English summary

In the Danish marine monitoring programme, UV oxidation has replaced oxidation by autoclaving since 2010 for measurements of total nitrogen (TN) and since 2016 for measurements of total phosphorus (TP). UV is believed to be less efficient for oxidation of organic matter and therefore the introduction of this oxidation method might have introduced a general bias in TN and TP measurements. Since the oxidation method only affects the organic part of TN and TP, comparison of methods was carried out on concentrations of organic nitrogen (ON) and organic phosphorus (OP).

The potential bias was investigated by comparing monitoring data (1992-2016) from open-water stations in the Danish Straits that have shared monitoring between Denmark, Germany and Sweden. Country-specific data show diverging trends for Danish data after the shift in oxidation methods for both TN and TP, strongly indicating less efficient oxidation with the UV method. The change of analysis method for TP in Sweden also introduced a significant shift, and similar shift may be present in German data as well.

In order to analyse the difference between UV and autoclave oxidation, a total of 50 samples were collected in October 2017 and subsampled for TN and TP analyses with the two oxidation methods at three different laboratories, although only one laboratory performed both oxidation methods for TN and no laboratory performed both oxidation methods for TP. Analyses of these data clearly document an underperformance of the UV oxidation method.

ON concentrations were on average 16% lower when measured with UV oxidation compared to autoclave oxidation, but the relative underestimation with UV oxidation was not constant for all samples, but varied with both salinity and sampling depth of the sample, reflecting that the efficiency of the UV method depends on the degradability of the organic material, which depends on the given type of water mass, UV exposure and production of fresh organic matter.

For OP concentrations, it was not directly possible to discriminate the effect of oxidation method from laboratory effect. Higher OP concentrations were measured with UV oxidation in the lower range of measurements and higher OP concentrations were measured with autoclave oxidation in the higher range of measurements. In addition to lower oxidation efficiency with the UV method, this unexpected pattern suggests that interference from chlorine gas, which develops during autoclave oxidation, with the TP measurement was not accounted for.

It is possible to adjust for the systematic bias introduced with UV oxidation for TN, but since the present data do not fully encapsulate all variations related to e.g. season and type of water mass, a larger set of data would likely increase the precision. For TP, the analysis issues with both UV and autoclave oxidation need to be resolved before any adjustments are considered.