

The sediment-water interface is characterized by high biological activity and steep concentration gradients of many chemical species. Ordinary chemical analysis in these steep gradients is often impossible to perform with sufficient depth resolution, and the only alternative is to use microsensors. Presently, electrochemical microsensors for  $O_2$ , pH,  $N_2O$ , dissolved sulfide, and redox potential have been used in marine research, and in fresh water environments it is furthermore possible to analyze  $NO_3^-$  and  $NH_4^+$ . Work is currently being conducted to expand the arsenal with a microsensor for dissolved inorganic carbon ( $CO_2$  or bicarbonate). In addition to the chemical sensors fiber-optic light sensors for irradiance and scalar irradiance have been developed. Chemical microsensors with optical signal detection (optrodes) have been developed, and such optical sensors may in the future significantly expand our arsenal of chemical species which can be analyzed.

The analysis of by use of microsensors may be performed on sediment cores brought to the laboratory, but it is also possible to do in situ analysis. Simple in situ analysis at shallow water depth can be done with laboratory equipment which is brought to the field, but analysis in the deep sea requires sophisticated computerized equipment. Jens Gundersen and Bo Barker Jørgensen in our group have developed a lander which can be used down to 6000 m water depth and which can record 8 simultaneous microprofiles at 25  $\mu m$  depth resolution. The microsensors which have been used until now are those for  $O_2$ , pH, and dissolved sulfide. The microsensors are identical to those used in the laboratory except that they are pressure compensated by a flexible rubber bulb filled with paraffin oil. Even in the deep sea, profiles can be recorded with extreme accuracy in terms of both concentration and spatial resolution. Among the interesting results obtained from the deep sea work is the finding that the analysis of near-interface pore water chemistry on sediment cores brought to the surface and exposed to atmospheric pressure will result in very erroneous results.

Sediments from shallow depths are exposed to daylight, and the photosynthetic activity by microorganisms within the uppermost sediment layers very much affects the pore water chemistry and thereby all microbial metabolism. We have previously shown how photosynthesis in sediments by use of microsensors can be analyzed at 0.1 mm depth resolution. The transformation and assimilation of inorganic nitrogen species were studied in various types of biofilms and sediments using  $^{15}N$  and microsensor methods. By use of microsensors for  $O_2$ ,  $N_2O$ , and  $NO_3^-$  it was possible to localize the depth horizons active in nitrification and denitrification, and it was also possible to obtain depth profiles of reaction rates. Nitrification occurred in the oxic surface layer, and in dark incubated sediments it was sometimes possible to distinguish two distinct nitrification maxima where the upper one located near the sediment surface was based on  $NH_4^+$  from the waterphase and the lower one just above the oxic-anoxic interface was based on diffusion from deeper sediment layers. Some of the formed  $NO_3^-$  diffused out of the sediment (uncoupled nitrification) whereas the rest diffused down into anoxic layers where it was denitrified (coupled nitrification-denitrification). Denitrification was always restricted to the deeper anoxic or almost anoxic layers where  $NO_3^-$  was the most favorable electron acceptor present. The denitrification zone could be extremely thin ( $< 100 \mu m$ ) at low  $NO_3^-$  concentrations in the overlying water and at low nitrification rates, but could also be several millimeters thick at high  $NO_3^-$ . The concentration of  $NO_3^-$  in any specific layer was not limiting denitrification as long as more than ca.  $10 \mu M$   $NO_3^-$  was present. Photosynthetic biofilms exhibited pronounced diurnal cycles in assimilation of  $NO_3^-$ , nitrification, and denitrification. Denitrification in the photic zone stopped when the sediment was illuminated and oxygen was produced by photosynthesis, but denitrification started immediately again after darkening and onset of anoxic conditions. A new  $^{15}N$  isotope method, which is based on monitoring the frequency of  $^{15}N_2$ ,  $^{14}N_2$ , and  $^{14}N_2$  in  $N_2$  gas evolved after adding  $^{15}NO_3^-$  to the overlying water, was used to determine rates of nitrification and denitrification. Determination of total nitrification rates was only possible when also the isotope dilution in waterphase  $NO_3^-$  was monitored. This new isotope technique has for the first time enabled us to do determinations of nitrification and denitrification (including coupled nitrification-denitrification) in all types of biofilms and sediments without the addition of artifact-creating artificial inhibitors of metabolic processes. Investigations of a thick photosynthetic biofilm showed that coupled nitrification-denitrification was two times higher during illumination than during darkness due to better oxygen conditions for nitrification. Denitrification based on  $NO_3^-$  in the overlying water was reduced to about half during illumination due to the longer diffusion path to the denitrifying anoxic layers. Assimilation by the microflora was high in the light and remained high for many hours after darkening. This high rate of dark  $NO_3^-$  assimilation has previously erroneously been interpreted as dissimilatory reduction to  $NH_4^+$  as mediated by strictly anaerobic bacteria.