6 Summary

Within the first part of the present work, a specially designed filtration/extraction device was used for the extraction of large volume water samples from different parts of the North Sea. The choice of solid-phase extraction by means of a polymeric sorbent enabled the extraction of a broad range of organic compounds from the water phase, far beyond the scope previously covered in analytical marine chemistry by liquid/liquid extraction or by the use of alkyl-silica based solid-phase sorbent. The thus obtained extracts were screened for the presence of organic contaminants by means of gas chromatography-mass spectroscopy. In the course of these investigations PAHs, PCBs, alkylbenzenes, chlorobenzenes, chloronitrobenzenes, bis(dichloropropyl)ethers, chloroanilines, dichlobenil, HCHs, and triazine herbicides were detected. Furthermore, a number of compounds was identified, which had not been reported before to be present in the water of the North Sea, including 1-chloronaphthalene, dichloropyridines, *N*-ethyltoluidine, DEET, tris(chloropropyl)phosphates, triphenylphosphine oxide and presumably biogenic mono-, di-, and tribromoindoles. The detection of caffeine and some pharmaceutically active compounds as for example propyphenazone, carbamazepine and clofibric acid was of special interest, since no information had been available before on the occurrence of this class of substances in marine ecosystems.

Based on the results of the GC-MS screening of the North Sea water extracts the applied extraction and determination method was validated for the quantification of a set of selected target analytes. This resulted not only in high recovery rates for the polar neutral analytes. Also the investigated acidic compounds such as clofibric acid, ibuprofen and diclofenac were recovered at remarkable 40 % or higher under the given conditions (pH 8.3). Characteristic distribution patterns of the target analytes were obtained by the application of the method to North Sea water samples. Caffeine was detected in relatively high concentrations (2 - 16 ng/L) at all stations. The distribution pattern points to rivers as important sources, with indications for additional contributions from shipping and offshore installations of the oil and gas industry. Clofibric acid, active metabolite of the lipid lowering agents clofibrate and etofibrate, was clearly detectable in the German Bight and off the Danish and Norwegian coasts. Concentrations of this compound ranged between 0.3 and 1.3 ng/L in these areas and thus in the same order of magnitude as classical organic pollutants, e.g., γ-HCH. In the Central North Sea and off the British east coast clofibric acid was either not detected or present below the quantification limit. The rivers Elbe and Rhine appear to be major sources for this compound. The insect repellent DEET showed a distribution pattern similar to that of clofibric acid at concentrations around 1 ng/L in the German Bight. In the case of DEET, the Rhine seems to be more relevant for the input into the North Sea than the

Elbe. Among the investigated pesticides, the distribution of the herbicide dichlobenil is noteworthy. Elevated concentrations (1.1 - 1.4 ng/L) were only observed at the sampling stations influenced by the River Rhine plume, while concentrations at all other stations ranged between 0.3 and 0.4 ng/L. This may be an indication for the contribution of atmospheric inputs to the contamination of the North Sea with this compound, which remains to be verified by the investigation of deposition samples. Further pesticides (e.g., metolachlor and terbuthylazine) showed a distribution pattern typical for predominant riverine input with highest values in the German Bight and along the Danish and Norwegian west coasts and concentrations that were non-detectable or below the limit of quantification in the Central North Sea and off the British east coast. Out of the six isomers of dichloropyridine, which have not been reported as contaminants of the aquatic environment to date, four isomers were identified in samples from the Elbe estuary. 2,6-Dichloropyridine was the dominant isomer, present in a concentration of 8.8 ng/L. In the North Sea, only the 2,6-isomer was detected occasionally, in most cases below or around the quantification limit of 0.1 ng/L. The observed distribution pattern of this compound does not allow unequivocal estimations of its sources, an atmospheric input in addition to the observed contribution of the River Elbe cannot be excluded. For the flame retardant tris(chloropropyl)phosphate first values for its distribution in the water of the North Sea were presented. Estimated concentrations calculated for the technical mixture ranged between 1 and 8 ng/L.

The second part of the present work focussed on the development and application of an analytical method for the simultaneous extraction of acidic, polar neutral and basic pharmaceuticals from environmental water samples at neutral pH. Under these conditions, recoveries of 70 - 100 % were obtained for most target analytes. Only the highly hydrophilic metabolite carboxy-ibuprofen, having a log Kow of -2.8 at pH 7 [109], showed an unsatisfactory recovery (30 %) under these extraction conditions. The developed method was applied to the determination of the concentrations of relevant pharmaceuticals (including some of their metabolites) as well as of caffeine in communal sewage and seawater from Tromsø/Norway and sewage and surface water from Hamburg/Germany. In Tromsø sewage caffeine proved to be a dominant component (concentration range 30 - 300 µg/L). Ibuprofen and its main metabolites hydroxy- and carboxy-ibuprofen were present in all samples in concentrations of up to 20 µg/L (sum of the three single compounds), while diclofenac, the antidepressants paroxetine, sertraline and fluoxetine as well as the ß-blocking agents propranolol and metoprolol were predominantly detected in sewage samples with contributions of hospital effluents. In seawater from the Tromsø area, exclusively caffeine and the compounds of the ibuprofen group were detected. Caffeine was measured in amazingly high concentrations. These were between 17 and 87 ng/L in the Tromsø-Sound and still just below 10 ng/L at the very sparsely populated coast of the open Arctic Ocean. Ibuprofen, hydroxy- and carboxy-ibuprofen were identified for the first time in seawater, their concentrations in the Tromsø-Sound reached values of up to 7.5 ng/L (sum of the three single compounds). Most of the target analytes were detected in surface water from Hamburg (river Elbe and lake Alster). In Elbe water, caffeine was determined in concentrations of 100 - 150 ng/L, clofibric acid 3 - 8 ng/L, ibuprofen 5 - 32 ng/L, hydroxy-ibuprofen 20 - 100 ng/L, carboxy-ibuprofen from below the quantification limit to 32 ng/L, diclofenac 30 - 70 ng/L, DEET 16 - 38 ng/L. The more lipophilic compound triclosan was only detected occasionally in the water phase (up to 4 ng/L). In the water of the lake Alster the concentrations of the investigated pharmaceuticals were generally lower compared to the Elbe (in the range of 2 - 25 ng/L), while the concentration of caffeine (176 ng/L) was slightly higher than in the river. The concentration of the herbicide mecoprop was even three-fold higher in lake water (22 ng/L).

An interesting aspect revealed the comparison of the relations of the concentrations of ibuprofen and its two main metabolites in the different types of investigated water samples. While in the non-biologically treated effluent of the Tromsø sewage treatment plant (STP) and in the influent of the Hamburg STP the relative amounts were comparable to those known from human urine (pharmacokinetic studies), deviations from this pattern were obvious in biologically treated sewage as well as in river water and seawater. These variations have to be attributed to the differences in transformability of the three compounds under the prevailing conditions in the different types of sampled water. The determination of the characteristic relative amount patterns may be a valuable tool for the elucidation of the environmental behaviour and fate of residues of pharmaceuticals in aquatic ecosystems. This holds especially when it is supplemented by the determination of enantiomeric ratios in the case of chiral compounds as for example ibuprofen, which may contribute information for a distinction between biotic and abiotic transformation.