Tracers – Making the Invisible Visible

Tracers are tools used in environmental research both to make processes more visible and to discover unknown processes. Tracers were used, for example in marine research, to answer the question about where the Gulf Stream ends. EAWAG is investigating similar questions about streams and lakes by using isotope tracers. Trace compounds in environmental repositories can be used to reconstruct changes in climatic conditions. A relatively recent development is the use of indicators of biological processes; biomarkers allow us to assess the effects of various pollutants on organisms.

Tracing the Gulf Stream

We enjoy a mild climate because the Gulf Stream directs warm water from the tropics towards Europe's shores. The Gulf Stream transports twenty times more water than all the world's streams combined; however, the water transported by the Gulf Stream must sink back down at some point or the North Atlantic would turn into a "water mountain". In the 1970s, a series of expeditions was undertaken to solve the mystery of the Gulf Stream. Temperature and salinity turned out to be reliable parameters to measure. Figure 1 shows two transects through the Atlantic Ocean [1]. On its way north, the Gulf Stream loses part of its volume through evaporation; western Europe receives this water in form of frequent well known precipitation. Evaporation increases the salinity of the Gulf Stream water. In addition, the water cools off on its way north and eventually mixes with the cold waters of the polar ocean, where the formation of the pack ice also increases salinity. North of Iceland, temperature and salinity reach a critical value. The density of the Gulf Stream water increases and the water masses drop to a depth of 3000 m, where it makes a turn south. After this point, the water is referred to as North Atlantic deep water. Near Gibraltar, warm and very salty water originating from the Mediterranean is layered above this deep current. At approximately the latitude of South Africa, two tongues of Antarctic water meet this current from the south. One part of the Antarctic water is colder but not as saline as the North Atlantic current and flows north along the ocean floor. This example demonstrates how we can make these very deep and slow currents visible with the help of just two parameters, temperature and salinity. Such parameters, revealing invisible processes, are called tracers. The temperature of a water body not only reveals the large-scale flow patterns; temperature measurements taken at a high spatial resolution can also give us quantitative clues about turbulent mixing processes on a small scale. The article by A. Wüest on p. 16 describes how such measurements of the temperature fine structure can be evaluated in a lake system.

Sources and Sinks

Since prehistoric times, humans have been curious about where the water in a spring comes from or where a stream that disappears in a seep hole ultimately goes. Tracer experiments in streams are almost 2000

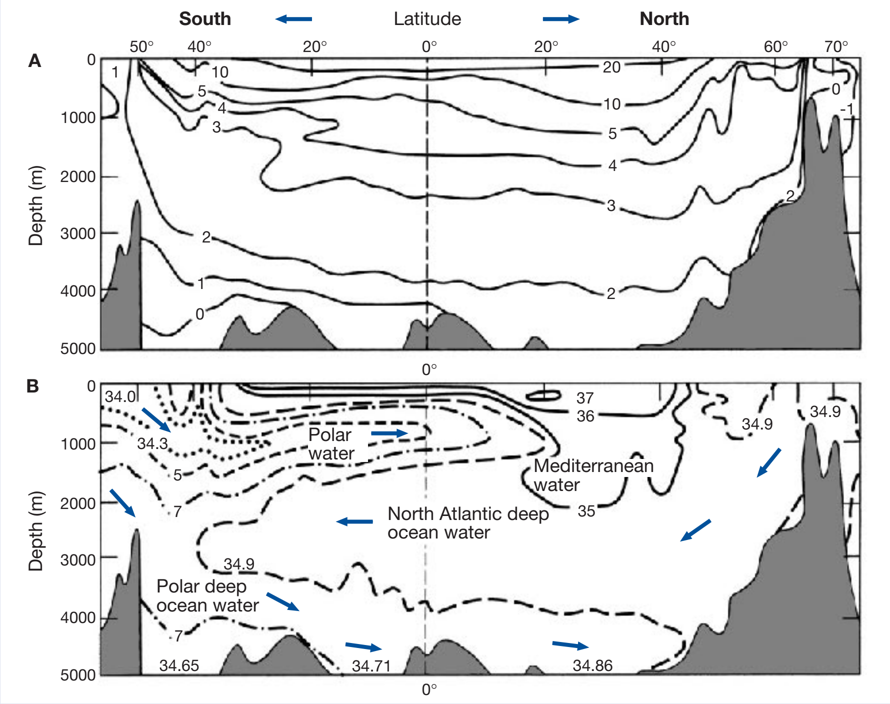

Fig. 1: Cross-section through the Atlantic Ocean. Lines indicate (A) zones of constant temperature, expressed in °C, and (B) zones of constant salinity, expressed as ‰. Figure modified after [1].

years old. During Roman times, the waters of the Jordan River were marked with chaff in an effort to trace the subterranean connection to a karst spring [2]. Over the last 50 years, fluorescent dyes, added to the system from the outside, have been used for this purpose. It is more elegant, however, to use natural compounds that are already present in the environment. Such tracers can be either naturally occurring or of anthropogenic origin (coming from human activity). An example of a naturally occurring tracer is the ratio of the oxygen isotopes $^{18}O/^{16}O$ in rainwater [3]. The ratio of the two isotopes is a function of the elevation above sea level at which the precipitation fell (Fig. 2). Thanks to technical advances in sample processing, measurements of isotopic ratios in water are far less difficult today than they were even ten years ago. We are now able to obtain a very good estimate of the mean elevation at which the water in a surface stream or a groundwater aquifer fell.

Looking Back in Time

Information on the residence time of water in groundwater aquifers is important in drinking water production, risk analysis in the case of chemical spills, and in the analysis of ecosystems that depend on ground water, such as flood plains. Just as a detective asks a suspect about his or her whereabouts on a certain date and time, the "environmental detective" wants to know how long the water has been in a particular groundwater aquifer. A number of anthropogenic tracers are available for investigating this type of question. Freon or CFC's (chlorofluoro-carbons) did not exist in the past. Because of their special properties, CFC's were used more and more as propellants in spray cans and as cooling liquids in refrigerators. As a consequence, their atmospheric concentrations increased continually (see Fig. 3), until their devastating effect on the ozone layer was recognized [4]. Today, the production of freon is limited by the terms of the Montreal Protocol and substitute compounds are now being used. For the period of the last 50 years, there is a well-defined atmospheric CFC concentration at any point in time, corresponding to an equally well-defined equilibrium concentration of CFC's in water. Measuring freon concentrations in a spring, groundwater aquifer or a deep layer of a lake allows us to determine the time when the water was last in contact with the atmosphere. Noble gases are another class of tracers suitable for dating ground water, as is discussed in the article by R. Kipfer on page 20.

The best known tracers for the determination of ages and time constants in environmental processes are radioisotopes. Radioisotopes follow the laws of radioactive decay, and their half-lives are known precisely. In stream research, for example, it is important that the rate of water exchange between the stream and the pore spaces in the gravel bed at the stream bottom is known. Intensive exchange between stream water and near-shore ground water is essential for the health of a stream. The interstitial water in the streambed is an important habitat for benthic organisms, and it controls the exchange of nutrients between the stream and its surroundings. The article by E. Hoehn on page 18 discusses how groundwater habitats within a flood plain can be recognized using radon, a natural radioisotope. Fortunately, we now have extremely sensitive detection methods for radioisotopes. It is possible, for example, to detect radioactive ^{14}C down to levels of 10^{-15} g (or one million atoms). The development of accelerator mass spectrometry has dramatically expanded the areas in which such tracer and age determination methods can be employed.

Rummaging in Environmental Archives

Other projects investigate the temporal dimension of environmental processes. Here the "environmental detective" faces a new kind of problem. In order to study the behavior of systems on large time scales, one has to have access to samples representing comparable periods of time. Typical research projects cover periods of a few years at most. Slow processes are typically studied by reconstructing the temporal development of the system under investigation. Obviously, one cannot expect that someone collected appropriate samples or even conducted the necessary measurements in wise foresight; one therefore has to rely on archives in which the relevant information has been stored or recorded in a temporal sequence.

A good example of such an archive is the sediment deposited in a lake. The sediments are a continuous, layer-by-layer record, storing a wide range of information on the chemical, physical and biological processes within the lake and its surroundings (Fig. 4). The challenge is to read and to interpret this information. The article by W. Giger on page 10 shows how detergents leave traces in the sediments and how sediment analyses can give us information about the original product composition and degradation processes in sewage treatment plants. The sediments can also tell us about natural processes. Geochemical indicators are often used to gain information about the intensity of a natural process from environmental archives, as demonstrated in the article by G. Friedl on page 14. Other groups at EAWAG are currently participating in international research projects attempting to reconstruct environmental conditions in the distant past. They use ice cores from Greenland glaciers and sediment cores from Lake Baikal in Siberia. These interdisciplinary programs try to better understand current environmental conditions and future

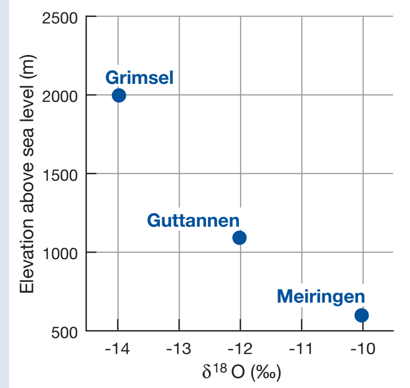

Fig. 2: The oxygen isotope δ^{18}O in precipitation collected at three weather stations within the same geographical area, but at different elevations. δ^{18}O: deviation of the $^{18}O/^{16}O$-ratio from a standard in ‰.

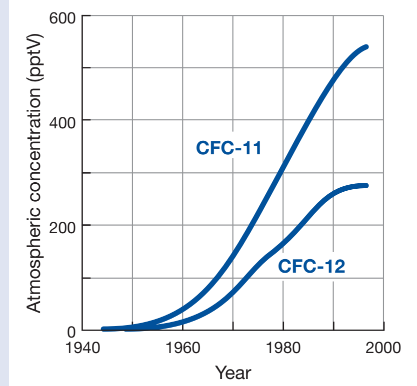

Fig. 3: Increase of atmospheric CFC concentrations (CFC-11 and CFC-12) since 1950. Unit pptV = 10^{-9} volume parts.

developments by comparing them to conditions and changes over the last several thousand years. The beryllium radioisotope ^{10}Be, for example, is formed in the atmosphere by cosmic radiation [5]. Its presence in Greenland ice may be used as a tracer for solar activity levels in the past. With these data, we can improve our understanding of the effect of solar radiation on climatic changes, which is important in determining the role that human activity plays in global climate change. A comparison between ^{10}Be and ^{14}C has revealed a reduction in the global ocean circulation at the end of the last ice age [6], which implies that even the Gulf Stream has a complex and ever changing history.

A Window into the Complexity of the Biosphere

The biosphere is a dynamic system of extraordinary complexity. With the sun as the driving force, innumerable biological processes occur on different temporal and spatial levels, but are usually coupled to one another. Three methodologies have become particularly useful in identifying individual processes: stable isotopes, gene probes and biomarkers. In biological processes, such as photosynthesis or denitrification, the lighter isotopes of a particular element are processed slightly faster than the heavier ones. Generally, this leads to enrichment of lighter isotopes (^{12}C or ^{14}N) in the biological products, while the heavier isotopes (^{13}C or ^{15}N) become enriched in the substrate. A shift in isotopic ratio, as compared to the natural abundances, can therefore be used to assess the type and intensity of biological processes. Additionally, we can use substances enriched in a certain isotope (e.g., nitrate, $^{15}NO_3^-$) as a tracer. Stable isotope tracers have the advantage that they are not radioactive and can be used in environmental studies without doing any harm. Nitrate is used in biological systems in many different pathways. Heterotrophic microorganisms use nitrate to produce atmospheric nitrogen (N_2) or ammonia (NH_4^+), while plants absorb nitrate as a nutrient and produce organically bound nitrogen. Using a mass spectrometer, we can, in some fortunate cases, follow the sources and the sinks of natural nitrate in the environment [7]. With isotopically-labeled nitrate, we can determine denitrification rates in surface waters [8]. The article by L. Zwank on page 6 illustrates the use of stable isotope tracers in studying the degradation of chemical pollutants in ground water. In this type of situation, the question often is whether an apparent drop in pollutant concentration along the flow path is simply a result of dilution or is due to microbial or chemical degradation. Biological degradation can typically be identified by a significant shift in isotopic ratios.

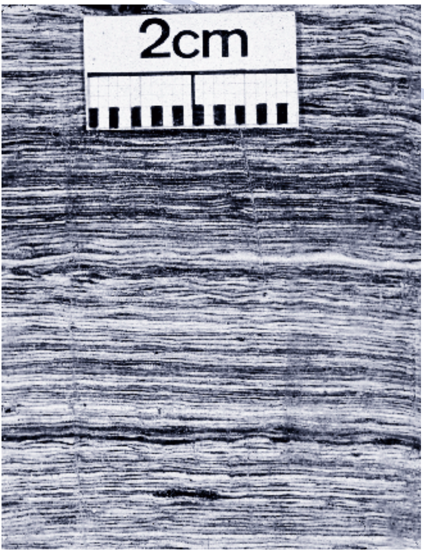
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Fig. 4: Sediment core from Lake Baldegg.

Modern microbial ecology, however, is interested in more than simply the question of which compound is transformed at what rate. One would like to know which microbes are active when and where. Today, gene probes allow us to determine the specific distribution of microorganisms in environmental samples. To achieve this, a short genetic sequence of ribosomal RNA is marked with a fluorescent tag. This type of biomolecular tracer marks specific groups of organisms, e.g., methanogens, in a water or sediment sample and can subsequently be analyzed microscopically. The advantage of this technique lies in the fact that we are examining active microorganisms, which often cannot be cultivated under laboratory conditions. The article by K. Zepp on page 12 discusses these techniques in more detail.

As information about the genetic make-up of organisms becomes available, we will have better tools to identify the players in complex interactions within the biosphere. Even more complex, however, is the information reflected in the wide array of proteins involved in the metabolism of organisms. This is where a relatively new tracer concept comes to the fore – that of biomarkers. Analyses of the metabolic products of an organism can tell us, for example, whether the organism had been exposed to toxic compounds. More about this new approach can be found in the article by R. Eggen on page 8.

This short overview has hopefully demonstrated how the various tracer techniques have evolved into extremely useful and very precise tools in environmental research. The success of this type of research, however, depends on whether the questions we are trying to answer are relevant, interesting and looking toward the future.

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