The determination of polychlorinated biphenyls in municipal sewage sludges using microwave-assisted extraction and gas chromatography-mass spectrometry

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The presence of organic micropollutants [such as poly(chlorobiphenyls)] in municipal sewage sludges is a major problem on account of risks associated with the agricultural valorisation of the sludges. In France, since January 1998, maximum values for trace organic pollutants are imposed [0.8 mg kg^{-1} dry matter for the sum of seven poly(chlorobiphenyls)]. The aim of this study was to develop a reliable, accurate and fast analytical procedure (extraction, clean-up, quantification) in order to determine polychlorinated biphenyls in municipal sewage sludges. Such pollutants could be efficiently extracted from dried sewage sludge samples using microwave-assisted extraction. This technique affords several advantages as compared to the classical Soxhlet extraction, mainly rapidity and reduction in solvent consumption. Extractions (10 min under 30 W with 30 ml hexane–acetone 1 : 1) were conducted in the presence of copper to avoid sulfur interferences in the extracts. The latter were further concentrated and purified onto disposable silica cartridges. After final concentration and addition of the internal standard, they were analysed by gas chromatography coupled to mass spectrometry (in the selected ion monitoring mode). Two types of sludges (from Achères and Valenton sewage treatment plants near Paris, France) were analysed, whose polychlorobiphenyl concentrations differed largely (Achères sludge being the most contaminated). The microwave extraction compared favourably with the classical Soxhlet extraction. In addition, the sludge concentrations found with our experimental procedure were close to the analyses made by another laboratory, even though some discrepancy was noted.

Aim of investigation

Polychlorinated biphenyls (PCBs) have been an important environmental problem for many years, because of the large quantities released into the environment, their persistence, and their potential toxicity to a broad spectrum of organisms, including humans (their lipophilic nature contributes to their high bioaccumulation potential). PCBs were marketed worldwide in large quantities for many years as transformer and capacitor oils, cutting oils, hydraulic oils, heat transfer fluids, and metalcasting release oils. They were also used in carbonless copy paper, paints and pesticides.

There are 209 PCB isomers and congeners.[1] Several studies reported their gas chromatographic analysis with either electron capture detection or mass spectrometry (GC-MS).[2–4] However, the separation of all PCBs remains quite a challenge, even with high resolution capillary GC.[2,5] For that reason, only seven congeners are recommended by the Community Bureau of Reference; these are PCB 28, 52, 101, 118, 153, 138 and 180. These congeners have been selected as indicators on the basis of their wide range of chlorination and of their relatively high concentrations in technical PCB mixtures and in the environment.

PCBs have been sought in different environmental matrices. Their extraction from sediments and sludges generally includes extraction with an organic solvent, removal of sulfur and clean-up.[2,6,7] Extraction is usually achieved using classical techniques, mainly Soxhlet extraction,[2,6,8–11] which is time and solvent consuming. So, recent techniques have been developed in the past few years to enable their rapid extraction from environmental matrices. In particular, microwave-assisted extraction (MAE) gave efficient recoveries of PCBs in reasonable times from water[12] as well as soils and sediments,[13–16] mostly using closed systems.

The concern about the presence of PCBs in sewage sludges is rather recent,[17] even though sewage sludges have been used for the fertilization of cultivated lands for several years. In France, the new regulation of 8 January 1998 imposes a maximum acceptable limit for the sum of the seven PCBs (0.8 mg kg^{-1} dry weight). A few studies have been conducted to determine PCB concentrations in sludge samples, giving several values for the sum of PCBs depending on the sludges: 3.3 mg kg^{-1} dry weight,[18] 1.3 mg kg^{-1} dry weight[6] and from 0.106 to 0.712 mg kg^{-1} dry weight.[11] In addition, PCBs were found persistent in sewage-sludge amended soils.[6,9,10,19] However, severe discrepancy has been observed between results obtained by different laboratories.[20] For that reason, there is a need for a fast analytical method that enables accurate determination of PCBs in sewage sludges. Thus, this study was undertaken to develop a fast and efficient analytical procedure to accurately determine PCBs in sewage sludges. Pollutants were extracted from the matrix under microwave energy, purified onto silica, and further analysed using GC-MS. Extraction efficiencies were compared to results obtained using classical Soxhlet extraction (precognised in the US Environmental Protection Agency (EPA) Method 3540 for the determination of PCBs in solid matrices).[8] Finally, our results were compared to the values determined by an independent laboratory in order to validate our method.

Experimental

Sewage sludge samples

Sewage sludge samples were obtained from two municipal wastewater stations near Paris, Achères and Valenton. Sludge samples from Achères came from only one sampling (January 1997). In contrast, samples from Valenton were received every two weeks (between July and September 1998), and were supposed to be composite samples over that period.

Upon their reception in the laboratory, sludges were kept frozen in order to avoid any sludge modification. Before their analysis, large samples (200 g) were taken and dried in an oven (60 °C, 18 h); they were further homogeneized with a mortar. This treatment was reported to minimize possible losses. They were bottled in a polypropylene box (the absence of contamination from the polypropylene was checked) and stored in the dark at room temperature (to keep them dry). The absence of water should make the matrix more accessible to the organic extractant solvent.[2] However, as drying at moderate temperature may result in the presence of residual water, dried sludge samples (10 g) were also kept at 105 °C in an oven for 24 h in order to correctly determine their dry weight.

In a few experiments, dried sludge samples were spiked with the PCB congeners before the extraction (at 0.15 mg kg^{-1} dry weight), in order to estimate the extraction recoveries.

Reagents and chemicals

Reagents and chemicals were supplied as follows: a standard solution of the seven PCB congeners (10 mg l^{-1}) in isooctane (PCB 28, 52, 101, 118, 138, 153 and 180), and individual standard solutions, 1,2,3,4-tetrachloronaphthalene (TCN), octachloronaphthalene (OCN) or PCB 29 (each at 10 mg l^{-1}) in isooctane by CIL Cluzeau (Paris, France); analytical-reagent grade copper metal and nitric acid solution 68% by Prolabo (Briare, France); HPLC-grade isooctane by Merck (Nogent-sur-Marne, France) and HPLC-grade acetone and *n*-hexane by Prolabo (Briare, France). PCBs purities were guaranteed between 97 and 99.7%. Other purities were stated to be higher than 99%. Blank experiments were conducted in order to check the absence of PCB contamination in concentrated solvent volumes (*i.e.*, 50 ml concentrated to around 0.6 ml).

Five stock standard solutions (at the following concentrations: 20, 50, 80, 150 and 200 μg l^{-1}) were prepared by diluting the PCB solution in isooctane. A stock standard solution (1 μg ml^{-1}) of TCN (internal standard) was prepared by dilution in isooctane. The internal standard was added and diluted (50 μg l^{-1}) in all calibration standards and sample extracts before injection. All solutions were stored at 5 °C in the dark. All glassware was washed first with a water-detergent solution, next cleaned for 24 h in a nitric acid solution (20%) and then dried at 250 °C for 8 h.

Activated copper bars (0.5 cm long) were cut and immersed in 30% nitric acid for 30 s. The bars were cleaned sequentially with acetone and hexane. They were further added to the samples before extraction in order to remove sulfur interferences.

Estimation of PCBs in ambient air of the laboratory

The air concentration was estimated, as possible contamination could occur if paints and rubbers contain PCBs.[2] This was done by placing Petri dishes containing 2 g of octadecyl-bonded silica (Lichroprep RP-18, 40–63 μm, from Merck, Darmstadt, Germany) in several rooms of the laboratory for two weeks. After this period, the silica was transferred to a glass column and eluted with diethyl ether–hexane 1 : 9 (10 ml). The extract was further concentrated to around 0.6 ml and analysed by GC-MS (after the internal standard addition).

Microwave-assisted extraction

MAE experiments were performed with a Soxwave 100 open microwave solvent extraction system (Prolabo, Briare, France) whose maximum power is 300 W. A 1 g aliquot of dried sewage sludge was weighted in the extraction cell. The mixture hexane–acetone 1 : 1 (30 ml) was then added to the sample and the solution stirred; this solvent was used as it gave efficient extractions under microwave energy.[14,21] Activated copper bars (1 g) were added to each sample just before extraction to remove sulfur by sulfide formation.[2,8] Extractions were performed at 30 W during 10 min (unless other conditions specified in the text), as such conditions enabled satisfactory extraction of several pollutants from soils and sediments.[22] After cooling to room temperature, the extracts were filtered (using ashless filter papers, 110 mm, Prolabo) to remove the copper and the matrix (no contamination from the filter papers was observed). The glassware was rinsed with 5 ml of hexane–acetone 1 : 1. Next, the extracts were concentrated to approximately 2 ml using a rotary evaporator at room temperature and reduced pressure. The flask was then rinsed two times with 5 ml of *n*-hexane; this volume was added to the extracts, which were finally concentrated under a gentle stream of nitrogen to approximately 2 ml before clean-up.

Soxhlet extraction

Extractions were performed with a Soxhlet apparatus as suggested by the US EPA method 3540B.[8] Initially, a dried sludge sample (1 g) was extracted with a mixture of hexane–acetone 1 : 1 (250 ml). Activated copper bars (1 g) were added to the sample before extraction in order to remove sulfur compounds. Extractions were performed during 6 h (4–5 cycles per hour) as already performed in another study.[6] After cooling to room temperature, the extracts were concentrated to approximately 2 ml using a rotary evaporator at room temperature and reduced pressure. The flask was then rinsed two times with 5 ml of *n*-hexane; this volume was added to the extracts, which were finally concentrated under a stream of nitrogen to approximately 2 ml before clean-up.

Clean-up method

The determination of trace pollutants in sewage sludges requires a clean-up step to remove lipids and fats. This is usually achieved on an adsorbent, either silica or Florisil.[6] Thus, purification was performed onto disposable solid-phase extraction silica cartridges (Supelclean LC-Si, 1 g, 6 ml, supplied by Supelco, Saint-Quentin Fallavier, France). A Visiprep vacuum manifold system (Supelco) was used. Cartridges were conditioned with 4 ml of *n*-hexane (the solvent was allowed to soak the entire cartridge for 5 min before passing through the cartridge). Care was taken to ensure that cartridges never dried before sample application. The extracts (2 ml) were transferred on top of the cartridge and allowed to pass through (at approximately 2 ml min^{-1}). When the entire extracts were passed through, the sample vials were rinsed with an additional 0.5 ml of solvent. This volume was added to the cartridges. The PCB congeners were finally eluted with 5 ml of hexane (the solvent was allowed to soak the cartridge before elution). Then, the extracts were concentrated under a stream of nitrogen to an appropriate volume (0.6 ml). The internal standard was added and diluted (50 μg l^{-1}) in the extracts. Blank experiments were conducted in order to check the absence of PCB contamination from the solid-phase extraction silica cartridges.

Gas chromatography-mass spectrometry

Extracts were analysed on a Hewlett-Packard (Avondale, PA, USA) Model 5890 Series II gas chromatograph interfaced to a Hewlett-Packard 5971A MS Engine mass spectrometer MS/DOS ChemStation and equipped for some extracts with a Hewlett-Packard 6890 Series autosampler. The acquisition was performed with the G1034C© program (M03.65.06 Version by Hewlett-Packard 1989-94). The samples were analysed on a 50 m × 0.22 mm id × 0.25 μm film thickness HT-8 (or 1,7-dicarba-*closo*-dodecarborane phenylmethyl siloxane) silica capillary open-tubular column, as this column gave enhanced selectivity in the analysis of PCBs and supported elevated temperatures.[5] The column was protected with a 1 m × 0.22 mm id deactivated non-polar fused-silica capillary column. Unless specified, the column temperature was held at 50 °C for 1 min and then increased at 30 °C min^{-1} to 180 °C, subsequently programmed at 6 °C min^{-1} to 300 °C and finally increased at 30 °C min^{-1} to 360 °C where it was held for 5 min. The total analysis time was 32.3 min. The carrier gas was hydrogen at a linear velocity of 35–40 cm s^{-1} for 250 °C (column head pressure: 18 psi). The injection volume was 1.5 μl and the injection temperature 290 °C. The injector was set in the splitless mode with split vent closed during 1 min after injection. The interface temperature was 300 °C. The electron energy was set at 70 eV and spectral data were acquired at a rate of 4.1 scan s^{-1}. The MS detector was operating in the selected ion monitoring (SIM) mode and the *m/z* values monitored were 256 and 258 for dichlorobiphenyls (PCB 28 and 29), 292 and 294 for tetrachlorobiphenyl (PCB 52), 266 and 268 for TCN (internal standard), 326 and 328 for pentachlorobiphenyls (PCBs 101 and 118), 360 and 362 for hexachlorobiphenyls (PCB 138 and 153), and 324 and 326 for heptachlorobiphenyl (PCB 180). When OCN was used as an internal standard, monitored *m/z* values for this compound were 402 and 404. The instrument was tuned weekly with perfluorotributylamine using the Automatic Tune internal program. In addition, to increase sensitivity, a 200 V overpotential was applied to the electronic multiplier.

Results and discussion

Choice of the chromatographic conditions

Separation of the seven congeners and the internal standard was easily achieved using a low ramp temperature as indicated in the experimental part of this paper. The final column temperature was rather high (*i.e.*, 360 °C) in order to remove contaminants from the column, and thereby to increase the column life. In our preliminary experiments, OCN was used as the internal standard, as suggested by several previous results.[1] However, this compound had a retention time (37.4 min) very different from the seven congeners, due to its much lower volatility. So, we found it preferable to use an internal standard whose volatility is closer to the seven PCB volatility, to avoid discrimination inside the injector as well as to reduce the total analysis time. So, TCN was chosen as precognised by several studies;[2,6] in that way, complete separation could be achieved within 32.3 min.

In the splitless injection mode, the residence time of the needle inside the injector chamber is of prime importance to achieve satisfactory and repeatable injections. As illustrated in Table 1, results from a Soxhlet extract showed a higher overall precision with slow injections (*i.e.*, 3 s). Besides, for the less volatile compounds (PCB 153, 138 and 180) the concentrations determined increased upon slow injection (from 20 to 45%); this clearly shows that these compounds were insufficiently volatilised during rapid injection (*i.e.*, 1 s). As this injection time effect was not observed with standard solutions, it was due to matrix effects. We assumed that the presence of the matrix hindered PCB volatilisation (due to preferential volatilisation of matrix interferences), leading to better results with slow injections.

Successive injections of sludge extracts resulted in frequent clogging of the mass spectrometer, leading to severe sensitivity loss. As an illustration, Table 2 presents the variations of the congener response coefficients (relative to the internal standard TCN) over a period of about six months. Due to elevated values of the relative standard deviations (RSDs), the calibration standard solutions were injected alternately with sludge extracts, in order to redraw the internal calibration curves daily. It can also be noted that the mass spectrometer sensitivity decreased as the number of chlorine atoms in the molecule increased. As an example, the response coefficient of PCB 180 was six times lower than that of PCB 28.

Efficiency of the clean-up step

The efficiency of the silica clean-up step was first investigated with standard solutions of the seven congeners. Solutions at the 100 μg l^{-1} level (for each PCB) in hexane–acetone 1 : 1 (2 ml) were applied on top of silica cartridges, already conditioned with hexane–acetone 1 : 1. PCBs were analysed in the hexane–acetone 1 : 1 fraction (5 ml). Recoveries were quite low (68–81%) due to incomplete retention of the PCBs as well as insufficient elution of the retained compounds. To improve this step, similar experiments were performed, replacing hexane–acetone by hexane in each step (conditioning, sample solvent, and elution solvent). This led to improved efficiencies (mean recoveries between 85 and 109%). Quantitative recoveries were obtained for most of the congeners; the slightly lower values for PCB 28 and 52 are probably the result of volatilisation upon the extract concentration under a gentle stream of nitrogen. In addition, during the purification of sludge extracts, we noted that hexane–acetone was a less selective eluting solvent, as polar interferences were eluted by acetone. So, hexane was used

Table 1 Influence of the injection time on the PCB concentrations found in a sludge extract

	PCB congeners						
	28	52	101	118	153	138	180
Injection time: 1 s							
Concentration in the extract/μg l^{-1}	20.1	15.9	26.0	19.4	54.0	37.3	39.3
RSD (%)	13.7	17.3	4.4	8.7	10.3	9.4	10
Injection time: 3 s							
Concentration in the extract/μg l^{-1}	23.1	19.9	25.2	21.5	63.7	45.5	56.7
RSD (%)	10.5	12.9	5.8	6.6	4.4	4.1	3.6

Table 2 Mean values of the response coefficient (relative to TCN as the internal standard) for the seven congeners, along with variation over time[a]

	PCB congeners						
	28	52	101	118	153	138	180
Relative response coefficient	1.33	0.84	0.54	0.52	0.29	0.28	0.22
RSD (%)	15.37	20.19	26.29	23.37	31.41	27.27	26.69

[a] This study was conducted over nearly six months, using 31 calibration curves.

as the extract solvent before the clean-up step, and as the elution solvent.

Due to the high selectivity of the SIM detection mode, only minor modifications of the chromatogram were obtained upon purification. Indeed, a large peak around 12 min was eliminated. However, the purification step was required to minimize the mass spectrometer clogging and column contamination.

Estimation of PCBs in ambient air of the laboratory

The presence of the more volatile PCBs (congeners 28, 52, 101 and 118) was found in two rooms, where either extraction (and further evaporatory concentration) or clean-up were performed. The corresponding concentrations in the C18 bonded silica extract are given in Table 3. The observed concentrations were over 0.5 ng g^{-1}, thereby indicating a significant contamination in the air.[2] This ambient air contamination was assumed to be due to partial losses of these volatile compounds during the experimental procedure, especially during the evaporatory concentration step. Blank experiments (with solvent extraction) were conducted to check that the presence of PCBs in ambient air did not result in extracts contamination.

Efficiency of the MAE extraction

Evaluation of the extraction efficiency was performed with spiked sludge samples (from Valenton). All extractions were performed in triplicate, and each extract was injected three times in the gas chromatograph. Sludge samples were pre-extracted under similar conditions to remove the initial PCBs; then, once the residual solvent had been completely evaporated, these samples were spiked with 150 μl of a standard solution containing the seven congeners at the 1 mg l^{-1} level, leading to a sludge spiking of 150 μg kg^{-1} dry weight (*i.e.*, close to the initial sludge concentrations). Extraction efficiencies were estimated based upon final analysis of the purified extracts. Satisfactory results could be obtained, the overall recoveries ranging from 88 to 105% (mean recovery: 94.6%). As these values take into account several steps additional to the extraction (concentration, purification, and final concentration), we considered that microwave-assisted extractions were satisfactory.

Table 3 Concentrations of the PCB congeners found in octadecyl-bonded silica (2 g) to estimate contamination in an ambient air laboratory

	PCB congeners			
	28	52	101	118
Concentration/μg kg^{-1}				
Extraction room	3.7	47.5	33.3	9.2
Clean-up room	1.6	4.6	3.2	Traces

Comparison of MAE and Soxhlet extractions

Extractions of Achères sludge samples carried out by MAE and Soxhlet apparatus were compared. They were performed in triplicate, and each extract was injected three times in the gas chromatograph. Results are presented in Table 4. Even though overall better extractions were achieved by Soxhlet, efficiencies of MAE were satisfactory (between 81 and 116%) with regard to the time required (10 min for MAE *versus* 6 h for Soxhlet). The lower precision for MAE results was partly attributed to the filtration step required after MAE, as it may lead to partial losses. The PCB 28 was slightly better recovered using MAE than Soxhlet extraction; this could be related to the stronger concentration of the extract in the latter case (because of a larger solvent volume), resulting in higher losses of this volatile compound. This was confirmed by the presence of this compound (as well as traces of PCB 52 and 101) in the laboratory ambient air.

Effects of MAE parameters

MAE recoveries may be influenced by the extraction time, the microwave power supplied, and the solvent volume used. So, their effect has been investigated. Results presented in Fig. 1 show that increasing the extraction time (from 10 to 30 min) resulted in lower mean recoveries, possibly due to losses upon volatilization. Slightly better results were obtained with 10 min extractions under 90 W instead of 30 W. Yet, as this power resulted in strong heating of the sample (experiments conducted under 120 W showed excessive heating, with possible explosions), a power of 30 W was preferable. Finally, the solvent

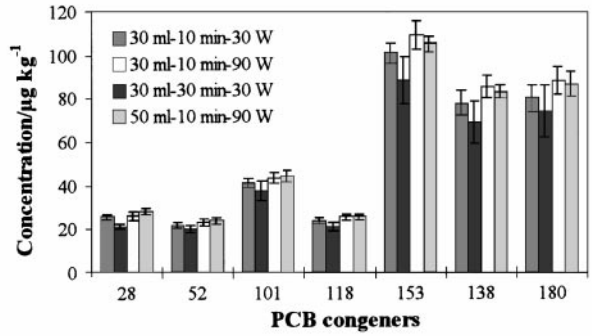

Fig. 1 Influence of MAE conditions on the PCB concentrations found in Achères sludge samples. GC conditions: autosampler injection (3 s); column temperature: 50 °C (1 min)–180 °C at 30 °C min^{-1}, to 300 °C at 6 °C min^{-1}, to 360 °C (5 min) at 30 °C min^{-1} (total analysis time: 32.3 min).

Table 4 Comparison of Achères sludge concentrations determined with either MAE[a] or Soxhlet extraction[b]

	PCB congeners							
	28	52	101	118	153	138	180	Sum
MAE								
Sludge concentration/μg kg^{-1}	85.9	48.8	82.4	60.0	174.2	117.2	128.8	697.3
RSD (%)	21.0	39.0	31.7	27.9	32.8	30.6	29.9	27.4
Soxhlet								
Sludge concentration/μg kg^{-1}	73.8	48.9	89.3	73.0	211.5	141.9	159.2	797.5
RSD (%)	17.9	32.2	13.5	17.8	10.4	12.2	12.5	10.0
MAE/Soxhlet (%)	116.4	99.8	92.3	82.3	82.4	82.6	80.8	87.4

[a] Dried sludge (1 g) + activated copper (1 g) extracted with 30 ml hexane–acetone 1 : 1 during 10 min under 30 W (injection time for GC: 1 s). [b] Dried sludge (1 g) + activated copper (1 g) extracted with 250 ml hexane–acetone 1 : 1 during 6 h (injection time for GC: 1 s).

volume (50 ml instead of 30 ml) had no significant influence on the recoveries. So, the following conditions were chosen: 30 ml solvent, 10 min extraction under 30 W.

Additional experiments were conducted in order to estimate losses of volatile PCBs throughout the experimental procedure, as evidence of such losses has been given (*i.e.*, recovery of spiked PCB 28 around 80%, and presence of volatile congeners in laboratory ambient air). So Valenton sludge samples were spiked with PCB 29 (at the 50 μg kg^{-1} level) as this non-natural congener is often suggested as a recovery standard (because its volatility allows the detection of evaporation losses).[2] The overall recoveries were around 65–70% for this compound. As the congeners 28, 52 and 101 are less volatile than PCB 29, their recoveries should be higher as already estimated for sludge samples spiked with the native PCBs.

Finally, our complete experimental procedure is detailed in Fig. 2.

Comparison of our results with those of an independent laboratory

Sludge samples were regularly taken in the Valenton plant in order to make composite samples over two weeks. These samples were further divided in two parts. The first one was analysed by our laboratory, and the second one by an independent laboratory (Institut Pasteur, Lille, France). The experimental procedure used in this laboratory was as follows: Soxhlet extraction of dried sludge (4–5 g) with 100 ml hexane–acetone 1 : 1 during 6 h; then the extract was concentrated up to 1 ml and cleaned-up onto Florisil (1 g). PCBs were further eluted with hexane (10 ml). The final extract was again concentrated up to 1 ml and analysed by GC coupled to electron capture detection (after addition of an internal standard).

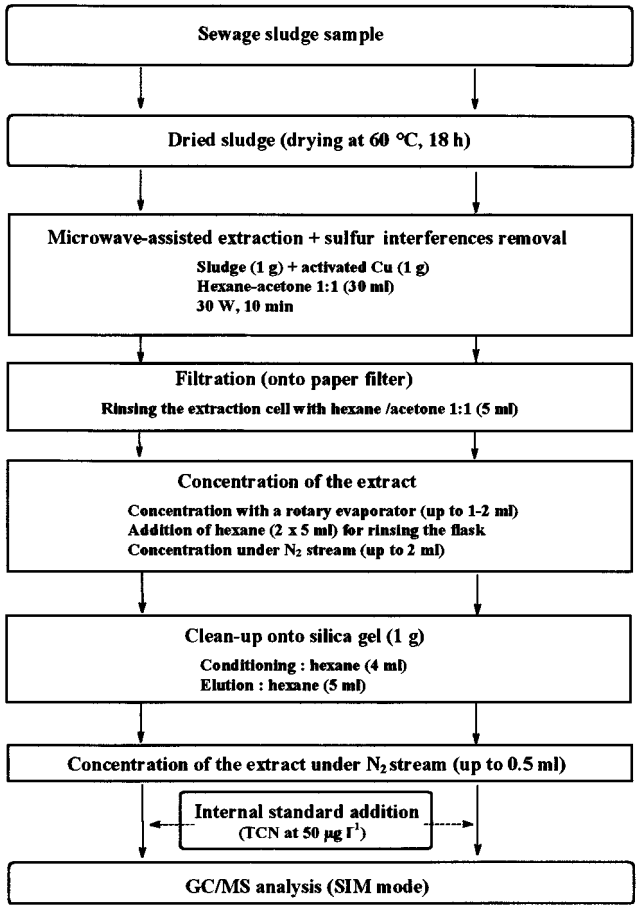

Fig. 2 Experimental procedure for the determination of PCB in sludge samples.

As shown in Figs. 3 and 4, our results compared favourably with the concentrations determined by the other laboratory. This was quite satisfactory, as previous results from interlaboratory studies on the determination of PCBs in sediment samples showed severe discrepancy between results (differences be-

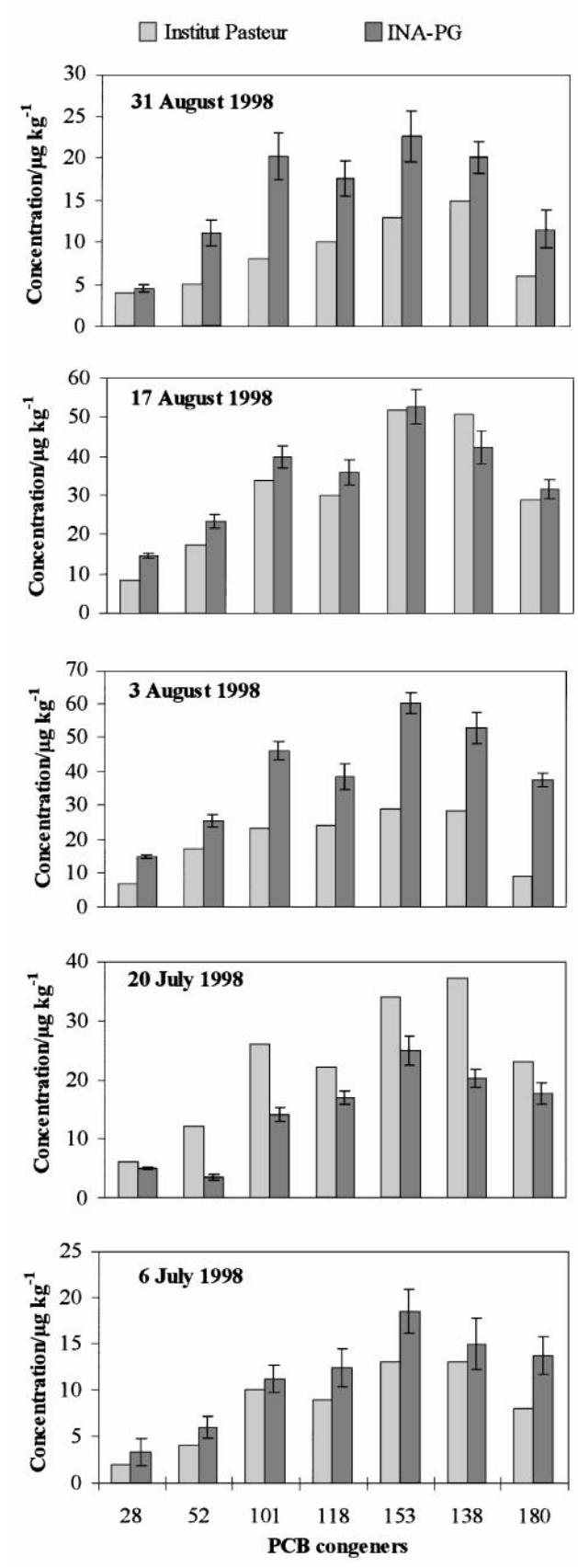

Fig. 3 Comparison of individual PCB concentrations determined in several Valenton sludge samples by our laboratory (INA-PG) and an independent laboratory (Institut Pasteur).

tween laboratories might be nearly one order of magnitude).[1] However, depending on the sample to be analysed, differences occurred between their results and our values. In fact, it must be pointed out that the samples received by both laboratories might have differed somewhat, as sludge samples had been taken from a sludge tank, and sent immediately to the laboratories without any treatment. In particular, they had not been homogeneized, so that the samples received in both laboratories were not exactly the same. So, future experiments will be conducted on composite samples that will be homogeneized in the wastewater treatment plant, before being divided in sub-samples sent to the laboratories involved in the study. This will avoid variability due to the sample heterogeneity (which is crucial for sewage sludges).

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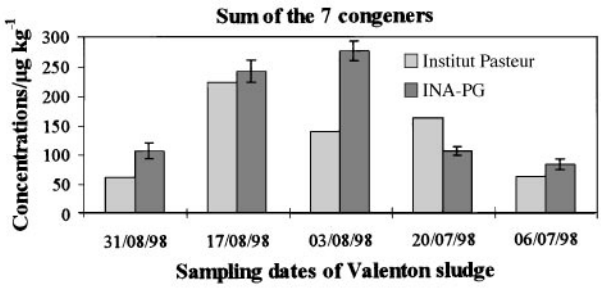

Fig. 4 Comparison of the concentrations determined for the sum of the seven congeners in several Valenton sludge samples by our laboratory (INA-PG) and an independent laboratory (Institut Pasteur).

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