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# PCB Trace Enrichment From Contaminated Natural Water at the Sub ppt Level on C<sub>18</sub> Microcartridges

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A novel micromethod of PCB trace enrichment from contaminated water at the sub ppt level is described. This procedure involves quantitative adsorption of PCB on C<sub>18</sub> microcartridges. This sorbent is a covalently bonded silicagel with octadecyl groups. PCBs are retained on the modified surface and subsequently eluted by appropriate apolar solvent prior to high resolution capillary gas chromatography. PCB recovery efficiency has been investigated in the concentration range from 0.01 to 10 ppb. This extraction method appears to result in high performance and rapid purification of dissolved PCB in natural water. The mean recovery percentage reached indeed 95.2% (SD=6.1%) within an overall procedure ranging 10 min. As a consequence, the simplicity of use of this PCB trace enrichment makes it useful for field sampling as well as for laboratory experiments.

KEY WORDS: PCB, aquatic ecosystem, C<sub>18</sub> microcartridges, extraction method.

## INTRODUCTION

A recent survey of the distribution and amount of persistent toxics in the Belgian environment emphasized that the aquatic ecosystems are particularly contaminated by PCB.<sup>1</sup> Analysis of trace amounts

of organic xenobiotics such as PCB in water requires usually recovery into a small volume of solvent before determination by gas chromatography. The most usual PCB extraction method from natural or waste waters is the well-known liquid-liquid extraction.<sup>2-3</sup> Other analytical procedures which are frequently employed for measuring low level of organic micropollutants in water in the range from 10 to 100 ppb involve charcoal or XAD resin adsorption followed by selective desorption using appropriate eluents.<sup>4-7</sup> These methods require large volume of water (up to 5l) and water non miscible solvent (up to 200ml) in order to obtain a sufficient recovery of organic micropollutants. Moreover, these procedures involve concentration of extraction solvent to have a sufficient sensitivity in the ppt range. Furthermore, the concentration step, even carefully performed, could induce losses of volatile compounds and concentration of solvent impurities which disturb analysis to a large extent.<sup>4-8</sup> As a consequence, micropollutant extraction methods which avoid important solvent concentration step appear to be more advisable for the recovery of trace organics in water.

The present paper deals with quantitative PCB trace enrichment at the sub ppt level from contaminated water on C<sub>18</sub> microcartridges. This sorbent is a covalently bonded silicagel with octadecyl groups particularly convenient to receive non polar compounds dissolved in a polar solvent.

## EXPERIMENTAL

### Analytical procedures

Trace enrichment of PCB from contaminated water using C<sub>18</sub> microcolumns was tested on a commercial mixture of Aroclor 1260 (Monsanto, USA). All solvents (hexane, acetone, methanol) were HPLC and pesticide grade. Analytical standards and solvents have been purchased from Alltech Belgium (Eke, Belgium). PCB extractions were carried out using microcolumns filled with 100mg C<sub>18</sub>, particles of which were 40 μ of diameter (Bond Elut C<sub>18</sub>, Analytichem International, Harbor City, California, USA). Stock solutions of Aroclor 1260 were made up in acetone containing 1 ng/μl, 0.1 ng/μl and 0.01 ng/μl. Given amounts of water distilled in glass

ranged from 100 to 500 ml have been spiked with these solutions according to the desired PCB concentrations (0.01, 0.05, 0.1, 0.5, 1, 2, 5 and 10  $\mu\text{g/l}$ ). All glassware was washed with acetone and *n*-hexane before use.

Adsorption of PCB onto the inner surface of glass was prevented by treatment with dimethylchlorosilane (DMCS 10% in *n*-hexane). This step in the analytical process is of first importance. Indeed, preliminary experiments have obviously shown that the amounts of PCB adsorbed on the inner surface of the glassware were significantly lower in the silicized vessel ( $4\% \pm 0.3$ ) than in the non treated one ( $25\% \pm 5.2$ ).

Maximum efficiency of PCB trace enrichment onto  $C_{18}$  micro-columns was achieved by successive treatment with 1 ml *n*-hexane, acetone, methanol and methanol in water (1:1; v/v). PCB spiked water samples (100 ml to 500 ml) were then passed through the column so treated at a flow rate of 10 ml/min (vacuum pressure = 0.9 bar). Vacuum was maintained for a few minutes in order to dry the columns. Most interfering polar compounds retained on the sorbent medium were eliminated by elution with 0.2 ml of methanol/water (1:1; v/v). PCBs were then eluted with 2 ml hexane. Prior ECD capillary gas chromatography analysis, extracts were evaporated up to 100  $\mu\text{l}$  under a gentle stream of nitrogen according to the PCB concentrations in water.

### Gas chromatography analysis

Samples of 1  $\mu\text{l}$  were injected in the splitless mode at 260°C (gas holded time = 30 s) using a Carlo Erba Fractovap capillary gas chromatograph (Carlo Erba Instrumentazione, Milano, Italy) equipped with a  $\text{Ni}^{63}$  ECD at 275°C. Samples were analysed on a 25 m  $\times$  0.25 mm ID glass capillary coated with 0.15  $\mu\text{m}$  of chemically immobilized SE-52. This analytical column was prepared according to Grob<sup>9</sup> and was kindly provided by Dr Termonia, IRC, Tervueren, Belgium. The column was temperature programmed from 60°C (initial hold = 1 min) to 240°C at 7.5°C/min with a hydrogen carrier gas flow rate of 1 ml/min and a  $\text{Ar/CH}_4$  (90:10) make up gas flow rate of 30 ml/min.

### Quantitation of PCB

PCB peaks were identified by retention time. In order to calculate the amounts of PCB retained on  $C_{18}$ , we used 10 major components of Aroclor 1260 which represent mainly hexa- and heptachlorobiphenyls (Figure 1). The total PCB concentration (expressed as Aroclor 1260) was calculated using the sum of areas of these 10 peaks in water sample extract and in Aroclor 1260 external standard ( $1 \text{ ng}/\mu\text{l}$ ).

### EFFICIENCY OF PCB TRACE ENRICHMENT METHOD

In a preliminary series of experiments, the recovery efficiency of the 10 analysed individual components of Aroclor 1260 has been tested.

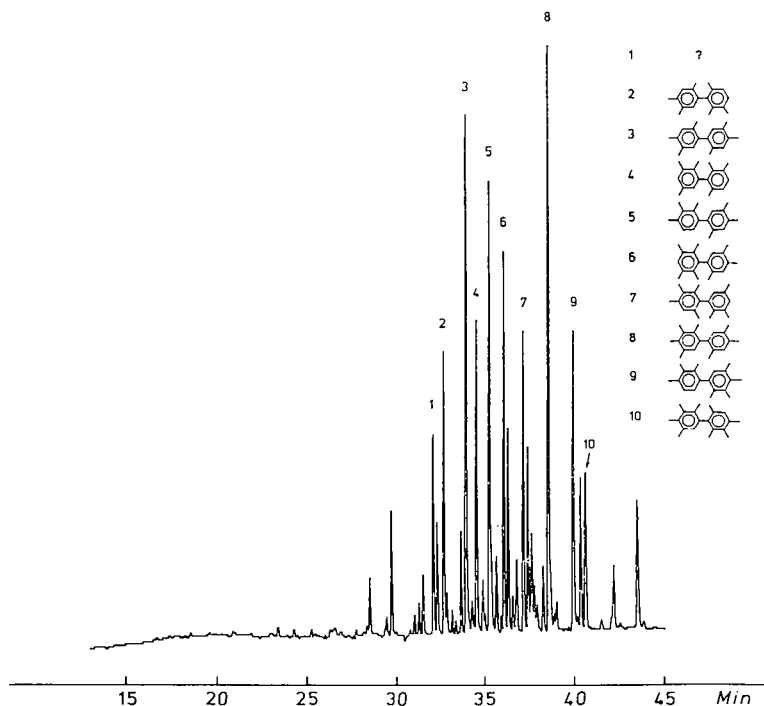


FIGURE 1 A typical chromatogram of Aroclor 1260 standard ( $1 \text{ ng}/\mu\text{l}$ ) and identification of the 10 pure PCB components used to determine the PCB concentrations in water samples. These components represent 95% of the PCB mixture Aroclor 1260.

For that purpose, 3 replications of PCB spiked water ( $1\ \mu\text{g}/\text{l}$ ) extractions have been performed on  $\text{C}_{18}$  microcartridges. A typical result of this experiment is shown in Figure 2. The data reported in Table I show that the mean recovery percentage reached about 97% for each of the 10 components taken into consideration.

In another set of experiments, we have tested the possibility of an effect of the PCB concentration on the percentage of the recovery efficiency. Data are reported on Figure 3. At low PCB concentrations, ranging from 0.01 to 1 ppb, high and reproducible recovery percentages support the idea that the adsorption of PCB onto  $\text{C}_{18}$  microcartridges is efficient enough to retain a significant amount of the PCB present in analysed water. Conversely, at higher PCB concentrations ranging from 2 to 10 ppb, the extraction efficiency drops down to 50%. These drastic changes in PCB adsorption

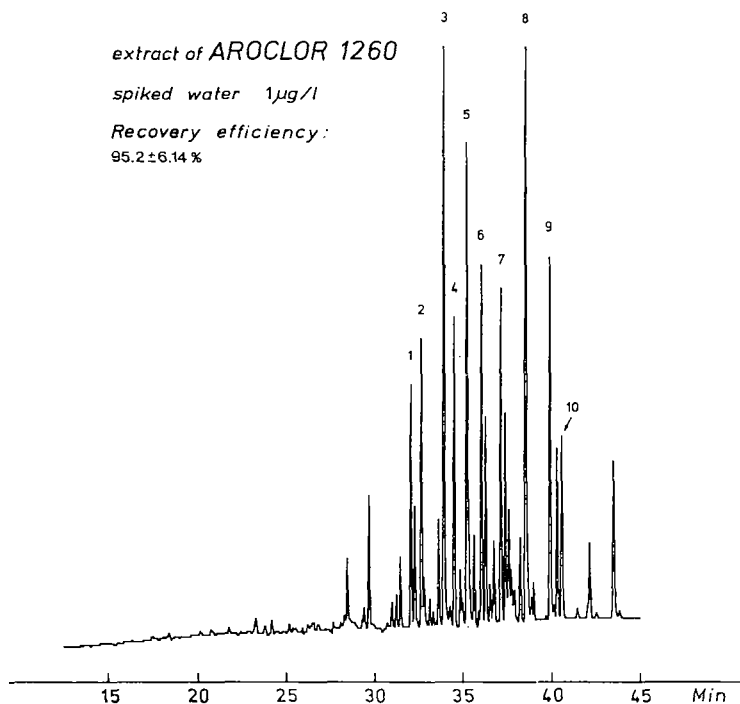


FIGURE 2 Recovery of PCB extracted from Aroclor 1260 spiked water ( $1\ \text{ppb}$ ) and performed on  $\text{C}_{18}$  microcartridges.

TABLE I

Recovery efficiency of the set of 10 individual components of Aroclor 1260 from 1 ppb spiked water.

Peak No.	IUPAC No.	Recovery efficiency (%) ±SD
1	?	96.5±2.1
2	149 2,4,5,2',3',6'	110.9±22.5
3	153 2,4,5,2',4',5'	95.3±2.1
4	151 2,3,5,6,2',5'	97.8±4.3
5	138 2,3,4,2',4',5'	97.9±8.3
6	187 2,3,5,6,2',4',5'	94.9±2.9
7	174 2,3,4,5,2',3',6'	95.8±4.8
8	180 2,3,4,5,2',4',5'	92.7±9.1
9	170 2,3,4,5,2',3',4'	91.1±2.7
10	196 2,3,4,5,2',3',4',6'	80.0±5.7
		Mean recovery efficiency: 95.2±6.1

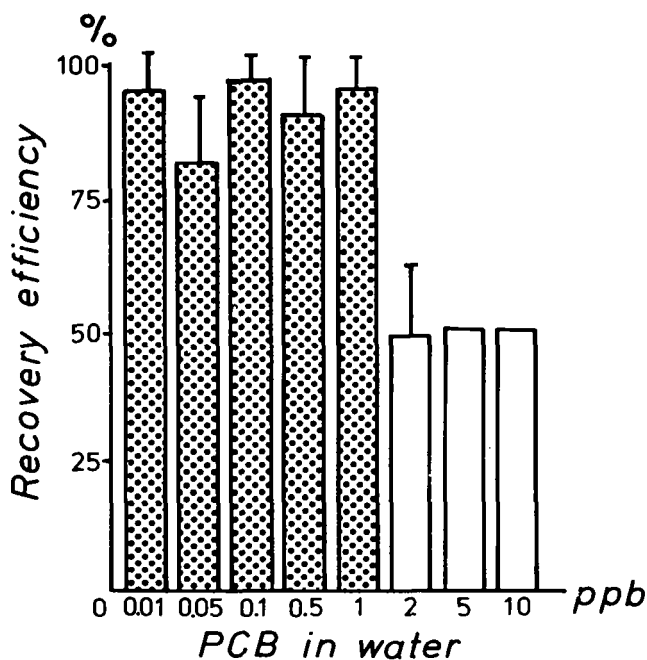


FIGURE 3 Recovery efficiency (in percent) of PCB after  $C_{18}$  enrichment vs PCB concentrations in Aroclor 1260 spiked water.

onto  $C_{18}$  are undoubtedly in relation with the solubility limit (about  $1 \mu\text{g/l}$ ) of the hexachlorobiphenyls, i.e. the major components of Aroclor 1260.<sup>10</sup>

These results are of significant interest when considered in the context of the usual PCB concentration measured in aquatic environment. Indeed, maximum concentrations in highly polluted Meuse river in Belgium reached  $0.6 \mu\text{g/l}$  ( $\text{SD}=0.35$ ) as shown in Figure 4.

According to Lafontaine and Delforge,<sup>11</sup> a concentration of  $0.5 \mu\text{g/l}$  of PCB in natural water corresponds to a high pollution level. As a consequence, the accuracy of the PCB trace enrichment method described is sufficient enough to investigate the difficult analytical problems of the distribution of PCB in natural water.

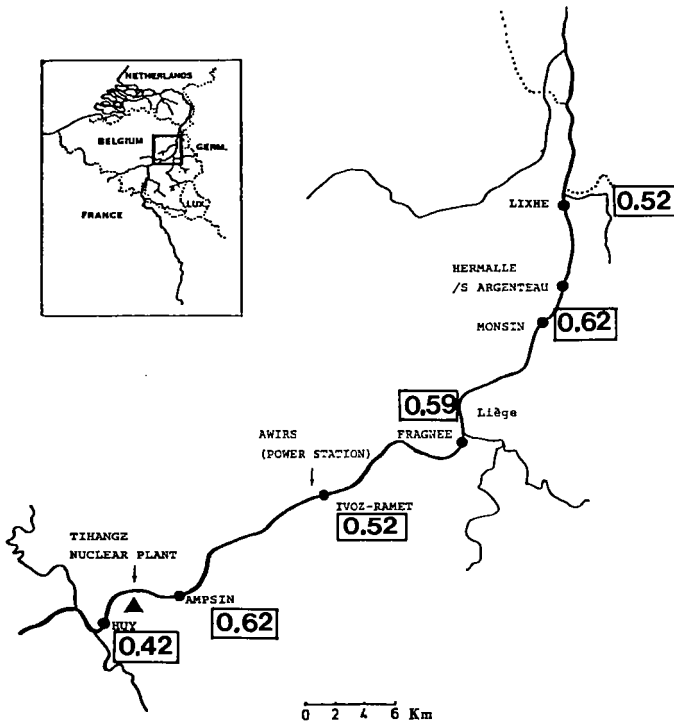


FIGURE 4 Mean PCB concentrations in different sampling places in Meuse river in Belgium. (Concentrations are expressed in ppb).



### PCB adsorption equilibrium on C<sub>18</sub> microcartridges

In aquatic environment, PCBs are known to accumulate on particle matter at higher concentrations than in water.<sup>12</sup> At the same time, PCB accumulation onto suspended matter was found to be correlated to PCB concentration in water, and could be described by a formula analogous to that of a Freundlich plot.<sup>13</sup>

Relationships between maximum capacity of PCB on the adsorbing agent, C<sub>18</sub>, and PCB concentration in solution were tested (Figure 5). This Figure shows a typical Freundlich plot. The quasiequilibrium adsorptions of PCB on C<sub>18</sub> particles were assumed capable of treatment by a Freundlich isotherm equation:

$$q = KC^{1/n}$$

where  $k$  and  $n$  are constants, and  $q$  is the final concentration on the adsorbent. The value of  $n$  for 40  $\mu$  C<sub>18</sub> particles is 1.12. A state of equilibrium was assumed to be maintained between C<sub>18</sub> adsorbent and its interstitial water though the method used involved a dynamic flow of PCB contamination water through C<sub>18</sub> microcartridges instead of a steady state system. However, the results are in quite good agreement with Hiraizumi *et al.*,<sup>13</sup> who suggest the maximum capacity of PCB adsorption can be reached by the adsorption equilibrium of PCB.

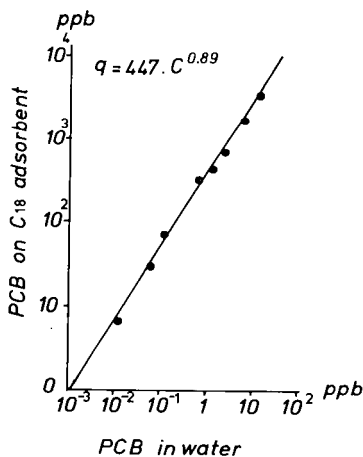


FIGURE 5 Adsorption isotherm for PCB on C<sub>18</sub> adsorbent.

## CONCLUSIONS

From this work, it is clear that PCB trace enrichment on C<sub>18</sub> microcartridges constitute a highly efficient PCB extraction method from contaminated water which could find favourable application to micropollutants analysis. Moreover, because of its high level of efficiency, its velocity and its simplicity of use, PCB C<sub>18</sub> extraction appears to be useful for field sampling as well as for laboratory practice.

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