The annual inputs to maintain the pool of DOM come from internal sources (phytoplankton etc., 99%), from the atmosphere (0.5%) and rivers (0.5%). Williams stated that unless such groups as "total carbohydrates" (of which few specific substances have been identified) are included, it is not possible to account for more than at most 10% of the total organic material known to be present.

The composition of the dissolved fraction can be divided into two principal categories on the basis of their biological activity. The first group of components is generally present at extremely low (threshold) concentrations since at higher concentrations they are rapidly metabolized by heterotrophic activity. Some of the compounds are the organic metabolites which serve as ecolog-

ical communicators. Many marine organisms have well developed chemo-receptors. There is no doubt that some of these act as aids in locating food, spawning grounds and mating partners.

The second group of compounds in the dissolved fraction consists of refractory materials which make up the bulk of the total organic carbon dissolved in sea water. They include carbohydrates, proteins and their derivatives, aliphatic carboxylic and hydroxycarboxylic acids, vitamins and auxins, humic acids, phenolic compounds and biogenic hydrocarbons.

From the ageing of DOC in deep water it is apparent that these compounds are not readily metabolized and may find their way into the sediments. The apparent age of refractory organic matter in the deep water of the NE Pacific Ocean has been estimated to be 3400 years by Williams et al. (1969). Skopintsev (1972) has calculated the residence time of refractory organic carbon in the deep World Ocean to be between 1000 and 1500 years. The long residence time might be due to retardation in biochemical processes caused by high pressure and low temperature (Sorokin 1978).

Is it possible, then, to identify a water mass on the basis of certain metabolites or compounds released during decomposition of the dead organisms belonging to the specific water mass? We can discuss some compounds mentioned in the recent literature.

The chemical composition of excreted material from phytoplankton has been examined by several investigators (see Williams 1975). It seems that glycolic acid (often more than 10%), proteins (a few %), carbohydrates (notably mannitol, glycerol, arabinose and glucose) and vitamins as thiamine, biotin and vitamin B12 are common. In fact they are so common that their usefulness as markers is limited. The present author is not aware of any algal species in a defined geographical area releasing an

identified, specific compound in sufficient amounts to be used as a marker on a routine basis. The use of bromoform released by red algae has been suggested (Dyrssen and Fogelqvist 1981) but red algae are benthic (only the genus *Porphyridium* is planktonic) and occur along most coastlines.

Marine animals release metabolites, some soluble components along with faeces plus residual digestive enzymes contained in the faeces. Faeces have their flora and fauna of bacteria and other micro-organisms. These, together with new types of micro-organisms continue the further breakdown of the organic material and in the process release a multitude of new compounds to the water. Organic phosphorus and organic nitrogen compounds are quite common among the metabolites, e.g. amino acids. If every type of water mass contained a very common organisms with a unique set of amino acids our problems would be simpler. But that is biochemically very unlikely (Raymont et al. 1975).

Dissolved compounds in the sea can be physically transported from one area to another by advection. Eddy-diffusive processes can result in moving compounds from one parcel of water to another. In addition DOM is increased by the sinking of particulate organic matter and by vertical migration of plankton and nekton.

Studies of transport and distribution of specific compounds seem to be relatively limited.

A fair number of studies has concentrated upon bulk properties of DOM (and POM for that matter). The data on temporal changes in the total DOM content of sea water indicate that observed increases probably result from decomposition rather than from excretion during the plankton bloom. The total DOM does not show the same clear seasonal variation as does the plankton in the upper layers in the middle and higher latitudes. The existing data provide no evidence for significant or regular differ-

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ences between the various oceans or their climatic zones. Even between nitrate-rich and nitrate-poor waters the difference is small. Menzel (1974), reviewing the literature, felt that seasonal and geographical differences in total DOM had failed to correlate with clearly identifiable water mass structures or movements. There seem to be two main reasons for this: 1) the distinction between POM and DOM is not clear, and 2) there are sampling and analytical difficulties. Gagosian and Lee (1981) agreed with Menzel's conclusions.

Methane is a reduced gas present in slight supersaturation in surface water relative to the marine atmosphere (Lamontagne et al. 1971, in Williams 1975). It also originates from microbial processes in anoxic water and in sediments. Lately methane has been found in large quantities in conjunction with gas escaping from so-called pockmarks in the North Sea and the Norwegian Trough. This methane is of thermogenic origin (Hovland et al., in press). Knowledge of methane concentrations might aid in studies of advective and eddy diffusive processes. Other interesting hydrocarbons are ethylene and polypropylene which are produced by photochemical decomposition of organic material originating from algae.

Amino acids are interesting with respect to our problem. Concentration variations of the combined amino-acid fraction in the water column suggest their potential use as an additional water mass indicator (Lee and Bada 1975). The Cromwell Current, which originates in the area of limited productivity in the western equatorial Pacific, has low concentrations of combined amino-acids. The current could be traced as far as to the Galapagos Islands (Lee and Bada 1975).

Sterols are involved in metabolic processes and act as hormonal regulators of respiration, growth and reproduction in most marine organisms. They are also present in organisms as lipoproteins. Gagosian and Nigrelli (1979) found large variations in specific

sterol concentrations in the upper 100 m of the water column in the Sargasso Sea. They hypothesized that the changes observed are governed for the most part by 1) physical mixing processes which control surface primary productivity, and 2) particulate transport to the deeper water where grazing by bacteria and other organisms occurs. The useful properties are that 1) individual sterols can be identified, and 2) the residence time for sterols in the euphotic zone is approximately one month, whereas it is 20–150 years in deep water.

The n-alkanes of the hydrocarbons can be used as an aid in determining the source of organic material. Odd-chain 25–31 carbon atoms n-alkanes are mainly of terrestrial origin whereas the 15–21 group are mainly derived from marine organisms (Gagosian and Lee 1981).

Lipids seem to be fairly evenly distributed over a depth range of more than 3000 m (Jeffrey 1970). There is little systematic quantitative difference between samples from an estuary and those from oceanic waters (Stauffer and MacIntyre 1970).

Carbohydrates are not promising. Degens et al. (1964) found no decrease in concentration of total carbohydrates with depth. Individual sugar concentrations normally fall in the range from the undetectable to 20 μg/l.

Among the vitamins the B group (biotin, thiamine and vitamin B12) is best known. B12 usually shows a very characteristic intermediate maximum in vertical profiles. In less than 100 m depth the concentration is typically <1 ng/l, in 200–500 m 3–5 ng/l, and in >1000 m <1 ng/l (see Williams 1975). In waters of high latitudes this compound might be useful.

Nucleic acids are probably highly resistant. Concentrations of 13–80 μg/l are known from inshore waters. Data for oceanic waters are very few (cf. Williams 1975).

182

Algal nutrients

Under some circumstances it is of interest to know the past history of a water mass. This may often be traced, at least partly, from T-S data, but it is also possible to obtain information on the biological history of water from its oxygen and nutrient content (Redfield et al. 1963; Stefánsson and Richards 1964; Richards 1965; Park 1967). The amount of oxygen which will dissolve in the sea at the surface is for a given atmospheric pressure a function of sea water temperature and salinity. The difference between the oxygen content expected from the known solubility and that measured is called the "apparent oxygen utilization" (AOU or $\triangle O_2$). The oxygen measured can be higher than the equilibrium solubility value due to photosynthesis (negative AOU) or lowered due to mineralization of organic matter (positive AOU). Thus the measured nitrate and phosphate can be expressed as

$$P_M = P_P + P_{Ox} \quad \text{and} \quad N_M = N_P + N_{Ox}$$

where P_M and N_M are the measured concentrations, P_P and N_P the preformed concentrations (carried by the water when it leaves the surface), P_{Ox} and N_{Ox} are the concentrations of inorganic phosphate and nitrate respectively derived from the oxidation of organic matter. According to the relationship proposed by Redfield et al. (1963) and the model of Richards (1965) the changes in the moles of dissolved oxygen, carbon and nutrients can be represented by

$$\triangle O_2 : \triangle C : \triangle N : \triangle P = 138:106:16:1$$

Although notable exceptions have been found to this statistical relationship which applies to uptake as well as regeneration in oxygen-containing waters and to the average composition in plankton, it has been found to hold reasonably well for large ocean areas. From this relationship it follows that:

$$P_P = P_M - (1/138) \cdot AOU$$
$$N_P = N_M - (16/138) \cdot AOU$$

where all units are in micromoles per litre. A slight modification of Richard's model has been proposed by Dyrssen (1984).

The preformed nutrients are by definition a conservative property of sea water (Redfield et al. 1963) and as such they can be used to characterize water masses. The value of these parameters for hydrographic studies has been demonstrated by many investigators. Thus Stefánsson (1968) has used preformed nutrients as a means of identifying water masses in the Irminger Sea. As shown by Pytkowicz (1971) these relationships can be extended to mixtures of several water masses. However, there are various sources of error and uncertainties in the estimation of preformed nutrients. Hence this technique should be used with caution (Wangersky 1978).

Broecker (1974) tackled the problem in a different manner. He constructed a composite property, "NO", which is closely related to the concept of preformed nutrients. He proposed to combine O_2 data and NO_3^- data in such a manner that the alteration due to respiration is canceled. The basis is that for each mole of oxygen consumed roughly 1/9th of a mole of bound nitrogen is released as nitrate ion. Thus the sum of $9 NO_3^- + O_2 = $ "NO" should be nearly conservative. In the same way "PO" is defined as "PO" $= 135PO_4 + O_2$. Data presented by Broecker (1974) and Broecker and Takahashi (1981) strongly supported the idea that "NO" is a sensitive, reliable and useful water-mass tracer.

Observations of nutrients as routine measurements in hydrography have until recently been a laborious task. Auto-analyzers with a digital print-out connected to the research vessel's computer are now becoming standard instrumentation on modern research vessels. The use of such a system (Føyn et al. 1981) has provided data for nu-

trient distribution off Norway that clearly indicate that the main nutrient source for the plankton bloom in Norwegian coastal waters is a more or less continuous inflow of nutrient-rich Atlantic water up into the euphotic zone. Fjord waters and Skagerrak winter-water could be ruled out as a source of importance (Føyn and Rey 1981).

I have the impression that many physical oceanographers do not make full use of existing information of this kind. Data on nutrient levels can often yield valuable information in studies of water mass transport or mixing, e.g. in fjords (P. Johannessen pers. comm.). I suggest that a careful selection of nutrient variables should be included in standard programmes for hydrographical stations and that such sampling should be extended to well below the euphotic zone. And in general where tracers other than temperature and salinity are needed for oceanographic studies, interdisciplinary cooperation between physical oceanographers, marine chemists and biologists is strongly recommended.

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184

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