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Evaluation of PCB fluxes in the environment

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SUMMARY

Since the early 1970s a variety of stringent measures have been taken by (international) governments to reduce the risks posed by the presence of polychlorinated biphenyls (PCBs) in the environment. A crucial question is whether these measures have achieved the desired result. The present report reviews, for the Netherlands, the major PCB flows in the (abiotic) environment during the period 1980-1993. In addition, PCB flows in the year 2000 have been calculated for two scenarios: with and without additional policy measures.
Sources of PCB emissions have been inventoried extensively in the Netherlands and the surrounding countries. Over the period 1980-1990 there has been a major decline in PCB emissions to the air, water and soil. Today the main influx of PCBs to the Netherlands is from other countries, *viz.* transboundary influx via the major rivers and via atmospheric deposition. PCB concentrations in the major rivers have also clearly decreased over the period 1980-1990. It is noteworthy, however, that this decline has not subsequently continued. Since 1989 PCB concentrations in nationally administered Dutch waterways have fluctuated around a virtually constant level. This level exceeds the current statutory limit value for PCBs. A similar pattern holds for the coastal waters of the Netherlands. The scarce monitoring data available for soil indicate that wide-scale transgression of the target value for PCBs is unlikely. Expectations are that, under the terms of current policy, the main PCB flows will continue to decrease during the period 1990-2000. An accelerated decline could be achieved if additional measures were taken in neighbouring countries. The most effective approach to reducing foreign PCB emissions to the atmosphere would be to tackle (unintentional) emissions from a variety of industrial processes. A clean-up of upstream river sediments would reduce the PCB influx via the major rivers. Because a substantial proportion of PCBs ultimately enters the North Sea via these rivers, upstream clean-up would also have a positive impact on the Dutch input of PCBs to the marine ecosystem. Further tightening-up of policy in the Netherlands, including accelerated collection of fluorescent lighting ballasts and capacitors, will have scarcely any effect on the situation in the year 2000, because of the relatively small share of these sources in aggregate PCB flows.
The present report provides an inventory of PCB flows in the abiotic environment. On its own, though, this inventory does not answer the key question of whether the PCB concentrations currently observed in the Netherlands imply a risk for the human population or for ecosystems. It is therefore recommended that a supplementary risk assessment be carried out, as an important follow-up to this study. This is fully in line with scheduled Dutch policy to re-evaluate the environmental quality standards for PCBs on the basis of new insights in the environmental chemistry and toxicology

of this group of substances.

SAMENVATTING

Sinds het begin van de jaren zeventig heeft de (internationale) overheid een aantal stringente maatregelen genomen om de risico's van polychloorbifenylen (PCB's) in het milieu te verminderen. Een belangrijke vraag is of deze maatregelen tot het gewenste resultaat hebben geleid. Het voorliggende rapport geeft voor Nederland een overzicht van de belangrijkste PCB-stromen in het (abiotische) milieu gedurende de periode 1980-1993. Voorts is een tweetal scenario's doorgerekend voor de PCB-stromen in het jaar 2000, respectievelijk met en zonder aanvullende beleidsmaatregelen.

De bronnen van PCB-emissies in Nederland en de omringende landen zijn uitgebreid geïnventariseerd. In de periode 1980-1990 zijn de emissies van PCB's naar lucht, water en bodem sterk gedaald. De aanvoer van PCB's in Nederland is momenteel vooral afkomstig uit het buitenland. Het gaat dan om grensoverschrijdende instroom via de grote rivieren en via atmosferische depositie. De PCB-concentraties in de grote rivieren zijn eveneens duidelijk afgenomen in de periode 1980-1990. Opvallend is echter dat deze daling zich niet heeft doorgezet. Sinds 1989 fluctueren de PCB-gehalten in de rijkswateren rond een nagenoeg constant niveau. Dit niveau bevindt zich boven de huidige grenswaarde voor PCB's. Eenzelfde patroon is zichtbaar voor de Nederlandse kustwateren. De schaarse meetgegevens voor de landbodem laten zien dat de streefwaarde voor PCB's waarschijnlijk niet op grote schaal wordt overschreden.

De verwachting is dat met het thans gevoerde beleid de belangrijkste PCB-stromen verder zullen afnemen in de periode 1990-2000. Een versnelde sanering zou mogelijk zijn door het treffen van aanvullende maatregelen in het buitenland. Voor het terugdringen van de PCB-emissies naar lucht zou men zich hierbij kunnen richten op het (ongewenst) vrijkomen van deze stoffen bij diverse industriële processen. Waterbodemsanering in bovenstroomse gebieden kan de PCB-instroom via de grote rivieren verminderen. Omdat een aanzienlijk deel van de PCB's uit de grote rivieren uiteindelijk in de Noordzee terecht komt, heeft zo'n bovenstroomse waterbodemsanering ook invloed op de Nederlandse aanvoer van PCB's naar het mariene ecosysteem. Een verdere aanscherping van de beleidsmaatregelen in Nederland, zoals een versnelde inzameling van TL-armaturen en condensatoren, zal nauwelijks invloed hebben op het beeld voor het jaar 2000. Dit vanwege het relatief geringe aandeel van deze bronnen op de totale PCB-stromen.

Het voorliggende rapport heeft de PCB-stromen in het abiotische milieu in kaart gebracht. De belangrijke vraag of de thans waargenomen PCB-concentraties in Nederland risicovol zijn voor mens of ecosystemen is daarmee echter nog niet

beantwoord. Een nadere risicoschatting dient dan ook een belangrijke vervolg-stap te zijn op dit projekt. Dit sluit direkt aan bij het beleidsvoornemen in Nederland om op basis van nieuwe inzichten in de milieuchemie en toxicologie van PCB's, de milieukwaliteitseisen voor deze groep van stoffen te her-evalueren.

1. INTRODUCTION

1.1. Background

At the Third North Sea Ministers Conference in 1990 it was decided that the risks of PCBs for man and the environment should be reduced in 1995 (optionally) and at the latest in 1999. A variety of measures were taken to achieve this goal (North Sea Action Plan, 1990). The subsequent question is whether these measures have indeed led to a significant decline of PCB levels in the environment. The SPEED Document 'Stofstromen van PCB's' (IVM, 1993), which was published under the authority of the Dutch Ministry of Environment (VROM), provided policy makers with a first global overview of the current situation in the Netherlands. The main conclusion of the SPEED Document was that PCBs are still a cause for concern in the Netherlands. After a significant initial decline, PCBs appear to be stabilizing at unacceptable levels in the environment. It should be noted, however, that there are major uncertainties in the estimates of PCB levels since recent monitoring data are very scarce. Furthermore, the contribution of several new PCB sources remains unclear.

1.2. Aim of the document

The present study can be seen as a follow-up to the SPEED Document. It is designed to fill - as far as possible - the gaps which emerged in the SPEED Document, creating a sound basis for an international debate on possible additional PCB policy strategies. The Ministry of Environment (VROM) has requested the Netherlands National Institute of Public Health and Environmental Protection (RIVM) to pay particular attention to the following items:

- greater clarity about the role of atmospheric PCB deposition in surface water loads
- further quantification of the PCB input and output vis-à-vis major Dutch rivers
- estimate of current PCB burden in sediments and magnitude of delayed release (re-emission); potential success of sediment clean-up activities
- comparison of current PCB fluxes to soil with critical loads in susceptible receptor areas
- research results of industrial emissions to air
- impact of collection of small and large PCB-containing appliances
- monitoring/estimation of PCBs in landfill percolate
- estimate of overall PCB fluxes.

In the past, greatest attention has been paid to the predominant PCB congeners in the abiotic and biotic environment (i.e. PCB 28, 52, 101, 138, 153 and 180). However, recent mechanistic toxicological studies on PCBs have shown that the non-ortho and mono-ortho congeners, which were only present at very low levels in the original PCB mixtures, are major contributors to the overall toxicity of dioxins and PCBs (for further details see Paragraph 2.1). In the present document a distinction will be made - as far as possible - between the (abiotic) fluxes of the aforementioned groups of PCBs. This more congener-specific approach anticipates the next step in the risk evaluation process of PCBs, namely the quantitative comparison of exposure and effect data. The actual evaluation of the risks of PCBs for man and the environment will be presented in the future in a separate document.

1.3. Outline of the document

In Chapter 2 a general overview is given of the physical and chemical properties of PCBs and their behaviour in the environment. Chapter 3 focuses on sources and emissions of PCBs in the Netherlands and abroad. Chapter 4 integrates sources, emissions and environmental behaviour of PCBs, resulting in an estimate of overall PCB fluxes in the environment. In Chapters 3 and 4 the present situation is compared with that prior to 1980. Next, several scenarios are calculated for PCB fluxes in the (near) future (Chapter 5). These scenarios demonstrate the impact of additional abatement measures. Chapter 6, finally, presents the conclusions and further recommendations.

2. COMPOUND PROPERTIES AND ENVIRONMENTAL BEHAVIOUR

2.1. Compound properties

Polychlorinated biphenyls (PCBs) are a family of compounds produced commercially by the direct chlorination of biphenyl. The biphenyl molecule is made up of two connected rings of six carbon atoms each (Fig. 2.1), and a PCB is any molecule having multiple chlorines attached to the biphenyl nucleus. Chlorines can be placed at any or all of the ten available sites, with 209 different PCB compounds theoretically possible, varying in the number and position of the attached chlorines. The individual isomers and homologues are generically referred to as congeners. The position of the chlorines can be indicated in two ways: the general position relative to the phenyl-phenyl bond (ortho, meta and para) and by numbering the carbon atoms (Fig. 2.1). The individual congeners can also be indicated by their IUPAC number (Table 2.1).

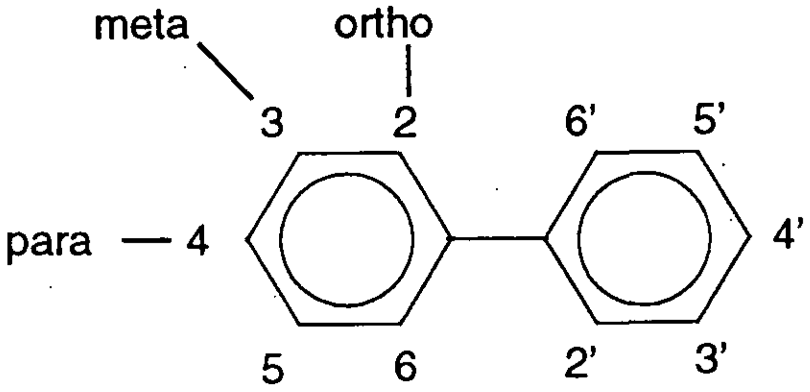


Fig. 2.1. Numbering of the chlorine substitution positions in the biphenyl molecule and the general spatial terms for chlorine substitution (ortho, meta, and para).

Initially, environmental analyses focused on the predominant congeners in biotic and abiotic matrices (i.e. PCB 28, 52, 101, 138, 153 and 180) (Table 2.1). To what extent these six congeners represent the total PCB concentration in the environment depends on the original mixtures used (e.g. Aroclor 1242, Aroclor 1260, Clophen A30, Clophen A50) and the possible changes in PCB composition due to differences in environmental behaviour of the individual congeners. Total PCB concentrations can be estimated by assuming that the sum of the six congeners represents 20% of the

Table 2.1. IUPAC numbering and chemical structures of six frequently reported PCB congeners.

IUPAC no.	structure	CAS no.
28	2,4,4’-trichlorobiphenyl	7012-37-5
52	2,2’,5,5’-tetrachlorobiphenyl	35693-99-3
101	2,2’,4,5,5’-pentachlorobiphenyl	37680-73-2
138	2,2’,3,4,4’,5’-hexachlorobiphenyl	35065-28-2
153	2,2’,4,4’,5,5’-hexachlorobiphenyl	35065-27-1
180	2,2’3,4,4’,5,5’-heptachlorobiphenyl	35065-29-3

total PCB concentration (Schulte & Malisch, 1984), which is an average value found in several PCB mixtures and environmental samples (see Appendix 1). Throughout this document the total PCB concentrations and loads are estimated by the following equations:

$$\textbf{total PCB} = \mathbf{5 * \Sigma 6}\ \textbf{PCBs}$$

$$\mathbf{\Sigma 6}\ \textbf{PCBs} = \textbf{PCB}\ \mathbf{28 + 52 + 101 + 138 + 153 + 180.}$$

Owing to new insights in toxicity mechanisms attention has recently shifted to another group of PCB congeners. Congeners that contain two para and at least two meta chlorines resemble 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) in their biochemical and toxic effects, while the addition of ortho chlorines reduces this effect significantly (Safe, 1990). The highly toxic non-ortho and mono-ortho chlorine-substituted congeners were present at trace levels in the original PCB mixtures (Hong *et al.*, 1993), but are now considered to be mainly responsible for the adverse effects of PCBs (de Voogt *et al.*, 1990). The dioxin-like toxicity of non-ortho, mono-ortho and di-ortho substituted PCB congeners is now widely established. The reduced fertility of seals and cormorants are two examples of the deleterious impact now observed (Reijnders, 1986; Van den Berg *et al.*, 1994). These PCB congeners appear to contribute substantially to the overall dioxin effects in the environment. Based on the similarity between these toxic PCBs and 2,3,7,8-TCDD, factors have been proposed that relate PCB toxicity to 2,3,7,8-TCDD toxicity (Table 2.2). Recent inventories demonstrate that the concentrations of non-ortho (especially PCB 126) and mono-ortho PCBs may pose a greater toxic threat than the 2,3,7,8-chlorinated dioxins and furans to humans and wildlife when expressed as 2,3,7,8-TCDD toxic equivalents (Tanabe, 1988; Järnberg *et al.*, 1993).

Table 2.2. Toxicity Equivalency Factors (TEFs) for non-ortho, mono-ortho and di-ortho chlorine-substituted PCBs (Ahlborg *et al.*, 1994).

IUPAC no.	structure	TEF
non-ortho:		
77	3,3',4,4'-tetra-	0.0005
126	3,3',4,4',5-penta-	0.1
169	3,3',4,4',5,5'-hexa-	0.01
mono-ortho:		
105	2,3,3',4,4'-penta-	0.0001
114	2,3,4,4',5-penta-	0.0005
118	2,3',4,4',5-penta-	0.0001
123	2',3,4,4',5-penta-	0.0001
156	2,3,3',4,4',5-hexa-	0.0005
157	2,3,3',4,4',5'-hexa-	0.0005
167	2,3',4,4',5,5'-hexa-	0.00001
189	2,3,3',4,4',5,5'-hepta-	0.00001
di-ortho:		
170	2,2',3,3',4,4',5-hepta-	0.0001
180	2,2',3,4,4',5,5'-hepta-	0.00001

Of the 209 possible congeners, only about half have been actually produced in commercial synthesis (Abramowicz, 1990). The environmental fate and behaviour of individual PCB congeners is strongly influenced by their physico-chemical properties; in particular volatility, aqueous solubility and lipophility (Tables 2.3 and 2.4). Lower-chlorinated congeners such as PCB 28 and PCB 52 possess comparatively greater vapour pressures and water solubilities than higher-chlorinated PCBs such as PCB 138 and PCB 180, whilst the higher-chlorinated congeners are more lipophilic. Such differences have a profound effect on the partitioning of individual congeners between different environmental compartments. The organic-carbon-normalized sediment/water partition coefficient (K_{oc}) is included in Table 2.4 as a measure of the affinity of PCBs to sediments. Although K_{oc} values are generally assumed to be constant, recent observations indicate that these values may depend on environmental conditions and contact times between solid matrix and contaminant. The listed values were determined in field-contaminated sediment and can be considered as representative for this environmental compartment.

Table 2.3. Physico-chemical properties of some selected congeners (all values at 25°C).

Congener IUPAC no	Vapour pressure[a] (Pa)	Water solubility[b] (mol/m^3)	Henry's Law Constant[c] (log HLC in $atm.m^3/mol$)
28	2.77×10^{-2}	1.21×10^{-3}	-3.544
52	1.93×10^{-2}	3.62×10^{-4}	-3.496
101	3.58×10^{-3}	1.09×10^{-4}	-3.610
138	4.87×10^{-4}	4.40×10^{-5}	-3.886
153	6.63×10^{-4}	3.70×10^{-5}	-3.783
180	5.06×10^{-4}	1.66×10^{-5}	-3.969
77	1.40×10^{-3}	3.19×10^{-4}	-3.989
126	2.74×10^{-4}	9.84×10^{-5}	-4.087
169	5.36×10^{-5}	3.41×10^{-5}	-4.186
105	7.07×10^{-4}	1.24×10^{-4}	-4.003
114	4.43×10^{-3}	1.24×10^{-4}	-3.845
118	9.62×10^{-4}	1.03×10^{-4}	-3.901
123	9.01×10^{-4}	1.02×10^{-4}	-3.759
156	7.34×10^{-4}	4.20×10^{-5}	-4.053
157	1.39×10^{-4}	4.20×10^{-5}	-4.073
167	1.88×10^{-4}	3.54×10^{-5}	-3.959
189	1.44×10^{-4}	1.60×10^{-5}	-4.177
170	3.72×10^{-4}	1.94×10^{-5}	-4.059

Sources:
[a] Holmes *et al.*, 1993: average uncertainty ±75%.
[b] Holmes *et al.*, 1993: average uncertainty ±96%.
[c] Dunnivant *et al.*, 1992.

2.2. Behaviour in soil

The most important transport processes of PCBs in the unsaturated zone of the soil are 1) mixing of soil layers, 2) sorption to soil particles (mainly the organic matter fraction of the soil), 3) transformation and 4) volatilization to the atmosphere. Intensive mixing of soil layers is generally restricted to agricultural (arable) fields. It is reasonable to assume that the PCB concentration in the ploughed layer of these soils is fairly homogeneous (over a time span of several years). Sorption of PCBs will mainly occur on the organic matter of soils, owing to the lipophilic character of the compounds. As a first approximation, sorption of PCBs can be assessed from the octanol/water partitioning coefficient. Via regression, K_{oc}-values (see Paragraph 2.1)

Table 2.4. Partition coefficients of some selected PCB congeners (all values at 25°C).

Congener IUPAC no.	Octanol/water partition coefficient (log K_{ow})		Sediment/water partition coefficient (log K_{oc})	
	I[a]	II[b]	I[c]	II[d]
28	5.67		6.31	6.52
52	5.84		6.56	6.50
101	6.38		7.34	7.31
138	6.83		8.00	8.21
153	6.92		8.13	8.08
180	7.36		8.78	8.66
77	6.36	6.63	7.32	
126	6.89		8.09	
169	7.42	7.41	8.86	
105	6.65		7.74	8.09
114	6.65		7.74	
118	6.74		7.87	7.69
123	6.74		7.87	
156	7.18		8.51	
157	7.18		8.51	
167	7.27		8.64	
189	7.71		9.29	
170	7.27		8.64	8.72

Sources:
[a] Hawker & Connel, 1988, extrapolation from gas chromatographic data.
[b] De Bruijn *et al.*, 1989, experimental determination.
[c] Evers & Smedes, 1993, calculated values based on the following equation: $\log K_{oc} = 1.46 \cdot \log K_{ow} - 1.97$, ($r^2 = 0.98$).
[d] Evers & Smedes, 1993, cosolvent method using field-contaminated sediment.

or K_{om}-values (partitioning constant between organic matter of the soil and water) can be obtained. Table 2.4 presents several K_{oc}-values, which may also be used for the soil compartment. The sorption of the PCBs will be such that very high retardation factors (with respect to water movement in the soil) may be expected. Therefore the compounds can be classified as immobile. Henry's law constants are relatively high and thus some transport via the gas phase of the soil may occur. This may lead to some dispersion of the PCBs through the soil (unsaturated zone). The relative high Henry's law constants may also lead to an exchange of PCBs with the air compartment. Whether this will result in a net loss or gain of PCBs in soil depends on the concentrations in the gaseous phases. In a recent study in the United Kingdom a significant reduction in soil PCB content was observed since the early 1970s, mainly attributed to volatilization (Alcock *et al.*, 1993). In a U.K. mass balance study for PCBs, it was concluded that there is currently a net loss from soil to atmosphere, i.e. volatilization exceeds deposition (Harrad *et al.*, 1994). The results of such calculations are highly dependent on the applied partition coefficient values, which may vary by more than one order of magnitude.

Transformation of PCBs in soil has been found for a few PCBs (especially for those with 5 Cl atoms) (Scheunert, 1987). Under laboratory conditions it has been shown that PCBs mineralize to some extent to CO_2, with low-substituted PCBs mineralizing faster than high-substituted PCBs (see also paragraph 2.3.2. and Figure 2.2A). Transformation rates were not established in this study, however. Fries and Manow (1984) used an originally uncontaminated soil to study the aerobic degradability of ^{14}C-labeled PCBs. Monochlorinated biphenyls were mineralized (CO_2 production) with half-lives of 300 days. Tetra- and hexachlorinated biphenyls remained unaltered in their experiments. Brunner *et al.* (1985) added ^{14}C-labeled Aroclor 1242 (containing mainly di-, tri-, and tetrachlorinated biphenyls) to originally uncontaminated soil and observed no significant mineralization (<3% recovered as $^{14}CO_2$) over a 210-day period. Addition of biphenyl (analog enrichment) or addition of specific microbial strains resulted in mineralization.

Unfortunately, no data are available on PCB degradability by native organisms in PCB-polluted soils. Prolonged exposure to PCBs may stimulate the development of enzymes/organisms with an enhanced capacity for degrading a broader range of PCBs, at higher rates.

Information on PCB transformation in the saturated zone of the soil is lacking. Depending on the redox conditions of the aquifers, the transformation rates found for PCB in sediments may provide an initial indication of the possible transformation in aquifers.

2.3. Behaviour in aquatic environments

2.3.1. Transport processes

Surface water

Sorption to sediments and volatilization to the atmosphere are two transport mechanisms that contribute to the removal of PCBs from the water column. PCBs sorb rapidly to the suspended solids in the water column due to their hydrophobic character (Table 2.4). Once associated with suspended matter, settlement to the sediment bed may occur if flow velocities decrease. Consequently, PCBs are usually found in much higher concentrations in sediments than in the overlying water.

The Henry's law constants of PCBs are rather low, and volatilization was long considered to be a minor process. Recently, however, detailed field research has made clear that a net PCB transfer from the water to the air exists in the Great Lakes (US) (Achman *et al.*, 1993). These authors state that volatilization of PCBs is as important as sedimentation to the overall lake mass balance. The total PCB flux values ranged from 13 to 1300 ng/m^2·day, depending on wind speed and dissolved PCB concentrations in the water (Achman *et al.*, 1993; Jeremiason *et al.*, 1994). Moreover, additional data demonstrate that volatilization of PCBs from contaminated waters is a major source of the PCB flux to the local atmosphere near the US Great Lakes (Hornbuckle *et al.*, 1993).

Unfortunately, data on PCB volatilization from lakes in the Netherlands or from the North Sea are lacking, with only estimates available (see Paragraph 4.6).

Sediment

Transport of PCBs with percolating water from sediment to groundwater is expected to be an extremely slow process. Even the least hydrophobic congener, 4-monochlorobiphenyl, proved to be immobile in a field column test (Winters and Lee, 1987).

2.3.2. Degradation reactions

Surface water

The photolysis of PCBs has been demonstrated in non-aqueous solvents. Comparison of rates in oxygen-saturated and anaerobic solutions indicated that oxygen suppresses photolysis, apparently by acting as a free-radical quencher. Higher-chlorinated PCBs photodegrade faster than lower-chlorinated PCBs. From laboratory studies it has been predicted that dechlorination via photolysis is a very slow process in the aquatic environment (Safe *et al.*, 1976; Bunce *et al.*, 1978).

PCBs are extremely resistant to chemical oxidation and hydrolysis (Hutzinger *et al.*, 1974) and, hence, these processes are not expected to be significant in the aquatic environment.

Individual PCBs vary widely in their susceptibility to biodegradation. Under aerobic conditions, which generally prevail in the water column, PCBs with four or fewer chlorine atoms per molecule can be biodegraded by many microorganisms (Bedard *et al.*, 1986; Pettigrew *et al.*, 1990; Thomas *et al.*, 1992). The predominant metabolic

pathways catalyze the hydroxylation of unsubstituted carbons at positions 2 and 3 or at unsubstituted 3,4 positions. Microbial metabolism under aerobic conditions results in the formation of chlorobenzoic acids or even in a complete mineralization to carbon dioxide, chlorine and biomass (Kong and Sayler, 1983). Aerobic degradation of lower-chlorinated PCBs has been demonstrated to occur naturally in the Hudson River (US), resulting in the formation of chlorobenzoic acids (Flanagan and May, 1993; Figure 2.2A).
Information on aerobic degradation rates in surface waters is scarce. Extrapolation of kinetic data obtained in laboratory incubations with pure cultures and high substrate concentrations to the environment is highly speculative. Degradation rates are influenced by compound properties (number and position of the chlorine atoms) and environmental factors (e.g. density of active microbial population, temperature, co-substrates, co-contaminants). A half-life of 0.2 to 3 years for di- and trichlorobiphenyls in aerobic surface waters has been found under environmental conditions (Rapaport and Eisenreich, 1988). These values, far below the rates observed in laboratory experiments, may be used as an approximate estimate for rates in Dutch fresh waters.

Sediment

In sediments abiotic PCB degradation reactions appear to be negligible. Microbial reactions similar to those in the aerobic water column may take place in the top layer of sediments, where aerobic conditions may exist. Mixed bacterial cultures obtained from PCB-contaminated river sediments are capable of degrading monochlorinated biphenyls ($8 < t_{1/2} < 16$ days) aerobically under simulated natural conditions (Kong and Sayler, 1983). In these experiments chlorinated benzoates were detected as major metabolites; total mineralization was demonstrated for 4-chlorobiphenyl ($t_{1/2} = 12$ days). Sunlight enhances the rate of mineralization by approx. 400% (Kong and Sayler, 1983). Bacterial strains isolated from PCB-contaminated sediment were able to mineralize monochlorinated biphenyls and to transform di-, tri- and tetrachlorobiphenyls, with half-lives ranging from 3 to 80 days (Sugiura, 1992). The majority of sediment is anaerobic, however, and the only significant process that affects PCB concentrations in anaerobic sediments is microbial reductive dechlorination (Quensen *et al.*, 1990; Alder *et al.*, 1993; Abramowicz *et al.*, 1993). In this process chlorines in the PCB molecule are replaced by hydrogen atoms, yielding lower-chlorinated PCB isomers (Figure 2.2B). It is now well established that microbial dechlorination has significantly altered the PCB composition in river sediments, e.g. in the severely polluted Hudson River (US) (Brown *et al.*, 1987; Lake *et al.*, 1992). Various patterns of PCB dechlorination are observed at different sites (Mohn and Tiedje, 1992) and may lead to an accumulation of mono- and dichlorobiphenyls. Dechlorination of PCBs has several significant consequences: a) it yields less hydrophobic congeners and consequently reduces the bioaccumulation potential of PCBs in the environment; b) since dechlorination involves mainly the removal of meta and para chlorines, significant reduction in the TCDD-like toxicity associated with PCBs may result; c) dechlorination might be the first step in achieving biological decontamination of polluted sediments. In contrast to their parent compounds, the lower-chlorinated congeners produced are suitable substrates for aerobic microbial mineralization (Abramowicz, 1990).

PCB dechlorination rates in contaminated sediments vary between several years and several decades (Dolfing and Beurskens, 1994).

The disappearance of several polychlorinated biphenyls was observed in the deeper anaerobic sediment layers of Lake Ketelmeer, a sedimentation area of the Rhine River (Beurskens *et al.*, 1993). Laboratory studies with an anaerobic consortium from this area demonstrated the potential for PCB transformation. The field and laboratory observations indicate that the disappearance of PCBs in the sediment might be caused by *in situ* microbial dechlorination. Although microbial dechlorination results in the formation of other PCBs, the transformation appeared to alter the dioxin-like toxicity of the PCBs significantly. The PCB toxicity of four reactive congeners was lowered by 75% over the last two decades (Beurskens *et al.*, submitted).

2.4. Behaviour in the atmosphere

2.4.1. Transport in air

The virtually universal distribution of PCBs throughout the world, including remote areas such as the Arctic and remote Pacific ocean, indicates that atmospheric transport is the main route for the distribution of PCBs. PCBs in the atmosphere occur mainly (90 - 100 %) in the vapour phase. The tendency to adsorb on particles increases with the degree of chlorination (Atlas *et al.* 1986; Eisenreich *et al.* 1981). Loss from the atmosphere occurs by chemical and photochemical degradation and by wet and dry deposition processes.

2.4.2. Degradation

The main processes governing the chemical loss of organic compounds present in the gas phase in the atmosphere are photolysis and chemical reaction with OH and NO_3 radicals and with O_3, with the OH radical reaction the most important of these processes for the majority of organic compounds (Finlayson-Pitts & Pitts, 1986;

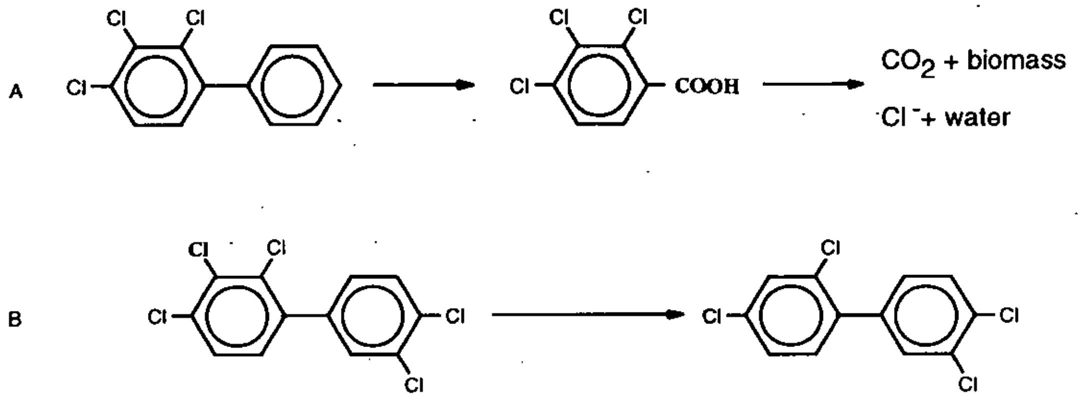


Figure 2.2. Biodegradation reactions that may occur under aerobic conditions in soil and surface waters (A) and under anaerobic conditions in sediments (B).

Atkinson, 1986). It appears to be very hard to obtain reliable experimental data concerning the gas-phase reactions of PCBs, owing to the low vapour pressure and tendency to adsorb on reaction chamber walls. Consequently, only a few experimental data are presently available concerning the gas-phase reactions of PCBs. Thus rate constants have been measured at room temperature for the reaction of biphenyl and the three monochloro-biphenyl isomers with the OH radical (Atkinson & Aschmann, 1985; Atkinson *et al.* 1984), and an upper limit rate constant has been determined for biphenyl (Atkinson *et al.* 1984).

Experimental data for several di-, tri-, and tetra-chlorobiphenyls indicate that PCBs are stable to photolysis under atmospheric conditions. The main degradation route in the atmosphere will be by reaction with the OH radical. Atkinson (1987) estimated the reaction rate constants and atmospheric lifetimes for PCBs based on the reaction with the hydroxyl radical. The reaction rate depends on the degree of chlorination. Rates decrease with increasing chlorination and range from 2.9×10^{-12} $cm^3.molec^{-1}.s^{-1}$ for di-chlorinated compounds to 0.2×10^{-12} $cm^3.molec^{-1}.s^{-1}$ for penta-chlorinated compounds. Using an annual diurnally averaged OH concentration of 5×10^5 cm^{-3}, this results in an atmospheric lifetime due to chemical degradation of 8 to 120 days, respectively (Table 2.5)

Table 2.5. Estimated rate constants for the reaction with the OH radical and experimental data, together with calculated tropospheric lifetimes due to the gas-phase loss.

No. of Cl substituents	$k \times 10^{-12}$, cm^3 $molecule^{-1}$ s^{-1}		Calculated tropospheric lifetime, days
	calculated	observed	
0	7.9	5.8 - 8.2	3
1	3.1 - 4.7	2.8 - 5.2	5 - 11
2	1.4 - 2.9		8 - 17
3	0.7 - 1.6		14 - 30
4	0.4 - 0.9		25 - 60
5	0.2 - 0.4		60 - 120

2.4.3. Dry deposition

PCBs occur mainly (>90 %) in the vapour phase. This, combined with the low solubilities of the compounds, means that dry deposition is an important removal process from the atmosphere. Early (in the seventies) measurements of dry deposition included deposition measurements to oil- and glycerol-coated plates and glycerol-water pans (Eisenreich, 1981). In these experiments no discrimination could be made between particle and vapour deposition. The resulting dry deposition velocities (particle and gas) ranged from 0.1 to 0.5 $cm.s^{-1}$, but are not very reliable.
There has been only one study which determined experimentally the deposition velocity of a PCB congener (PCB-52) onto sea water (Baart *et al.*, 1991). The dry deposition velocity over (PCB-free) North Sea water amounted to 0.07 $cm.s^{-1}$. Using this value as an upper limit of the dry deposition velocity gives a lifetime of approximately 17 days due to dry deposition.

The magnitude (and direction) of the gas exchange of PCBs across the air/water air/soil boundary has been the subject of controversy in recent years, particulary with reference to the Great Lakes ecosystem (North America). Although at one time they were a sink to atmospheric PCB, restrictions on the input of PCB into the environment seem to have reversed the direction of the flux. (Hornbuckle *et al.*, 1994; Jeremiason, J.D. 1994; Aschman *et al.* 1993; Swackhamer *et al.* 1988; Baker *et al.* 1990).

For the Great Lakes a seasonal variation in the direction of the flux has been found (volatilization is dominating). Vapour deposition is indicated in April to May (0-

3°C). The larger volatilization fluxes were measured in the fall. The direction of the flux is directly related to the water temperature and the PCB air/water concentration ratio (Hornbuckle *et al.* 1994).

Model calculations for the Netherlands indicate deposition over land and a transition from deposition to emission over water between 1990 and 2000 (Baart *et al.*, 1995); see Section 4.6.

2.4.4. Wet deposition

Because gas-phase scavenging of PCBs is thought to be minimal, and the fact that 90 to 100 % of the PCBs occur in the gas phase, wet deposition is less important than dry deposition. From 1979 to 1989 the concentration of PCBs in rainwater was measured by RIVM/KNMI at three locations in the Netherlands (CCRX 1989; Raad *et al.* 1993). Measurements up to 1985 were hampered by concentrations below the detection limits and an inadequate sampling and analysis method. In 1985 in half of the monthly samples PCB-153 was detected, with an average concentration of 2 $ng.l^{-1}$. PCBs were detected in only a few samples in 1986 and in even less in 1987. In 1988 only one sample was found containing PCB: 1 $ng.l^{-1}$ of PCB-128. In 1989 the measurement were discontinued.

In 1989 three rainwater samples were analysed for PCB (7 congeners): the average concentration was 0.02 $\mu g.l^{-1}$ (Raad *et al.* 1993). This concentration, and a yearly averaged annual rainfall of 76 cm, results in a wet deposition flux of 0.15 $g.ha^{-1}.y^{-1}$. This flux should be regarded as an upper limit since, owing to the sampling method, part of this flux will have been caused by dry deposition.

2.5. Summary and conclusions

During the last decade new insights have been gained into the effects and environmental behaviour of PCBs, particularly with regard to toxicity mechanisms, volatilization and degradation in sediments.

The fact that PCBs contribute to the overall dioxin-like effects has resulted in renewed attention being given to the environmental behaviour of this group of chemicals. However, important data for the overall assessment of this behaviour are still lacking. The analysis of current PCB behaviour and future developments are highly dependent on the choice of the partition constants used in distribution models. Because there is a considerable amount of variation in these values, environmental quality forecasts for PCBs may still contain major uncertainties.

Decreasing PCB concentrations in the atmosphere may result in volatilization of

PCBs from surface waters and soils to the atmosphere, where long-range transport may occur. Volatilization may become an important process determining long-term PCB concentrations in surface waters and soils.

In 1987 the first reports were published indicating that PCBs can be transformed in anaerobic sediments. Since then a large number of studies has confirmed the shift from higher- to lower-chlorinated PCBs in sediments. Laboratory experiments have demonstrated that anaerobic microbial populations in sediments are able to dechlorinate PCBs and produce lower-chlorinated biphenyls as products. Although these reactions only transform PCBs, rather than completely eliminating them (mineralization), microbial dechlorination results in a significant reduction of the dioxin-like toxicity and the bioaccumulation potential of PCBs.

3. PRODUCTION, APPLICATIONS, SOURCES AND EMISSIONS

3.1. Production and applications

In Europe, PCBs were formerly produced in the EC countries Germany (former FRG), France, United Kingdom and Spain. In these countries production was terminated in the first half of the 1980s. Outside the EC, PCBs were produced in the former Warsaw Pact countries Germany (former GDR), Poland, the former Soviet Union and the former Czechoslovakia. It is unlikely that production still continues in these countries; the Chemko factory in Czechoslovakia presumably ended production in 1985 (still 500 tonnes in 1985) (De Voogt, 1994), whereas in that period Russia still produced about 500 tonnes yearly, though formulation had already been discontinued for ecological reasons (De Voogt, 1994). A summary of the production process and amounts produced is given in the SPEED Document (Raad *et al.*, 1993). Undesirable production of PCBs may take place during several reactions in which chlorinated compounds are involved (e.g. the production of phthalocyanine pigments with chlorobenzenes as a solvent) and incineration processes (e.g. waste incineration, coal combustion).

Table 3.1. Possible applications of PCBs (Raad *et al.*, 1993)

closed applications	open applications
transformers	lubricating oils, metal-working fluids (additive)
capacitors (large)	hydraulic fluids, gear oils
fluorescent lighting units	plasticizer (paint, printing ink, polymers, etc.)
small capacitors (e.g. in home appliances)	impregnating agent for paper, textiles, etc.
pre-connection appliances	

The applications of PCBs may be *open* or *closed*. Closed application means that - in principle - PCBs cannot be released to the environment during use (for example applied as a dielectric fluid in transformers).
Table 3.1 presents the applications for which PCBs have been used, or still are in use.

Since 1972 several measures have been taken to protect the environment against PCBs:

- in 1972 Dutch industry decided voluntary to ban the use of open PCB applications;
- in the period 1979-1985 the Dutch government banned the sale of closed PCB applications. Regulations were introduced to encourage replacement and destruction for the applications in use. An incentive scheme was set up to replace capacitors (cos phi) in fluorescent lighting units;
- in the period 1985-1988 the Dutch government tightened up regulations for PCB-containing waste materials;
- in most countries cessation or limitation of PCB production and discontinuation of open-system application have been encouraged and have actually taken place.

As a result of these measures, there has been a substantial reduction in the use of PCBs. Since the publication of the SPEED Document (Raad *et al.*, 1993) no more recent data on PCBs present in transformers and large capacitors have become available (Ligthart, 1994). No estimate could be made of the quantities of PCBs present in home appliances. No data on the amounts of replaced capacitors are available (Meijer, 1994).
Dutch producers used PCBs in a few open applications, a practice that was ended in 1973 (Raad *et al.*, 1993). Import of PCB-containing products could have occurred over a longer period.
According to (Anon., 1994a) the percentage of mineral oil contaminated with PCBs at levels of 50-500 ppm is about zero in the Netherlands.

3.2. Sources and emissions in the Netherlands

Due to the cessation (in most countries) or limitation of PCB production and the ending of open-system application, the major sources of PCB emissions to air, water and soil have shifted from the open applications to accidental release from closed systems still in use.
In this chapter the most important source categories are reviewed. Available data are presented with - as far as possible - a range of uncertainty. The major focus is on emissions of the predominant PCB congeners in the abiotic and biotic environment (expressed as 'total PCB'; see Chapter 2), with some attention also being given to emissions of the non-ortho and mono-ortho congeners.

Deposition and volatilization from contaminated water and soil are important routes of PCBs entering surface water and soil and air. These fluxes will be treated extensively in Chapter 4. In this chapter only the magnitude of these fluxes will be presented, so that emission and deposition/volatilization fluxes can be compared.

3.3. Emissions to air

3.3.1. Emissions to the air in the Netherlands

Emissions in the Netherlands have been estimated by combining emission factors with data on source categories. The emissions are presented as approximations for 1990 and 1980 in Table 3.2.

The range of uncertainty in the figures in Table 3.2 is high. In the following pages this uncertainty will be explained for each source category. Taking these uncertainties into account, we come to three conclusions:

- PCB emissions to air had decreased in 1990 relative to 1980. We think that an emission of about zero from open applications in 1980 is more probable than an emission of thousands of kilos. Based on this assumption, a decrease can be calculated of approximately 50%;
- processes where PCBs may be formed unintentionally (processes with footnote a) in Table 3.2) have become relatively more important;
- it is probable that in 1990 volatilization from surface water is of the same order of magnitude as direct air emissions from Dutch anthropogenic sources.

Use of open applications

It is unknown when the use of open applications actually ceased. As mentioned in Paragraph 3.1, Dutch producers ended open PCB applications in 1973 (Raad *et al.*, 1993). By the beginning of the eighties, the only possible emission sources were import and use of PCB-containing products. There are no data available on this import. It is likely that in 1980 use of open PCB applications in the Netherlands was already very low (around zero). However, to give an indication of the uncertainty, a rough estimate has been made of the emission in the case of open systems still being in use. The volume of PCBs in open applications in the OECD countries has been derived from production and sales data (Bletchly, 1983). In these statistics, figures are given for production and application in closed systems for the OECD countries as a whole. A figure is also given which might include open applications, but is probably mainly export to non-OECD countries. A distinction between those two possibilities cannot be made. In a 'worst case' calculation we assume that this figure represents totally the amounts of PCBs used in open systems. The figure is distributed between the countries according to their gross national product (GNP), differentiating between producer and non-producer countries (the ratio is assumed to be equal to the ratio for PCB use in electrical equipment). Using an emission factor of 7% (Duiser, 1989), evaporation from open applications in the Netherlands around 1980 could amounted to 5600 kg per year. Taking the assumptions into account, this amount is probably much too high. For the calculation of deposition in 1980,

Table 3.2. Estimates of PCB emissions (total PCB) to air in the Netherlands in 1980 and 1990, compared to volatilization estimates (in the bottom two rows).

Source	Emissions in 1980 (kg.year^{-1})	Emissions in 1990 (kg.year^{-1})	Remark
Open applications	0 - 5600	0	less than 1% is non-ortho- and mono-ortho
Spills/leaks from transformers	40	5	less than 1% is non-ortho- and mono-ortho
Spills/leaks from large capacitors	230	60	less than 1% is non-ortho- and mono-ortho
Spills/leaks from small capacitors	180	80	less than 1% is non-ortho- and mono-ortho
Waste incineration[a)]	15[a)]	15[a)]	1-25% is non-ortho- and mono-ortho[a)]
Incineration of coal and lignite[a)]	30[a)]	30[a)]	1% is non-ortho- and mono-ortho[a)]
Primary steel production (cokes, sinter)[a)]	40[a)]	40[a)]	2-5% is non-ortho- and mono-ortho[a)]
Other high-temperature processes[a)]	20[a)]	20[a)]	wide range[a)]
Totals	560 - 6100	250	
Volatilization from water[b)]	260	260	
Volatilization from soil[b)]	6	6	

[a)] PCBs (PCB 28, 52, 101, 118, 153, 138, 180) emitted in combustion and industrial processes where also dioxins are formed, based on Bremmer *et al.*(1995). The amount of total PCB is unknown.

[b)] No trend can be given because of the uncertainties in the calculation method (see Paragraph 4.6.1) we have used an open-application emission of zero, because we consider it far more probable that in 1980 these emissions were already very low.

Due to the cessation of PCB production and formulation in most countries around the world in the 1980s, we assume that in 1990 emissions from open applications in the Netherlands were zero.

Leaks and spills from PCB-equipment

Emissions may result from leaks, accidental damage or rupture of closed systems, such as transformers, capacitors and other electrical equipment.

Estimates of leakage/spillage rates for PCB-equipment in the U.S. have been made by the Edison Electric Institute and the Utility Solid Wastes Activity Group for the EPA, using data from the electric utility industry (Callahan *et al.*, 1983; EPA, 1987). According to these estimates, PCB-transformers and PCB-capacitors contain 99 per cent of all PCBs in electrical equipment and are responsible for 99 per cent of the amount spilled or leaked.

For the electric utility industry it was estimated (from data on mineral oil transformers) that about 2% of the PCB-transformers developed leaks annually, with an average quantity of PCBs spilled of about 30 kg. Most of the time the spills were caused by transformer leaks. In a quarter of the cases they involved accidental damage.

The leakage frequency for large PCB-capacitors was estimated to be 3%, with an average amount spilled of 8 kg PCBs. The spills were mostly caused by rupture. Capacitor leaks formed the second most important cause.

By combining these leakage data with data on the amounts of PCB applied in U.S. PCB-equipment (EPA, 1987; Bletchly, 1983; Callahan *et al.*, 1983) it can be deduced that 0.06% of the total PCBs in use in PCB-transformers are spilled per year. For large capacitors a leakage/spillage rate of 1.6% of the PCBs in use in this equipment can be derived. In this study these figures are used.

Some other studies on leaks of PCB-equipment in the chemical industry and in government buildings have been conducted, which yielded different data for the percentage of leaking transformers and capacitors (Callahan *et al.*, 1983). From inspection reports in the chemical industry in the U.S. it was found that 19% of the PCB-transformers started to leak within a year. However, for mineral oil transformers this appeared to be about 2.5%. An inspection programme in U.S. government buildings showed that about 20% of the transformers develop leaks in much less than a year. These estimates are higher (by up to more than ten times) than those for the utility study. For large PCB-capacitors in the chemical industry the inspection reports revealed that 0.18% start to leak annually. This is less than one tenth of the fre-

quency in the utility industry.
These studies cannot be used to deduce an emission factor, because they contain no estimates of the amounts of PCBs spilled. However, they indicate that caution is required when using the utility industry data to estimate emissions for other situations. Assuming the same values for average amounts of spilled PCBs, the leakage/spillage rate of transformers based on the chemical industry studies would be up to ten times higher (0.6% instead of 0.06%). For large capacitors the rate would be more than ten times lower (0.1% instead of 1.6%). These figures give an indication of the uncertainty range.

No data are available on small PCB-capacitors, although they contain a considerable proportion of the total PCBs in use in electrical equipment. They are therefore likely to be an important source. The leakage/spillage rate of large capacitors can serve as a first rough estimate.

The proportion of the spilled amount that evaporates depends on many factors, such as the PCB composition, the surface onto which PCBs are spilled, temperature, wind speed and the rapidity with which spills are cleaned up. This large variation in factors makes it difficult to estimate an emission factor (EPA, 1987). An indication can be derived from a study on the vapour behaviour of PCBs (Haque *et al.*, 1974). The vapour loss of Aroclor 1254 from itself has been found to be 2 $\mu g.day^{-1}.cm^{-2}$ at 26 °C and 89 $\mu g.day^{-1}.cm^{-2}$ at 60 °C. Assuming a thickness of the spilled/leaked liquid layer of 0.5 cm (viscous liquid) and a density of 1.5 $g.cm^{-3}$, the evaporation rate is then 0.1% (at 26 °C) to 4% (at 60 °C) at the amount spilled per year. For less chlorinated PCB mixtures such as Arochlor 1242 and 1016 the evaporation rate is about 5 to 6 times higher (according to the difference in vapour pressure) and can be estimated to be 0.6% to 24%. No data are available on the proportion of the different PCB blends used in electrical equipment. Therefore, as a rough approximation, an emission of 10% of the amount spilled is applied. This is probably an overestimate, especially for countries that have regulations on the control of PCB equipment. Following the foregoing, the emission factors used in this study are 0.006% of the PCBs used in transformers and 0.16% of the PCBs used in capacitors.

The pattern of PCB congeners in the emissions will qualitatively be the same as in the technical blend used in the equipment. The lower-chlorinated congeners will volatilize faster. Compared to the distribution of congeners in the technical blend, there will be a shift towards the lower molecular weight compounds (tri- and tetrabiphenyls).

The numbers of PCB-transformers and PCB-capacitors in use in the Netherlands have been derived from Raad *et al.* (1993). For transformers and large capacitors, the data have been based on registration data from the Ministry of Housing, Physical Planning and Environment. In 1990, 83 tonnes of PCBs were in use in transformers and 37 tonnes in large capacitors. For 1980 the data from the first registration year, 1985, have been assumed, i.e. 592 tonnes of PCBs in transformers and 143 tonnes in large capacitors. For small capacitors the amounts have been based on estimates of fluorescent light ballasts by TEBODIN (1980, 1982) and an assumed service life of 15 years. In 1980 and 1990, respectively, 112 and 52 tonnes of PCBs were in use in small capacitors.

Estimates of emissions have been made by combining the emission factors with the PCB amounts in use. In view of the uncertainties the results should be treated with caution.

Waste incineration, incineration of coal and lignite, primary steel production (sinter), metal industry and other

In Bremmer *et al.* (1995) an estimate is made of PCB emissions from processes where dioxins are emitted. They selected processes with an elevated temperature and the presence of organic matter and chlorine in the raw materials. In Table 3.2 the calculated emissions for these processes are presented. The PCB congener pattern of these sources appears to be different from that of the 'classic' PCB emission sources: in general, more of the more toxic ortho- and non-ortho congeners are emitted. Concerning the origin of the PCBs, Bremmer *et al.* (1995) concluded that PCB 126 may be formed by 'de novo synthesis', that the occurrence of (some) dioxin-like PCBs (non-ortho and mono-ortho congeners) may depend on different factors than those causing formation of toxic dioxins, and that possibly some of the PCBs already present in the raw materials are emitted to the air.

The emission estimates are based on a limited set of measurements: waste incineration is based on five measurements, sinter processes on two and incineration of coal and lignite on only one. Based on these very small number of measurements, an emission factor per process is derived, which is multiplied by an activity level, resulting in a rough emission estimate. In this mode of calculation, two main points of uncertainty can be pointed out:

- in time, emission factors for a process will vary because of changing raw material composition and process parameters (such as temperature). With only a few measurements, this variation cannot be seen; the resulting emission factor could be accidentally high or low;
- the emission factor is in fact only applicable for the plant where measurements

have taken place. However, we have used the factor for a whole range of activities with only the raw materials in common: waste, sinter and coal.

These two points in particular introduce a high level of uncertainty. Therefore, the emission figures should be interpreted as order-of-magnitude estimates.

Because of the high level of uncertainty, we assume the emission figures in Bremmer *et al.* (1995), which they present as 1994 figures, to be representative for 1990, too. Although in 1980, for example, less waste and steel was produced, we have assumed the same level of emission in 1980 and 1990, because of the lower standard of emission abatement technology in 1980 and the possibly higher PCB levels in waste and steel scrap in 1980.

Finally, it should be pointed out that for the processes in which PCB formation plays a role, the emission estimates are given for PCB 28, 52, 101, 118, 153, 138 and 180 'only'. These congeners have been measured. We know of no way to translate the quantity of these PCBs into a 'total-PCB' figure. This could imply that the relative contribution of these sources to the total PCB emission to the air (see Table 3.2) has been underestimated.

3.3.2. Emissions to air in other European countries

In Table 3.3 an overview is given of PCB emissions to air in a selection of European countries in 1980 and 1990. In Appendix 2 the figures for all European countries are presented.

For the Netherlands, there was also an emission reduction between 1980 and 1990 (see Table 3.3).

For 1980, the volume of PCBs applied in open applications can be assumed to be negligible in OECD countries (lower part of the 1980 range). For the case that open systems were still in use, an estimate has been made of the amounts used around this period on the basis of production and sales data and differentiating between producer and non-producer countries (upper part of the 1980 range). The same procedure has been used for the calculating Dutch emissions (see Paragraph 3.3.1). The range gives an indication of the high uncertainty of the presented figures. The lower part of the 1980 range has been used in the deposition calculation for the year 1980.

For the non-OECD countries, the amounts still used in open applications in 1980 are based on figures from Czechoslovakia (Holoubek *et al.*, 1993). It is estimated from these figures that approximately 200 tonnes of PCBs were used in Czechoslovakia in 1980 for plasticizer applications. The calculated GNP-related amount has been extrapolated to other countries, correcting for the difference between producer and non-producer countries (see Paragraph 3.3.1).

Table 3.3. PCB emissions to the air in a selection of European countries (excluding re-emission, i.e. volatilization from surface water and soil).

	1980 (kg.year^{-1})	1990 (kg.year^{-1})
Belgium	6,400 -10,000	5,200
Germany	70,000 - 170,000	43,000
France	31,000 - 101,000	20,000
United Kingdom	15,000 - 64,000	8,900
Others	221,000 - 310,000	46,000

On the basis of the GNP-related PCB volumes, estimates have been made of the PCBs used in transformers and capacitors for the European countries for which no data were available. In view of the difference in PCB use between producer and non-producer countries, the average GNP-related PCB volumes for non-producer countries has been used to arrive at a rough estimate for these other European countries (all of which are non-producer countries). The results give merely an indication of the order of magnitude.

3.4. Emissions to surface water

Table 3.4 presents PCB emissions to surface water. For all sources, the share of the non-ortho and mono-ortho congeners is less than 1%.
The emissions to surface water are difficult to estimate, and the figures should be considered as order-of-magnitude estimates. Nevertheless, a downward trend from 1980 to 1990 is likely.

In estimating the emissions to surface water, we have analysed the PCB flow to and from sewage treatment plants in 1990 (see Figure 3.1).
The flow is based on three measurements.

1) At the beginning of the 1990s the total-PCB content of communal sewage sludge was about 0.4 mg.kg^{-1} sludge (d.w.) (based on CBS, 1994; standard deviation 0.43 mg.kg^{-1} sludge (d.w.)). This figure is in accordance with the PCB content of British sewage sludge (Harrad *et al.*, 1994). Production of sewage sludge in 1990 amounted to 315 million kg, resulting in a total PCB sludge content of about 130

kg.

2) Somers *et al.* (1994) surveyed STP influents in the province of Brabant. In 8% of the samples they could detect PCBs (total number of samples 1169). In the samples where PCBs remained below the detection limit, they assumed a PCB content of 50% of the detection limit. Based on these data, for the province of Brabant Somers *et al.* (1994) calculated a total-PCB (5*Σ7PCB) load in influent of about 100 kg, and, assuming a sewage treatment efficiency of 90%, an effluent load of 10 kg. For the Netherlands the total emission from STPs can be estimated to be about 70 kg.year^{-1} in 1990 (based on the ratio of inhabitants). This amount is not in exact accordance with the total-PCB volume in sewage sludge. Taking the sludge content into account and assuming a treatment efficiency of 90%, one would expect an emission of about 10-20 kg.

Table 3.4. PCB emissions (total-PCBs) to surface water in the Netherlands (kg.year^{-1}), compared to deposition (the two bottom rows). STP means 'sewage treatment plant'.

Source	1980	1990
Households		
- indirect (via STP)	10	3
- direct	5	1
	15	5
Industry		
- Indirect (via STP)	15	5
- PCB-equipment (leaks)	900	300
- Paper & cardboard	0 - 5	0 - 5
- Metal scrap	>6 - 20	5 - 15
- Other	unknown	unknown
	930	320
Total	950	320
Indirect deposition (via communal STPs)	10	5
Direct deposition	80	40

Considering all the uncertainties, we have chosen a figure of 20 kg, giving order-of-magnitude accordance for the two methods of calculation.

3) In the period 1984-1987 STORA (1985) and RIZA (1992) measured PCB concentrations in household wastewater (adopted from Raad *et al.*, 1993). They estimated an emission factor of 1.8 total-PCB mg.inhabitant^{-1}.year^{-1} (STORA, 1985) and 9 total-PCB mg.inhabitant^{-1}.year^{-1} (RIZA, 1989). Arbitrarily, we have taken the high emission factor for the year 1980 and the low emission factor for the year 1990. We assume a downward trend because recent research has shown the PCB content of household wastewater to be below the detection limit (RIZA, 1992).

A share of the total deposition to soil (see Chapter 4) is estimated to end up in STP effluent (based on Dutch wastewater streams; see Coppoolse *et al.*, 1993, p.121). The contribution of deposition drained to STP effluents is calculated to be 70 kg total-PCBs in 1980 and 50 kg in 1990.

The contribution of industry to STP is a balance item: industry = surface water + sludge minus households + deposition.

The 1980 flow is obtained by using the 1980 household input to STP, using the 1990 industry input increased by a factor based on the amounts of PCBs in use and on the deposition input in 1980.

Households

PCBs in domestic waste water (from households) probably originate mainly from the intake of food, followed by excretion.

Industry

Via STP's

In Figure 3.1 this route is described. We assume that most of the PCB originates from leaks and spills from PCB-equipment.

Leaks and spills from PCB-equipment

The magnitude of emissions to water from leaks and spills is highly dependent on the type of location where the PCB-containing equipment is installed. If the equipment is installed indoors, there may be a connection to a communal sewer (see previous item) or to a private sewer installation. Alternatively, the equipment may be installed outdoors, with some portion of PCB spills being emitted directly via run-off to surface water. Here, a rough estimate is used of 20% direct run-off at an application rate of 25% for outdoor situations and 20% indirect emissions (via private sewer or untreated) at an application rate of 75% for indoor situations. Based on the same amounts of the PCBs in use, emissions to surface water from leaks and spills have been calculated as presented in Table 3.4.

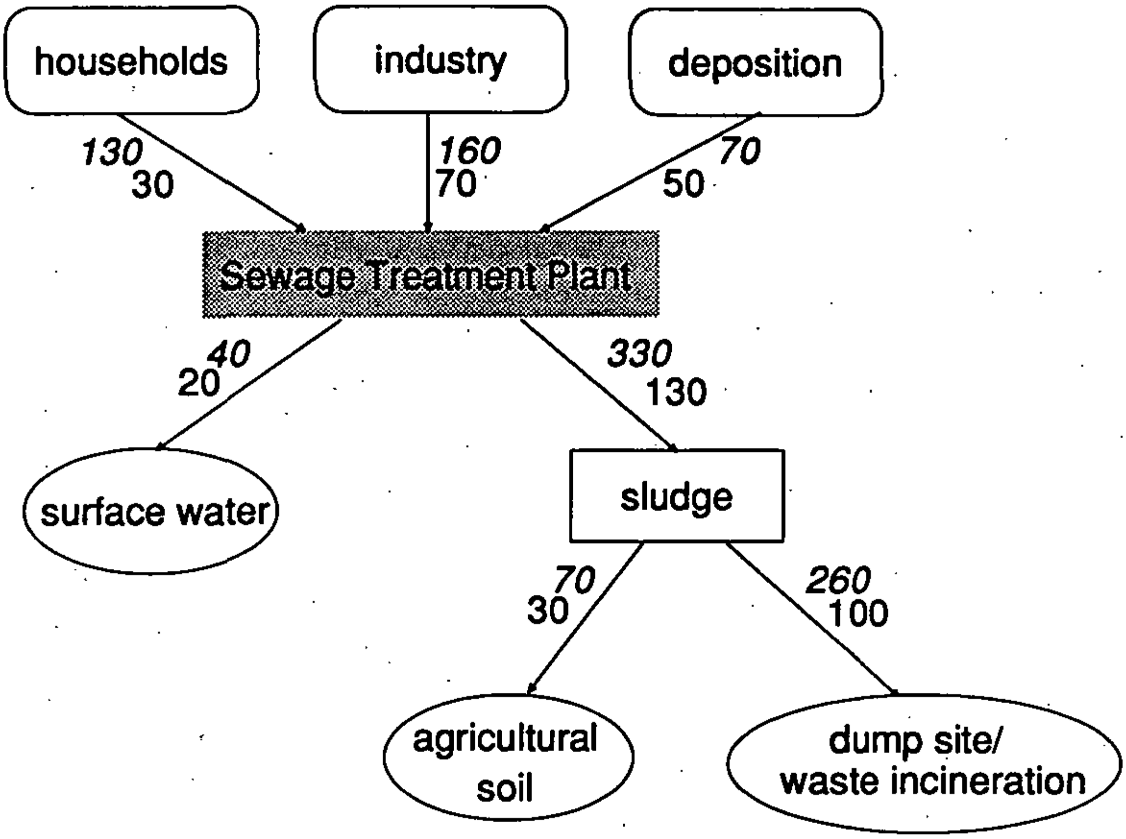


Figure 3.1. PCB flow (simplified) to and from a sewage treatment plant for 1990 (in kg; upper figure: 1980, lower figure: 1990)

Chemical industry

In the chemical industry only one factory, in the colorant industry, was investigated with regard to PCBs in wastewater (Van Luin *et al.*, 1987); the concentration of $\Sigma 7$ PCB was 0.07 µg/l. The SPEED Document (Raad *et al.*, 1993) gives two possible processes in the colorant industry where PCBs may be formed. In production of phthalocyanines (if produced at all in the Netherlands), it is unlikely that dichlorobenzene and/or trichlorobenzene are used as solvents and thus unlikely that PCBs are formed. The 'Criteria Document' on chlorobenzenes does not mention application as a solvent (Slooff *et al.*, 1991). Production of dichlorobenzidine in the Netherlands (and other European countries) is similarly unlikely. In a survey carried out on chemical substances, including the benzidine dyes Trypan blue and Direct Red 39, it appeared that only in very few cases are benzidine dyes still produced elsewhere in Europe, and dichlorobenzidine dyes not at all (Van der Poel *et al.*, 1988; Van der Poel *et al.*, 1981).

Other chemical industry categories producing derivatives of chlorobenzenes and chlorophenols are the pharmaceutical and pesticide industries. The likelihood that significant amounts of PCBs are formed and released to surface water and/or wastewater seems to be small, comparable to the formation of dioxins in these branches (Bremmer, 1994). Many large chemical factories have private STPs.

Paper and cardboard industry

Many paper and cardboard producers have their own private STPs. Their annual emission direct to surface water is estimated to be 0-3 kg Σ6-PCB (0-5 kg total-PCBs) (Raad *et al.*, 1994). This estimate is for 1990; for 1980 it has been assumed that the fraction of paper containing PCBs was larger and that the PCB level in this paper was higher.

Direct emissions have been investigated at 6 plants, which showed concentrations of 0.01 (detection limit) - 0.16 μg Σ6-PCB/l (Raad *et al.*, 1993). Although the quantities of water discharged annually are not known, it is expected that the loads will be negligible.

Metal scrap production, storage and transhipment

In secondary metal production scrap is used (recycled) to produce new metal. In primary metal production, too, a certain fraction of scrap is used. Analogous to dioxins, PCBs may be present in the residues of metal-working fluids present in metal scrap (Bremmer, 1987). Especially in the case of steel scrap, it is possible that PCBs may also come from contaminated (lubricating) oil.

At Rotterdam, large volumes of metal scrap are stored and transhipped. Direct emission routes to surface water are:

a) run-off from (unmetalled) storage yards;
b) spills during transhipment;
c) rinse and rain water from transport vehicles.

From a confidential memorandum (Anon., 1994b) it appears that:

sub a) The run-off may contain a few tenths of μg/l of PCBs. The end-of-pipe measure usually proposed is removal of suspended matter (including activated carbon adsorption).

sub b) There are instances of dredging activities adjacent to the quay recovering over ten per cent of the scrap. Presumably, there are demonstrable influences on the local sediment quality. Recently preventive measures (adaptation of machinery) and good housekeeping measures (if possible) have been introduced in licenses.

sub c) Investigations of the dredging loads due to harbour activities have shown elevated PCB concentrations at the cleaning sites of tug-pushed dump barges in the range of 0.5-1 mg/kg. In the waste from these barges, 4 kg of PCBs have been found (calculation for one year), which is presumably an underestimate, as the scrap fraction had been removed. Cleaning of tug-pushed dump barges involves large volumes of water: up to several m^3 per barge. Once the regulation on cargo residues comes into effect under the Surface Waters Act, direct releases to surface water of water (and other waste) will be prohibited. A similar measure is in preparation for other means of transportation.

Most of the metal scrap transported via international inland shipping comes from Germany (about 90%) (Anon., 1994b). The largest share, approximately 80%, is stored and transhipped in the harbour area of Rijnmond for export. In the Netherlands, metal scrap is produced by 7 shredder facilities, with a total capacity of 790,000 tonnes/year (Raad *et al.*, 1993). At three of them, (random) samples have been investigated (Luijten *et al.*, 1988) of their wastewater, which is discharged directly to surface water. For one (large) installation, an estimate was made of the amount discharged annually to surface water (approx. 1 kg). It was concluded (Luijten *et al.*, 1988) that the PCBs present in the wastewater originated from capacitors present in the household appliance fraction. The rainwater drained from the premises, which is usually released via an oil skimmer to the sewerage or surface water, may presumably also contain considerable amounts of PCBs (Luijten *et al.*, 1988). As PCBs are no longer applied in capacitors, this emission will diminish over the years.

For both the scrap transhipment activities and the shredder installations, rough estimates have been made for 1980 and 1990. Because of the decrease over the years of PCB-containing elements in the scrap produced, for 1980 a 20% higher emission is assumed. For transhipment a further decrease has been assumed, because in some cases measures will have been taken at that time owing to the introduction of regulations.

Other industries, service industries and health care

Of the other industries where measurements have been made of PCBs in wastewater, it is likely that the PCBs found originate from contaminated materials (Raad *et al.*, 1994). In the case of garages and a mechanical repair centre for ship's engines, contaminated oils may be a potential source of PCBs. For those industries where PCBs were found, the amount was quantified: >0.3 kg/year (Raad *et al.*, 1993). Extrapolation for the Netherlands as a whole on the basis of these measurements, carried out for such a limited number of firms, is impossible.

For other private STPs, no data are available (Anon., 1994c; Baas, 1994) on concentrations in influent/effluent and sludge. Some branches of industry may be important to investigate, as the amounts of wastewater treated and sludge produced are significant (communal STP : private STP sludge production = 323 : 250 in 1992 (Anon., 1994c).

Mining slag

In the past PCBs were extensively used in coal mines (Belgium and Germany) in hydraulic fluids. In Germany hundreds of tonnes of PCBs were spilled every year (TAUW, 1986).

In the Netherlands several types of mining slag are used for several purposes (civil construction). In an investigation of leaching from slag, samples were analysed for many components, among them PCBs (TAUW, 1986). In 2 out of 21 samples PCBs were detected clearly above the detection limit, viz. 85 and 800 μg/kg. The highest concentration was found in a sample of stone deposit, which is certainly not imported as such (it may just be present to some extent in the slag).

It is possible that the mining slag currently imported will no longer be an important source, as PCBs in hydraulic fluids have been abandoned for over 5 years. However, it is advised to give due attention to PCBs for a verifiable and environmentally well-founded application of mining slag (TAUW, 1986; Faasen, 1995).

Leaching of PCB-containing products

The amount (or concentrations) of PCBs in articles applied outdoors are unknown. For waste materials it is known that the rubber/leather fraction, in particular, contains PCBs (Janssens *et al.*, 1988). Van Luin *et al.* (1987) also mention the presence of PCBs in the rubber industry.

It is advised to investigate the origin of PCBs in rubber (formed during production of synthetic rubbers or present in the raw materials used).

3.5. Emissions to soil and groundwater

Direct emissions to soil may originate from applications by industry and the service industry, and from leaching of products containing PCBs. Indirect emissions may occur through landfilling (or storage) of waste materials, waste incineration products (slags and filter ashes), dredgings and sewage sludge, and the application of composted fruit, vegetable and garden waste and sewage sludge.

Table 3.5 presents PCB emissions to soil. Emissions to soil were 60% lower in 1990 than in 1980, mainly as a result of the replacement of PCBs in closed applications. Deposition dominates the load of PCBs to soil, especially in 1990.

Each source will now be treated separately.

PCB-equipment (Raad *et al.*, 1993)
The only current application of PCBs is in transformers and capacitors (Sections 3.3 and 3.4). The direct emissions, which can be estimated assuming 75% indoor use with 5% of the leaks and spills going to soil, and 25% outdoor use with 25% going to soil, are presented in Table 3.5.

Sewage sludge
A fraction of the PCBs in influent (originating from households, industry and deposition; see Figure 3.1) end up in the sewage sludge of the STPs. This sludge is used as a fertilizer. We have assumed a downward trend from 1980 to 1990, based on the higher influent levels in 1980 compared to 1990.

Landfilling
Since the SPEED Document (Raad *et al.*, 1993) was published, no new data have been found about the amount of PCBs entering landfills. In 1990 approximately 3500 kg of total-PCBs were landfilled in all kinds of waste materials. This figure is exclusive of industrial waste. Solid waste from shredders belongs to the category of industrial waste. The amount of PCBs in solid waste from shredders (27% of the

Table 3.5. Emissions of total-PCBs to soil (kg.year^{-1}), compared to deposition.

Source	1980	1990	Remark
Transformers (leaks)	40	5	
Large capacitors (leaks)	230	60	
Small capacitors (leaks)	180	80	
Sewage sludge to soil	70	30	see Figure 3.1
Landfilling (leaching to soil and groundwater)	0	0	based on limited measurements
Total	520	180	
Deposition	940	630	

input) may be considerable (0-100 mg.kg^{-1}) (Vos *et al.*, 1991). At a rough estimate, the amount of PCBs dumped with this solid waste category (140,000 tonnes in 1988; Vos *et al.*, 1991) is thus 0-14,000 kg. Greater attention should therefore be paid to shredder waste, as this source may exceed the total load of PCBs to soil from all other waste materials.

We do not consider landfilling as an 'emission'. Rather, emissions may occur through leaching of PCBs from landfills to the soil and groundwater. In the Netherlands PCBs are not continually analysed in the percolate of dump sites. In two cases (where it was known that PCBs were present in the waste), PCBs were measured in the percolate. All congener levels were below the detection limit. We assume that PCBs are contained at the waste sites for a very long period.

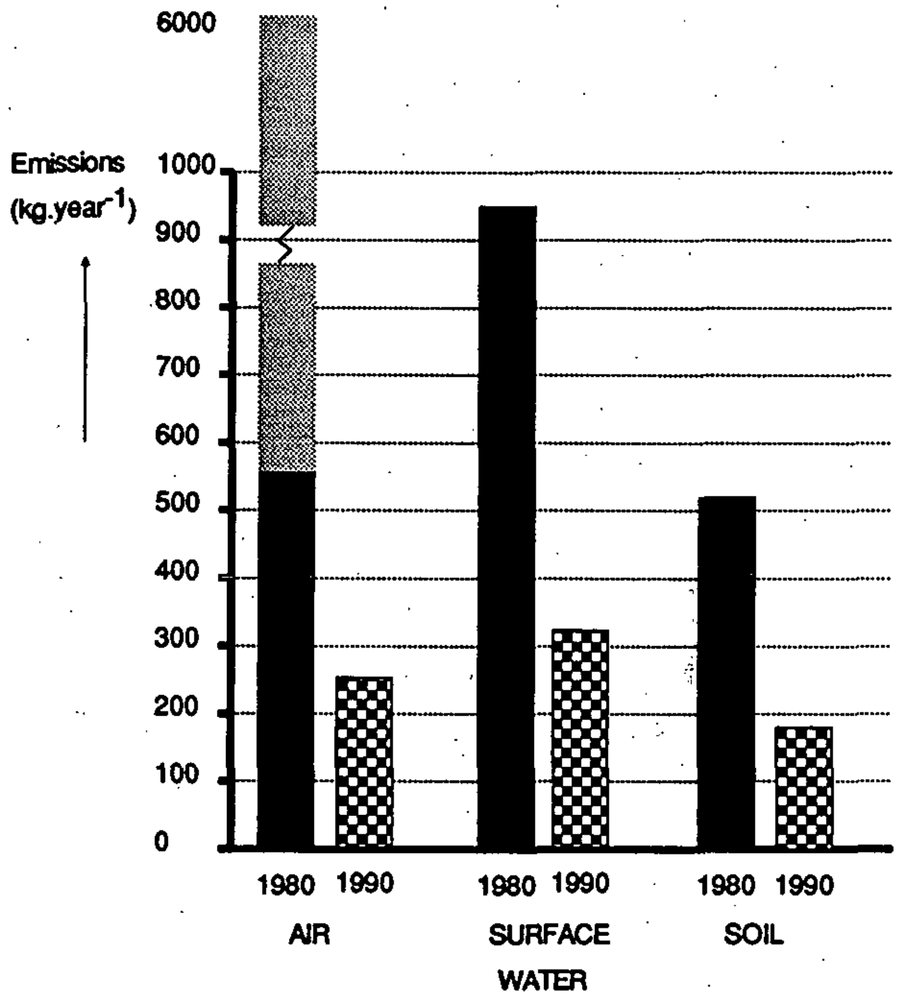


Figure 3.2 Emissions of total-PCBs to air, surface water and soil in 1980 and 1990.

3.6. Summary and conclusions

PCB policy measures in the past have led to a downward emission trend. Figure 3.2 gives an overall view of this trend. We stress that most emission estimates are uncertain, because valid data are scarce. In compiling this overview of PCB emissions, therefore, several theoretical assumptions have had to be made. For example, in the present document it is assumed that around 1980 the use of PCBs had already stopped. However, if open applications still existed at that time, emissions to air could have amounted to up to 6000 kg per year in the beginning of the 1980s (see Figure 3.2). Despite all these uncertainties, it is clear that PCB emissions to air, surface water and soil have decreased from thousands of kilograms (1000-8000 kg) around 1980 to hundreds of kilograms (100-900 kg) around 1990. Spills and leaks from PCB-containing equipment are the main source of emissions. Processes in which PCBs may be formed unintentionally have become relatively important sources of emissions to air. Emissions to soil take place mainly at industrial sites (via leaks and spills).

4. CONCENTRATIONS AND FLUXES IN THE ENVIRONMENT

4.1. Chemical analyses

Polychlorinated biphenyls are difficult to analyse in environmental samples. This is due to the usually low concentration levels of a large number of PCB congeners, each with their own characteristics. In addition, other, related contaminants (e.g. halogenated pesticides, PCDDs and PCDFs) are often simultaneously present in samples.

During the last two decades the analytical methodology for PCBs has evolved considerably. Detection techniques have gradually shifted from the use of packed column chromatography for 'total-PCBs' to capillary column chromatography for individual congeners. This change in analysis technique concurred with the shift in attention towards specific PCB congeners, resulting from new insights in toxicity mechanisms (see Paragraph 2.1). The congener-specific analysis of PCBs has been reviewed in detail by Wells (1988), IPCS (1993) and De Voogt *et al.* (1990).

Table 4.1. Environmental quality standards for PCBs in soil and sediment (in µg/kg), normalized to 10% organic matter and 25% lutum (Evaluatienota Water).

compound	target value	limit value		intervention value
	(streefwaarde)	(grenswaarde)	toetsingswaarde	(interventiewaarde)
PCB 28	1	4	30	
PCB 52	1	4	30	
PCB 101	4	4	30	
PCB 118	4	4	30	
PCB 138	4	4	30	
PCB 153	4	4	30	
PCB 180	4	4	30	
Σ6 PCBs (excl. 118)	20			
Σ7 PCBs			200	1000

Currently, various different analytical methodologies are used. As a consequence, available PCB data from different laboratories may not be directly comparable. It is generally accepted that there is a major need for well-defined protocols for the analysis of polychlorinated biphenyls. Fortunately, there is growing international consensus on the procedures for sampling, extraction, clean-up and analysis of PCBs.

Furthermore, several national and international organizations (e.g. NNI, KIWA, CEN and WHO) are supporting interlaboratory comparison studies for PCB analysis. Despite these efforts towards harmonization, the greatest possible caution should be taken when comparing existing monitoring data from different sources (or periods). Differences of up to a factor of 1000 or more have been reported (IPCS, 1993). This complicates the assessment of PCB pollution trends.

4.2. Environmental quality objectives

The environmental quality standards for soil and sediment are summarized in Table 4.1. No PCB quality standards are reported for surface waters. The majority of PCBs are associated with suspended solids in water. Since the normalized organic matter content of suspended solids is based on 20% organic matter, the quality standards for suspended solids can be derived from the soil/sediment quality standards by multiplying the latter by 2.

Table 4.2 Combinations of soil use and type of soil investigated.

1	pasture	sandy soil
2	pasture	sandy soil (humous)
3	pasture	peaty soil
4	arable land	clayey soil
5	arable land	sandy soil
6	arable land	sandy soil (humous)
7	orchard	clayey soil
8	orchard	clayey soil (humous)
9	pine forest	sandy soil (leemarme veldpodzol)
10	pine forest	sandy soil (leemarme vlakvaaggrond)

4.3. Levels in soil and groundwater

4.3.1. Soil

At the national level, 2 studies have been carried out to date to obtain information about the occurrence of PCBs in Dutch soils as a result of the general dispersion of

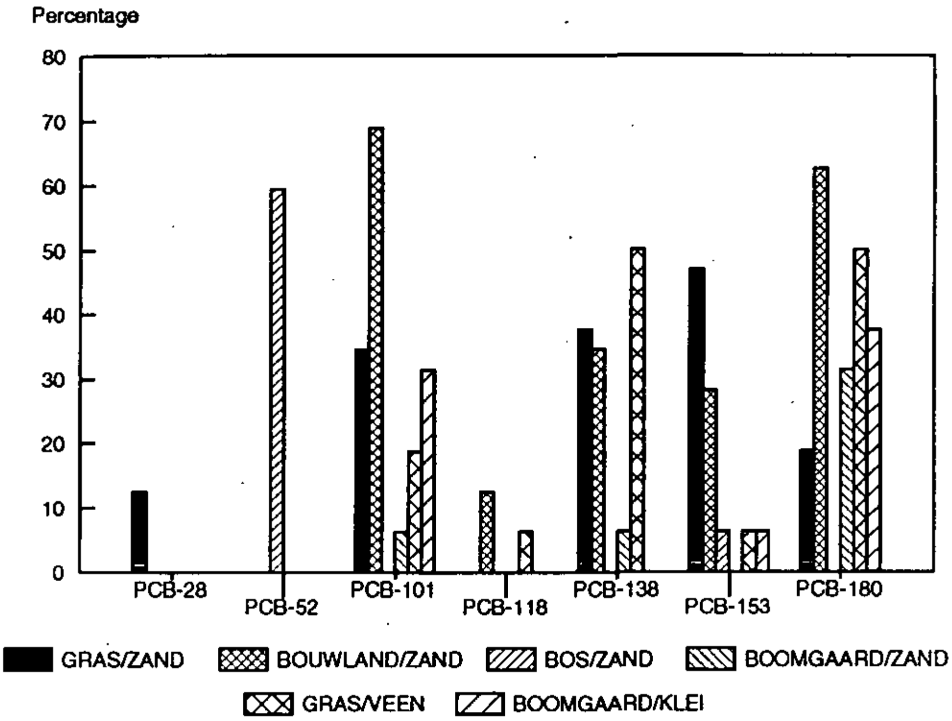


Fig. 4.1. Percentage of analysis results above detection limit (Van Duijvenbooden *et al.*, 1992).

PCBs in the environment. Within this framework, no attention has been paid to specific, locally polluted sites. In the period 1989-1991 an investigation was carried out focusing on 10 combinations of soil type and soil use (see Table 4.2) and on the occurrence of a wide variety of pollutants in the top soil, including PCBs (Greve *et al.*, 1989; Van Duijvenbooden *et al.*, 1992/1994). For every combination, 4 locations were examined. Sampling took place at 2 depths (0-10 cm-l.s. and 10-30 cm-l.s., except for arable land: 30-50 cm-l.s.). Four samples were analysed from each location and depth, each consisting of a mix of 40 individual samples. The results are presented in Table 4.3.

In general, it can be concluded that in many samples no PCBs could be detected (detection limit: 0.5 µg. kg^{-1}; see Figure 4.1). In about 7% of the analysis results, the target values in force were exceeded by a factor of 1 to 6. In the top soil (0-10 cm-l.s.) concentrations were generally higher than in the deeper strata (10-50 cm-l.s.). In forest regions lower concentrations were generally found compared with cultivated regions.

In 1993 a study was carried out focusing on the occurrence of PCBs in the top soils of the 13 agricultural regions of the Netherlands (Lagas *et al.*, 1994). In the framework of this study, samples were taken from the 3 or 4 most important combinations of soil use and type of soils in these regions. For every combination chosen in a region, a soil sample was analysed composed of 20 mixed samples, each of these

Table 4.3. Average concentrations of PCBs in Dutch soils in µg.kg^{-1} (Van Duijvenbooden *et al.*, 1994).

Combination of type of soil / soil use 2)										
top level (0-10 cm-l.s.)										
parameter	1	2	3	4	5	6	7	8	9	10
PCB-28	-	1.0	-	-	-	-	-	-	-	-
-52	-	-	-	-	0.58	2.48	-	-	0.96	-
-101	-	1.03	0.89	1.05	1.43	0.54	0.77	0.53	-	-
-118	-	-	0.51	-	0.58	-	-	-	-	-
-138	-	2.68	4.49	-	0.68	0.82	-	0.54	-	-
-153	-	1.6	1.2	-	0.6	0.6	1.0	-	0.8	-
-180	-	0.8	2.6	-	1.7	0.54	0.9	0.7	-	-
second level (10-30 cm-l.s.; arable land 30-50 cm-l.s.)										
PCB-28	-	-	-	-	-	-	-	-	-	-
-52	-	-	-	-	0.51	5.1	-	-	0.59	-
-101	-	0.68	0.78	-	0.59	-	0.51	-	-	-
-118	-	-	0.52	-	0.56	-	-	-	-	-
-138	-	0.83	2.26	-	0.51	0.52	-	-	-	-
-153	-	1.09	2.47	-	-	-	0.58	1.39	0.51	-
-180	-	0.67	1.2	-	0.56	-	0.71	0.71	-	-
1) Detection limit: 0.5 µg.kg^{-1}										
2) See Table 1										

mixed samples again being composed of 40 individual samples. A total of 43 samples were analysed. Only 4 samples indicated concentrations of 1 to 4 times the target values, with most of the other samples generally showing concentrations far below the target value and sometimes even below the detection limit (0.1 μg.kg^{-1}). The integral analysis results are presented in Figure 4.2.

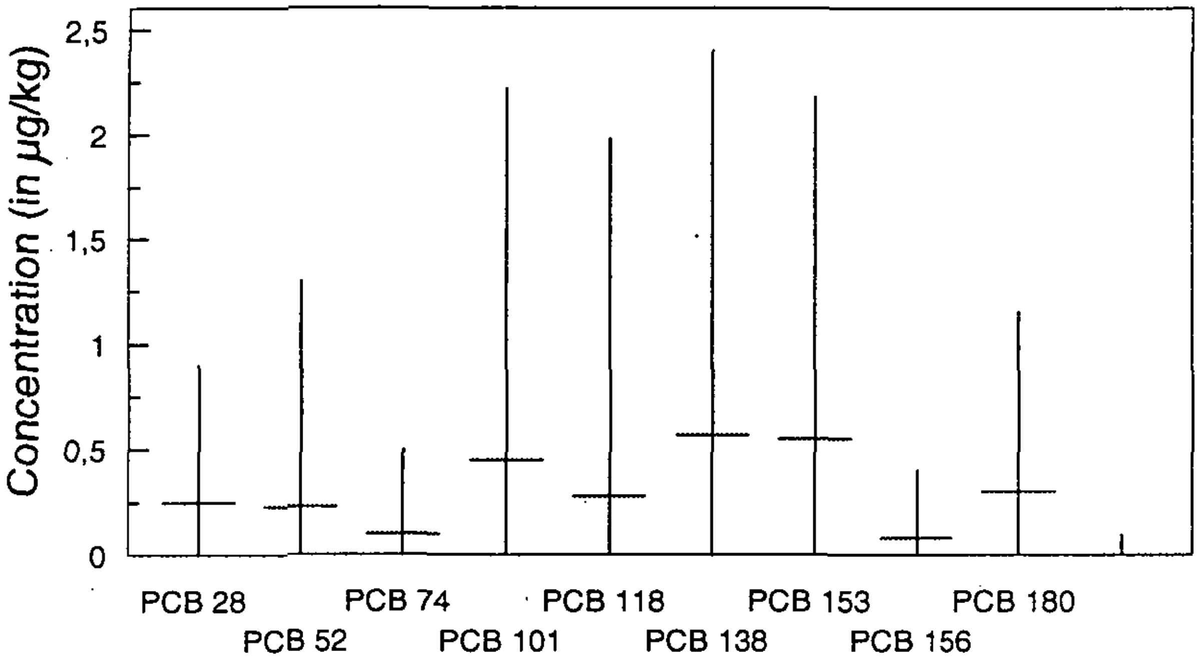


Fig. 4.2. PCB concentrations (mean, maximum and minimum) in Dutch top soils in μg.kg^{-1} (detection limit: 0.1 μg.kg^{-1}; top soil 0-5 cm-l.s.; arable land 0-20 cm-l.s.); Lagas *et al.*, 1994)

Unfortunately, no information is available on the vertical distribution of PCBs in soil. The same holds for a reconstruction of PCB soil pollution history in the Netherlands.

The total PCB burden in the top 5 cm of Dutch soils has been estimated to be about 23 tonnes. The calculation procedure was as follows:

total soil surface area of the Netherlands:	34 835 x 10^6 m^2
minus urban areas and area below surface water	5 937 x 10^6 m^2
	28 898 x 10^6 m^2
average dry soil bulk density	1300 kg m^{-3}
top 5 cm of Dutch topsoil will weigh:	
0.05 m * 28 898 x 10^6 m^2 * 1300 =	1.88 x 10^{12} kg

4.3.2. Groundwater

Based on chemical characteristics, it is to be expected that PCBs will not generally be found in groundwater. Nevertheless, in 1987 a study was carried out to investigate the presence of PCBs in Dutch groundwaters. A total of 24 monitoring wells of the Dutch National Groundwater Quality Monitoring Network were sampled at a depth of about 10 m-l.s. Half of these wells were situated in municipal regions. The study focused on the occurrence of PCB nos. 28, 52, 101, 118, 138, 153 and 180. All the analysis results indicated concentrations below the detection limit (0.01 mg.m^{-3})

Table 4.4. PCB burden in top 5 cm of Dutch soil around 1990.

PCB	conc. µg.kg^{-1}*	burden in kg
28	0.25	470
52	0.2	376
101	0.45	846
138	0.6	1128
153	0.6	1128
180	0.35	658
ΣPCBs	2.45	4606
total PCBs (5*ΣPCBs)		23030

*Mean PCB concentrations from Figure 4.2.

4.4. Levels in surface water and sediments

4.4.1. Fresh water

Determination of PCBs in small water samples is fraught with many uncertainties owing to the relatively low concentrations involved. Since 1988 measurements have been conducted on the suspended solids in the main Dutch rivers (so-called 'rijkswateren') using high-volume water samples. Comparison of levels in surface waters in the past with present levels is hampered by changes in sampling and analytical techniques. For the most recent years (since 1988) such a comparison has been made. Unfortunately, only data for the traditionally measured congeners are available for the main surface waters in the Netherlands. The PCB concentrations in suspended solids were, in general, somewhat higher in 1988 and 1989 relative to the period 1990 - 1993. Nevertheless, differences in PCB levels in the subsequent years are relatively small and concentrations in suspended solids remain constant. The PCB content in the IJsselmeer (Vrouwezand) was systematically the lowest value during the observation period.

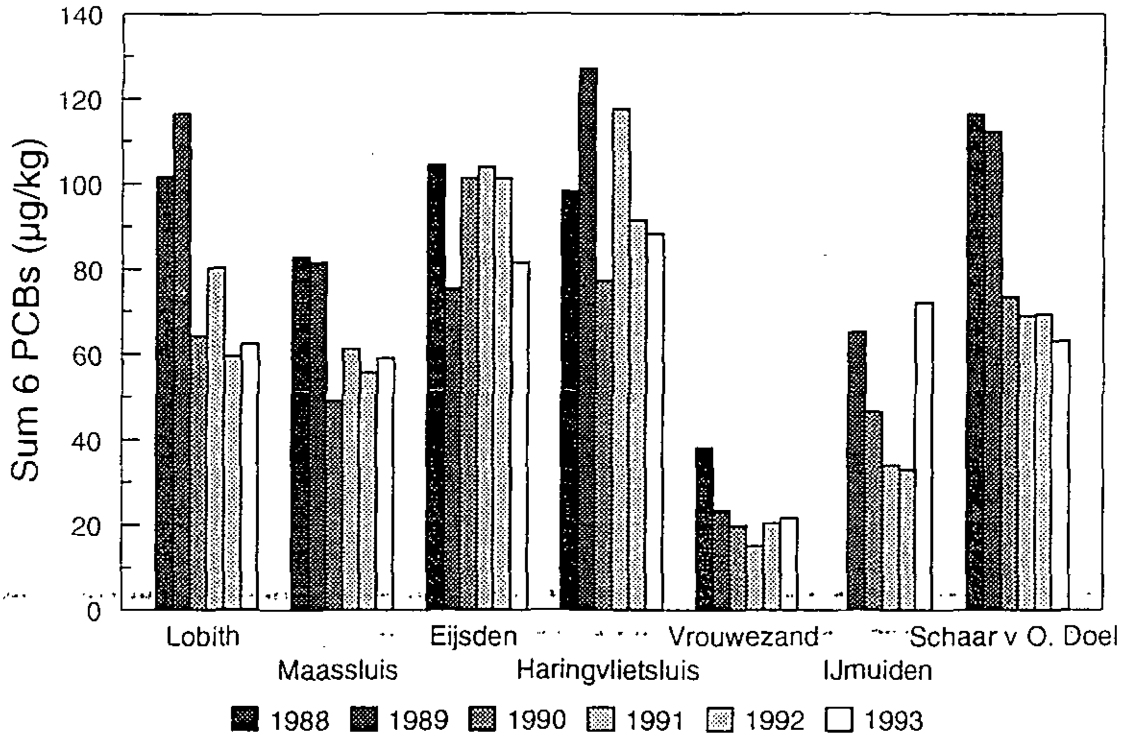


Fig. 4.3. Mean PCB content of suspended solids in surface waters (Σ6 PCBs, not standardized with respect to organic matter content) during a 6-year period (source: RIZA).

Table 4.5 gives congener-specific data for 1990. The PCB concentrations in Rhine and Scheldt water are higher than those in the Maas. The PCB concentrations in Lake IJsselmeer are fairly low. The PCB concentrations in suspended solids around 1990 exceed the limit value (8 µg/kg) by a factor of 2 to 5 for the individual congeners in all three rivers. Only the PCB concentrations in IJsselmeer are below the limit values.

Concentrations of PCBs in water samples from small waterways are not available.

4.4.2. Coastal waters

The mean PCB concentrations in suspended solids from coastal waters in the period 1989-1993 are shown in Figure 4.4. The concentrations in coastal waters were relatively high in 1989, but were lower in subsequent years, although concentrations tended to increase in 1992 and 1993.

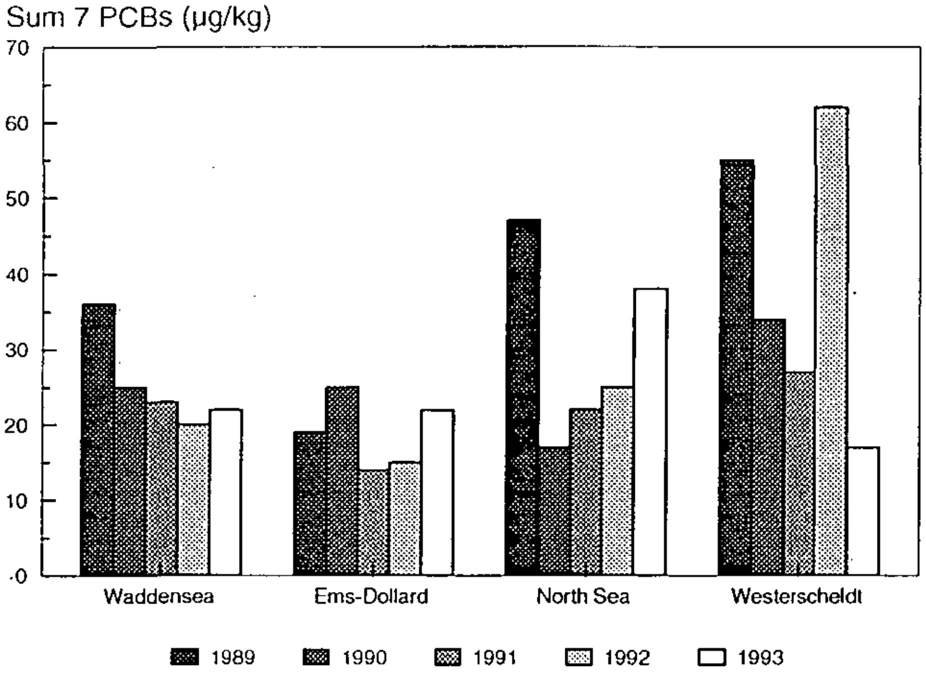


Figure 4.4. PCB concentrations (Σ7 PCBs) in suspended solids from coastal waters; springtime measurements (source: CCRX, 1993).

4.4.3. Sediments

The suspended solids with their bound PCBs settle in the downstream stretches of rivers and the relatively persistent PCBs consequently accumulate in sediments. PCB levels in the major sedimentation areas of the Netherlands are summarized in Table 4.6.

Historical sediment samples, collected in 1972 from the top layer of Ketelmeer sediment and analysed in 1990, have been included to indicate the change in pollution levels. The levels in the 1972 samples do not exceed the intervention value (1000 µg/kg Σ7 PCBs)). The present input of PCBs to the sediment is about 5 to 10 times below the levels of the 1970s. PCB concentrations in recently deposited sediment layers exceed the limit value. Only for Ketelmeer sediment are concentrations of the planar PCBs available. In the past, the levels of these planar congeners were much higher than in the recently deposited sediments (Table 4.6); the dioxin-like toxicity (TEQ) has decreased by a factor 10.

Current contamination with PCBs is still high in Ketelmeer sediment relative to the levels in IJsselmeer or Scheldt sediment. Based on more than 6000 sediment samples from the major waterways ('rijkswateren'), the following distribution in sediment classes was obtained: unclassified: 15%, class 0: 68%, class 3: 14%, class 4: 3% (Geenen, 1994).

Table 4.5. Mean PCB concentration in suspended solids from major surface waters, in µg/kg d.w. (standardized organic matter content: 20%).

Location	Rhine Lobith 1990 n=11	Maas Eijsden 1990 n=9	Scheldt S. v. Ouden Doel 1990 n=10	IJsselmeer IJ23 1990 n=6
PCB 28	15	4	10	2
PCB 52	18	13	33	1
PCB 101	23	15	38	3
PCB 118	16	9	22	3
PCB 138	28	18	44	4
PCB 153	28	19	44	4
PCB 180	20	16	36	2
Σ6 PCB (excl. 118)	132	85	205	16
total PCB (=5*Σ6 PCB)	660	425	1025	80

Source: Venema, 1991.

Potential transformations in anaerobic sediments may alter the composition of PCBs and therefore sediment cores cannot be used to reconstruct the PCB pollution history of the Rhine, for example. Another option to reconstruct the pollution history of the Rhine is provided by the flood-plain samples collected by IB-DLO (Haren). In flood-plain soils aerobic conditions prevail and PCB composition is influenced only by aerobic degradation or volatilization. These processes are expected to have only a minor impact. Since 1958 soil samples from flood-plains have been collected and stored. These samples were recently analysed (Japenga *et al.*, 1988). Together with a new inventory (CSO, 1992) a fairly complete picture can be obtained (Figure 4.5). From these data a clear decrease in PCB concentrations can be observed since the early 1970s: recent flood-plain samples contain 5 times less PCBs than those of the early 1970s.

Table 4.6. Mean concentrations of PCBs in surface sediments of some major surface waters (µg/kg d.w.).

Congener	Historical levels:		Recent levels:			
	±1972		1986-1989		1986-1989	1984-1991
	Lake Ketelmeer[1] (n=5)		Lake Ketelmeer[2] (n=18)		Lake IJsselmeer[2] (n=28)	Scheldt River[3] (n=38)
28	143		52		6	4
52	119		44		6	7
101	128		39		4	10
138	147		34		7	18
153	131		34		6	15
180	98		21		4	10
ΣPCB	766		224		33	64
total PCB(=5xΣPCB)	3830		1120		165	320
		TEQ		TEQ		
77	3.2	0.0016	1.0	0.0005		
105	140	0.014	10	0.001		
118	135	0.0135	15	0.0015		
126	0.16	0.016	0.02	0.002		
156	46	0.023	2	0.001		
169	0.1	0.001	<0.01	-		
ΣTEQ		0.0691		0.006		

[1] Lake Ketelmeer is a sedimentation area of the Rhine River; data from Beurskens *et al.*, 1993; sediment samples collected in 1972 from top layer, average organic carbon content: 5%.

[2] Data from Winkels *et al.*, 1993; sediment layer deposited between 1986-1989; concentrations normalized to 5% organic carbon content.

[3] Concentration in suspended solids, collected in the period 1984-1991, normalized to 5% organic carbon content; pers. comm. B. van Eck, Tidal Waters Division, Rijkswaterstaat, Middelburg, The Netherlands.

There are major variations in PCB concentrations in sediments from small waterways (so-called 'regionale wateren'), depending on the source of PCB contamination. As an example of a rather uncontaminated sediment, influenced only by atmospheric

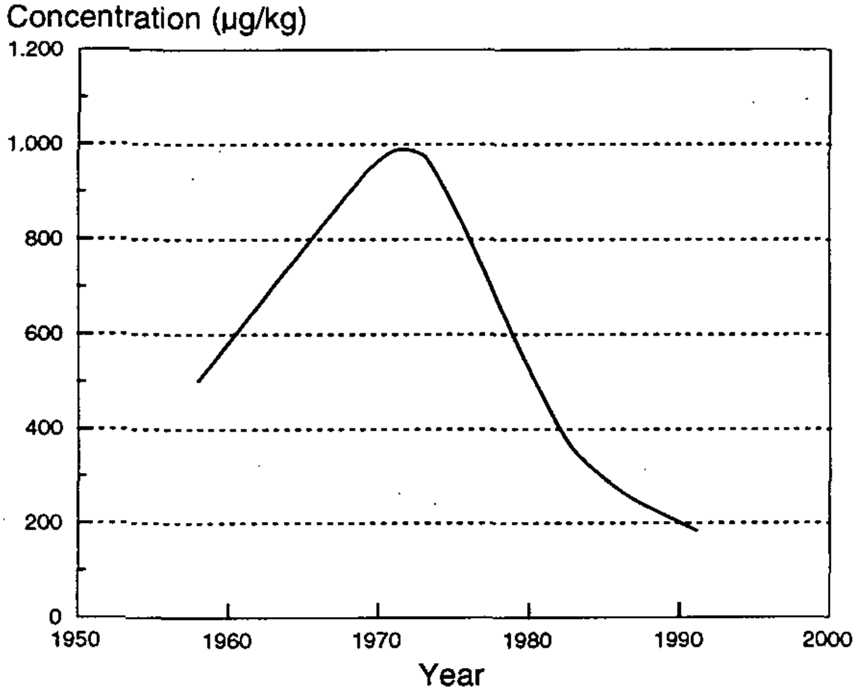


Figure 4.5. Reconstruction of PCB concentrations in flood-plain soils along Rhine/Waal over three decades. The concentrations of the sum of six congeners (28, 52, 101, 138, 153, 180) are shown. Data for 1958, 1970, 1972 and 1982 are from Japenga *et al.*, 1988; multiple samples from 7 locations along the Rhine were used. Values are expressed on a 5.8% organic carbon basis. Data for 1991 are from CSO (CSO, 1992); 74 samples from Waal flood-plains were analysed and expressed on a 5% organic carbon basis.

deposition, the levels in a recently created pond (1989, Het Bil, Friesland) are shown in Table 4.7. Another location, Zandmeer, influenced by IJsselmeer water, has clearly elevated sediment PCB levels. The sediment of a small ditch that received waste water from a former transistor-producing facility is still highly contaminated with PCBs, which can be regarded as an example of an extreme PCB-contaminated site that can still be found in the Netherlands. An overall picture of the present and historical PCB contamination of smaller waterways is difficult to construct. Nevertheless, it is expected that locations that are not in close proximity to a point source (currently or in the past) currently have much lower contamination levels than 10 to 15 years ago. Based on almost 5000 sediment samples from small waterways, the following distribution in sediment classes was obtained regarding PCB contamination: unclassified:5%, class 0: 92%, class 3: 3% (Geenen, 1994).

Table 4.7. PCB concentrations in sediment from small waterways (in μg/kg).

	Het Bil[1] Friesland	Zandmeer[1] Friesland	Maasnielderbeek[2] Limburg
28	1.5	14	15700
52	0.7	9	4600
101	0.5	14	1000
118	0.3	9	1200
138	0.3	20	1700
153	0.5	18	1200
180	0.2	15	370
ΣPCB (excl. PCB 118)	3.7	90	24570
total PCB (=5xΣPCB)	18.5	450	122850

[1] Data from Van Hattum *et al.*, 1992; concentrations on a 5% organic carbon content basis.

[2] Data from Van den Heuvel *et al.*, 1994; organic carbon content 6%.

The total PCB burden in sediments is estimated to be 78,000 kg, calculated as follows:

contaminated sediment in the Netherlands: 150 10^6 m^3
density: 1300 kg m^{-3}
total: 195 10^9 kg contaminated sediment in the Netherlands
mean concentration for sum of 6 congeners: 80 μg/kg (< intervention value: class 2)
thus total PCB concentration: 400 μg/kg
total burden: 78,000 kg PCBs

4.5. Levels in the atmosphere

PCB concentrations in the atmosphere depend on numerous factors, including proximity to local sources, source emission strengths and meteorological variables. Indoor concentrations in homes and offices typically contain several hundred $ng.m^{-3}$ PCB (Atlas 1986; Balfanz *et al.* 1993).
Outdoors, levels over 40 $\mu g.m^{-3}$ have been found over a direct PCB spill (Atlas, 1986). Away from direct sources, concentrations are highest near urban centres, typically in the range of 1 - 10 $ng.m^{-3}$. Concentrations in rural areas range from 0.1

to 0.5 ng.m^{-3} (Atlas *et al.* 1986; Bidleman *et al.* 1987; Halsall *et al.* 1993). The concentration in the Great Lakes area has remained virtually constant for more than ten years, despite a ban on all use of these chemicals in the USA and Canada within this period (Hornbuckle *et al.* 1993). Volatilization (re-emission) from contaminated aquatic and terrestrial systems may act to buffer atmospheric concentrations of PCBs. There are very few measurements of atmospheric PCB levels in the Netherlands. During 1979-1981 PCB levels in Delft were measured 55 times. The average concentration was approximately 0.9 ng.m^{-3}. In 1983 PCB concentrations were measured at three locations (Vlaardingen, de Bilt, Witteveen). More or less identical levels were found, with an average of 0.9 ng.m^{-3} and a maximum of 2.7 ng.m^{-3}.

4.6. Fluxes in the environment

4.6.1. Re-emission from contaminated water and soil to atmosphere

Recent studies have demonstrated that water and soil contaminated with PCBs can be important sources of PCB fluxes to the atmosphere. Historically, the atmosphere has been a source of PCBs entering surface waters and soil by deposition. Decreased production, use and emissions may have reversed the direction of the gas exchange across the air-water and air-soil interface. Relatively highly contaminated sites may have become net sources. This re-emission phenomenon has been demonstrated in studies using artificial ponds in Sweden (Larsson & Södergren, 1987) and in the Great Lakes region in North America (Swackhamer *et al.*, 1988; Baker and Eisenreich, 1990; Achman *et al.*, 1993; Hornbuckle *et al.*, 1994; Jeremiason *et al.*, 1994).

The most frequently used model to assess the transfer of chemicals across the air-water or air-soil interface is the two-film resistance model (Achman *et al.*, 1993). There are two difficulties in estimating the emissions from water and soil to the atmosphere: the uncertainties of the parameter values and the variations in the values due to the differences between individual PCBs and differences in environmental factors. Parameter values used in the various different studies can differ considerably.

Despite these difficulties, a rough estimate of the re-emission has been made using a two-film model as described in the models SOILBOX and WATERBOX (Bakker & Van den Hout, 1993). In view of the differences in volatility between the individual PCBs, these models calculate emissions of for the five homologue groups occurring most frequently in the environment: tri-, tetra-, penta-, hexa- and hepta-PCBs. The results have been summed to give a total PCB emission. Assumptions with regard to the concentrations of the homologue groups in soil and surface water were deduced from data on concentrations in British and Dutch soils (Alcock *et al.*, 1993, Lagas *et al.*, 1994) and concentrations in the Great Lakes (Baker & Eisenreich, 1990). The soil emissions were assessed for two soil types with different properties as far as volatilization is concerned: sand with a low and loam with a high content of organic matter. The results were averaged. The mass transfer coefficients were chosen according to RIVM *et al.* (1994).

To permit the re-emission to be compared with the anthropogenic emissions, a 'gross' flux is calculated. The deposition flux is not taken into account. In the model the concentration in the air is assumed to be zero. The input parameters are given in Appendix 3.

The calculated volatilization rate from surface water is 0.77 $g.ha^{-1}$ per year. This is in the same order of magnitude as the volatilization rates found in the Great Lakes in the U.S.

For soil the calculated volatilization rate is 0.018 $g.ha^{-1}$ per year. Harrad *et al.* (1994) estimated a much higher rate (by a factor 100) of 1.6 $g.ha^{-1}$. This is derived from model calculations by Eduljee (1988). The difference is due mainly to differences in a few important parameters. Eduljee (1988) took much lower K_{oc} values and higher H values, derived from chemical properties for a number of technical PCB mixtures (Mackay *et al.* 1986). The K_{oc} values were calculated based on a general equation for organic chemicals. In this study a specific equation derived from measurements on some individual PCB congeners in PCB-contaminated sediment is used (see Table 2.4). The H values in this study are derived from measurements on individual PCBs as well (see Table 2.4). Furthermore, Harrad *et al.* (1994) based their estimate on a higher PCB concentration in U.K. soils. The parameter values employed in Harrad *et al.* (1994) and Eduljee (1988) were considered to be rough estimates. Although the values of K_{oc} and H used in this study are assumed to be more accurate, other parameters in the model are uncertain and the result should still be considered as a rough estimate.

Volatilization of PCBs from soils and surface waters from temperate latitudes results in long-range transport and ultimately leads to an accumulation of PCBs in polar regions. Further international strategies on PCB reduction may be necessary with regard to this aspect.

4.6.2. Deposition fluxes

Baart *et al.* (1995) calculated the annual averaged total deposition flux over the Netherlands, based on estimated European emissions. Calculations were performed

for three emission scenarios: 1980, 1990 and 2000 (Business As Usual). The volatilization of PCBs from inland surface waters (re-emission) to the atmosphere has been taken into account. Although still a minor source in most of Western Europe, this process is becoming increasingly significant as direct emissions decrease. In the Netherlands, the fraction of the total emission due to re-emission has increased from approx. 1% in 1980 to 60% in 2000.
From 1980 to 2000, deposition will prevail over emission in the Netherlands. However, the difference between the re-emission and deposition flux will tend to level out. Even from 1990 to 2000 this could result in a net emission from inland waters. The results are given in Table 4.8. Over 90% of the deposition on the Netherlands stems from emissions abroad; for the deposition on the North Sea the relative contribution of various countries is given in Table 4.9.

Table 4.8. Calculated deposition fluxes of summed PCBs averaged over the Netherlands [1].

Year	Total deposition ton.y^{-1}	Deposition flux over land g.ha^{-1}.y^{-1}	Deposition flux over water g.ha^{-1}.y^{-1}
1980	1.2	0.3	- 0.5 (= emission)
1990	0.8	0.2	- 0.6 (= emission)
2000	0.4	0.1	- 0.5 (= emission)

[1] Values already corrected for re-emission. Negative values indicate that the re-emission flux is larger than the deposition flux.

4.6.3. PCB loads in the hydrosphere

Total PCB loads entering the Netherlands by way of the major rivers and subsequently entering the North Sea have been calculated onwards from 1988, when PCB analyses of suspended solids began. During the years 1988, 1989 and 1990 a clear downward trend can be observed in the annual PCB load entering the Netherlands via the major rivers (Figure 4.6). The PCB loads in 1991 and 1992 were rather constant and comparable with the levels in 1990. In 1993, however, the PCB load was higher than in 1992; this is due mainly to a substantially higher load of suspended solids in the rivers in 1993. The PCB load entering the North Sea shows the same trend, although the annual load is systematically lower than the load entering the Netherlands, because of sedimentation and volatilization of PCBs from surface waters. The average PCB load entering the Netherlands was 980 kg in the years

Table 4.9. Relative contribution of individual countries to the atmospheric deposition on the North Sea.

	1980	1990	2000
Netherlands	1.3	1.3	2.7
Germany	33.3	33.4	40.1
Belgium/Luxembourg	7.6	9.9	11.7
France	11.3	11.8	12.1
United Kingdom	31.8	31.4	14.4
Denmark	1.8	2.4	3.0
Norway	1.2	1.8	3.9
Sweden	1.4	2.0	3.7
other	10.3	6.0	8.4

1989, 1990 and 1991. The average PCB load entering the North Sea via the three main rivers was 575 kg in these three years. This means that about 400 kg of total PCBs is retained in sediments or volatilized to the atmosphere. Obviously, PCBs emitted to surface waters in the Netherlands that are deposited in the sedimentation areas are not accounted for in this calculation.

An additional PCB load entering the North Sea is caused by disposal of dredged harbour sediments in the North Sea. The total PCB load from dredging Dutch harbours and subsequent disposal in the North Sea is estimated to be 700 kg in 1990 (based on 180 kg given for the sum of 7 congeners in Wulffraat *et al.*, 1993, p.103).

4.6.4. Fluxes influencing the PCB burden in soils

In the past there has been relatively high atmospheric deposition of PCBs on the soil. Such removal processes as volatilization, degradation, downward transport and removal during harvest may reduce the accumulation of PCBs in soil. UK studies have indicated a significant decrease in PCB concentrations in soil over the past 20 years, attributed to volatilization (Harrad *et al.*, 1994). Whether PCB levels have decreased in Dutch top soils is unclear, since measurements are lacking. Based on model calculations, a substantial accumulation in soil is to be expected (removal only by a relatively low degree of volatilization). This calculations depend mainly on the values of partition constants applied in the models. Only additional measurements can clarify this aspect.

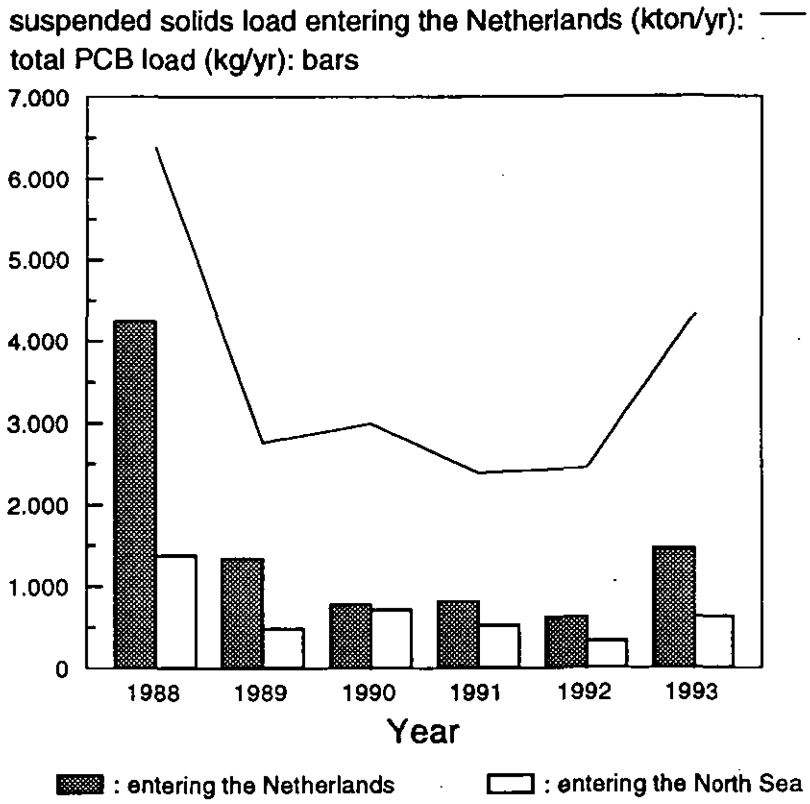


Figure 4.6. Annual PCB load (total PCBs = 5*Σ6 PCBs, in kg) entering the Netherlands via the major rivers (Rhine/Lobith, Meuse/Eijsden and Scheldt/Schaar van Ouden Doel) and annual loads entering the North Sea via the major Dutch river outlets (Maassluis, Haringvlietsluizen and Vrouwezand) (Source: RIZA). The PCB load is determined mainly by the suspended solids load entering the Netherlands via the major rivers, as indicated by the line.

A critical PCB load in soil, based on the target value for PCBs and taking into account slow PCB removal rates from soil, has been determined using two scenarios:

A worst-case scenario:
-peat soil (high binding capacity)
-no volatilization
-only removal by downward transport
The critical load to soil is: 0.26 $mg.ha^{-1}.yr^{-1}$

A less conservative scenario:
-sandy soil
-including volatilization as a removal process
The critical load to soil is: 4.2 $mg.ha^{-1}.yr^{-1}$

These calculations indicate that the actual atmospheric deposition, 200 $mg.ha^{-1}.yr^{-1}$ in 1990 (see Table 4.8), exceeds the critical load by a factor of 50 to 800. Consequently, accumulation of PCBs in soil is to be expected. The environmental significance of atmospheric deposition exceeding the critical load can be illustrated by estimating the accumulation rate of PCBs in soil and relating it to the quality standards and the actually observed concentrations:

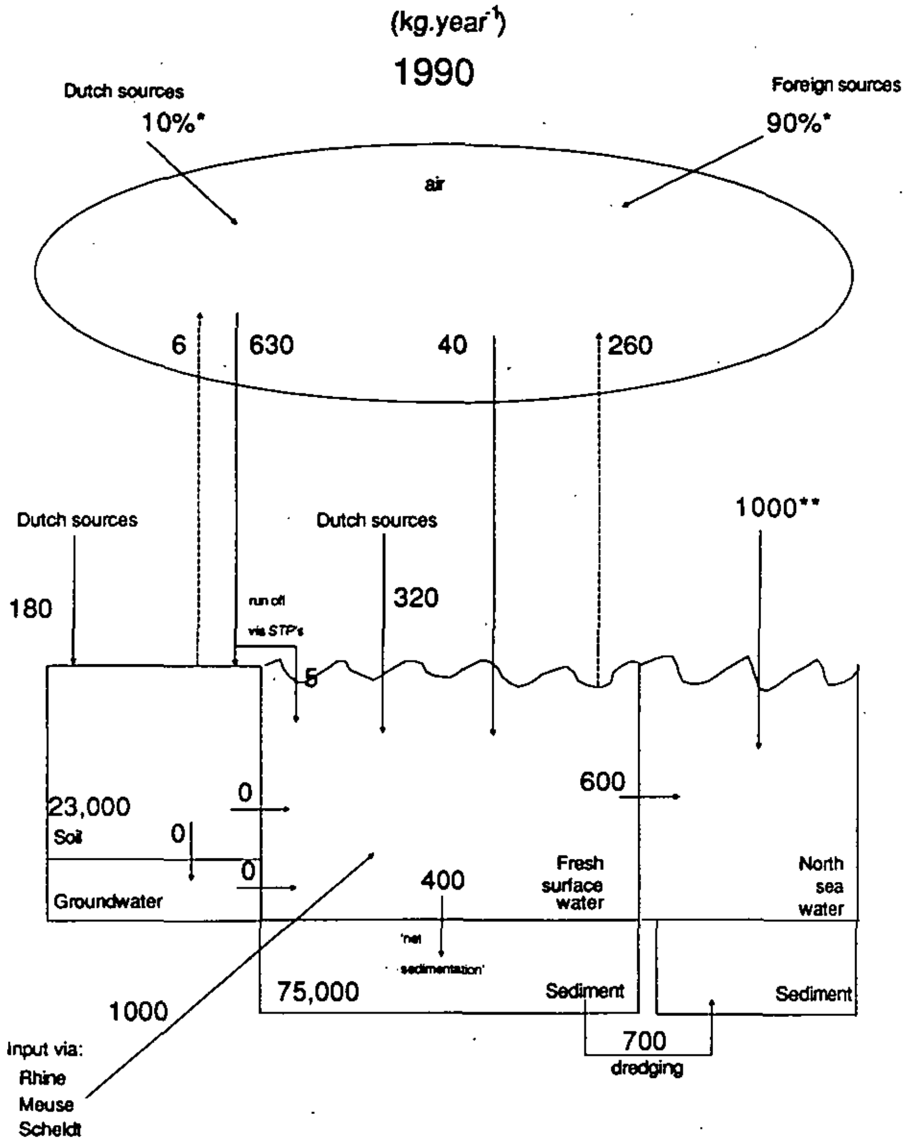
in 1990: 200 mg/ha.yr (Table 4.7) net deposition of total PCBs
for Σ6 PCBs: 200/5 = 40 mg/ha.yr
1 ha: 0.1 metre homogenized soil top layer: volume: 1000 m^3
dry soil bulk density: 1400 kg/m^3
in 1 ha: 1,400,000 kg dry soil
thus the 1990 atmospheric deposition leads to: 40/1,400,000 = 0.0286 μg Σ6 PCBs/kg dry soil per yr.
target value Σ6 PCBs = 20 μg/kg

Assuming volatilization as the only relevant PCB removal process in soil, and absence of downward transport, the target value will be reached in a 700-year period if the PCB input remains constant with time and equals to the 1990 value.
It is highly likely that in the last 20 years atmospheric deposition was higher than the 1990 value assumed for the aforementioned estimate. Nevertheless, on the basis of the estimate one may expect that present PCB levels in soil will not exceed the target value. The recent soil inventory described in Paragraph 4.3.1 indeed shows that the mean concentration in soil is 2.45 μg/kg (Σ6 PCBs; see Table 4.4), clearly below the target value of 20 μg/kg. Moreover, taking into account the decrease in atmospheric deposition in the future (Table 4.8), it is highly likely that the average PCB content in Dutch soils will remain below the target value in the next 1000 years.

4.7. Summary and conclusions

The PCB burdens in the various environmental compartments and the exchange fluxes for 1990 are summarized in Figure 4.7. The bulk of the Dutch environmental burden of PCBs is associated with sediments (78 tonnes) and soils (23 tonnes). Transboundary transport of PCBs with the major rivers and atmospheric deposition are currently the main input sources of PCBs into the Netherlands.
The total amount of PCBs in the Dutch environment can be subdivided into two fractions:

1. A cycling fraction in top layers of soils, water, top layers of sediments and



* contribution (in %) to the deposition on the Netherlands

** total deposition on the North sea. The contribution from Dutch sources is approximately 1%.

Figure 4.7. PCB fluxes in 1990 (in kg/year).

the atmosphere, in which soil appears to be a major sink for PCBs. In *soils and surface waters a small fraction of the lower-chlorinated* biphenyls (less than 4 chlorines) may be eliminated due to biodegradation. In addition, as early as in 1980 volatilization from surface waters to the atmosphere began to exceed deposition.

2. A trapped fraction in deeper soil and sediment layers and in landfills. This fraction does not readily participate in the exchange processes between environmental compartments. Polychlorinated biphenyls trapped in sediments are subject to significant microbial reductive dechlorination, which reduces the dioxin-like toxicity and bioaccumulation potential of PCBs.

A reconstruction of the Rhine PCB pollution history (flood-plain samples) showed a continuous decrease in PCB concentrations during the 1970s and 1980s. This concurred with restrictions on their manufacture and use. However, since the early 1990s PCB concentrations have been found to level off. A similar PCB contamination pattern was observed in suspended solids from coastal waters during the period 1989-1993.

It is stressed that present PCB levels in the major rivers still exceed the limit value ('grenswaarde') by a factor of 2 to 5. High levels are found particularly in the major sedimentation areas in the Netherlands.

In contrast to the aquatic environment, where current PCB concentrations clearly exceed contemporary quality objectives, PCB concentrations in soil are presently below the target value ('streefwaarde').

5. PROJECTION OF PCB FLUXES IN THE FUTURE

5.1. No additional policy measures

In this paragraph the consequences for PCB fluxes in the Netherlands are evaluated for the case that no additional policy measures are taken. Figure 5.1 shows the result.

In calculating the flux for the year 2000 a scenario was constructed that comprised the following items:

Air

Replacement of PCBs in closed application will continue. If no additional measures are taken, the rate of this replacement is determined by the life time of the existing equipment. Based on historical data, it is assumed that 75% of the equipment still in use in the year 1990 will be replaced. Consequently, emissions from leakage and spillage will decrease by 75%.

In Chapter 3 it was shown that in several industrial processes (e.g. sintering, incineration) PCBs are formed unintentionally. Besides PCBs dioxins may also be released from these processes. From a physico-chemical point of view, dioxins and PCBs have strong similarities. Since there is already a strong (inter)national policy to abate dioxin emissions, it is expected that the PCB emissions from these processes will concurrently decrease: in 2000 by approximately 30% of contemporary levels (Bremmer *et al.*, 1995). Table 5.1 shows the consequences of these assumptions.

Table 5.1 further indicates that volatilization will possibly become the most important emission route of PCBs to air in 2000. It also shows that processes where PCBs are formed unintentionally are becoming very important emission sources.

It is assumed that the atmospheric emissions from other European countries will decrease by the same order of magnitude as Dutch emissions (about 50-60%). The projected emissions in European countries are given in Appendix 2.

The deposition is calculated based on the air emissions in 2000 (and re-emission data).

Surface water

The assumption is that the amount of PCBs entering the Netherlands via the major rivers will decrease by 40% by 2000 compared to 1990. This is in accordance with international agreements (Rhine and North Sea Action Programme), which include an emission reduction agreement of 50% in 1995 compared to 1985. It is assumed that

Table 5.1. Emissions to air (kg.y^{-1}) in 1980, 1990 and 2000, compared to volatilization.

Source	1980	1990	2000
Open applications	0 - 5600	0	0
Spills/leaks	450	150	40
Processes where PCBs may be formed	100	100	70
Total	550 - 6200	250	110
Volatilization	260	260	260

in 1990 part of this pledge agreement had already been fulfilled.
For the Dutch sources, owing to the continuing replacement of PCBs
an emission reduction of about 70% has been used in the scenario calculations.

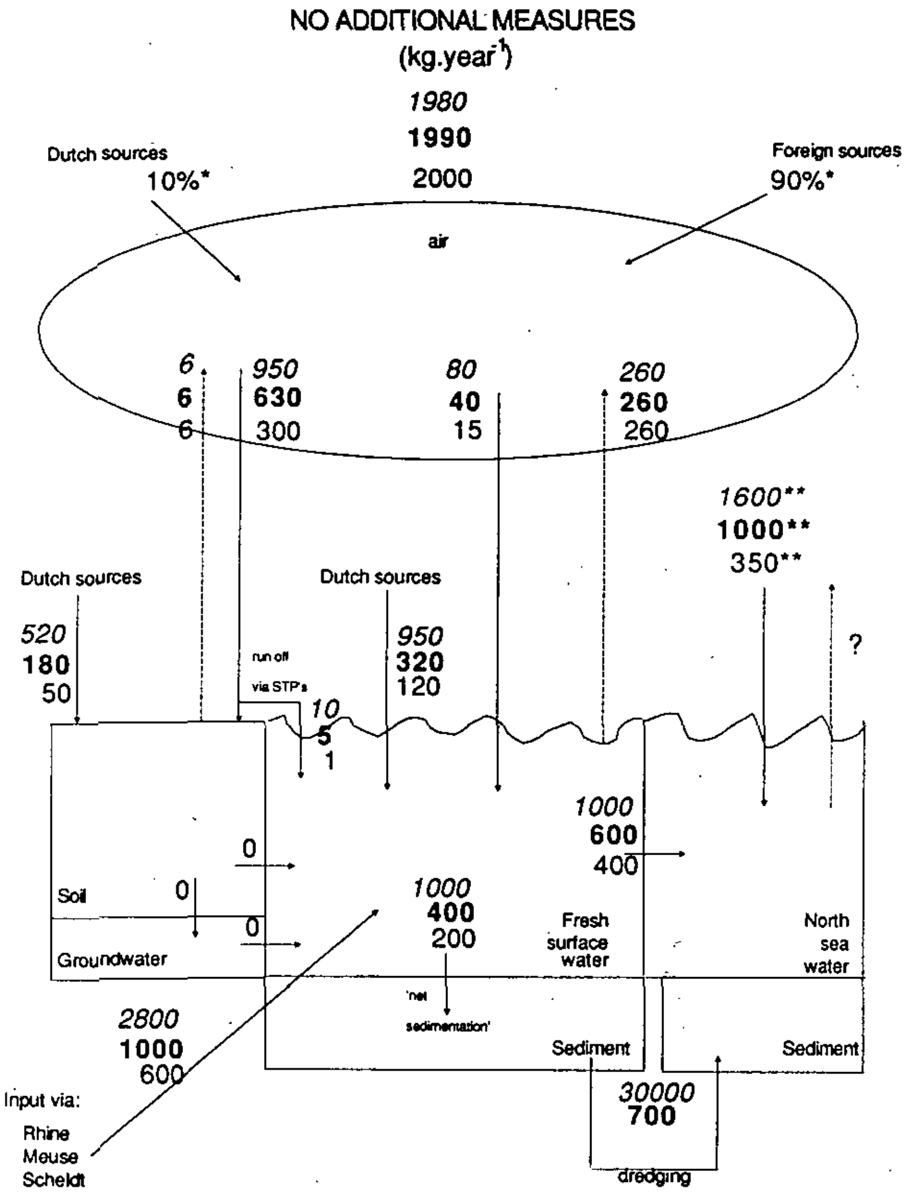
Soil

In the scenario an emission reduction of about 70% is assumed, owing to the continuing replacement of PCB-containing equipment. The use of sewage sludge as a fertilizer on agricultural soil will stop due to the so-called BOOM policy regulation (Decree on quality and use of other organic fertilizers).

Results

The total surface water load in 2000 is estimated to be approximately 50% lower than in 1990. This decrease is due mainly to emission reductions in foreign countries, resulting in a lower input via the major rivers. A lower input to surface water leads to less PCB sedimentation and a lower PCB input to the North Sea. Assuming a constant suspended matter content, our analysis indicates an approximately 50% lower PCB concentration (by a factor 2) in suspended matter in 2000. In Chapter 4 it was shown that PCB congeners still exceed the limit values in suspended solids by a factor of 2 to 5. Thus, without additional measures it seems that a decrease within this range is possible.

In this scenario, the total load to soil will decrease from 1500 kg in 1980 and 800 kg in 1990 to 350 kg in the year 2000. This reduction can be attributed almost entirely to decreasing PCB deposition, which is dominated by foreign emission sources. In our flux an accumulation of PCBs in soil may still occur in 2000. However, it should be emphasized that the re-emission figure, especially, is highly uncertain (see also Chapters 2 and 4).



* contribution (in %) to the deposition on the Netherlands

** total deposition on the North sea. The contribution from Dutch sources is approximately 1%.

Figure 5.1. Fluxes of total-PCBs in 1980, 1990 and 2000 (no additional measures).

5.2. Additional measures

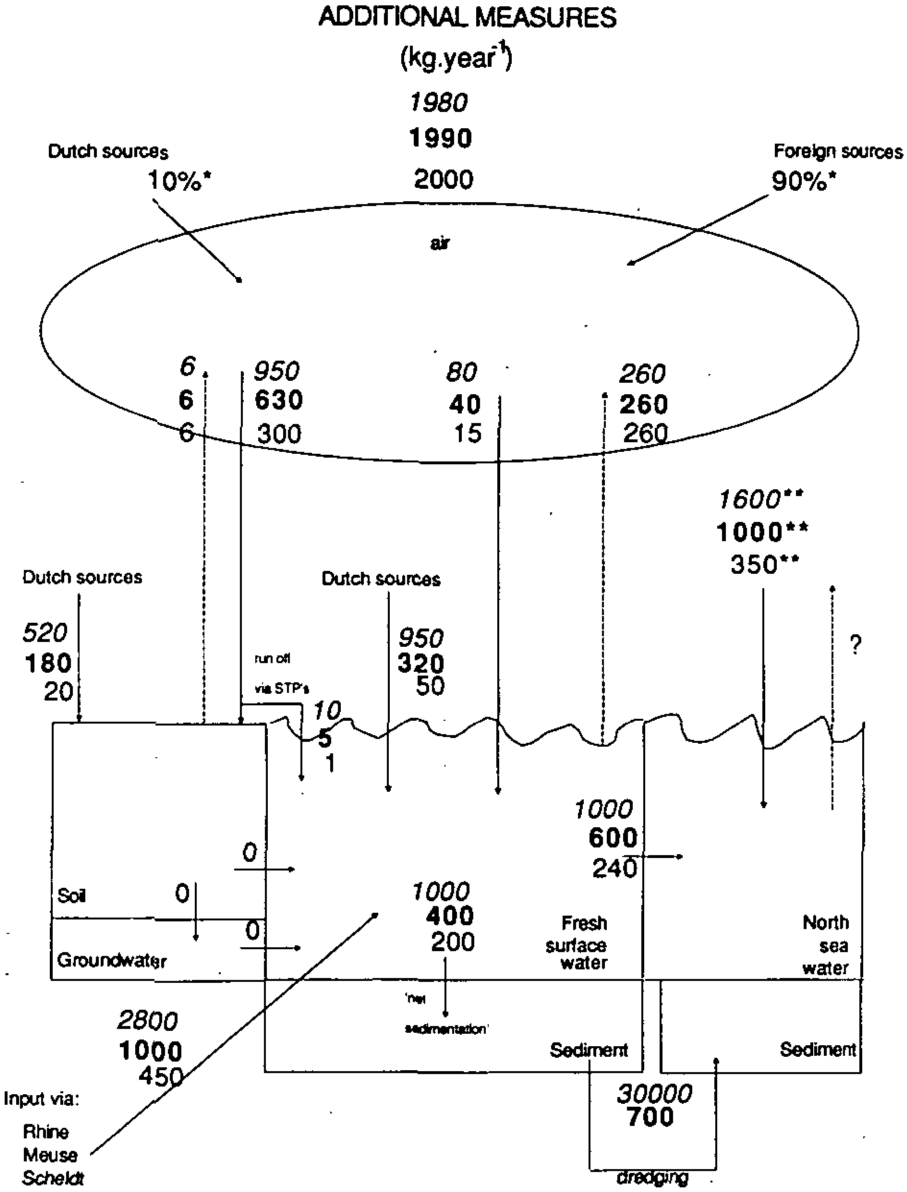
In this paragraph the consequences for the PCB flux in the Netherlands are evaluated for the case that additional policy measures are taken in the Netherlands. Figure 5.2 shows the results.

In calculating this 'additionally reduced' flux, we have taken the following possible measures into account:

- Enhanced replacement of PCB-containing equipment. We assume a further emission reduction to air, surface water and soil of 50% compared to the emission levels in 2000 without additional measures;
- Dredging upstream hot spots. The PCB concentrations in the suspended solids of the rivers Rhine and Maas still exceed the quality objectives, and it does not appear that the Rhine Action Programme PCB reduction target will be met in 2000. Present PCB contamination of these rivers is attributed mainly to diffuse emission sources, which are difficult to reduce by additional policy development.

  The possible diffuse sources are currently unknown. PCB hot spots in upstream sediments may contribute to this 'diffuse' PCB pollution. These hot spots may be the result of emissions in the past to the Rhine or its tributaries. Owing to erosion from these areas, PCBs can be transported downstream to the Netherlands.

  The significance of this hypothesis has been tested by a calculation (see Appendix 3). This calculation shows that if upstream a hot spot exists with the assumed erosion rate and magnitude, dredging of this hot spot will reduce PCB input to the Netherlands by about 20%.
- Dredging the major downstream sedimentation areas. Contaminated sediments may pose a risk either through exposure of aquatic biota to high levels of contaminants or by vertical (groundwater) or horizontal (downstream) transport of contaminants. In the major sedimentation areas in the Netherlands, where undisturbed sedimentation occurs, the sediment top layers are less contaminated than the deeper sediment layers deposited in the past. This is the result of a substantial decrease of PCB concentrations in the major rivers over the past 20 years. Vertical transport (with infiltrating water) is the only relevant transport direction in this situation. Taking into account the immobile character of PCBs, vertical transport is unlikely to occur. This means that a major fraction of the total PCB burden in sediments is trapped. Exposure of aquatic biota is probably restricted to sediment-dwelling organisms such as eels. To what extent these organisms really reach the deeper, highly contaminated sediment layers is unknown. Consequently, sediment dredging at locations where high PCB concentrations are trapped in the



* contribution (in %) to the deposition on the Netherlands

** total deposition on the North sea. The contribution from Dutch sources is approximately 1%.

Figure 5.2. Fluxes of total-PCBs in 1980, 1990 and 2000 (additional measures).

deeper layers (>10 cm below sediment surface) appears to have only a limited impact, because in this case exposure and transport are limited.
If sedimentation is disturbed and the sediment layers from the 1960s and 1970s are still the top layers, exposure and horizontal transport may occur and pose acute risks. This situation is found in small areas in the Ketelmeer and Hollands Diep lakes, but these areas do not generally exceed 10% of the total sediment surface area. At these locations, with high levels in the top layers, dredging will significantly reduce the risks associated with PCB presence in sediments. We assume that dredging of the major sedimentation areas would result in a 20% lower PCB input to the North Sea.

Results

Compared to the flux in the year 2000 in Figure 5.1 (no additional measures), enhanced replacement of PCB-containing equipment in the Netherlands is not very effective. The loads in soil and surface water, sediment and the North Sea change slightly. The dredging measures seem more effective: a 40% lower output to sea will occur compared to the 'no additional measure scenario'. It should be stressed that the *figures are merely indicative*.
Assuming a constant suspended matter content, the 'additional-measure scenario' indicates an approximately 60% lower PCB concentration (concentrations decreasing by a factor 2.5) in suspended matter in 2000. The difference with the 'no additional measure scenario' is too small to conclude with any certainty whether the selected additional measures are really required to meet the target values.

5.3. Summary and conclusions

A 'no additional measure scenario' for PCBs will lead to significantly lower loads of PCBs in surface waters and soil in the Netherlands. The decrease in PCB fluxes is due mainly to the assumed PCB emission reductions in foreign countries, resulting in both lower deposition and lower input via the major rivers. The 'additional measure scenario' indicates that new measures to curb national sources will have hardly any impact on future PCB fluxes. A further reduction of PCB loads can be reached by intensifying restrictive measures on air and water emissions in foreign countries and, probably, by dredging upstream hot spots.

6. GENERAL CONCLUSIONS AND RECOMMENDATIONS

The restrictive measures for the manufacture and use of PCBs have had a significant impact on the emissions of PCBs in the Netherlands. Emissions to air have declined from 560-6100 kg/y in 1980 to 250 kg/y in 1990. Emissions of PCBs to water and soil have decreased by 50% since 1980. At present, transboundary transport of PCBs via the major rivers and atmospheric deposition are the most important input sources of PCBs in the Netherlands. The PCB output from Dutch surface waters to the North Sea is directly related to this influx via the Rhine, Maas and Scheldt. With respect to air, it is emphasized that the relative importance of 'spills and leaks' and the unintentional production of PCBs (e.g. steel production and coal incineration) has increased.

PCB concentrations in the aquatic environment initially reflected the trend in emissions: levels in sediments decreased significantly in the period 1970-1990. However, since 1990 this decrease has been found to level off for the major Dutch surface waters; concentrations even appear to stabilize above the limit value ('grenswaarde') for the individual PCBs in suspended solids. In marine suspended solids, too, PCB levels remained constant during the period 1989-1993. For soils it is much more difficult to obtain an accurate idea of the historical changes, since data for before 1990 are scarce. Nevertheless, the available data for soil indicate that current levels are lower than the target value ('streefwaarde').

Owing to high emissions in the past and the relative persistence of PCBs, their current total burdens in Dutch soil and sediment are estimated to be still 75,000 and 25,000 kg, respectively.
The total quantity of PCBs in the Netherlands can be subdivided into two fractions:
1) a cycling fraction in the top layers of soils and sediments, water and atmosphere, with the soil appearing to be a sink for PCBs. In soil and surface waters a small fraction of the lower-chlorinated biphenyls may be eliminated due to biodegradation. In surface waters volatilization was shown to be another influential elimination process for PCBs: today, it exceeds deposition.
2) a trapped fraction in deeper soil and sediment layers and in landfills. This fraction does not readily participate in the exchange processes between the environmental compartments. In sediments this fraction is subject to significant microbial reductive dechlorination, which reduces both the toxicity and bioaccumulation potential of PCBs.

The role of soil as a PCB sink is still uncertain, owing to a lack of knowledge on removal processes. Assuming low removal factors, current deposition exceeds the 'critical load' for Dutch soils by a factor of 40-800. However, taking into account the expected decrease in atmospheric PCB deposition in the future, the average PCB levels in Dutch soils will remain below the target value for - at least - the next 1000 years.

Without additional restrictive measures, all environmental PCB fluxes will continue to decrease in the Netherlands (see Figure 5.1). This prognosis is based on an autonomous, further reduction of foreign PCB emissions, resulting in lower deposition and lower input via the major rivers.
An accelerated decrease can be achieved by taking additional measures in other countries to reduce PCB emissions to air and water. With respect to air, special attention should be paid to the unintentional production of PCBs. For the aquatic environment, it is recommended to trace the most important upstream PCB pollution sources to rivers, so that adequate measures may be taken. If major PCB-contaminated upstream sediments ('hot spots') exist, dredging of these areas can be another effective step to reduce the PCB input to the Netherlands. A further intensification of the collection of fluorescent lighting fittings and large capacitors on a national scale will hardly affect future PCB fluxes. These sources make only a minor contribution to overall PCB fluxes in the Netherlands.

With or without additional restrictive measures, the general trend is a further reduction of PCB levels in the Dutch environment. It should be emphasized, however, that this does not answer the question of whether current (and future) PCB levels still pose any threat to man and the environment. For such a risk evaluation, an in-depth comparison of exposure and effect data must be made. This crucial aspect was beyond the scope of this document, but will certainly be investigated in a subsequent study. This research will probably be initiated after the revision of the environmental quality objectives (target and limit values) for PCBs in the Netherlands (in 1996). In the present study the congener-specific approach (see Chapter 1) could hardly be pursued, owing to a lack of specific data. It is recommended that future PCB measurements should also include non-ortho and mono-ortho congeners.

This document comprises the most recent data on actual PCB fluxes in the Netherlands. However, various uncertainties remain in our knowledge of PCB presence and behaviour in the environment. Deposition and volatilization were shown to be important routes in the total PCB flux scheme. It should be realized, however, that the figures for these two processes are based solely on model calculations. It is advisable to carry out a specific set of measurements so that these calculations can be validated.

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APPENDICES

Appendix 1. PCB composition of commercial mixtures and in soil samples with regard to the 6 traditionally measured congeners.

	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Σ6 PCBs	Σ6 PCBs
de Voogt, 1990 in wt.%							assuming <2 = 0	assuming <2 = 1
Aroclor 1242	13.3	4.1	<2	<2	<2	<2	17.4%	21.4%*
Aroclor 1254	<2	<2	7.0	4.2	3.3	<2	14.5%	17.5%*
Aroclor 1260	<2	<2	5.0	5.0	8.2	7.2	25.4%	27.4%*
Clophen A30	9.9	3.1	<2	<2	<2	<2	13.0%	17.0%*
Clophen A40	4.0	7.3	2.3	<2	<2	<2	13.6%	16.6%*
Clophen A50	<2	6.8	6.1	6.0	3.2	<2	22.1%	24.1%*
Clophen A60	<2	5.0	4.1	11.3	8.6	8.9	37.9%	38.9%*
Quensen, 1990 in mol%								
Aroclor 1242	7.4	3.8	1	0	0.05	0	12.3%	12.3%
Aroclor 1254	0.15	6.1	6.9	5.5	5.8	0	24.5%	24.5%
Aroclor 1260	0.1	0.25	1.75	7.25	9.6	9.3	28.3%	28.3%
Alcock, 1993 in wt.%								
soil samples	4.5	2.3	3.5	4.3	3.7	8.1	26.1%	26.1%
average							21%	23%

APPENDIX 2 EMISSIONS TO AIR IN EUROPEAN COUNTRIES

Table 1 PCB emissions into the air in European countries in 1980 assuming no use of open applications in OECD-countries

		PCB emission (kg/year)											
Country	Total	Open uses	Leaks/spills electrical equipment			Stationary combustion		Primary iron & steel		Land-fills	MWIs	Re-emission	
			trans-form.	large cap.	small cap.	large comb. plants	resid. comb.	cokes	sinter			soil	water
Albania	379	245	1	21	3	0	0	0	0	0,0	0,1	5	104
Austria	1408	0	56	1044	175	10	7	6	9	0,1	1,1	15	86
Belgium	6476	0	360	4000	2000	25	10	20	27	0,1	6,8	5	22
Bulgaria	1867	1513	8	141	24	104	24	4	3	0,0	0,3	20	28
Czechoslovakia	16921	14000	95	1680	840	154	58	38	25	0,1	0,5	23	8
Denmark	1303	0	1	800	400	34	3	0	0	0,0	4,5	7	54
Finland	5402	0	15	2400	480	11	4	2	6	0,1	0,2	54	2430
France	31173	0	3900	13440	13440	39	45	26	48	0,4	30,2	97	108
Germany	70752	16785	1876	33406	16235	1234	259	149	143	0,8	32,4	62	569
Greece	378	0	2	51	26	183	6	0	0	0,2	0,0	23	88
Hungary	2945	2547	11	213	36	41	20	2	4	0,1	1,1	16	53
Ireland	194	0	1	40	20	7	6	0	0	0,0	0,0	12	107
Italy	8652	0	720	4800	2400	46	14	23	31	0,6	10,1	52	555
Luxembourg	116	0	4	77	13	0	1	0	11	0,0	0,5	1	9
Netherlands	794	0	36	229	179	30	0	19	23	0,2	9,7	6	263
Norway	1801	0	2	320	160	2	1	0	0	0,0	1,6	54	1260
Poland	7099	5255	25	458	77	425	93	61	22	0,1	1,3	54	629
Portugal	701	0	23	407	204	12	3	1	1	0,1	0,0	16	34
Romania	4289	3192	15	270	45	128	13	16	17	0,1	0,8	41	551
Spain	11021	0	972	6240	3120	144	16	12	14	0,3	2,9	88	412
Sweden	5513	0	12	1600	800	4	3	4	7	0,0	5,4	73	3006
Switzerland	2279	0	225	1120	800	0	2	0	0	0,0	7,9	7	117
United Kingdom	15295	0	180	8000	6400	301	50	30	32	1,2	8,6	43	249
USSR	159393	134747	607	11290	1889	579	541	229	219	0,9	3,1	3027	6260
Yugoslavia	8287	7241	28	517	87	268	22	8	6	0,1	0,8	45	63
Total	364439	185526	9173	92565	49852	3780	1200	650	648	6	130	3846	17063

Table 2 PCB emissions into the air in European countries in 1980 assuming the use of open applications in the OECD-countries

	PCB emission (kg/year)												
Country	Total	Open uses	Leaks/spills electrical equipment			Stationary combustion		Primary iron & steel		Land-fills	MWIs	Re-emission	
			trans-form,	large cap.	small cap.	large comb. plants	resid. comb.	cokes	sinter			soil	water
Albania	379	245	1	21	3	0	0	0	0	0,0	0,1	5	104
Austria	3849	2441	56	1044	175	10	7	6	9	0,1	1,1	15	86
Belgium	10345	3869	360	4000	2000	25	10	20	27	0,1	6,8	5	22
Bulgaria	1867	1513	8	141	24	104	24	4	3	0,0	0,3	20	28
Czechoslovakia	16921	14000	95	1680	840	154	58	38	25	0,1	0,5	23	8
Denmark	*3480*	*2177*	1	*800*	*400*	34	3	*0*	*0*	*0,0*	4,5	7	54
Finland	6967	1565	15	2400	480	11	4	2	6	0,1	0,2	54	2430
France	101132	69959	3900	13440	13440	39	45	26	48	0,4	30,2	97	108
Germany	169869	115903	1876	33406	16235	1234	259	149	143	0,8	32,4	62	569
Greece	1743	1365	2	51	26	183	6	0	0	0,2	0,0	23	88
Hungary	2945	2547	11	213	36	41	20	2	4	0,1	1,1	16	53
Ireland	750	556	1	40	20	7	6	0	0	0,0	0,0	12	107
Italy	54990	46337	720	4800	2400	46	14	23	31	0,6	10,1	52	555
Luxembourg	292	176	4	77	13	0	1	0	11	0,0	0,5	1	9
Netherlands	6400	5606	36	229	179	30	0	19	23	0,2	9,7	6	263
Norway	3506	1705	2	320	160	2	1	0	0	0,0	1,6	54	1260
Poland	7099	5255	25	458	77	425	93	61	22	0,1	1,3	54	629
Portugal	1452	751	23	407	204	12	3	1	1	0,1	0,0	16	34
Romania	4289	3192	15	270	45	128	13	16	17	0,1	0,8	41	551
Spain	32795	21775	972	6240	3120	144	16	12	14	0,3	2,9	88	412
Sweden	9393	3880	12	1600	800	4	3	4	7	0,0	5,4	73	3006
Switzerland	5850	3571	225	1120	800	0	2	0	0	0,0	7,9	7	117
United Kingdom	64445	49150	180	8000	6400	301	50	30	32	1,2	8,6	43	249
USSR	159393	134747	607	11290	1889	579	541	229	219	0,9	3,1	3027	6260
Yugoslavia	8287	7241	28	517	87	268	22	8	6	0,1	0,8	45	63
Total	678439	499526	9173	92565	49852	3780	1200	650	648	6	130	3846	17063

Table 3 PCB emissions into the air in European countries in 1990

	PCB emission (kg/year)											
Country	Total	Leaks/spills electrical equipment			Stationary combustion		Primary iron & steel		Land-fills	MWIs	Re-emission	
		trans-form.	large cap.	small cap.	large comb. plants	resid. comb.	cokes	sinter			soil	water
Albania	134	1	21	3	0	0	0	0	0,0	0,1	5	104
Austria	1408	56	1044	175	10	7	6	9	0,1	1,1	15	86
Belgium	5216	360	4000	740	25	10	20	27	0,1	6,8	5	22
Bulgaria	355	8	141	24	104	24	4	3	0,0	0,3	20	28
Czechoslovakia	2921	95	1680	840	154	58	38	25	0,1	0,5	23	8
Denmark	1051	1	800	148	34	3	0	0	0,0	4,5	7	54
Finland	5100	15	2400	178	11	4	2	6	0,1	0,2	54	2430
France	19871	3081	11424	4973	39	45	26	48	0,4	30,2	97	108
Germany	43548	1858	33086	6155	1234	259	149	143	0,8	32,4	62	569
Greece	362	2	51	9	183	6	0	0	0,2	0,0	23	88
Hungary	398	11	213	36	41	20	2	4	0,1	1,1	16	53
Ireland	182	1	40	7	7	6	0	0	0,0	0,0	12	107
Italy	6423	626	4176	888	46	14	23	31	0,6	10,1	52	555
Luxembourg	116	4	77	13	0	1	0	11	0,0	0,5	1	9
Netherlands	498	5	59	83	30	0	19	23	0,2	9,7	6	263
Norway	1700	2	320	59	2	1	0	0	0,0	1,6	54	1260
Poland	1844	25	458	77	425	93	61	22	0,2	1,3	54	629
Portugal	572	23	407	75	12	3	1	1	0,1	0,0	16	34
Romania	1097	15	270	45	128	13	16	17	0,1	0,8	41	551
Spain	9024	1128	6053	1154	144	16	12	14	0,4	2,9	88	412
Sweden	5009	12	1600	296	4	3	4	7	0,0	5,4	73	3006
Switzerland	1775	225	1120	296	0	2	0	0	0,1	7,9	7	117
United Kingdom	9222	139	6000	2368	301	50	30	32	1,2	8,6	43	249
USSR	24646	607	11290	1889	579	541	229	219	1,0	3,1	3027	6260
Yugoslavia	1045	28	517	87	268	22	8	6	0,1	0,8	45	63
Total	143517	8326	87248	20619	3780	1200	650	648	6	130	3846	17063

Table 4 PCB emissions into the air in European countries in 2000

	PCB emission (kg/year)										
Country	Total	Leaks/spills electrical equipment		Stationary combustion		Primary iron & steel		Land-fills	MWIs	Re-emission	
		trans-form.	large cap.	large comb. plants	res. comb	cokes	sinter			soil	water
Albania	120	1	10	0	0	0	0	0,0	0,1	5	104
Austria	665	30	501	10	7	6	9	0,1	1,1	15	86
Belgium	2230	194	1920	25	10	20	27	0,1	6,8	5	22
Bulgaria	255	4	68	104	24	4	3	0,0	0,3	20	28
Czechoslovakia	1165	51	806	154	58	38	25	0,1	0,5	23	8
Denmark	486	0	384	34	3	0	0	0,0	4,5	7	54
Finland	3667	8	1152	11	4	2	6	0,1	0,2	54	2430
France	7351	1017	5940	39	45	26	48	0,4	30,2	97	108
Germany	19227	896	15881	1234	259	149	143	0,8	32,4	62	569
Greece	325	1	25	183	6	0	0	0,2	0,0	23	88
Hungary	245	6	102	41	20	2	4	0,1	1,1	16	53
Ireland	153	1	19	7	6	0	0	0,0	0,0	12	107
Italy	2068	251	1086	46	14	23	31	0,6	10,1	52	555
Luxembourg	61	2	37	0	1	0	11	0,0	0,5	1	9
Netherlands	382	3	28	30	0	19	23	0,2	9,7	6	263
Norway	1473	1	154	2	1	0	0	0,0	1,6	54	1260
Poland	1518	13	220	425	93	61	22	0,2	1,3	54	629
Portugal	274	12	196	12	3	1	1	0,1	0,0	16	34
Romania	905	8	130	128	13	16	17	0,1	0,8	41	551
Spain	3745	575	2482	144	16	12	14	0,4	2,9	88	412
Sweden	3876	6	768	4	3	4	7	0,0	5,4	73	3006
Switzerland	793	122	538	0	2	0	0	0,1	7,9	7	117
United Kingdom	1455	19	720	301	50	30	32	1,2	8,6	43	249
USSR	16606	328	5419	579	541	229	219	1,0	3,1	3027	6260
Yugoslavia	676	15	248	268	22	8	6	0,1	0,8	45	63
Total	69723	3565	38834	3780	1200	650	648	6	130	3846	17065

Appendix 3 Input parameters in the re-emission calculation

Homologue group	**tri**	**tetra**	**penta**	**hexa**	**hepta**
Soil conc. (μg.kg^{-1})	1	2	2	2.5	0.5
Water conc. (μg.m^{-3})	0.2	0.2	0.2	0.2	0.2
Partition coeff. K_{oc}	$2.0*10^6$	$3.6*10^6$	$4.0*10^7$	$1.3*10^8$	$6.0*10^8$
Henry's law constant	0.004	0.004	0.002	0.001	0.0005
Soil properties		sand		peat	
Bulk density (kg.m^{-3})		1500		450	
Porosity (%)		40		75	
Water content (%)		20		60	
Organic matter cont. (%)		1		45	
Mass transfer coefficients					
air-side of air-water interface			$1.39*10^{-3}$		
water-side of air-water interface			$1.39*10^{-5}$		
air-side of air-soil interface			$1.39*10^{-3}$		
soil-air-side of air-soil interface			$5.56*10^{-6}$		
soil-water-side of air-soil interface			$5.56*10^{-10}$		