Atmospheric deposition of organic contaminants into the North Sea and the western Baltic Sea

Summary

The aim of this study was the assessment of the exchange processes of organic pollutants between the marine atmosphere and the surface seawater of the German EEZ, the wider North Sea and the Baltic Sea with emphasis upon the occurrence and contribution of atmospheric deposition to the seawater contamination. 87 organic pollutants, routinely monitored as surface seawater contaminants by the BSH, were targeted in this study. Concentrations of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), currently used pesticides (CUPs), perfluorinated compounds (PFCs), organophosphorus / brominated flame retardants and pharmaceuticals were simultaneously quantified in the surface seawater and the marine atmosphere during two research cruises in the German EEZ in May/Jun. 2009 and May 2010 as well as during a further research cruise in the North Sea in Aug./Sep. 2009. Air samples of the gaseous mass fraction of the Baltic Sea atmosphere of April 2009 were provided by the University of Hamburg. Air samples were collected using high-volume active air samplers operated on the top deck of the respective research vessels. Furthermore, PUF disk passive air samples were exposed at an urban land based sampling site (Sülldorf/Hamburg) and at a rural coastal sampling site (Tinnum/Sylt) between October 2009 and December 2010, respectively. Moreover, PUF disks were installed at the FINO research platforms in the German EEZ in various heights above sea level. Seasonal and vertical fluctuations of atmospheric concentrations could be successfully monitored by passive air sampling providing further indications of sources, occurrences and distributions of the organic pollutants in the marine atmosphere. The application of standard active and passive air sampling methodologies at research ships required a continuing optimization and adaptation of the sampling equipment and sampler design to the extreme weather and working conditions at sea. Methods of sample preparation were developed and validated which allowed the reliable quantification of 87 organic pollutants from a single air sample (GFFs, PUF disks, PUF plugs, PUF/XAD-2/PUF adsorber cartridges). Estimations on wet deposition fluxes to the surface seawater were based on substance concentration levels in precipitation at Zingst (Baltic Sea) and Tinnum/Sylt (German EEZ/North Sea) provided by the Federal Environmental Agency of Germany for 2009 and 2010. Dry particulate fluxes were derived from the concentrations of organic pollutants in the particle associated mass fraction of the marine aerosol and an estimated deposition velocity of 0.02 cm/s.

All processes contributing to air-sea exchange of organic pollutants, i.e. atmospheric deposition and volatilisation from the surface seawater could be documented in this study. The most frequently observed exchange mechanism of the target analytes was the atmospheric deposition. A significant contribution of atmospheric deposition to the surface water contamination of the open sea could be demonstrated for phenanthrene, fluorene, lindane, dieldrin, *p,p´*-DDE and CUPs. While the spatial distribution of most target compounds in the surface seawater appeared to be dominated by riverine input and subsequent transport with sea currents, increased surface water concentrations beyond river plumes and/or characteristic changes in distribution patterns with season were found and might be ascribed to the influence of atmospheric deposition. The occurrence and widespread distribution of organic contaminants in the marine atmosphere as well as seasonally extended atmospheric concentrations were in agreement with these perceptions: For example, fluorene and phenanthrene, the main PAH components in the marine atmosphere, displayed almost constant or only slightly decreasing surface water concentrations throughout the German EEZ unaffected by the suspended particulate matter and riverine fresh water content. In contrast, other PAH components occurring in lower atmospheric abundances revealed strong concentration gradients from the coastal waters to the open sea. Similar observations are made for the DDT metabolites. Although *p,p´*-DDD was quantified in higher concentrations than *p,p´*-DDE in the coastal surface waters, exclusively *p,p´*-DDE could be quantified in the central North Sea. This shift in distribution patterns pointed to an atmospheric deposition of *p,p´*-DDE, which was found to be the main DDT metabolite in the marine atmosphere. A further example was dieldrin. Dieldrin exhibited increased surface water concentrations in the south-central part of the North Sea (Dogger Bank region), which could be excluded to originate from riverine input due to the prevailing sea currents. However, elevated atmospheric concentrations of

dieldrin were observed in air masses originating from central England above or in proximity to this sea region. These might be possible sources of dieldrin to the Dogger Bank. In particular, the CUPs exhibited highest variability in atmospheric concentrations, which were consistent with the seasonal changes of their concentrations in surface seawater. Correlations in the seasons of highest atmospheric abundances and highest concentrations in the surface seawater, in particular in regions beyond riverine input, were assumed to originate rather from a fast atmospheric transport and subsequent deposition than from the comparable slower riverine transport and distribution along the sea currents. Such correlations were observed for a variety of the targeted CUPs: Terbuthylazine was found to be the currently most extensively used triazine herbicide with a main application season in May/June. Metolachlor exhibited the same main application season. The phenoxyethanoic acids (24-D, MCPA) exhibited highest air and water concentrations in spring, whereas pendimethalin, trifluralin and metazachlor had a main application season from September to October. Furthermore, anomalous distribution patterns in the surface seawater as observed for trifluralin and pendimethalin, which were incoherent with the prevailing sea currents and riverine sources, but consistent with their seasonally increased atmospheric abundances, gave evidence that atmospheric deposition was a major source of surface seawater pollution. Other CUPs exhibiting a short persistence in the environment like pirimicarb and the organophosphate herbicides were scarcely detected in the marine atmosphere and the surface seawater. However, their sporadic occurrence in air and water even at remote sampling sites might indicate an atmospheric deposition to the surface seawater. Air mass history indicated that advection of contaminated air masses from the continent resulted in a widespread distribution of organic pollutants in the marine atmosphere and deposition to the surface seawater. This was additionally suggested by the vertical pollutant profiles obtained from the FINO stations, which displayed an almost even distribution with height. Air-sea exchange close to equilibrium was documented for some “classical” OCPs like hexachlorobenzene and α-HCH and was even assumed for the low molecular weight PCBs (CB28 and CB 52) in the Baltic Sea environment. Besides, hexachlorocylcohexane isomers (α-HCH, lindane) and fluorene, a low molecular weight PAH, displayed a significant trend of net volatilisation from highly contaminated coastal waters (river plume of the Elbe) in summer. The targeted pharmaceuticals and PFCs were scarcely detected in the marine atmosphere in concentrations close to or below the respective LOQs. In consequence, the contribution of atmospheric deposition to the surface seawater contamination by these pollutants was expected to be negligible. In contrast, the continuous and widespread occurrence of PFOA in the marine atmosphere independent of air mass history indicated a marine particle source, such as sea spray (occurring in wave breakings and during precipitation). Organophosphorus flame retardants were found to be major contaminants of the marine atmosphere. Although surface water data was not available, the increased concentrations and their predominant occurrence in the particle associated mass fraction was indicative of an extended atmospheric deposition to the surface seawater.