Comparative GC/MS and LC/MS detection of hexabromocyclododecane (HBCD) in soil and water samples

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Introduction

Hexabromocyclododecane (HBCD) is a crucial additive flame retardant (FR) for FR Polystyrene insulation foams (both expandable (EPS) as well as extrudable polystyrene (XPS)), polystyrene masterbatches and textile FR coatings. The total consumption of HBCD within the European Union (EU) is estimated to be about 10,000 tons out of 16,700 worldwide per year[1]. The technical HBCD product usually is a mixture of the three diastereoisomers α-, β- and γ-HBCD with the γ-isomer as main component. Compared to other flame retardants only few data on HBCD levels in the environment have been published [e.g. 2, 3, 4].

BSEF (Bromine Science and Environmental Forum) representing the major HBCD producers, launched, in coordination with user industries, a product-stewardship (PS) programme for the major brominated flame retardants, including HBCD. Objective of this voluntary industry PS programme is to minimise and continuously reduce environmental exposure.
As first step an environmental monitoring study in five EU member states was carried out for BSEF by the Dutch National Institute for Fishery Research (RIVO). These findings triggered the second step carried out by our institute; a plant emission monitoring programme at 7 representative user sites in five different EU member states, covering all known applications. Complementary to the efforts of BSEF, the EPS and XPS foam producers, associated within CEFIC (European Chemical Industry Council) carried out a similar monitoring programme under their own responsabilities.
Results from our study demonstrate that emission control of HBCD is both feasible, also for small/medium sized enterprises, the typical customer basket outside the EPS and XPS foam industry, and effective.

Within this study a series of soil and water samples from HBCD processing plants was analysed by GC/MS (LRMS-EI). Besides GC/MS, also liquid chromatography coupled to mass spectrometry (LC/MS) is often used for HBCD detection in

environmental samples. Whilst GC/MS only provides information about the total of the three HBCD isomers, LC/MS is able to selectively monitor and quantify the three components. On the other hand GC/MS usually has the advantage of a higher sensitivity[5,6].

In order to verify the GC/MS results and to check the comparability to LC/MS analytical data, five soil and five water samples showing a wide range of HBCD concentrations were analysed by using both techniques. The comparative analyses by means of LC/MS confirmed the HBCD identification and quantification of the GC/MS. The differences between the total HBCD results of the GC/MS and the LC/MS analyses were less than 24%. The γ- isomer proved to be the main HBCD diastereoisomer in the soil and water samples tested.

Methods and Material

All soil and water samples were taken by GfA at different HBCD processing plants in various European countries. Each soil sample was collected from an area of approximately 100 m² by taking 10 partial samples from the upper 0.1 m. The soil and water samples were collected in pre-cleaned amber glassware and kept cool for transport and storage. Soil samples were air-dried and sieved (mesh size 2 mm). According to international standards only the fraction < 2 mm was used for the analysis. Approximately 15 g of the fine fraction were Soxhlet-extracted by means of toluene for 12 hours. Water samples were filtrated for separation of suspended solid matter, if present. The filtrate was liquid/liquid extracted by means of toluene. After drying, the filter with the solid matter was Soxhlet-extracted by using the toluene from the liquid/liquid extraction of the aqueous phase. Consequently, the resulting raw extract covered both, the dissolved and the particle-bound HBCD of a water sample.

For the determination of HBCD by means of GC/MS an internal standard was added to an aliquot of the raw extract prior to the clean-up. Since no $^{13}C_{12}$-labelled HBCD standard was commercially available so far, $^{13}C_{12}$-labelled hexabromodiphenyl ether (hexa-BDE) was used as internal standard for the quantification of the HBCD isomers. The aliquot of the raw extract was treated with sulphuric acid and further cleaned-up by column chromatography using basic alumina. Finally, $^{13}C_{12}$-labelled heptabromodiphenyl ether (hepta-BDE) was added to the HBCD fraction as recovery standard. Recoveries of the internal standard were in the range of 100 $\pm$ 10 % for the soil and water sample analyses.

The gaschromatographic separation was performed on a 15 m non-polar HP-5 column. Details of the instrumental parameters can be seen from Table 1. As mentioned before, the non-polar GC columns used for the HBCD analyses are not able to separate the three diastereoisomers. Since the mass spectrometric detector also cannot distinguish between α-, β- and γ-HBCD, only the total of the three HBCD isomers can be determined. Examples of GC/MS chromatograms showing the HBCD peak of a calibration mixture and of a soil sample (S4) are presented in Figures 1a and 1b. The typical peak broadening due to the presence of the three diastereoisomers can be seen from both chromatograms.

For HBCD detection by means of GC/MS, the mass spectrometer was operated in the so-called EI-Mode (Electron Impact Mode) monitoring selected HBCD fragment ions ($[M\text{-}HBr]^+$-cluster) and molecular ions of the internal and the recovery standard. Identification of HBCD was verified by the retention time relative to the internal standard, by the isotope ratio and by monitored masses. Quantification was done via the internal $^{13}C_{12}$-labelled HexaBDE standard by means of relative response factors.

Since separate GC-injections of native α-, β- and γ-HBCD standards showed different response factors relative to the internal standard (up to 36% difference), mixtures containing 1:1:1 concentrations of α-, β- and γ-HBCD were prepared for calibration. This corresponds to the application of a mean HBCD response factor for the GC/MS analysis. The total HBCD content of the calibration mixtures varied between 25 and 5000 ng while the internal $^{13}C_{12}$-labelled HexaBDE standard was kept constant. The GC/MS calibration curve of total HBCD proved not to be linear. A quadratic calibration function was fitted to the calibration points and used for quantification. By applying GC/MS, the limits of quantification for total HBCD were in the range of 25 µg/kg for soil samples and 25 ng/l for water samples.

A series of method blanks, duplicate analyses and spike tests was performed for all kinds of matrices analysed within this study. Method blanks were all below the LOQs. Duplicate analyses showed differences in the HBCD values between 2 and 27 %. Portions of the raw extracts of 6 samples were spiked with similar HBCD amounts as detected in the previous analyses and analysed again. Recoveries of the spiked HBCD between 87 % and 118 % were found.

For verification of the HBCD detection in the soil and water samples by means of LC/MS, the cleaned-up extracts from the GC/MS analyses were used. For this purpose the solutions were evaporated to near dryness, re-dissolved in methanol and finally injected into the LC/MS system. Instrumentation and operation conditions can be seen from Table 1. Whilst the GC/MS analyses

were carried out by eurofins / GfA, Münster, the LC/MS analyses were performed by eurofins / WEJ, Hamburg.

Calibration functions were established by injection of 6 mixtures of equal proportions of α-, β- and γ-HBCD at different concentration levels. Since the LC system was able to chromatographically separate the three HBCD isomers, separate calibration curves were received for each of the HBCD compounds. The LC/MS calibration curves proved to be linear over the calibrated range (injection of 100 ng to 2000 ng per HBCD isomer). External quantification was applied in case of the LC/MS detection. Examples of LC/MS chromatograms of a HBCD calibration mixture and of the soil sample S4 are presented in Figures 1c and 1d. By applying LC/MS, the limits of quantification for total HBCD were in the range of 100 µg/kg for soil samples and 100 ng/l for water samples.

Table 1: GC/MS and LC/MS operation parameters for the detection of Hexabromocyclododecane (HBCD) in soil and water samples

	GC/MS	LC/MS
Instrumentation	Capillary gaschromatograph (HRGC) Hewlett Packard/Agilent 6890 coupled with low resolution mass spectrometer (LRMS) Hewlett Packard/Agilent 5973	Liquid Chromatograph / Mass Spectrometer Agilent 1100
Injection	PTV injection, 2 µl injection volume	20 µl injection volume
Column	HP-5 capillary column (Hewlett Packard) 15 m x 0.32 mm ID, film thickness: 0.25 µm	Develosil C30-UG-3
Temperature program / Gradient	90 °C (4 min) – 120 °C/min to 170 °C (2 min) - 7°C/min to 320 °C (8 min)	80 % methanol / 20 % H_2O linear gradient to 100 % methanol within 20 min
Ionization	Electron impact (EI), 70 eV	atmospheric pressure chemical ionization (APCI)
Detection	SIM (selected ion monitoring) Monitoring fragment ions of native HBCD, $[M\text{-}HBr]^+$ ion cluster	Scan Mode (scanned from 638 m/z to 642 m/z); Monitoring masses of native HBCD molecular ion cluster

Results and discussion

For the comparative detection of HBCD by different techniques, soil samples with total HBCD concentrations between 100 and 24,000 $\mu g/kg_{dm}$ were selected. Samples with higher concentrations resulted from areas within HBCD-processing plants close to an emission source. Soil samples with lower concentrations came from undisturbed areas or greenland at distances of 100 to 500 m down-

wind of the plants. Soil samples in case of which no HBCD was detected by means of GC/MS (e.g. from larger distances to the plants) were not included in the comparison.

The water samples which were selected for the comparative analyses showed total HBCD concentrations between 9 and 21,000 µg/l. The high HBCD values resulted from untreated process water before treatment in the plant-own waste-water facilities. Lower concentrated samples represent waste water released to the external waste-water system. All water samples were analysed including suspended particulate matter if present.

The results of the GC/MS and LC/MS analyses of the 5 water and 5 soil samples for HBCD are compared in Table 2. The LC/MS data are presented as total of the three HBCD isomers and as concentrations of the individual HBCD components. GC/MS only provides total HBCD data. For two soil samples the concentrations were below the calibration range and below the limit of quantification of the LC/MS system, so that the data cannot be compared to that of the GC/MS analysis. For the other soil and water samples the total HBCD values were in good agreement over the whole concentration range. Differences between the GC/MS and LC/MS determined HBCD totals were below 24%. There is no indication that one of the methods leads to systematically higher or lower values. The differences are in the range of deviations found for duplicate GC/MS determinations within this study (up to 27%).

The deviations in the total HBCD results are to be attributed to the instrumental analyses and calibration only since the cleaned-up extract portions from the GC/MS analysis were taken for the LC/MS analysis. Taking calibration mixtures with similar α-, β- and γ-HBCD composition like found in environmental samples (instead of 1:1:1 mixtures) may lead to a slightly improved accuracy in GC/MS analysis. Since the internal standard used for GC/MS quantification was not suitable for the LC/MS analysis, quantification was done externally in the latter case. Moreover, using a suitable internal standard for LC/MS should also further improve the accuracy of the LC/MS quantification. Independent of these facts, the comparative analyses of soil and water samples for total HBCD by GC/MS and LC/MS carried out within this study indicate that both techniques lead to the same result and may both be applied for HBCD determination in environmental samples.

Acknowledgement
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Table 2: Comparison of the results of the exemplary analysis of some water and soil samples for HBCD by using different detection techniques (GC/MS and LC/MS)

Sample			HBCD concentration				
			GC/MS analysis	LC/MS analysis			
No.	**Matrix**	**Unit**	**Total HBCD[b]**	**Total HBCD[b]**	**alpha- HBCD[b]**	**beta-HBCD[b]**	**gamma-HBCD[b]**
W 1	Water	µg/l	20300	19000	7580	3230	8220
W 2	Water	µg/l	30.4	36.0	3.8	3.5	28.7
W 3	Water	µg/l	318	361	76	17	268
W 4	Water	µg/l	9.1	11.0	1.6	0.6	8.8
W 5	Water	µg/l	206	205	51	39	115
S 1	Soil	$\mu g/kg_{dm}$	597	569	80	56	433
S 2	Soil	$\mu g/kg_{dm}$	171	135	33	18	84
S 3	Soil	$\mu g/kg_{dm}$	344	(137)[a]	(28)[a]	n.d.	(109)[a]
S 4	Soil	$\mu g/kg_{dm}$	23200	20600	2930	1520	16100
S 5	Soil	$\mu g/kg_{dm}$	111	(59.0)[a]	(18)[a]	n.d.	(41)[a]

dm dry mass
a Values in the range of the detection limit and below the limit of quantification
b HBCD concentrations of water samples include both, particle-bound and dissolved HBCD
n.d. not detected

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Figure 1. GC/MS and LC/MS chromatograms of a calibration mixture and a soil sample, showing the HBCD peaks (x-axis: time; y-axis: abundance; LC/MS elution order: α-, γ-, β-HBCD)

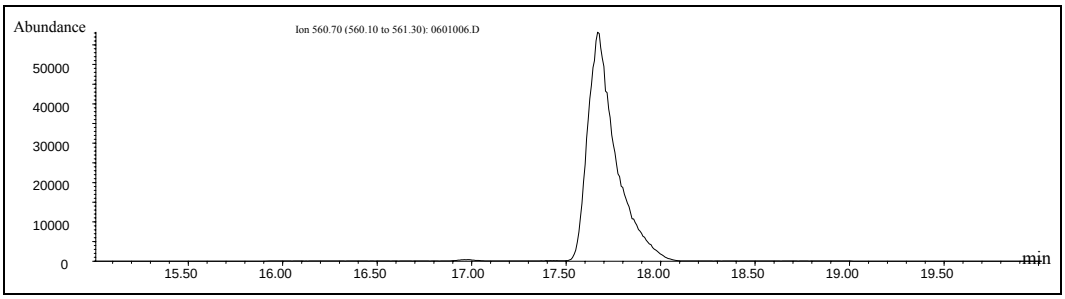

Figure 1a. GC/MS chromatogram of calibration solution (1:1:1 mixture), total HBCD peak

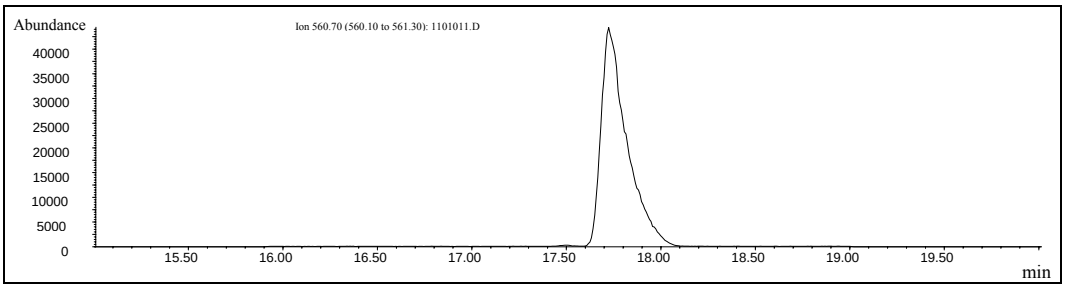

Figure 1b. GC/MS chromatogram of soil sample S4, total HBCD peak

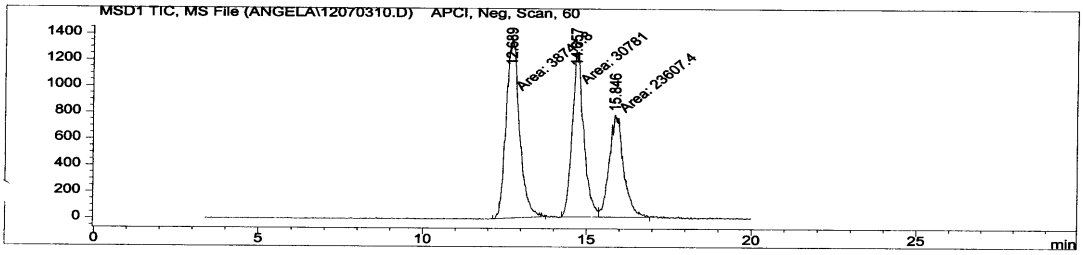

Figure 1c. LC/MS chromatogram of calibration solution (1:1:1 mixture of α-, γ- and β-HBCD)

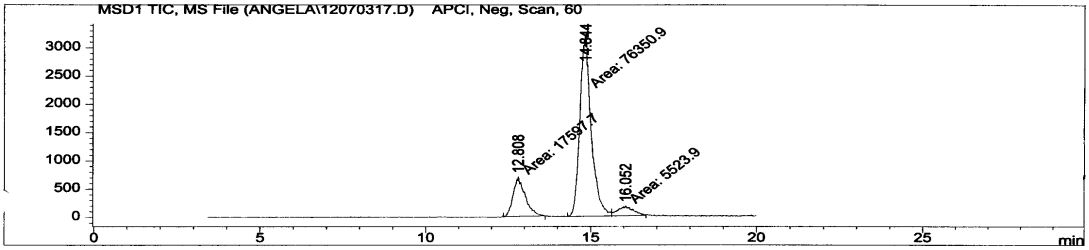

Figure 1d. LC/MS chromatogram of soil sample S4 showing the α-, γ- and β-HBCD peaks