

Potential risk of organic micro pollutants on marine phytoplankton in the greater North Sea: integration of modelling and experimental approaches

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A complex chemical cocktail, with unknown composition and concentrations, is present in marine waters. Although the awareness of the vulnerability of marine ecosystems to pollution-induced changes increased, the ecotoxicological effects of chemical pollutants on marine ecosystems are poorly understood. Even in intensively monitored regions such as the North Sea, current knowledge of the ecotoxicological effects of chemicals is limited to few (priority) substances and few (model) species. To partly address this knowledge gap, in the present work it was assessed how marine ecosystems respond to the presence of organic chemicals. By analysing existing data and performing laboratory experiments, ecotoxicological effects of organic chemicals to marine organisms and ecosystem functions were quantified. Specific aims of this work were: (1) to infer spatiotemporal trends of concentrations of organic chemicals; (2) to investigate the impact of primary and secondary emissions on the spatiotemporal trends of organic chemicals; (3) to examine the partitioning of organic chemicals in different environmental compartments; (4) to assess the potential ecotoxicological effect of realistic mixtures of organic chemicals on marine phytoplankton species; and (5) to quantify the relative contribution of organic chemicals to the phytoplankton growth dynamics.

Spatiotemporal trends of polychlorinated biphenyl (PCB) concentrations were inferred based on an extensive set of concentrations monitored between 1991 and 2010 in sediments of the Belgian Coastal Zone (BCZ) and the Western Scheldt. The time trends unravelled two to three-fold decreases of the PCB concentrations in the BCZ during the last 20 years. In the Western Scheldt estuary, time trends were spatially heterogeneous and not significantly decreasing. These results demonstrated that international efforts to cut down emissions of PCBs have been effective to reduce concentrations in open water ecosystems like the BCZ but had little effect in the urbanized and industrialized area of the Scheldt estuary. Most likely, estuaries were subject to secondary emissions from historical pollution.

The spatiotemporal trends of PCB concentrations in the Belgian marine waters were confirmed at larger spatiotemporal scales. To do so, multidecadal field observations (1979–2012) in the North Sea and Celtic Sea were analyzed to characterize the spatiotemporal concentrations of PCBs in mussels (*Mytilus edulis*) and in sediments. Decreasing interannual PCB concentrations were found in North Sea sediments and mussels. In addition, interannual changes of PCB concentrations were separated from seasonal variability. By doing so, superimposed to the generally decreasing interannual trends, seasonally variable PCB concentrations were observed. These seasonal variations were tightly coupled with seasonally variable chlorophyll *a* concentrations and organic carbon concentrations. Indeed, the timing of phytoplankton blooms in spring and autumn corresponded to the annual maxima of the organic carbon content and the PCB concentrations in sediments. These results demonstrated the role of seasonal phytoplankton dynamics (biological pump) in the environmental fate of PCBs at large spatiotemporal scales. The latter was a novel result since the working of the biological pump was never assessed before based on field data collected at the scale of a regional sea and in multiple decades.

Despite the generally decreasing spatiotemporal trends of PCBs, it was not clear whether current concentrations (still) pose a risk to marine ecosystems. Therefore, the spatiotemporal trends were used to assess the ecological risk of PCBs to marine life in the North Sea and Celtic Sea. To do so, PCB concentrations were compared with environmental assessment criteria (EAC). It was found that the potential ecotoxicological risk of PCBs changed considerably over time and in space. Risk quotients (RQs) of PCBs in marine sediments primarily depended on the location of the monitoring site, i.e. the closer to the coast, the higher the RQ. Especially in summer, when PCB concentrations in sediments are high, PCBs present in marine coastal sediments may have posed an environmental risk. By contrast, RQs in mussel depended first on the interannual changes of PCB concentrations. At present, in the Celtic Sea, RQs in mussels are below the value of 1, suggesting no potential environmental risk. In the North Sea, however, PCBs in mussels may still exceed the prescribed

environmental quality criteria. Overall, it was demonstrated that the spatiotemporal variability in PCB concentrations should be considered in future environmental risk assessments.

Comparing concentrations of chemicals with quality thresholds (e.g. EAC) only suggests a potential ecological risk. Therefore, if risk quotients exceed the value of 1, additional assessments are recommended. Hence, additional experimental studies were performed in which a marine diatom was exposed to a realistic mixture of organic contaminants. To do so, passive samplers were used to achieve exposure to realistic mixtures of organic chemicals close to ambient concentrations. The main conclusion was that organic chemicals present in Belgian marine waters did not affect the intrinsic growth rate of *Phaeodactylum tricornutum*. The relative contribution of several environmental factors to the growth of *P. tricornutum* was examined and it was found that natural drivers such as nutrients regime, light intensity and temperature explained about 85% of the observed variability in the experimental data. The main effect of organic chemicals to the growth of *P. tricornutum* was limited to about 1%. In this context, caution is needed prior to extrapolating these results to field conditions. In the present research, results were obtained under laboratory controlled conditions with one single species and thus neglecting possible species interactions. Therefore, it is suggested to assess the validity of the results in a mesocosm experiment (including multiple species and different trophic levels) or under field conditions.

It was not realistic to use only one algal species to represent the ecotoxicological effects of organic chemicals on the entire phytoplankton community. Therefore, an ecosystem model was used to assess the potential adverse effects of organic contaminants on the total primary production. To do so, we modelled phytoplankton dynamics using four classical drivers (light and nutrient availability, temperature and zooplankton grazing) and tested whether extending this model with a chemical-induced growth limitation term improved the model fit. As the inclusion of monitored concentrations of PCBs and pesticides did not lead to a better model fit, it was suggested that the chemical-related growth limitation of marine phytoplankton in the North Sea and the Kattegat was small compared to the limitations caused by the classical drivers. The inferred contribution of organic chemicals to phytoplankton growth limitation was about 1% in Belgian coastal waters, but in the Kattegat the organic chemicals explained about 10% of the phytoplankton growth limitation. These results suggested that there are regional differences in the contribution of organic chemicals to the phytoplankton growth limitation.

This dissertation evaluated the potential risk of organic micropollutants in the marine environment. By integration of existing monitoring data, experimental data and advanced statistical analyses, it is shown that the spatiotemporal variability of PCB concentrations should be considered in future environmental risk assessments and that ambient concentrations of the organic chemicals present are not major drivers of phytoplankton growth. Concentrations of PCBs and pesticides have generally decreased over time in open waters. In coastal waters and in estuaries, however, concentrations remained relatively unchanged. These results demonstrate that international efforts to decrease emissions of PCBs have been effective to reduce concentrations in open water ecosystems, but had little effect in urbanized and industrialized estuaries. The latter is reflected in the relatively high risk quotients (>1) close to the coast. Based on the outcome of the traditional risk assessment, two extra analyses, one model-based approach and one laboratory-based experiment, were performed. Despite the fact that the risk assessment identified a potential ecotoxicological effect of organic chemicals, neither the lab-based study, nor the model-based study indicated that organic chemicals have a major ecotoxicological effect on marine phytoplankton. By contrast, it was demonstrated that phytoplankton, by means of the biological pump, is an important driver in the fate of organic chemicals. The latter is a novel result since the effectiveness of the biological pump was never assessed before based on field data collected at the scale of a regional sea in multiple decades. Overall, natural factors such as nutrients, temperature, light availability and zooplankton grazing are much more important drivers of the marine phytoplankton growth than organic chemicals. In future research, the validity of these conclusions should be further assessed for other substances, other species and higher trophic levels.