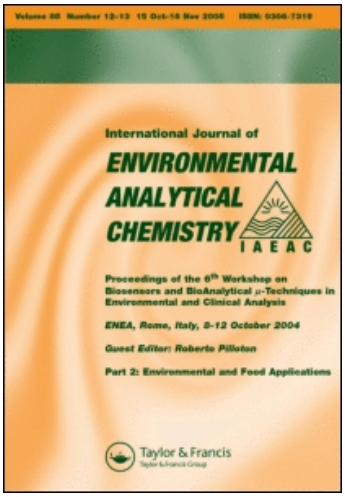

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High Resolution PCB Analysis of Kanechlor, Phenoclor and Sovol Mixtures Using Multidimensional Gas Chromatography

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HIGH RESOLUTION PCB ANALYSIS OF KANECHLOR, PHENOCLOR AND SOVOL MIXTURES USING MULTIDIMENSIONAL GAS CHROMATOGRAPHY

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Kanechlor-300, -400, -500 and -600, Phenoclor DP-3, -4, -5 and -6 and Sovol mixtures were analyzed for their chlorobiphenyl (CB) composition using high-resolution one-dimensional and multidimensional gas chromatography-electron capture detection (MDGC-ECD) techniques. The congener patterns of tested Kanechlor and Phenoclor mixtures resembled Aroclor 1016, 1242, 1254 and 1260. However, differences in the percentage contribution of minor constituents were noticed among these mixtures, which could be due to variations in the boiling-point fractionation of these commercial products. CB pattern of Sovol was different from the rest of the mixtures tested. It showed a composition in between ca. 30%, 40%, 50% and 60% overall chlorine levels. MDGC-ECD study showed the presence of hitherto unnoticed non-CB compounds coeluting with CBs in some commercial PCBs. The use of these mixtures as quantitation standards should be considered with caution. CB patterns of Sovol and a water extract of the Gulf of Finland matched closely, indicating a point source contamination to these waters.

KEY WORDS: Kanechlor, Phenoclor, Sovol, polychlorinated biphenyls, multidimensional gas chromatography-electron capture detection (MDGC-ECD), composition of commercial PCBs.

INTRODUCTION

Polychlorinated biphenyls (PCBs) have been widely used in completely closed systems such as capacitors and transformers, in nominally closed systems such as hydraulic and heat transfer exchange systems and in open-ended applications e.g., as plasticizers, paints, inks, adhesives, pesticide extenders and microencapsulation of dyes for carbonless copy paper[1]. It has been estimated that 1 054 800 tonnes have been produced by the western industrialized nations till the end of 1980; the USA contributed 61.4%. The other major producers of PCBs and their percentage contributions are: Germany 12.4, France 9.6, UK 6.3, Japan 5.6, Spain 2.4 and Italy 2.2. Similar data from the producers in eastern Europe is not available[1].

Since commercially produced PCBs are the ultimate source of chlorobiphenyls (CBs) in the environment, analyses of those mixtures have been attempted from the

early 70s onwards. The main components of Kanechlor-400, which caused the "Yusho disease" were analyzed soon after 1968, the year of "Yusho" incident using preparative gas chromatography and UV spectrometry[2]. Jensen and Sundström analyzed the German mixtures Clophen A50 and A60 with the aid of charcoal chromatography and packed column gas chromatography-electron capture detection (ECD)[3]. A few other mixtures (Clophen A30, A60) were analyzed in a later study using capillary gas chromatography-ECD[4]. Various attempts were made to analyze the Aroclor mixtures, using GLC-NMR and MS[5], GLC-ECD[6,7], GLC-MS[7,8], HRGC-ECD[9–12], HRGC-MS[13–15].

Characterization of the CB mixtures in all these analyses were not complete, because only in two cases[10,11] all 209 theoretically possible congeners were available as reference compounds and in most other cases the number was much smaller. The CBs in commercial mixtures and in environmental samples are so complex that even capillary chromatography could not separate all congeners[16]. Some problems associated with coeluting congeners have been solved by GC-MS techniques in the case of commercial mixtures[7,17]. However, this method is less accurate for congeners with low relative contribution to a peak and, moreover, it can not distinguish coeluting congeners with the same number of chlorine atoms.

Multidimensional gas chromatography (MDGC) has been applied in this laboratory to tackle the problems encountered before[16]. Using the high sensitivity and selectivity of MDGC-ECD with the retention time data of all 209 CB congeners on a capillary SE-54 column[10] and all 209 CBs as reference compounds, Schulz *et al.*[18] characterized five Aroclor and four Clophen mixtures completely.

The present work examines the composition of French, Japanese and Russian commercial mixtures. The French and the Japanese together contribute more than 15% of the global production. The production data is not available from the Soviet Union, where PCBs have been manufactured and marketed for domestic consumption under the name Sovol. An understanding of the composition of these mixtures may assist in evaluating the ecodynamics and sources of PCBs in the environment.

EXPERIMENTAL

The compositional analysis of commercial PCBs was carried out on one dimensional GC-ECD system with a SE-54 capillary column as well as a multidimensional GC-ECD system with SE-54 and OV-210 capillary columns in series.

One-dimensional gas chromatography—ECD was carried out on a Siemens Sichromat-I gas chromatograph equipped with a 60 m, 0.32 mm i.d., 0.25 μm film thickness SE-54 capillary column. Carrier gas: H_2 at 1 bar pressure. Temperature programme: 100°C – 1 min, 100–250°C at 4°C min^{-1}.

The instrumentation and analytical details of MDGC-ECD technique have been presented elsewhere[19,20]. The MDGC-ECD technique involves the use of two columns of different polarities in series, each in a separate temperature-controlled oven and each equipped with an ECD. The eluate of the first column passes either through the monitor detector or through the second column and the main

detector. In the latter mode, a preselected small fraction is cut from the eluate of the first column and transferred to the second column. This can be achieved efficiently, quantitatively and reproducibly. The usual ECD chromatogram is recorded by the monitor detector, only interrupted during the cut time. The chromatogram recorded by the main ECD shows one or only a few peaks depending on the components included in that cut (Figure 1c). The identity of the CB congeners potentially included in the cut is known from the retention times on the first column[10] i.e., SE-54. This allows them to be identified on the basis of retention time data on the two columns in series and to be quantitated by analyzing, under identical cut conditions, quantitative mixtures of the relevant congeners. Schulz *et al.*[18] identified 87 chromatographic domains in Aroclor and Clophen mixtures using a 50 m SE-54 fused silica column, each of which contained either one well resolved peak or a cluster of unresolved peaks. The domains were further resolved using selective heart-cuts on MDGC-ECD. Thus 132 congeners in these technical mixtures were identified and quantitated. The experience gained during those analyses formed the basis for the identification in the present work.

MDGC-ECD analyses were carried out with a Siemens SiCHROMAT-2. First column: 25 m fused silica SE-54 (0.25 mm, 0.32 mm i.d.), second column: 25 m fused silica OV-210 (0.25 mm, 0.32 mm i.d.). The gas pressure (H_2) was maintained at 0.8 bar on the first and at 0.4 bar on the second. Temperature programming conditions: first column 140–250°C at 4°C min^{-1}, second column at 170°C until 20 min after injection, then increase to 240°C at 4°C min^{-1}.

The Phenoclor mixtures DP-3, DP-4, DP-5 and DP-6 were a gift of Dr. A. Abarnou, IFREMER, France. The Kanechlor mixtures KC-300, KC-400, KC-500 and KC-600 were donated by Prof. T. Wakimoto, Ehime University, Japan. The Sovol product was obtained from a Chemistry Laboratory in Moscow. A working solution of 1 $\mu g\ ml^{-1}$ was prepared for the analysis in MDGC-ECD from a stock solution of approximately 100 $\mu g\ ml^{-1}$ (in hexane).

Chlorobiphenyl congeners are referred by their IUPAC numbers.

RESULTS AND DISCUSSION

Initially, recordings were made using one-dimensional GC-ECD for Kanechlor KC-300, 400, 500 and 600; Phenoclor DP-3, 4, 5 and 6 and the Sovol mixtures. Representative chromatograms are given in Figures 1 and 5.

In comparison with the corresponding Aroclor mixtures studied earlier[18] no other chlorobiphenyl congeners were found than the 132 congeners identified, in Kanechlor and Phenoclor mixtures. The congener patterns of KC-300, 400, 500, 600 and DP-3, 4, 5, 6 resembled closely that of Aroclor 1016, 1242, 1254 and 1260. This facilitated the identification of individual chlorobiphenyls in the former mixtures. Identification of CBs in Sovol, which hardly resembled any one of the other mixtures, was also achieved from the detailed information on different Aroclors[18].

The percentage contribution of each individual congener was calculated on the basis of the ratio of the relative peak height with respect to the sum of the peak

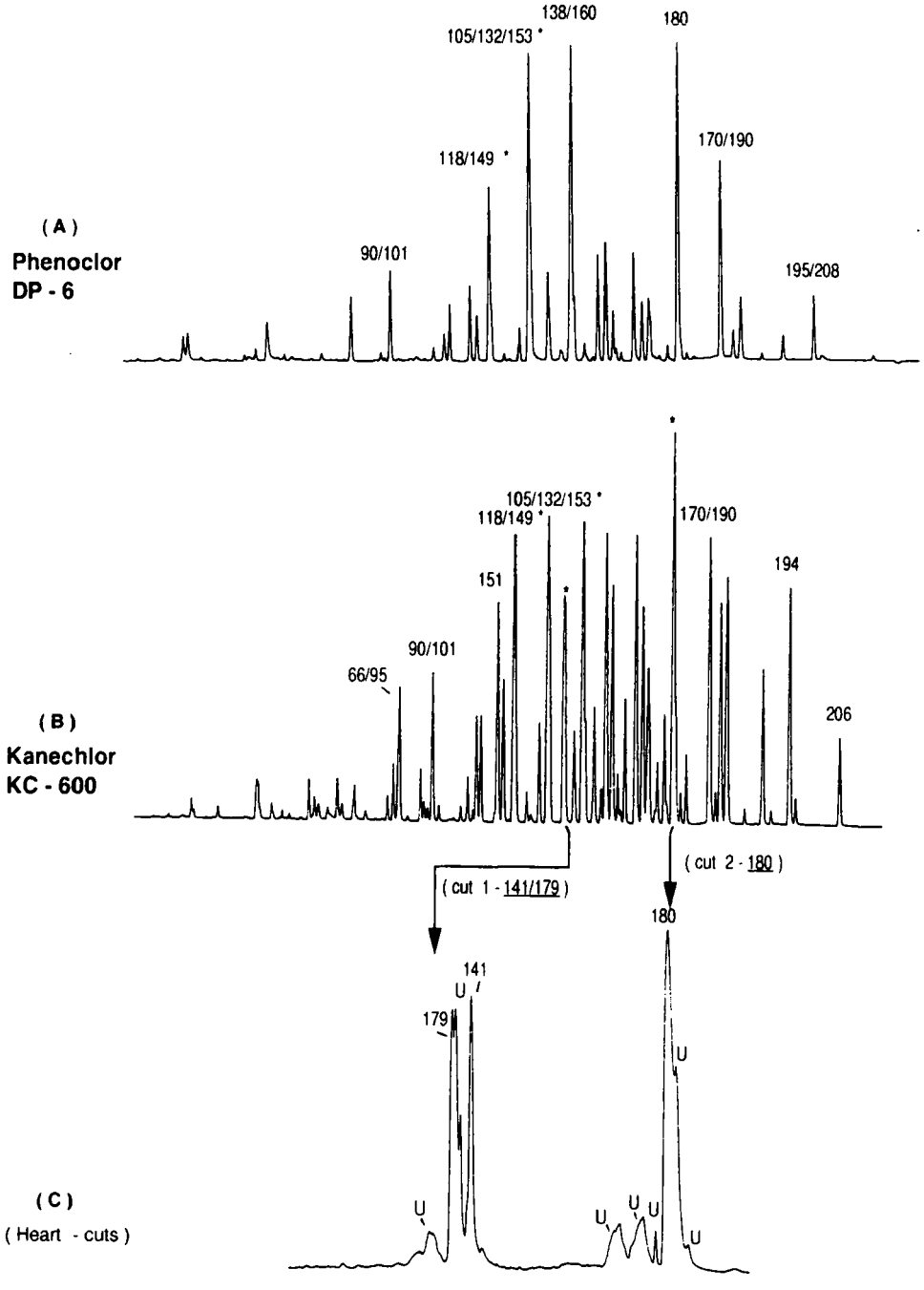

Figure 1 One-dimensional GC-ECD chromatograms of Phenoclor DP-6 (A) and Kanechlor KC-600 (B): * mark indicates points of heart-cuts in MDGC-ECD. Additional cuts were performed (Cut 1 and 2) at 141/179 and 180 in KC-600. C) Multidimensional GC-ECD chromatogram of those heart-cuts recorded by the main detector. 'U' represents unknown substances coeluting with 179, 141 and 180.

heights of all congeners identified in each mixture. A comparison between the composition of Kanechlor, Phenoclor and the corresponding Aroclor and Clophen mixtures is presented in Figure 2 and Table 1. A striking similarity exists in the composition of dominant congeners among the Japanese, French, American and German mixtures at each overall chlorine content at approximately 30%, 40%, 50% and 60% (Figure 2). For example, the dominant congeners in Aroclor 1016 are also the dominant ones in the mixtures KC-300, DP-3 and A-30. Thus:

i) KC-300 and DP-3 are composed largely of di-, tri-, and tetrachlorobiphenyls;

ii) KC-400 and DP-4 are composed mostly of tri-, tetra-, and pentachlorobiphenyls;

iii) KC-500 and DP-5 are composed predominantly of tetra-, penta-, and hexachlorobiphenyls and,

iv) KC-600 and DP-6 are composed largely of hexa-, hepta-, and octachlorobiphenyls.

However, there are some differences between the mixtures. For example, the congener pair 5/8 which contributes 7% in Aroclor 1242 is either absent or present at low levels in DP-4 and KC-400, respectively. The quantitative aspect of these differences will be discussed in a different section.

The composition of Sovol has no exact match among the various mixtures studied so far (Figure 3). Sovol resembles Aroclor 1254 to a limited extent.

Examples of the differences between the mixtures for minor components are shown in Table 1 and can be summarized as follows:

1. In both KC-300 and DP-3 there are only 3 congeners at 1–2% level. The pair 77/110 being present in KC-300 is absent (i.e. below the detection limit of 0.05%) in DP-3. The 13 congeners, among the 15 identified at less than 1% level, are also present in KC-300 at the same low level. Additionally, 21 other congeners are present in KC-300.

2. While KC-400 showed the presence of 29 congeners which are also present in DP-4 at 0.2–2.0% level, it has some 13 more congeners at comparatively elevated levels. Among them are the congeners 16/32, 26, 25, 63, 141/179, 170/190 which occur at less than 0.2% level in DP-4. Interestingly, the congeners 25, 87, 151, 131, 122, 172, 198, 199, 194 are exclusively present in KC-400 at less than 0.5% level. They are virtually absent in Aroclor 1242, Clophen A40 and Phenoclor DP-4.

3. At the 2–10% level the congener composition between DP-5 and KC-500 match very closely, except that 128 and 180 are at higher level in DP-5 compared to KC-500. DP-5 has all peaks at the 0.5–2.0% level present in KC-500 and possesses six more congeners. At $<0.5\%$ level KC-600 has five more congeners than DP-5.

4. Except for congeners 77/110 and 158, the other congeners constituting the 1–2% level in KC-600 and DP-6 are very different. KC-600 has more congeners (59) present at $<1\%$ level than DP-6. Among the 20 congeners identified in DP-6 at $<1\%$ ten are also present in KC-600.

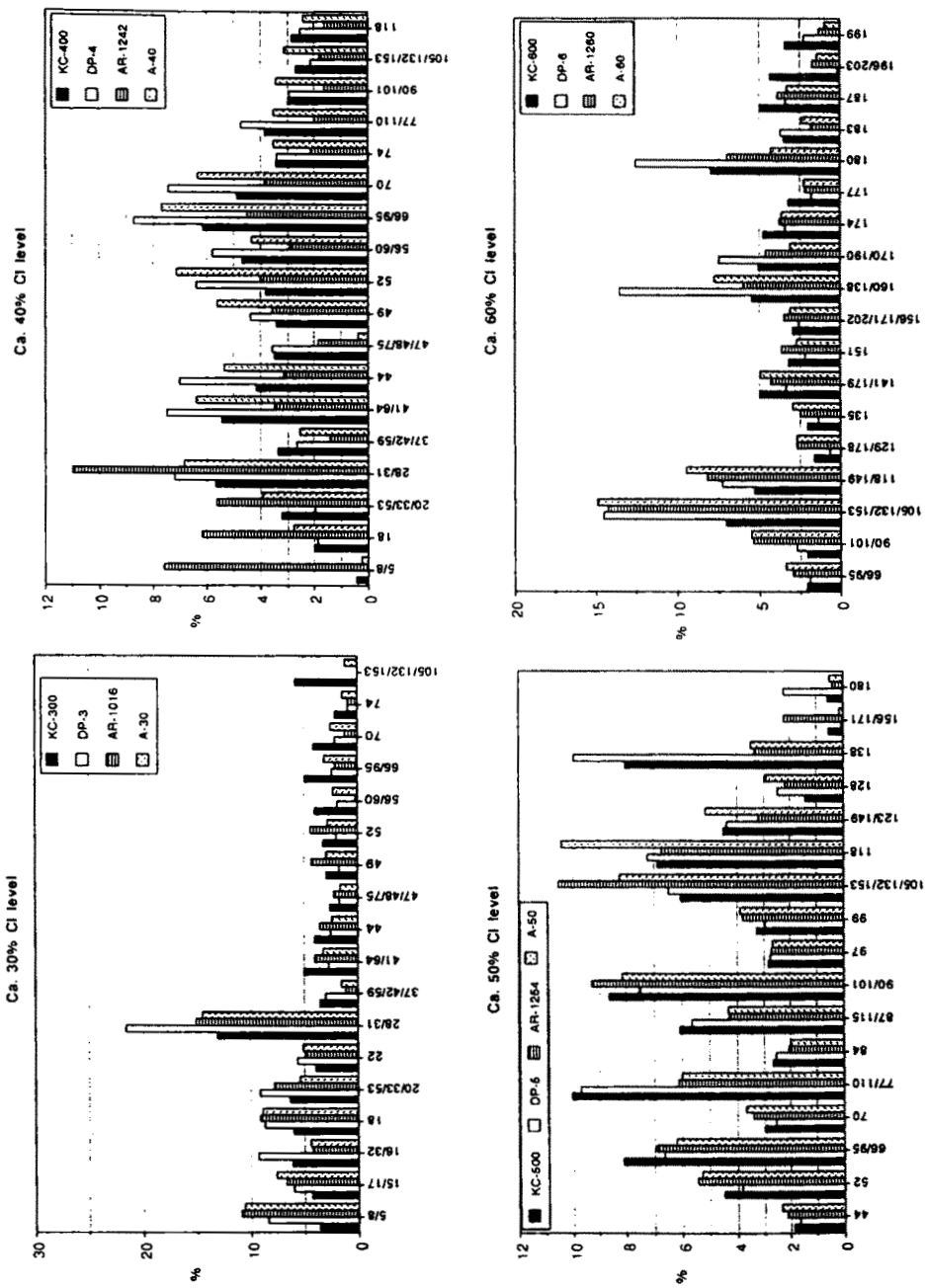

Figure 2 Percentage contributions of major components in Kanechlor (KC), Phenoclor (DP), Aroclor (AR) and Clophen (A) commercial mixtures at approximately 30%, 40%, 50% and 60% overall Cl levels. Contributions are in % (see text for calculation). CB-numbers are given in the horizontal axis. For example, 105/132/153 represent a cluster of coeluting peaks in one dimensional chromatography.

Table 1 Percentage contribution of individual chlorobiphenyls in Japanese, French and Russian PCBs.

IUPAC No.	*KC-300*	*KC-400*	*KC-500*	*KC-600*	*DP-3*	*DP-4*	*DP-5*	*DP-6*	*Sovol*
4/10	+	+	–	–	+ +	+ +	–	–	–
5/8	+ + +	+	+	+	+ + +	–	–	–	–
6	+	–	–	–	–	–	–	–	–
7/9	+	–	–	–	+ +	–	–	–	–
15/17	+ +	+ +	–	+	+ +	+	–	–	–
16/32	+ + +	+ +	–	+	+ + +	–	–	–	–
18	+ + +	+ + +	+	+	+ + +	+ +	–	–	+
19	+ +	+	–	–	+ +	–	–	–	–
20/33/53	+ + +	+ + +	+	+	+ + +	+ +	–	–	+
22/51	+ + +	+ +	–	+	+ + +	+ +	–	–	+
24/27	+ +	+	–	–	+ +	+ +	–	–	–
25	+ +	+	–	–	+ +	–	–	–	+
26	+ +	+ +	–	–	+ +	+	–	–	–
28/31	+ + +	+ + +	+	+	+ + +	+ + +	+ +	+ +	+
29	+	–	–	–	–	–	–	–	–
34	–	–	–	–	–	–	–	–	–
35	+ +	+	+ +	+	+ +	+ +	+ +	+ +	+
37/42/59	+ + +	+ + +	–	+	+ + +	+ + +	–	+	+
40	+ +	+ +	+	–	+ +	+ +	–	–	+
41/64	+ + +	+ + +	+ +	+	+ + +	+ + +	+	–	+ +
44	+ + +	+ + +	+ +	+	+ + +	+ + +	+ +	–	+ + +
45	+ +	+ +	–	–	+ +	+ +	–	–	–
46	+	+ +	–	+	+	+	–	–	–
47/48/75	+ +	–	+	+	+ +	–	+	+	+
49	+ + +	+ + +	+ +	+	+ + +	+ + +	+ +	–	+ +
52	+ + +	+ + +	+ + +	+	+ + +	+ + +	+ + +	+	+
56/60	+ + +	+ + +	+	+	+ +	+ + +	+	–	+
63	+	+	–	–	–	+	–	–	–
66/95	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+ +	+ + +

(*continued*)

Table 1 (*continued*)

IUPAC No.	*KC-300*	*KC-400*	*KC-500*	*KC-600*	*DP-3*	*DP-4*	*DP-5*	*DP-6*	*Sovol*
67/100	+	+	−	+	+	+	−	−	+
69	−	−	−	−	−	−	−	−	−
70	+ + +	+ + +	+ + +	+ +	+ + +	+ + +	+ + +	−	+ + +
74	+ + +	+ + +	+	+	+ +	+ + +	+	−	+ +
77/110	+ +	+ + +	+ + +	+ +	−	+ + +	+ + +	+ +	+ + +
82/151	+	+	−	+	−	−	−	−	−
83	+	+	+	+	−	+	+ +	−	+
84	+	+ +	+ + +	+	−	+ +	+ + +	−	+ + +
85	+	+ +	+ +	+	−	+ +	+ +	−	+ + +
87/115	+	+ + +	+ + +	+	−	+ + +	+ + +	+	+ + +
88	−	−	−	−	−	−	+	−	−
90/101	+	+ + +	+ + +	+ + +	+	+ + +	+ + +	+ + +	+ + +
91	+	+ +	+ +	+	−	+ +	+ +	−	+ +
92	+	+ +	+ +	+	−	+	+ +	+	+ +
96	−	+	−	−	−	−	−	−	−
97	+	+ +	+ + +	+	−	+ +	+ + +	−	+ + +
99	+	+ + +	+ + +	+	−	+ +	+ + +	−	+ + +
107	−	−	−	+	−	−	−	−	+ +
114/122/131	−	−	−	−	−	−	−	−	+
119	−	−	−	−	−	−	−	−	+
126/129/178	−	+	+	+ +	−	−	+	+ +	+ +
128	+	+	+ +	+ +	−	−	+ + +	+ +	+ + +
130	−	−	+	−	−	−	+	−	−
134	−	+	−	+	−	−	−	−	+
135	−	+	+ +	+ + +	−	−	+ +	+ +	+ +
136	−	+	+ +	+ +	−	−	+ +	+ +	+ +
137/176	−	+	+	−	−	−	+ +	−	+ +
138/158/160	+	+ +	+ + +	+ + +	+	+	+ + +	+ + +	+ + +

141/179	−	+	+ +	+ + +	−	+	+ +	+ + +	+ +
146	−	+	+ +	+ +	−	−	+ +	+ +	+ +
156/171/202	−	+	+ +	+ + +	−	+	+	+ + +	+ +
157/173/201	−	+	−	+ +	−	−	−	+	+
167	−	+	+	+	−	+	+	+	+
170/190	−	+	+	−	−	+	+ +	−	+ +
172	−	−	−	+ +	−	−	−	+	+
174	−	+	+	+ + +	−	+	+ +	+ + +	+
175	−	−	−	+	−	−	−	+	+
177	−	+	+	+ +	−	+	+	+ +	+
180	+	+	+ +	+ + +	−	+	+ + +	+ + +	+ +
183	−	+	+	+ + +	−	+	+	+ + +	+
185	−	−	−	+ +	−	−	−	−	−
187	−	+	+	+ + +	−	+	+	+ + +	+
189	−	−	−	+	−	−	−	+ +	−
191	−	−	−	+	−	−	−	−	−
193	−	−	−	−	−	−	−	−	−
194	−	+	−	+ + +	−	−	−	−	−
195/208	−	−	−	+ + +	−	−	−	+ + +	−
196/203	−	−	−	+ + +	−	−	−	+	−
197	−	−	−	−	−	−	−	−	−
198	−	+	−	+	−	−	−	+ +	−
199	−	+	−	+ + +	−	−	−	+ + +	−
200	−	−	−	+ +	−	−	−	−	−
205	−	−	−	+	−	−	−	+	−
206	−	−	−	+	−	−	−	+	−
207	−	−	−	+	−	−	−	−	−
209	−	−	−	−	−	−	−	−	−

+ + + = >2%; + + = >0.5 − 2%; + = >0.05 − 0.5%; − = <0.05%.

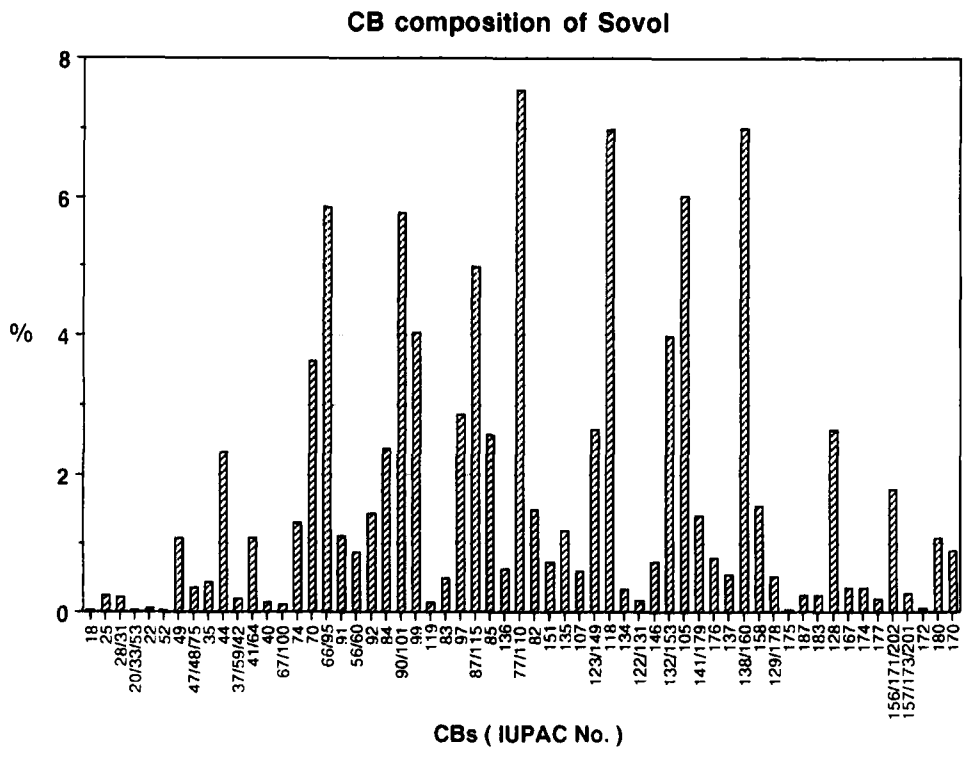

Figure 3 Composition of Sovol. See text for % calculation.

5. At the 1–2% level there is close agreement between Sovol and KC-500/DP-5. The congeners present in Sovol at $<1\%$ could only be seen in one of the following mixtures at similar levels: KC-600, KC-500 and KC-400.

These differences in the composition of minor compounds could arise from differences in the boiling-point fractionations of PCB mixtures between the various manufacturers. We have no information whether Sovol represents the only PCB mixture available in the Soviet Union or what we obtained was one among the various boiling-point fractions available in that country.

Complete quantitation of all the individual congeners was attempted earlier (for example in Aroclor and Clophen mixtures)[18]. A different approach was taken in the present study being much less time consuming, still resulting in useful information. Sixteen congeners, i.e. CB-18, 26, 44, 49, 52, 101, 118, 128, 138, 149, 151, 170, 180, 183, 187 and 194 were quantitated using a standard mixture of extremely pure chlorobiphenyls. They elute as base-line separated peaks on a SE-54 column allowing their quantitation. Problem in the complete separation of 118 and 149 congeners was experienced, however. There are three other congeners which are environmentally significant but analytically difficult to determine with one-dimensional GC-ECD, i.e. CB-105, -132 and -153. These five congeners were quantitated by MDGC-ECD. The

important criteria of selection of these 19 CBs are bioaccumulation and toxicity. These congeners constitute more than 80% of chlorobiphenyl residues determined in porpoise blubber[21], more than 68% in ducks[22], and more than 65% in fish[23]. This set also include some of the most important mono-*ortho* Cl CBs of significant toxicity[24]. The quantitative results are presented in Figure 4. The data for the corresponding Aroclor and Clophen mixtures are included for comparison. The individual contributions (%) represents the relative contributions to the sum of concentrations (wt/wt) of 19 CBs. They are represented at four different overall chlorine levels.

Compositional differences among the various commercial PCBs are clearer from this representation than from Figure 2. We shall discuss some aspects for each of the four overall chlorine levels.

30% Cl level (Figure 4A)

Congeners 44, 49, 52, 101 and 138 occur at equal levels in KC-300 and DP-3. A difference of more than 20% is present for the dominant congener No. 18. CB-149 and 132 are virtually absent in DP-3, a fact deducible only using MDGC-ECD. Concentration ratios differ between DP-3 and KC-300 (rather high in the latter). The congeners and the difference (KC-300/DP-3) are: CB-118: 47, CB-153: 47, and CB-105: 41. Although Aroclor and Clophen mixtures show less differences between them, they differ greatly from Kanechlor and Phenoclor mixtures.

40% Cl level (Figure 4B)

Congeners 18, 44, 49, 52, 101, 118, 153 and 138 are the prominant ones in KC-400 and DP-4. There are quantitative differences among these congeners in those mixtures. For example, in DP-4 congeners 44, 52, 105, 118, 153 are 1.4, 1.4, 2.9, 1.8, 1.7, times higher than in KC-400, and CB-18, 26, 128, 138, 149, 151, 170 and 180 are 1.3, 6.7, 4.8, 2.7, 2.1, 17, 1.7 and 2 times higher in KC-400. The contribution of CB-18 and 52 is highest in Aroclor 1242.

50% Cl level (Figure 4C)

The following ten congeners are present at near equal concentrations in KC-500 and DP-5: CB-26, 44, 49, 52, 101, 105, 151, 153, 183, and 187. KC-500 contains CB-132 and 149 at 1.4 and 6 times higher levels than DP-5 but CB-118 and 138 are 1.3 and 1.7 times higher in DP-5.

60% Cl level (Figure 4D)

Among the dominant ones, congeners 132, 138, 149, 170 and 180 showed comparable contributions in KC-600 and DP-6. The contribution of CB-153 is two times higher in DP-6 than KC-600. The contribution of CB-101 is nearly equal in Aroclor-1260 and Clophen A-60, being two times higher in KC-600 and DP-6.

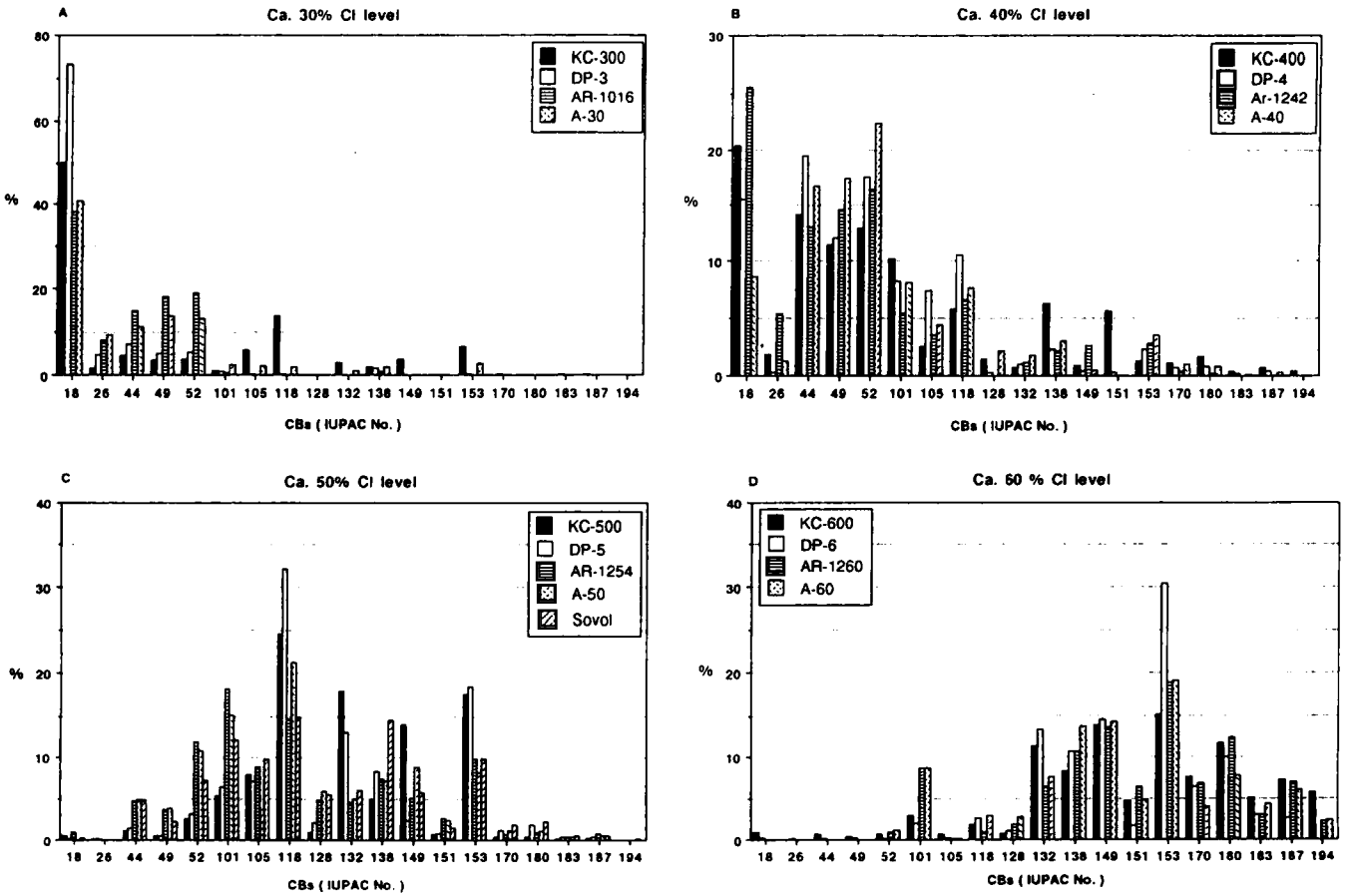

Figure 4 Relative concentration (X/sum of 19 CBs × 100) of selected CB congeners in Kanechlor (KC), Phenoclor (DP), Aroclor (AR), Clophen (A) and Sovol commercial mixtures at ca. 30%, 40%, 50% and 60% Cl level.

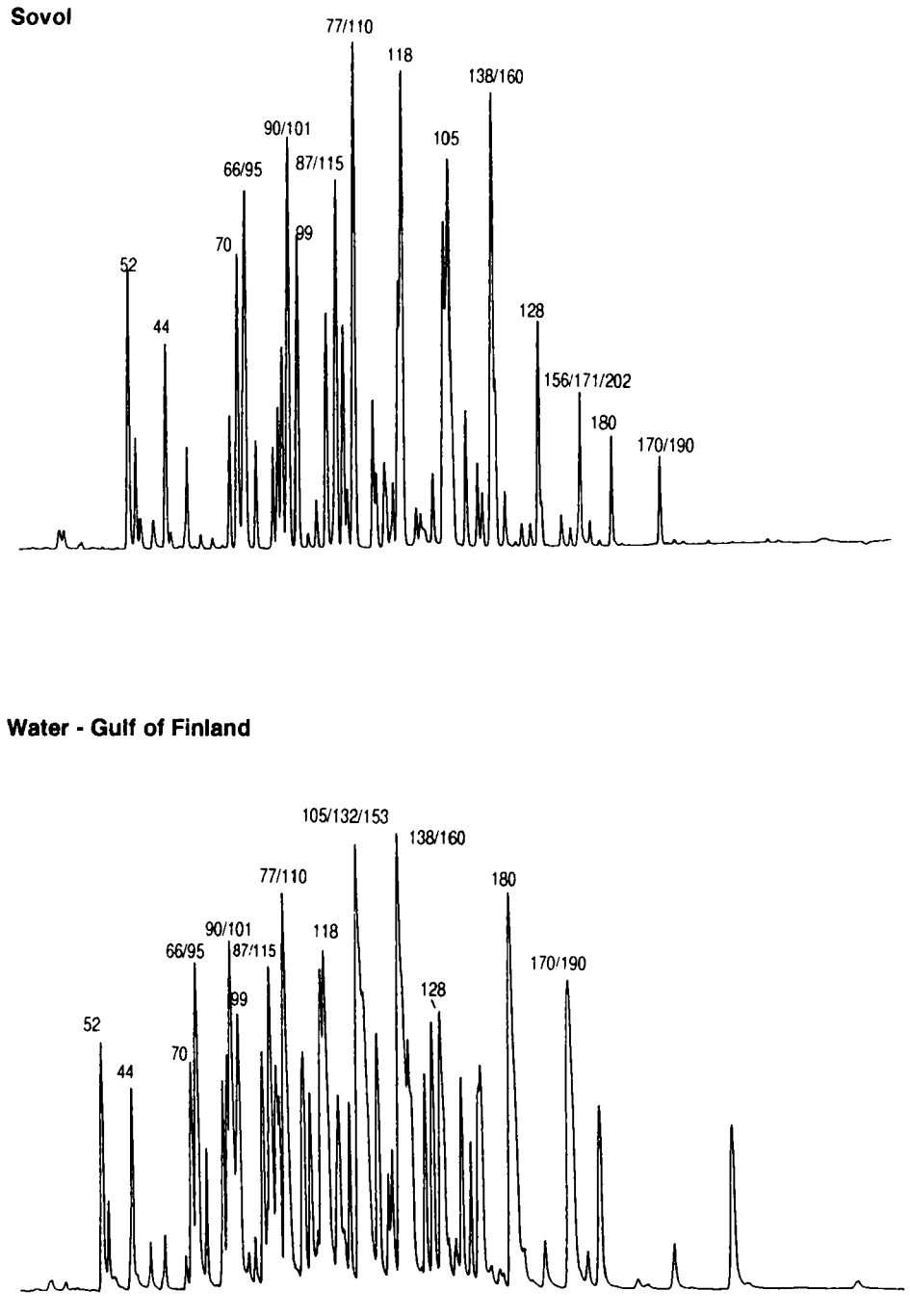

Figure 5 Identification of point source contamination for the waters of Gulf of Finland by Sovol. a) GC-ECD chromatogram of Sovol technical mixture b) Chromatogram of water sample extract. Both chromatograms were obtained by one-dimensional GC-ECD.

Sovol (Figure 4C)

The results for Sovol are presented along with other PCBs at the ca. 50% Cl level. It is unique in some respects. For example, the 12% contribution of CB-101 is comparable to that of 10% contribution in KC-400. The 15% contribution of 118 in Sovol is comparable to the 14% and 11% contribution in KC-300 and DP-4. The 15% contribution of 138 in Sovol is not comparable in any other mixture except in DP-6 (11%). Thus Sovol resembles a composition in between 30%, 40%, 50% and 60% Cl levels of other commercial mixtures.

The analysis of commercial PCBs using MDGC-ECD revealed another interesting aspect of quantitation of environmental samples using commercial PCBs as technical standards. It has been observed earlier during the analysis of Clophen in MDGC-ECD that two non-CB compounds coeluted with congeners 138 and 180[25]. Once again, we noticed co-elution of unknown substances along with target CBs, this time in KC-600 (Figure 1B and C). Heart-cuts at the retention times of congeners 141/179 and 180 revealed several unknown substances coeluting with these congeners. For example, two major and two small clusters of unknown substances coelute with 141 and 179. The peak 180 is accompanied by several clusters of unknown substances. The implication is that the use of Kanechlor mixtures as quantitation standards[26] may cause errors because of the presence of hitherto unnoticed substances in those mixtures. It is to be investigated whether GC-MS measurements in the single ion monitoring mode eliminates this problem. The use of commercial mixtures as quantitation standards has been discouraged on the basis of the lack of agreement between their composition and those in environmental samples[13,27]. The present observation is an additional argument to support this view.

Understanding the composition of commercial PCBs has additional benefits. Water from the Gulf of Finland was analysed for PCBs during a recent survey of the Baltic. The CB pattern was found to be very different from all our earlier water sample analyses. A striking similarity was found between the chromatograms of the water sample and the Sovol (Figure 5). This indicates a point-source of PCB contamination to the Gulf of Finland, receiving large volumes of fresh water from the River Neva from the Soviet Union.

Special emphasis has been given in recent years for the measurement of non-*ortho* Cl substituted congeners (especially, 77, 126 and 169) in CB analysis for reasons of toxicity[16,24,28]. In a recent publication[29] we noted that the use of clean charcoal material and MDGC-ECD were essential for the unambiguous identification and quantitation of these congeners occurring at ultra trace levels. Those important congeners will be reported as result of a study using an improved charcoal HPLC-MDGC-ECD system.

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