

Abstract

Phosphororganic flame retardants and plasticisers are important contaminants in the aquatic environment. Whereas the non-chlorinated alkylphosphates were partly eliminated in wastewater treatment plants the amounts of the chlorinated flame retardants were hardly reduced. Thus these compounds are discharged into the aquatic environment by STP-effluents. The elimination efficiency of wastewater treatment depends on the one hand on the dimension of the respective STP and on the other hand on the treatment technique that is applied. The elimination was higher in larger STP (inhabitant equivalent values (IEV) 300,000-1,000,000) than in smaller ones (IEV below 100,000). Lower elimination rates were observed for the trickling filter plant that was sampled in comparison to the activated sludge plants. In degradation experiments of the selected organophosphates with activated sludge in batch reactors, bis-(2-chloroethyl) phosphate was identified as metabolite of tris-(2-chloroethyl) phosphate under aerobic conditions.

The selected organophosphate esters were detected in surface water that is used for drinking water purification. Thus it was studied if the drinking water quality is affected by these compounds. For this purpose samples from different waterworks in the Ruhr catchment area were analysed. Moreover the elimination efficiency of diverse treatment processes such as slow sand filtration, ozonisation and activated carbon filtration was studied. In the finished water the concentrations of the organophosphates were below the respective limit of quantification (LOQ).

The chlorinated alkylphosphates are very persistent in the aquatic environment as they have been detected and quantified in pristine waterbodies such as the German Bight and Lake Ontario. A reduction of these compounds in the German Bight was traced back to dilution effects only. The concentrations of the phosphororganic flame retardants in marine samples were one order of magnitude higher than for other contaminants such as herbicides and by-products of pesticide production. The non-chlorinated alkylphosphates have only been detected in the river Elbe plume. Similar results were obtained for samples of Lake Ontario.

As expected from the respective log K_{OW} values of the selected organophosphate esters the bioaccumulation of these substances in fish is low. The concentrations of tri-*n*-butylphosphate (*TnBP*), tri-*iso*-butylphosphate (*TiBP*), triphenylphosphate (*TPP*) and tris-(chloro*isopropyl*) phosphate *T*CPP in bream muscle from different sampling locations in Germany were in the lower ng/g range (dry weight). Tris-(chloroethyl) phosphate (*TCEP*), tris-(dichloro*isopropyl*) phosphate (*TDCP*), tris-(butoxyethyl) phosphate (*TBEP*) and ethylhexyldiphenylphosphate (*EHDPP*) were not detected in any fish sample. Moreover a temporal trend in the concentrations was observed. The sampling location seems to be an important factor that influences the detected levels of these substances in fish muscle as in the conurbation area higher amounts were detected than in riverine ecosystems.

For the extraction of the selected organophosphate esters from water samples liquid-liquid extraction (LLE) and solid phase extraction (SPE) has been applied. Fish samples were extracted by accelerated solvent extraction (ASE) in combination with different clean up steps (SPE on silica gel and size exclusion chromatography (SEC)). The different compounds were detected by gas chromatography mass spectrometry with electron impact ionization (GC-EI-MS). For quantification purposes the isotopic labelled internal standards tri-*n*-butylphosphate d_{27} (*TnBP* d_{27}) and triphenylphosphate d_{15} (*TPP* d_{15}) were used. *TPP* d_{15} was synthesized from phenol d_6 and phosphorus oxytrichloride. The empiric formula of the product was confirmed by electrospray high resolution time of flight mass spectrometry (ESI-HR-TOF-MS).

The metabolites bis-(2-chloroethyl) phosphate (*BCEP*), bis-(methyl, 2-chloroethyl) phosphate (*BCPP*) and bis-(butoxyethyl) phosphate (*BBEP*) were synthesized from phosphorus oxytrichloride and the respective alcohols chloroethanol, 1-chloro-2-propanol and butoxyethanol. For the control of the reaction the respective products were measured after derivatisation with trimethylsulphoniumhydroxide (*TMSH*) by GC-EI-MS and gas chromatography positive chemical ionisation mass spectrometry (GC-PCI-MS).