

C 11
166

FORMATION OF POLYCHLORINATED DIBENZOFURANS (PCDFs)
FROM THE PYROLYSIS OF PCBs

Hans Rudolf Buser and Hans-Paul Buehhardt
Swiss Federal Research Station
CH - 8820 Wädenswil, Switzerland

and

Christoffer Rappe
Department of Organic Chemistry, University of Umeå
S - 901 87 Umeå, Sweden

(Received in UK 3 January 1973; accepted for publication 5 January 1978)

Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals of wide use and now known to be widely distributed in the environment. The commercial products are complex mixtures of at least 80 different substances. Due to their extreme stability in ecological systems, the use of PCBs is now restricted to sealed systems like capacitors and transformers. However, prior to 1972, PCBs due to their good thermal and chemical stability were used in a variety of other applications; in particular the use as heat transfer fluids and casting waxes was associated with the thermal stability.

Very closely related to the PCBs are the polybrominated biphenyls (PBBs), some of which have been used as flame retardants. Of special interest is Fire Master BP-6 or Fire Master FF-1, which were shown to consist mainly of 2,4,5,2',4',5'-hexabromobiphenyl.¹ Intoxication with this PBB has been directly associated with a wide-spread agricultural calamity in Michigan (USA) in 1973-74.²

Part of the PCBs found in the environment has escaped open applications and closed systems, some probably during incineration and burning. Karlsson and Rosen³ have studied the thermal stability of PCBs; laboratory experiments and theoretical calculations showed that at temperatures higher than 800°C PCBs are thermodynamically unstable. The main decomposition products were found to be C(s), CO, CO₂, HCl and Cl₂.

In 1970 Vos *et al.*⁴ identified polychlorinated dibenzofurans (PCDFs) as toxic impurities in European PCBs at the ppm-level, and the same has also been reported for American and Japanese PCBs.^{5,6} The toxic effects of the PCDFs are very similar to those reported for the polychlorinated dibenzo-p-dioxins (PCDDs). In both cases, the 2,3,7,8-tetrachloro compounds are the most toxic isomers, having LD₅₀-values in the range of 1-10 µg/kg (guinea pig).^{7,8} Like PCDDs, the PCDFs have been found to increase cytochrome P-450 activity and a number of drug metabolizing enzymes.^{8,9}

Morita *et al.*¹⁰ have reported increased amounts of PCDFs in a sample of PCB sealed with air in a glass tube and heated at 300°C for two weeks.

In this paper, we report on the formation of PCDFs from the pyrolysis of a commercial PCB (Aroclor 1254) in the presence of air in a sealed quartz tube. In order to study the mechanism of the reaction, we have included individual PCB isomers as model compounds.

Experimental

Materials

2,6,2',6'-Tetra-, 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl were prepared according to known methods.¹¹ Aroclor 1254 and Firemaster BP-6 were from commercial sources. Analysis of the two hexachlorobiphenyls on glass capillary columns showed single peaks, pentachlorobiphenyls being present as impurities at levels of 1% in 2,4,5,2',4',5'- and of 0.5% in 2,4,6,2',4',6'-hexachlorobiphenyl. None of the individual PCB isomers or Aroclor 1254 did contain detectable quantities (< 0.001-0.01%) of PCDFs, polychlorinated benzenes, diphenyl ethers or biphenylols. Standard solutions of the PCBs were prepared at concentrations of 1 and 10 mg/ml in n-hexane or benzene.

Microb

Q

of the

a micr

placed

a elig

heat ti

approx

1:7.5 :

Th

to temp

in an

ampoule

heat th

the tim

if

broken

dilutio

effects

and 50%

GC-MS

An

electro

25 and

the ion

145°, 5

2°/min

tively.

Micropyrolysis

Quartz mini-ampoules were made from quartz tubing using a gas-oxygen burner; the lengths of these ampoules were 25-30 mm, the internal diameters 3.4 mm and the volumes 0.3 ml. Using a micro-syringe, 10 μ l of a standard solution (corresponding to 10 or 100 μ g of compound) was placed into the tip of an ampoule. After complete evaporation of the solvent with the aid of a slight vacuum, the ampoules were closed using a very small flame; care was taken not to heat the tips containing the compounds. The volume of 0.3 ml air in an ampoule was kept approximately constant. The molar ratios of PCB to oxygen in an ampoule were about 1:75 and 1:7.5 for amounts of 10 and 100 μ g of PCB, respectively.

The quartz mini-ampoules were placed in an electrical oven (max. temp. 1000°C) preheated to temperatures ranging from 550 to 850°C. The temperature was controlled with a thermocouple in an ampoule placed next to the samples. Heating periods (time between placing a sample ampoule into the oven and removing it) were kept constant at 60 sec. The time required to heat the mini-ampoules up to a temperature within 20°C of the preset value was around 55 sec, the time of a sample at actual pyrolysis temperature thus around 5 sec.

After removing and immediate cooling to room temperature, the tips of the ampoules were broken and 200 μ l of benzene added. A 2- μ l aliquot was used directly for analysis. Further dilution was required for samples with low decomposition of PCBs to overcome overloading effects of the GC-MS system. Some samples were cleaned-up on an alumina-microcolumn, using 2% and 50% methylenechloride in n-hexane to separately elute PCBs and PCDFs.¹²

GC-MS Analysis

Analyses were carried out on a Finnigan 4000 quadrupole GC-MS instrument equipped with electron-impact ion-source and a Finnigan 6111 data-system. OV-17 glass capillary columns of 25 and 50 m length (0.36 mm ID) were coupled via a platinum interface leading directly into the ion-source. The column conditions were as follows: 100°, 2 min isothermal, 15°/min to 145°, 5°/min to 230°C for the 25 m OV-17 column; 100°, 2 min isothermal, 20°/min to 160°, 2°/min to 230° for the 50 m OV-17 column; helium carrier gas at 0.80 and 1.40 at, respectively. Samples were splitlessly introduced with the vaporizer at 260°C.

All samples were directly analyzed on the 25 m OV-17 column by repetitive scanning of complete mass spectra (m/e 35-460 in 1.4 sec) using the data system. After data acquisition, the mass spectra (up to 1000) were searched for PCBs, PCDFs and other possible reaction products by running and plotting mass chromatograms.

For optimal isomer separation some of the samples were reanalyzed on the 50 m OV-17 glass capillary column. Mass specific detection (mass fragmentography) of PCDFs was carried out by continuously monitoring molecular ions at m/e 202, 236, 270, 304, 338 and 372 for the mono- to hexachloro compounds.

Results

Pyrolysis of 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl

In Tables 1 and 2 we report the results of the pyrolysis of two hexachlorobiphenyls at temperatures ranging from 550 to 850°C. As indicated, 37% of the 2,4,5,2',4',5'- and 22% of the 2,4,6,2',4',6'-hexachlorobiphenyl decomposed at 550°C. Both compounds were decomposed to > 90% at 650°C. Complete destruction occurred at 700°C and above. No isomerization of these hexachlorobiphenyls or dechlorination to lower chlorinated biphenyls was observed in this temperature range.

Table 1 Pyrolysis of 2,4,5,2',4',5'-hexachlorobiphenyl (100 µg) in quartz mini-ampoules

Temperature (°C)	Decomposition (%)	PCDFs formed ⁺ (%)	
		tetra-CDF	penta-CDF
550	37	1.6	0.2 + 0.15
600	83	0.3	0.35 + 0.1
650	97	0.2	1.1 + 0.1
700	> 99.99	< 0.01	< 0.01
850	> 99.99	< 0.01	< 0.01

+ 1 tetra- and 2 penta-CDF isomers formed

Tetra- and pentachlorodibenzofurans (tetra- and penta-CDFs) were formed at temperatures of 550-650°C. The levels were 0.2-1.6% and 0.1-0.5% for 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl. At temperatures of 700°C and above, complete destruction of these PCDFs occurred. No di-, tri- or hexa-CDFs were formed at any of these temperatures.

Table 2 Pyrolysis of 2,4,6,2',4',6'-hexachlorobiphenyl (100 µg) in quartz mini-ampoules

Temperature (°C)	Decomposition (%)	PCDFs formed* (%)	
		tetra-CDF	penta-CDF
550	22	0.5	0.1
600	90	0.5	0.3
650	94	0.35	0.35
700	> 99.99	< 0.01	< 0.01
850	> 99.99	< 0.01	< 0.01

* 1 tetra- and 1 penta-CDF isomer formed

The formation of penta- and hexachlorobenzene was observed with both PCB isomers at temperatures of 650°C (0.05%) and 700°C (0.5-1%). The lower chlorinated benzenes would have escaped detection (elution from capillary column prior to starting of MS scanning). Both, penta- and hexachlorobenzene were decomposed at 850°C.

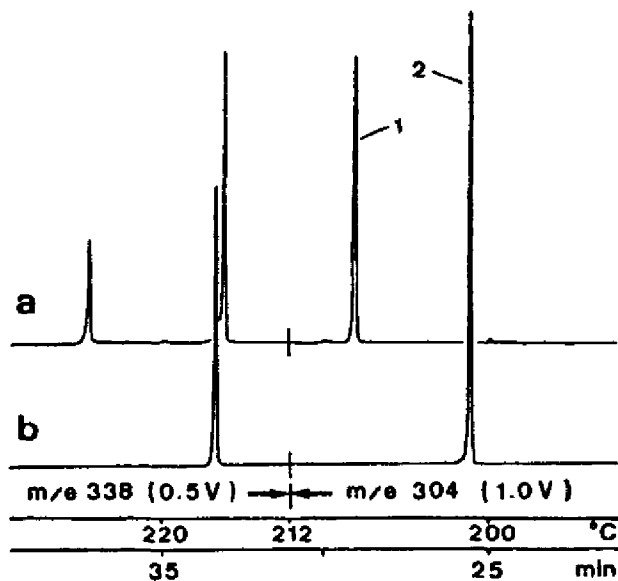
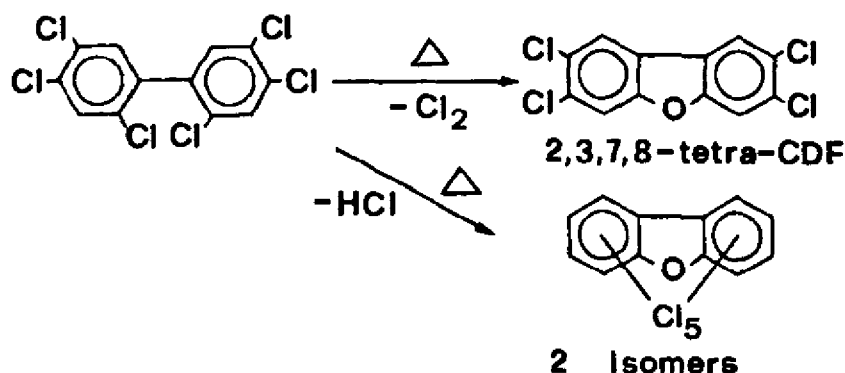


Figure 1 Partial mass fragmentograms (50 m OV-17, m/e 304 and 338) showing elution of tetra- and penta-CDFs in a) pyrolyzed 2,4,5,2',4',5- and b) pyrolyzed 2,4,6,2',4',6'-hexachlorobiphenyl. 1 = 2,3,7,8-tetra-, 2 = presumably 1,3,7,9-tetra-CDF.

In Figure 1 mass fragmentograms of both hexachlorobiphenyls pyrolyzed at 600° show the elution of tetra- and penta-CDFs on the 50 m OV-17 glass capillary column. The pyrolysis of 2,4,5,2',4',5'-hexachlorobiphenyl did yield one tetra- and two penta-CDF isomers. By comparison with an authentic standard, it could be shown that the Cl₄-isomer is the very toxic 2,3,7,8-tetra-CDF. Consequently, no rearrangement is involved in the cyclization forming this isomer. In the case of the two penta-CDFs, it is evident that a rearrangement must be involved. The nonrearranged product should be the 1,3,4,7,8-penta-CDF, but additional work is needed to establish the identity of these penta-CDFs.



The pyrolysis of 2,4,6,2',4',6'-hexachlorobiphenyl did yield one tetra- and one penta-CDF isomer. The Cl₄-isomer presumably is the 1,3,7,9-tetra-CDF, but this cannot be confirmed due to lack of an authentic standard. The penta-CDF is formed in a rearrangement and its structure is still unknown. No additional PCDFs were formed in a mixed pyrolysis of the two hexachlorobiphenyls indicating only intramolecular cyclization processes.

Pyrolysis of Aroclor 1254

Aroclor 1254 is a commercial PCB containing tri-, tetra-, penta- and hexachlorobiphenyls as the major constituents. GC-MS analysis using the 50 m OV-17 glass capillary column showed the presence of the 2,4,5,2',4',5'-substituted isomer as one of the major

hexachlorobiphenyls. No 2,4,6,2',4',6'-hexachlorobiphenyl was detected (<1% relative to the 2,4,5,2',4',5'-isomer).

Table 3 Pyrolysis of Aroclor 1254 in quartz mini-ampoules

Temp. (°C)	Amt. (µg)	Decomp. (%)	PCDFs formed* (%)				
			mono-	di-	tri-	tetra-	penta-
550	100	12	0.25	0.65	0.90	0.75	0.20
"	10	80	0.02	0.40	0.70	0.70	0.15
600	100	45	0.10	0.40	0.70	0.60	0.12
"	10	90	< 0.01	0.10	0.25	0.35	0.05
650	100	90	< 0.01	0.02	0.18	0.25	0.12
"	10	98	0.01	0.12	0.25	0.12	< 0.02
700	100	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02
"	10	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02
850	100	> 99.9	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02

* combined values of all isomers of a PCDF

In Table 3 the results of the pyrolysis of Aroclor 1254 in the temperature range of 550-850°C and levels of 10 and 100 µg are reported. At 550-650°C, the decomposition at the 100 µg-level ranged from 12% to 90%, at the 10 µg level from 80 to 98%. Aroclor 1254 was completely destroyed at temperatures of 700°C and above. These decomposition values are based on the hexachlorobiphenyls present. The decomposition of the lower chlorinated biphenyls was somewhat higher than the stated values. No penta- or hexachlorobenzene was detected at any temperature. Again, lower chlorinated benzenes would have escaped detection.

Mono- to penta-CDFs were found at 550-650°C at levels ranging from 0.1-0.9%. The maximum amounts found were at 550°C. Taking into consideration the amount of PCB recovered after pyrolysis, the total yield of PCDFs ranged from 3-25%. In addition to PCDFs, polychlorinated biphenyls as possible precursors were identified at levels of approximately one fifth of the amount of PCDFs present.

In Figure 2 mass fragmentograms of pyrolyzed Aroclor 1254 (100 µg at 600°C, cleaned-up sample) on a 50 m OV-17 glass capillary column are shown. The elution of up to 30 major and more than 25 minor PCDFs can be observed. They range from the mono- (all 4 theoretically possible isomers) to the penta-CDFs. Since 2,4,5,2',4',5'-hexachlorobiphenyl is one of the

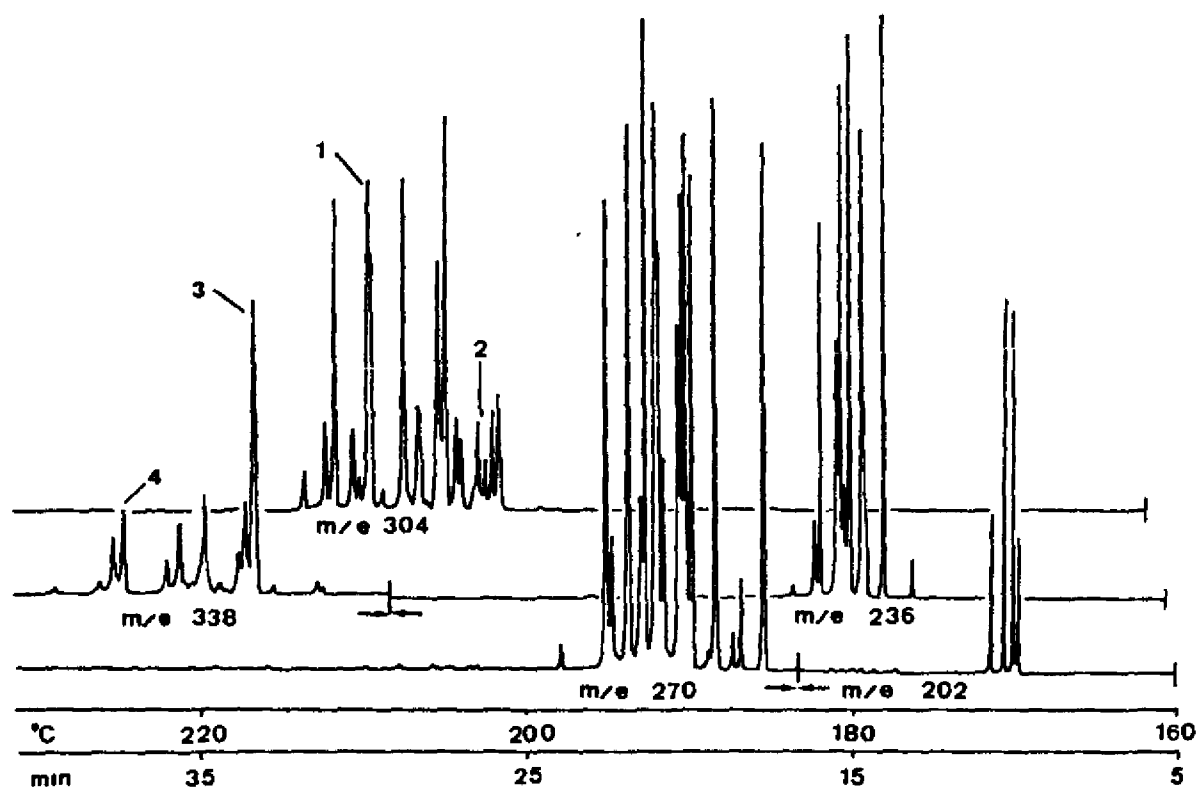


Figure 2 Mass fragmentograms (50 m OV-17, m/e 202, 236, 270, 304 and 338) showing elution of (right to left) mono-, di-, tri-, tetra- and penta-PCBs from pyrolyzed Aroclor 1254 (600°C). Sensitivities: mono- and di-: 2 V; tri- and tetra-: 1 V; penta-PCB: 0.5 V. Peak identifications: 1- 2,3,7,8-tetra-; 3 and 4- penta-PCBs from 2,4,5,2',4',5'-hexachlorobiphenyl; 2- position where tetra-PCB from 2,4,6,2',4',6'-hexachlorobiphenyl would elute.

MONS 213809

1
2.
3.
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15.
16.
17.
18.
19.
20.
21.
22.
23.
24.
25.
26.
27.
28.
29.
30.
31.
32.
33.
34.
35.
36.
37.
38.
39.
40.
41.
42.
43.
44.
45.
46.
47.
48.
49.
50.
51.
52.
53.
54.
55.
56.
57.
58.
59.
60.
61.
62.
63.
64.
65.
66.
67.
68.
69.
70.
71.
72.
73.
74.
75.
76.
77.
78.
79.
80.
81.
82.
83.
84.
85.
86.
87.
88.
89.
90.
91.
92.
93.
94.
95.
96.
97.
98.
99.
100.

tri- and tetra-: 1 V; penta-CDF: 0.5 V. Peak identifications: 1= 2,3,7,8-tetra-; 3 and 4= penta-CDFs from 2,4,5,2',4',5'-hexachlorobiphenyl; 2= position where tetra-CDF from 2,4,6,2',4',6'-hexachlorobiphenyl would elute.

main hexachlorobiphenyls in Aroclor 1254, it is of interest to confirm the presence of 2,3,7,8-tetra-CDF and of the two penta-CDFs in this complex mixture. The 2,3,7,8-tetra-CDF is not completely separated on this column from another tetra-CDF isomer. The tetra-CDF formed from 2,4,6,2',4',6'-hexachlorobiphenyl was not found to be present.

In case of the major isomers, the discrete PCDFs could be identified by running complete EI mass spectra. All mass spectra showed intense molecular ions with the expected ion clustering due to the chlorine isotopes and the characteristic fragmentation for PCDFs with formation of M^+-COCl and $M^+-COCl-Cl_2$.

Pyrolysis of additional compounds

Additionally we have studied the pyrolysis of 2,6,2',6'-tetrachlorobiphenyl and of Firemaster BP-6 (mainly 2,4,5,2',4',5'-hexabromobiphenyl). Tetrachlorobiphenyl formed at 550°C one di- and one tri-CDF isomer at levels of 1.6 and 2.5%, respectively. The tri-CDF must be formed in a rearrangement. At 700°C, the tetrachlorobiphenyl was completely destroyed and no PCDFs were found. Firemaster BP-6 was also completely destroyed at 700°C, but at 600°C new compounds were formed, one of which could be a tetrabromodibenzofuran ($M^+=480$, Br₄; major fragment M^+-Br_2 ; other fragments M^+-Br and M^+-COBr). In analogy with the corresponding PCB isomer, it seems most likely that it is the 2,3,7,8-tetra-BDF. The amount formed is about equal to the amount of tetra-CDF formed from the corresponding PCB.

Conclusions

The results reported in this paper suggest that uncontrolled burning of PCBs can be an important environmental source of the hazardous PCDFs. Although PCDFs have not yet been found in the environment, they have been identified in fly ash from municipal incinerators and industrial heating facilities.^{13,14} Moreover, Nagayama *et al.*¹⁵ have found highly increased levels of PCDFs in the PCB associated with the Yusho accident in Japan in 1968, and one of the main components was also the 2,3,7,8-tetra-CDF.¹⁶

In spite of being partly banned, large volumes of PCBs are still in use, especially in transformers and capacitors. In Sweden the amount now in use in capacitors is about 2500 tons; a similar amount applies for Switzerland according to a survey by the Swiss Federal Office of Public Health. It is evident that all disposal of PCBs should be carefully

controlled in order to avoid accidental formation of hazardous PCDFs.

Our investigation also indicates that special processes may be associated with occupational health risks due to formation of PCDFs. One of these processes is the welding of leaking systems containing PCBs. Another process is the casting of iron using PCB containing casting waxes. /

Accidental burning of material impregnated with 2,4,5,2',4',5'-hexabromobiphenyl may yield gases containing the very toxic 2,3,7,8-tetra-BDF. Consequently, the use of this compound as a flame retardant should be carefully reconsidered.

References

1. K. Andersson, A. Norström, C. Rappe, B. Rasmussen and H. Swahlin, Env. Quality and Safety, Supp. Vol. III, p. 798 (1975).
2. Anonymous, Chem. Eng. News, February 24, p. 7 (1975).
3. L. Karlsson and E. Rosen, Chemica Scripta, 1, 61 (1971).
4. J.G. Vos, J.H. Koeman, H.L. van der Maas, M.C. ten Noever de Brauw and R.H. de Vos, Fd. Cosmet. Toxicol., 8, 625 (1970).
5. J.A.G. Roach and I.H. Pomerantz, Bull. Environ. Contam. Toxicol., 12, 338 (1974).
6. G.W. Bowes, M.J. Mulvihill, B.R.T. Simoneit, A.L. Burlingame and R.W. Risebrough, Nature, 256, 305 (1975).
7. J.D. McKinney, K. Chae, B.M. Gupta, J.A. Moore and J.A. Goldstein, Toxicol. Appl. Pharmacol., 36, 65 (1976).
8. E.E. McConnell, J.A. Moore, J.K. Haseman and M.W. Harris, Toxicol. Appl. Pharmacol., 37, 146 (1976).
9. A. Poland, E. Glover, A.B. Kende, J. Biol. Chem., 251, 4936 (1976).
10. M. Morita, J. Nakagawa, K. Akiyama, S. Mimura and M. Isono, Bull. Environ. Contam. Toxicol., 18, 67 (1977).
11. O. Hutzinger, S. Safe and V. Zitko, The Chemistry of PCBs, CRC Press, Cleveland, Ohio (1974).
12. H.R. Buser, J. Chromatogr., 107, 295 (1975).

13. K. Olie, P.L. Vermeulen and O. Hutzinger, Chemosphere, 8, 455 (1977).
14. H.R. Buser and H.-P. Bosshardt, Mitt. Geb. Lebensmittelunters. u. Hyg., in press (1978).
15. J. Nagayama, M. Kuratsune and Y. Masuda, Bull. Environ. Contam. Toxicol., 15, 9 (1976).
16. C. Rappe, A. Gara, H.R. Buser and H.-P. Bosshardt, Chemosphere, 5, 231 (1977).