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Saioa Zorita^a; Lennart Mathiasson^a

^a Lund University, SE-22100 Lund, Sweden

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Determination of dissolved and particle-bound PCB congeners at ultra-trace concentrations in water

SAIOA ZORITA and LENNART MATHIASSEN*

Lund University, PO Box 124, SE-22100 Lund, Sweden

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Adsorption of 10 PCB congeners in aqueous solutions on glass-fibre filters taken from different boxes but of the same type were not significantly different. The standard deviations using filters from the same box were below 10% at concentration levels of 4.1 ng L^{-1} . At this level, the adsorption of dissolved PCB at the filters was in the range of 5–20% depending on the congener. This led to a procedure for determination of dissolved and particle-bound congener in authentic landfill leachate, which included correction for adsorption losses. The procedure was based on filtration through glass-fibre filters, followed by trapping of the PCB in the eluate on solid-phase extraction (SPE) disks. After separate supercritical fluid (SFE) extractions, with carbon dioxide, of the filters as well as of the SPE disks, the extracts were analysed on a two-column capillary GC-ECD system. Corrections for congener adsorption on glass-fibre filters were made, from which corrected distribution constants between particle-bound and dissolved PCB congener in the water phase could be obtained for authentic landfill leachate. These values (10^4 – 10^5) agreed well with those obtained by others.

Keywords: Dissolved and particle-bound PCB; Filter adsorption; Wastewater

1. Introduction

To estimate transport of pollutants in an aqueous system, knowledge about concentrations of particle-bound and dissolved pollutants is essential. One common procedure to achieve this knowledge is to filter the sample on a glass-fibre filter and then to determine separately the pollutants trapped on the filter and the pollutants remaining in the eluate [1–3]. This can be done by extracting both the filter and the eluate with an organic solvent [4, 5] or with a supercritical fluid [6, 7]. In the latter case, the eluate passing the glass-fibre filter is preferably trapped on a solid-phase extraction (SPE) disk before the supercritical extraction step.

Irrespective of the method used for the final analysis, the amount of pollutants found on the filter is normally ascribed as the particle-bound fraction and the

*Corresponding author. Fax: +46-46-2224544. Email: lennart.mathiasson@analykem.lu.se

amount found in the eluate as the dissolved pollutant fraction [2, 3]. With this approach, the possibility that pollutants dissolved in the water phase might be trapped on the filter is totally neglected. If this occurs, the particle-bound fraction will be overestimated and the dissolved fraction accordingly underestimated.

In this article, we have investigated adsorption losses of PCB congeners, dissolved in an aqueous phase, on different types of glass-fibre filters. For the first time, a high-quality analytical procedure based on supercritical fluid extraction has been used to quantify adsorption on glass-fibre filter. A procedure for correction of distribution constants between particle-bound and dissolved PCB congeners has also been developed based on these results. The use of low concentrations ensures that the results obtained can be used to predict the behaviour of authentic samples, where PCB concentrations generally are far below $1\text{ }\mu\text{g L}^{-1}$. For the determination of PCBs at these low concentrations, the methodology recently developed by us was used [8, 9].

2. Experimental

2.1 Chemicals and sample

The PCB standard used for recovery studies was a certified reference material, NIST 2262 (Gaithersburg, MD), utilized for preparation of calibration standards, containing 28 certified PCBs. Seven calibration solutions in isooctane were prepared in the range of $1\text{--}40\text{ ng mL}^{-1}$. The study was limited to 10 congeners: 28, 52, 101, 118, 153, 105, 138, 128, 180 and 170 for which there were comparative data available from others studies [8, 9] and their references.

PCB 35 (as time reference) and 169 (for quantification, Larodan Fine Chemicals AB, Malmö, Sweden) in *n*-heptane were used as internal standards (I.S.). The concentrations in the solution were 540 ng mL^{-1} and 400 ng mL^{-1} for PCB 35 and PCB 169, respectively. These concentrations are well within the linear range of their external calibration lines and give a high signal-to-noise ratio, which improves the precision in the measurements.

Reagent water was obtained from Milli-Q water purity system (Millipore Corp. Bedford, MA). Methanol, isooctane and *n*-pentane (residue analysis, Fluka Chemie, Buchs, Switzerland) and *n*-heptane (pestanal[®], Riedel-de Haën[®], Seelze, Germany), were used in the experiments.

Sodium chloride (GR for analysis) was obtained from Merck, Germany. Leachate samples from Rassebygd Landfill, close to Emmaboda, Sweden, were studied. The DOC in this water was 29.4 mg L^{-1} . The samples were stored in a refrigerator at 4°C until their extraction.

2.2 Analytical procedures

The total analytical procedure used in this work included filtration of PCB-contaminated water samples through a glass-fibre filter, collection of the dried filter and a subsequent solid-phase extraction (SPE) step for the eluate using SPE disks. The glass-fibre filters and the SPE disks were then extracted separately using supercritical fluid extraction (SFE) with carbon dioxide as supercritical fluid. Finally, the extracts were run by GC with electron capture detector [9].

2.2.1. Filtration. The aqueous samples were filtrated through a package of three 47 mm glass microfibre filters (D/C/F, pore size 2.7, 1.2 and 0.7 μm , respectively, corresponding to $\geq 98\%$ retention of particles above the diameters cited, Whatman, UK) in this order. Before use, the filters were cleaned with pentane/methanol/water by the same procedure as for the SPE disks. Filtration was performed within 1 h after the preparation of the reagent water samples. The filters were dried under vacuum suction for 15 min and 24 h in a desiccator before extraction by SFE.

2.2.2. Solid-phase extraction. SPE was done using Empore disks (EmporeTM, 47 mm, C₁₈, 3M Center, St. Paul, MN) and a Millipore 47 mm filter apparatus (Millipore Corp. Bedford, MA) that were rebuilt to facilitate the cleaning and extraction steps [8]. The normal sintered piece of glass acting as support for the glass-fibre filters and SPE disks was removed. Instead, a removable Teflon O-ring and a removable stainless steel support with small drilled holes (40% of the total area) were introduced. One glass-fibre filter (type D) was placed under the Empore disk to prevent the SPE disk attaching directly to the stainless steel support, which would decrease the total area available for the water samples to pass through the disk. This glass-fibre filter was always extracted together with the Empore disk. An MZ 2C vacuum pump (Vacuubrand, Wertheim, Germany) was connected to the filter equipment.

Before applying the sample, the disk was washed with 10 mL of *n*-pentane and dried by applying vacuum. This was followed by an activation step with 10 mL of methanol. About 3 mL of methanol was sucked through the disk after which it was allowed to stand for 1 min before passing further ca 4 mL of methanol. Remaining methanol was replaced by 10 mL reagent water in a subsequent conditioning step. The aqueous sample was passed through the SPE disk, which was then allowed to dry under vacuum for 15 min and 24 h in a desiccator. Then, the SPE disk was inserted in the extraction cell of the SFE equipment.

2.2.3. Supercritical fluid extraction. All supercritical fluid extractions were performed using an ISCO SFX 3560 (Isco, Lincoln, NE) automated system with a 260 D syringe pump. High-purity carbon dioxide (4.8; 99.998%, AGA Gas AB, Sweden) was used as extraction fluid and food quality CO₂ (AGA Gas AB, Sweden) as cooling gas.

The SFE conditions after the optimization of the method were as follows: pressure 350 bar, temperature 100°C, extraction time 45 min, dynamic mode with a flow rate of 1.5 mL min⁻¹, collection temperature -5°C, and trapping solvent 10 mL of isooctane.

A volume of 50 μL of IS was added before the reduction in the SFE extract volume from ca 10 mL to ca 1 mL under gentle stream of nitrogen. An aliquot of this was injected into the GC system.

2.2.4. GC analysis. Analysis of the extracted samples was performed by gas chromatography with electron capture detector (GC-ECD) using a Agilent 6890N series GC system (Agilent, Palo Alto, CA) equipped with an agilent 7683 series injector and an Agilent 7683 series autosampler. The GC system was equipped with a ⁶³Ni electron capture detector held at 300°C and purged with 60 mL min⁻¹ of nitrogen (5.5, >99.9995% purity, AGA Gas AB, Sweden). A dual-column system was utilized for separation of analytes. One system was an HP-5ms (30 m \times 0.25 mm, 0.25 μm

5%-phenyl-methylpolysiloxane) column coupled in series to a HT-5 (25 m \times 0.22 mm, 0.10 μ m 5% phenyl-polycarboransiloxane; Scientific Glass Engineering Europe Ltd, Milton Keynes, UK) column. The second column system was a DB-17 (60 m \times 0.25 mm, 0.25 μ m 50% phenyl-methylpolysiloxane) column. These two column systems were coupled in parallel to the inlet via a deactivated retention gap (2 m \times 0.530 mm deactivated fused silica) using a quick-seal glass 'T'. The columns HP-5ms, DB-17 and the retention gap were obtained from Agilent (Palo Alto, CA).

A volume of 1 μ L was injected. Hydrogen was used as carrier gas at a constant linear velocity of 46 cm s⁻¹, giving a volumetric flow rate of 2.1 mL min⁻¹, and using the two-column system described above the flow ratio was calculated to be close to 1:1. The oven temperature was held at 90°C for 2 min and then raised to 170°C at a rate of 20°C min⁻¹, keeping the temperature constant at 170°C for 7.5 min. Thereafter, the temperature was raised to 285°C with a speed of 3°C min⁻¹ and then held constant at 285°C for 8 min. The complete cycle corresponded to a time of 60 min. The Chemstation software (Agilent, Palo Alto, CA) was used to run the system and interpret the chromatograms. Data evaluation was made by means of peak-height measurements.

3. Results

3.1 *Investigation of the reproducibility of physico-chemical properties of glass-fibre filters from different packages*

The possibility of generalizing adsorption of water-soluble PCB congeners on glass-fibre filters depends on the reproducibility of adsorptive properties of manufactured filters. Accordingly, experiments on commercially available glass-fibre filters were first performed.

After spiking 1 L of water, with 100 μ L of a PCB mixture of 10 congeners, each at a concentration of 41 ng mL⁻¹, the sample was filtered through three filters with different pore sizes from different packages as described by Westbom [8]. Supercritical fluid extraction of these filters was performed separately. A triplicate and a blank were analysed for each filter package. The blank showed no peaks above the detection limit (0.1–0.2 ng L⁻¹) except for PCB 170. The value of this PCB in the blank was 0.23 ng L⁻¹. Results are shown in table 1. Owing to a problem with one extraction of the D filter, only two values could be used to calculate the average.

A parallel *t*-test showed that there were no significant differences in total congener adsorption between the two boxes for any of the filter types at the 95% confidence level. However, for individual PCB congeners, there were in a few cases a significant difference at the 95% confidence level, namely for PCB 128 on the C filter and F filter and for PCB 138 on the F filter. Only for PCB 128 on F filter is it of a magnitude with which one should take care. The RSD values within a certain box range between 3 and 42% for the D filter, between 4 and 28% for the C filter, and between 1 and 22% for the F filter; the average RSD value for adsorption on filter D is 21%, on filter C 11% and on filter F 10%, which is acceptable.

These results indicate that it is possible to measure the adsorption of different PCB congeners on glass-fibre filter and to use this value for correction of adsorption in unknown sample. This idea was further developed below.

Table 1. Adsorption of PCB congeners at concentrations of 4.1 ng L^{-1} onto glass-fibre filters D, C, and F.^a

	D		C		F	
	Box 1	Box 2	Box 1	Box 2	Box 1	Box 2
PCB 28	0.53	0.50	0.45	0.40	0.44	0.39
PCB 52	0.14	0.15	0.19	0.16	0.19	0.18
PCB 101	1.04	1.12	1.14	1.07	1.12	1.13
PCB 118	1.54	1.53	1.12	1.09	1.05	1.22
PCB 153	1.11	1.17	0.79	0.77	0.74	0.85
PCB 105	1.09	0.84	0.29	0.35	0.29	0.41
PCB 138	2.06	2.12	1.40	1.38	1.26	1.44
PCB 128	1.20	1.24	0.24	0.31	0.25	0.38
PCB 180	1.80	2.01	0.89	0.94	0.82	0.95
PCB 170	1.59	1.70	0.42	0.44	0.34	0.45

^aTwo different boxes were used, and average values based on two measurements (filter D) or three measurements (filter C and F) for each box are given in the table.

3.2 Adsorption behaviour of different congeners in particle-free reagent water

One would expect that filters with different pore sizes would have different adsorption characteristics, but also the hydrophobicity and the concentrations of the PCB congeners studied would have an impact on the adsorption. The first two features were studied using a mixture of 10 PCB congeners at concentrations of ca 4.1 ng L^{-1} , respectively. One problem in an investigation of this type is that some dissolved PCBs may be lost on the surface of the bottle, as described by Lung *et al.* [10], and hence will never pass the filter. However, in the timescale ($< 1 \text{ h}$) we used between sample preparation and filtration, we observed no significant differences between the calculated PCB values and the added known amounts. We have found that in waters with large concentrations of solid particulate matter (SPM), several filters with varying pore sizes may be needed. In this experiment, particle-free reagent water containing the PCB mixture passed three filters (D,C,F) in this order, the filter package was placed in the SFE cell, and the adsorbed PCBs were subsequently extracted with supercritical carbon dioxide. The results can be seen in figure 1. A sample volume of 1 L passed the filters.

For the most volatile congener PCB 28, the average contribution from the second filter (C) is markedly larger. For the other congeners, the contribution from the first filter with largest pore size is noticeably larger. This filter (D) meets the sample first followed by the C and finally the F filter. The most probable explanation to this behaviour is that the three filters act as a short chromatographic column. The most volatile and/or less hydrophobic PCB, with lower partition coefficients, will then move faster through this column in this dynamic system. This means that a larger portion of these PCB congeners is transferred from the first to the two other filters.

The influence of different concentrations of the PCB congeners on the adsorption behaviour is illustrated in figure 2. The experimental set-up was as above, and the sample volume was 1 L.

For low-chlorinated PCBs, the adsorption is relatively constant. It is suspected that for each congener, there is a limitation of adsorption sites with sufficient strength for

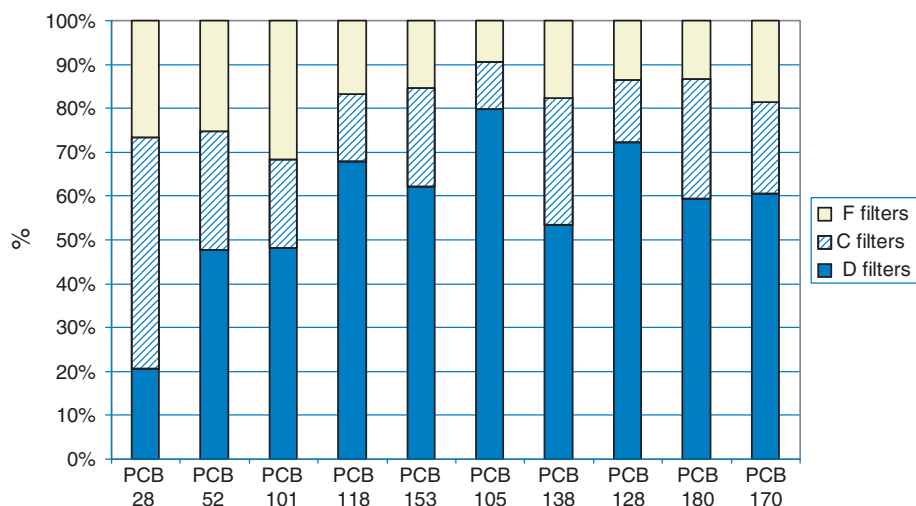


Figure 1. Proportional PCB adsorption onto glass-fibre filters, D/C/F, where the D filter first meets the sample solution ($n = 3$).

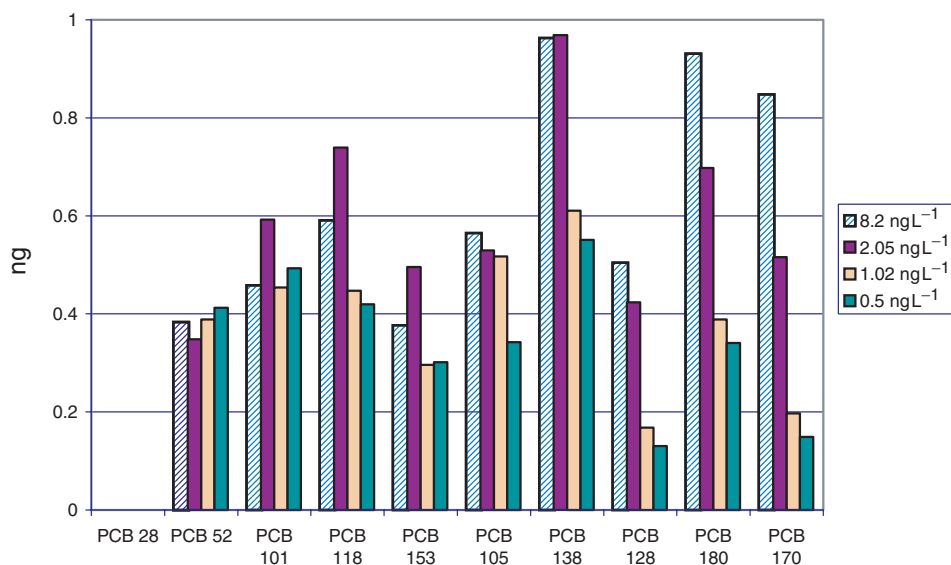


Figure 2. Amount of PCBs (ng) adsorbed onto glass-fibre filter package (D/C/F) for different standard concentrations ($n = 3$).

efficient adsorption of these congeners. This is obvious for PCB 52, with an average of 0.383 ng, adsorbed onto glass-fibre filters with an RSD of 7%. More hydrophobic congeners as PCB 170 or PCB 180 have a different behaviour in the concentration range studied. They appear not to reach such adsorption limits; instead, the adsorbed amounts increase with increasing PCB concentration. The adsorption of PCB 170 is unexpectedly low for the two lowest concentrations considering its relatively high hydrophobicity.

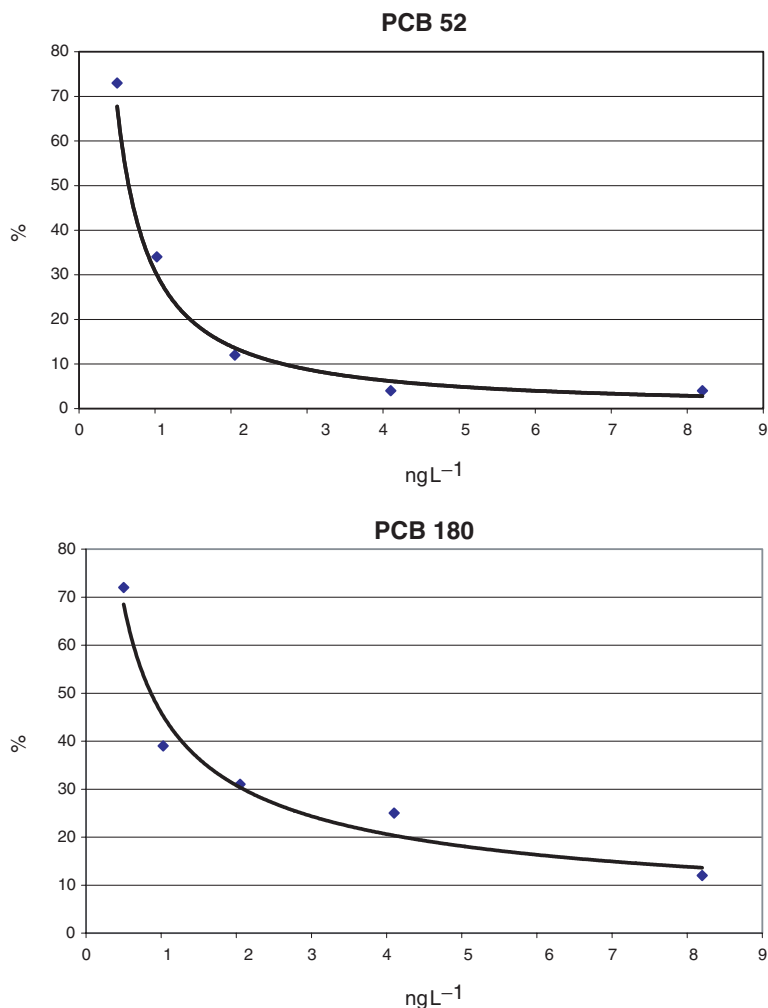


Figure 3. Percentage of adsorption of congeners PCB 52 and PCB 180 on a glass-fibre filter package (D/C/F) at different concentrations ($n=2$).

Instead of considering the total amount of PCB congener trapped on the filter, the extent of adsorption can be expressed as a function of PCB congener concentration. This is illustrated in figure 3 for two of the considered congeners representing different hydrophobicities. The other congener behaves in a similar way. Generally, the curves are quite similar in shape. Table 2 also shows the results of curve fitting for all the congeners, based on an equation of the general form $y = Ax^b$ where y is the extent of adsorption, x is the congener concentration and A and b are constants for a given congener. In all cases, the general equation above describes the behaviour of the congeners quite well, as reflected by the r^2 values given in table 2, which also include values of the constants A and b in the aforementioned equation.

With the aid of the equations in table 2, describing the relation between congener concentration in water and extent of adsorption, values of adsorption have been

Table 2. Values of the constants A and b and the coefficient of determination r^2 in the equation $y = Ax^b$ describing the relation between congener concentration in water and extent of adsorption on a glass-fibre filter.

	A	$-b$	r^2
PCB 52	30.8	1.140	0.947
PCB 101	42.7	1.221	0.919
PCB 118	50.2	0.956	0.956
PCB 153	33.7	0.953	0.953
PCB 105	48.3	0.932	0.932
PCB 138	59.9	0.743	0.984
PCB 128	27.8	0.543	0.895
PCB 180	45.9	0.578	0.951
PCB 170	25.9	0.358	0.903

Table 3. Theoretical values of relative adsorption at different concentration for different PCB congeners on a glass-fibre filter package with D, C, and F filters in this order.^a

Congener	Relative adsorption (%)					
	100 ng L ⁻¹	20 ng L ⁻¹	10 ng L ⁻¹	5 ng L ⁻¹	1 ng L ⁻¹	0.5 ng L ⁻¹
PCB 52	0.2	1.0	2.2	4.9	30.8	67.9
PCB 101	0.2	1.1	2.6	6.0	42.7	99.4
PCB 118	1.1	4.3	7.5	13.3	50.2	88.9
PCB 153	0.6	2.3	4.3	8.0	33.7	62.5
PCB 105	1.2	4.3	7.6	13.2	48.3	84.4
PCB 138	2.0	6.5	10.8	18.1	59.9	100.2
PCB 128	0.0	0.6	4.8	13.0	29.3	32.4
PCB 180	3.2	8.1	12.2	18.1	46.0	68.6
PCB 170	5.0	8.8	11.3	14.5	25.9	33.2

^aThe values are calculated from the equations given in table 2.

calculated within the investigated concentration range. An estimation is shown in table 3 of the absorption contributions of higher concentrations, calculated using the equations given in table 2.

It is clear from table 3 that the importance of adsorption decreases when the concentration increases. The hygienic threshold limit within EU for drinking water pollution by one persistent organic pollutant as a PCB congener [11] is 100 ng L⁻¹. At this concentration, the error due to adsorption on filter never exceeds 5% and can generally be neglected or corrected for using information in the table 3. Of course the values at 100 ng L⁻¹ should be considered as somewhat tentative, as they are outside the experimental concentration range.

3.3 Influence of sodium chloride on adsorption of PCB

On many occasions when waste water is considered, especially concerning leachate from landfill, high concentrations of salts are found. Here, one has to take into consideration matrix influences on pollutant adsorption. This is expected to be different for waters with a high ionic strength, since the salting-out effect should increase the adsorption contribution. To get an estimation of the magnitude of this effect,

a comparison was made between reagent water spiked with the PCB mixture above at congener concentrations of 4.1 ng L^{-1} and the same water containing additionally 3000 mg L^{-1} of chloride ions, added as sodium chloride. Both these solutions were then filtered through the glass-fibre filter package described above. At these high chloride concentrations in reagent water, the trend was that the PCB congener adsorption generally increased with 5–6% compared with reagent water, except for the three PCB congeners with lowest chlorination, where the increase in adsorption was only about 1–2%. These findings are in agreement with observations on pyrene made by Karickhoff [12], who, in 1979, had already observed an increase in the distribution constant between particle-bound and dissolved congener of 15% when comparing pure water and sodium chloride solution at a concentration of 0.34 M.

If not corrected for, the changes of adsorption on the glass-fibre filter package with varying chloride concentrations will lead to errors in the calculations of particle-bound PCB congener at low ng L^{-1} analyte concentrations. However, if the particle concentration is not too low (above 10 mg L^{-1}), and the distribution constants are at least above 10,000, these errors will be negligible.

3.4 Determination of distribution constants for PCB congeners in spiked leachate from landfills

Leachate water from Rassebygd municipal landfill close to Emmaboda, Sweden, was spiked with the same PCB mixture as before. Possible concentrations of PCB in this water were below the detection limits for the congeners. The total concentration of each PCB congener in the water passing a glass-fibre package and an SPE disk in this order was determined by a separate extraction of the fibre package as well as the SPE disk with supercritical carbon dioxide. Two samples with an average PCB concentration before equilibrium of each congener in the aqueous phase of $ca. 2.05 \text{ ng L}^{-1}$ and $ca. 4.1 \text{ ng L}^{-1}$, respectively were investigated. The analytical procedure was the one described in section 2. Since the content of sulphur in this water was low, no extra clean-up procedure, as described in [9], was needed. The volume of the processed samples was 1 L. The concentrations of particles in these two samples were 8.9 and 16.9 mg L^{-1} , respectively. These values are quite low and thus less precise. We think that the measured values may differ by about 1–3 mg from the true values, and this leads to uncertainties in the order of 10–30% in the determination of K_d values.

The concentration of particle-bound PCB congener (C_s) was obtained by subtracting the value obtained on the filter package with the estimated adsorption in the filter pores of PCB dissolved in the water phase. This adsorption value was obtained using the equations given in table 2 and the concentration value of the aqueous phase. The concentration value of a PCB congener in the aqueous phase (C_w) at equilibrium was obtained by taking into consideration that some part of each congener was adsorbed on particles, the extent given by table 2. Starting with 2.0 or 4.1 ng L^{-1} , a recursion procedure already gave a good agreement after two iterations. The (C_w) values obtained after the second iteration were then used to calculate the distribution constant $K_d = C_s/C_w$. Table 4 lists the distribution constants (K_d) between particle-bound and dissolved congener, the ratio between uncorrected (K'_d) and corrected (K_d) distribution constants as well as the extent of overestimation of the particle-bound fraction for some of the PCB congeners. Uncorrected distribution constants had no corrections for adsorption of PCB congeners in the aqueous phase onto glass-fibre filters.

Table 4. Values for K_d and K'_d/K_d (where K_d is the corrected and K'_d the uncorrected distribution constants between particle-bound and dissolved PCB congener in spiked leachate), and values for the overestimation of uncorrected PCB congener concentration on particles ($\Delta C_{\text{particles}}$).

Congener	K_d		K'_d/K_d		Overestimation $\Delta C_{\text{particles}}\%$	
	2.05 ng L ⁻¹	4.1 ng L ⁻¹	2.05 ng L ⁻¹	4.1 ng L ⁻¹	2.05 ng L ⁻¹	4.1 ng L ⁻¹
PCB 52	9672	10954	3.0	1.4	158	33
PCB 101	25384	19218	2.2	1.3	79	23
PCB 118	(4001) ^a	17538	(12.2) ^a	1.8	(781) ^a	53
PCB 153	116514	56848	1.4	1.2	17	10
PCB 105	91043	22595	1.8	1.7	33	40
PCB 138	92148	40792	2.2	1.6	43	30
PCB 128	154797	52585	1.4	1.3	14	14
PCB 180	71516	35772	2.1	1.7	47	33
PCB 170	120863	81556	1.5	1.3	19	11

^aValue considered as an outlier.

The estimation of K_d will obviously become quite erroneous at low concentrations, if the adsorption is not corrected for. Furthermore, the K_d values in table 4 seem to be dependent on the total PCB congener concentration in that a higher concentration leads to lower K_d values. This may depend on the small amounts of particles in the considered samples, which may lead to a less efficient multilayer adsorption of the congeners at higher total concentrations. However, as mentioned previously, there is also a relatively high uncertainty in the determination of the amount of particles on the filter. As in all determinations based on filtration, the PCBs adsorbed on very small particles passing the filters will be considered as dissolved PCBs, which might give some overestimation of the dissolved fraction.

However, in comparison with other measurements on PCB distribution constants, the values obtained here agree quite well. The values given by other authors [13–15] are between 10^4 and 10^5 .

4. Discussion

Taking into consideration the results obtained above, the method described for measuring dissolved and particle-bound pollutant can be applied for PCBs with tolerable accuracy, without correction for losses of dissolved PCBs on the types of glass-fibre filter investigated, for concentrations above $0.1 \mu\text{g L}^{-1}$. At lower concentrations, a correction factor should be applied. For determination of concentrations of PCBs in other leachate waters, correction factors obtained from experiments like those above are expected to give a fairly good estimate of the real situation. However, if the chloride concentrations and ionic strength differ considerably compared with the concentrations investigated in this article, it may be wise to carry out some experiments to estimate the salting-out effect. Values on chloride and ionic strength are generally accessible from control programs measurements on this type of waste water. For pollutants, more hydrophobic than PCBs, like high molecular-weight polybrominated diphenyl ethers (PBDEs), the adsorption on glass-fibre filter might be even more important, shifting the concentration level, where a correction is needed further upwards compared with PCBs. The same may be true for other types

of compounds like phthalate esters or alkyl phosphates, which are normally found in landfill leachate. Some of them, like di-(2-ethylhexyl) phthalate, often occur at comparably high concentrations in landfill leachates. There are also other parameters like DOC, which could affect the adsorption of dissolved PCB and other pollutants like PBDEs. Competing adsorption from other species in DOC could lead to some displacement in the filters of the target PCB compounds, which would lead to somewhat less PCB adsorption. An investigation of this problem was not addressed in this article but is surely of interest. Such an investigation is quite complicated as the concentrations of DOC as well as the composition of DOC show large variations between different leachates. In the water from the Rassebygd landfill described above, the DOC value was low, which indicates a limited influence on the results. As an indication of this, the calculated values of the distribution constants for different PCB congeners agreed well with results obtained by others. Knowledge on bound and dissolved pollutant concentrations of different types of organic compounds is scarce, and further measurements are certainly needed.

5. Conclusions

It has been shown that at low ng L^{-1} levels, the adsorption of dissolved PCB congeners on glass-fibre filters can be large, giving overestimated values of particle-bound PCB concentrations. The adsorption problem on glass-fibre increases when the PCB congeners become more hydrophobic. However, at concentrations above 10 ng L^{-1} , the systematic error in an uncorrected determination of dissolved and particle-bound PCB congeners is estimated to be less than 10% in general, and at 100 ng L^{-1} , it is reduced to a few percent. The results imply that caution is needed in determining dissolved and particle-bound fractions of PCB congeners as well as other hydrophobic compounds. However, by taking into consideration experimentally determined values on the extent of adsorption in the filters used to separate particle-bound and dissolved pollutant concentrations, it should be possible to obtain reliable results concerning dissolved and particle-bound pollutant concentrations, even at very low concentrations.

References

- [1] J.C. Moltó, Y. Picó, J. Mañes, G. Font. *J. AOAC Int.*, **75**, 714 (1992).
- [2] D.L. Swachhamer, D.E. Armstrong. *J. Great Lakes Res.*, **13**, 24 (1987).
- [3] X. Jiang, D. Martens, K.W. Schramm, A. Kettrup, S.F. Xu, L.S. Wang. *Chemosphere*, **41**, 901 (2000).
- [4] J.J. Ridal, M.E. Fox, C.A. Sullivan, R.J. Maguire, A. Mazumder, D.R.S. Lean. *Anal. Chem.*, **69**, 711 (1997).
- [5] J. Dachs, J.M. Bayona. *Chemosphere*, **35**, 1669 (1997).
- [6] J.S. Ho, P.H. Tang, J.W. Eichelberger, W.L. Budde. *J. Chromatogr. Sci.*, **33**, 1 (1995).
- [7] D.C. Messer, L.T. Taylor. *LC-GC*, **14**, 134 (1996).
- [8] R. Westbom, L. Thörneby, S. Zorita, L. Mathiasson, E. Björklund. *J. Chromatogr. A*, **1033**, 1 (2004).
- [9] S. Zorita, R. Westbom, L. Thörneby, E. Björklund, L. Mathiasson. *J. Chromatogr. A* (Submitted).
- [10] S-C. Lung, Y. Yanagisawa, T.E. Ford, J.D. Spengler. *Chemosphere*, **41**, 1857 (2000).
- [11] 80/778/CEE. *EU Official J.*, **229**, 11 (1980-08-30).
- [12] S.W. Karickhoff, D.S. Brown, T.A. Scott. *Wat. Res.*, **13**, 241 (1979).
- [13] G. Font, J. Mañes, J.C. Moltó, Y. Picó. *J. Chromatogr. A*, **733**, 449 (1996).
- [14] M. Chevreuil, L. Granier, A. Chesterikoff, R. Létolle. *Wat. Res.*, **24**, 1325 (1990).
- [15] J.H. Hermans, F. Smedes, J.W. Hofstraat, W.P. Cofino. *Environ. Sci. Technol.*, **26**, 2028 (1992).