

Thermal Degradation of Selected Chlorinated Herbicides

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With a view toward the disposal of large quantities of waste pesticides by incineration, degradation temperatures of chloramben, linuron, and propanil were determined in open crucibles and sealed ampules. There was evidence that vaporization prior to degradation could occur in the open crucibles. Degradation temperatures determined in sealed ampules were 275 °C for chloramben and linuron, and 125 °C for propanil. Gaseous products produced by incinerating the herbicides at 400 °C were identified by mass spectrometry and gas chromatography. Gases identified included HCN, NO, CH₃NH₂, HCl, NO₂, CH₃Cl, C₂H₃Cl, and C₂H₅Cl. Products resulting from complete combustion were predicted by a series of chemical equilibrium composition calculations. The major products were CO₂, CO, N₂, NO, H₂O, HCl, and Cl₂.

The disposal of waste pesticides without contamination of the environment is a major problem of modern agriculture. This problem is complicated by the wide variety of chemicals used as pesticides, making it difficult to develop a single method of disposal.

Woodland et al. (1965) reported that the following four methods of disposal of chemical wastes have traditionally been employed: (1) settling ponds, (2) ground burial, (3) deep-well injection, and (4) incineration. The settling pond method is inadequate for pesticides because of their toxicity to plant and animal life. Burial of pesticides does not guarantee that they will remain stationary (Stojanovic et al., 1972). Because most pesticides move through soil in the direction of the water movement, the ground water and run-off water could easily be contaminated by the original chemicals or by their toxic by-products. The pesticide disposal problem is further complicated by the fact that high concentrations of many pesticides do not decompose within a reasonable length of time (Kennedy et al., 1972a). Furthermore, in studies concerning decomposition of linuron in soil, Hance and McKone (1971) found that the rate of decomposition decreased as the herbicide concentration increased. Thus, the methods of ground burial and deep-well injection could prove to be extremely hazardous.

Incineration has shown promise of being an efficient means for the disposal of a variety of pesticides (Kennedy et al., 1969). However, for incineration to be acceptable, the combustion must be complete and the system must be equipped with scrubbers capable of absorbing the toxic gases which are often produced (Kennedy et al., 1972a,b; Anderson, 1971). At the present time, additional information concerning the thermal degradation of pesticides is urgently needed in order to fully evaluate the process of incineration as a method of waste pesticide disposal. For instance, degradation temperatures and the identities of the gaseous pollutants are only two of the factors that must be determined before a pesticide can be safely incinerated on a large scale.

Ideal conditions for pesticide incineration are those which would effect complete decomposition of these toxic chemicals. However, actual operating conditions in an incinerator may very likely not be ideal since neither the combustion temperature nor the pesticide:fuel:air ratio are

static, but may vary over fairly wide ranges (Shih et al., 1973). Moreover, during a malfunction of the system, combustion conditions may be far from optimum. Therefore, any comprehensive investigation of pesticide combustion products must include products of incomplete combustion as well as those produced under ideal burning conditions. The purpose of the present investigation was to determine the degradation temperatures of three chlorine-containing herbicides and to identify the gases produced under optimum and nonoptimum conditions of incineration.

MATERIALS AND METHODS

Herbicides. Analytical standards and commercial formulations of the herbicides used in this study were supplied by the respective manufacturers of the formulations. The chemical names of the herbicides and the formulations used in the study were: chloramben, 3-amino-2,5-dichlorobenzoic acid; liquid chloramben containing 22% active ingredient; linuron, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea; Lorox wettable powder containing 50% active ingredient; propanil, 3',4'-dichloropropionanilide; liquid Stam F-34 containing 35% active ingredient.

Herbicide Analyses. The concentration of active ingredient in each herbicide was established by ten determinations. The mean values obtained are given in Table I. Chloramben was analyzed by a spectroscopic method (AOAC, 1971), and gas-liquid chromatographic procedures were used for linuron and propanil. Samples (100–300 mg) of these two herbicides were weighed into 50-ml volumetric flasks and brought to volume with the appropriate solvent. The solvent used for linuron was a 1:1 methanol-isooctane mixture (McKone, 1969), and that for propanil was a 1:1 acetone-benzene mixture (Zweig and Sherma, 1972). Aliquots of these solutions were diluted with isooctane and hexane, respectively, to concentrations appropriate for the electron capture detector. All solvents used in this study were pesticide quality from Burdick and Jackson Laboratories, Inc.

A Barber-Colman 5000 series gas chromatograph equipped with a tritium electron capture detector was used. A 6 ft × 5 mm i.d. stainless steel column packed with 5% E-301 on 60/80 mesh Gas-Chrom Q was used for the linuron analyses (McKone, 1969). Injector, column, and detector temperatures were 265, 140, and 200 °C, respectively. Retention time of linuron was 4 min. Propanil was analyzed on a 6 ft × 4 mm i.d. glass column packed with 1.5% OV-17, 1.95% QF-1 on 100/120 mesh Chromosorb W (Thompson, 1972). Injector, column, and detector temperatures were 225, 200, and 210 °C, re-

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Table I. Temperatures Required for Herbicide Degradation in Open and Closed Systems

Herbicide	Mp, °C	Obsd act. ingred., %	Degrad. temp open crucible, °C	Wt loss at degrad. temp, %	Max wt loss, %	Degrad. temp sealed ampule, °C
Chloramben	201	23.1	300	83.0	99.9	275
Linuron	93-94	51.8	300	56.7	65.3	275
Propanil	85-89	35.3	400	94.7	99.5	125

spectively. The retention time of propanil was 2 min. Nitrogen at a flow rate of 100 ml/min was used as carrier gas for all analyses. The peak height method was used for quantitation with two standards bracketing each peak.

Degradation Temperature Determinations. Degradation temperatures were determined in open and closed systems. For the open system determination, samples of the herbicide formulations were weighed in Coors No. 0 porcelain crucibles and incinerated in the muffle furnace at 100 °C increments from 100 to 1000 °C. Each determination was conducted in triplicate in the temperature range of 100 to 500 °C, and in duplicate at the higher temperatures. The optimum time of incineration for each herbicide was established by varying the time of incineration at 100, 500, and 800 °C. A heating time of 45 min was found to be sufficient to reach a point of no further reaction. The cooled samples were analyzed for weight loss and active ingredient content by the methods described previously. The criterion used to establish the degradation temperature was no detectable amount of pesticide at the milligram per milliliter level of residue concentration. In addition, an untreated sample of the commercial formulation was analyzed as a quality control sample along with each group of incinerated samples.

For the closed system determinations, analytical standard herbicides were sealed in 10-ml ampules and heated in a muffle furnace in increments of 25 °C beginning at their melting points and continuing to some temperature at which degradation was confirmed. Sample sizes were approximately 30 mg and heating time was 15 min at each temperature. The temperature at which the infrared spectrum deviated from that of the untreated herbicide and/or a change in physical appearance were the criteria used to establish the thermal degradation temperature. All infrared spectra were obtained as 13-mm KBr pellets or CS₂ solutions using a Perkin-Elmer 337 grating spectrophotometer. Spectra of the untreated herbicides were compared to those in the Sadtler Index when possible (Sadtler Research Laboratories, 1968).

Pollutant Gas Analyses. Two investigations were conducted to determine the volatile products of herbicide incineration. The first study was the experimental determination of the gaseous products formed during incineration at 400 °C. Analytical grade herbicides (50-100 mg) were sealed in 10-ml ampules and incinerated in a muffle furnace for 15 min. Identification of the gaseous products was accomplished by a combination of mass spectrometry and gas chromatography. The mass spectrometer was a Varian Anaspect EM-600 equipped with an EM-6270 gas sampling adapter. Gaseous samples were introduced with the adapter at an inlet temperature of 180 °C. Spectra were obtained at ionizing voltages of 70 eV and approximately 25 eV and were interpreted by using a computer program. The program listed all possible combinations of the elements contained in a herbicide which would give each of the masses present in the spectrum of its gaseous products. The most probable gas (or gases) were selected for possible confirmation by gas chromatography using a Barber-Colman 5000 series chromatograph equipped with a thermal conductivity detector. A glass column (6 ft × 4 mm i.d.) packed with

80/100 mesh Deactigel was employed. Injector, column, and detector temperatures were 120, 120, and 125 °C, respectively, and the carrier gas was helium at a flow rate of 50 ml/min (Thronsberry, 1971).

The second study was the theoretical prediction of the combustion products that would result from incineration of the herbicides under conditions of complete combustion. Complete combustion was determined by the addition of successive amounts of air until a ratio was obtained at which a small excess of diatomic oxygen was present. Temperatures studied were 127 and 27 °C. The NASA/LEWIS Chemical Equilibrium Composition Computer Program (Gordon and McBride, 1971) was used to predict the products which would be thermodynamically stable under these conditions. This program, which contained the thermochemical properties of most of the combustion products to be expected from incineration of typical halogenated hydrocarbons, was amended to include the thermochemical properties of other compounds indicated to be present by the experimental data. The thermodynamic data were obtained from a number of sources (Barin and Knacke, 1973; Chase et al., 1974; National Bureau of Standards, 1971; Rossini et al., 1952).

RESULTS AND DISCUSSION

Degradation Temperatures. Temperatures of herbicide degradation determined in the open crucibles and the accompanying weight losses at these temperatures are given in Table I. There are several possible pathways of herbicide loss during these treatments. Three of the possibilities are decomposition with volatilization, decomposition followed by volatilization of the products, and volatilization without decomposition. The weight losses indicated that considerable quantities of gases were evolved in each instance. Observations during the heating of chloramben led to the suspicion that volatilization prior to degradation might be occurring. Appearance of white crystals around the door of the furnace at temperatures greater than 150 °C indicated that sublimation might be occurring. Subsequent gas chromatographic analysis of the crystals proved them to be chloramben, and no peaks that might have been thermal decomposition products were noted in any of the chromatograms. On the basis of this evidence, it is concluded that accurate degradation temperatures could not be determined in an open system because of the possibility of herbicide volatilization prior to decomposition.

To prevent vaporization, the degradation temperatures were determined in a closed system. Table I contains the results of this study. Comparison of the degradation temperatures shows that chloramben and linuron were degraded in the sealed ampules at temperatures similar to those determined in the open crucibles. In both instances, vaporization was observed at temperatures below the degradation temperatures. Propanil, however, degraded at a much lower temperature in the ampule than in the crucible. The physical appearances of the untreated herbicide and the cooled residue in the ampule were identical. The degraded herbicide, however, had melted during treatment. Vaporization was also observed at 100 °C. The infrared spectra of the untreated herbicide and

Table II. Mass Spectral Data for Chlorinated Herbicides Heated at 400 °C

amu	Chloramben		Linuron		Propanil	
	Assignment	Confirmed by GC	Assignment	Confirmed by GC	Assignment	Confirmed by GC
14	N ⁺ , CH ₂ ⁺		N ⁺ , CH ⁺		N ⁺ , CH ₂ ⁺	
15	— ^a		NH ⁺ , CH ₃ ⁺		NH ⁺ , CH ₃ ⁺	
16	O ⁺ , NH ₂ ⁺ , CH ₄ ⁺		O ⁺ , NH ₂ ⁺ , CH ₄ ⁺		O ⁺ , NH ₂ ⁺ , CH ₄ ⁺	
17	OH ⁺ , NH ₃ ⁺		OH ⁺ , NH ₃ ⁺		OH ⁺ , NH ₃ ⁺	
18	H ₂ O ⁺		H ₂ O ⁺		H ₂ O ⁺	
26	—		—		CN ⁺	
27	HCN ⁺		HCN ⁺		HCN ⁺	
28	N ₂ ⁺ , CO ⁺		N ₂ ⁺ , CO ⁺		N ₂ ⁺ , CO ⁺	
29	^{14,15} N ₂ ⁺		^{14,15} N ₂ ⁺		^{14,15} N ₂ ⁺	
30	—		NO ⁺		NO ⁺	
31	—		CH ₃ NH ₂ ⁺		—	
32	O ₂ ⁺		O ₂ ⁺		O ₂ ⁺	
35	Cl ⁺		Cl ⁺		—	
36	—		—		HCl ⁺	
38	—		—		H(³⁷ Cl) ⁺	
40	Ar ⁺		Ar ⁺		Ar ⁺	
41	—		—		CH ₃ CN ⁺	
43	—		—		CHON ⁺	
44	CO ₂ ⁺	Yes	CO ₂ ⁺	Yes	CO ₂ ⁺	Yes
	N ₂ O ⁺		N ₂ O ⁺		N ₂ O ⁺	
45	CO ₂ H ⁺ , CH ₃ NO ⁺		CO ₂ H ⁺ , CH ₃ NO ⁺		CO ₂ H ⁺ , CH ₃ NO ⁺	
46	NO ₂ ⁺		NO ₂ ⁺		NO ₂ ⁺	
47	CCl ⁺		CCl ⁺		—	
48	CHCl ⁺		—		—	
50	—		CH ₃ Cl ⁺		CH ₃ Cl ⁺	Yes
52	—		CH ₃ (³⁷ Cl) ⁺		CH ₃ (³⁷ Cl) ⁺	Yes
57	—		—		C ₃ H ₅ O ⁺	
61	C ₂ H ₅ Cl ⁺		—		—	
62	C ₂ H ₅ ³⁷ Cl ⁺		C ₂ H ₅ Cl ⁺		—	
64	C ₂ H ₅ (³⁷ Cl) ⁺ , C ₂ H ₅ Cl ⁺		—		—	

^a A dash indicates that no peak occurred at the specified mass number.

the residue were similar, but there were noticeable differences in the 1600–1200- and 900–800-cm⁻¹ regions.

The temperatures of degradation determined in the sealed ampules were very likely more accurate than the temperatures determined in open crucibles, since the herbicide could not escape via volatilization before degradation. However, degradation at these temperatures did not lead to complete combustion; these were only the minimum temperatures at which any degradation occurred.

Incomplete Combustion Products. The temperature of 400 °C used in the incomplete combustion study was selected on the basis of the degradation temperatures determined in the sealed ampules which indicated it to be well above the minimum temperature required to initiate degradation of these herbicides. The burning conditions were designed to simulate a malfunction during which complete combustion could not occur because of the low temperature and the lack of sufficient oxygen.

Discussion of the gaseous combustion products will be limited to pollutant gases, although the product mixtures did contain a number of other gases. The mass spectra indicated that nitrogen, oxygen, and argon from the atmosphere and the combustion products, water vapor and carbon dioxide, were present in all of the mixtures. The presence of oxygen may have resulted from a leak in the gas sampling system. No special attempts were made to confirm any of these gases because they are not environmental hazards. The presence of CO was also not confirmed since it is a known product of incomplete combustion.

The residue remaining after incineration of chloramben was carbonaceous. The mass spectrum of the gaseous products contained 18 peaks, the assignments of which are listed in Table II. Several of the pollutant gases (CH₄,

NH₃, CO, and N₂O) cannot be positively identified because their masses are identical with the masses of other species (O, OH, N₂, and CO₂) which were present in all of the spectra. In addition to these gases, trace quantities of HCN, NO₂, C₂H₃Cl, and C₂H₅Cl were tentatively identified from the mass spectrum of the chloramben gaseous product mixture.

Incineration of linuron produced a black liquid. Assignments of the 20 peaks present in the mass spectrum of the gaseous products are given in Table II. Gases produced included traces of HCN, NO, CH₃NH₂, NO₂, CH₃Cl, and C₂H₃Cl. The retention times of the latter two gases were identical on the Deactigel column. Passage of the gaseous product mixture through this column produced a peak with the same retention time as these gases. Further investigation is presently underway to determine the identity of the gas(es) in this mixture.

Heating propanil produced a carbonaceous residue. Table II contains assignments for the 22 peaks present in the mass spectrum of the gaseous products. Propanil yielded trace quantities of HCN, NO, HCl, CH₃CN, NO₂, and CH₃Cl. The presence of CH₃Cl was confirmed on the Deactigel column.

Complete Combustion Products. The number of moles of air required for complete combustion of 1 mol of herbicide was 45 for chloramben, 50 for linuron, and 55 for propanil. The combustion products formed by these compounds are given in Table III. The higher temperature represents the operating range of commercial incinerators, while the lower temperature simulates the cooled exhaust.

The major products formed under these combustion conditions were rather simple for all three herbicides. The carbon component was oxidized primarily to CO₂ with small quantities of CO also being formed. Most of the

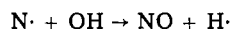
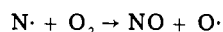
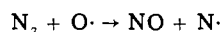
Table III. Combustion Products^a of Chlorinated Herbicides in Air

Product	Combustion temp, °C					
	Chloramben		Linuron		Propanil	
	1727	27	1727	27	1727	27
Ar	8.48×10^{-3}	8.58×10^{-3}	8.29×10^{-3}	8.38×10^{-3}	8.55×10^{-3}	8.63×10^{-3}
CO	8.19×10^{-4}	0.00	2.30×10^{-3}	0.00	1.39×10^{-3}	0.00
COCl	2.54×10^{-9}	0.00	2.97×10^{-9}	0.00	2.25×10^{-9}	0.00
CO ₂	1.14×10^{-1}	1.44×10^{-1}	1.58×10^{-1}	1.62×10^{-1}	1.49×10^{-1}	1.52×10^{-1}
Cl	6.38×10^{-3}	7.65×10^{-20}	2.65×10^{-3}	6.84×10^{-20}	3.32×10^{-3}	6.84×10^{-20}
ClO	2.15×10^{-5}	3.26×10^{-19}	3.56×10^{-6}	5.99×10^{-23}	6.96×10^{-6}	1.60×10^{-19}
ClO ₂	6.41×10^{-10}	3.12×10^{-24}	0.00	0.00	1.30×10^{-10}	8.38×10^{-25}
Cl ₂	7.33×10^{-5}	2.05×10^{-2}	1.27×10^{-5}	1.71×10^{-2}	1.99×10^{-5}	1.69×10^{-2}
H	1.06×10^{-5}	0.00	3.46×10^{-5}	0.00	1.79×10^{-5}	0.00
HCl	3.40×10^{-2}	2.89×10^{-5}	3.30×10^{-2}	1.80×10^{-3}	3.00×10^{-2}	3.49×10^{-5}
HNO	1.01×10^{-8}	0.00	9.34×10^{-9}	0.00	1.07×10^{-8}	0.00
HO ₂	2.87×10^{-7}	3.05×10^{-28}	1.06×10^{-7}	8.63×10^{-34}	1.89×10^{-7}	1.20×10^{-28}
H ₂	4.25×10^{-5}	0.00	2.31×10^{-4}	0.00	1.23×10^{-4}	0.00
H ₂ O(l)	0.00	1.73×10^{-2}	0.00	5.66×10^{-2}	0.00	4.29×10^{-2}
H ₂ O	3.32×10^{-2}	3.39×10^{-2}	7.20×10^{-2}	3.26×10^{-2}	5.96×10^{-2}	3.31×10^{-2}
H ₂ O ₂	1.42×10^{-8}	2.54×10^{-24}	1.23×10^{-8}	5.03×10^{-28}	1.59×10^{-8}	1.36×10^{-24}
N	7.62×10^{-10}	0.00	7.58×10^{-10}	0.00	7.65×10^{-10}	0.00
NH	0.00	0.00	2.00×10^{-10}	0.00	1.47×10^{-10}	0.00
NO	3.83×10^{-3}	1.53×10^{-16}	1.52×10^{-3}	3.05×10^{-20}	2.38×10^{-3}	8.25×10^{-17}
NOCl	2.65×10^{-7}	7.78×10^{-14}	4.38×10^{-8}	1.45×10^{-17}	8.63×10^{-8}	3.87×10^{-14}
NO ₂	3.03×10^{-6}	4.40×10^{-11}	4.79×10^{-7}	1.81×10^{-18}	1.18×10^{-6}	1.31×10^{-11}
N ₂	7.20×10^{-1}	7.31×10^{-1}	7.13×10^{-1}	7.21×10^{-1}	7.25×10^{-1}	7.33×10^{-1}
N ₂ O	1.85×10^{-7}	1.08×10^{-19}	7.29×10^{-8}	2.19×10^{-23}	1.16×10^{-7}	5.92×10^{-20}
O	1.50×10^{-4}	0.00	5.97×10^{-5}	0.00	9.32×10^{-5}	0.00
OH	8.09×10^{-4}	8.77×10^{-28}	7.53×10^{-4}	1.21×10^{-29}	8.56×10^{-4}	6.32×10^{-28}
O ₂	5.08×10^{-2}	4.47×10^{-2}	8.09×10^{-3}	1.81×10^{-9}	1.97×10^{-2}	1.30×10^{-2}
O ₃	5.88×10^{-10}	3.57×10^{-31}	0.00	0.00	1.41×10^{-10}	5.71×10^{-32}

^a Mole fractions; l = liquid.

hydrogen was converted to H₂O and HCl and the chlorine to HCl and Cl₂. Herbicide nitrogen was converted primarily to N₂ with a small amount forming NO.

The results of the incineration of these herbicides were somewhat simplified by the fact that the NASA/LEWIS program does not consider reaction kinetics, but predicts the products of combustion solely on the basis of their thermodynamic stability under the specified conditions. Two of the systems affected by the neglect of kinetics were the CO and NO systems, both of which have been studied extensively in recent years (Newhall, 1969; Breen et al., 1971). Actual CO concentrations in automobile exhaust have been found to correspond more closely to the equilibrium values at the combustion temperatures than to the equilibrium values at the cooler exhaust temperatures. This finding indicates that there will be considerable quantities of CO present in the incinerator exhaust, even though none was predicted by the thermodynamic model at ambient temperature. Formation of NO has been found to occur by two routes. The first path is via oxidation of atmospheric N₂ by the following three reactions:



However, these reactions produce NO only above 1760 °C. The other route is the oxidation of herbicide nitrogen, the kinetics of which are of the same order as the combustion process. Kinetics of NO destruction, however, are limited during expansion. As a result, the actual NO concentration in incinerator exhaust will probably be considerably higher than that predicted by the calculations.

CONCLUSIONS

Incineration of chlorinated herbicides under both optimum and very inefficient conditions of incineration

produced a number of toxic gases. On a practical basis, all of these pollutants would have to be removed from the incinerator effluent prior to its discharge into the atmosphere. Therefore, for incineration to be acceptable as a method of herbicide disposal, a scrubber or series of scrubbers capable of trapping these gases must be developed.

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Fate of Polybrominated Biphenyls (PBB's) in Soils. Persistence and Plant Uptake

Lee W. Jacobs,* Sheng-Fu Chou, and James M. Tiedje

The flame retardant, PBB, which contaminated animal feeds in Michigan, was found to be comprised of 2,2',4,4',5,5'-hexabromobiphenyl as the major component, two isomers of pentabromobiphenyl, three additional isomers of hexabromobiphenyl, and two isomers of heptabromobiphenyl. The PBB's were extremely persistent with only one pentabromobiphenyl isomer showing any significant disappearance after 24 weeks of incubation in soils. Orchard grass and carrots grown in soil contaminated with PBB's showed none or only very minor uptake of PBB's, respectively. PBB's were detected in soils from a field which had received manure from a PBB-contaminated dairy herd 10 months earlier.

In 1973 an industrial flame retardant (fireMaster BP6, manufactured by Michigan Chemical Corporation, St. Louis, Mich.) was accidentally added to livestock feed in place of magnesium oxide (Carter, 1976; Isleib and Whitehead, 1975; Robertson and Chynoweth, 1975). The addition of this chemical, which is a mixture of several polybrominated biphenyl (PBB) isomers, into livestock rations had a catastrophic impact on Michigan's livestock industry and resulted in more than 23 000 cattle, 4000 swine, 1.5 million chickens, and tons of eggs, milk, butter, cheese, and feed having to be destroyed (D. R. Isleib, personal communication). This incident has been termed the most costly and disastrous accidental contamination ever to occur in United States agriculture (Isleib and Whitehead, 1975).

Attention immediately focused on the effects of PBB on animals and humans. Several reports (Fries et al., 1973; Jackson and Halbert, 1974; Babish et al., 1975; Gutenmann and Lisk, 1975) regarding uptake of PBB by and its effect on animals have been published. Information on the contamination of other ecosystem components such as plants, soil, water, and air is needed to better evaluate the fate of PBB's inadvertently added to soils by contaminated manure, milk, carcasses, etc.

We report here on the chemical characterization of fireMaster BP6, persistence of PBB in soils, and uptake of PBB by plants.

EXPERIMENTAL PROCEDURES

Soil Incubations. The susceptibility of PBB's to biodegradation was evaluated using Brookston loam and Spinks sandy loam soils which were freshly collected from the University Experimental Farms. Twenty-five grams of soil which had passed through a 2-mm sieve was placed

in a 125-ml Erlenmeyer flask. One milliliter containing 100 μ g of PBB in acetone was distributed in microdrops over the soil surface. The soil in each flask was then moistened with 5 ml of basal salt solution. Half of the flasks received additional organic matter in the basal salts in an attempt to stimulate cometabolism. This amendment per flask was 0.2% glucose, 0.2% peptone, 0.2% sodium acetate, and 0.05% *m*-bromobenzoic acid per gram fresh weight of soil. The flasks were closed with a rubber stopper and incubated in the dark at 28 °C, except for one set of Brookston soils with the organic amendment which was incubated at room temperature in an anaerobic glove box ($E_h < 0.05$ mV). Three flasks were analyzed for each treatment after 0, 6, 12, and 24 weeks of incubation.

Plant Uptake. A greenhouse experiment was established using a Spinks loamy sand (characterized by Filonov et al., 1976) amended with varying levels of fireMaster BP6 and cropped with two plant species. Five concentrations of PBB (0, 0.1, 1.0, 10, and 100 ppm) with three replicates of each concentration were used for each plant species: Nordstern orchard grass (*Dactylis glomerata* L.) and Spartan Delite carrots (*Daucus carota*). The soil was prepared by mixing powdered PBB with air-dried soil at a PBB concentration of 100 ppm and diluting this mixture with additional soil to achieve the desired concentrations.

Four kilograms of the PBB-amended soil was placed in a tin container lined with a polyethylene bag for each replicate and treated with nutrient solutions initially and during growth to satisfy the needs of each crop. The soil was watered daily to 10% moisture. The orchard grass was grown for about 5 weeks before the first harvest and then allowed to regrow for three additional harvests. Grass was cut about 2.5 cm above the soil for each harvest. The carrots were harvested after 11 weeks growth when roots were about "finger" size. Carrot tops were separated from the roots, and the roots washed thoroughly to remove all soil particles. All plant tissue was refrigerated following harvest until analyzed for PBB.

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