Polychlorinated Terphenyls as Potential Contaminants of Animal Products

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Abstract

The polychlorinated terphenyl (PCT), Aroclor 5460, has been used in a sealant for concrete stave silos. PCT residues were found in samples of wall scrappings, silage, and milk from farms known to have affected silos. The PCTs are complex mixtures making identification and quantitation difficult. The samples were reacted with $SbCl_5$ to form the three tetradecachloroterphenyl derivatives. Formation of the derivatives facilitated identification of PCT residues by gas-liquid chromatography. It also appears to be the most promising approach to a quantitative method.

In recent years there has been considerable public concern about the presence of polychlorinated biphenyl (PCB) residues in the environment. Many studies are being conducted to determine the extent and significance of PCB residues. Regulatory guidelines have been established and actions taken when PCB residues were found in foods (6).

MONS 039921

However, little attention has been given to possible residues of the polychlorinated terphenyls (PCT) compounds that are similar in chemical characteristics and uses to the PCBs (7).

General structural formulas for the PCTs are presented in Fig. 1. Commercial formulations of PCTs could be expected to be much more complex than the PCBs. There are not only more positions and combinations of positions available for chlorination, but the phenyl rings could also have three possible arrangements.

In common with the PCBs, the PCTs are marketed in the U.S. as Aroclors,[1] and the formulations are described by a four-digit number (7). The first two digits indicate that the materials are PCBs (12), PCTs (54), or a mixture of PCBs and PCTs (25 and 44). The last two digits indicate the percent chlorine in the mixture.

There has been a recent report of PCT residues in environmentally obtained samples. Zitko et al (9) found PCT residues resembling Aroclor 5460 in eggs and fatty tissue of herring gulls (Larus argentatus). Residues were not present in eggs and fatty tissues of double-crested cormorants (Phalacrocorax auritus) from the same area.

It has come to our attention that Aroclor 5460 was used in a silo sealant with Aroclor 1254. The PCB residues in milk from the use of Aroclor 1254 has been the subject of regulatory (b) and research activity (4,5,8). This known use of a PCT provides the opportunity to determine if PCT residues can occur in milk. It also allows the comparison of the behavior of PCT residues with residues of Aroclor 1254.

[1]Aroclor is a registered trademark of the Monsanto Company.

It is the purpose of this paper to present evidence of PCT residues in milk from the use of Aroclor 5460 in silo sealants.

Materials and Methods

Samples. The samples examined in this study were obtained from farms known to have PCB contaminated silos. Most samples had been previously analyzed for PCBs and the results have been published (4). The samples include scrappings from silo walls, silage samples taken adjacent to the walls, and milk samples from cows fed silage. One sample of sealant, from which some solvent evaporated, was also obtained. In addition to the environmental samples, a cow was fed a single dose of 200 mg of Aroclor 5460. This provided samples of milk and feces that were high in residues and free of other contaminants.

Extraction and Clean-up. Milk and silage samples were exacted and cleaned up using FDA multipesticide residue methodology (3). A Florosil column was used for clean-up. Wall scrappings were extracted with hexane and examined without further clean-up. The sealant sample was diluted with hexane and examined without further clean-up.

Chlorination. The clean-up samples were chlorinated with $SbCl_5$ to provide confirmation of the residues. The method was similar to that of Berg et al (2). The cleaned-up samples were placed in a tube with a teflon-lined screw cap. The solvent was evaporated, 0.2 ml of $SbCl_5$ was added, and the tube was sealed. The tubes were heated at 175°C for 4 hours. After cooling, 1 ml of 10% HCl was added to suppress precipitation of antimony oxychloride. The solution was extracted several times with benzene. The benzene extracts were combined, shaken with

MONS 039923

aqueous $NaHCO_3$, and dried anhydrous Na_2SO_4. No further clean-up was used.

Detection. Gas liquid chromatography (GLC) with electron capture detection was used for detection of residues. A Hewlett-Packard Model 7620 instrument equipped with a ^{63}N electron capture detector and an electronic integrator was used. The 1/4 inch O.D. glass column was packed with 5% OV-17 on 80 - 100 mesh Gas-Chrom Q. The column length varied and will be specified in the results. The carrier gas was a 95% argon-5% methane mixture with a 120 ml/min flow rate. A purge gas was not used. Inlet and detector temperatures were 280 and 300°C respectively. The column temperature varied and will be specified in the results.

Results and Discussion

PCTs are not eluted at the maximum operating temperatures of GLC column such as SE-30 and DC-200, typically used for chlorinated hydrocarbon analysis. Therefore, we arbitrarily selected OV-17 as a column because of its suitability for high temperature work.

Typical chromatograms of Aroclor 5460, a silage sample and a milk sample using a 6-ft column at 250°C are presented in Fig. 2. As expected, Aroclor 5460 presents a complex chromatogram with many unresolved peaks. The peaks of the silage chromatogram are nearly identical in retention times and relative areas to the standard. The only exception was during the first five minutes when the Aroclor 1254 in this silage was eluted.

MONS 039924

The shape of the milk chromatograms was similar to the standard. The retention times of the peaks were generally the same, but there is some indication that the relative areas differed. The milk chromatogram in Fig. 2 is from the cow fed a single dose of Aroclor 5460. In general, the concentration of PCT in the environmentally exposed cows was too low to provide a distinctive pattern.

We adopted the chlorination method to overcome the difficulties in identifying and quantitating chromatograms of the type in Fig. 2. A typical chromatogram of the fully chlorinated Aroclor 5460 is presented in Fig. 3. The 6-ft column was operated at 270°C. Three components, two not completely resolved, were present. Three tetradecachloroterphenyls would be expected, but we have not compared the retention times to known compounds. The peak at 2.7 min. has the same retention as decachlorobiphenyl. The presence of a small amount of biphenyls in terphenyls should not be unexpected.

The retention times of the tetradecachloroterphenyls were too long for routine use with large numbers of samples. For this reason a 2-ft column was adopted for routine use. At 260°C the retention time of the last terphenyl peak was about 20.5 min. (Fig. 4). The two unresolved peaks with the 6-ft column (Fig. 3) appear as a single peak with the 2-ft column.

Decachlorobiphenyl had a retention time of 1.1 min. This was too short for adequate separation from the solvent and interfering peaks. For this reason dechlorobiphenyl was determined at the lower column

temperature of 225°C where its retention time was 4.0 min. The necessity for two GLC runs was not as great a problem as would appear. Because the PCT was several times greater and the peak was much narrower, it would have been necessary to use different concentrations of each sample for optimum detection and quantitation of each compound.

Chromatograms of the sealant, wall scrapping, silage, and milk samples are presented in Fig. 4 and 5. Residues of PCTs were detected in all samples. The early terphenyl peak was not present in the wall sample. Wall samples can be quite variable in composition, and an insufficient sample was used for the lesser peak to be detected.

These preliminary findings indicate that PCTs can become contaminants of animal products if they have been introduced to the animal food supply. Qualitatively, the movement of the PCT, Aroclor 5460, was similar to the PCB, Aroclor 1254. However, we have not established whether or not the quantitative rates are similar.

Concentrations of PCB and PCT in a number of silage and milk samples were calculated. However, because of a number of unresolved problems, no values will be presented.

The recoveries of PCB and PCT in the chlorination method have not been established. The recovery with decachlorobiphenyl as a starting material was 94% with a range of 90 to 97%. However, with a limited number of Aroclor 1254 samples the recovery was only 54% with a range of 43 to 71%. This low recovery was apparently also true for the milk and silage samples because the values were much lower than had been previously determined by conventional methods (4).

MONS 039926

Recovery of the tetradecachloroterphenyls was not determined because we did not have standards at the time. However, the relative areas of the peaks of several treated Aroclor 5460 samples ranged from 0.83 to 1.13 if the average area was assumed to be 1.0.

A second problem is the occurrence of interferences at the shorter retention times. This was particularly true with milk samples (Fig. 5). In some cases the interferences were great enough to preclude detection of decachlorobiphenyl. These interferences were not present before chlorination and presumably they were formed by chlorination of compounds that do not cause an electron capture response. We have not studied possible means of removing these interferences either before or after chlorination.

The optimum GLC columns and conditions also require investigation. The PCT peaks were quite broad and are not the most suitable for quantitation. It would also be desirable if the relative retention time of decachlorobiphenyl was greater. This would allow simultaneous determination of the two contaminants if the relative concentrations were appropriate. Zitko *et al.* (9) have used an OV-210 which allows operation at a lower temperature but the relative retention times were similar. The 3% Dexsil 300 column used by Addison *et al.* (1) appears to give much better resolution of the peaks of unaltered Aroclor 5460 than either OV-17 or OV-210.

MONS 039927

Conclusions

The data presented here as well as the report of PCT residues in birds (9) suggest that PCT residues in foods could occur if the material has been introduced into the environment. The prevalence and significance of the residues would require further study.

Our work demonstrates that milk produced on farms with contaminated silos will contain PCT residues. In a practical sense, this is not an important problem. It has already been established that most of these farms are producing milk with PCB residues exceeding the FDA guidelines. Since the PCB and PCT residues are from the same source, correction of the PCB problem will also eliminate the PCT residues.

The silo situation does provide good opportunity to study the comparative behavior of the two classes of compounds under environmental conditions. If the behavior is similar, it may be possible to predict the distribution and levels of PCT residues from information available on PCBs.

Mention of proprietary products does not imply endorsement or approval by the U.S. Department of Agriculture to the exclusion of other suitable products.

MONS 039928

References

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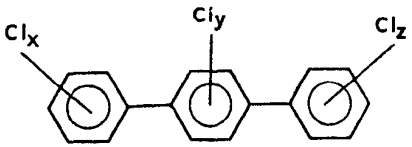
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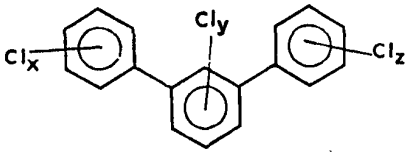
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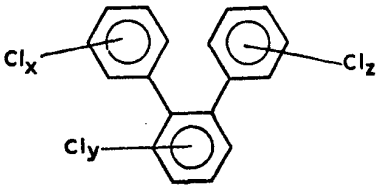
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Para



Meta



Ortho

Fig. 1. Formulas for polychlorinated terphenyls.

MONS 039930

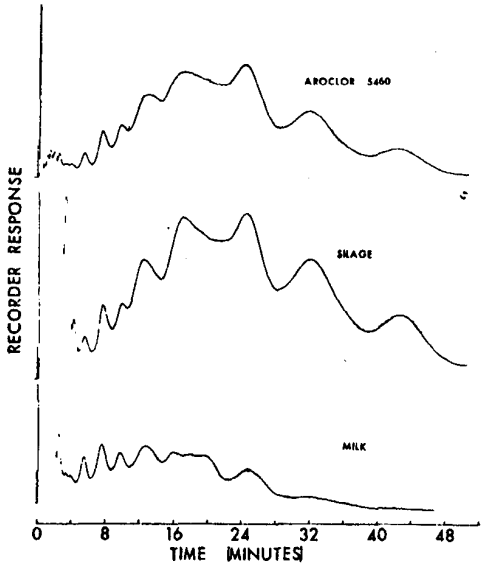


Fig. 2. GLC tracings of Aroclor 5460 and samples of silage and milk. Silage was from a silo coated with the sealant containing Aroclor 5460 and milk from a cow fed Aroclor 5460 in the laboratory. The 6-ft column was operated at 250°C.

MONS 039931

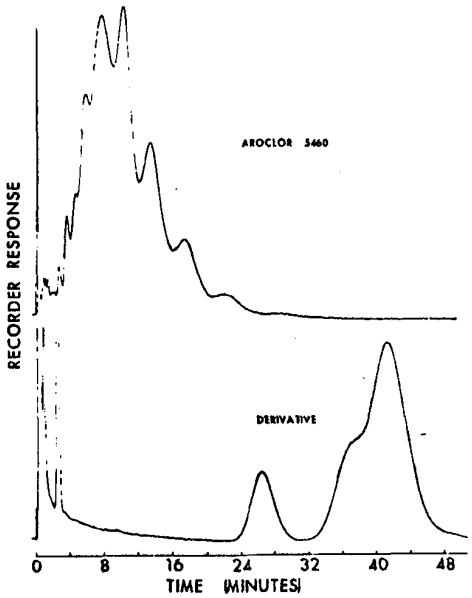


Fig. 3. GLC tracings of Aroclor 5460 and its derivatives formed by chlorination with $SbCl_5$. The 6-ft column was operated at 270°C.

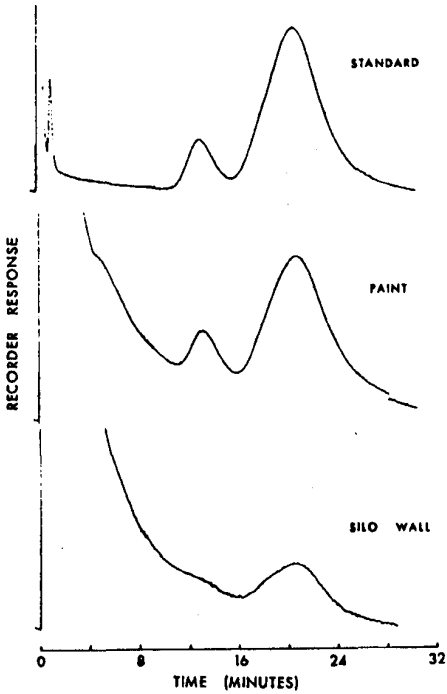


Fig. 4. GLC tracings of the chlorination products of Aroclor 5460, silo sealant, and extract of silo wall scrappings. The 2-ft column was operated at 260°C.

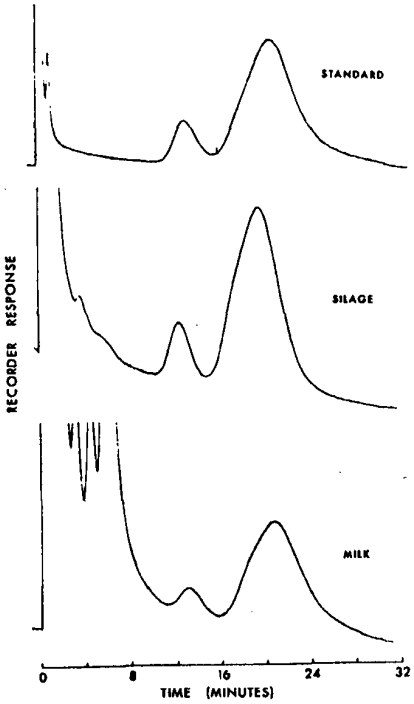


Fig. 5. GLC tracing of the chlorination products of Aroclor 5460 and samples of silage and milk. The samples were obtained from a farm that had used the silo sealant containing Aroclor 5460. The 2-ft column was operated at 260°C.

MONS 039934