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Review

Current developments in the analysis of water pollution by polychlorinated biphenyls

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Abstract

A review and discussion of the analytical developments of the last 10 years in the determination of polychlorinated biphenyls (PCBs) in water are presented, including sample treatment, clean-up, identification and determination. Some of the most significant advances have occurred in the area of sample preparation, such as the increased adoption of solid-phase extraction and on-line techniques and the chromatographic separation of PCB congeners, principally by mass spectrometry. Special attention is focused on applications to real samples.

Keywords: Reviews; Water analysis; Environmental analysis; Extraction methods; Sample handling; Polychlorinated biphenyls

Contents

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1. Introduction

There are 209 theoretically possible polychlorinated biphenyl (PCB) congeners. The commercial products [Aroclor (USA), Chlorphen (Germany) and Kaneclor (Japan)] are complex mixtures containing 132 congeners, and each mixture consists of different, but overlapping, assemblages of PCBs [1]. Their long-term heavy usage as dielectric fluids, in transformers and capacitors, hydraulic fluids, fire retardants, paints, pigments and the paper and cardboard industries, together with their high hydrophobicity, lipid solubility and persistence, have resulted in their widespread permeation into almost every environmental medium throughout the world [2–5].

Because of their ubiquity, PCBs are common environmental pollutants that are included in the priority pollutants list published by the US Environmental Protection Agency (EPA) [6] and by the European Union (EU) [7].

The toxicities of PCBs differ for each congener and range from highly toxic, which are potent inducers of enzymes (P-450 and glucuronil transferases), to moderately toxic, which are more potent inhibitors of dopamine and other neurotransmitters [8]. PCBs have immunosuppressive activity, are tumour promoters and interfere with calcium utilization (thus producing their well known negative effect on eggshell formation in birds) [9]. They are classified as carcinogens by both the EPA and the International Agency for Research on Cancer (IARC). Because of their persistence, potential for bioaccumulation and biomagnification, monitoring of PCBs is important for the conservation of the environment and biota [10].

Aquatic ecosystems have been contaminated by direct dumping of PCBs and waste fluids containing PCBs [11,12]. Their insoluble character causes their rapid binding to some organic entities, such as river and lake sediments [13,14], algae and protozoa [15–17].

The concentrations of PCBs in water are very low and can only be measured by sensitive techniques. The EU established a maximum level of 1–2 μg/l for natural waters [18] and a ten times lower value for drinking waters [19]. Concentrations in seawater in the low picogram per litre level have been reported for the most abundant congeners.

Therefore, adequate methods for monitoring the levels of these compounds in effluents and in waters affected by such effluents are required. To avoid this problem, some Marine Health programmes utilize biological indicators such as mussels to judge coastal contamination by PCBs. It has been suggested that this "mussel watch" could serve as an early warning system for ecological catastrophes [20–23].

This review examines the most important advances in the analysis of water pollution by PCBs and also reports real concentrations in environmental waters. The rising cost of sample preparation and the need to measure PCBs at the ultratrace level make automation and on-line systems necessary in routine analysis. The principles and practices of determining the recoveries of trace PCBs and the values obtained in the various studies are discussed.

2. Sampling

Water sampling is made difficult by the usually very low concentrations of PCBs in waters caused by the hydrophobic nature of these compounds [24,25]. Atmospheric transport is the major pathway of the global distribution of PCBs from land to water [26], with the river and ocean sediments serving as reservoirs of PCB residues [27]. The distribution of these contaminants in water is heterogeneous; there is a gradient of concentration occurring from the fresh water sources toward the sea. The water sample taken must be representative of the water environment [20].

In seawater samples, the concentration of PCBs is great in the surface layers. The air–sea interface is a point of interest because sea slicks may significantly accumulate PCBs [26]. There are specific microlayer samplers suitable for collecting the upper water layer of thickness 50–400 μm. However, to take a representative sample, possible contamination by the penetra-

tion of the sampler through this surface layer of the sea has to be excluded. For this purpose, different samplers have been designed: the Blumer sampler, the DHI sampler and a high-volume water sampler prepared to pump water from a defined depth below the sea surface outside the wake of the survey vessel [28].

Sampling is a time-consuming and error-prone step in the analytical procedure. Equipment used for sampling and storage must be treated according to the procedures commonly recommended in the literature [29,30].

A problem derived of the low water solubility is their adsorption on solid supports with a potential substantial effect on the results. Owing to adsorption, the use of polymers, other than PTFE, should generally be avoided during PCB analyses, as demonstrated in different experiments. Generally, water samples were collected in 50 l or larger stainless-steel drums to avoid these problems [24,31].

The adsorption on solids also complicates PCB determinations in surface water. In the water phase, material is present in a wide range of sizes and with many different characteristics. The range encompasses truly dissolved materials such as proteins, lipids and humic and fulvic acids, which constitute the dissolved organic matter (DOM), and also colloids and suspended solid matter (SPM) [32].

SPM is an operationally defined parameter; in practice, the SPA is usually defined as all particles that are retained by a 0.45-μm filter. Concentrations of PCBs in water containing suspended matter are almost completely determined by this SPM. Distribution coefficients between this SPM and solutions have been reported to be of order of 10^5 [24]. Removal of the SPM therefore is necessary. Different devices such as glass-fibre filters, which have nominal 1-μm pores [32–35], tangetial flow membrane filters with exact 0.45-μm pores [32] and continuous-flow centrifugation [32,36] are available. Possible artifacts with filtration, such as clogging during filtration and adsorption of PCBs on the filter, have been investigated.

It is generally appreciated by environmental analytical chemists that the binding of organic chemicals to DOM remaining in the water samples can also affect the recoveries obtained on extracting PCBs from filtered or centrifuged water [24].

The subsequent processing of the water samples may include different steps that allow both the extraction and enrichment of the PCBs with high selectivity [25,37–39].

3. Isolation and clean-up procedures

In general, liquid–liquid or liquid–solid extraction techniques are applied [40–42], but analysts are continually exploring new techniques and new aspects of the old techniques. Alternative approaches that should still be studied intensively are mentioned in the literature: dialysis [43], solvent-filled dialysis membranes [44], adsorption on uncoated capillary columns [45,46], gas purging [47] and in situ extraction with a fluidized bed-type extractor [48].

An interesting selective concentration method was developed by Hess et al. [49], in which PCBs (24 congeners) were concentrated by adsorption on magnesium hydroxide and precipitated in situ. The precipitate was removed by centrifugation and dissolved in a small volume of acidic buffered solution for analysis. The method is selective for polycyclic aromatic hydrocarbons (PAHs) and PCBs of high molecular mass.

3.1. Liquid–liquid partitioning (LLP)

Although it uses large amounts of potentially toxic organic solvents, LLP is one of the time-tested conventional sample preparation methods in environmental analysis for measuring organic pollutants in water and waste water samples.

A review of the literature about methods used to extract and isolate PCB residues in water (Table 1) reflects that the majority of LLP methods for isolating PCBs are now well established. Table 1 shows the type of water analysed, the isolation and clean-up methods used, the PCBs determined, the amounts spiked into the water and the recoveries determined, the limits

Table 1
LLP and GC detection method for the determination of PCBs in water

Water	Isolation and clean-up	PCB congener tested	Concentration (μg/l)	Recovery (%)	Detection limit (ng/l)	Other compounds	Detection	Ref.
Waste water (1 l), pH adjusted to 2, 7, 10	3 × 50 ml of DCM or DCM–hexane and clean-up by Florisil and alumina	Aroclor 1016	25	92–101	–	OCPs	ECD	[51]
		1221	55	90–102				
		1232	55	86–100				
		1242	28	83–97				
		1248	40	87–99				
		1254	50	91–95				
		1260	80	91–95				
Water, 10–100 ml	SDE with *n*-pentane	Aroclor 1260	10	81–103	–	OCPs	ECD	[52]
Water samples (4 × 4 l)	4 × 80 ml of *n*-hexane clean-up with acid silica gel	18	0.0032	97	–	CBs	ECD	[53]
		40	0.0048	96		HCBDs		
		101	0.0023	87		CTs		
		153	0.0054	93				
		194	0.0038	98				
Reagent, tap and river water (1 l)	Water, pH 8 3 × 50 ml DCM **EPA 680**	Aroclor 1016	0.05–2	–	0.1	OCPs Chlorinated benzenes	MSD	[54]
		1221						
		1232						
		1242						
		1248						
		1254						
		1260						
		1262						
Waste water (1 l) (without filtering)	3 × 50 ml of 15% DCM in *n*-hexane Clean up with Florisil Removal of elemental sulphur with metallic mercury	36 components	0.02–1.2	–	–	–	ECD	[55]
Reagent, tap and river water	Water (without pH adjustment) 3 × 60 ml DCM **EPA 680**	1	27–130	–	–	OCPs	MSD	[56]
		5						
		29						
		50						
		87						
		154						
		188						
		200						
		207						
		209						
Water (about 2 l)	250 ml of *n*-hexane Clean-up with acid and oxidant treatment	PCBs	–	–	–	OCPs	ECD	[57]
Tap, river and waste water (1 l)	Water (without pH adjustment) 3 × 60 ml of 15% diethyl ether in hexane Acid and alkaline treatments	Aroclor 1254	380	101.8	–	OCPs	ECD	[58]
		1260	420	99				

Water samples (1 l)	**EPA 680** 3 × 50 ml DCM	1 5 29 50 87 154 188 200 209	148	60	–	OCPs	MSD	[59]
Sea water (50–100 l)	Cyclohexane (250 ml) continuous	PCBs	–	–	–	*n*-Alkanes Carboxylic acids	ECD	[34]
Waste water (300 ml)	3 × 60 ml DCM Clean-up with silica and with Florisil Removal of elemental sulphur Tetramethylammonium sulphite	Aroclor 1016 1260	– –	114–122 99–102	500–900	OCPs	ECD	[60]
	EPA 608							
Water (100 ml)	20 ml DCM Silica gel for separation	Chlophen A50	50–1	80–90	–	OCPs	ECD	[61]
Water (20 l) (pH 1, 12 and 7.4)	500 ml DCM Clean-up with silica gel	15 101 151 118 153 141 138 187 180 170 201 196 195 194	0.038 0.0045 0.0026 0.0020 0.0017 0.0014 0.0021 0.0017 0.0015 0.0016 0.0022 0.0018 0.0013 0.0012	56–65 69–92 71–76 107–115 96–111 65–74 81–99 64–82 76–79 50–71 56–71 51–69 42–61 53–68	–	–	ECD	[62]
River water (2 l)	50 ml of hexane	Cl_1–Cl_{10}	–	86.5	–	–	MSD	[63]
Water sample (1 l)	125 ml of *n*-pentane in a rotary evaporator	28 52 101 138 153 180	0.01–0.05	70	2–15	OCPs Chlorobenzene	ECD	[64]
Water sample (1 l)	10 ml of pentane	28 52 101 138 153 180	0.01–0.05	80–90	3–5	OCPs Chlorobenzene	ECD	[64]

(Continued on p. 454)

Table 1 (*continued*)

Water	Isolation and clean-up	PCB congener tested	Concentration ($\mu g/l$)	Recovery (%)	Detection limit (ng/l)	Other compounds	Detection	Ref.
Water sample (1 l)	SDE with hexane	28 52 101 138 153 180		<70	35	OCPs Chlorobenzene	ECD	[64]
Water sample (500 ml)	SDE with *n*-hexane	DP 6	2	100	–	OCPs	ECD	[65]
Waste water (2 l)	2 × 120 ml DCM Clean-up with Florisil	Aroclor 1260	1	70	30	–	ECD ELCD	[66]
River water (1.5 l)	2 × 50 ml DCM	PCBs	–	80–96	6	OCPs	ECD	[67]
River water	3 × 50 ml of *n*-hexane	PCBs	0.896	81–94	–	OCPs	ECD	[68]
Sea water (10 l)	Continuous extraction with *n*-pentane Clean-up with silica Removal of elemental sulphur Tetramethylammonium sulphite	18 31 28 52 49 44 101 118 153 105 138 187 180	–	>95	5 2.8 2.8 2.7 1.0 1.3 13 3.7 12 7 2.5 3.3 2.3	OCPs	ECD	[32]
Tap and river water (2 l)	Water, pH 5–9 3 × 60 ml of *n*-hexane Acid treatment	Aroclor 1254 1260	2–20	63 83	1	OCPs Chlorophenols	ECD	[69]
River water (60 l) (pH 11)	2 × 500 ml DCM Clean-up with Florisil	PCBs	$(7–13)\cdot10^{-6}$	90	0.007–0.013	OCPs	ECD	[35]
Water (100 ml)	SDE equipment with *n*-pentane	101 77 151 118 153 105 138 126 167 156 180 169 170 194	0.01–1	57–98 93–98 101–113 71–100 97–115 92–103 100–126 68–105 94–105 76–105 102–114 93–113 103–112 102–109	–	PCDDs PCDFs	ECD	[24]

of detection (LODs), other compounds that can be extracted together with PCBs and the detector employed.

Recovery measurements are one of the more difficult and ill-defined aspects of trace organic analysis. Experiments designed to obtain the efficiency of an analytical method often implicitly assume that this also includes the efficiency of the extraction from the matrix.

Differences in behaviour between spiked PCBs and those already present in the water phase have induced some researchers to perform recovery measurements by comparing several extraction methods [34]. At present, the way to calculate properly the recovery of a method using spiked water samples is well established. The PCBs are added below the surface of the sample in a small volume (ca. 1–2 ml) of water-miscible solvent. The water must be completely mixed and allowed to stand at least overnight prior to extraction to allow the PCBs to come into equilibrium with the other organic materials, particularly humic materials. The spiked water samples must be analysed in them entirely, including the inner surfaces of the container, either separately or as a single determination [32,50]. Some of them are recommended by different environmental protection agencies. For example, the EPA published the 500 series of methods for drinking water analysis and the 600 series for waste water [70,71].

Eleven pesticides and PCBs are measured with method 505 [72,73]. A 35-ml water sample is extracted with 2 ml of hexane in a liquid–liquid extraction (LLE) procedure. Similarly, separation, identification and measurement are via capillary GC–electron-capture detection (ECD) using one capillary column.

Method 508 requires that the sample was collected with the mercury(II) chloride as bactericide. A 1-l volume of water is buffered to neutral pH and dechlorinated; salt is added to decrease the pesticide solubility and the sample is shaken with 300 ml of dichloromethane (DCM). Method 505 is cheaper and easier to use than Method 508.

PCB determinations in waste water are resolved by EPA Methods 608, 617 and 680 [74]. Waste water typically requires extraction (with DCM or DCM–hexane mixtures), concentration and clean-up with silica or Florisil before injection into the GC system.

There are other well established testing procedures such as American Society for Testing and Materials (ATSM) methods or Standard Methods for the Examination of Water and Waste Water [75].

The simplest LLP technique is shaking or stirring the sample with an appropriate organic solvent at room temperature without pH adjustment, that is, at about neutral pH [74]. However, the effect of pH on the extraction efficiency of PCBs and chlorinated pesticides from filtered Niagara river water has been demonstrated [62]. In 43 samples collected in 1985–86, the basic extract contained 40% of the PCBs and chlorinated pesticides, the acidic extract contained 15% and the suspended solids 45%. This phenomenon may be the result of the binding of lipophilic chemicals to DOM, binding that is not disrupted by organic solvent extraction at acidic or neutral pH but is at least partially disrupted by extraction at high pH.

LLP procedures with samples up to 100 l and using reverse continuous-flow extractors have been published [32,34]. These extractors should be used when the sample is very diluted (such as occurs in sea water).

Simultaneous steam distillation–solvent extraction (SDE) procedures have been reported [24,64,65]. The compounds are first distilled and then extracted into an organic solvent. These techniques were initially laborious and required solvent concentration by evaporation [37]. More recently, micro-extraction procedures, using different solvents, such as *n*-pentane [24,52] or *n*-hexane [65], have yielded good recoveries of PCBs from water and are ecologically beneficial, because they need only small amounts of solvents (<10 ml). In contradiction, Geisller and Schöler [64] found unacceptably low recoveries with SDE.

3.2. Solid-phase extraction (SPE)

In SPE processes, a compound is isolated from

a liquid sample by differences in its relative solubility between a liquid mobile phase and a stationary phase. The process is often performed by packing a stationary phase into a cartridge, passing the water sample through the cartridge and eluting the retained analytes with a solvent of the appropriate strength [76–78]. Table 2 shows the SPE method applied to the water analysis for PCBs.

A wide variety of solid sorbents exhibiting various chemistries are available [78]. C_{18} sorbents are efficient for trapping PCBs using sample volumes between 1 and 10 l [88,94], which are generally sufficient to achieve a detection limit of 0.1 μg/l. The use of Amberlites or polyurethane foams is recommended when high volumes (>16 l) of sample are to be analysed [34,80].

The SPE recovery depends on factors such as the type of water sample (presence of particulate matter, presence of interfering compounds such as surfactants, ionic strength of the water), pH and sorbent treatment [78]. All these factors have been studied for water analysis for PCBs by SPE using C_{18} [88]. pH does not affect the recovery. However, the presence of organic matter and surfactants diminishes considerably the efficiency of the process.

SPE has advantages over the LLP such as avoiding manipulations with large volumes of solvents and being rapid and easily automated, and because of this it has been proposed by the EPA in a draft method [73] for the determination of 43 organic contaminants, including PCBs. The cartridge procedure, as presented in EPA Method 525, requires a 1000-ml water sample acidified to pH 2 and elution with ethyl acetate–DCM (1:1).

A goal of SPE would be the integration of the entire sample extraction, separation, analyte identification and analyte measurement procedures into a totally automated system. A simple on-line technique for the determination of PCBs in water has been achieved [84]. A retention gap coupled to the capillary column served as the recipient of relatively large sample volumes (ca. 199 μl) introduced into the GC system. Recoveries of more than 95% were observed and detection limits of less than 1 pg/l were found. A deterioration of the ECD performance, caused by the introduction of water, represented the main problem.

A new generation of SPE devices that borrow the disk configuration of membrane filters has recently emerged. These devices include flat disks with high cross-sectional areas that provide advantages not found with cartridges [87,90,94].

The performance of disk extraction was evaluated for PCBs and compared with the results obtained using cartridge extraction for reagent, tap, ground and river water samples [87,90]. The results presented demonstrate that the speed of routine analysis and consequently the productivity of a testing laboratory can be increased considerably by using the extraction disk in place of packed columns with practically the same reliability under normal conditions.

SPE reduces the solvent volume required to less than 25 ml [78]. In order to increase the reduction in the use of organic solvents, supercritical fluid elution (SFE) was proposed [90,94] to replace solvent elution. The results of these studies demonstrated that this alternative technique produces good precision and accuracy data for the analytes studied.

3.3. Comparisons between LLP and SPE procedures

Liquid–liquid extraction and adsorption on polyurethane foam and Amberlite XAD-2 have been compared for the determination of PCBs and other compounds [34]. The authors reported that LLE is the method providing these components in higher relative amounts, and Amberlite XAD-2 adsorption is the method yielding a lower proportion. Adsorption on polyurethane foam represents an intermediate case. This trend appears to be independent of the operational conditions used.

Geissler and Schöler [64] compared three established procedures: liquid–liquid extraction, solid–liquid extraction with C_{18} cartridges and extractive steam distillation. The best enrichment results were obtained with the LLE method. However, Moltó et al. [88], comparing the results obtained in extracting PCBs from fortified tap

Table 2
SPE and GC detection methods for determination of PCBs in water

Water	Isolation and clean-up	PCB congener tested	Concentration (μg/l)	Recovery (%)	Detection limit (ng/l)	Other compounds	Detection	Ref.
Water (50 ml)	C_{18} extraction 2 ml methanol elution Redissolved in DCM	Aroclor 1248	500	80	–	–	MSD	[79]
Tap water (16–19 l) (pH 8)	XAD-4 extraction 250 ml DCM elution	Aroclor 1232	10	93	10	Carbamates OCPs Triazines OPPs Chlorophenols	ECD	[80]
Water (100–500 ml)	100 mg C_{18} extraction 2 ml hexane elution	Aroclor 1260	0.01–1	95.2	–	–	ECD	[81]
		149		110.9				
		153		95.3				
		151		97.8				
		138		97.9				
		187	1	94.9				
		174		95.8				
		180		92.7				
		170		91.1				
		196		80.0				
Sea water (50 l)	XAD-2 200 ml hexane	28 52 101 118 138 153 180	–	70–80	0.050	OCPs	ECD	[82]
Sea water (20–50 l)	XAD-2 3 × 30 ml DCM	PCBs	0.1–0.9	90	10	OCPs	ECD	[83]
Water (1 ml)	C_{18} LC microprecolumn 85 μl *n*-hexane elution	Aroclor 1254	2.5	95–105	1	OCPs	On-line ECD	[84]
Sea water (50–100 l)	100 ml XAD-2 220 ml acetone–water elution and recovered in (3 × 30 ml) *n*-hexane Clean-up by alkali treatment Polyurethane 500 ml actone followed by 500 ml *h*-hexane Clean-up by alkali treatment	PCBs	–	–	–	*n*-Alkanes Carboxylic acids	ECD	[34]
Water (1 l)	C_{18} extraction 1 ml *n*-hexane	Aroclor 1221	11.9	91.2–79.4	–	–	ECD	[85]

(Continued on p. 458)

Table 2 (*continued*)

Water	Isolation and clean-up	PCB congener tested	Concentration (μg/l)	Recovery (%)	Detection limit (ng/l)	Other compounds	Detection	Ref.
Water (10 l)	C_{18} extraction 90 ml methanol elution NaCl solution added and re-extracted with *n*-hexane for clean-up	Clorphen 60	0.1	78	100	Toxaphene	ECD	[86]
Water (1 l)	500 mg C_{18} 3×1 ml hexane	28	0.01–0.05	80–100	5	OCPs	ECD	[64]
		52			33	Chlorobenze		
		101			2.5			
		138			2.5			
		153			5			
		180			2.5			
Water (1 l) (pH 2)	47 mm Empore extraction disk (C_8) 10 ml ethyl acetate–DCM	1	0.2–2.0	78–112	–	OCPs	MSD	[87]
		5		101–125		Triazines		
		29		90–108		Phthalates		
		47		97–144				
		98		106–118				
		154		95–131				
		171		15–30				
		200		45–102				
River water	500 mg C_{18} in a glass column for extraction 10 ml hexane elution	1	0.5	92	10–100 (as Aroclors)	–	ECD	[88]
		4	0.3	94				
		7	0.05	100				
		15	0.3	92				
		29	0.03	108				
		77	0.03	91				
		101	0.016	85				
		153	0.012	86				
		209	0.006	83				
Drinking and river water (1 l)	C_{18} extraction *n*-Hexane elution Florisil clean-up	2	337.4	83.2	20	OCPs	ECD	[89]
		7	137.4	78.2	9	OPPs		
		28	56.9	78.3	3	Pyrethrins		
		52	78.5	79.3	0.3	Carbamates		
		47			0.4	Triazines		
		101	91.4	81.2	0.3			
		118			0.2			
		153	150.0	80.7	0.08			
		138	150.0	82.1	0.1			
		180	150.0	79.4	0.05			
		194			0.05			
		206			0.01			
		209	53.8	81.9	0.002			

Reagent	47 mm diameter Empore	1	4	92	–	PAHs	MSD	[90]
	disk for extraction	5		99				
	SFE elution with CO_2	29		83				
		47		94				
		88		86				
		158		72				
		188		103				
Water	After in situ acetylation	28	40	103.2	2.0	OCPs	ECD	[91]
(1 l)	C_{18} solid-phase extraction	52		107.1	2.0	Chlorophenols		
	2 ml *n*-hexane elution	101		107.8	2.0	PAHs		
		138		108.0	2.0	Chlorophenoxy		
		153		106.9	1.0	acids		
		180		106.8	1.0			
Natural	500 mg C_{18} in a glass	1	0.1–100	>89	1238	OCPs	ECD	[92]
waters	column for extraction	4			990	OPPs		
	10 ml ethyl acetate–hexane	7			89	Carbamates		
	elution	15			992	Triazines		
		29			79			
		77			62			
		101			41			
		153			15			
		209			10			
River water	500 mg C_{18} in a glass	1	5–35	64–97	–	OCPs	ECD	[93]
	column for extraction	4	4–28	68–97				
	10 ml ethyl acetate–hexane	7	0.6–3.6	0–97				
	elution	15	4–24.5	0–99				
	Confirmation by acid,	29	0.4–2.4	60–98				
	alkali and chromic acid	77	0.4–1.8	0–97				
	treatment	101	0.2–1.3	94–97				
		153	0.2–0.6	96–98				
		209	0.1–0.5	95–99				
		Aroclor 1242	0.4–2.6	87–98				
		1248	0.2–2	91–97				
		1254	0.2–2	95–97				
		1260	0.1–1.5	96–98				
		1262	0.1–1.6	95–98				
Tap water,	47 mm diameter Empore	1	2	99	20	Phthalates	MSD	[94]
river water	disk for extraction	5	2	100	40	PAHs		
Ground water	SFE elution with CO_2 and	29	2	94	80	OCPs		
(1 l)	acetone	47	2	99	30			
		88	2	99	110			
		158	2	93	80			
		188	2	100	160			
		200	2	91	60			

water with those obtained using classic solvent extraction methods, demonstrated that PCBs can be extracted from water using C_{18} with at least the same recoveries as those obtained using LLE methods.

The differences in the results reported by various authors may be because the recovery in SPE depends both on the sample volume percolate and on the breakthrough volume, which is related to the chromatographic retention volumes in water, and thus on the nature and amount of sorbent [95]. In SPE, it is always possible to show examples with recoveries of 100% by decreasing the sample volume. A simple calculation indicates whether handling of this volume will allow the detection level required. Some comparisons between LLP and SPE have been made without taking this parameter into account and samples up to 500 l have been percolated [34].

The main disadvantages reported for SPE have been the risk of overloading the column or an early breakthrough due to blocking of the pores by percolating unknown samples with a high content of contaminants [76,78].

The lower recoveries observed with SPE when water samples with high contents of organic matter, DOM or SPM, have also been reported with LLP [32,35,62], although the mechanisms implicated seem to be different [95].

SPE presents some advantages over LLP such as speed and simplicity, no emulsion formation, safety, low cost, flexibility and sampling in the field.

3.4. Clean-up

As is well known, the extent of clean-up required is dependent on the type of sample being analysed, the detection limit demanded and the detection technique employed [42]. As might be expected, about 60% of the reported methods for the analysis of water samples, summarized in Tables 1 and 2, did not require clean-up of extracts.

However, the extraction techniques selected for the PCB determinations are also suitable for the determination of a wide range of different contaminants present in water (see Tables 1 and 2). When there are matrix interferences or overlapping of other compounds, different clean-up schemes should be performed.

The clean-up procedures reported for water samples for PCB determinations are mainly based on the use of solid phases and chemical treatments. Liquid–liquid partitioning with hexane was reported only in one study [86].

Chromatographic clean-up has been developed in the normal-phase mode using silica [53,60–62], alumina [51,96] and Florisil [32,51,55,60,89,97]. The solid phase is suitable both for removing interfering compounds and for separating PCBs from other organochlorine pesticide (OCP) contaminants in different fractions. Clean-up with Florisil and alumina was compared [51]. Recoveries from both columns were excellent and there is no reason to choose one phase over the other.

To separate PCBs from the OCP compounds and, at the same time, to remove interfering compounds, a fractionation procedure was developed [60]. Several extract clean-up procedures based on silica and Florisil chromatography were investigated. Regardless of the reproducibility of the fractionation, it is apparent that the Florisil fractionation method is not suitable for samples that contain OCPs and PCBs.

Chemical treatment followed by GC determination is probably one of the most useful approaches for confirmation because of its simplicity, specificity and sensitivity. The process can be carried out with concentrated sulphuric acid [57,69] or ethanolic KOH [34]. The effect of both procedures was studied with several treatment times for the confirmation of PCBs [58]. The behaviour of OCPs and PCBs (individual congeners and Aroclors) on treatment with sulphuric acid, potassium hydroxide and chromium(VI) oxide has been studied [93]. PCBs resist both acid and alkali attack. Chromium(VI) oxide is the best of the three treatments for Aroclors but some low-chloride PCBs are totally or partially destroyed by oxidative treatment.

Elemental sulphur, which may be present in waste waters, gives GC peaks that mask the

region of PCBs. Several methods are available for the removal of sulphur from extracts. Shaking with metallic mercury [55], activated copper and Raney nickel and tetramethyl ammonium sulphite [32,60] have been reported for the clean-up of extracts from waste water prior to determining PCBs by GC.

4. Identification and determination

The identification and determination of PCBs in water samples are complicated by the fact that there are 209 individual congeners. The selected method to determine PCBs is GC. Early measurements of PCBs were made using packed GC columns and commercial mixtures such as Aroclor, Clorphen and Kanechlors [98,99].

Environmental contamination may be derived from these mixtures or from incidentally generated chlorobiphenyls, whose profiles do not resemble mixture patterns. In the environment their composition could be altered by biological and chemical processes. Taking into consideration such factors, this quantification method is inadequate [100,101].

Moreover, PCBs differ in their physico-chemical characteristics and in their toxicological properties. The ideal analytical procedure is one that identifies and measures each individual chlorobiphenyl isomer. The need for congener-specific analysis was stressed at the beginning of the 1980s [102].

It is surprising that industrial formulations are still used for qualitative and quantitative analysis, but it occurs. Many laboratories use packed columns [51,57,58,61,65,69]. They do not give sufficient peak resolution and summed peak areas on the low-resolution chromatogram are quantified.

Techniques for the quantification of PCBs based on perchlorination of all individual congeners to fully chlorinated decachlorobiphenyl have been reported [103]. Dechlorination of PCBs has also been used as an alternative to perchlorination [104]. The advantage of these approaches is the conversion into a single derivative for each positional perchlorinated isomer.

Another important approach is the use of capillary columns but quantifying using commercial mixtures [66,81,88], although the irrelevance of this quantification has been pointed out by Druinker et al. [105].

It is also not uncommon that PCBs in water samples are quantified on the basis of characteristic groups (homologues), based on the number of chlorine atoms in the PCB molecule. A principal components multivariate statistical method based on SIMCA (soft independent method of class analogy) has been applied [106]. The results from principal components modelling of samples and Aroclors by using both isomers and Cl_1–Cl_{10} homologue concentrations were compared. Modelling of normalized data from Aroclors or their mixtures gave similar sample score plots for both data sets. However, modelling environmental sample congener concentrations gave erroneous classification results when compared with results from modelling isomer data [107].

All the modern approaches depend on reliable, accurate and unambiguous measurements of PCBs in water. The main problem in achieving this has been the commercial unavailability of many of the 209 PCB congeners. Considerable effort has gone into the production of individual, pure PCBs.

Nowadays, selected PCBs are available as certified or well characterized materials for monitoring and toxicological studies [108]. Non-*ortho*-chlorine-substituted congeners such as 3,3′,4,4′-tetrachlorobiphenyl, 3,3′,4,4′,5-pentachlorobiphenyl and 3,3′,4,4′,5,5′-hexachlorobiphenyl are far more toxic than other congeners, but on the other hand *ortho*-chlorine-substituted congeners are more abundant.

As even high-resolution chromatographic peaks of the non-*ortho*- and mono-*ortho*-PCBs may overlap those of multi-*ortho*-PCBs, in addition all mono-*ortho*- and non-*ortho*-PCBs are present at substantially lower concentrations compared with the remaining PCBs. It is therefore necessary to perform a series of group separations prior to the final resolution of the PCBs by HRGC.

PCBs are present in environmental waters in

trace amounts, at the picogram per litre level. In European countries, the drinking water ordinance is set at a limiting concentration of 0.5 μg/l for the sum of all isomers and 0.1 μg/l for each isomer, so that detection limits below the 0.1 μg/l level are required for monitoring drinking water. Such low detection limits are also necessary for studying the fate and the transport of PCBs directly in environmental waters. A method has been described for calculating analytical values for water quality parameters from sub-detection limit measurements [109].

A selected method to determine PCBs is the GC with a capillary column. Other determination methods have also been proposed for PCB detection and quantification in water samples, such as combustion tube decomposition and molecular emission cavity analysis [110], fluorescent excitation and emission characteristics in α- and β-cyclodextrin [99,111] and supercritical fluid chromatography using a microbore C_{18} column, and open-tubular capillary column coated with SE-52 and CO_2 as supercritical fluid [112].

4.1. Group separation

The possibility of separating PCBs according to planarity (and hence toxicity) is very useful. Although the number of analyses for toxicity evaluation is increasing, and there is much evidence about the extreme toxic potential of these coplanar PCBs, very little information is available on their water concentration [113]. The most probable cause is that the concentration of the most abundant PCBs in water samples is very low and it is noted that monochlorobiphenyls constituted as much as one-third of the total PCBs in water [114]. In spite of this, several systems are available which can perform these separations in the extracts.

Adsorption chromatography using Florisil, silica or alumina has been investigated to separate non-*ortho*- and mono-*ortho*-substituted from the remaining PCBs. Three main problems were observed: lipid removal cannot be effected simultaneously on the same column, the volume of eluents used is greatly increased and the planar congeners were only partially eluted [115,116].

Activate carbon has been used extensively to separate the toxic congeners. There are many papers dealing with the testing of the efficiency of various types of activated carbon (Norit, Darco, AX-21, PX-21, etc.) and the suitability of various supports such as polyurethane foam, sand, glass-fibre and Chromosorb. PCBs are fractionated by column chromatography using mixtures of cyclohexane, toluene, dichloromethane and methanol as eluents [117–121].

HPLC on porous graphite columns has also provided satisfactory results in the field [122,123]. Various types of semi-automated apparatus, that include an active carbon column with reversed elution, have been introduced [124].

Other special chromatographic materials such as a silica bonded phase, 2-(1-pyrenyl)ethyldimethylsilylated (PYE) material [125–127], dinitroanilinopropylsilica (DNAP), a tetranitrofluoreneaminopropylsilica (TENF) [128] and poly(styrene–divinylbenzene) (PSDVB) covalently bonded to C_{60} and C_{70} fullerenes [129] offer new electron donor–acceptor (EDA) adsorbents with high sample capacity, and are of use in HPLC to fractionate and enrich coplanar PCBs from other isomers. They separate the *ortho*- and non-*ortho*-chloro-PCBs on the basis of the degree of planarity and chlorination. Hexane provides the best mobile phase.

4.2. High-resolution gas chromatography (HRGC)

The selection of the capillary column and GC conditions is very important to obtain good identification and quantification of the PCB residues present in water samples.

4.2.1. HRGC columns

The complexity of PCB separations often requires the separation to be achieved by capillary columns, and many standard GC methods are being revised to substitute the use of packed columns by these capillary columns [130,131].

Currently there are two general types of capil-

lary columns, conventional (0.10–0.25 mm I.D.) and wide-bore capillary columns (0.53 mm I.D.). A study was performed to determine the relative retention times (RRTs) of OCPs and PCBs using three wide-bore capillary columns and two different packed columns [132]. Although these capillary columns are now considered to be packed columns, they offer much higher separation efficiency and are more inert than packed columns.

The only complete set of retention time data for a capillary column so far available for all 209 congeners was obtained by Mullin et al. [133] for the SE-54 5% diphenyl–1% divinyldimethylsiloxane. Because this is very useful, some analyses have been based on the phase [32,53,57]. Measurements of the retention times of 51 PCBs on seven narrow-bore columns, CPSil8, CPSil12, CPSil19, CPSil88, C_{18}, SB Smectic and FFAP, have been reported [134]. These data can be used for choosing the optimum column combination for multi-dimensional GC separations. However, the most commonly employed GC phase in the determination of PCBs in water (see Table 3) is 5% phenyl–methylsiloxane [24,55,56,59,60,86–90,92–94]. DB-17, 50% phenyl–methylsilicone, has also been employed mainly as a confirmatory column [88,89,93].

Some workers have measured PCBs using narrow-bore columns, CPSil8 CB [64] and CPSil19 CB [32]. Fifteen PCBs were also separated on a fused-silica capillary column coated with β-cyclodextrin on OV-1701 with hydrogen as the carrier gas and flame ionization detection [136]. The temperature is programmed from an initial low temperature (ca. 80°C) to high temperatures (ca. 270°C) at a low gradient rate.

Although the use of single capillary column is essential to the determination of specific PCB congeners, no single column is available that can separate all 209 PCB congeners. Different methodologies have been proposed to solve this problem, as follows.

Quantification of individual isomers of toxicological importance. The separation of PCB congeners by HRGC on a 50% *n*-octyl–methylpolysiloxane phase was reported [137]. The separation mechanism for PCBs on this phase, normally used in SFC, can be described as a separation resting on increasing planarity of the molecules as defined by the number of chlorine atoms in the 2,2′- and 6,6′-positions. A similar behaviour has been observed in RP-HPLC. Consequently, the last-eluting congeners of each chlorination degree are those without "*ortho*" chlorine atoms. These congeners can easily be determined without preseparation if mass-selective detection is used.

Confirmation of PCB isomer identity. At least a second confirmatory column is required. An improved method for the determination of PCBs using the parallel capillary column technique has been described; the method employs two capillary columns of different polarity in parallel from the common injector to separate detectors [98,138,139].

Mixtures of chlorobiphenyls can be determined unambiguously in terms of the individuals PCBs by multi-dimensional gas chromatographic (MDGC) techniques. The separation of complex isomeric mixtures was optimized using an MDGC system containing two capillary columns of different polarities, operated within a double-oven instrument [140]. As an alternative for the determination of PCBs the use of column switching eliminates the need to concentrate the sample extract. PCBs can be measured using a rotary valve and two capillary columns in DCM with an electron-capture detector [141].

4.2.2. Injection systems

The most commonly employed injection technique is the splitless mode with injection volumes between 1 and 5 μl [24,32,62,64,87–90,92–94] followed by on-column injection [84,91].

The Community Bureau of Reference (BCR) organized a collaborative interlaboratory project to improve the analytical protocol for some specific PCBs within the EU. A series of test procedures were prescribed to optimize the GC conditions for splitless and on-column injection, which substantially improved the quality of the data obtained. No significant difference could be

Table 3
Chromatographic conditions used for determination of PCBs in extract from water samples

Column systems	Detection system	Ref.
HTS–OV-1, Hewlett-Packard (30 m × 0.33 mm I.D.)	ECD	[52]
Two capillary columns in parallel to separate ECD: OV-1, Hewlett-Packard (25 m × 0.22 mm I.D. × 0.11 μm) SE-54, Hewlett-Packard (25 m × 0.22 mm I.D. × 0.11 μm)	ECD	[53]
10 m OV-101 stationary phase on glass capillary (WCOT) columns	MSD Scan/SIM	[79]
DB-1701, J & W Scientific (30 m × 0.25 mm I.D. × 0.25 μm)	ECD	[80]
12 m × 0.21 mm I.D. OV-101 (methylsilicone, Carbowax deactivated) fused-silica capillary column	GC–CI–SIM[a] (methane)	[54]
Packed column (2 m × 3 mm I.D.), 5% QF-1 on Gas Chrom Q (100–200 mesh) Retention gap (2 m × 0.3 mm I.D.) and SE-54, home-made (50 m × 0.25 mm I.D. × 0.25 μm)	ECD	[57]
SPB-5, Supelco (30 m × 0.24 mm I.D.) SE-30 (50 m × 0.25 mm I.D.)	ECD	[55]
DB-5 from J & W Scientific (30 m × 0.32 mm I.D. × 0.25 μm)	MSD	[56]
SE-52 (25 m × 0.25 mm I.D. × 0.15 μm)	ECD	[81]
DB-5 (30 m × 0.25 mm or 0.32 mm I.D.)	MSD Scan	[59]
DB-5, J & W Scientific (30 m × 0.25 mm I.D. × 0.25 μm) SPB-608, Supelco (30 m × 0.25 mm I.D. × 0.25 μm)	ECD	[60]
Capillary column	ECD	[85]
SE-52 (25 m × 0.25 mm I.D.)	ECD	[34]
5 m fused-silica retention gap (0.50 mm O.D., 0.32 mm I.D.) + CP Sil 5 CB fused-silica capillary column (25 m × 0.22 mm I.D. × 0.13 μm)	ECD	[84]
Two capillary columns in parallel to separate ECD: (25 m × 0.22 mm I.D. × 0.17 μm)	ECD	[62]
Retention gap (2.5 m × 0.32 mm I.D.); analytical column CP-Sil-8 CB, Chrompack (50 m × 0.32 mm I.D. × 0.25 μm)	ECD	[64]
DB-5, J & W Scientific (30 m × 0.25 mm I.D. × 0.25 μm)	MSD Scan	[87]
Packed columns OV-101, OV-225, OV-17 + QF1	ECD	[65]
Two capillary columns in parallel to separate ECD: CP Sil-19 CB, Chrompack (50 m × 0.32 mm I.D. × 0.2 μm) SE-54, Chrompak (50 m × 0.32 mm I.D. × 0.2 μm)	ECD	[32]
RSL-200 (30 m)	ECD	[135]
Fused-silica capillary column, Hewlett-Packard Ultra 2 cross-linked 5% phenyl–methylsilicone (5 m × 0.32 mm I.D. × 0.33 μm)	ECD	[86]
Single injection into two capillary columns of different polarity (DB-5 and DB-17 from J & W Scientific, both 30 m × 0.25 mm I.D. × 0.25 μm)	Switching valve and ECD and NPD (for other compounds)	[89]
HP-1, Hewlett-Packard (10 m × 0.53 mm I.D. × 2.65 μm)	ECD	[91]
BP-5 Scientific Glass Engineering (25 m × 0.25 μm) and to confirm DB-17, J & W Scientific (30 m × 0.25 cm I.D. × 0.25 μm)	ECD	[88,93]
BP-5, Scientific Glass Engineering (25 m × 0.25 μm)	ECD and NPD (for other compounds)	[92]
DB-5, J & W Scientific (60 m × 0.25 cm I.D. × 0.25 μm)	ECD	[24]
DB-5, J & W Scientific (30 m × 0.25 cm I.D. × 0.25 μm)	GC–ITD-MS[b]	[90,94]

[a] GC–CI–SIM = gas chromatography–chemical ionization–selected ion monitoring.
[b] GC–ITD-MS = gas chromatography–ion-trap detection mass spectrometry.

found between splitless and on-column injection [142].

The injection of larger extract volumes into a programmed-temperature vaporized (PTV) system operating in the solvent-venting mode was described [86] for the sensitive determination of PCBs and toxaphene in water. This injection technique allows the elimination of the solvent before the sample transfer to the capillary column and reconcentration of toxaphene and PCB components having relatively low volatilities.

4.2.3. Detection systems

GC detection methods mainly used in PCB determinations are electron-capture detection (ECD) and mass spectrometric detection (MSD). The electron-capture detector is optimized using a modified simplex technique for the determination of PCBs. Pulse voltage, temperature, make-up gas flow-rate and reference current (or pulse frequency) using the signal-to-noise ratio as criteria must be optimized [143].

The similarity of most PCB mass spectra sometimes decreases the specificity of the technique in identifying each congener, particularly when GC peaks are unresolved [144]. Different MS approaches are employed such as selected-ion monitoring (SIM) and negative-ion chemical ionization (NICI). The latter has made this detector considerably more amenable to the identification and measurement of PCBs at the trace level with similar precision to the ECD [145]. Some investigations have dealt with the systematic determination of PCBs in water [146].

When the identification is difficult because GC peaks are unresolved, electron impact (EI) ionization with NICI-MS has been demonstrated to be a powerful tool [145]. The use of ECD with NICI-MS (with methane as reagent gas) has been investigated as a possible means of discriminating PCBs in the presence of interferences [147].

The "*ortho* effect" resulting from the loss of halogen atoms relative to the molecular ion can be combined with the GC retention index for isomer-specific identification by GC–MS [148]. Collision-induced dissociation mass spectra are sensitive and specific for the detection of PCBs without isobaric interferences from congeners with higher levels of chlorination [149].

Quantitative measurement of PCB isomers by response factor calibration (RFC) was evaluated with GC and a Hall electrolytic conductivity detector. These RFC measurements provide quantitative analysis in the absence of a standard for each measured component [150].

GC with electrolytic conductivity detection (ELCD) and ECD in combination with GC–MS, operated in the EC-NICI mode, were evaluated by Greaves et al. [66] for the determination of PCBs in waste water from an industrial facility. The specificity of ELCD reduces the sample turnround time because the extract could be analysed without fractionation or clean-up. ECD was subject to interferences from non-halogenated compounds and required additional sample clean-up. EC-NICI-MS was highly specific and provided full mass spectra of PCB congeners at the same quantification limit.

Atomic emission detection allows the quantification of individual PCB congeners with an average error of ±3.2% at mg/l levels [151]. HRCG, coupled with the superior IR spectra produced by matrix isolation Fourier transform ED (FT) IR, yields powerful analytical tool [152].

5. Applications of the methods

The performance of extraction and clean-up methods for the determination of PCBs in water has been tested with spiked water samples (see Tables 1 and 2). In these studies good recoveries have been found in the determination of PCBs, but unfortunately these experiments are usually carried out on low ionic strength and particle colloid-free aqueous samples representing a matrix rather different from natural waters, and particularly from sea water.

The interest in establishing all this methodology suitable for the determination of PCBs in water samples is its application to the knowledge of the environmental water pollution level by

Table 4
PCB contents in environmental waters

Sample	PCB	Concentration range (ng/l)	Ref.
Saline waters			
Baltic Sea (Germany) 1980–84	PCBs	5.5–46.0	[57]
Mediterranean Sea (Spain) 1987	PCBs	1.30–8.80	[34]
Atlantic Ocean[a] (Netherlands) 1988	28	0.79–0.11	[82]
	52	0.60–0.17	
	101	0.46–0.16	
	118	0.17–0.08	
	138	0.55–0.26	
	153	0.34–0.15	
	180	0.30–0.13	
Arctic Ocean (Canada) 1988	PCBs	2.0–6.3	[83]
North Sea (Netherlands) 1992	PCBs	0.07–0.19	[32]
Estuarine waters and brines			
Dutch Delta (Netherlands) 1989	PCBs	0.07–0.60	[20]
Surface waters (rivers, lakes, artificial impoundments, runoff, etc.) and drinking water			
Niagara River (Canada) 1980	18	0.22	[53]
	40	0.11	
	101	0.38	
	153	0.16	
	194	0.06	
Niagara River water (Canada) 1985–86	18	7	[62]
	15	27	
	54	57	
	31	22	
	52	53	
	49	37	
	44	85	
	60	11	
	101	49	
	87	21	
	77	164	
	154	4	
	151	8	
	118	63	
	114	12	
	153	86	
	105	26	
	141	12	
	137	5	
	138	79	
	159	2	
	182	5	
	187	4	
	183	17	
	180	27	
	191	6	
	201	17	
	209	1	

Table 4 (*continued*)

Sample	PCB	Concentration range (ng/l)	Ref.
Burlington Ship Canal (Canada) 1985–86	15	0.8	
	101	0.6–1.8	
	151	0.2–0.7	
	118	0.6	
	153	0.3–1.3	
	141	0.4	
	138	0.2–2.1	
	187	0.1–0.5	
	180	0.1–1.0	
	170	0.6–1.1	
	201	0.3	
	196	0.2	
	195	0.1	
	194	–	
Gran, Saugeen and Thames Rivers (Canada) 1986–90	PCBs	8	[67]
Shing Mung River (Hong Kong) 1991	Cl_1	6.22	[63]
	Cl_2	3.42	
	Cl_3	ND	
	Cl_4	ND	
	Cl_5	0.31	
	Cl_6	ND	
	Cl_8	0.13	
	Cl_{10}	ND	
River and drinking water (Croatia) 1988–89	Aroclor 1254	<1–3	[69]
	1260	<1–3	
Meuse River (Belgium) 1985	Aroclor 1260	420–620	[81]
River water of rural area, Valladolid (Spain) 1990	52	2–14	[89]
	101	2–42	
	153	6	
Guadalquir River (Spain) 1989	PCBs	85–222	[68]
River water, Valencia (Spain) 1990	Aroclor 1016	129	[88]
	1242	84–354	
	1254	212	
River water, Valencia (Spain) 1992	Aroclor 1248	10–313	[92]
Waste waters			
Waste water, Castellón (Spain) 1992	Aroclor 1254	3.4–1547	[58]
Waste water treatment plant, Fribourg (Switzerland) 1988	PCBs	3200–500	[55]
Waste water from industrial outfall (Carolina, USA) 1991	Aroclor 1260	100–600	[66]

[a] Results for samples taken at 100 and 4000 m depths.

PCBs, coupling them with the monitoring programmes established by regional, national or international regulations (e.g. EC Directives) or international conventions such as the Paris and Oslo conventions for the North Sea or the Barcelona convention for the Mediterranean Sea.

Table 4 lists the content of PCBs found in environmental waters. Many of the proposed extraction and determination methods (see Tables 1–3) have only been applied to spiked samples.

It is of interest that the River Rhine concentration data show a reduction over recent decades. Similarly, PCB concentrations in sea water, plankton and molluscs in the Mediterranean and in the coastal seas of the Netherlands and the Arctic in the same period showed a reduction by a factor of 2–5 [20].

In saline waters, which present the lowest levels among the natural waters, it has been observed that concentrations of PCBs identified in the early studies sometimes were significantly higher than those identified in samples collected after 1985. These observations may reflect a decline in PCB levels in the open ocean or an improvement in the analytical methods. These low PCB levels require their concentration from relatively large volumes of water, typically of the order of 100–1000 l, to reach the required detection levels.

As has been noted before, the distribution of PCBs in water is heterogeneous. Moreover, of the gradient established from river water to the sea, in surface waters there is a redistribution of the PCBs caused by turbulence and advection by the main current of the river [20,27]. However, in ocean water the redistribution is related to depth. The detection of OCPs synthesized only in the last few decades in abyssal water, biota and sediments indicates that vertical transfer processes exist from the surface to greater depths in the ocean.

Observations that sea water concentrations of PCBs appeared to be independent of depth in the Pacific Ocean were explained on the basis of the aqueous solubility. It was proposed that the less soluble PCBs would be more rapidly transported to depth on sinking particles, because a greater proportion of these compounds were associated with particulate material in the surface waters. Other studies, in the Mediterranean, have demonstrated that grazing zooplankton also contribute to the PCB flux bellow 100 m by the production of rapidly sinking faecal material [15].

Pollution prevention is the environmental objective of the 1990s. It replaces two decades of environmental policy based on mandatory regulations. Future environmental policy will emphasize pollution prevention and pollution source reduction.

Few studies have been performed to established mechanisms for the reduction of PCB levels. For example, Bush et al. [153] reported the precipitation of PCB congeners from aqueous solution by clay and Aly and Badawy [154] evaluated the efficiency of coagulation and chlorination for removal of PCBs from drinking water.

6. Conclusion

The solid-phase isolation and concentration process is faster than the liquid extraction procedure, and it is being adopted as the extraction technique of choice. The advantages of this technique are that no emulsions are formed and the passage of the sample through a column bed replaces repeated extractions and centrifugations.

It is clear that a large and very diverse number of studies exist describing the determination of PCBs by HRGC, and their interest is not diminished by the persistence of these contaminants. A selective detector can be used to enhance the response of the analytes. The most modern and accurate approach is to quantify PCBs in water on the basis of individual congeners. All the recent research on PCBs clearly indicates that it is time for PCBs to be measured and studied exclusively as individual chemical entities. Also, it is now the time to apply this advanced analytical methodology to real-world problems.

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