



## Dissolved organic phosphorus and its bioavailable fraction in the Baltic Sea

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In general, it is accepted that dissolved organic phosphorus (DOP) is besides dissolved inorganic phosphorus (DIP) a source for phosphorus nutrition of phyto- and bacterioplankton. If available, DIP is usually preferred to DOP. DOP becomes the most important source under DIP depleted conditions occurring in the Baltic Sea in summer. However, its contribution to nutrition and consequently its significance is very difficult to appraise because only the bioavailable fraction (BAP = bioavailable phosphorus) can be used by organisms. DOP comprises also inert compounds which persist over longer periods. Therefore, there is an urgent need to quantify the bioavailable DOP. In 2004 and 2005, DOP and BAP concentrations were detected in surface water at three stations in the central Baltic Sea from May until July. In June/July 2008 an intensive measuring campaign was performed throughout the whole Baltic Sea. DOP measurements were done from the entrance to the North Sea in the West until the innermost parts of the Gulf of Bothnia in the North and the Gulf of Finland in the East. BAP was determined at 14 stations in the central and northern parts.

DOP was determined using the alkaline potassium peroxidisulphate oxidation method followed by the manual DIP determination. BAP has been detected in time course experiments using 0.8  $\mu\text{m}$  filtered sea water containing free-living heterotrophic bacteria and amended with 7  $\mu\text{M}$  ammonium chloride and 1mg l-1 D-(+) glucosemonohydrate to prevent nitrogen and carbon limitation and increase the phosphorus demand in bacteria. BAP is defined as that proportion of DOP which is used by bacteria and calculated as the difference of DOP concentrations at the beginning and the lowest concentrations during an incubation for 4-6 days.

In 2004 and 2005, most DOP concentrations ranged between 0.18 and 0.32  $\mu\text{M}$ , with a declining tendency from spring to summer probably due to elevated uptake compared to its release caused by higher temperatures and DIP shortage. DOP concentrations of 0.54  $\mu\text{M}$  exceeding this range has been detected in a spring bloom. BAP concentrations ranged between 0.02 and 0.34  $\mu\text{M}$  comprising a proportion between 9 and 61% of the DOP. The amount of BAP was strongly correlated with the ambient DOP concentrations at the beginning of the experiments and can be described by the equation:  $\text{BAP} = (0.92 * \text{DOP}) - 0.14$ . The regression slope of 0.92 indicated that all DOP above the intercept with the abscissa is bioavailable and those variations in DOP were caused by fluctuations in BAP.

The remaining refractory DOP varied between 0.13 and 0.20  $\mu\text{M}$  and did not vary seasonally.

Parallel experiments in 2005 without carbon and nitrogen additions reveal the BAP utilization by heterotrophic bacteria under natural conditions. The bacterial uptake of BAP ranged between 18 and 78% and reached 100% during the summer bloom of diazotrophic cyanobacteria. BAP utilization despite the availability of DIP indicates that phosphorus uptake may be often carbon and/or nitrogen limited and the BAP could satisfy bacterial carbon or nitrogen demand. The limitation was repressed during the summer bloom of diazotrophic cyanobacteria. Here the BAP fulfils the phosphorus demand.

The spatial variability of DOP concentrations in summer 2008 shows a gradient in DOP concentrations from south to north. In the southern and central Baltic Sea, DOP values in the surface ranged between 0.25 and 0.39  $\mu\text{M}$ . In the Gulf of Finland, concentrations of around 0.25  $\mu\text{M}$  were found. In the Gulf of Bothnia, characterized by a phosphate limitation especially in the northern part, DOP concentrations decreased from 0.20  $\mu\text{M}$  in the southernmost part down to 0.12  $\mu\text{M}$  in the northernmost region. BAP amounted between 8% and 57% of DOP. High BAP proportions were detected in the Bornholm Basin (57%) and the Gulf of Finland (45%). The lowest percentage (8 %) was found in the northernmost part in the Gulf of Bothnia. Differing from the results in the central Baltic Sea in previous years, spatial changes in DOP were not only influenced by BAP but also by the

refractory DOP.

Summing up, our investigations give first data about concentrations of the bioavailable fraction of DOP for the Baltic Sea which has to be taken into account if nutrition and possible limitation of phytoplankton growth is evaluated.