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Air is Still Contaminated 40 Years after the Michigan Chemical Plant Disaster in St. Louis, Michigan

Angela A. Peverly, Amina Salamova, and Ronald A. Hites*

School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405, United States

S *Supporting Information*

ABSTRACT: The Michigan Chemical (also known as Velsicol Chemical) plant located in St. Louis, Michigan operated from 1936−1978. During this time, the plant manufactured polybrominated biphenyls (PBBs), hexabromobenzene (HBB), 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl) ethane (DDT), and *tris*(2,3-dibromopropyl) phosphate (TDBPP), among other products. Due to widespread PBB contamination of Michigan, the plant eventually became a Superfund site, and despite years of cleanup activities, many of the compounds can still be found in the local ecosystem. To investigate the current atmospheric levels and to determine their spatial distributions, we collected tree bark samples from around Michigan and measured the concentrations of these pollutants. For comparison, other organic pollutants, such as polybrominated diphenyl ethers (PBDEs) and organophosphate esters (OPEs), which were not manufactured at the Michigan Chemical plant, were also measured in the same tree bark samples. Our results show levels of PBBs, DDT, and HBB in tree bark collected within 10 km of the Velsicol Superfund site (43, 477, and 108 ng/g lipid wgt., respectively) are 1−2 orders of magnitude higher than at sites located more than 10 km from the site (0.36, 28, and 0.36 ng/g lipid wgt., respectively). Levels of PBDEs and OPEs did not depend on distance from St. Louis. This is the first study on the atmospheric distribution of these chemicals around the Superfund site.

INTRODUCTION

Through a mislabeling accident in 1973, the Michigan Chemical Corp. in St. Louis, Michigan, switched two of its products: polybrominated biphenyls (PBBs), which were intended to be used as a flame retardant in plastics, and magnesium oxide, which was intended to be used as a nutritional additive for dairy cow feed. The result was the widespread PBB contamination of dairy cows in the lower peninsula of Michigan. The public was widely exposed to PBBs by the consumption of milk from these cows, and dairy farmers and their families were exposed by the consumption of contaminated cow meat. Eventually, over 30,000 livestock (cattle and swine), 1,600,000 poultry, and thousands of pounds of eggs, milk, butter, cheese, and dairy feed had to be destroyed.[1,2]

The Michigan Bureau of Environmental Protection began its investigation of the Michigan Chemical plant in 1974.[3] Michigan Chemical ceased production of PBBs in 1974 and merged with Velsicol Chemical Corp in 1976, which closed the plant in 1978.[4−6] Early studies showed that the plant's soil, the town's groundwater, and the sediment and fish from the adjacent Pine River were contaminated with PBBs, hexabromobenzene (HBB), 1,1,1-trichloro-2,2-*bis*(4-chlorophenyl) ethane (DDT), and *tris*(2,3-dibromopropyl) phosphate (TDBPP).[7,8] In 1982, the U.S. Environmental Protection Agency (EPA) reported that the maximum concentrations in Pine River sediment of PBBs, DDT, and HBB were 330,

26,000, and 9,300 μg/g, respectively.[9] As a result, in 1982, Velsicol Chemical, the State of Michigan, and the EPA entered into a consent decree, and the main plant site was included on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) National Priorities List and became a Superfund site.[8,10] Velsicol was required to contain the 52 acre plant by constructing a 2 foot thick slurry wall around it and to cap the entire site with a 3 foot thick clay layer. At the same time, it was decided that the Pine River sediments would be left in place. The consent decree required Velsicol to conduct long-term maintenance at the site but cleared them from all liability for remediation of the Pine River sediments.

After collecting Pine River sediment in 1996 and 1997, the State of Michigan and the U.S. EPA reported that DDT levels were "extremely high" (up to 32,000 ppm) and that these levels had not decreased since 1980.[11] In 1998, the U.S. EPA decided to remove all sediment containing >3000 ppm of DDTs. This action was the result of the analyses of sediment and fish, which showed that the levels of DDTs in Pine River reservoir fish had actually increased from 11 to 23 ppm from 1989 to 1994.[8] In 2002, the EPA collected and removed 12,000 L of nonaqueous phase liquid (NAPL), which contained >70% DDTs, from the
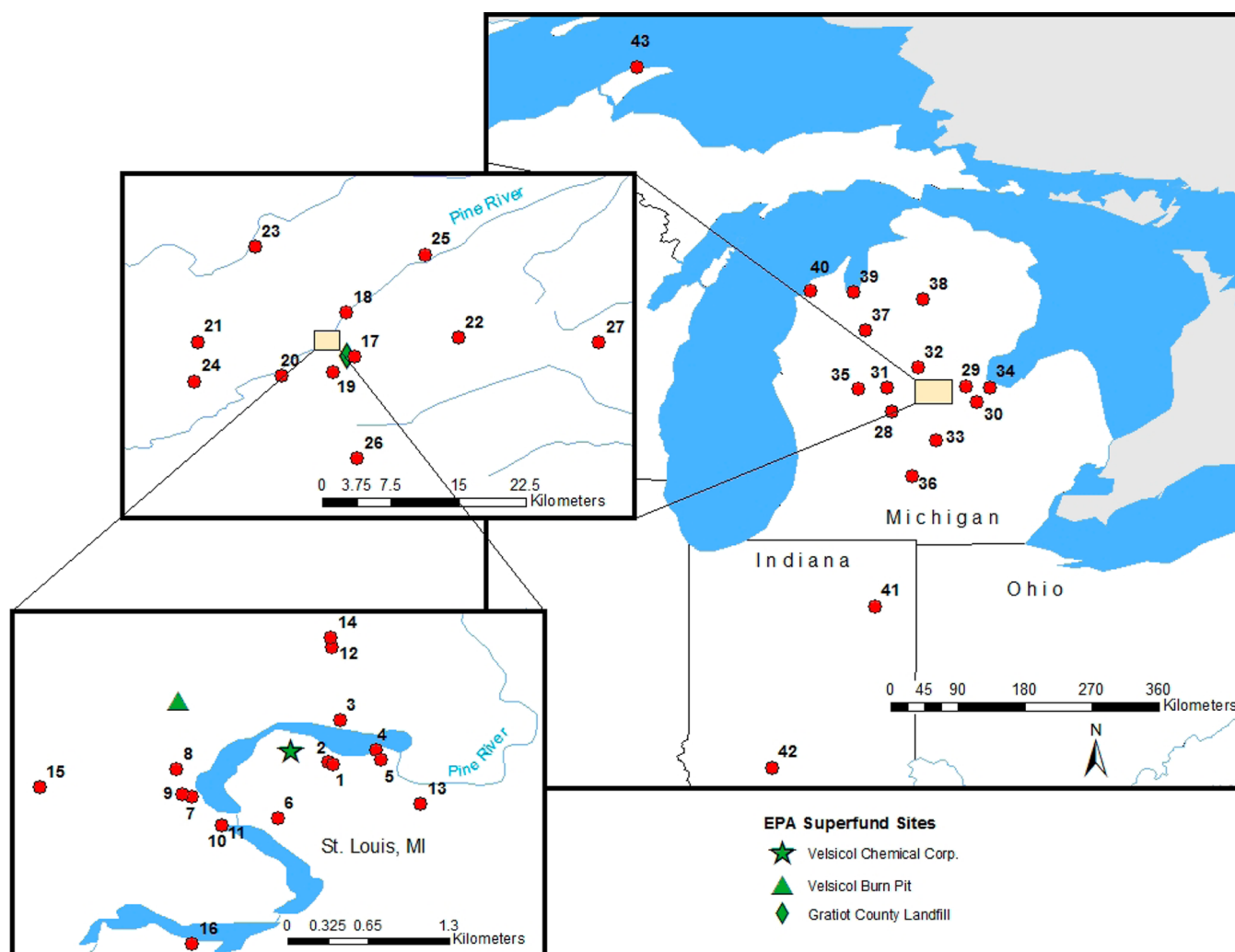
Figure 1. Map of sampling and Superfund sites centered on St. Louis, Michigan. Tree bark sampling sites are labeled with a red circle and their identification number. The Velsicol Chemical Corporation plant, burn pit, and the Gratiot County Landfill are labeled with a green star, triangle, and diamond, respectively. The geographical coordinates of each site are given in Table S1, Supporting Information. Samples 10 and 11 were from two different sets of trees located within 40 m of each other.

sediment of the Pine River.[8] More recently in 2012, dead robins frequently found at the site and in neighboring residential backyards were diagnosed with organochlorine poisoning from high levels of DDE (an environmental degradation product of DDT).[8] Even though the PBB incident was widely publicized, DDT contamination still remains the main concern of the U.S. EPA. As of 2006, they had spent nearly $100 million on sediment cleanup, and they expect to spend up to $350 million to reach their cleanup goals.[10,12]

In addition to the plant site itself, there are two other Superfund sites associated with the former Michigan Chemical site; these include the Velsicol Burn Pit (for some odd reason located on the Gratiot County Golf Course) and the Gratiot County Landfill. From 1956 until 1970, Velsicol used the burn pit to dispose of 7,500−11,400 L of hazardous waste including DDT. In 1982, Velsicol removed 52,000 m³ of soil from the burn pit and placed it under the clay cap on the plant site; nevertheless, contamination was still seen at the burn pit site in 2006.[13] The Gratiot County Landfill has been in continuous operation since 1971, and it was used for the disposal of domestic, commercial, and industrial solid waste including 122,000 kg of PBBs.[14] Ponds and aquifers in the vicinity of the

landfill have also been found to be contaminated by these chemicals.[14]

In this study, we investigated the current atmospheric levels of the chemicals that were produced by Michigan Chemical and dumped at and near the site after the plant was closed more than 40 years ago. These are the first published air quality results around the Velsicol Superfund site; the EPA only monitored air quality during remediation in 2000 and that data was not made public.[15] The compounds of interest here are HBB, PBBs (congeners 153 and 180), DDTs (*o,p'*- and *p,p'*-DDT, DDD, and DDE) and TDBPP. For comparison, the atmospheric levels of several chemicals that were presumably not produced at the St. Louis Superfund site, but represent widespread environmental pollutants, were also measured. These are pentabromobenzene (PBBZ), pentabromoethylbenzene (PBEB), hexabromocyclododecanes (HBCDs, measured as the sum of the *α*, *β*, and *γ* isomers), polybrominated diphenyl ethers (PBDEs) (including BDE-28, 47, 66, 99, 100, 153, 183, 196, 197, 201, 203, 204, and 206-209), and several organophosphate esters (OPEs), including *tris*(1,3-dichloro-2-propyl)phosphate (TDCPP), *tris*(1-chloro-2-propyl)phosphate (TCPP), tributyl phosphate (TnBP), tri(butoxyethyl)-

phosphate (TBEP), triphenyl phosphate (TPP), and 2-ethylhexyl diphenyl phosphate (EHDPP).

We used tree bark as a passive air sampler. Tree bark is an efficient passive atmospheric sampler because, due to its high lipid content, it accumulates lipophilic atmospheric pollutants from both the atmospheric vapor and particle phases. Bark gives an integrated relative measurement of the atmospheric concentrations over a time scale of 3−10 years, which is the time that the bark remains on the tree.[16,17] Concentrations of lipophilic pollutants in tree bark have been shown to correlate with atmospheric concentrations measured near the sampled tree.[16,18] Bark has been used for the analysis of persistent organic pollutants in numerous studies.[16−26] In this study, 43 tree bark samples were collected around central Michigan starting in St. Louis; see Figure 1. This wide geographical area gave us the opportunity to examine the spatial distribution of each pollutant.

■ MATERIALS AND METHODS

Sampling. Table S1, Supporting Information, contains information on the sampling sites used in this study. Tree bark samples were collected in July 2013 and March 2014 from coniferous trees with coarse bark, mainly pine trees (*Pinus sp.*). At most sites, three different trees were chosen that were located within about 50 m of one another. At each tree, approximately 100 g of bark was collected from two sides of the tree; the bark was removed with a precleaned chisel at a height of 1.5 m. The bark was then wrapped in aluminum foil, sealed in a plastic bag, and kept at ambient temperature until the samples were returned to the laboratory, where they were stored at −20 °C until extraction.

Sample Preparation. A previous method[19] was modified for this research. In brief, bark samples were cut into 1 cm pieces. For each site, the total mass of extracted bark was 3 g; that is, 1 g from each tree. Bark samples were weighed and then packed into a Soxhlet extraction thimble containing 10 g of granular anhydrous sodium sulfate (Fisher Chemical, Fair Lawn, NJ), and an additional 10 g of sodium sulfate was added on top of the bark sample to prevent floating. Each Soxhlet sample was spiked with known amounts of the recovery standards [BDE-77, BDE-166, $^{13}C_{12}$-BDE-209, ε-HCH, tris(2-chloroethyl)phosphate-d_{12}, and $^{13}C_{18}$-triphenyl phosphate] and then extracted for 24 h with 400 mL of a 1:1 (v/v) hexane in acetone solution.

After the extraction was complete, the lipid content was determined gravimetrically by removing an aliquot of the extract into a preweighed aluminum dish and evaporating the solvent. Then, acid-activated copper was added to the sample to remove sulfur; the copper was filtered off after about 8 h. The bark extract was then rotary evaporated to 2 mL with two solvent exchanges with 75 mL of hexane. Samples were cleaned and fractionated on a fully activated 10 g Florisil (PR; Sigma-Aldrich, St. Louis) column. This column was eluted with 15 mL of hexane (fraction 1, not analyzed), 70 mL of a 3:2 (v/v) dichloromethane in hexane solution (fraction 2), and then 90 mL of a 4:1 (v/v) acetone in dichloromethane solution (fraction 3). All compounds of interest eluted in fraction 2, except the OPEs, which eluted in fraction 3. These included TDBPP, TDCPP, TCPP, TnBP, TBEP, TPP, and EHDPP.

Fractions 2 and 3 were concentrated by rotary evaporation to 2 mL, with one and two solvent exchanges of 25 mL of hexane, respectively. Extracts were transferred to 4 mL vials, blown down with dry N$_2$ to 2 mL, and spiked with known amounts of internal quantitation standards (BDE-118, BDE-181, anthracene-d_{10}, and perylene-d_{12}). Fraction 2 was further concentrated with N$_2$ blow-down to a volume of 100 μL and analyzed for the halogenated compounds by electron capture negative ionization (ECNI) gas chromatographic mass spectrometry. Fraction 3 was analyzed for OPEs by electron impact (EI) gas chromatographic mass spectrometry.

Instrumental Analysis. Fraction 2 [containing HBB, PBBs, DDTs, PBBZ, PBEB, HBCDs (measured as the sum of the α, β, and γ isomers), and PBDEs] was analyzed on an Agilent 7890 series gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) operating in ECNI mode using methane as the reagent gas. The mass spectrometer ion source and quadrupole temperatures were maintained at 200 and 140 °C, respectively. One μL of the sample was injected in the pulsed splitless mode at 240 °C. Chromatographic resolution was achieved with an Rtx-1614 (15 m × 250 μm i.d., 0.1 μm film thickness) fused silica capillary GC column (Restek Corporation, Bellefonte, CA). The carrier gas was helium (99.999%; Liquid Carbonic, Chicago) regulated at a constant flow of 1.5 mL/min. The GC/MS transfer line was maintained at 320 °C. For analysis of PBDEs, HBB, PBBZ, HBCDs, and PBEB, the GC oven temperature was programmed as follows: 100 °C for 2 min, 25 °C/min to 250 °C, 3 °C/min to 270 °C, 25 °C/min to 320 °C, and 320 °C for 9 min. For analysis of PBBs and DDTs, the GC oven temperature was programed as follows: 120 °C for 2 min, 0.8 °C/min to 150 °C, 5 °C/min to 200 °C, 25 °C/min to 320 °C, and 320 °C for 5 min.

Selected ion monitoring of the two bromide ions at m/z 79 and 81 was used to quantitate most of the target compounds. The exceptions were m/z 79, 81, and 279 for the quantitation of BDE-28 and BDE-47; m/z 409 and 411 for BDE-197; m/z 720 and 722 for BDE-201; m/z 562 and 564 for BDE-203 and BDE-196; m/z 79, 81, and 562 for BDE-183; m/z 487 and 489 for BDE-204 and BDE-206 to BDE-209. For the analysis of the two PBB congeners, m/z 79 and 81 were also used for quantitation, but m/z 468 and 628 were included for confirmation of PBB-153 and PBB-180, respectively. To quantitate DDTs, m/z 35 and 37 were used along with m/z 246 for o,p'-DDD and p,p'-DDD and m/z 246 and 281 for o,p'- and p,p'-DDT and DDE.

Analysis of fraction 3 was performed on an Agilent 6890 series GC coupled to an Agilent 5973 MS operating in EI mode. The mass spectrometer ion source temperature and electron energy were maintained at 230 °C and 70 eV, respectively. Injections were performed in the pulsed splitless mode at 280 °C for 1 μL samples. Chromatographic resolution was achieved with a DB-5MS Ultra Inert capillary column (30 m × 250 μm i.d., 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA). The carrier gas was helium (99.999%; Liquid Carbonic, Chicago) regulated at a constant flow of 1.5 mL/min. The GC/MS transfer line was maintained at 300 °C. For analysis of OPEs, the GC oven temperature was programed as follows: 70 °C for 3 min, 10 °C/min to 170 °C, held for 5 min, 10 °C/min to 230 °C, held for 5 min, 5 °C/min to 250 °C, and then 10 °C/min to 300 °C for 4 min. Selected ion monitoring of the following ions was used to quantitate TDBPP, TDCPP, TCPP, TnBP, TBEP, TPP, and EHDPP: 119 and 137, 191, 125, 99, 85, 326, and 251, respectively. All compounds were quantitated using the internal standard method using anthracene-d_{10} and perylene-d_{12} for OPEs and BDE-118 and BDE-181 for the remaining compounds.
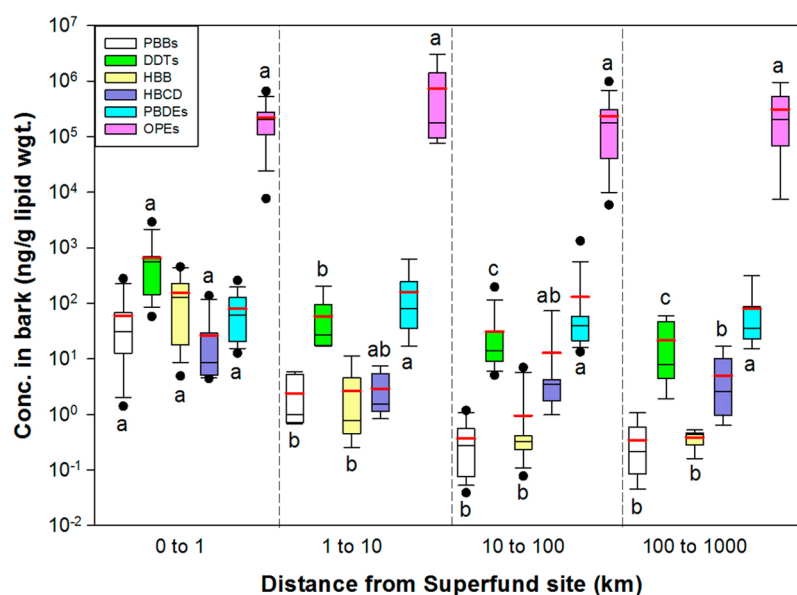
Figure 2. Boxplots of concentrations of pollutants according to distance from the Velsicol Superfund site in St. Louis, Michigan. All concentrations in tree bark are reported in ng/g lipid weight. The thin black lines represent the median, the thick red lines represent the mean, the boxes represent the 25th and 75th percentiles, the whiskers represent the 5th and 95th percentiles, and outliers are displayed by circles. ANOVA results using logarithmically transformed concentrations are shown; the concentration distributions sharing the same letter are not statistically different at the $P < 0.05$ level.

Materials. A PBDE standard mixture (BFR-PAR) was purchased from Wellington Laboratories, Guelph, ON. This solution contained all PBDE congeners of interest along with HBB and PBEB. Additionally, PBBZ, $^{13}C_{12}$-BDE-209 from Wellington Laboratories, and α-HBCD and BDE-118 from AccuStandard, New Haven, CT, were added individually to the calibration standard. BDE-77, BDE-166, BDE-181, TDCPP, TCPP, TnBP, TBEP, TPP, EHDPP, and $^{13}C_{18}$-triphenyl phosphate were purchased from Wellington Laboratories. TBPP and *tris*(2-chloroethyl) phosphate-d_{12} were purchased from Sigma-Aldrich, St. Louis, MO. *p,p'*-DDD was purchased from Supelco Analytical, Bellefonte, PA. The remaining DDTs and ε-HCH were purchased from Ultra Scientific, North Kingstown, RI. PBB-153, PBB-180, and TDBPP were purchased from AccuStandard. The PAH standards, anthracene-d_{10} and perylene-d_{12}, were purchased from Chem Service, Inc., West Chester, PA. All solvents used for the extraction and cleanup processes were residue analysis grade. Glassware was baked at 500 °C for at least 6 h prior to use.

Quality Assurance and Quality Control. To ensure the correct identification and quantitation of the target compounds, three criteria were used: (a) The GC retention times matched those of the standard compounds within ±0.1 min. (b) The signal-to-noise ratio was greater than 3:1. (c) The isotopic ratios for selected ion pairs were within ±15% of the theoretical values. Six recovery standards were added to each sample before extraction with average recoveries (±standard errors) of 71 ± 12%, 62 ± 12%, 43 ± 9%, 55 ± 12%, 50 ± 11%, and 71 ± 9% for BDE-77, BDE-166, $^{13}C_{12}$-BDE-209, ε-HCH, *tris*(2-chloroethyl)phosphate-d_{12}, and $^{13}C_{18}$-triphenyl phosphate, respectively. At least one blank was included in each set of 6−8 extracted samples. The masses of all of the compounds in the blanks were <30% of the average mass measured in the tree bark samples, except for PBDEs and OPEs which were 33% and 31% of the average mass detected in the bark samples. Blanks consisted of 10 g of sodium sulfate, which was spiked with the same amount of recovery standards. Samples were not blank or recovery corrected; sample concentrations below the procedural blank, in the sample's respective set, were treated as nondetects.

RESULTS AND DISCUSSION

Concentrations for all target compounds at each site are given in Table S1, Supporting Information. All concentrations are given in ng/g (or μg/g) lipid weight (as opposed to bark weight) because this approach has been shown to normalize for variations in the sampled tree species.[26] A visual representation of the data is given in Figure 2, which shows the data as box plots grouped by distance from the Velsicol Superfund site, which is located at 43.4129 N, 84.6152 W.

As expected, the concentrations of PBBs decrease with distance from the Velsicol Superfund site. The highest concentration of PBBs was 278 ng/g at site 10, which is located <1 km from the site. PBB concentrations decrease until a background level of about 0.4 ng/g is reached at >10 km from the site. This background level is higher than that measured in tree bark from a 2006 study, which sampled trees from various areas of the United States (average concentration for PBB-153 only was 0.06 ng/g lipid).[23] The mean PBB concentrations at 0−1 km from the site are at least 100 times higher than those 100−1,000 km from the site (see Figure 2). This sharp decrease in concentration with distance was also reported in 1974 for sediment samples taken from the Pine River; PBB concentrations decreased from 6,200 to 100 μg/kg in about 46 km.[3] Yun and co-workers[27] showed that the sediment concentrations of PBB decreased by a factor of 100−300 from the Pine River to the upper reaches of the Saginaw River.

The highest level of DDTs was 2,910 ng/g at site 13, which is a park located about 0.9 km southeast of the site. As seen in Figure 2, the average DDT concentration decreases from about 656 ng/g near the site to about 35 ng/g at distances >1 km from the site. On average, *p,p'*-DDT dominates the distribution

profile (Figure S1, Supporting Information), comprising 48% of the total DDTs, with p,p'-DDE being the next most abundant at 29%. The relatively high background and similar distribution throughout the study are probably due to the old use of DDT throughout Michigan, where it remains in the soil.[28] DDT concentrations, compared to those of PBB and HBB, continue to remain high in sediment from the Pine River; in 2010, they were 2,000 μg/kg around the site.[8] Hermanson et al.[28] investigated the levels of atmospheric DDTs in Michigan from 1992 to 1994 and observed an average atmospheric concentration of 55 pg/m^3 except for South Haven, Michigan, where DDT was thought to have been used extensively and where its concentration was 1,200 pg/m^3. Figure 3 shows that
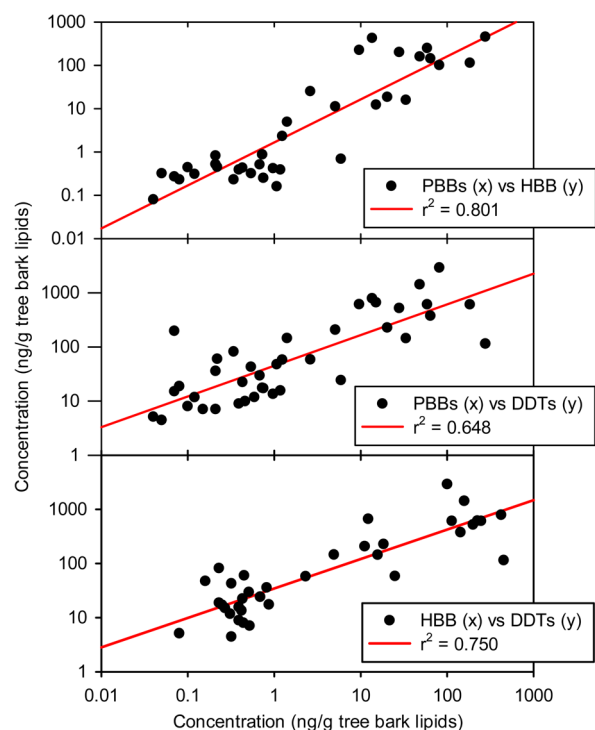

Figure 3. Plots of the PBB, DDT, and HBB concentrations vs one another, showing the regressions and correlation coefficients. All other correlation coefficients are given in Table 1.

DDT concentrations correlate well with those of PBBs and HBB ($r^2 = 0.648$, $P < 0.001$ and $r^2 = 0.750$, $P < 0.001$, respectively) indicating that DDTs came from the same source as PBBs and HBB.

Levels of HBB are about 153 ng/g at distances <1 km from the site and about 1 ng/g at distances >1 km from the site (Figure 2). This is the largest change in concentration with distance that we observed. The highest concentration was 454 ng/g at site 10, which is about 0.73 km from the site. Figure 3 shows that PBB and HBB concentrations correlate very well with each other ($r^2 = 0.801$, $P < 0.001$), indicating that they were produced at the same location. As mentioned above, HBB concentrations correlate well with those of DDTs even though DDT has higher background levels.

The concentrations of pentabromobenzene (PBBZ) and pentabromoethylbenzene (PBEB) are included only in Table S1, Supporting Information, because their average levels are low (about 0.73 and 0.22 ng/g, respectively). However, Table 1 shows that the levels of these two compounds correlate well with those of the other brominated compounds produced by

Michigan Chemical. PBBZ concentrations show an $r^2 = 0.867$ ($P < 0.001$) for HBB, $r^2 = 0.731$ ($P < 0.001$) for PBBs, and $r^2 = 0.712$ ($P = 0.001$) for DDTs. Similarly, PBEB concentrations show an $r^2 = 0.395$ ($P = 0.001$) for HBB, $r^2 = 0.507$ ($P < 0.001$) for PBBs, and $r^2 = 0.354$ ($P = 0.002$) for DDT. These observations suggest that PBBZ and PBEB may be impurities in the production of HBB and PBBs, which were made by the bromination of benzene or biphenyl, respectively.[29] It is likely that the benzene and biphenyl used for these purposes were technical grade materials and that they contained toluene, ethylbenzene, and xylenes as impurities. Partial bromination of benzene would yield PBBZ, and bromination of toluene and or ethylbenzene would yield pentabromotoluene (PBT), which we did not observe in a preliminary study of these samples, and PBEB, respectively (see the scheme below). The maximum concentrations of PBBZ and PBEB were 20.6 and 1.31 ng/g, respectively, at site 12, which is <1 km from the Velsicol Superfund site.
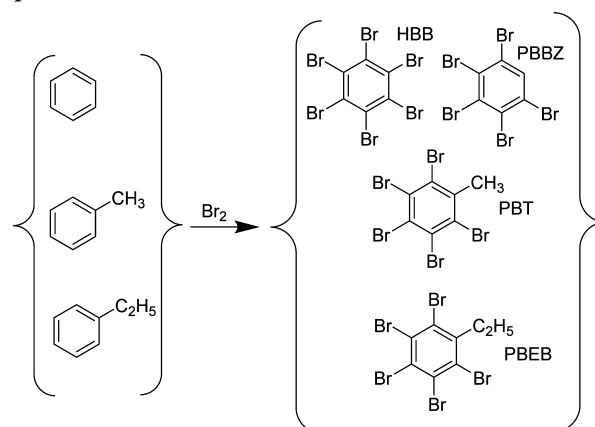
HBCDs, PBDEs, and OPEs are widely used flame retardants and plasticizers and represent ubiquitous environmental organic pollutants, but they were not known to be products of the Michigan Chemical plant. Hence, we thought these chemicals would not show a dependence on distance from the plant. This was confirmed for PBDEs and for OPEs (Figure 2), which do not have elevated concentrations near the plant. On the other hand, the concentrations of HBCDs are somewhat elevated near the plant (Figure 2). In fact, HBCD concentrations show an $r^2 = 0.319$ ($P = 0.003$) for HBB, $r^2 = 0.320$ ($P = 0.002$) for PBBs, and $r^2 = 0.290$ ($P = 0.003$) for DDTs (Table 1). These relationships suggest that HBCDs could have been manufactured at the Michigan Chemical plant, more on this later.

The concentrations of PBDEs in these tree bark samples were not related to distance from the Velsicol Superfund site (Figure 2), indicating that these compounds were not made at this site. In fact, PBDEs were not produced much, if at all, until PBBs were taken off the market in 1978.[4] An interesting finding was that PBDE levels (and those of HBCDs) were particularly high at site 29, which was in Midland, Michigan, home to the Dow Chemical Company, a company known to have used both of these flame retardants.[30,31] In 2006, PBDEs were measured in tree bark from around the United States, and the authors reported similar concentrations for sites not located near PBDE's manufacturing plants. Our highest measured PBDE value (1,320 ng/g) is similar to concentrations found at sites in Missouri and Mississippi (1,600 and 1,500 ng/g lipid, respectively) but lower than the 5,700 ng/g lipid level found in Arkansas, which was near PBDE's manufacturing site.[23] Congener profiles are given in Figure S1, Supporting

Table 1. Correlation Coefficients (r^2) and Probabilities of the Insignificance of the Correlation for the Concentrations of Halogenated Compounds Measured in Tree Bark in Michigan

	HBB	PBBs	DDTs	HBCDs	PBBZ	PBEB	TDBPP
PBBs	0.801 0.000						
DDTs	0.750 0.000	0.648 0.000					
HBCDs	0.319 0.003	0.320 0.002	0.290 0.003				
PBBZ	0.867 0.000	0.731 0.000	0.712 0.001	0.436 0.075			
PBEB	0.395 0.001	0.507 0.000	0.354 0.002	0.333 0.015	0.701 0.019		
TDBPP	0.004 0.759	0.044 0.296	0.030 0.388	0.027 0.505	0.158 0.290	0.002 0.860	
TDCPP	0.405 0.000	0.291 0.007	0.288 0.001	0.002 0.841	0.285 0.112	0.029 0.460	0.010 0.634

Information, for PBDEs. Overall, the profiles did not change with distance from the site, and the dominant congener throughout was BDE-209 (an overall 67% of the total PBDEs).

By far, the most abundant group of chemicals seen in tree bark are the OPEs, the concentrations of which are 1000–10,000 times higher than those of the other target compounds (Figure 2). Of the OPEs, the most abundant compounds are TDBPP and TDCPP, which are (on average) 48% and 43% of the total OPE concentrations, respectively. The third halogenated OPE, TCPP, compromises 4% of the OPEs. It is known that TDBPP was made at the Michigan Chemical site; however, the concentrations of TDBPP do not decrease with distance from the site and do not correlate with those of HBB ($r^2 = 0.004$, $P = 0.759$), PBBs ($r^2 = 0.044$, $P = 0.296$), or DDTs ($r^2 = 0.030$, $P = 0.388$). The one exception is TDCPP, the concentrations of which do decrease with distance from the Velsicol Superfund site and do correlate with those of HBB ($r^2 = 0.405$, $P < 0.001$), PBBs ($r^2 = 0.291$, $P = 0.007$), and DDTs ($r^2 = 0.288$, $P = 0.001$). This finding led to an interesting discovery: According to EPA's documentation,[7,8] TDCPP and HBCDs were not made at the Velsicol plant; however, in 1977, the National Institute for Occupational Safety and Health (NIOSH) listed 27 chemicals used in production processes at this site, and TDCPP and HBCDs were among them.[32] This could explain the significant correlations of TDCPP and HBCD concentrations with those of HBB, PBBs, and DDTs.

It is evident that those chemicals that were made in St. Louis, Michigan, are behaving differently in the atmosphere than those that were not. To further demonstrate this point, the correlation coefficients between the levels of these compounds in tree bark and the distance from the site were examined (see Figure S2, Supporting Information). For the sum of HBB, PBB, HBCDs, PBBZ, and PBEB (total brominated compounds), $r^2 = 0.535$ ($P < 0.001$); for the total DDT-related compounds, $r^2 = 0.524$ ($P < 0.001$), but for the PBDEs, $r^2 = 0.002$ ($P = 0.776$). Clearly, the levels of HBB, DDTs, and PBBs are elevated close to the manufacturing site with a sharp decrease after 10 km, whereas the levels of PBDEs and OPE are constant with distance from the site. The Velsicol Superfund site is still a point source of this pollution to surrounding areas even after 40 years, and people living within a 10 km radius of the site are still being subject to relatively high levels of HBB, PBBs, and DDTs

in the air they breathe. The EPA has focused on the remediation of soil, sediment, and water; however, humans can control what they eat and touch but not what they breathe. This study suggests that air monitoring around Superfund sites should be continued before, throughout, and long after remediation. Tree bark analysis provides an inexpensive method for examining air quality and could be easily implemented at other Superfund sites.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Table with the identification numbers for the tree bark sampling sites, locations, lipid percentages, distances from the Velsicol Superfund site, and concentrations (in ng/g tree bark lipids or μg/g tree bark lipids) of PBBs, DDTs, HBB, HBCDs, PBBZ, PBEB, PBDEs, OPEs, TDBPP, TDCPP, TCPP, TnBP, TBEP, TPP, and EHDPP; figures of congener distributions of DDTs and PBDEs and total brominated compound concentrations, total DDT-related compound concentrations, and total PBDE concentrations as a function of distance from the Velsicol Superfund site. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: hitesr@indiana.edu.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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