

# Identification of Isopropylbiphenyl, Alkyl Diphenylmethanes, Diisopropyl-naphthalene, Linear Alkyl Benzenes and Other Polychlorinated Biphenyl Replacement Compounds in Effluents, Sediments and Fish in the Fox River System, Wisconsin

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Five polychlorinated biphenyl replacement dye solvents and a diluent present in carbonless copy paper were identified by gas chromatography/mass spectrometry in the following matrices: effluents from a de-inking-recycling paper mill and a municipal wastewater treatment plant receiving wastewaters from a carbonless copy paper manufacturing plant; sediments; and fish collected near both discharges in the Fox River System, Wisconsin. An isopropylbiphenyl dye solvent mixture included mono-, di- and triisopropylbiphenyls. Also identified were two dye solvent mixtures marketed under the trade name Santosol. Santosol 100 comprised ethyl-diphenylmethanes (DPMs), benzyl-ethyl-DPMs, and dibenzyl-ethyl-DPMs. Similarly, Santosol 150 comprised dimethyl-DPMs, benzyl-dimethyl-DPMs, and dibenzyl-dimethyl-DPMs. Diisopropyl-naphthalenes, widely used as a dye solvent in Japan, were identified for the first time in the US environment. *sec*-Butylbiphenyls and di-*sec*-butylbiphenyls, likely constituents of a *sec*-butylbiphenyl dye solvent mixture, were tentatively identified. Linear alkyl benzenes (C<sub>10</sub> to C<sub>13</sub>-LABs) constituted the Alkylate 215 diluent mixture. Although known to occur as minor constituents in linear alkyl sulfonate detergents, LAB residues have not been previously attributed to commercial use of LABs.

## INTRODUCTION

The past use of polychlorinated biphenyls (PCBs) in carbonless copy paper was a main factor leading to this research. During 1957-1971, 21 million kg of PCBs (as Aroclor 1242) were used by the National Cash Register Co.† (NCR Corp.) to make carbonless copy paper.<sup>1</sup> Manufacturing techniques and chemical constituents of carbonless copy paper have been described.<sup>2</sup> Microcapsules containing the dye solvent (PCBs) were produced at a plant in Portage, Wisconsin. The PCBs were released into the environment in many ways. In Wisconsin, major point sources included the carbonless copy paper plant and paper mills that recycled waste-paper, including carbonless copy paper.<sup>3,4</sup> In 1971, when PCBs were becoming known as ubiquitous environmental contaminants, they were no longer sold to open system users.<sup>1</sup> Other compounds, many claimed to be proprietary, replaced the PCBs. When exclusive patents on carbonless copy paper expired, other companies often chose different PCB replacements. The

names and several characteristics of pertinent PCB replacements are listed in Table 1.

Why study the PCB replacements? After reviewing their use in dielectric fluids, Addison<sup>5</sup> concluded: 'Much less is known about PCB replacements—whose production and use are apparently accepted—than about the PCBs themselves, which are banned.' In this work, we report for the first time the identification of several PCB replacement mixtures associated with carbonless copy paper in two surface water systems: the Lower and Upper Fox rivers in Wisconsin. The topography, setting, industrial activities, and PCB contamination in these two distinct segments of the Fox River have previously been described.<sup>4,6-9</sup> Also, another 100 compounds, both chlorinated and non-chlorinated, were identified in the Lower Fox River system by using gas chromatography/mass spectrometry (GC/MS).<sup>8</sup>

We now report the identification and GC/MS characterization of a series of non-chlorinated compounds that are constituents of several PCB replacement dye solvent mixtures. (Mono- to trichlorinated derivatives are to be discussed in a later paper). The non-chlorinated PCB replacement compounds have been found in wastewaters, sediments and fish in both the Upper and Lower Fox rivers, where several specific point sources have been identified. Two in particular are a municipal

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‡ Reference to trade names or manufacturers does not imply government endorsement of commercial products.

Table 1. PCB replacement compounds found in the Fox River–Green Bay

Mixture (dates used)	Constituents	Abbreviations used in text	M <sub>r</sub>	Structure
Isopropylbiphenyl (~1971–)	Isopropylbiphenyl	IPB	196	
	Diisopropylbiphenyl	DIPB	238	
	Triisopropylbiphenyl	TIPB	280	
Santosol 100 (~1976–79?)	Ethyl-diphenylmethane	Ethyl-DPM	196	
	Benzyl-ethyl-diphenylmethane	Benzyl-ethyl-DPM	286	
	Dibenzyl-ethyl-diphenylmethane	Dibenzyl-ethyl-DPM	376	
Santosol 150 (~1979–)	Dimethyl-diphenylmethane	Dimethyl-DPM	196	
	Benzyl-dimethyl-diphenylmethane	Benzyl-dimethyl-DPM	286	
	Dibenzyl-dimethyl-diphenylmethane	Dibenzyl-dimethyl-DPM	376	
Suresol 290 (~1981–)	sec-Butylbiphenyl		210	
	Di-sec-Butylbiphenyl		266	
Diisopropylnaphthalene (unknown)	Diisopropylnaphthalene	DIPN	212	
Alkylate 215 (~1971–)	C <sub>10</sub> –C <sub>13</sub> Linear alkyl benzenes	LABs	218 232 246 260	

wastewater treatment plant (Portage WWTP) that receives carbonless copy paper manufacturing wastes, and a paper mill at Neenah, Wisconsin, that de-inks and recycles wastepaper, which can include carbonless copy paper. Because many of these newly identified contaminants were related to two different activities in the paper-making process, we decided that they warranted further study. Aquatic toxicities for some are unknown. We found that most of the non-chlorinated PCB replacement compounds behaved in a similar manner as the PCBs, i.e. they accumulated in fish inhabiting receiving waters near both point sources.

## EXPERIMENTAL

### Sample collection, extraction and clean-up

Wastewater, adult fish and some sediment samples from both study sites were collected by personnel of the Wisconsin Department of Natural Resources (WDNR) during 1977–1982. Sample collection and compositing procedures were previously described.<sup>7</sup> Fish samples of particular interest that were collected in May 1977 from the Lower Fox River (site 1) were a common carp, *Cyprinus carpio*, and walleyes, *Stizostedion vitreum vitreum* (a composite of three specimens 33, 41 and 42 cm in total length). A 3.2 kg, 58 cm common carp was collected from the Upper Fox River (site 2), 0.6 km downstream from the Portage WWTP in July 1981. Also, ten adult walleyes, averaging 0.7 kg and 40 cm long, were

collected in May 1984 from the mouth of the Lower Fox River at Green Bay, Wisconsin, by US Fish and Wildlife Service (FWS) personnel. Near the FWS collection site, 60 km downstream from site 1, effluents from several paper mills, including a recycling mill, are discharged into the river. An FWS walleye composite sample was prepared by thoroughly mixing 20% of all tissue ground from the ten fish.

Extraction and clean-up protocols used for wastewater, sediment and fish collected by the WDNR followed previously described methods.<sup>6–9</sup> The FWS walleye composite was processed by using a method for polycyclic aromatic hydrocarbons (PAHs). The sample was saponified with KOH, extracted with CH<sub>2</sub>Cl<sub>2</sub> in cyclopentane, fractionated first on potassium silicate/silica gel, and then by gel permeation chromatography (S-X3). Several deuterated PAHs and monochloro-PAHs were added as instrumental internal standards.

### GC and GC/MS analyses

For GC/FID analyses before 1981, we used an Ultra-Bond 20M packed column (1.8 or 3.2 m × 2 mm i.d.), temperature programmed from 100 °C (4 min hold) to 260 °C at 4 °C min<sup>-1</sup>, then held 16 min. Later, we used a 15 m × 0.25 mm i.d. SE-54 (0.25 μm) capillary column with splitless injections and a helium linear velocity of 30 cm s<sup>-1</sup>. The initial oven temperature, 125 °C, was chosen for an optimum 'solvent effect'<sup>10</sup> with nonane (Burdick & Jackson, b.p. 153 °C) used as a 'keeper' in the sample extract. After a 15 min initial hold, the oven was ramped to 131 °C at 1 °C min<sup>-1</sup>, to 247 °C at 4 °C

min<sup>-1</sup> and to 280 °C at 8 °C min<sup>-1</sup> with a 15 min final hold. For reference, five *n*-alkane compounds eluted at the following retention times (min): C<sub>18</sub>H<sub>38</sub> (29.45), C<sub>19</sub>H<sub>40</sub> (33.10), C<sub>20</sub>H<sub>42</sub> (36.30), C<sub>24</sub>H<sub>50</sub> (46.00) and C<sub>28</sub>H<sub>58</sub> (53.90). For the FWS fish extract, capillary GC (30 m DB-5, H<sub>2</sub> carrier gas) with a photoionization detector (GC/PID) preceded GC/MS.

Early GC/MS analyses were similarly performed by using the Ultra-Bond 20M column with a Finnigan model 9500/3100D/6000 gas chromatograph/mass spectrometer/data system.<sup>7</sup> For later analyses we used a 30 m × 0.25 mm i.d. DB-5 capillary column (J&W Scientific) with a Finnigan model 9600 gas chromatograph coupled to either a model 4023 or 4510 mass spectrometer with an INCOS data system. The sweep valve was opened 48 s after 1–2 µL splitless injections. The oven temperature was typically programmed either from 120 °C to 280 °C at 4 °C min<sup>-1</sup> or from 120 °C to 200 °C at 3 °C min<sup>-1</sup>, then 200 °C to 280 °C at 8 °C min<sup>-1</sup> (final hold 15 min). For the FWS fish extract, the oven was programmed from 60 °C (1 min hold) to 210 °C at 10 °C min<sup>-1</sup> then 210 °C to 295 °C at 5 °C min<sup>-1</sup>. For determining retention indices (RIs) according to Lee *et al.*,<sup>11</sup> the oven was programmed from 45 °C (no hold) to 300 °C at 4 °C min<sup>-1</sup>. Electron ionization mass spectra from *m/z* 35 to 500 were repetitively acquired at 70 eV every 1.0 s. Perfluorotributylamine (PFTBA) (FC-43) and decafluorotriphenylphosphine (DFTPP) were used for instrument calibration.<sup>12</sup> Methane chemical ionization mass spectra from *m/z* 120 to 500 were similarly acquired for the Santosol 100 and 150 mixtures to verify their constituent molecular masses.

### Source of standards

Isopropylbiphenyl (electric fluid or capacitor grade) was furnished by Tanatex Chemical Corp., Lyndhurst, New Jersey, a subsidiary of Sybron Corp. Alkylate 215 and

Santosols 100 and 150 standards were obtained from Appleton Papers (formerly NCR) at Portage, Wisconsin, and from Monsanto Industrial Chemicals Co., St. Louis, Missouri. Diisopropylanthracene (DIPN) was furnished by American Cyanamid Co., Wayne, New Jersey.

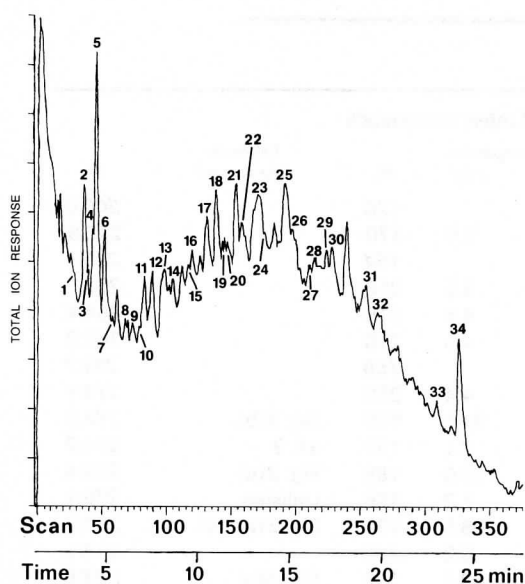
## RESULTS AND DISCUSSION

To the best of our knowledge, the first four PCB replacement mixtures in Table 1 have not been previously identified in a contiguous environmental setting. Except for the detection of DIPN in Japan,<sup>13</sup> none have been definitively associated with pulp and paper mill activities. Our earliest GC/MS analyses detected two early PCB replacements, isopropylbiphenyl (IPB) and Santosol 100 mixtures, in samples from the Lower Fox River (site 1). Their presence indicated that various PCB replacements were released into the environment from either different brands or vintages of carbonless copy paper.

### GC/MS analysis of fish from Lower Fox River (site 1)

A total ion chromatogram (Fig. 1) depicts the analysis of an extract (6% ether in hexane eluate from Florisil) from the WDNR walleye sample. The peaks numbered 1–34 in Fig. 1 are listed in Table 2 and have either been confirmed with standards or tentatively identified by mass spectral interpretation. The fish sample (8.7% lipid) also contained 12 µg g<sup>-1</sup> PCBs (representing Aroclors 1248/1242) and 0.4 µg g<sup>-1</sup> pentachloroanisole. We were particularly interested in the non-chlorinated PCB replacement compounds (and their chlorinated derivatives) present in µg g<sup>-1</sup> concentrations. These compounds were first described in an unpublished thesis<sup>9</sup> and are discussed here in detail with supplementary data to enable other researchers to recognize and differentiate them.

Several PCB replacement compounds have the same molecular weight (*M<sub>r</sub>*), elute closely even from DB-5 capillary columns, and their mass spectra resemble each other. The various constituents of the PCB replacement mixtures are collectively listed in their GC elution order in Table 3. Constituents are denoted according to labeled GC peaks in capillary chromatographic and mass spectral figures discussed later. To assist other researchers to pinpoint these compounds, RIs according to Lee *et al.*<sup>11</sup> are given. Vassilaros *et al.*<sup>14</sup> reported that, although RIs provide essential information on elution order and intervals, they should be viewed as 'good working estimates under given conditions ... but the actual numbers should not be expected to be absolute'. Our GC/MS-derived RIs for 49 compound peaks listed in Table 3 closely compare with our GC/PID-derived RIs, differing by a mean ± SD of 0.67 ± 0.25 RI. For several reference PAHs listed in Table 3, our GC/MS-derived RIs were within 0.5 RI and 2.2 RI units, from those of Vassilaros *et al.*<sup>14</sup> and Lee *et al.*,<sup>11</sup> respectively, who used gas chromatographs with SE-52 capillary columns.



**Figure 1.** Total ion chromatogram of a Lower Fox River fish extract chromatographed by using the Ultra-Bond 20M packed column temperature programmed 100–220 °C at 4 °C min<sup>-1</sup>. Numbered peaks are identified in Table 2.



min<sup>-1</sup> and to 280°C at 8°C min<sup>-1</sup> with a 15 min final hold. For reference, five *n*-alkane compounds eluted at the following retention times (min): C<sub>18</sub>H<sub>38</sub> (29.45), C<sub>19</sub>H<sub>40</sub> (33.10), C<sub>20</sub>H<sub>42</sub> (36.30), C<sub>24</sub>H<sub>50</sub> (46.00) and C<sub>28</sub>H<sub>58</sub> (53.90). For the FWS fish extract, capillary GC (30 m DB-5, H<sub>2</sub> carrier gas) with a photoionization detector (GC/PID) preceded GC/MS.

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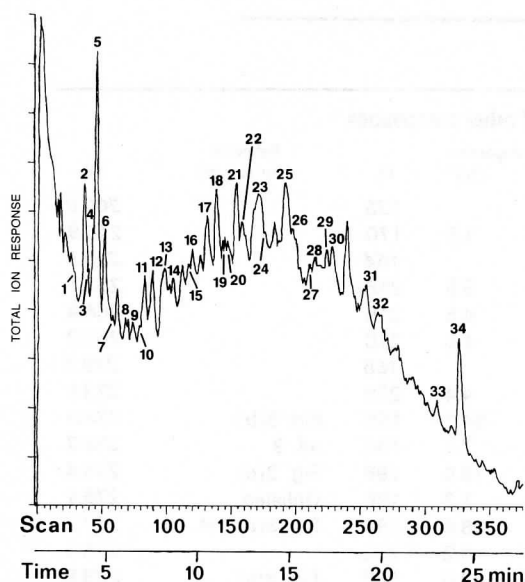
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**Table 2. Compounds identified in a Lower Fox River walleye extract**

Peak no. <sup>a</sup>	Compound name	Mixture derived from <sup>c</sup>
1	(1-Pentylhexyl)-benzene and (1-butylheptyl)-benzene	A 215-e A 215-f
2	2-Ethyl-diphenylmethane (DPM)	S 100-a
3	3-Ethyl-DPM	S 100-b
4	3-Isopropylbiphenyl	IPB
5	4-Ethyl-DPM	S 100-c
6	4-Isopropylbiphenyl	IPB
7	Pentachloroanisole	
8	Chloro-isopropylbiphenyl <sup>b</sup>	
9	Chloro-isopropylbiphenyl <sup>b</sup>	
10	Chloro-isopropylbiphenyl <sup>b</sup> and dichlorobiphenyl	PCB
11	Diisopropylbiphenyl	IPB
12	Chloro-ethyl-DPM <sup>b</sup>	
13	Chloro-ethyl-DPM <sup>b</sup>	
14	Trichlorobiphenyl	PCB
15	Dichloro-isopropylbiphenyl <sup>b</sup>	
16	Dichloro-(ethyl-DPM or isopropylbiphenyl) <sup>b</sup> and trichlorobiphenyl	PCB
17	Trichlorobiphenyl	PCB
18	Dichloro-ethyl-DPM <sup>b</sup> and dibutyl phthalate	
19	Dichloro-(ethyl-DPM or isopropylbiphenyl) <sup>b</sup>	
20	Dichloro-(ethyl-DPM or isopropylbiphenyl) <sup>b</sup>	
21	Tetrachlorobiphenyl	PCB
22	Dichloro-ethyl-DPM <sup>b</sup>	
23-24	Tetrachlorobiphenyl	PCB
25	Tetrachlorobiphenyl and pentachlorobiphenyl	PCB
26-29	Pentachlorobiphenyl	PCB
30	Pentachlorobiphenyl and 4,4'-DDE	PCB
31	Benzyl-ethyl-DPM	S 100-e
32	Benzyl-ethyl-DPM	S 100-f
33	Benzyl-ethyl-DPM and dioctyl phthalate	S 100-m
34	Squalene <sup>b</sup>	

<sup>a</sup> Peaks numbered in Fig. 1.<sup>b</sup> Tentatively identified by GC/MS. All other compounds confirmed by matching both GC retention times and mass spectra of standard or standard mixture.<sup>c</sup> Commercial mixture comprises this compound: A 215-a denotes Alkylate 215, component a as labeled in Fig. 8; S 100-a denotes Santosol 100, component a as labeled in elution order; IPB denotes isopropylbiphenyl, PCB denotes polychlorinated biphenyl.**Table 3. Retention index for PCB replacement compounds and other compounds**

Compound name <sup>a</sup>	CAS number <sup>b</sup>	Mixture <sup>c</sup>	Composition (%) <sup>d</sup>	M <sub>r</sub>	Reference mass spectra <sup>e</sup>	RI <sup>f</sup>
<i>Naphthalene</i>				128		200.0
Isopropyl-naphthalene	29253-36-9	DIPN	1.6	170		248.9
<i>Acenaphthene</i>				154		253.5
1-(Butyl-hexyl)-benzene	4537-11-5	A 215-a	5.5	218		263.1
1-(Propyl-heptyl)-benzene	4537-12-6	A 215-b	4.5	218		264.4
1-(Ethyl-octyl)-benzene	4621-36-7	A 215-c	4.5	218		267.3
<i>Fluorene</i>				166		269.7
1-(Methyl-nonyl)-benzene	4537-13-7	A 215-d	4.4	218		273.1
2-Ethyl-diphenylmethane (DPM)	28122-25-0 <sup>g</sup>	S 100-a	34.1	196	Fig. 3(b)	274.0
3-Ethyl-DPM	28122-24-9 <sup>g</sup>	S 100-b	7.1	196	ref. 9	274.7
2,6-Dimethyl-DPM	28122-29-4 <sup>g</sup>	S 150-a	18.0	196	Fig. 3(d)	275.4
3,5-Dimethyl-DPM	28122-27-2 <sup>g</sup>	S 150-b	1.3	196	Unlisted	276.1
3-Isopropylbiphenyl	20282-30-8 <sup>g</sup>	IPB	58.5	196	Fig. 3(a), ref. 19	277.7
1-(Pentyl-hexyl)-benzene	4537-14-8	A 215-e	6.2	232		278.1
2,4-Dimethyl-DPM	28122-28-3 <sup>g</sup>	S 150-c	62.5	196	Fig. 3(e)	278.5
4-Ethyl-DPM	620-85-9 <sup>g</sup>	S 100-c	43.7	196	Fig. 3(c)	278.6
1-(Butyl-heptyl)-benzene	4537-15-9	A 215-f	10.7	232		278.7
1-(Propyl-octyl)-benzene	4536-86-1	A 215-g	8.3	232		280.2
4-Isopropylbiphenyl	7116-95-2 <sup>g</sup>	IPB	38.6	196	refs. 9, 19	282.2
1-(Ethyl-nonyl)-benzene	4536-87-2	A 215-h	7.4	232		283.3
Diisopropyl-naphthalene	38640-62-9 <sup>h</sup>	DIPN a	5.4	212	Unlisted	285.1

Table 3—continued

Compound name <sup>a</sup>	CAS number <sup>b</sup>	Mixture <sup>c</sup>	Composition (%) <sup>d</sup>	<i>M<sub>r</sub></i>	Reference mass spectra <sup>e</sup>	RI <sup>f</sup>
Diisopropylnaphthalene	38640-62-9 <sup>h</sup>	DIPN b	5.0	212	Unlisted	285.9
1-(Methyl-decyl)-benzene	4536-88-3	A 215-i	6.5	232		289.0
<i>sec</i> -Butylbiphenyl (A)	38784-93-9			210	ref. 9	290 <sup>i</sup>
Diisopropylnaphthalene	38640-62-9 <sup>h</sup>	DIPN c	37.2	212	Unlisted	291.6
<i>Pentachloroanisole</i>				278		291.7
Diisopropylnaphthalene	38640-62-9 <sup>h</sup>	DIPN d	44.6	212	ref. 45	292.7
1-(Pentyl-heptyl)-benzene	2719-62-2	A 215-j	11.9	246		293.0
1-(Butyl-octyl)-benzene	2719-63-3	A 215-k	11.0	246		293.7
<i>sec</i> -Butylbiphenyl (B)	38784-93-9			210	ref. 9	294 <sup>i</sup>
1-(Propyl-nonyl)-benzene	2719-64-4	A 215-l	7.5	246		295.5
<i>Dibenzothiophene</i>				184		295.9
Diisopropylnaphthalene	38640-62-9 <sup>h</sup>	DIPN e	0.8	212	Unlisted	296.6
Diisopropylnaphthalene	38640-62-9 <sup>h</sup>	DIPN f	0.4	212	Unlisted	297.4
1-(Ethyl-decyl)-benzene	2400-00-2	A 215-m	5.8	246		298.6
<i>Phenanthrene</i>				178		300.0
1-(Methyl-undecyl)-benzene	2719-61-1	A 215-n	3.1	246		304.8
1-(Hexyl-heptyl)-benzene	2400-01-3	A 215	0.2	260		308.3
Diisopropylbiphenyl	69009-90-1	IPB	1.1	238	ref. 9	308.4
1-(Pentyl-octyl)-benzene	4534-49-0	A 215-o	0.6	260		308.5
1-(Butyl-nonyl)-benzene	4534-50-3	A 215-p	0.4	260		309.5
Di- <i>sec</i> -butylbiphenyl (A)	79725-05-6			266	ref. 9	313 <sup>i</sup>
Diisopropylbiphenyl	69009-90-1	IPB	0.9	238	ref. 9	313.9
Di- <i>sec</i> -butylbiphenyl (B)	79725-05-6			266	ref. 9	318 <sup>i</sup>
Triisopropylnaphthalene	35860-37-8	DIPN	0.8	254	Unlisted	318.8
Diisopropylbiphenyl	69009-90-1	IPB	0.2	238	ref. 9	321.2
Triisopropylnaphthalene	35860-37-8	DIPN	0.9	254	unlisted	324.3
Diisopropylbiphenyl	69009-90-1	IPB	0.1	238	Unlisted	326.7
Di- <i>sec</i> -butylbiphenyl (C)	79725-05-6			266	ref. 9	332 <sup>i</sup>
Di- <i>sec</i> -butylbiphenyl (D)	79725-05-6			266	ref. 9	340 <sup>i</sup>
<i>Fluoranthene</i>				202		344.6
Di- <i>sec</i> -butylbiphenyl (E)	79725-05-6			266	ref. 9	351 <sup>i</sup>
<i>Pyrene</i>				202		352.3
4,4'-DDE				316		362.9
Benzyl-ethyl-DPM	42504-55-2	S 100-d	0.4	286	ref. 9	378.4
Methyl-benzyl-dimethyl-DPM	Unknown	S 150-d	0.4	300	Fig. 7(a)	379.0
Benzyl-dimethyl-DPM	50851-34-8	S 150-e	1.2	286	Fig. 7(b)	380.2
Benzyl-ethyl-DPM	42504-55-2	S 100-e	3.5	286	Fig. 5(a)	381.2
Benzyl-ethyl-DPM	42504-55-2	S 100-f	0.5	286	Unlisted	382.7
Benzyl-ethyl-DPM	42504-55-2	S 100-g	5.1	286	Fig. 5(b)	385.5
Benzyl-dimethyl-DPM	50851-34-8	S 150-f	0.3	286	Fig. 7(c)	386.1
Benzyl-ethyl-DPM	42504-55-2	S 100-h	1.1	286	Fig. 5(c)	386.8
Benzyl-ethyl-DPM	42504-55-2	S 100-i	0.6	286	ref. 9	388.3
Benzyl-dimethyl-DPM	50851-34-8	S 150-g	8.0	286	Fig. 7(d)	389.1
Benzyl-ethyl-DPM	42504-55-2	S 100-j	1.4	286	ref. 9	390.1
Benzyl-ethyl-DPM	42504-55-2	S 100-k	0.3	286	Unlisted	390.9
Benzyl-dimethyl-DPM	50851-34-8	S 150-h	0.4	286	ref. 9	392.1
Benzyl-dimethyl-DPM	50851-34-8	S 150-i	6.5	286	ref. 9	393.4
Benzyl-ethyl-DPM	42504-55-2	S 100-l	0.8	286	Fig. 5(d)	396.3
Benzyl-dimethyl-DPM	50851-34-8	S 150-j	0.1	286	ref. 9	397.4
<i>Chrysene</i>				228		400.0
Benzyl-dimethyl-DPM	50851-34-8	S 150-k	0.7	286	Fig. 7(e)	400.7
Benzyl-ethyl-DPM	42504-55-2	S 100-m	1.2	286	Fig. 5(e)	401.3

<sup>a</sup> Compound name listing and identification criteria: All are PCB replacement compounds (printed in roman type), except for ten other compounds included for reference (printed in italics). Compounds constituting a mixture were confidently identified by combining mass spectral and GC chromatographic properties with known or expected synthetic reaction products described in patent literature. Two *sec*-butylbiphenyls and five di-*sec*-butylbiphenyls were tentatively identified based on mass spectral interpretation.

<sup>b</sup> Chemical Abstracts Service registry numbers are listed only for PCB replacement compounds discussed here.

<sup>c</sup> Commercial mixture comprising this compound: A 215-a denotes Alkylate 215, component a as labeled in Fig. 8; S 100-a denotes Santosol 100, component a as labeled in elution order; S 150-a denotes Santosol 150, component a as labeled in elution order; IPB denotes isopropylbiphenyl; DIPN denotes diisopropylnaphthalene.

<sup>d</sup> Percentage composition of the mixture determined by GC/MS.

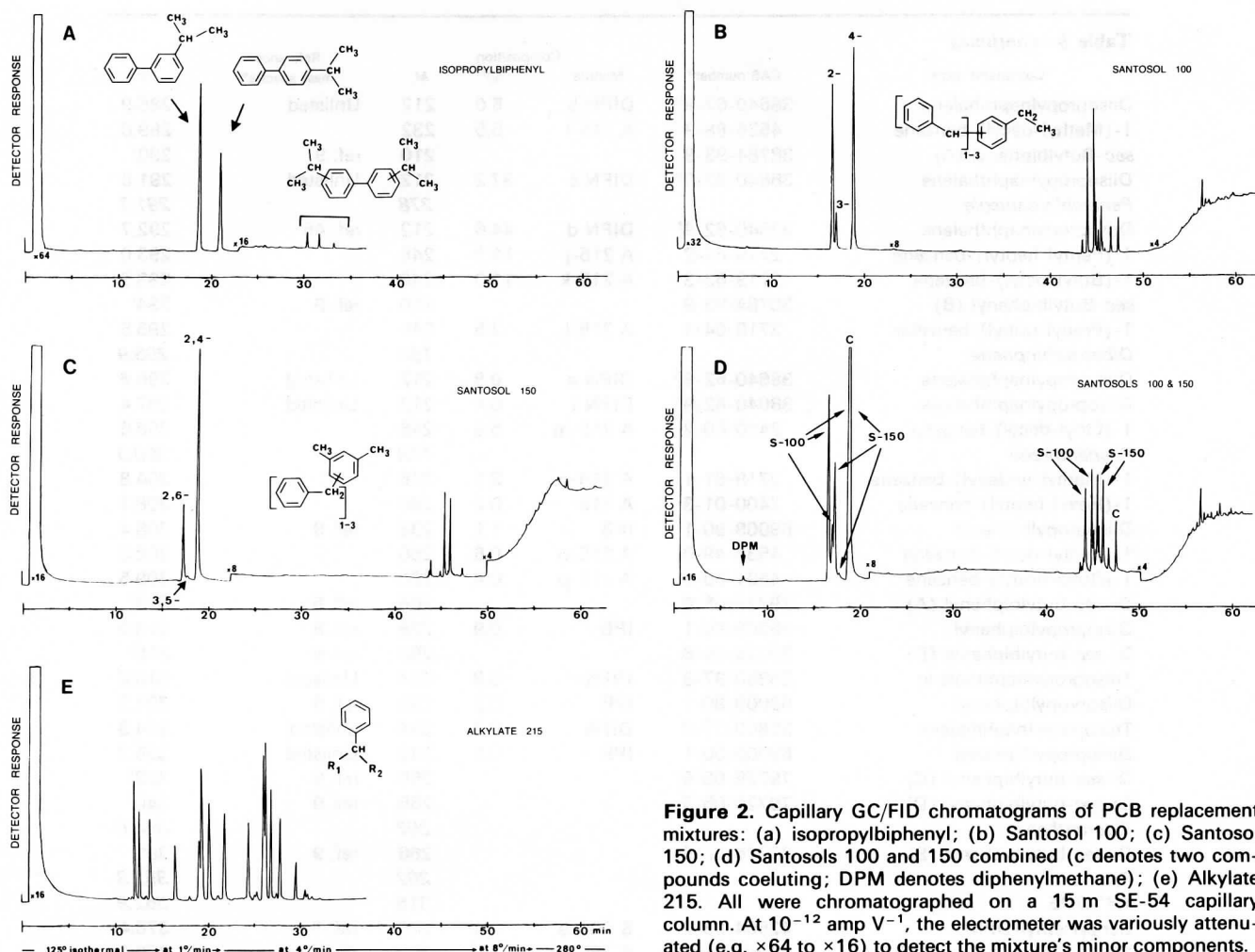
<sup>e</sup> Reference mass spectra are in NIST (EPA/NIH) Library<sup>36</sup> unless designated.

<sup>f</sup> Denotes retention index developed by Lee *et al.*,<sup>11</sup> but using a 30 m × 0.25 mm DB-5 capillary column instead of their 12 m × 0.3 mm SE-52 column. Our GC/MS column was temperature programmed from 45°C (no hold) to 300°C at 4°C min<sup>-1</sup>.

<sup>g</sup> Isomer substitution as hypothesized in text. See also CAS 42504-54-1 for unspecified ethyl-DPM, CAS 32518-97-71 for unspecified dimethyl-DPM, and CAS 25640-78-2 for unspecified IPB.

<sup>h</sup> CAS number for unspecified DIPN. CAS numbers exist for six isomers; four are in commercial use.

<sup>i</sup> RI estimated from sample analyses using different GC conditions.



**Figure 2.** Capillary GC/FID chromatograms of PCB replacement mixtures: (a) isopropylbiphenyl; (b) Santosol 100; (c) Santosol 150; (d) Santosols 100 and 150 combined (c denotes two compounds coeluting; DPM denotes diphenylmethane); (e) Alkylate 215. All were chromatographed on a 15 m SE-54 capillary column. At  $10^{-12}$  amp  $V^{-1}$ , the electrometer was variously attenuated (e.g.  $\times 64$  to  $\times 16$ ) to detect the mixture's minor components.

### IPB mixture identification

The use of IPB as a PCB replacement has been reviewed.<sup>5,15-17</sup> Besides its use as a dielectric fluid in capacitors, this chemical was one of the first PCB replacement leuco dye solvents in carbonless copy paper. Users included NCR Corp./Appleton Papers from about 1971 to 1976<sup>18</sup> and Mead Corp.<sup>19</sup> Because most companies have switched to other PCB replacements, only 0.16–1.6 million kg were sold in 1982 for the manufacture of carbonless copy paper.<sup>16</sup>

A commercial dielectric fluid mixture, Wemcol, that was analyzed<sup>20</sup> not only contained two isomers, 3- and 4-IPB, but also small amounts of diisopropylbiphenyls (DIPBs). Triisopropylbiphenyls (TIPBs) can be trace constituents.<sup>16</sup> The Wemcol composition was similar to that of the capacitor grade furnished to us. The PG and MPG grades (Sybron Corp.) used in carbonless copy paper are chemically similar but contain larger amounts of the DIPBs.<sup>16</sup>

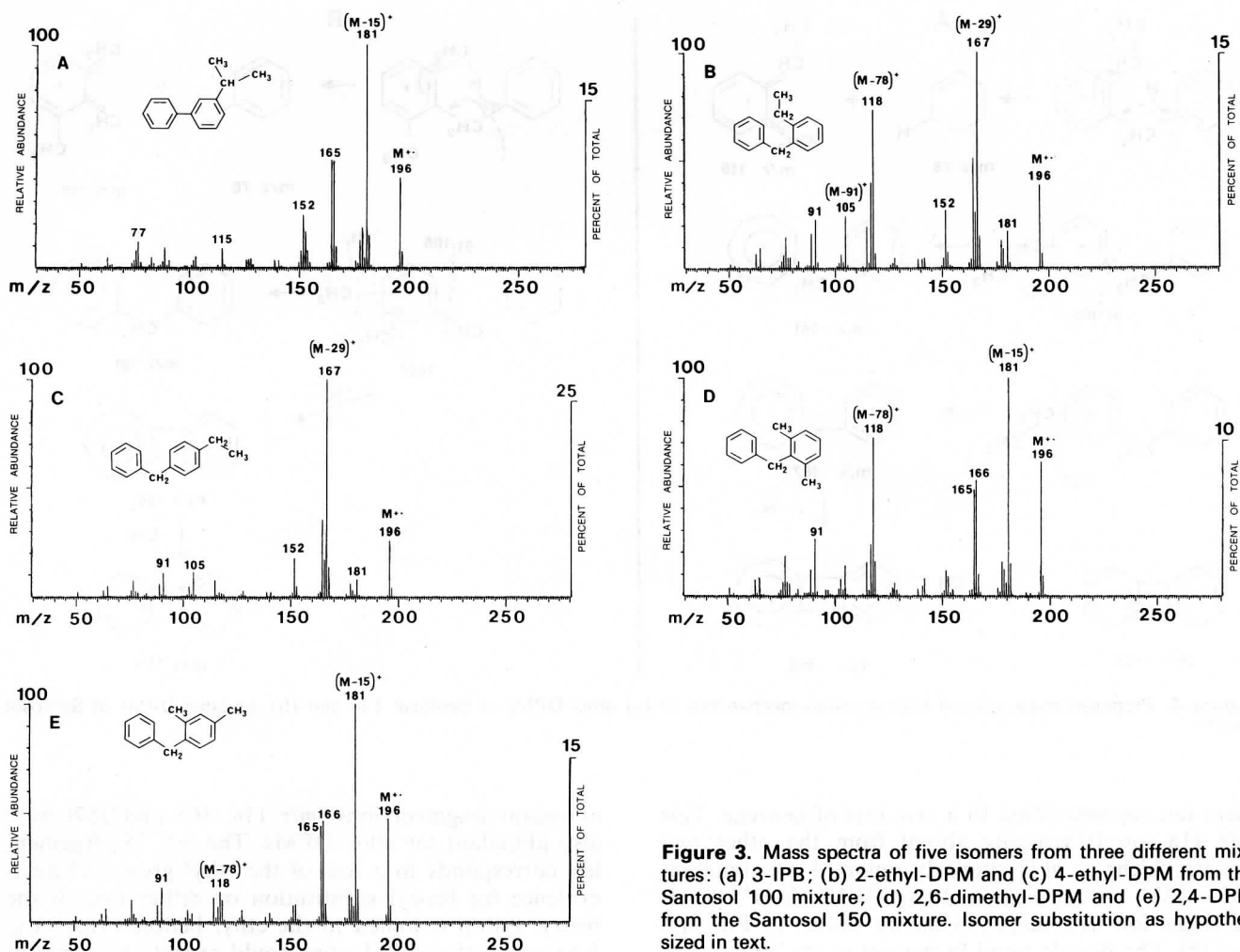
In Fig. 2, capillary GC/FID chromatograms of several PCB replacement mixtures discussed below are compared. The IPB mixture is shown in Fig. 2(a). Similarly in Fig. 3, mass spectra of several related PCB replacement compounds are compared. The mass spectrum of 3-IPB, shown in Fig. 3(a), is representative of both IPB isomers.<sup>9,20</sup> Initially, the two isomers were

differentiated by their GC elution order from the same low-loaded Carbowax 20M gas chromatograph column packing as done by Tulp *et al.*<sup>20</sup> This same elution order held for the capillary column (Fig. 2(a)).

In the walleye sample (Fig. 1), the earliest eluting DIPB isomer was definitively detected as peak 11; traces of the other DIPB isomers from the IPB mixture were detected amidst peaks 12–14. Though difficult to confirm in this fish, DIPBs were confirmed both in wastewaters of the de-inking–recycling mill and in the common carp sample. To avoid confusing DIPBs with another  $M_r$  238 compound, tetrahydroretene, reported by Wakeham *et al.*,<sup>21</sup> analysts should match both GC retention times or RIs and mass spectra.

TIPBs were detected in only one wastewater, a grab sample collected in 1977 when the concentration of the IPB mixture was sufficiently high ( $\sim 0.5$ – $1$  mg  $L^{-1}$ ) to enable detection of all constituents of the mixture (IPBs, DIOBs and TIPBs). Distinctive ions of TIPB mass spectra are the molecular ion  $m/z$  280 (70%),  $m/z$  265 (100%) and  $m/z$  181 (35%). An added secondary treatment stage later helped reduce IPB mixture residues in the mill's wastewaters, but the main reduction occurred when major carbonless copy paper plants switched to the next recent PCB replacement, the alkyl diphenylmethanes of the Santosol 100 mixture.





**Figure 3.** Mass spectra of five isomers from three different mixtures: (a) 3-IPB; (b) 2-ethyl-DPM and (c) 4-ethyl-DPM from the Santosol 100 mixture; (d) 2,6-dimethyl-DPM and (e) 2,4-DPM from the Santosol 150 mixture. Isomer substitution as hypothesized in text.

### Santosol 100 identification

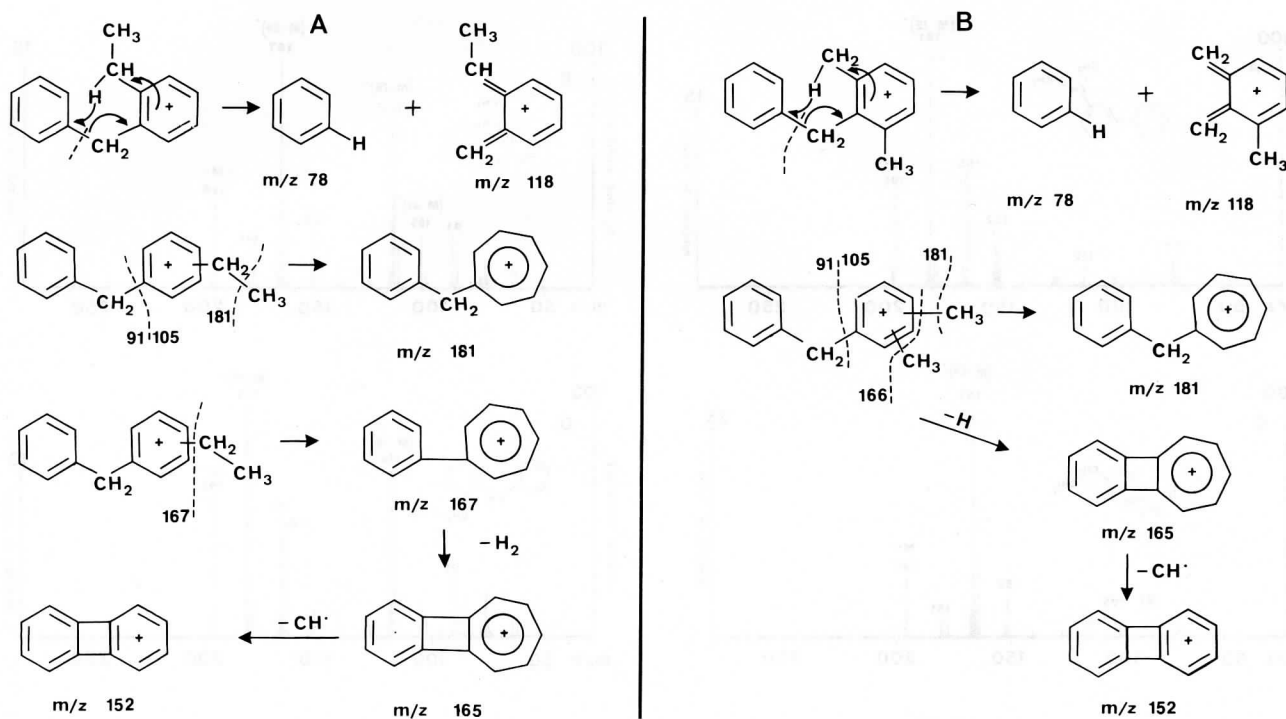
Our analysis of the Santosol 100 dye solvent mixture and our confirmed identification of it in the environment is unprecedented. Chemical production volume is unavailable. It is composed of three groups of related isomers spanning a wide volatility range, as shown by a representative GC/FID chromatogram (Fig. 2(b)).

The ethyl-diphenylmethane (DPM) structure for the first isomer group,  $C_{15}H_{16}$  and  $M_r$  196, was disclosed by Weber.<sup>22</sup> The IUPAC name is ethyl-(phenylmethyl)-benzene. We report this in detail, since they are isomers of IPB and other compounds. Santosol 100 is a mixture of benzylated ethyl benzenes made by reacting benzyl chloride with ethyl benzene. Though additional details were not revealed by the manufacturer, it is known that such a reaction follows a Friedel-Crafts alkylation mechanism.<sup>23</sup> Since the ethyl group in ethyl benzene is *ortho*, *para* directing, it follows that the benzylation would prefer to follow this reaction mechanism. Mixtures of polyalkylated products are often formed.<sup>24</sup> Benzylation occurs several times for Santosol 100, accounting for the three groups of isomers chromatographed (Fig. 2(b)). The presence of mono- to tri-benzylated compounds composing 70%, 25% and 7% within a dye solvent was disclosed in a patent granted to Appleton Papers.<sup>25</sup>

Of the first group of three peaks (Fig. 2(b)), the two largest are very likely the *ortho*- and *para*-substituted isomers, and the smallest is very likely *meta*-substituted. Supporting evidence for specific isomer assignments is based on both GC relative retention and mass spectral differences of these isomers. Louwerse<sup>26</sup> and Habboush and Al-Bazi<sup>27</sup> reported the phenomenon of the *ortho* effect, i.e. *ortho*-substituted compounds eluted earliest through GC columns. Tulp *et al.*<sup>28</sup> used this phenomenon to identify methoxyhalobiphenyls by GC/MS. For either a chlorine or a methoxy substituent, the elution order remained the same, namely, *ortho* < *meta* < *para*. This same order occurs for the ethyl-DPM isomers of Santosol 100 as listed in Table 3.

Mass spectra of 2-ethyl-DPM and 4-ethyl-DPM are shown in Fig. 3(b) and (c). Besides matching peaks 2, 3 and 5 from Fig. 1, they match those from the de-inking-recycling paper mill wastewaters reported previously as characterized, but unidentified spectra.<sup>7</sup> They also match those detected in the Portage WWTP wastewater, which receives process water from the carbonless copy paper manufacturer. The mass spectrum of 3-ethyl-DPM is not included here because it closely matches that of 4-ethyl-DPM.<sup>9</sup>

The mass spectrum of the suspected *ortho* isomer (2-ethyl-DPM) differs from the others. The abundant  $m/z$  118 ion in this spectrum represents a  $[M - 78]^+$  frag-



**Figure 4.** Proposed mass spectral fragmentation mechanisms of (a) ethyl-DPMs of Santosol 100 and (b) dimethyl-DPMs of Santosol 150.<sup>30</sup>

ment ion corresponding to a rare loss of benzene. This  $m/z$  118 ion is virtually absent from the other two spectra. Liehr *et al.*<sup>29</sup> similarly reported an abundant  $[M - 78]^+$  ion for *ortho*-hydroxy-DPM. Hites<sup>30</sup> developed the ion fragmentation theory shown in Fig. 4(a) and (b). The double bond formation at the ring site of each alkyl substituent would enhance this ion's stability and abundance in the mass spectrum.

Compared with IPB mass spectra, the ethyl-DPM mass spectra show significant differences. The  $m/z$  167 ion, representing an ethyl group loss, is abundant in all ethyl-DPM spectra, in contrast to the abundant  $m/z$  181 ion, representing a methyl group loss in IPB spectra. The  $m/z$  91 ion is moderately abundant in the ethyl-DPM spectra but is essentially non-detected in the IPB spectra.

Additional constituents of the Santosol 100 mixture include 10 benzyl-ethyl-DPM isomers having  $C_{22}H_{22}$  and  $M_r$  286. They compose the middle group of peaks shown in Fig. 2(b), which elute between 378.4 and 401.3 RI units. Three of the peaks (31, 32 and 33, Fig. 1) were resolved and identified through GC/MS analysis of the walleye composite extract. The benzyl-ethyl-DPMs were also present in the effluent of the de-inking-recycling mill (site 1), as well as in the wastewaters of the Portage WWTP and in fish collected nearby (site 2). The compounds are derived by the dibenylation of ethyl benzene. Based on the *ortho*, *para* directing nature of the ethyl substituent, the benzyl group would be more likely to substitute on the same ring.

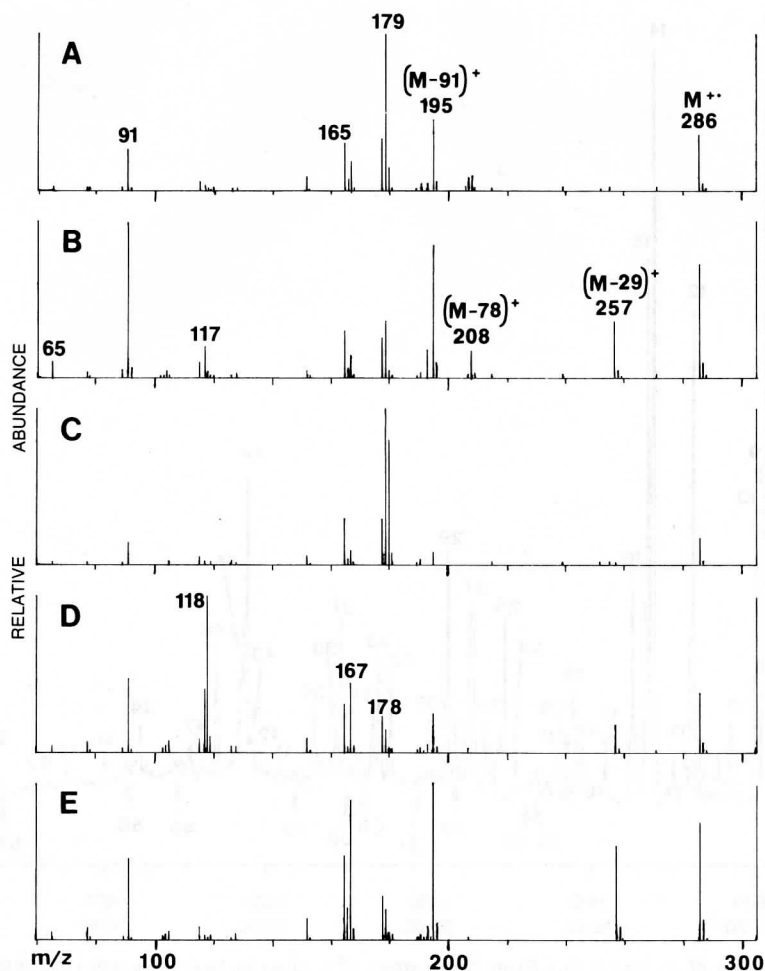
Definitive mass spectra were obtained for eight benzyl-ethyl-DPM peaks (Table 3) that were sufficiently resolved by capillary GC. Because several spectra were very similar, five mass spectra representative of these isomers are shown in Fig. 5. Not surprisingly, some

abundant fragment ions ( $m/z$  118, 165 and 167) were also abundant for ethyl-DPMs. The  $m/z$  257 fragment ion corresponds to a loss of the ethyl group. There is evidence for benzyl substitution on either ring. If the benzyl group is joined to the ethyl benzene ring—e.g. 5-benzyl-2-ethyl-DPM—one could expect an abundant  $m/z$  91 ion and  $[M - 91]^+$  fragment ion at  $m/z$  195, a less abundant  $m/z$  117 ion and a benzene loss of  $[M - 78]^+$  at  $m/z$  208. Spectrum B (Fig. 5) fulfills these postulates. If it is joined to the other ring—e.g. 4'-benzyl-2-ethyl-DPM—the abundant  $m/z$  118 ion discussed earlier (Fig. 4(a)) would be very likely, as in spectrum D (Fig. 5).

The third group of isomers of Santosol 100 consists of several small, very late-eluting peaks (Fig. 2(b)) that correspond to dibenzyl-ethyl-DPMs with  $M_r$  376. Distinctive ions of a representative mass spectrum include  $m/z$  376 (54%),  $m/z$  347 (3%),  $m/z$  285 (36%),  $m/z$  207 (50%) and  $m/z$  91 (100%).

#### GC/MS analysis of a common carp from the Upper Fox River (site 2)

We next discuss additional non-chlorinated PCB replacement compounds identified from the Santosol 150 and Alkylate 215 mixtures. A total ion chromatogram of an extract of the common carp tissue is shown in Fig. 6. The 64 peaks identified are listed in Table 4. Besides  $Cl_{2-5}$  PCBs and several alkanes from  $C_{15}$  to  $C_{22}$ , compounds from three different mixtures (Santosols 100 and 150 and Alkylate 215) were detected. No chlorinated derivatives were present because there was no major use of chlorinating agents at the Portage WWTP, aside from the relatively mild 30 min disinfection-chlorination step performed at the plant.



**Figure 5.** Representative mass spectra of benzyl-ethyl-DPM isomers detected in the Santosol 100 mixture, shown in elution order from top to bottom: (a) peak e; (b) peak g; (c) peak h; (d) peak i; (e) peak m.

### Santosol 150 identification

It was necessary to thoroughly characterize the Santosol 150 dye solvent mixture because the manufacturer's product manager, Weber,<sup>22</sup> disclosed nothing about it other than that it was similar to the Santosol 100 mixture. Comparing the GC/FID chromatograms of Santosol 100 and 150 (Fig. 2), somewhat fewer peaks compose the three groups of Santosol 150 peaks spanning a wide volatility range. When both mixtures are chromatographed together (Fig. 2(d)), a major component of each mixture co-elute at RI 278.5 (Table 3). The mass spectra of the three groups of Santosol 150 peaks also contain molecular ions at  $m/z$  196, 286 and 376, respectively. The additions of 90 daltons each and the diminishing amounts of the higher mass isomers are consistent with the Friedel-Crafts benzylation reaction. Because the groups of isomers produced have the same molecular masses as those of Santosol 100, it follows that Santosol 150 is a mixture of mono-, di- and tri-benzylated xylene(s).

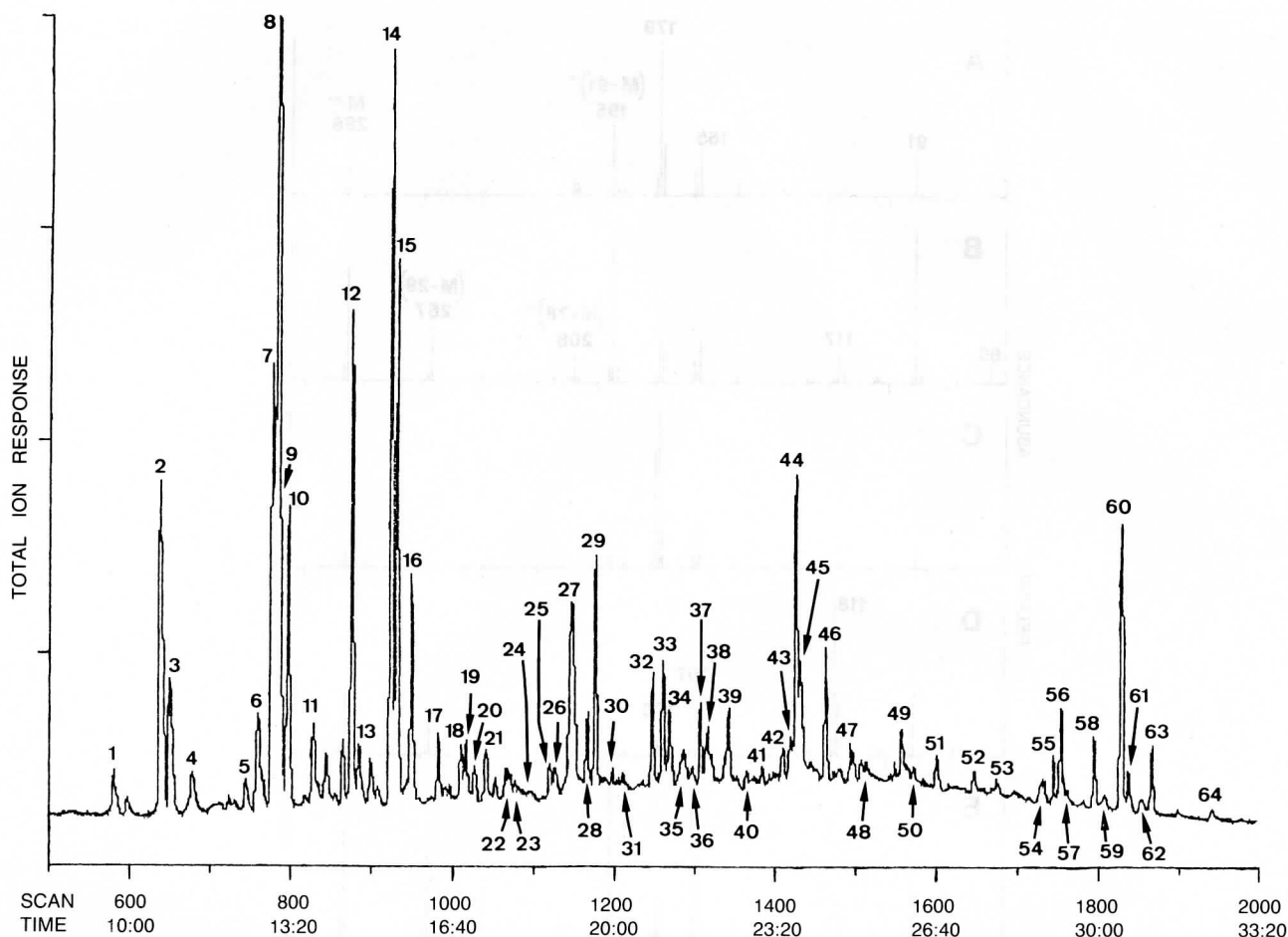
Subsequently, the Santosol 150 mixture was listed as benzylated *m*-xylene.<sup>31</sup> The IUPAC name of the simplest component is 1,3-dimethyl-(phenylmethyl)-benzene or a dimethyl-DPM. Other constituents are benzyl<sub>1-2</sub>-dimethyl-DPMs. Mixed xylenes were not

reactants, because five different  $M_r$  196 isomers would have been formed. The relative amounts of the three early-eluting dimethyl-DPMs are consistent with those expected from benzyl-1,3-dimethyl benzene. The benzyl group would probably not substitute at the 5-position, which is *meta* to each methyl group. Steric considerations would hinder the benzylation at the 2-position (*ortho* to each methyl group), especially between two *meta* substituents.<sup>23</sup> Therefore the 4-position (*ortho*, *para* to the methyl groups) would be the most preferred.

The patent by Wygant<sup>32</sup> explained that only mixtures of benzylated *m*-xylene, *p*-xylene and mixed *m*-, *p*-xylenes have suitably low odor to be superior dye solvents useful in pressure-sensitive copying paper systems. Benzylated *o*-xylene, IPBs and the ethyl-DPMs of Santosol 100 do not have the desired low-odor property, which is apparently the reason that these other mixtures were replaced by at least one manufacturer of carbon-less copy paper.

The mass spectra of the two main dimethyl-DPM peaks of Santosol 150 are shown in Fig. 3(d) and (e). In contrast to the mass spectra of the ethyl-DPMs from Santosol 100 (Fig. 3(b) and (c)), the base peak of each of these is  $m/z$  181. This fragmentation corresponds to the same methyl loss as discussed for the IPB mass spectra (Fig. 3(a)). Similarly, many of the other ions—e.g.  $m/z$





**Figure 6.** Total ion chromatogram of an Upper Fox River carp extract (6% ether in hexanes eluate) chromatographed on a 30 m DB-5 capillary column, temperature programmed from 120 °C (1 min hold) to 280 °C at 4 °C min<sup>-1</sup>. Numbered peaks are identified in Table 4.

166, 165, 152, 115 and 77—compare closely to those in the IPB spectra. Although the mass spectra of both major dimethyl-DPM peaks can be recognized by an  $m/z$  118 fragment ion corresponding to the loss of benzene (Fig. 3(d) and (e)), this ion is abundant only in the mass spectrum of the earliest eluting dimethyl-DPM isomer (RI 275.4).

The early-eluting GC property from the *ortho* effect, and the presence of an abundant  $m/z$  118 ion, both strongly suggest at least one *ortho*-substituted benzyl group as discussed for Santosol 100. In 2,6-dimethyl-DPM at RI 275.4, the benzyl group is *ortho*-substituted to both methyl groups. As discussed above, the second main isomer at RI 278.5 should be the *ortho*, *para*-substituted 2,4-dimethyl-DPM. The very small peak between the two main peaks (Fig. 2(c) at RI 276.1 should be 3,5-dimethyl-DPM.

The second group of Santosol 150 peaks (Figs 2(c) and 6) are very likely benzyl-2,4-dimethyl-DPMs (Table 4), based on the same reaction tendencies ascribed to the benzyl-ethyl-DPMs of Santosol 100. These elute later than 1-C<sub>22</sub>H<sub>46</sub> (Fig. 6) and within the RI range 379–401 (Table 3). Mass spectra of all eight peaks resolved by GC were tabulated.<sup>9</sup> Seven of eight show a molecular ion of  $m/z$  286, whereas one (Fig. 7(a)) represents a methyl-benzyl-dimethyl-DPM having a molecular ion of  $m/z$  300. This compound could arise from

rearrangement of alkyl groups, which may occur with Friedel–Crafts reactions.<sup>23</sup> Because several spectra were very similar, five representative ones are compared (Fig. 7). The four  $M_r$  286 spectra differ slightly from those of Santosol 100 (Fig. 5). Spectra (b), (d) and (e) (Fig. 7) show the  $m/z$  271 ion corresponding to a methyl loss, whereas the corresponding Santosol 100 spectra (Fig. 5) show an  $m/z$  257 ion from an ethyl loss.

Trace components identified in the Santosol 150 mixture include several very late-eluting  $M_r$  376 isomers and an  $M_r$  390 moiety. The  $M_r$  376 isomers correspond to dibenzyl-2,4-dimethyl-DPMs. Compared with that of the  $M_r$  376 isomers of Santosol 100, the mass spectra contain a small  $m/z$  361 ion from a methyl loss, rather than a small  $m/z$  347 ion from an ethyl loss.

#### Alkylate 215 linear alkyl benzene (LAB) identification

The Alkylate 215 mixture, specified in a patent,<sup>33</sup> is a diluent used in the manufacture of carbonless copy paper at Portage, Wisconsin. Production volume is unknown. Its secondary C<sub>10–13</sub>-substituted LAB constituents were previously reported,<sup>7</sup> but their association with one commercial mixture was previously unknown. A GC/FID chromatogram of the mixture is shown in Fig. 2(e). The mixture's 16 components desig-

**Table 4. Compounds identified in an Upper Fox River carp extract**

Peak no. <sup>a</sup>	Compound name	Mixture derived from <sup>c</sup>
1	1-Pentadecane	
2	(1-Butylhexyl)-benzene	A 215-a
3	(1-Propylheptyl)-benzene	A 215-b
4	(1-Ethylloctyl)-benzene	A 215-c
5	2-Ethyl-diphenylmethane (DPM)	S 100-a
6	2,6-Dimethyl-DPM	S 150-a
7	(1-Pentylhexyl)-benzene	A 215-e
8	(1-Butylheptyl)-benzene	A 215-f
9	2,4-Dimethyl-DPM and 4-ethyl-DPM	S 150-c S 100-c
10	(1-Propylloctyl)-benzene	A 215-g
11	(1-Ethylnonyl)-benzene	A 215-h
12	1-Heptadecane	
13	(1-Methyldecyl)-benzene and dichlorobiphenyl	A 215-i PCB
14	(1-Pentylheptyl)-benzene	A 215-j
15	(1-Butylloctyl)-benzene	A 215-k
16	(1-Propylononyl)-benzene	A 215-l
17	(1-Ethyldecyl)-benzene	A 215-m
18-19	Trichlorobiphenyl	PCB
20	2-Octadecane	
21	1-Octadecane, (1-Methylundecyl)-benzene and trichlorobiphenyl	A 215-n PCB
22	Trichlorobiphenyl	PCB
23	(1-Pentylloctyl)-benzene and diisopropylbiphenyl	A 215-o IPB
24	(1-Butylononyl)-benzene	A 215-p
25-27	Trichlorobiphenyl	PCB
28	2-Nonadecane <sup>b</sup>	
29	1-Nonadecane	
30	Trichlorobiphenyl	PCB
31-34	Tetrachlorobiphenyl	PCB
35	2-Eicosane <sup>b</sup>	
36	1-Eicosane	
37-43	Tetrachlorobiphenyl	PCB
44	2-Heneicosane <sup>b</sup>	
45	Tetrachlorobiphenyl and pentachlorobiphenyl	PCB PCB
46	1-Heneicosane	
47-48	Pentachlorobiphenyl	PCB
49	Unknown hydrocarbon	
50-51	Pentachlorobiphenyl	PCB
52	1-Docosane	
53	Pentachlorobiphenyl	PCB
54	Methyl-benzyl-dimethyl-DPM	S 150-d
55	Benzyl-dimethyl-DPM	S 150-e
56	Benzyl-ethyl-DPM	S 100-e
57	Benzyl-dimethyl-DPM	S 150-f
58	Benzyl-ethyl-DPM	S 100-g
59	Benzyl-ethyl-DPM	S 100-h
60	Benzyl-dimethyl-DPM	S 150-g
61	Benzyl-ethyl-DPM	S 100-j
62	Methyl-benzyl-ethyl-DPM	S 100
63	Benzyl-dimethyl-DPM	S 150-i
64	Benzyl-dimethyl-DPM	S 150-k

<sup>a</sup> Peaks numbered in Fig. 7.<sup>b</sup> Tentatively identified by GC/MS. All other compounds confirmed by matching both GC retention times and mass spectra of standard or standard mixture.<sup>c</sup> Commercial mixture comprises this compound: A 215-a denotes Alkylate 215, component a as labeled in Fig. 8; S 100-a denotes Santosol 100, component a as labeled in elution order; S 150-a denotes Santosol 150, component a as labeled in elution order; IPB denotes isopropylbiphenyl; PCB denotes polychlorinated biphenyl.

nated with letters 'a-p' in elution order are shown in Fig. 8 with mass chromatograms of their respective molecular ions. All 16 components elute between 1-C<sub>15</sub> and 1-C<sub>19</sub> alkanes and 13 of them elute within the RI range 263.1-309.5 (Table 3). Our GC/MS data resemble those reported for detergent alkylates or LABs.<sup>34,35</sup>

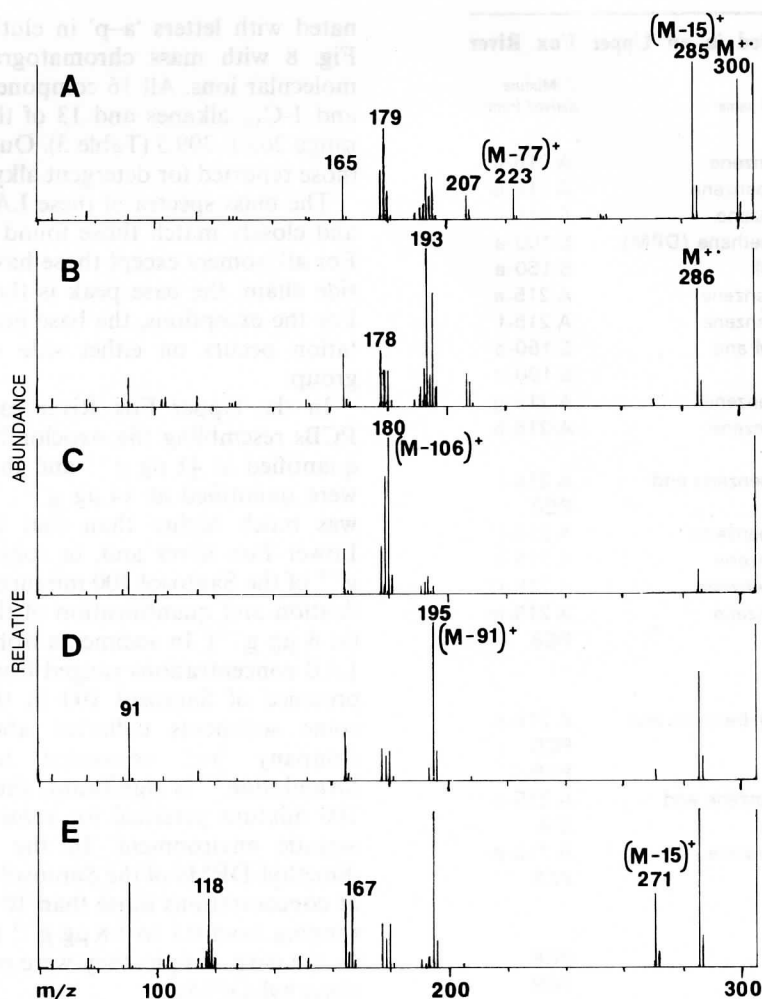
The mass spectra of these LABs have been reported<sup>9</sup> and closely match those found in the NIST Library.<sup>36</sup> For all isomers except those having a methyl group as a side chain, the base peak is the tropylium ion, *m/z* 91. For the exceptions, the base peak is *m/z* 105. Fragmentation occurs on either side of the phenylmethyle group.

In the Upper Fox River carp sample (4.7% lipid), PCBs resembling the Aroclor 1242/1248 mixtures were quantified at 41 µg g<sup>-1</sup> and the LABs as Alkylate 215 were quantified at 44 µg g<sup>-1</sup>. The LAB concentration was much higher than that found in fish from the Lower Fox River and, in conjunction with several µg g<sup>-1</sup> of the Santosol 100 mixture, complicated the identification and quantification of the Santosol 150 mixture (at 8 µg g<sup>-1</sup>). In sediments from the Upper Fox River, LAB concentrations ranged from 0.2 to 26 µg g<sup>-1</sup>. The presence of Santosol 100 in the carp sample and in some sediments collected about 2 years after the company had converted to the Santosol 150 formulation<sup>37</sup> is significant, showing that the Santosol 100 mixture persisted for some time in that particular aquatic environment. In the sediments, the benzyl-dimethyl-DPMs of the Santosol 150 mixture were found at concentrations more than 10 times higher than those ranging from 0.1 to 1.8 µg g<sup>-1</sup> for the dimethyl-DPMs. In the carp sample, they were only twice as high as the dimethyl-DPMs.

From the total ion chromatogram of the carp sample (Fig. 6) and compounds identified in the extract (Table 4), it is clear that certain LABs were selectively degraded as similarly reported by Eganhouse *et al.*<sup>35</sup> Although most were environmentally persistent, LAB isomers progressively degraded according to how close the phenyl group was to the end of the alkyl chain.<sup>35</sup> In our carp sample, other fish and sediment samples, and even to some extent in wastewaters from the Fox River area, some LABs were selectively degraded, especially component 'd', (1-methylnonyl)-benzene. Bayona *et al.*<sup>38</sup> demonstrated such selective biodegradation by aerobic bacteria. Albaigés *et al.*<sup>39</sup> found LABs in fish from the western Mediterranean Sea.

#### Tentative identification of *sec*-butylbiphenyls

Other PCB replacements associated with carbonless copy paper were tentatively identified, and are included in Table 3. Two *sec*-butylbiphenyls and at least three di-*sec*-butylbiphenyls were tentatively identified by GC/MS in an effluent sample collected in late 1981 from the Portage WWTP and in the FWS walleye sample. Full range mass spectra have been reported.<sup>9</sup> In brief, for *sec*-butylbiphenyl, the molecular ion is *m/z* 210 (55%) and characteristic ions are *m/z* 181 (base peak), *m/z* 165 (30%), *m/z* 166 (25%) and *m/z* 152 (15%). For di-*sec*-butylbiphenyl spectra, the molecular ion is *m/z* 266 (45%) and the base peak is also the [M - 29]<sup>+</sup>



**Figure 7.** Representative mass spectra of the second group of peaks detected in the Santosol 150 mixture, shown in elution order from top to bottom: (a) peak d; (b) peak e; (c) peak f; (d) peak g; (e) peak k.

fragment ion,  $m/z$  237. Less abundant ions (<20%) include  $m/z$  209, 181, 165 and 152. The loss of 29 is consistent with that of two *sec*-butyl compounds<sup>40</sup> and the added mass of 56 corresponds to an additional butyl group.

Confirmation was not possible because a standard was not available, but supporting evidence exists. The mixture Suresol 290 (Koch Industries) has been listed as a dye solvent for carbonless copy paper;<sup>41</sup> its use was acknowledged,<sup>42</sup> but chemical production volume is unavailable. The relative amounts of *sec*-butylbiphenyls and di-*sec*-butylbiphenyls detected were consistent with those reported in a patent.<sup>43</sup> The dye solvent (*sec*-butylbiphenyl) and the diluent ( $C_{10-13}$  alkyl benzenes) were specified in a recent patent for carbonless copy paper.<sup>44</sup>

#### GC/MS analysis of FWS fish sample from the Lower Fox River, Green Bay, Wisconsin

In the FWS walleye composite sample prepared for PAH analyses, all PCB replacement mixtures listed in Table 3 except the Alkylate 215 mixture were detected. Also tentatively identified were several chlorinated  $C_2$ -DPMs. The LABs of Alkylate 215 may have been excluded by the sample enrichment procedure. In addition

to those already discussed, four isomers of diisopropylnaphthalene (DIPN) at RI 285.1, 285.9, 291.6 and 292.7 were also identified on the basis of GC and mass spectral comparisons with a commercial mixture of DIPNs. Mass spectra of all four isomers have similar ions with only slight variations in abundance, and, except for the lack of  $m/z$  78, matched the abbreviated mass spectrum previously reported.<sup>45</sup> The molecular ion  $m/z$  212 ranged from 65 to 90% of the base peak  $m/z$  197 and the fragment ion  $m/z$  155 ranged from 35 to 65%.

The relative amounts of the DIPN isomers detected in the fish extract differ significantly from the standard mixture furnished to us and also from those detected in sludge and wastewater from a paper mill outside the Fox River area at Oconto Falls, Wisconsin. In our standard mixture, six DIPN isomeric peaks eluted in three pairs. The earliest DIPN isomers (a and b) each constituted about 5%; later-eluting isomers (c and d) constituted 37% and 45%, respectively, and latest-eluting isomers (e and f) each constituted less than 1%. In the fish extract, the concentrations of isomers a and c were about equal; isomers b and d were half that of a and c; and isomers e and f were not detected. DIPN used for carbonless copy paper may differ or our method may



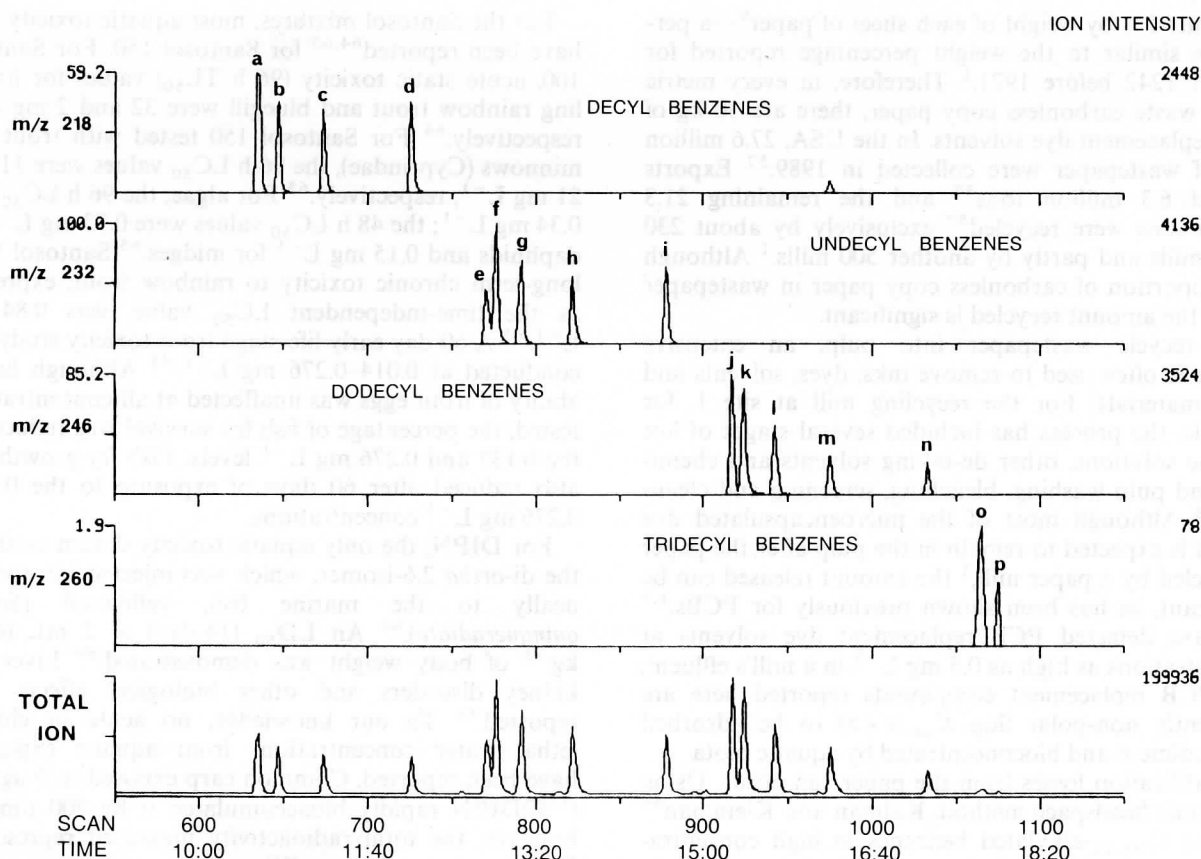


Figure 8. GC/MS analysis of the Alkylate 215 mixture chromatographed on a 30 m DB-5 column with the same conditions as given in Fig. 6.

have discriminated against certain isomers; however, it is much more likely that the fish selectively metabolized certain DIPN isomers, as found in an exposure study.<sup>45</sup> Isopropyl-naphthalene, triisopropyl-naphthalenes and other minor constituents (<1%) of the DIPN mixture were not detected in the fish sample.

DIPN has been widely used as a dye solvent in carbonless copy paper made in Japan and may now be similarly used in the USA.<sup>46,47</sup> Two chemical company representatives reported knowing no other uses.<sup>46</sup> According to the TSCA database of September 1983,<sup>48</sup> DIPN was produced by five US companies, two of which also imported it. Of those reporting, American Cyanamid Co., Pleasants, West Virginia, had the largest amount, ranging from 4.5 to 22.5 million kg yr<sup>-1</sup>.<sup>48</sup>

In Japan, DIPN has been detected in fish,<sup>49</sup> river sediment downstream from a wastepaper recycling plant,<sup>13,50</sup> river water and sediments<sup>53</sup> and Tokyo Bay.<sup>54</sup> In river sediments, Sato<sup>50</sup> reported DIPN concentrations of 0.3–23 µg g<sup>-1</sup>.

Although 191 PAHs were found totaling 313 µg g<sup>-1</sup> in Lower Fox River sediment collected nearby,<sup>53</sup> few PAHs were detected in the FWS fish sample; most were less than 50 ng g<sup>-1</sup>. Fish are known to metabolize PAHs, often to carcinogenic forms.<sup>54</sup> In the FWS fish sample, PCBs totaled 16 µg g<sup>-1</sup>, PCB replacements 2 µg g<sup>-1</sup>, and PAHs 0.5 µg g<sup>-1</sup>. Concentrations of PCB replacements are estimates, however, because method-spiked recoveries are unavailable. Santosol 150 components totaled 0.9 µg g<sup>-1</sup>, *sec*-butylbiphenyls 0.4 µg

g<sup>-1</sup>, Santosol 100 components 0.2 µg g<sup>-1</sup>, diisopropyl-naphthalenes 0.1 µg g<sup>-1</sup> and isopropylbiphenyls 0.07 µg g<sup>-1</sup>.

In summary, a variety of non-polar PCB replacement compounds (Table 3) have been detected together in a complex sample extract and separately in fractions that also contained PCBs, organochlorine pesticides and PAHs. From Florisil, LABs elute similar to that of PCBs. From Silica gel, C<sub>2</sub>-DPMs elute similar to that of 4-ring PAHs, but benzyl-C<sub>2</sub>-DPMs require a stronger eluant. The specific procedures and measured concentrations of these PCB replacements in wastewater, sludge, river water, sediment and fish of the Upper Fox River System is to be reported later. Also, PCB replacement compounds have been reported elsewhere in Wisconsin<sup>55</sup> (based on our laboratory results). In samples collected for the National Contaminant Bio-monitoring Program<sup>56</sup> and analyzed by GC/MS, PCB replacement compounds were found in fish from the Hudson River, New York; Raritan River, New Jersey; and Ohio River, Ohio. Alkyl-DPMs were found in three samples, IPBs and LABs in two, and DIPNs and *sec*-butylbiphenyls in one sample each.

#### Potential for environmental occurrence of PCB replacement compounds used in carbonless copy paper

During the manufacture of carbonless copy paper, PCB replacement compounds are microencapsulated,<sup>2</sup> and

constitute 3% by weight of each sheet of paper<sup>9</sup>—a percentage similar to the weight percentage reported for Aroclor 1242 before 1971.<sup>1</sup> Therefore, in every metric ton of waste carbonless copy paper, there are 30 kg of PCB replacement dye solvents. In the USA, 27.6 million tons of wastepaper were collected in 1989.<sup>57</sup> Exports totalled 6.3 million tons<sup>57</sup> and the remaining 21.3 million tons were recycled<sup>57</sup> exclusively by about 230 paper mills and partly by another 500 mills.<sup>1</sup> Although the proportion of carbonless copy paper in wastepaper varies, the amount recycled is significant.

To recycle wastepaper into pulp, an extensive process is often used to remove inks, dyes, solvents and other materials. For the recycling mill at site 1, for example, the process has included several stages of hot alkaline solutions, other de-inking solvents and chemicals, and pulp washing, bleaching, screening and cleaning.<sup>1,58</sup> Although most of the microencapsulated dye solvent is expected to remain in the pulp after the paper is recycled by a paper mill,<sup>1</sup> the amount released can be significant, as has been shown previously for PCBs.<sup>1,7</sup> We have detected PCB replacement dye solvents at concentrations as high as 0.5 mg L<sup>-1</sup> in a mill's effluent. The PCB replacement compounds reported here are sufficiently non-polar (log  $K_{ow} \geq 4.8$ ) to be adsorbed onto sediment and bioconcentrated by aquatic biota.

Volatilization losses from the paper can occur. Using a dynamic headspace method, Kalman and Kleinman<sup>59</sup> detected C<sub>10-12</sub>-alkylated benzenes in high concentrations in a closed atmosphere surrounding carbonless copy paper. During an indoor air investigation in Europe, 'santosol' content in paper was reported;<sup>60</sup> however, the composition of hydrogenated terphenyls, very likely from the Santosol 340 or HB40 mixtures,<sup>15,61</sup> differed from that in the Santosols 100 and 150 mixtures used in the USA.

#### Reported aquatic toxicity and preliminary assessment of environmental significance of PCB replacement compounds used in carbonless copy paper

Static fish toxicity data for the IPB mixture (Wemcol) have been reported.<sup>62</sup> Acute 96 h LC<sub>50</sub> toxicity of 4.0 mg L<sup>-1</sup> for bluegill (*Lepomis macrochirus*) and 2.5 mg L<sup>-1</sup> for rainbow trout (*Oncorhynchus mykiss*) approach the mixtures's solubility of 10 mg L<sup>-1</sup> in water.<sup>62</sup> A river die-away test showed that more than 80% of IPB biodegraded in 48 h in both river soil and water.<sup>62</sup> For point sources such as a recycling paper mill whose releases may be continual, this test may be unrealistic. When reviewing IPB, Mercier<sup>62</sup> acknowledged that when high levels of any material are repeatedly introduced into the environment, excessive and potentially toxic residual levels can build up, despite the fact that the material is biodegradable.

For the LAB mixture, Alkylate 215, and for other LAB mixtures, aquatic toxicity data are not available. LAB microbial degradation was recently compared with LAB degradation in river and Tokyo Bay sediments.<sup>63</sup> Although the total LAB mixture degraded rapidly (45%) after 3 days of aerobic incubation, certain LAB isomers persisted and have persisted in sediments for years.<sup>63</sup> During 6 days of anaerobic incubation, all LABs degraded very slowly.<sup>63</sup>

For the Santosol mixtures, most aquatic toxicity data have been reported<sup>64,65</sup> for Santosol 150. For Santosol 100, acute static toxicity (96 h TL<sub>50</sub>) values for fingerling rainbow trout and bluegill were 32 and 2 mg L<sup>-1</sup>, respectively.<sup>64</sup> For Santosol 150 tested with trout and minnows (Cyprinidae), the 96 h LC<sub>50</sub> values were 11 and 21 mg L<sup>-1</sup>, respectively.<sup>65</sup> For algae, the 96 h LC<sub>50</sub> was 0.34 mg L<sup>-1</sup>; the 48 h LC<sub>50</sub> values were 0.72 mg L<sup>-1</sup> for daphnids and 0.15 mg L<sup>-1</sup> for midges.<sup>65</sup> Santosol 150's long-term chronic toxicity to rainbow trout, expressed as the time-independent LC<sub>50</sub> value, was 0.84 mg L<sup>-1</sup>.<sup>65</sup> A 60-day early life-stage trout toxicity study was conducted at 0.014–0.276 mg L<sup>-1</sup>.<sup>65</sup> Although hatchability of trout eggs was unaffected at all concentrations tested, the percentage of fish fry survival was reduced at the 0.137 and 0.276 mg L<sup>-1</sup> levels. Fish fry growth was also reduced after 60 days of exposure to the 0.061–0.276 mg L<sup>-1</sup> concentrations.

For DIPN, the only aquatic toxicity datum exists for the di-*ortho* 2,6-isomer, which was injected intraperitoneally to the marine fish, yellowtail (*Seriola quinqueradiata*).<sup>66</sup> An LD<sub>50</sub> (14-day) of 2 mL (or g) kg<sup>-1</sup> of body weight was demonstrated.<sup>66</sup> Liver and kidney disorders and other biological effects were reported.<sup>66</sup> To our knowledge, no acute or chronic lethal water concentrations from aquatic exposures have been reported. Common carp exposed to 5 µg L<sup>-1</sup> (<sup>14</sup>C)DIPN rapidly bioaccumulated it by 200 times;<sup>67</sup> however, the total radioactivity measured represented DIPN and metabolites. When removed to clean water, the carp cleared 50% within 56 h. Several metabolites of 2,6-DIPN have been identified,<sup>68,69</sup> but their toxicological significance is unknown.

The US Interagency Testing Committee associated with the Toxic Substances Control Act reviewed DIPN before it was significantly used in the USA.<sup>46</sup> DIPN isomers were expected to partition onto soil organic matter and to show a tendency to bioconcentrate. However, bioconcentration would be limited by moderately rapid metabolism.<sup>46</sup>

Obviously, more aquatic research is needed on these PCB replacements. Bioavailability, acute and chronic toxicity, metabolism, persistence and fate should be studied.

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## CONCLUSIONS

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Initially, our environmental monitoring for PCBs led to the discovery of non-chlorinated PCB replacement dye solvents and related chlorinated derivatives by GC/MS. With GC/MS analyses of the commercial mixtures, we confirmed our identifications and detailed both chromatographic RIs and mass spectra. Except for the LABs, no mass spectra of any other PCB replacement compounds discussed here have yet been cataloged in either the NIST Library<sup>36</sup> or the Wiley Library.<sup>70</sup> Until our submitted mass spectra are cataloged by NIST, analysts using GC/MS with a survey-analytical approach may not recognize these PCB replacements. One researcher<sup>71</sup> reported finding no Santosol components in fish collected from the Fox River; however, dimethyl-phenylmethyl-benzene was tentatively identi-

fied and was likely a major component of the Santosol 150 mixture.

Constituting about 3% by weight of carbonless copy paper, dye solvents can be inadvertently released to the aquatic environment from wastepaper in significant amounts by de-inking-recycling paper mills. Chlorinated derivatives of PCB replacement dye solvents can be formed when chlorinating agents are present in high concentrations; e.g. when pulp is bleached. Such chlorinated PCB replacement compounds include alkyl-PCBs. Extant evidence suggests that both non-chlorinated and chlorinated compounds are lipophilic, accumulate in sediment and to some extent in fish, and most are moderately toxic. Our findings suggested that the environmental fate of new PCB replacement chemicals used in open systems such as carbonless copy paper should be studied more thoroughly. Investigations should be performed in other aquatic systems

where similar PCB replacement manufacturing plants and paper mills that recycle wastepaper are located. Aquatic research should assess bioavailability, acute and chronic toxicity, metabolism and persistence.

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