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Contamination of Silos in Switzerland by PCB Residues in Coatings

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Polychlorinated biphenyls (PCBs) have received considerable attention in the last 15 years, since studies have shown their extreme persistence in the world wide environment (Risembrough et al. 1968; Jensen et al. 1970).

Willet and Hess (1975) in the United States have reported results of a case of milk contamination by PCBs, principally AROCLOR 1254 from a silo coating named CUMAR. From the end of 1982 to the beginning of 1983 some Swiss Cantonal Laboratories for Food Control have detected high levels of PCBs in the milk output from several dairy farms at Laufental, in the northwest of Switzerland. These investigations showed that the silo coatings and consequently the silage from these silos were at the origin of the milk contamination. Four farms which produced the most polluted milk were investigated, specifically to determine PCB migration from coating material into the concrete walls and silage. Table 1 gives the characteristics of these 4 silos. This paper presents the results of this investigation.

Table 1 : Characteristics of the 4 silos investigated

Silo	PCB levels in milk (mg/kg fat weight) a)	Year of construction of the silo
A	3,80	1964
B	0,95	1962
C	1,30	1968
D	0,80	1955

a) Maximum level permited in Switzerland : 0,5 mg/kg fat weight

PCB residues come from a blue, plastic like coating material which has been applied to silos when these were built, 15 or 20 years ago. Its function was to fill the concrete pores and reduce the surface vulnerable to organic acids attack. Acid juices, principally acetic and lactic acid, are formed when silage components ferment. It has been shown that PCBs may be soluble in acetic acid (Hutzinger et al. 1974). It is difficult to estimate the formulation of the coating and the number of silos which have been treated, the factory being closed many years ago. However, it seems that the name of these coatings were SUPERASCOLIN and SILOGRUEN.

MATERIALS AND METHODS

All sampling materials were washed with distilled water, acetone and n-hexane. Silo coating has been detached by simple scraping with a knife and uniformely homogenized in a mortar before extraction. Silage has been drawn out with tweezers, chopped and analyzed. Concrete samples from silos B, C and D have been taken by means of an electric drill provided with a crown which extracts carrots with a diameter of 32 mm and a length of 40 mm. To exclude contaminations by the crown, external sides of the carrots were filed off with a fine grain file. Then, to study PCB penetration inside concrete walls, the filings taken from the carrots at three different levels, each 0,5 cm, were analyzed. At farm A, an electric drill provided with an auger-bit of 1,5 cm diameter was utilized; the powder was collected on aluminium foil and analyzed. Sand residues from scraping have been taken with a scoop, mixed uniformely and analyzed.
Although all precautions have been taken to avoid errors due to external contamination of the samples, caution is recommended when examining our test results. Extremely high levels of PCBs in some samples, for ex. 80'000 mg/kg, do not exclude contamination during sampling or analysis.

All solvents and chemicals were pesticide grade. Glassware was washed as described for sampling materials. PCB residues from silage, concrete and sand residues were extracted by 20 % acetone in n-hexane (v/v) in a mechanical agitator, four times 15 minutes each.
PCBs in coating materials were extracted by 50 % acetone in n-hexane (v/v) also in a mechanical agitator, four times 15 minutes each.

All extracts were filtered on anhydrous Na_2SO_4. Extracts from concrete, coating and sand residues were cleaned by agitation and later centrifugation with fuming H_2SO_4,7%. Silage extracts were cleaned on a florisil column. Extracts were concentrated and injected in GC-ECD with a capillary column. GC-ECD Ni_{63}, WCOT capillary-column SE-54, 30 m x 0,25 mm ID. Split mode. Quantitative determination was obtained by pattern comparison either with an AROCLOR 1260 standard of with one AROCLOR standard mixture of 1242, 1254 and 1260.

RESULTS AND DISCUSSION

The chromatograms of PCB residues found in the silo coating of all four silos correspond to AROCLOR 1260 type, figure 1. Less chlorinated biphenyls are also present, but in very low concentrations.

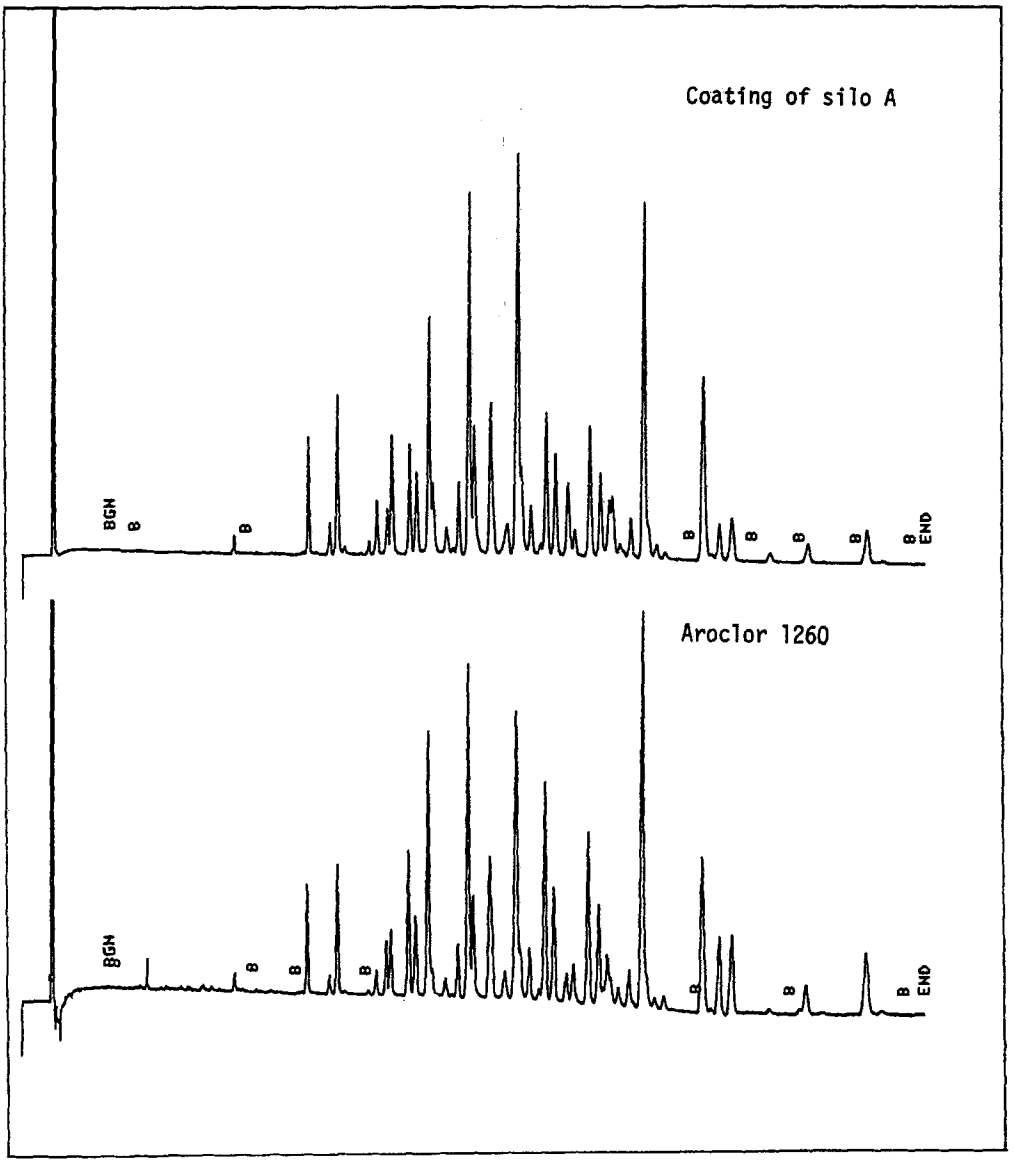

Figure 1 : Chromatogram patterns of PCB residues extracted from coating materials and Aroclor 1260. (For chromatographic conditions see text).

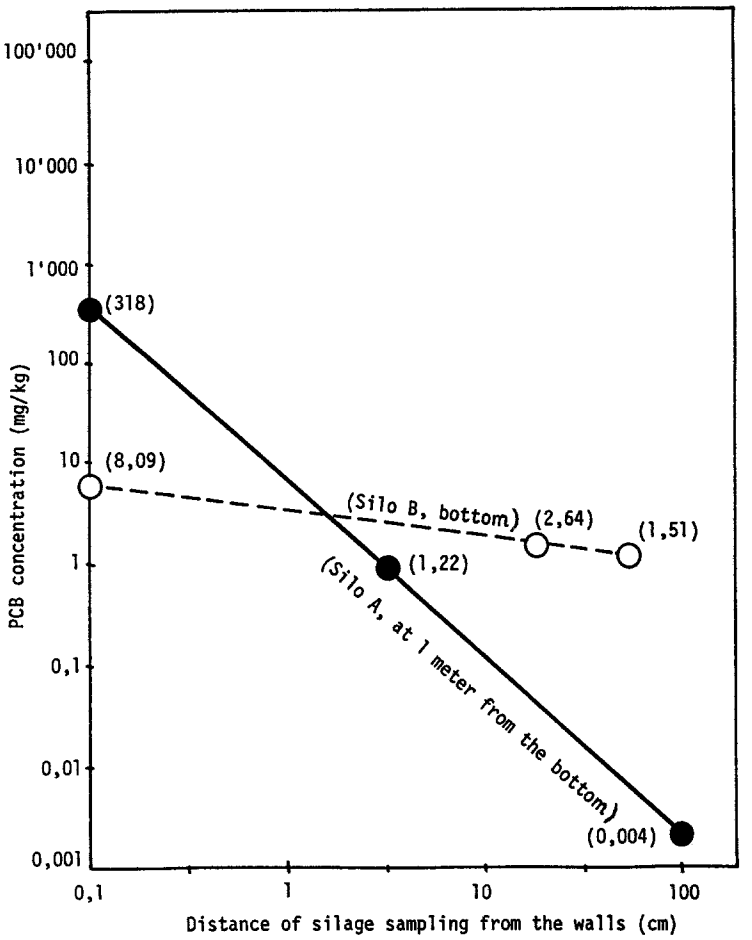

Figure 2 : PCB levels in silage

Silage : Only silos A and B still had fresh silage, the others had only old rests on the bottom or adhered to the silo walls. Results are shown in figure 2.
PCB levels in silage from these silos decrease as function of the logarithm of the distance from the wall. Only the first centimeters of the silage near the wall can be considered as very polluted. These results are similar to those found by different authors in the United States between 1971 and 1974 (Skrentny et al 1971, Willet 1974). The old silage adhered to the walls had high levels of PCB (300 mg/kg or more) and it is not impossible that little scraps of coating materials were present in the sample when sampling or analyzing.
PCB dissolution in acid juice, mechanical erosion of coatings and volatilisation of the coating surface seem to be the principal mechanisms which explain the PCB migration from coating to silage. In silo A, samples were taken of the silage having a height of one meter. Silo B had only a few centimeters of silage on the bottom. Differences between PCB levels corresponding to the distance from the walls are less pronounced than in silo A. It may suggest gravitational effect carry away of PCB from walls to the bottom and therefore a more uniforme distribution.

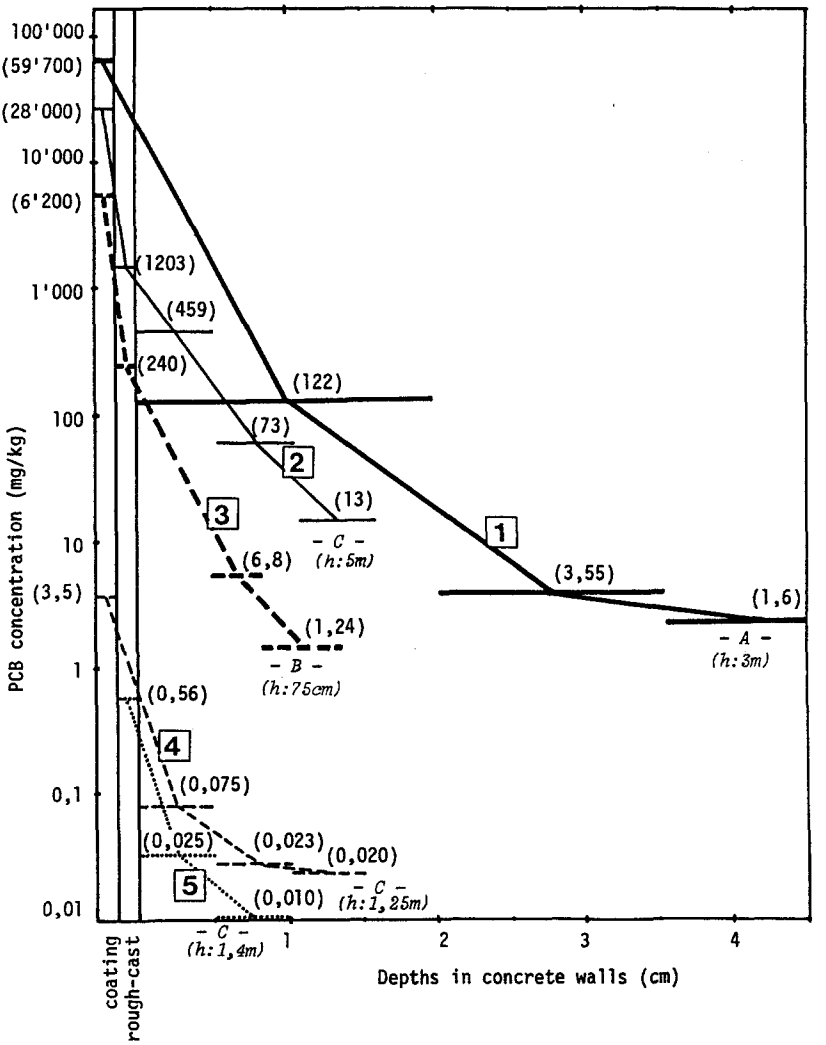

Figure 3 : PCB migration into silo walls

PCB residues in silo walls :

Generally PCB residues in the concrete walls were of the same type as the PCBs in the coatings, i.e. type AROCLOR 1260. However, at farm B, althouth the coating analyzed showed PCBs as AROCLOR 1260 concrete analyzis showed an important concentration of less chlorinated isomers like AROCLOR 1242. It could be possible that the coating formula in this silo was different from the others. Also, light PCB isomers had less viscosity in comparison with heavy isomers and thus perhaps they can penetrate more easily into concrete.

Figure 3 shows PCB concentration inside the concrete walls. Curves 1, 2 and 3 correspond to carrots which were taken under the coating material having a high PCB concentration and that seems to have relatively good conservation. Curves 4 and 5 correspond to carrots taken where the coating material was worn.

Figure 3 shows that, generally, PCB concentration in the wall seems to decrease logarithmically with depth. Concerning curves 1, 2 and 3, it seems that contamination affects principally the first two centimeters. Curves 4 and 5 concern the worn coating material and show a weak concentration in the concrete. It is possible that, when the coating is worn, organic acids dissolved the PCBs which had penetrated into the concrete.

The decontamination of silos polluted with PCB has been realized by scraping the walls with a high pressure sand jet. Residues ran between 500 and 700 kg per silo of 80 m^3. Values given in table 2 are to be examined with precaution because it was impossible to obtain a homogeneous sample of this quantity of sand. Consequently, silo decontamination by sand scraping produces a great quantity of toxic wastes and it is important to correctly eliminate them. The utilisation of plastic foil to cover the inside walls may be a less expensive and less polluting alternative to silo decontamination.

Table 2 : PCB levels in sand residues

Silo	PCB concentration (mg/kg)
A	484
B	183
C	1831

Investigations should be undertaken to study possible contamination of humans resulting from consumption of products from dairy farms, as well as the efficiency of the decontamination technics.

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