Monsanto INDUSTRIAL CHEMICALS CO.

FROM (NAME & LOCATION): R. E. Keller - T1B - St. Louis

DATE: August 15, 1975

SUBJECT: CHLORINATED DIBENZOFURANS

REFERENCE:

TO: R. Baxter
LLN - 5045

cc: H. S. Bergen - B2SL
R. A. Liggett - LLN - 5045
J. P. Moeure - T2F
R. H. Munch - T1B
W. B. Papageorge - B2SK
W. R. Richard - T3A
D. Wood - B2SD

Dick,

In June this year a plan was developed with Bill Papageorge and others to learn more about chlorinated dibenzofurans in our Aroclor products. As a part of this plan it was decided that furans standards should be prepared and analytical methodology developed for the detection of at least 0.1 ppm for each furan homolog. Laboratory mixtures of monochloro- through hexachlorodibenzofurans have been prepared and characterization for homolog distribution is underway. Also, we have about one-man continuous effort on the method development work.

As part of the plan it was decided that we should determine if Bayer has carried out "in-house" work of this type. The attached June 16 memo from Dave Wood to J. N. Haggart covers a request for this information. We have had no reply to this correspondence to our knowledge. Any information or assistance you can provide on this point will be appreciated.

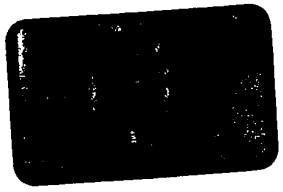
During the past week a publication has appeared in the literature entitled "Identification of Chlorinated Dibenzofurans in American Polychlorinated Biphenyls" by R. W. Risebrough et al. of the University of California. A copy of this paper is attached. It shows the identification of chlorinated dibenzofurans in our Aroclor products except Aroclor 1016. We are now anxious to develop our own data for comparison with this publication.

Regards,

Bob K

R. E. Keller

SS
Attachments(2)





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D. Wood - St. Louis

① Xc R Kailer

June 16, 1975

② CHLORINATED DIBENZYLFURANS

H. S. Bergen - B2SL
W. B. Papageorge - B2SK
J. Mieure - T2F
R. H. Munch - T1B
C. Paton - B2SC

J. N. Haggart
5040

John,

You will recall that Dutch researchers (Voss et al) found furans in chlorinated biphenyls produced by Prodelec and Bayer some four years ago.

Recently FDA has claimed to have detected these products in Aroclor and we will possibly see increased publication about these toxic contaminants develop.

It would be appropriate to establish a technical dialogue with Bayer if they have carried out "in house" work in this area and Ralph Much will be writing to Dick Baxter about this.

We need to develop our own methods to determine if indeed the chlorinated dibenzylfurans are present and what is the potential hazard. I am asking Ralph to send copies to you when he contacts Dick in case there are any business implications in establishing such a technical contact of which we are not aware.

Regards,

D. Wood

/pep

Bob - As I recall Ralph or Ralph and yourself jointly were going to follow up on my advice to brunels product group.

David

I suggest you write to Baxter referencing my Hoeme to Haggart

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(2)

(3)

San Francisco. These conditions would lead to increased tree growth during the following growing season (Fig. 4).

Autumn and winter climatic anomaly features, combined with spring climate and the year-to-year autocorrelation of tree-ring widths, produce the other ring-width anomaly features in Fig. 4 for the following growing season. Narrow ring widths south of San Francisco, for example, imply below normal precipitation—an expected feature since winter precipitation in the Pacific North-west is negatively correlated with winter precipitation in southern California[6].

The reconstructed values of albacore catch distribution data (Fig. 3) and inferred population distribution also seem to exhibit long term changes over intervals of 100 yr or more, which suggest the possibility that long term fluctuations in the ocean–atmosphere system may be involved.

The success of the calibration of tree rings with albacore catch indicates the possibility of relating tree-ring variations to any type of biological variations which are affected by large scale climatic fluctuations. Such relationships may be quantified and used to reconstruct objectively other climatically-caused biotic variations in the past.

N. E. Clark

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Oats may grow better in water depleted in oxygen 18 and deuterium

While growing oats at different temperatures in water of different ^{18}O and deuterium (D) abundances, we noticed that oats grown in Antarctic water in which is depleted in ^{18}O and D by $-49‰$ and $-400‰$ relative to standard mean ocean water (SMOW used as a comparative reference in hydrogen and oxygen isotope studies), showed initial growth 1–2 weeks sooner than did oats grown in water containing greater ^{18}O and D concentrations. The oats seemed to grow better in water which was most depleted in the stable isotopes throughout the growth period.

The oats were grown from the same batch of seeds in two sealed glass-covered glass jars (approximately 10 l). Twenty-five oat seeds were added to each jar, containing the same amount of vermiculite and 500 ml water to which 5.0 g Rapid-Gro, a commercial fertiliser, had been added. One jar contained melted glacial ice from the Antarctic with isotope concentrations of $-49‰$ $\delta^{18}O$ (SMOW) and $-400‰$ δD (SMOW). The other jar contained distilled ocean water with $+1.0‰$ $\delta^{18}O$ (SMOW) and $+17‰$ δD (SMOW). Both jars were placed in the chamber at the same time.

The experiment was repeated three times with new materials: once the growth chamber was maintained between 1.7 and 3.3 C; once between 24 and 26.6 C; and once the temperature fluctuated between 1.7 and 26.6 °C. Each time the oats in the jar containing water depleted in the heavy isotopes showed germination 1–2 weeks earlier and seemed to grow better throughout the growth period, than oats grown in distilled ocean water.

Using oats grown at 15 °C, the first sign of germination in the jar containing water depleted in the heavy isotopes was 4 d after planting. On the day 6, eight plants (out of 25) had attained a height of 6 cm. The first sign of germination in the jar with water containing the heavier isotope concentration, was after 17 d. By the time five plants had attained a height of 6 cm in this jar, in that with water depleted in the isotopes, 23 plants that had reached the top of the jar (approximately 25 cm).

Kashutin[1] observed that snow-water depleted in D increases the yield of cucumbers, radishes and spring wheat compared with controls grown in ordinary water of unspecified isotopic composition. He cites experiments on the egg productivity of hens and the weight gain of suckling pigs. In both cases water depleted in D was especially efficient in promoting productivity.

Although much has been done on the effect of D-enriched water on biological systems, we suggest that research on the effect D-depleted water on plant and animal growth may prove fruitful. A major source of water depleted in D by over $-400‰$ ($-40°$) compared with SMOW is snow and ice from the Antarctic polar plateau. Water depleted by -150 to $-180‰$ is readily available in the USA from Rocky Mountain snow precipitating above 10,000 feet elevation.

Jim D. Gleason
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Identification of chlorinated dibenzofurans in American polychlorinated biphenyls

Mortality of embryos has contributed to the reproductive failures of several bird species, including the sparrowhawks (*Accipiter nisus*) of southern Scotland[1], the white-tailed eagles (*Haliaeetus albicilla*) of Schleswig Holstein[2], and the herring

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gulls (*Larus argentatus*) of Lake Ontario[3]. Suspected [illegible] include *p,p'*-DDE [2,2-bis-(*p*-chlorophenyl)-1,1-dichlor[illegible]lene], other chlorinated biocides and/or their deriv[illegible], and the polychlorinated biphenyls (PCBs), all of which are present as contaminants in the eggs[1-3]. PCBs are present in high concentrations in the bird populations which suffer embryonic mortality[1-3]. Other organochlorine compounds which may be present in food webs include the chlorinated dibenzodioxins and the chlorinated dibenzofurans (Fig. 1), which are toxic to embryos in amounts[4-7] less than 1 μg. They are therefore among the most toxic substances known and are possible causes of the observed mortality.

The chlorinated dibenzodioxins and chlorinated dibenzofurans, however, have proved exceedingly difficult to detect in environmental samples in the concentrations at which they are expected to be embryotoxic[8-10]. The chlorinated dibenzodioxins enter the environment as contaminants in preparations of the herbicide 2,4,5-T (refs 5 and 11) and the fungicide pentachlorophenol[12,13]. Chlorinated dibenzofurans have been found in a French (Phenoclor DP6) and a German (Clophen A60) PCB and were shown to be the active embryotoxic agent in these preparations[6]. The techniques used, however, did not detect chlorinated dibenzofurans in an American PCB, Aroclor 1260. We report here the presence of chlorinated dibenzofurans in Aroclor PCB, widely used in North America and Great Britain, and in the same Aroclor 1260 preparation examined previously with negative findings[6].

Samples of PCB examined include: Aroclor 1248, 1254, and 1260 (1969); Aroclor 1254 (1970); Aroclor 1016 (1972); and the same three preparations studied by Vos *et al.*[6]: Aroclor 1260, lot No. AK-3; Clophen A-60, lot No. 912434; and Phenoclor DP-6, lot not specified. The latter three PCBs were obtained from Dr Vos, the others from the Monsanto Company in the years indicated in parentheses.

PCBs extracted from environmental samples most often have gas chromatographic profiles similar to those of PCB formulations containing approximately 48, 54 or 60% chlorine. In the Aroclor series, the former two PCBs are equivalent to Aroclor 1248 and Aroclor 1254, respectively. Aroclor 1260, Phenoclor DP6, and Clophen A60 all contain approximately 60% chlorine.

Chlorinated dibenzofurans were identified in all Aroclor preparations except Aroclor 1016, as well as in Clophen A60 and Phenoclor DP6. Aroclor 1016 is a PCB mixture containing approximately 42% chlorine and has replaced Aroclor 1242 in many applications, principally as the dielectric fluid in capacitors[14]. Values reported in Table 1 represent the total of those compounds found in 400 ml Florisil fractions 2-6. A total of 10-12 isomers was identified in each PCB. Two chlorinated dibenzofuran contaminants have been reported for the Clophen and Phenoclor previously[6]; our first analyses of the Clophen revealed an additional five chlorinated dibenzofurans[9]. The structures contained four to six chlorine atoms. Other dibenzofurans including those chlorinated to a lesser extent may have been present in the first 400 ml fraction but this was not examined in detail as it contained substantial PCB interference. Recently synthesised 2,3,7,8-tetra-, 2,3,4,7,8-penta- and 2,3,4,6,7,8-hexachlorodibenzofuran were used to quantify tetra-, penta-, and hexachlorodibenzofurans, respectively. The former two authentic standards had retention times on the OV1 column the same as those of two dibenzofurans isolated from the PCB.

Vos *et al.*[6] detected no chlorinated dibenzofurans in an Aroclor 1260 preparation at a detection limit of 1 p.p.m. Fractionation and examination of the identical Aroclor 1260 in our study confirm their findings based on the stated limit, but reveal the presence of 11 chlorinated dibenzofurans in the preparation, having a total concentration of 0.6 μg g^{-1} PCB (Table 1). The same workers also found diethyl ether extracts of the Clophen A60 and Phenoclor DP6 to be much more toxic to chick embryos than diethyl ether extracts of Aroclor 1260. Our study confirms those findings on the basis of chlorinated

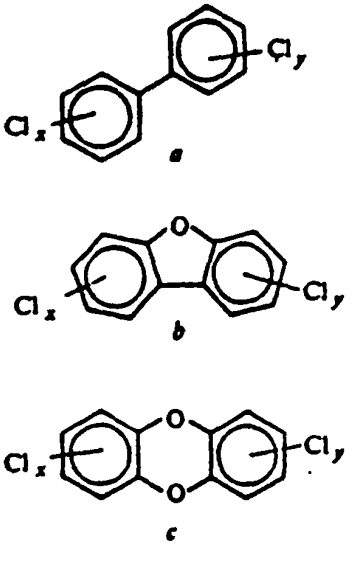
Table 1 Chlorinated dibenzofuran concentrations* in Aroclor, Clophen and Phenoclor

PCB	4-Cl	5-Cl	6-Cl	Total
Aroclor 1248 (1969)	0.5 (25)	1.2 (61)	0.3 (15)	2.0
Aroclor 1254 (1969)	0.1 (6)	0.2 (12)	1.4 (82)	1.7
Aroclor 1254 (1970)	0.2 (13)	0.4 (27)	0.9 (60)	1.5
Aroclor 1260 (1969)	0.1 (10)	0.4 (40)	0.5 (50)	1.0
Aroclor 1260 (lot. AK3)	0.2 (25)	0.3 (38)	0.3 (38)	0.8
Aroclor 1016 (1972)	ND	ND	ND	—
Clophen A-60	1.4 (17)	5.0 (59)	2.2 (26)	8.4
Phenoclor DP-6	0.7 (5)	10.0 (74)	2.9 (21)	13.6

*Expressed as μg g^{-1} PCB. Values in parentheses represent quantity as percentage total dibenzofuran.
ND, not detected (< 0.001 μg g^{-1}).

Amounts of PCB ranging from 1.0 to 2.0 g were dissolved in 400 ml hexane, placed on a Florisil column (130 g, internal diameter 31.5 mm), and eluted with: an additional 1,600 ml hexane, and successive 800 ml volumes each of 5% diethyl-ether–hexane, 25% diethyl-ether–hexane and acetone, at a rate of approximately 7 ml min^{-1}. The major portion of the PCB was eluted in the hexane fraction, which was discarded. On addition of the 5% mixture, the eluates were collected in six successive 400 ml volumes. To eliminate the polar solvents, each eluate was evaporated twice just to dryness and taken up each time in a minimal amount of hexane. Each fraction, in 1 ml hexane, was placed on a microalumina column[15] and eluted with 10 ml each of 1% and 20% methylene chloride in hexane. These were also taken twice just to dryness and made to up a volume of 1 ml in hexane to eliminate the methylene chloride before gas chromatographic analysis. Aliquots of all fractions obtained before and after partitioning on alumina were injected into a six foot glass column containing 3% OV1 on 100-120 mesh Supelcoport in Tracor MT220 and Hewlett-Packard 5700 gas chromatographs equipped with ^{63}Ni electron-capture detectors. PCBs were found to be present in each fraction eluted from the Florisil column in amounts sufficient to interfere with the detection of trace contaminants. Partitioning on the alumina columns separated most of the PCB interference into the 1% methylene chloride fractions. On removal of this interference, different peak patterns appeared in the chromatograms of the 20% methylene chloride fractions. Compounds eluting in the 20% methylene chloride fraction were collected for mass spectrometric analysis using a 20:1 effluent splitter, and a trap consisting of a capillary tube (1 mm internal diameter, 100 mm long) bent to a U shape, immersed in a liquid nitrogen bath. Methylene chloride (20%; 4 μl) in hexane was injected into the capillary as a rinse, removed with a 10 μl micropipette, and placed directly on the mass spectrometer probe. The probe was inserted into a GEC AEI MS902 high resolution mass spectrometer and the solvent removed by the force pump. The probe was rapidly inserted into the ion source and multiple scans were recorded in the on-line high resolution mode[16].

Fig. 1 Skeletal structures of: *a*, chlorinated biphenyl, $x+y = 1$–10; *b*, chlorinated dibenzofurans, $x+y = 1$–8; *c*, chlorinated dibenzodioxins, $x+y = 1$–8.



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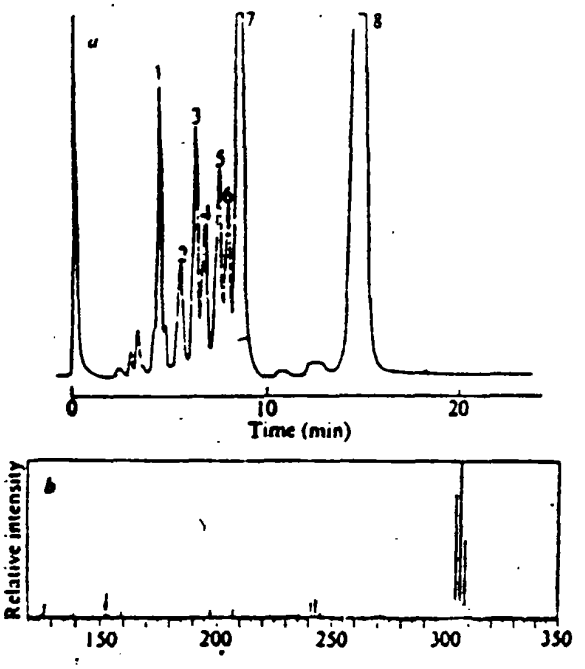

Fig. 2 *a*, Gas chromatogram of a fraction of Aroclor 1254 containing a mixture of chlorinated biphenyls, dibenzofurans, and naphthalenes. Identities of peaks are given in the text. *b*, Mass spectrum of peak 2, a tetrachlorodibenzofuran.

dibenzofuran content: the identical Clophen and Phenoclor contain 11 and 17 times more total chlorinated dibenzofurans, respectively, than the Aroclor 1260.

A gas chromatogram showing components derived from the Aroclor 1254 obtained in 1969 is represented in Fig. 2. The components were eluted in the second 400 ml Florisil fraction and recovered from the alumina column in 20% methylene chloride–hexane. Each of the numbered peaks was trapped as described here, and identified by mass spectrometric analysis. A nominal mass plot of the high resolution mass spectrum of peak 2 is shown in Fig. 2. The plot includes all the ions with elemental compositions ranging to the maximum empirical formula $C_{12}H_6O^{35}Cl_3^{37}Cl_1^{13}C_1$. The molecular ion cluster at nominal *m/e* 304–310 fragments by successive losses of Cl to yield the ions at *m/e* 269–275 and CO to the ions at *m/e* 241–245. A minor loss of Cl from the peaks at *m/e* 269–275 also occurs to yield the ions at *m/e* 234–238, followed by CO elimination to *m/e* 206–210.

The group of peaks at *m/e* 152–154 are the doubly charged molecular ions. An identical spectrum was obtained from an authentic standard of 2,3,7,8-tetrachlorodibenzofuran. This latter compound has a retention time identical to that of peak 4. Peak 2 is, therefore, a positional isomer. The accurate mass measurements for the characteristic ions are within 2 p.p.m. of the calculated exact masses. Peaks identified on this chromatogram and their retention times relative to dieldrin are as follows: a mixture of tetra- and pentachlorobiphenyl (1.02); tetrachlorodibenzofuran (1.30); pentachlorobiphenyl (1.46); tetrachlorodibenzofuran (1.57); hexachloronaphthalene (1.75); pentachlorobiphenyl (1.86); hexachloronaphthalene (2.00); and heptachloronaphthalene (3.46). An aliquot of combined fractions derived from the same Aroclor 1254 was treated with diazomethane to assess whether any chlorinated ortho-hydroxybiphenyls (pre-furans) were present. Gas chromatographic analysis of the sample before and after treatment resulted in identical chromatograms.

As large quantities of PCBs have entered the global environment[17–20], it may be assumed that the contaminant dibenzofurans also have been [illegible]sed in proportional amounts. Their persistence, effects, [illegible] significance remain to be determined.

We thank J. A. Burke, M. L. Porter and J. G. Vos for discussions; A. S. Kende for standards of chlorinated dibenzofurans; and F. C. Walls for assistance with the mass spectrometry. This work was supported by the Canadian Wildlife Service, National Science Foundation, and NASA.

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Niche breadth in Bryozoa as a test of competition theory

COMPETITION theory predicts that intraspecific and interspecific competition should often have opposite effects on the use of resources by a population, the former increasing, the latter decreasing, the range of resource actually used[1–3]. Field data supporting these predictions are well known for the interspecific case[3–5] but are scarce for the intraspecific condition, and we have been unable to find any reference demonstrating both effects within a single species. We therefore report here the verification of both predictions in respect of competition for space by the epiphytic bryozoan *Alcyonidium hirsutum*; less extensive data suggesting the same effects within other bryozoans are also reported.

Intraspecific competition should result in an increase in the range of a resource spectrum used by a species, as at high population levels the advantages to any individual of being at the competition-free optimum of a resource gradient are offset by the intense intraspecific competition found there (Fig. 1*a*); this is the 'principle of equal opportunity' of MacArthur[1]. Interspecific competition, on the other hand, should tend to restrict the range of the resource spectrum used by a species, as individuals attempting to exploit marginal resources cannot do so as efficiently as

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