

Polychlorinated Biphenyl Contamination of Domestic Turkeys from Building Materials

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A field investigation was undertaken to determine the source of polychlorinated biphenyl (PCB) contamination in commercially reared turkeys. The sporadic nature of the residues indicated a source other than feed; 206 samples were collected from the farm, 105 samples were analyzed, and 32 were positive for PCBs. The positive samples consisted primarily of turkey tissues and building materials. A ceiling vapor seal/insulation consisting of white plastic, brown adhesive, and a small amount of retained spun glass contained over 500 ppm PCB, similar to an Aroclor 1254/1260 mixture. The congener profile in turkey fat was consistent with that of the vapor seal when the influences of weathering and biodegradation/bioaccumulation were considered. The old vapor seal, pieces of which were observed to fall into the turkey pens, was apparently consumed by the birds and resulted in the violative residues in a small proportion of the flock. Removing loose plastic and recovering with newer materials reportedly alleviated the turkey residue problem.

Polychlorinated biphenyls (PCBs) are highly stable compounds, commercially produced as mixtures for a wide variety of industrial applications. Production and use declined rapidly in the mid-1970s after their worldwide accumulation in the environment was confirmed and accompanied by cases of widespread human and animal contamination and poisoning (Hansen, 1987a,b). PCBs are ubiquitous in the atmosphere, hydrosphere, and lithosphere. Geographical distinctions are decreasing as dispersion followed declining use and disposal (Eisler, 1986; Hansen, 1987a); nevertheless, there are several large foci of greater contamination and hazard as well as smaller areas of higher PCB concentrations but limited environmental impact. Monitoring of the food supply occasionally detects unexpected sources of PCB exposure.

PCBs have a low acute toxicity, and levels of exposure below current U.S. Food and Drug Administration (FDA) guidelines of 0.2-5.0 ppm do not appear to present a hazard to consumers. Subacute and chronic health effects, however, are complex and not fully understood. People eating large amounts of older fish from moderately contaminated sources (DHEW, 1978) or large proportions of contaminated animal products (Hansen, 1987b) are at the greatest health risk. Because of the food processing and distribution system in the United States, it is unlikely that most consumers will be exposed to more than occasional pulses of dietary PCB; however, primary producers who eat mostly their own products do not enjoy the attenuating influence of dilution and a mix of sources. A well-known example is the exposure of families from farms using PCB contaminated silos (Hansen, 1987b).

In April 1987, routine premarket screening indicated unacceptable PCB contamination in turkeys from a large producer in the southeastern United States. The variable residues indicated an unusual source of contamination. Staff of the University of Illinois Animal Poison Information Center investigated the problem, determining the major sources of contamination to be certain building materials in the 25-year-old range houses. After routine PCB estimation procedures, specific ion monitoring GC-MS was used to confirm the presence of PCBs and to assist

in matching sources with animal residues.

MATERIALS AND METHODS

On 10 April 1987, a composite prepurchase fat sample from the producer was shown by the packer to contain a concentration of PCBs greater than the FDA tolerance of 3.0 ppm for poultry fat. Resampling of turkeys from the range houses containing the affected birds confirmed the presence of PCBs, and the packer refused to accept the birds. The Illinois Animal Poison Information Center was contacted on 1 May 1987 and visited the facility on 5 and 6 May.

The facility consisted of six range houses, a brooder house, and associated office, storage, and machine sheds. The two implicated range houses (#2 and #3) were near two additional range houses (#4 and #5), somewhat separated from the brooder house (#1) and more distant from range houses #6 and #7. A systematic sampling of turkey tissues, feeds, water, medications, soils, litter, lubricants, and building materials yielded 206 samples. Of these, 105 were analyzed and 32 were positive for PCBs. Two separate laboratories were involved in the analyses, both of which employ glassware cleaning procedures, solvent and apparatus blanks, and daily quantitation as is customary for PCB analyses (Erickson, 1986).

The feed and fat samples were extracted with hot isooctane and screened by packed-column gas-liquid chromatography (GC) at the State Animal Disease Laboratory in Centralia, IL. Positive samples were quantitated by capillary column GC, total PCB estimations being based on the seven major peaks in Aroclor 1254/1260 standards. Samples with a minimum of five matching peaks (retention times and proportions) were reported as positive. These methods in this laboratory are FDA certified for 98% recovery.

For the remaining samples a slightly more rigorous procedure was employed in our laboratory. Aliquots of 5 g were extracted by shaking for 2 h at 80 °C in a water bath with 10 mL or more of isooctane. Of the extract 1 mL was adsorbed onto 1 g of activated Florisil and extracted from a disc filter cartridge with 3 × 2 mL of petroleum ether-ethyl ether (94:6). The solvent was then evaporated under nitrogen and the residue resuspended in 1 mL of isooctane for analysis by capillary column GC with temperature programming and electron capture detection. A Hewlett-Packard 5840A GC equipped with a J&W DB-5 30 m

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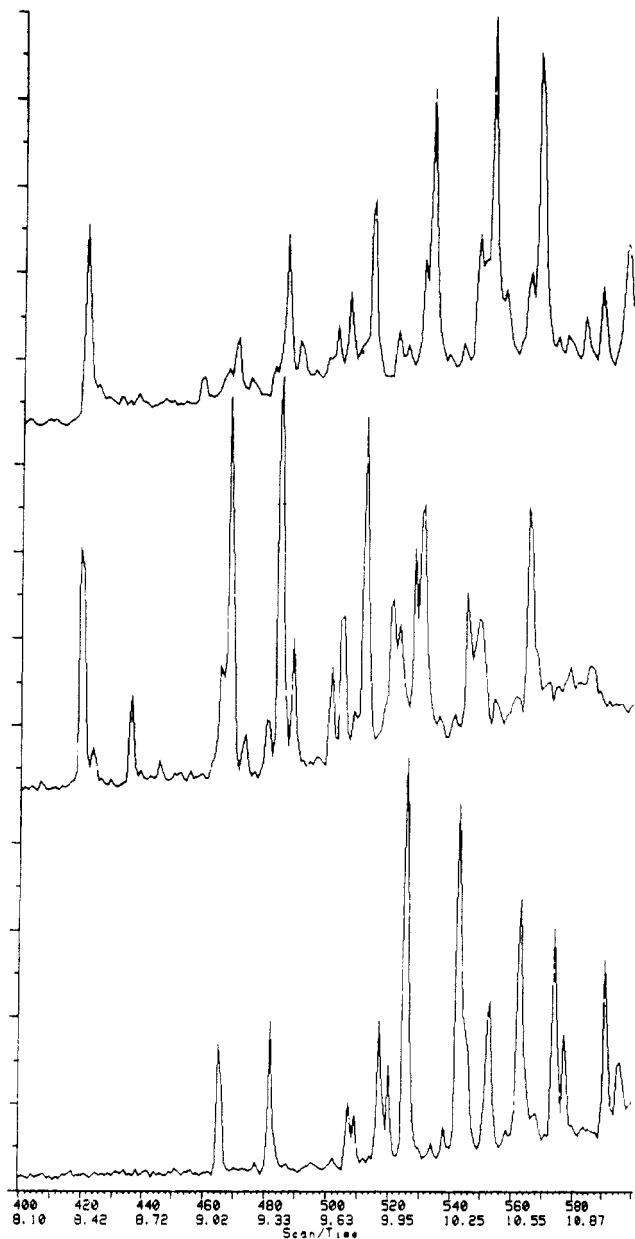


Figure 1. Gas-liquid chromatograms of Aroclor 1260 (bottom), Aroclor 1254 (middle), and an extract of the ceiling vapor seal (top). Detection by electron impact mass spectroscopy (total ion current).

$\times 0.53$ mm column (J&W Scientific, Folsom, CA) was used. Temperatures: injector, 270 °C; detector, 300 °C; column oven, 160 °C programmed to 260 °C at 4 °C/min with a hold time of 5 min. The column gas flow was 7 mL/min hydrogen.

Recoveries were not determined from each of the separate matrices but can be safely considered to be greater than 75% for the plastics since this matrix is less tenacious than animal fats and recovery following Florisil cleanup is nearly quantitative (Erickson, 1986). A separate extraction of a different aliquot of sample 178 (vapor seal) was performed several months later by refluxing 1.0 g in 75 mL of acetone-hexane (1:1, v/v) for 2 h, drying with sodium sulfate, and evaporating into 0.5 mL of isoctane. GC-ECD analysis following Florisil cleanup (mean recovery of five congeners, 95%; range, 84–112%) yielded an estimate of 693 ppm PCB as Aroclors 1254/1260 compared to 516 ppm in the first sample.

The two turkey fats and the four building material samples with the highest PCB residues were further re-

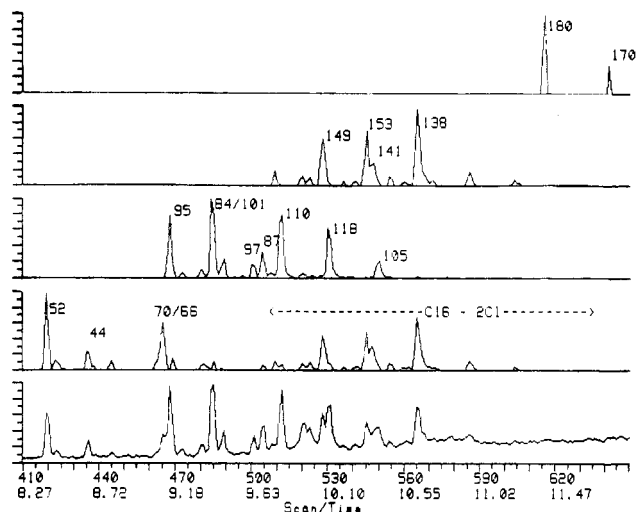


Figure 2. Single-ion chromatograms of Aroclor 1254 resolving (from top to bottom) hepta-, hexa-, penta-, and tetrachlorobiphenyls within the total ion chromatogram (bottommost). 100% responses were 44, 967, 2248, 987, and 103925, respectively. Specific congeners are identified by IUPAC number (see Table III). The area contributing from the fragment ions of the hexachlorobiphenyls ($M - 2Cl$) to tetrachlorobiphenyl chromatograms is indicated.

solved by capillary column GC/mass spectroscopy (GC/MS) (Figure 1). Mass spectrometry was performed on an Extranuclear Simulscan quadrupole mass spectrometer interfaced with a capillary gas chromatograph (Extrel Corp., Pittsburg, PA). Spectra were acquired in the electron impact mode at 70 eV, scanning from 45 to 550 amu at 750 amu/s. The source temperature was 200 °C. Calibration was accomplished with perfluorotributylamine reference standard. The gas chromatograph was equipped with a J&W DB-5 30 m \times 0.25 mm fused silica column with 0.25- μ m film thickness, interfaced directly with the MS source through an interface operating at 300 °C. The GC operating parameters were as follows: injector, 270 °C; column oven, 90 °C programmed to 320 °C at 20 °C/min with a hold time of 5 min. Gas flows: column flow, 50 cm/s helium; split vent, 30 mL/min; septum purge, 2 mL/min. Injections were 1 μ L, with the split vent opening 30 s after the injection was made.

Single-ion chromatograms for the molecular ion masses of the PCB congeners were used to identify the congener groups: tetra-CB m/z 290; penta-CB m/z 326; hexa-CB m/z 360; hepta-CB m/z = 394. Figure 2 illustrates the separation for the Aroclor 1254 standard and the most likely IUPAC number (Ballschmiter and Zell, 1980) of the PCB congener in some of the major peaks. In the mass spectra of the higher chlorinated PCB's, the fragmentation corresponding to loss of two chlorines from the molecular ion is abundant ($M - 2Cl$). The identity of the higher chlorinated congeners can then be further confirmed by looking at the single-ion chromatogram for the congener with two fewer chlorines. With some of the samples, the $M - 2Cl$ peaks of the hexachlorobiphenyls were great enough to diminish the tetrachlorobiphenyl peaks so that minor portions were isolated from the total ion chromatogram in order to diminish the interference and visualize the tetrachlorobiphenyls.

RESULTS AND DISCUSSION

Routine sampling had detected PCB residues above 3 ppm in bird fat, and two subsequent samplings of 30 birds each had indicated residues from below detection to 17 ppm. The objective of further sampling was to assist in

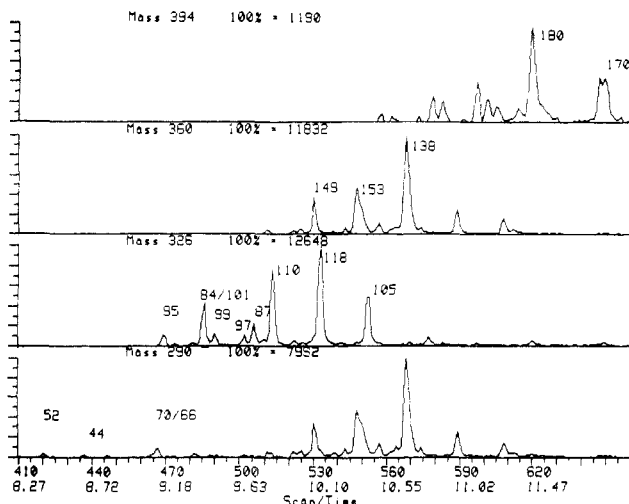


Figure 4. Single-ion chromatograms of vapor seal extract. Congeners identified as in Figures 2 and 3.

clearly confirmed the presence of common peaks (Figure 4).

Table III indicates the most probable identities of the Aroclor and sample peaks and a subjective summary of the relative amounts present. While several references (see below) have been consulted, it should be noted that none agree entirely on the identities of each peak. For example, early work established the presence of PCBs 84 and 110 in Aroclor 1254 (Sissons and Welti, 1971; Webb and McCall, 1972) and later studies confirmed their presence in both Aroclors 1254 and 1260, PCB 110 being a major component of 1254 and Clophen A50 and a significant component of 1260 (Bush et al., 1983; Safe et al., 1985; Duinker et al., 1988). Nevertheless, these PCBs are not included in the analysis by Ballschmiter and Zell (1980) or Schwartz et al. (1987). Ballschmiter et al. (1987), however, have recently revised their assignments to include these congeners. Schwartz et al. (1987) used 105 congeners as standards while Safe et al. (1984) synthesized all 209 congeners in their laboratory and were able to resolve 195 of the 209 (Mullin et al., 1984).

The relative retention times for all 209 congeners (Mullin et al., 1984) and the single-ion chromatogram resolution of isomers were used to confirm our initial peak identifications. As further confirmation, samples of pure PCBs 52, 95, 118, and 153 were compared by GC/MS to the proposed peaks in Aroclor 1254. Retention times and electron impact fragmentation patterns confirmed the identity of these congeners with the peaks in Aroclor 1254 as proposed in Table III.

Comparing specific ion chromatographs of the vapor seal (sample 178, Figure 4) with that of turkey fat (sample 137, Figure 3) reveals little change in the heptachlorobiphenyls present. Of the hexachlorobiphenyls, the relative amount of PCB 149 declines in the fat sample while the relative contribution of PCB 153 increases. Pentachlorobiphenyl 118 can serve as a reference peak in fat and vapor seal. PCBs 95 and, especially, 84/101 and 110 are lower in fat (relative to PCB 118) while PCBs 105 and 99 are relatively higher in the fat as compared to the vapor seal, the suspected major source of contamination. Significant tetrachlorobiphenyls in the vapor seal are PCBs 52 and 44 and a peak that should be PCB 70 and/or 66. The contribution of tetrachlorobiphenyls in the fat sample is readily masked by the large contribution of fragment ions from the hexachlorobiphenyls ($M - 2 Cl$); scans excluding this influence reveal little PCB 52 and 44, but a significant peak for 66/70. The same congener pattern was seen in the second

fat sample (sample 158, Table I) except that PCBs 95 and 110 were not present at detectable concentrations.

PCBs 95, 84, and 149 are present at lower relative concentrations in the vapor seal than would be expected from an Aroclor 1254/1260 mixture; the presence of three ortho chlorines in these congeners greatly influences volatility, and their GC retention times are shorter than would be expected; this may also influence their weathering out of the vapor seal. PCBs 95, 110, and 149 did not accumulate in bird fat in the proportions found in the vapor seal; these PCBs have the labile 2,3,6-substitution and generally do not accumulate in animals (Hansen, 1987a,b). PCBs 118, 105, 153, and 138 accumulate readily as would be expected from animal experiments (Hansen, 1987a,b).

Thus, allowing for physical properties and susceptibility to biodegradation, it appears that pieces of the vapor seal falling from the ceiling and eaten by the turkeys provided the majority of the congeners found in the turkey fat. The vapor seal most likely contained a combination of Aroclor 1254 and Aroclor 1260. Recent contact with the producer indicated that the residue problem was alleviated by removing loose plastic and covering the remaining material with a different plastic.

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Registry No. PCB 149, 38380-04-0; PCB 153, 35065-27-1; PCB 118, 31508-00-6; PCB 95, 38379-99-6; PCB 101, 37680-73-2; PCB 110, 38380-03-9; PCB 105, 32598-14-4; PCB 99, 38380-01-7; PCB 52, 35693-99-3; PCB 44, 41464-39-5; PCB 66, 32598-10-0; PCB 138, 35065-28-2; PCB 180, 35065-29-3; PCB 170, 35065-30-6; aroclor 1254, 11097-69-1; aroclor 1260, 11096-82-5.

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Volatile Constituents of Guava Fruits (*Psidium guajava* L.) and Canned Puree

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Essences of fresh guava (*Psidium guajava* L.) with white and pink flesh, respectively, were obtained by direct extraction of flesh juices with dichloromethane. Commercial canned puree of guava was water distilled, and the distillate was extracted with dichloromethane. The three essences were analyzed by fused silica capillary gas chromatography and gas chromatography/mass spectroscopy. A total of 122 volatile components were identified: 13 aldehydes, 17 ketones, 31 alcohols, 10 acids, 28 esters, 10 hydrocarbons, and 13 miscellaneous compounds. Quantitatively, the major constituents of fresh fruits were C₆ compounds. The total amount of C₆ aldehydes, alcohols, and acids comprised 20% of the essence of fresh white and 44% of the essence of fresh pink. The canned puree contained acetoin, which comprised 81% of the essence, as the major constituent.

The guava (*Psidium guajava* L.), which has a unique quince- and banana-like odor, is native to Central America. It was distributed into other parts of tropical and subtropical areas such as Asia, South Africa, Egypt, and Brazil by the early 17th century and is now cultivated in nearly 60 countries. The production of guava in the world is still much less than those of other major tropical fruits, but it is economically important in certain countries. In addition to consumption as fresh fruit, guava has been processed into many different foods: jellies, jams, cheese, ketchup, puree, juice powder, nectar, and juices.

A pioneer study on volatile components in guava was done in the early 1960s (Kunishi and Seale, 1961). The aroma constituents of guava were not, however, reported until Stevens et al. (1970) identified 22 aroma components of Hawaiian guava. They suggested that β -ionone, which has a low odor threshold and intense violet aroma, contributed floral flavor to the fruit. Wilson and Shaw (1978), who identified 12 terpenes in an extract of guava puree, described that β -caryophyllene plays an important role in guava aroma. Later, MacLeod and de Troconis (1982) reported that 2-methylpropyl acetate, hexyl acetate, and benzaldehyde had a guava-like odor among 40 volatiles identified in guava from Venezuela. Most recently, Idstein and Schreier (1985) identified 154 compounds in guava from Brazil including 115 compounds described for the first time. In the present study, volatile components of fresh guava fruit from Amami Island, Japan, and canned guava puree from South Africa were identified.

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EXPERIMENTAL SECTION

Materials. Fresh ripe guava fruits (pink and white) were obtained from Amami Island located 300 miles south of the mainland of Japan. Canned guava puree was purchased from the Potona Canning and Production Co., Ltd. Authentic chemicals for gas chromatographic analysis were purchased from reliable commercial sources or were donated by Ogawa & Co., Ltd., Tokyo, Japan.

Sample Preparations. Fresh guava with white flesh (white) and fresh guava with pink flesh (pink) were treated and analyzed separately. The fruit flesh (1.5 kg) was separated from peel and seeds, sliced into small pieces (3 cm), and homogenized with an electric blender. The homogenized sample was mixed with 1.5 L of deionized water, and stone cells were removed with a centrifuge. The fresh juice (2 L) was extracted with 150 mL of dichloromethane with use of a liquid-liquid continuous extractor for 12 h. After the extract was dried over anhydrous sodium sulfate, the solvent was removed on a Vigreux column at 42 °C. The solvent was further removed with a purified nitrogen stream, and approximately 0.3 mL of a fresh fruit essence was obtained.

Canned puree (1.5 kg) was also homogenized with 1.5 L of deionized water and was water-distilled under reduced pressure (40 mmHg) in a nitrogen stream at 40 °C. The distillation was continued until 1.5 L of distillate was obtained. The distillate was extracted with 150 mL of dichloromethane with use of a liquid-liquid continuous extractor for 12 h. The extract was treated in the same manner as the one from fresh fruit, and approximately 0.5 mL of essence was obtained.

Analysis of Volatiles. Identification of volatile constituents of the guava samples was made by comparison of their Kovats gas chromatographic retention indices and mass spectra to those of authentic compounds.