Bull. Environ. Contam. Toxicol. (1985) 35:51–60

Bulletin of Environmental Contamination and Toxicology

Quantification and Distribution of Polychlorinated Biphenyls in Farm Silos[1]

L. B. Willett,[1] Ting-Ting Y. Liu,[1] Holly I. Durst,[1] Burton D. Cardwell,[2] and Edwin D. Renkie[2]

[1]Department of Dairy Science, Ohio State University, Ohio Agricultural Research and Development Center, Wooster, OH 44691 and [2]Toxic Substances and Emergency Services Office, Michigan Department of Agriculture, P.O. Box 30017, Lansing, MI 48909

One source of polychlorinated biphenyls (PCBs) in the human food chain has been concrete stave farm silos that were treated with a coating material called Cumar (Willett and Hess, 1975; Willett, 1980). This coating was formulated in 1941 to aid the proper curing of concrete and protect the staves and joint mortar from the erosive actions of the organic acids which are produced during fermentation of silage.

Willett and Hess (1975) reported that Cumar contained approximately 19% Aroclor 1254, a PCB mixture, and 5.4% Aroclor 5460, a mixture of polychlorinated terphenyls. Once applied to the silo wall, and the carrier solvents evaporated, the cured coating contained 32.6% PCB. Typically, 2.45 m^2 of silo wall were covered per liter. Thus, in the case of a freshly coated silo, if completely coated, the concentration of Aroclor 1254 equaled 467 ppm on a whole silo basis. If coated only on joint mortar, a frequently used procedure, the concentration equaled 109 ppm. The PCB content of silos declined with use as the coating disintegrated and flaked off the silo wall. Studies have revealed that the PCBs were soluble in the organic acids, including lactic and acetic, that were produced during the fermentation process. Once dissolved in these acids, the residues diffused toward the center and leached toward the bottom of the silo (Willett, 1974).

According to the "Toxic Substances Control Act of 1979", materials which contain more than 50 µg/g of PCBs require special handling and disposal. Usually, scrapings are taken from the surface of silos to determine if a silo is contaminated. The concentration of PCB in scrapings generally exceeds the 50 µg/g limit. However, scrapings represent only the concentration of PCBs directly on the inner surface of the silo and are not representative of the entire structure.

In order to determine the relationship between the concentration of PCBs in scrapings from the silo wall and the concentration in the entire structure a study was conducted to determine the extent of penetration of PCBs into concrete silo staves, and develop equations whereby the concentration of PCBs in the entire silo can be predicted from the concentration of PCBs in scrapings from the inner silo surface.

MATERIALS AND METHODS

Silo staves from Michigan and Ohio, known to be contaminated with polychlorinated biphenyls, were collected to determine the depth of penetration of PCB residues. Staves used in this study were manufactured by National, C & B, Interlocken and Michigan Silo Companies and included both plain- and waxed-stave construction from the latter manufacturer. Staves represented silos of various conditions, from those with Cumar coating intact to those cleaned and recoated. A brief description of the staves is in Table 1.

Silo staves were weighed and measured, and their condition and history recorded. Five locations were selected in each full stave for sampling, positions A-E (Figure 1). Positions represented both edge and center locations. Each sample position was cut in four to six cross-sections through the stave on a masonry saw with a diamond blade. The size and weight of sections were recorded with each approximately 25 x 25 mm on the face and 10 mm thick. Sections were labeled consecutively with 1 designating the inside surface. Sections were also cut from a control stave to monitor method cross-contamination. Sections were gently rinsed, and air dried to remove residual dust from cutting.

Sections were crushed in a mortar and pestle to approximately 1 mm in diameter. Crushed sections were ground (20,000 rpm for 2.5 min.) to a fine powder in a mill equipped with a tungsten carbide blade (A-20 Universal Mill, Tekmar Company, Cincinnati, OH). To prevent cross-contamination, section were ground by descending sample number and 5-7 grams of absorbant clay was ground between sections. Surfaces of the mill, mortar and pestle were cleaned with acetone between samples. Blanks were ground prior to each stave. In addition scrapings were taken from the inside surface adjacent to the sampling sites. Scraping thickness was influenced by density and condition of the stave surface. Scraping thickness ranged from .01 to 1.5 mm.

Two gram samples of the ground sections were weighed into tubes that had been prewashed with toluene and

Table 1. Silo staves used to determine the penetration of PCBs.

No.	Brand	Appearance & Condition	Positions[a] Sampled
OM-1[b]	Michigan[d]	Recoated, surface very good	A-E
OM-2[b]	Michigan[d]	Recoated, surface very good	A-E
OCB-1[b]	C & B[d]	Cumar coating intact, excellent	A-E
ON-1[b]	National[d]	PCB containing coating intact, excellent	A-E
MM-1[b]	Michigan[e]	Some erosion, good	A-E
MM-2[b]	Michigan[e]	No erosion, excellent	A-E
MM-3[b]	Michigan[e]	Recoated, coating & surface poor	A-E
MM-4[b]	Michigan[e]	Recoated, coating & surface poor	A-E
MM-5[b]	Michigan[e]	Some erosion, surface very good	A-E
MM-6[b]	Michigan[e]	Badly eroded, poor condition	A-F
MM-7[c]	Michigan[e]	Moderate surface erosion, fair	A-C
MM-8[c]	Michigan[e]	Minor erosion, good	D,E
MM-9[c]	Michigan[e]	Minor erosion, good	A-C
MI-1[c]	Interlocken[e]	Surface erosion, fair	A,B

[a] Figure 1.
[b] Entire stave available.
[c] Partial or broken stave available.
[d] Source - Ohio.
[e] Source - Michigan.

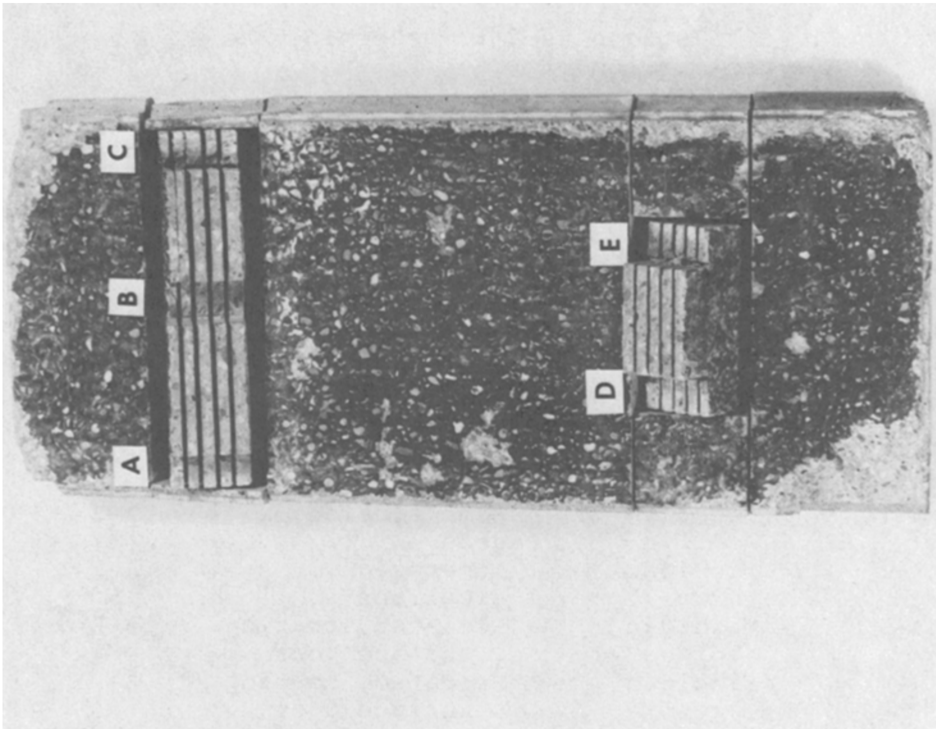

Figure 1. The cutting and sectioning pattern used on silo staves

acetone. Samples were extracted with 9 ml of 2% benzene in petroleum ether, agitated for 1 min, centrifuged at 1,240 x g for 3 min, and the supernatant decanted into similarly prewashed screw-top vials. Samples were reextracted as above and the supernatants combined. Method recovery and quality control were based on spiked control stave samples. Silo scrapings were extracted in the same manner using 9 ml of 2% benzene in petroleum ether regardless of sample weight. Sample analysis was by gas-liquid-chromatograph using a ^{63}Ni detector (5736-A Gas Chromatograph, Hewlett Packard, Avondale, PA). A 1.8 m glass column of 5% OV-101 on Gas-Chrom Q (80/100 mesh) was used with Argon-Methane (95:5) as carrier and purge. Running conditions were: oven 250°C, detector 300°C and injection port 300°C. Samples were diluted and injected to be within the linear detection range of the EC-cell. Quantification was based on electronically integrated area of peaks 3-9 (Figure 2).

RESULTS AND DISCUSSION

The procedures utilized in this study were adequate to reliably determine the penetration of polychlorinated biphenyls into concrete silo staves. Recovery of PCBs

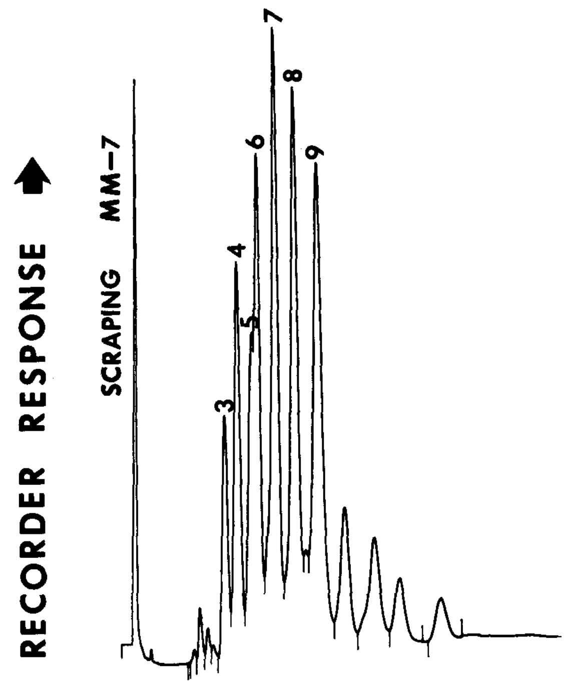

Figure 2. Typical chromatogram of polychlorinated biphenyls (Aroclor 1254) extracted from Cumar-treated silo staves. Quantification was based on integrated areas of peaks 3 through 9.

from spiked concrete was adequate and repeatable (86.47 ± 1.50%) utilizing 2% benzene in petroleum ether as the solvent. Chromatographic "clean-up" methods were not necessary as background and blank samples revealed no interfering peaks for the staves within the elution time for Aroclor 1254 congeners with our GLC conditions. The procedures employed did an excellent job of preventing cross-contamination despite great differences in residue concentration among sections. The procedure was reliable as the coefficient of variation for duplicate (> limit of analytical sensitivity) and rerun samples was 7.29%. During this study the limit of analytical sensitivity was 0.025 μg/g.

The 14 silo staves collected for this experiment seem to represent many possible stave conditions that can be encountered on farms (Table 1). Least-squares analyses of variance revealed significant stave and section differences ($P<.01$) where position effect was not significant ($P>.05$). Table 2 summarizes the PCB concentration in scrapings and sections of each stave. The data presented were averages of all positions sampled. When considering these results it is important that all of

Table 2. Penetration of PCB into silo staves.

	PCB Concentration in μg/g						
Stave No.	Scrapings	Section 1	Section 2	Section 3	Section 4	Section 5	Section 6
OM-1	2.14	.29	.00	.00	.02	.03	---
OM-2	85.51	10.98	.03	.00	.00	.00	---
OCB-1	259206.35	1639.51	.29	.14	.11	.08	.43
ON-1	997.58	221.23	20.09	.52	.00	.00	.17
MM-1	235.35	53.37	.03	.00	.00	.09	---
MM-2	445.19	49.01	1.40	.04	.01	.15	---
MM-3	3.13	.76	.00	.00	.00	.03	---
MM-4	2.14	.07	.00	.00	.00	.07	---
MM-5	10.95	3.80	.00	.00	.00	.18	---
MM-6	1.25	.82	.00	.00	.04	---	---
MM-7	586.13	92.96	.33	.05	.04	.30	---
MM-8	25.56	9.48	.04	.02	.04	.07	---
MM-9	18.39	9.50	.54	.47	.95	.38	---
MI-1	1.19	.04	.00	.00	.00	.03	---

the staves collected in Ohio were known to be coated across the entire inside surface (plain-staves). Michigan Brand silos from the Charlotte, Michigan, plant have been reported to be of waxed-stave construction, thus staves collected in Michigan most likely were coated only on the joint mortar. Records are not available to verify the coating procedures of the particular staves collected for this study, however, higher concentrations near the edges (Positions A & C) of some of these staves would suggest that the joints were Cumar treated.

Scrapings from the surface of all of the staves revealed the presence of polychlorinated biphenyls when compared to standard Aroclor 1254. The thickness of these scrapings varied with composition and condition of individual staves. The maximum and minimum particle thickness of scrapings for each stave were measured. The average maximum thickness was 0.834 ± 0.580 mm and the minimum averaged 0.100 ± 0.012 mm. The range of PCB concentration in scrapings from these staves was > 250,000 μg/g to ≃ 1 μg/g (Table 2). The former is particularly significant as Cumar coating was intact on the stave surface with concentrations of PCB approaching the theoretical maximum of 325,600 μg/g based on reported Cumar formulations.

When sections were cut from the staves all but one were found to be densely constructed of concrete and stone aggregate. The National brand stave (ON-1) from Ohio was visibly porous with traces of coating penetrating beyond the surface. The stave used in this study was experimentally coated in 1971 (Willett, 1974), thus there is little likelihood of National silos that contain Cumar.

The average residue pattern of Michigan brand silo stave MM-9 (Table 2) suggested that penetration of PCB may have occurred. However, residue concentrations were greatest in sections along the stave joints; thus Cumar may have penetrated between, not through, the stave.

Except for the aforementioned National (ON-1) and Michigan (MM-9) brand staves, these studies revealed little penetration of residual PCB into the silo wall. Table 3 summarizes the amount of PCB in each section, thus the majority of the PCB was found in the first section (inside) of each stave which included the surface and 9 to 14 mm of concrete. Residual PCB was either nondetectable or in very low concentrations in subsequent sections through the stave until the outer surface. Most outside sections had a low PCB content, probably resulting from silage juices carrying PCBs

Table 3. Distribution of PCB in silo staves.

Stave No.	Amount of PCB (% of total in sections)					
	Section 1	Section 2	Section 3	Section 4	Section 5	Section 6
OM-1	86.41	.00	.00	4.85	8.74	---
OM-2	99.76	.24	.00	.00	.00	---
OCB-1	99.94	.02	.01	.01	.01	.03
ON-1	91.77	7.95	.20	.00	.00	.07
MM-1	99.73	.05	.00	.00	.22	---
MM-2	97.55	2.09	.06	.02	.28	---
MM-3	97.10	.00	.00	.00	2.90	---
MM-4	96.36	.00	.00	.00	3.64	---
MM-5	96.50	.00	.00	.00	3.50	---
MM-6	97.42	.00	.00	2.58	---	---
MM-7	99.31	.28	.05	.03	.33	---
MM-8	98.58	.35	.19	.30	.57	---
MM-9	82.52	3.67	3.55	6.82	3.44	---
MI-1	65.85	.00	.00	.00	34.15	---

down the outside of the silo or cross-contamination of staves when stacked, after the silos were dismantled. Amounts of PCB detectable in all sections other than those adjacent to the inner wall (section 1) were considered to be insignificant.

These results have shown that PCBs from the silo coating called Cumar did not penetrate significantly into the concrete staves. Thus, with the majority of residual PCB on the inner surface of the silo, the PCB content scrapings from this surface can be used to estimate the PCB content of the entire silo assuming that the density of scrapings are equal to the entire stave (2.3 g/cm^3). The following formulas were developed to estimate the PCB content of a silo irrespective of size. For plain-stave silos, where the entire staves were coated, concentration is estimated by:

$$C_e = C_s \cdot \frac{D_s}{D_w}$$

where: C_e = concentration in entire silo
C_s = concentration in scrapings
D_s = depth of scrapings
D_w = thickness of silo wall

In the case of Michigan Brand silos, where only the joint mortar was coated with Cumar, less PCB is present. If the scrapings were collected from the joint mortar of one of these silos, the concentration estimate for the entire silo can be adjusted for the portion not coated by the equation:

$$C_e = .23 \cdot C_s \cdot \frac{D_s}{D_w}$$

This study has shown that most of the residual PCBs from Cumar-treated silos can be found on or within a few mm of the inner silo surface. Therefore, the PCB content of scrapings from that surface can be used to estimate the PCB content of the entire silo. Based on these estimates, the majority of PCB-contaminated silos would not exceed 50 μg/g in the total structure and thus would not require disposal in a hazardous waste facility. This is fortunate because such disposal would be tremendously expensive and would occupy a great deal of valuable space that could be utilized for more hazardous materials.

Presently, there are no uniform regulations defining the ultimate fate of silos which have been coated with Cumar. In some areas they may be allowed to remain in use as long as no residue problems result, while in others they may need to be completely abandoned.

Cumar-treated silos are now at least 13 years old since the last reported uses of this coating were in 1970. Some date back to the early 1950s and late 1940s and have reached the end of their usefulness. Unless these older structures were recoated with Cumar, it is highly unlikely that they would exceed the federal 50 µg/g regulation as most of the PCB has eroded or was dissolved from the silo wall. Since these staves contain only small amounts of PCBs, which are bound to the surface, they seem to represent only a minimal future environmental hazard once removed from direct contact with humans, food, feed, or livestock.

An extensive survey of 19,096 silos in Michigan has revealed 406 that contained between .7 and 140,000 µg/g PCB, with 50% < 1,000 and 90% < 8,500 µg/g in scrapings. Since the majority of these silos surveyed are reported to have been only coated on the joint mortar, few would exceed the 50 µg/g limit on a whole silo basis.

Acknowledgements. This study was supported in part by Environmental Protection Agency Grant No. CS-8079120 and gifts from Milk Marketing, Inc., and Michigan Milk Producers Assn. Journal Article No. 49-84, The Ohio State University, Ohio Agricultural Research and Development Center.

REFERENCES

Willett LB, Hess JF, Jr. (1975) Polychlorinated biphenyl residues in silos in the United States. Residue Reviews 73:135-147

Willett LB (1974) Coatings as barriers to prevent polychlorinated biphenyl contamination of silage. J Dairy Sci 57:816-825

Willett LB (1980) Polychlorinated biphenyls from dairy farms: Consequence in market milk. J Dairy Sci 63:1961-1965

Received July 27, 1984; accepted August 27, 1984.