Behaviour of brominated and chlorinated flame retardants during drinking water treatment
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ABSTRACT

Flame retardants are chemicals that are added to plastic materials in order to prevent them from catching fire and to slow down the burning process. Due to the widespread occurrence of flame retardants in the environment, it can be expected that especially the more hydrophilic compounds already contaminate raw water resources of water utilities. In this paper results of laboratory-scale experiments on the behaviour of ten brominated and chlorinated flame retardants during different steps of drinking water treatment will be presented. The target compounds were selected based on their production volumes and physical-chemical properties. The final list includes 1- and 2-bromostyrene, 2,4- and 2,6-dibromophenol, tetrabromophthalic acid, tetrachlorophthalic anhydride, chlorendic acid, tris(1,3-dichloro-2-propyl) phosphate, tris(2-chloroethyl) phosphate (TCEP), and tris(1-chloro-2-propyl) phosphate (TCPP). The results obtained from the laboratory-scale experiments clearly indicate that from the selected flame retardants only 1- and 2-bromostyrene are well biodegradable under aerobic conditions whereas the other flame retardants under investigation turned out to be persistent. Flocculation with either iron or aluminium salts is not an efficient option for removal of the selected flame retardants. For 1- and 2-bromostyrene removal rates of ca. 50% can be achieved whereas for the other compounds removal rates are in the range of 10 to 30% even when dosing 50 mg/L of flocculation agent. Oxidation with either ozone or ozone/hydrogen peroxide proved also to be rather inefficient for removal of the flame retardants under investigation, even at elevated doses of oxidant of 10 mg/L. However, results showed that the selected flame retardants adsorb well onto activated carbon and thus GAC adsorption seems to be a promising option for their removal.

Key words | activated carbon filtration, drinking water, flame retardants, flocculation, ozonation, underground passage

INTRODUCTION

Flame retardants are chemicals that are added to plastic materials used in electrical and electronic equipment, in cars and in aircrafts, or to paints, textiles, and furniture in order to prevent those materials from catching fire and to slow down the burning process (World Health Organisation 1997). At present, four different classes of flame retardants are used by chemical industries: inorganic flame retardants as alumina or aluminium polyphosphates, halogenated flame retardants, organophosphorus compounds, and nitrogen-based flame retardants. The “Index of Flame Retardants”, an international guide to more than 1,000 products by trade name, chemical, application, and manufacturer, contains more than 200 commercial flame retardant chemicals (Ash & Ash 1997). Different flame retardants show different modes of action and inhibit different steps of the combustion process (Alaee et al. 2003). Halogens and all types of halogenated organic compounds are able to effectively capture free radicals which are formed during
the combustion process and which are essential for a flame to propagate. Fluorinated compounds, however, are too expensive and, except for special cases, less effective than other halogenated compounds due to the strong C-F bond. Iodinated compounds on the other hand are also rather expensive and at the same time too unstable to be effective. Thus, mainly brominated and chlorinated flame retardants are of commercial relevance.

Due to their widespread use, flame retardants are released into the environment, either during manufacturing, transport, use, or disposal and can affect air, water and soil (Jansson et al. 1987). It can be expected that especially the more hydrophilic compounds already contaminate raw water resources of water utilities. However, although a lot of research has been performed in this field during the last years, only limited information is available about the behaviour of chlorinated and brominated flame retardants during drinking water treatment. Within a research project funded by the Water Research Foundation the relevance of brominated and chlorinated flame retardants and possible degradation products for drinking water utilities has been assessed. The initial selection of the flame retardants and degradation products was based on a literature search on the composition of fire retardants. During this literature search, a total of 118 brominated and chlorinated compounds that are used or have been used as flame retardants have been reviewed and 33 of them were selected for further investigations. For these 33 compounds the partition between solid and aqueous phase was determined for three different soil types following the procedure described in the OECD Technical Guideline 106. Based on their partition coefficients ten flame retardants, which exhibited $K_{OC}$ values below 2,000 cm$^3$/g and thus are not expected to predominantly adsorb onto particulate matter, were selected for investigating their behaviour during different steps of drinking water treatment. The removal of 2,4- and 2,6-dibromophenol, 1- and 2-bromostyrene, tetrabromophthalic acid, chlorendic acid, tetrachlorophthalic anhydride, tris(1,3-dichloro-2-propyl) phosphate (97% purity), tris(2-chloroethyl) phosphate (98.5% purity) and tris(1-chloro-2-propyl) phosphate (99.5% purity) were purchased from Dr. Ehrenstorfer (Augsburg, Germany), tetrabromophthalic acid (98% purity), 1-bromostyrene (90% purity), 2-bromostyrene (97% purity) and tetrachlorophthalic anhydride (98% purity) from ABCR (Karlsruhe, Germany), and chlorendic acid (99% purity) from TCI Europe (Eschborn, Germany). From all target compounds, 10 g/L stock solutions in acetone (analytical grade, Merck Eurolab GmbH, Darmstadt, Germany) were prepared. These stock solutions were stored in a refrigerator at −18°C and proved to be stable for at least 12 months. All solvents used for sample preparation or as mobile HPLC phase as well as hydrochloric acid for pH adjustment and sodium chloride were of analytical grade and were also obtained from Merck Eurolab GmbH.

**METHODS**

**Chemicals**

2,4-Dibromophenol (97.5% purity), 2,6-dibromophenol (99.5% purity), tris(1,3-dichloro-2-propyl) phosphate (97% purity), tris(2-chloroethyl) phosphate (98.5% purity) and tris(1-chloro-2-propyl) phosphate (99.5% purity) were purchased from Dr. Ehrenstorfer (Augsburg, Germany), tetrabromophthalic acid (98% purity), 1-bromostyrene (90% purity), 2-bromostyrene (97% purity) and tetrachlorophthalic anhydride (98% purity) from ABCR (Karlsruhe, Germany), and chlorendic acid (99% purity) from TCI Europe (Eschborn, Germany). From all target compounds, 10 g/L stock solutions in acetone (analytical grade, Merck Eurolab GmbH, Darmstadt, Germany) were prepared. These stock solutions were stored in a refrigerator at −18°C and proved to be stable for at least 12 months. All solvents used for sample preparation or as mobile HPLC phase as well as hydrochloric acid for pH adjustment and sodium chloride were of analytical grade and were also obtained from Merck Eurolab GmbH.

**Analytical method**

**Sample pre-treatment**

For the analysis of the flame retardants investigated a new method was developed, optimized and validated. This method is based on liquid-liquid extraction of the target analytes from 200 mL water sample with 25 mL methyl tertiary butyl ether (MTBE). The pH of the samples is adjusted to 2 by addition of hydrochloric acid. Twenty five grams of sodium chloride are added to each water sample to increase extraction yield. After extraction and separation of the organic phase the solvent volume is reduced in a stream of nitrogen to a final volume of 200 μL for injection into the gas chromatography/mass spectrometry (GC/MS) system.

**Instrumentation**

GC analysis was carried out with an 6,890 gas chromatograph from Agilent Technologies (Waldbronn, Germany) equipped with a split/splitless injector. Detection was done...
by an Agilent MSD 5973N mass spectrometer. A fused silica capillary column DB 5-MS (30 m x 0.25 mm I.D., 0.1 μm film thickness, purchased also from Agilent Technologies) was used for the separation of the analytes. Injection volume was 2 μL (splitless) and injector temperature was set constantly at 260°C. Helium from Air Liquide (Düsseldorf, Germany) with a purity of 99.9990% was used as carrier gas with an inlet pressure of 54.5 kPa corresponding to a flow-rate of 1.0 mL/min. The column oven temperature programme started at 50°C (held for 1 min), set at 5°C/min to 100°C (held for 1 min), set at 40°C/min to 220°C (held for 3 min), set at 25°C/min to 300°C and held isothermally at 300°C for another 8 min. Transfer line was set at 280°C, quadrupole temperature at 150°C, and source temperature at 230°C. To obtain maximum sensitivity, the quadrupole mass spectrometer was run in the SIM (single-ion monitoring) mode. For selection of fragment masses, full-scan spectra from m/z = 50 to m/z = 400 were recorded for each of the flame retardants.

**Method validation**

Method validation focused on the determination of recovery rates, repeatability data, limit of detection (LOD) and limit of quantification (LOQ). It could be shown that recoveries were above 80% and method variation for a 7-fold analysis was below 10% for all flame retardants under investigation. Furthermore, LOD values below 0.03 μg/L and LOQ values below 0.1 μg/L were obtained.

**Laboratory-scale experiments**

**Biodegradation**

The experimental set-up for the investigation of microbial degradation of the target compounds during underground passage or riverbank filtration consisted of a closed-loop test system which was filled with 10 L of water from river Rhine. In recent years this experimental method has been adapted and optimized for the study of the behaviour of single substances during bank filtration at environmental concentrations (Karrenbrock et al. 1999). The river water was slowly pumped over a carrier material of sintered porous glass beads to enhance biofilm formation and to thus accelerate microbial degradation. The flow rate was always adjusted to a value between 10 and 15 mL/min. Continuous aeration with ambient air guaranteed aerobic conditions throughout the experiments. To avoid any interference between the degradation processes, a separate experiment was performed for each of the flame retardants. For the initial experiments, the river water was spiked with the target compounds at a concentration level of 10 μg/L and samples were taken at regular time intervals to follow the variations in concentration of the spiked compounds. Two hours after spiking, a sample was taken to determine the initial concentration. To investigate the impact of concentration, an additional experiment was performed at a spiking level of 1 μg/L which was closer to the levels found (or expected) in the environment. For this experiment, a mixture of flame retardants was used.

**Coagulation/flocculation/sedimentation**

The removal of the flame retardants by flocculation and sedimentation was investigated in a non-continuous laboratory-scale test, the so-called Jar test (DVGW 1998). For this test, a flocculator with well-defined geometry was used and the stirring conditions were properly adjusted to simulate real-world conditions. All experiments were performed with tap water from Karlsruhe and surface water from river Rhine. The ten selected flame retardants were dosed at a concentration level of 10 μg/L, each. Polyaluminum chloride and iron chloride were tested as flocculants at concentration levels of 5, 10, 25, and 50 mg/L (calculated as Fe and Al, respectively). Following addition of the flocculant, the pH was adjusted to 6 by addition of caustic soda. Stirring conditions were: 250 min⁻¹ for 30 s, 50 min⁻¹ for 5 min, and 25 min⁻¹ for another 10 min. Then the flocs were allowed to settle for 30 min and pH and turbidity were measured in the supernatant. After sedimentation, the supernatant was filtered through a 0.45 μm membrane filter and the filtrate was analyzed for residual amounts of iron and aluminum, respectively and for concentrations of the spiked flame retardants. For determination of the initial concentration of the spiked flame retardants one experiment without dosage of flocculation agent was included in each set of experiments.
Oxidation

Ozonation experiments were performed in batch mode. In a 5 L glass vessel defined amounts of ozone stock solution prepared in a separate bubble column were added to spiked solutions of the flame retardants and metabolites under investigation. The concentration decline of the target compounds was determined by taking samples after defined time intervals and analyzing them for the parent compounds. The residual ozone concentration was also determined. Experiments were performed with tap water and river water. For the tap water experiments the pH value was adjusted to 5, 7, and 9 by addition of buffer solutions while the river water experiments were performed at the original pH of 8.2. By adjusting the pH for the tap water experiments the stability of the target flame retardants towards molecular ozone (pH 5) and hydroxyl radicals (pH 9) could be investigated. All experiments were performed with mixtures of the 10 selected flame retardants which were spiked at a concentration of 1 mg/L, each. Initial ozone dose for these experiments was 1 mg/L. Additionally experiments with some single compounds were performed in order to check whether any cross effects between the compounds in the mixture affect the results. All experiments with single compounds, however, confirmed the results of the experiments with the mixtures and thus cross-effects can be excluded.

Activated carbon adsorption

To investigate the effect of activated carbon on the removal of the selected flame retardants adsorption isotherms with powdered activated carbon were determined. All experiments were performed for single compounds in deionized water as well as river water. River water was used as matrix to study the impact of natural organic matter on the adsorption (Sacher et al. 2001). For the determination of the isotherms, samples of 200 mL water were spiked with each flame retardant at an initial concentration of 100 μg/L. This high initial concentration was necessary to follow the concentration decline due to adsorption of the spiked compound for at least two orders of magnitude. Different quantities of a coal-based powdered activated carbon of F300 type were added. As for most of the experiments the activated carbon had to be added in small portions (i.e. carbon concentrations below 10 mg/L) a suspension was used. This suspension of powdered activated carbon was prepared at a concentration of 0.2 g/L. After the addition of the charcoal the mixture was shaken for 24 h. Finally the water samples were filtered through 0.45 μm polycarbonate filters and analyzed for the spiked compound. Evaluation of the data was done according to the equation of Freundlich which gives a straight line if the loading of the coal q is plotted as a function of the residual concentration c in double logarithmic scale (Freundlich 1906). From such a plot, the Freundlich parameters K and n can be determined. The higher the K value the better the adsorbability of the respective compound.

RESULTS AND DISCUSSION

Biodegradation

The results of the experiments for microbial degradation at an initial concentration of the selected flame retardants of 1 μg/L are presented in Figure 1. It can be easily seen from the diagrams that only the two bromostyrene isomers show a distinct decline in concentration while all other flame retardants under investigation do not exhibit any significant change in concentration within 30 days. The variations in concentration observed for some of the compounds are mainly due to analytical uncertainties. For few compounds a limited solubility in water and thus a non-homogenous dispersion of the (highly concentrated) stock solution at the beginning of the experiments might also contribute to the observed variations. For all flame retardants under investigation, the results obtained at the spiking level of 10 μg/L were comparable to the results obtained at 1 μg/L. Additional efforts were taken to identify possible degradation products of the two bromostyrene isomers. However, analysis for styrene was negative and a GC/MS screening did not yield any significant peak. Thus, it can be concluded that the degradation products formed from the bromostyrene isomers are either not extractable by organic solvents or not amenable to GC analysis.

Coagulation/flocculation/sedimentation

The results of the flocculation experiments with iron and aluminum salts clearly showed that none of the flame
Figure 1 | Microbial degradation of flame retardants at a spiking level of 1 µg/L.
retardants under investigation was completely removed during the flocculation process, even after dosing of 50 mg/L flocculation agent. Best removal efficiencies were obtained for the two bromostyrene isomers, where removal rates of more than 50% could be achieved. Comparing the removal rates with iron and aluminum salts, slightly better results were obtained for the iron salts. In tap water flocculation with iron salts yielded removal rates of 10 to 30% for most of the flame retardants under investigation. Maximum removal rates were already obtained with a dosage of 10 mg/L Fe and when dosing higher amounts of flocculation agent no significant improvement could be achieved. For the two bromostyrene isomers removal rates with iron salts in tap water were between 50 and 70%. In river water lower removal rates were determined being in the range of 10% for most of the flame retardants (and ca. 30% for the bromostyrenes). This reduction in removal efficiency can be explained by the competition with natural organic matter in river water compared to tap water. Also for the flocculation with aluminum salts higher removal efficiencies were observed in tap water compared to river water. In tap water removal rates for most of the compounds were between 10 and 20% whereas in river water most of the removal rates were below 10%.

Oxidation

Figure 2 displays as an example the results which were obtained for the bromostyrene isomers, one bromophenol isomer, chlorendic acid and tetrabromophthalic acid for the tap water experiments at a pH at 7.

From these diagrams it can be observed that the flame retardants exhibit a diverse reactivity towards ozone: The bromostyrene isomers as well as the two bromophenol isomers (2,4- and 2,6-dibromophenol) react rather fast with ozone and even after a reaction time of only 1 minute the mother compounds can not be detected any more. The other flame retardants do not show any significant variation in concentration and thus can be considered as persistent towards a reaction with ozone. As the ozone measurements proved, even after 30 minutes contact time a significant amount of residual ozone was present and thus the observed non-reactivity can not be explained by shortage of ozone. Comparing the results obtained for tap water at
pH values of 5, 7 and 9 and the river water experiments, no significant differences can be observed. In each matrix and at each pH, the bromostyrene isomers and the two bromophenols react rather fast with ozone (or hydroxyl radicals, depending on pH) while the other flame retardants are not affected in concentration at all. Additional experiments proved that even by application of elevated ozone doses or of advanced oxidation processes which stimulate the formation of hydroxyl radicals complete elimination of the persistent flame retardants could not be achieved. Comparable results for the chlorinated flame retardants were published recently by other researchers (Andresen & Bester 2006; Watts & Linden 2009).

Activated carbon adsorption

Table 1 summarizes the Freundlich parameters of the target flame retardants determined from the adsorption isotherms in deionized water and in river water.

From the data it can be seen that for deionized water the \( n \) values of the flame retardants under investigation are in a range between 0.3 and 0.8 while all \( K \) values are above 100. As a rule, compounds with \( K \) values above 100 can be regarded as well adsorbable onto activated carbon (Sontheimer et al. 1988). The Freundlich parameters which were determined in river water exhibit slight differences to the values in deionized water. \( K \) values for all flame retardants are lower in river water than in deionized water which can easily be explained by the competition to natural organic matter (NOM) in environmental waters. NOM is mainly composed of large molecules that compete for the adsorption sites on the coal and thus reduce the capacity of the coal for micro-pollutants like flame retardants. For the bromophenols an additional effect might be relevant which explains the large difference of \( K \) values in deionized water and river water. For phenolic compounds adsorption depends on pH as adsorbability of the phenolate ion which is the dominant species at higher pH values is lower than the adsorbability of the phenol molecule. Consequently the higher pH in river water compared to deionized water leads to a lower adsorbability of the bromophenol isomers and thus a lower \( K \) value. However, even in river water the \( K \) values of all flame retardants are above 45, indicating still a good adsorbability of the target compounds.

CONCLUSIONS

The results obtained from the laboratory-scale experiments clearly indicate that the options for removal of brominated and chlorinated flame retardants during drinking water treatment are limited. Based on the results of this investigation, only the two bromostyrene isomers are well biodegradable whereas the other flame retardants are persistent under aerobic conditions and thus underground passage can not be regarded as a good option for the removal of these compounds. The same is true for the

<table>
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<th>Compound</th>
<th>Deionized water</th>
<th>River water</th>
</tr>
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<tr>
<td></td>
<td>( n )</td>
<td>( K )</td>
</tr>
<tr>
<td>1-Bromostyrene</td>
<td>0.72</td>
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<td>2-Bromostyrene</td>
<td>0.48</td>
<td>1,699</td>
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<td>2,4-Dibromophenol</td>
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<td>2,6-Dibromophenol</td>
<td>0.81</td>
<td>2,485</td>
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<tr>
<td>Chlorendic acid</td>
<td>0.61</td>
<td>353</td>
</tr>
<tr>
<td>Tetrabromophthalic acid</td>
<td>0.39</td>
<td>292</td>
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<td>Tetrachlorophthalic acid</td>
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<td>Tris(2-chloroethyl) phosphate (TCEP)</td>
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<td>249</td>
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<td>Tris(1-chloro-2-propyl) phosphate (TCPP)</td>
<td>0.45</td>
<td>504</td>
</tr>
<tr>
<td>Tris(1,3-dichloro-2-propyl) phosphate</td>
<td>0.80</td>
<td>3,776</td>
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coagulation/flocculation/sedimentation process with either iron or aluminum salts. For 1- and 2-bromostyrene removal rates of ca. 50% can be achieved whereas for the other selected compounds removal rates are in the range of 10 to 30% only even when dosing 50 mg/L of flocculation agent. Oxidation with ozone leads to a good removal of the bromostyrene isomers and the bromophenol isomers while it proved to be rather inefficient for the removal of the other flame retardants under investigation. Fortunately, the laboratory-scale experiments indicate that all of the selected flame retardants adsorb well onto activated carbon and thus GAC adsorption appears to be a promising option for their removal. However, additional column tests need to be performed in order to take into account kinetic effects which might especially be relevant for larger molecules. Furthermore, the experiments have to be complemented by full-scale measurements in order to confirm the results obtained in laboratory-scale.

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REFERENCES


