

Vos *et al.*¹⁶ 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 0.8 $\mu\text{g g}^{-1}$ PCB (Table II). 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

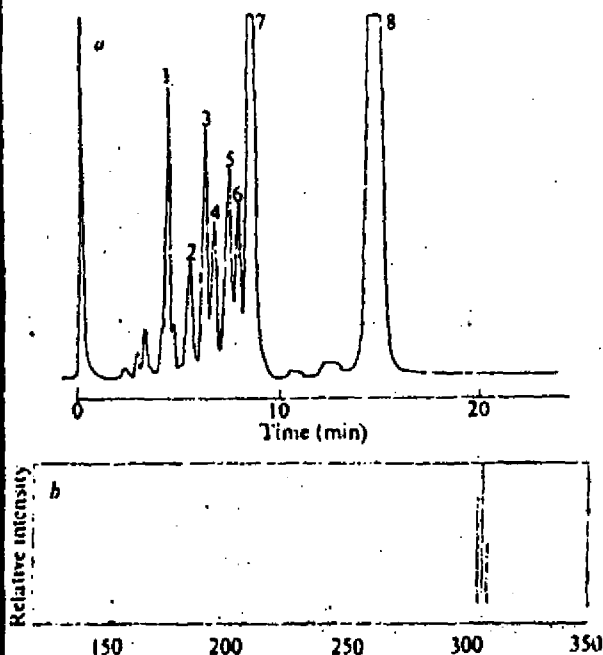


Fig. 2. a, Gas chromatogram of a fraction of Aroclor 1254 containing a mixture of chlorinated biphenyls, dibenzofurans, and naphthalenes. Identities of peaks are given in the text. b, Mass spectrum of peak 2, a tetrachlorodibenzofuran.

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 $\text{C}_{12}\text{H}_6\text{O}^{35}\text{Cl}_4^{37}\text{Cl}^{13}\text{C}$. 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^{17,18} it may be assumed that the contaminant dibenzofurans also have been released in proportional amounts. Their persistence, effects, and 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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1. Newton, L., and Bogan, J., *Nature*, **249**, 382–383 (1974).
2. Koeman, J. H., Madderling, R. H., and Byleveld, M. F. J., *Biol. Conserv.*, **4**, 373–377 (1972).
3. Gilbertson, M., and Hale, R., *Can. J. Fish. Aquat. Sci.*, **30**, 354–356 (1974).
4. Higginbotham, G. R., *et al.*, *Nature*, **228**, 702–703 (1968).
5. Sparschu, G. L., Dunn, F. L., and Rowe, V. S., *Food Cosmet. Toxicol.*, **9**, 405–412 (1971).
6. Vos, J. G., Koeman, J. H., Van der Maas, H., ten Noever de Brauw, M. C., and de Vos, R. H., *Food Cosmet. Toxicol.*, **8**, 623–633 (1970).
7. Vos, J. G., *Environ. High Press.*, **1**, 105–117 (1972).
8. Bowles, G. W., Simoneit, B. R., Burlingame, A. L., de Lappe, B. W., and Risebrough, R. W., *Environ. High Press.*, **5**, 191–197 (1973).
9. Baughman, R., and Nieselson, M., *Environ. High Press.*, **5**, 27–35 (1973).
10. Baughman, R., and Nieselson, M., *Adv. Chem.*, **130**, 92–104 (1973).
11. Report no. 2.4.5-T1 Executive Office of the President, Science Advisory Committee, Office of Science and Technology, March, 1973.
12. Jensen, S., and Renberg, L., *Ambio*, **1**, 62–63 (1972).
13. Firestone, D., Ress, J., Brown, N. L., Barton, R. P., and Damico, J. N., *J. Ass. Off. Anal. Chem.*, **55**, 85–92 (1972).
14. Porter, M. L., and Burke, J. A., *J. Ass. Off. Anal. Chem.*, **54**, 1426–1428 (1971).
15. Burlingame, A. L., Olsen, R. W., and McPhetson, R. V., *Adv. Mass Spectr.*, **8**, 1051–1059 (1974).
16. Nishit, I. C. T., and Sarofim, A. F., *Environ. High Press.*, **1**, 21–38 (1972).
17. Bowles, G. W., and Jonkel, C. J., *J. Fish. Res. Bd. Can.*, in the press.
18. Jensen, S., Juhnelt, A. G., Olson, M., and Otterlind, G., *Nature*, **224**, 247–250 (1969).
19. Koeman, J. H., ten Noever de Brauw, M. C., and de Vos, R. H., *Nature*, **221**, 1126–1128 (1969).
20. Risebrough, R. W., Reiche, P., Peakall, D. B., Herman, S. G., and Kirven, M. N., *Nature*, **220**, 1096–1102 (1968).

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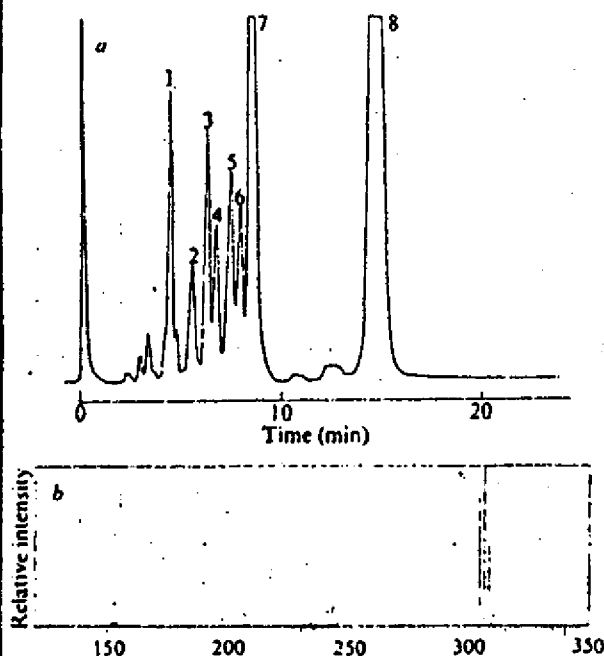


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2. Koeman, J. H., Haderling, R. H., and Buijveld, M. F. J., *Biol. Conserv.*, **4**, 373–377 (1972).
3. Gilbertson, M., and Hale, R., *Can. J. Fish. Aquat. Sci.*, **31**, 135–136 (1974).
4. Higginbotham, G. R., *et al.*, *Nature*, **220**, 702–703 (1968).
5. Spatich, G. L., Dunn, F. L., and Rowe, V. K., *Food Cosmet. Toxicol.*, **9**, 405–412 (1971).
6. Vos, J. G., Koeman, J. H., Van der Meer, H. L., ten Nouwer de Brauw, M. C., and de Vos, R. H., *Food Cosmet. Toxicol.*, **8**, 625–633 (1970).
7. Vos, J. G., *Environ. Hlth Persp.*, **1**, 105–117 (1972).
8. Bowes, G. W., Simoneit, B. R., Burlingame, A. L., de Lappe, B. W., and Risebrough, R. W., *Environ. Hlth Persp.*, **5**, 191–198 (1973).
9. Baughman, R., and Meselson, M., *Environ. Hlth Persp.*, **5**, 27–31 (1973).
10. Baughman, R., and Meselson, M., *Adv. Chem. Ser.*, **120**, 92–104 (1973).
11. Report on 2,4,5-T (Executive Office of the President, Science Advisory Committee, Office of Science and Technology, March, 1971).
12. Jensen, S., and Renberg, L., *Ambio*, **1**, 62–65 (1972).
13. Firestone, D., Ress, J., Brown, N. L., Barron, R. P., and Damico, J. N., *J. Ass. Off. Anal. Chem.*, **55**, 85–92 (1972).
14. Porter, M. L., and Burke, J. A., *J. Ass. Off. Anal. Chem.*, **54**, 1426–1428 (1971).
15. Burlingame, A. L., Olson, R. W., and McPherson, R. V., *Adv. Mass Spectr.*, **6**, 1051–1059 (1974).
16. Nickel, I. C. T., and Sasofm, A. F., *Environ. Hlth Persp.*, **1**, 21–28 (1972).
17. Bowes, G. W., and Jonkal, C. J., *J. Fish. Res. Bd. Can.*, in the press.
18. Jensen, S., Johnels, A. G., Olson, M., and Ottelblad, G., *Nature*, **224**, 247–250 (1969).
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20. Risebrough, R. W., Reiche, P., Peakall, D. B., Herman, S. G., and Kirven, M. N., *Nature*, **220**, 1098–1102 (1968).

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