6.9 to 7.0. The major isomer, 6 Br(I), was found in concentrations of 4.1, 5.7, and 4.4 ppb, respectively. Peaks corresponding in retention time to all six PBB components were also found. Additional evidence for the identity of these peaks as PBB's was the disappearance of the hexa- and heptabromobiphenyl peaks and the appearance of peaks with shorter retention time after exposure to uv light, as described in the confirmatory procedure of Erney (1975).

Since we do not have previous samples from this farm, we could not determine quantitative changes in PBB or changes in peak ratios with time; however, these analyses clearly show that PBB's can be detected in manured soils nearly a year after application. The quantities found are very small and appear to pose no future hazard. Since PBB's are sensitive to light (Ruzo and Zabik, 1975), surface applied manure may allow some photodegradation.

We conclude that the potential hazards from PBB-contaminated soils are low since PBB's are not taken up by plants or leached to ground water (Filonow et al., 1976) at concentrations expected to be present, and they are probably not volatilized due to their low vapor pressure (5.2×10^{-8} mmHg at 25 °C, calculated from Michigan Chemical Corp. Product Bulletin); however, they may remain in the soils for many years because of their resistance to degradation. Only low levels of contamination are expected in soils on most of the exposed farms because of dilution, as we found for the one farm examined. In certain rare and localized situations where high level contamination may have occurred, potential concern could arise from erosion of contaminated soils or manures into streams and the accumulation of PBB's in terrestrial and aquatic food chains.

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Fate of Polybrominated Biphenyls (PBB's) in Soils. Retention of Hexabromobiphenyl in Four Michigan Soils

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The adsorption of 2,2',4,4',5,5'-hexabromobiphenyl (HBB) by four Michigan soils conformed well to a Freundlich adsorption isotherm. Adsorption of HBB increased with increasing soil organic carbon (correlation, $r = 0.87$ to $r = 0.96$). Leaching studies using the same soils amended with 100 ppm of HBB showed that less than 0.6% of the HBB was lost from each soil with leachate quantities equivalent to 20 times the average annual rainfall in Michigan. Results suggest that PBB, which is present in some Michigan farm soils due to applications of PBB-contaminated manure, should not leach below the depth of incorporation.

Following widespread contamination of Michigan livestock by PBB's, concern developed for potential movement of PBB's from burial sites or from surface soils if the latter were found to be significantly contaminated.

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To acquire information regarding the retention and movement of PBB in contaminated soils, adsorption and leaching studies were conducted in the laboratory with four Michigan soils using 2,2',4,4',5,5'-hexabromobiphenyl (HBB). We report here on the results of these studies.

EXPERIMENTAL SECTION

Reagents. The 2,2',4,4',5,5'-hexabromobiphenyl (HBB) was chromatographically separated and purified (>95%) from fireMaster BP6 (lot no. 6244A), a mixture of polybrominated biphenyls (PBB). The identifications of the

Table I. Characteristics of Soils

| Soil | % | | | | |
	Org.[a] C	Sand[b] (2.0-0.05 mm)	Silt[b] (0.05-0.002 mm)	Clay[b] (<0.002 mm)	pH
Spinks ls	1.10	81.1	14.5	4.4	5.8
Miami sl (eroded)	1.18	56.5	26.3	17.2	7.7
Miami sl	2.12	54.2	33.7	12.1	6.0
Brookston sl	3.14	58.0	27.9	14.1	7.0

[a] Average of duplicate determinations by Walkley-Black method (Allison, 1965). [b] Average of duplicate determinations by pipet method (Kilmer and Alexander, 1949).

fireMaster components and of HBB are described elsewhere (Jacobs et al., 1976). Nanograde quality organic solvents and water redistilled from water containing permanganate were used in all experiments. Anhydrous sodium sulfate was washed with methylene chloride and dried prior to use, and glass fiber disks (Whatman GFC, 9 cm diameter) were used as received.

Instrumental Analyses. Gas–liquid chromatography was done on a Beckman GC-5 gas chromatograph equipped with a nonradioactive electron-capture detector and a Beckman 10-in. linear recorder (1 mV). The polarizing voltage was 550 V and the carbon dioxide and bias voltage set for optimum detector response. A 1.83-m glass column packed with 2% Dexsil 300-GC on 80/100 mesh Gas-Chrom Q was used with a carrier gas flow rate of 100 ml/min. The inlet, column, detector line, and detector temperatures were 220, 250, 270, and 300 °C, respectively. Using this column and operating conditions, the HBB peak retention time was 4 min, and the least detectable quantity was 20 pg of HBB. The coefficient of variability for HBB analyses in extracts was 5%.

Soils. Four soils obtained from the University Experimental Farms were used in adsorption and leaching experiments: a Spinks loamy sand (Psammentic Hapludalf); a Miami sandy loam, eroded phase (Typic Hapludalf); a Miami sandy loam (Typic Hapludalf); and a Brookston sandy loam (Typic Argiaquoll). The particle size distributions, organic carbon concentrations, and pH values of these soils are given in Table I. The soils were air-dried, passed through a 2-mm sieve, and stored in glass bottles until use.

EXPERIMENTAL PROCEDURES

Adsorption. A stock concentration of HBB in water was prepared by adding 0.4 ml of 10 000 μg/ml HBB in acetone to 20 l. of water stirred with a Teflon coated magnetic bar. Dilutions of this stock solution provided varying HBB concentrations for the adsorption experiments conducted by shaking 200 ml of HBB solution with 5.00 g of soil (10.00 g of Spinks soil) in a 300-ml flask at 24 °C. Preliminary work showed that 2 h of equilibration was sufficient for HBB adsorption, so a 4-h shaking time was used to ensure completeness of adsorption.

Four HBB concentrations were equilibrated with each soil and replicated five times for each concentration. Four flasks without soil were used for each HBB concentration as the control. After shaking, the soil–solution mixture was filtered through a Buchner funnel with a glass fiber disk into a suction flask containing 25 ml of benzene. Two controls at each concentration were filtered and two were not filtered prior to extraction of HBB.

Since HBB adsorbs to glassware, the quantity of HBB available for adsorption by soil was always determined by the difference in benzene extractable concentrations between controls and the flasks containing soil–solution mixtures. An estimate of the HBB retained on the glass filter was obtained by the difference between filtered and unfiltered controls. These differences were then used to determine the actual quantity of HBB removed from solution by each soil during equilibration.

Leaching. One kilogram of each soil (25% moisture) was mixed continuously for 5 min with acetone containing 100 mg of HBB. The acetone was evaporated with heat lamps until the soil was dry and free flowing (acetone odor absent). The resulting amended soil was extracted by three successive benzene–2-propanol (2:1) aliquots and the HBB concentrations in the soils determined. Results confirmed that the soils contained 100 ppm of HBB.

Amended soil was placed in a glass column (3.8 cm diameter × 70 cm) fitted with a removable stopcock adaptor, with glass wool placed above and below the soil column. Three columns, each containing 100 g of amended soil, were prepared for each soil and leached continuously with water. Soils were kept in a saturated state for the duration of the experiment, and a free water head of 50–55 cm was maintained above the soil surface. Leachate was collected in a glass bottle containing 50 ml of benzene which was wrapped with foil to prevent possible photodecomposition (Ruzo and Zabik, 1975).

The Brookston, Spinks, Miami, and Miami (eroded) soils were leached for 7, 11, 12, and 19 days, respectively. Leachate was collected continuously and samples analyzed for HBB at regular intervals which varied depending on the rate of water flow through the soil.

Water Analysis. Water samples collected from the adsorption and leaching studies were extracted three times with benzene. The extracts were combined, passed through sodium sulfate into a round-bottomed flask, and concentrated by placing the flask (fitted with a three-ball Snyder column) on hot sand (80–90 °C). The concentrated extract was then transferred, along with successive washings, into a volumetric flask, and the resulting HBB concentration determined by gas chromatography. Loss of HBB by volatilization during the concentration step was determined to be less than 5%, while the overall extraction efficiency with benzene was 90%.

RESULTS AND DISCUSSION

Adsorption Experiments. Table II shows the mean quantities of HBB adsorbed by soils during equilibration. Coefficients of variation for replicates were usually 10% or less. Adsorption was least with the Spinks soil which removed 2–4% of the available HBB and greatest with the Brookston soil which removed 10–14%. The two Miami soils had intermediate removals with the Miami (eroded) adsorbing 4–5% of the available HBB compared to 6–10% for the other Miami.

Adsorption of HBB by the four soils was influenced primarily by organic carbon content of the soils. The correlation between adsorption and organic carbon ranged from $r = 0.87$ ($x/m = 16$ ppb) to $r = 0.96$ ($x/m = 85$ ppb) for the four soils. Neither percent clay nor pH correlated well with HBB adsorption. Any effect which clay content may have had was apparently masked by the effect of

Table II. Mean Quantities of HBB Adsorbed by Soils for Varying Amounts of HBB in Solution

Soil	μg		
	HBB available in solution[a]	Mean[b] HBB adsorbed by soil	% of available adsorbed
Spinks ls	1.20	0.025	2.1
	3.00	0.083	2.8
	12.2	0.352	2.9
	29.4	1.12	3.8
Miami sl (eroded)	2.40	0.090	3.8
	3.60	0.178	4.9
	6.40	0.242	3.8
	13.4	0.516	3.8
Miami sl	3.20	0.334	10.4
	5.40	0.396	7.3
	9.20	0.576	6.3
	17.0	0.942	5.5
Brookston sl	3.00	0.316	10.5
	8.40	0.866	10.3
	11.6	1.28	11.0
	23.8	3.27	13.7

[a] Two hundred milliliters of HBB solution. [b] Mean of five replicate determinations.

Table III. HBB Adsorption by Different Soils (x/m) under Identical Equilibrium Concentrations[a]

HBB concn, ppb	ng/g			
	Spinks ls	Miami sl (eroded)	Miami sl	Brookston sl
16	72	126	301	307
27	137	211	421	558
46	263	358	595	1025
85	559	659	885	2067

[a] x/m calculated using regression equations in text.

organic carbon on adsorption. Haque et al. (1974) found that the adsorption of Aroclor 1254, a polychlorinated biphenyl, was similarly influenced by soil organic carbon.

Adsorption of HBB by each soil is plotted in Figure 1 using the log expression of the Freundlich adsorption isotherm, $\log x/m = \log K + 1/n \log C$, where x is micrograms of HBB adsorbed, m is the mass of adsorbent (grams of soil), C is the HBB concentration following equilibration, and K and $1/n$ are constants. The adsorption of HBB by these soils conformed very well to the Freundlich equation as did the adsorption of polychlorinated biphenyls (Haque et al., 1974).

Regression equations expressing Freundlich-type adsorption were developed for the soils: Spinks, $\log x/m = \log K + 1.22 \log C$, $K = 2.42$; Miami (eroded), $\log x/m = \log K + 0.99 \log C$, $K = 8.00$; Brookston, $\log x/m = \log K + 0.65 \log C$, $K = 12.94$; and Miami, $\log x/m = \log K + 1.14 \log C$, $K = 49.77$. The coefficients of correlation for all equations were $r = 0.96$ or greater, indicating that
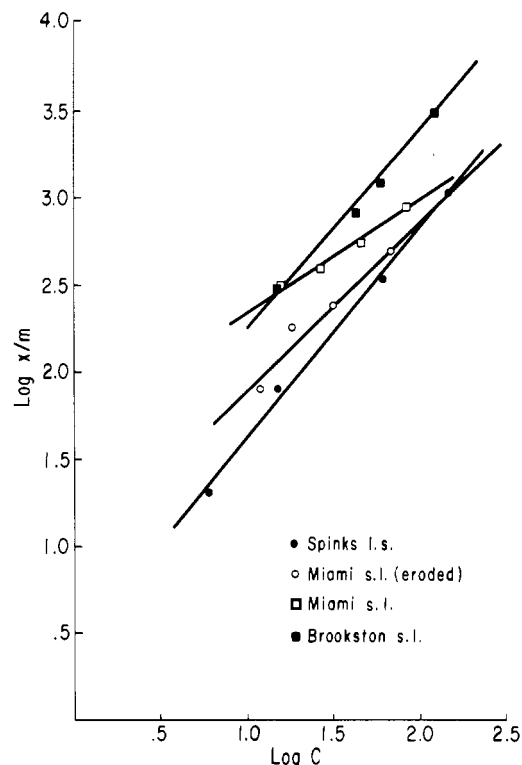

Figure 1. Freundlich isotherm showing adsorption of HBB onto four agricultural soils (C in parts per billion and x/m in nanograms of HBB/gram of soil).

adsorption data fit the Freundlich equation well. Using these equations, theoretical HBB adsorption values were calculated for identical equilibrium concentrations (Table III) for direct comparison among the four soils.

Leaching Experiments. The removal of HBB from the amended soils did not agree with the general order of HBB adsorption, as determined from the adsorption isotherms of the soils. However, the mechanisms responsible for adsorption of HBB in the four soils were probably not controlling the amount of HBB removed by leaching water. The basis for expecting other than desorption mechanisms to control loss of HBB from the amended soils follows.

Table IV shows the leachate volume collected for each soil, the amount of HBB removed by that water, and the average HBB concentration. All water collected from columns had HBB concentrations less than the lowest adsorption concentration (16 ppb) used in Table III. At the 16-ppb concentration, the maximum adsorption was only about 0.3 μg/g of soil. In contrast, the HBB amendment used for the leached soils was 100 μg/g, which greatly exceeds the adsorption capacity of the four soils. Therefore, this high amendment essentially amounts to a physical deposit of HBB in each soil which greatly exceeds any retention of HBB effected by physicochemical forces in each soil. Consequently, mechanisms other than

Table IV. Total HBB Recovered in Leachates from Soil Columns[a]

Soil	Leachate vol, l.	HBB recovered, μg	HBB concn in leachate, μg/l.	Av leaching rate, l./day
Miami sl (eroded)	3.47	11.08	3.19	0.18
Brookston sl	9.07	13.63	1.50	1.30
Miami sl	9.98	28.21	2.83	0.83
Spinks ls	18.05[b]	21.92	1.21	1.64

[a] Mean of three replicate columns. [b] Equivalent to rainfall of 1592 cm.

desorption are likely responsible for the amount of HBB which was removed from the soil by leaching water.

The rate of leaching generally declined as the percolating water increased settling and compaction. No definite relationship between leaching rate and the resulting HBB concentration of the leachate was evident. Such a relationship might be expected if the solubility of the HBB in water was the dominant mechanism controlling the loss of HBB from the amended soils. Some preliminary work suggested that when solid HBB was mixed with distilled water, the rate of HBB dissolution into the water was very slow, taking 21 days for 28 ppb of HBB to be dissolved. While a comparison between the average HBB concentration in the leachates and the average leaching rates (Table IV) between soils seems to indicate this possibility, this trend is not as evident when looking at individual column data. Therefore, other mechanisms of organic chemical transport in soils (Letey and Oddson, 1972) may be contributing to HBB loss from the amended soils.

An important aspect of considering leaching losses from a highly contaminated soil is in evaluating potential environmental pollution by movement of polybrominated biphenyls from the soil with water. If the average leachate concentrations for each soil (Table IV) are multiplied by the maximum leachate volume collected for the Spinks soil, the theoretical quantity of HBB that would be lost from each soil for that volume of water can be calculated. Under these conditions, the amount of HBB lost from each soil would be less than 0.6% of the total HBB present. These predicted losses suggest that HBB will not be readily leached even from highly contaminated soils by percolating water.

The results of the leaching and adsorption studies can be used to estimate PBB leaching in soils to which PBB-contaminated manure was applied. One should note, however, that our studies were with HBB which is approximately 20 times less soluble in water than PBB (fireMaster BP6). [The solubility of fireMaster BP6, lot no. 6244A, was estimated to be 610 ± 50 ppb (ng of PBB/ml) based on the mean analyses of redistilled water mixed continuously with solid PBB for 7, 14, and 56 days.]

Assuming that HBB adsorption values (Table III) are the same for PBB, adsorption of PBB by the four soils would range from 70 to 300 ng of PBB/g of soil if the PBB concentration in the soil solution was approximately 16 ppb. These adsorption capacities would be equivalent to about 0.16–0.68 kg of PBB/ha for the surface 15 cm of soil. With higher PBB concentrations in the soil solution, larger quantities of PBB would be adsorbed by the surface 15 cm of soil.

Livestock manure can contain very high PBB concentrations while the animals are eating contaminated feed but declines rapidly after the PBB source is discontinued (Willett and Irving, 1975). The highest PBB concentrations reported for dairy manure after PBB ingestion was discontinued are 2.79 ppm (Willett and Irving, 1975) and 1.54 ppm (R. M. Cook, personal communication). These concentrations occurred 7 days and several months, respectively, after PBB ingestion was stopped.

Since these concentrations were for highly contaminated cows, maximum PBB levels in most contaminated manure will likely be less than 2 ppm. At 23 and 46 metric tons/ha manure application rates, 0.046 and 0.092 kg of PBB/ha would be added, respectively, if a maximum 2-ppm concentration is assumed. These PBB additions are well within the adsorption capacities of the four soils given above. Consequently, applications should not result in any leaching losses of PBB below the depth of incorporation.

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