

Spray Irrigation of Treated Municipal Wastewater as a Potential Source of Atmospheric PBDEs

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Spray irrigation facilities utilizing treated municipal wastewater are a potential source of polybrominated diphenyl ethers (PBDEs) to the atmosphere. PBDEs are used as flame retardants in many household items and have been found in wastewaters and biosolids. Evidence of PBDE release from spray irrigation facilities was discovered during a multiyear project to measure semivolatile organic chemical concentrations in air. Four BDE congeners (47, 99, 100, and 154) were monitored at three remote/rural locations in Maryland and Delaware from 2001 to 2003. Average concentrations at two of the sites (BDE-47, 10–17 pg/m³; BDE-99, 5.3–7.7 pg/m³) reflect background levels. Average concentrations at the third location were 5–10 times higher (BDE-47, 175 pg/m³; BDE-99, 26 pg/m³) and were significantly correlated ($p < 0.0001$) with temperature indicating local source(s). Several spray irrigation facilities are located south and west of the third site, the prevailing wind direction during the spring and summer when most samples were collected. The fine mist released from the irrigation equipment may enhance release to the atmosphere via air–water gas exchange from water droplets. Temporal trends indicate that aerial concentrations of PBDEs in this area are increasing at an exponential rate; the atmospheric doubling times for the different congeners range from 1.1 to 1.7 yrs.

Introduction

Polybrominated diphenyl ethers (PBDEs), flame retardants that are widely incorporated into consumer products such as electronic appliances, construction materials, and upholstery, have been detected globally in many environmental compartments (1). The North American environment is more contaminated with PBDEs as compared to Europe, and levels

have increased at an exponential rate, doubling every 4–6 years (1). Although these compounds appear to have low acute and chronic toxicity, they are bioaccumulable and are likely to be more potent endocrine disruptors than many other classes of organohalogen compounds (2). Through an evaluative fate assessment procedure, Palm et al. (3) have deduced that tetra- and penta-brominated congeners are perhaps of greatest environmental concern since they tend to remain available in the environment. Not surprisingly, the constituents of the penta-BDE product (BDE-47, -99, -100, -153, and -154) are most commonly reported in the environment (1, 3).

Since many consumer products contain PBDEs, residues are delivered to municipal wastewater streams (4, 5) where, owing to their physical properties, PBDEs tend to focus in the resulting sludge material. Constituents of the penta-BDE product have been found in concentrations ranging from 1100 to 2290 $\mu\text{g}/\text{kg}$ (dry weight basis) in land applied sewage sludge (biosolids) from different parts of the United States (4, 6), and PBDE congener patterns in biosolids closely resemble that of the commercial penta-formulation, DE-71 (4). In the United States, over half of the sludge generated is now disposed of by application onto agricultural and other lands (7), and spray irrigation operations utilizing treated wastewater are becoming more popular as direct discharge of effluents is restricted in many waterways. As biosolids and wastewater are applied to soils, PBDEs may be accumulating in organic material at the soil surface and, therefore, are available for wider dissemination.

This research represents part of a greater effort to characterize the occurrence of contaminants in the atmosphere of the Chesapeake Bay region. The work included a multiyear air sampling effort at three locations on the Delmarva Peninsula (Figure 1). The air sample extracts were analyzed for four penta-BDE constituents (BDE-47, -99, -100, and -154). The Delmarva Peninsula, within the Chesapeake Bay airshed, is predominantly rural with 44% of the land under cultivation. Except for some large urban centers across the Bay on the western shore (Washington, DC and Baltimore, MD) and the Wilmington, DE industrial region to the north, there are no obvious sources of PBDEs. Since higher PBDE concentrations in air have been reported near urban areas (8, 9) the relatively remote locations of our sites is an important factor in this study. Elevated air concentrations of PBDEs at one of these three monitoring stations has prompted further investigation into potential local sources. This report provides evidence that several spray irrigation facilities located upwind from this site may be contributing to the higher air concentrations. Results suggest that spray irrigation of treated wastewater, containing relatively low concentrations of PBDEs (7), may facilitate movement of these chemicals into the atmosphere such that local air concentrations are increased.

Experimental Section

Sampling Sites and Techniques. High-volume air samples were collected at three sites on the Mid-Delmarva Peninsula (Figure 1). The Horn Point sampling site (38° 36' 04" N, 76° 07' 47" W) is situated on the campus of the University of Maryland Center for Environmental Studies, Cambridge, MD. It is a semi-rural region near the mouth of the Choptank River with no major industrial activity in the vicinity. The Washington, DC/Baltimore metropolitan area is approximately 90 km west-northwest.

The Lewes, DE sampling location (38° 46' 26" N, 75° 08' 20" W) is located on the campus of the University of Delaware

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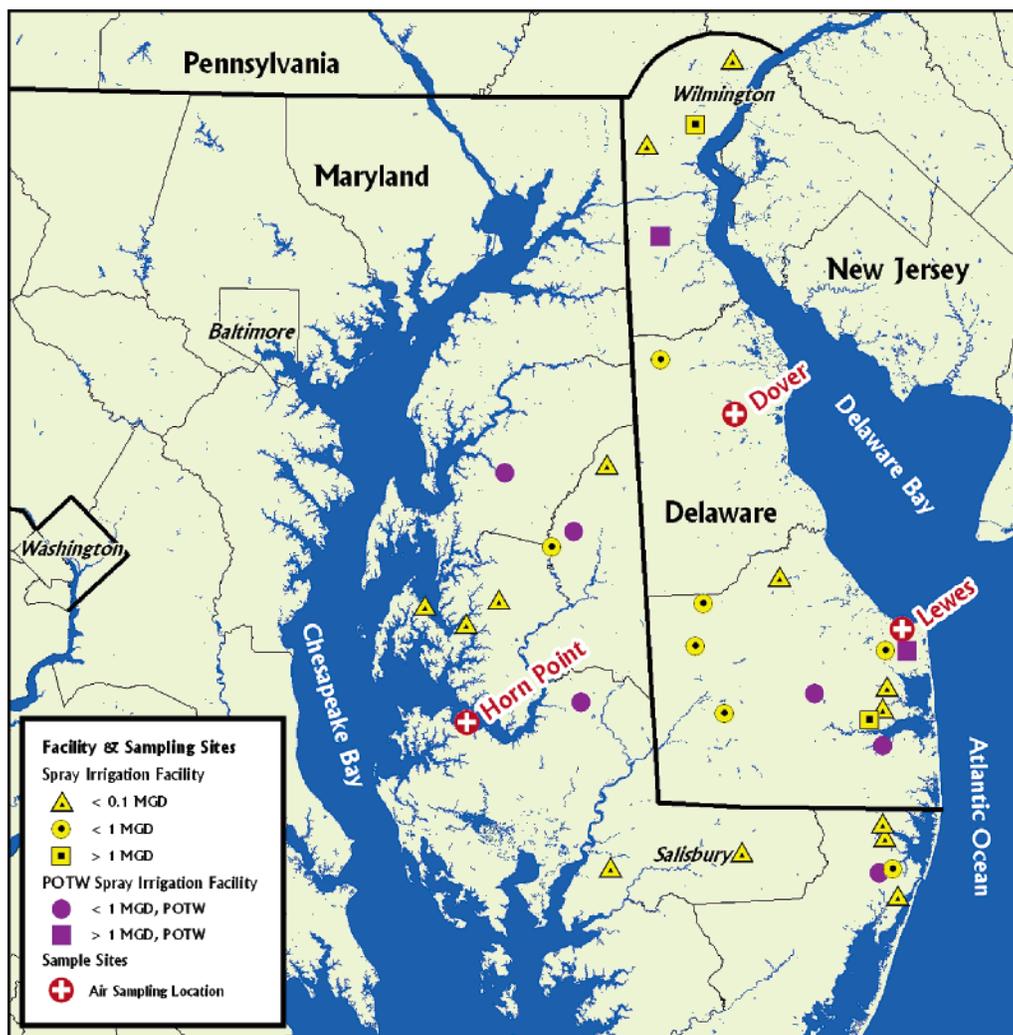


FIGURE 1. Location of sampling sites and spray irrigation facilities on the Delmarva Peninsula (POTW, publicly owned wastewater treatment works; MGD, million gallons per day).

at Lewes, on the southern junction of Delaware Bay and the Atlantic Ocean. The land use in southern Delaware is primarily rural—agriculture. The third site, at Dover, DE (39° 09' 29" N, 75° 31' 26" W), is located on the grounds of the St. Jones Estuarine Research Reserve on the banks of the St. Jones River. The sampling site is situated approximately 1.5 km southeast of the Dover Air Force Base and about 82 km south of Wilmington, DE. Of the three sites, Lewes is the most isolated in terms of proximity to large urban centers.

Air sample collection was conducted from 2001 to 2003 at Horn Point and Lewes and 2002 to 2003 at Dover. Samples were collected from April to November in 2001, March to November in 2002, and April to September in 2003. Weekly air samples were collected simultaneously from all three stations over a 24-h period (details provided in Supporting Information). This study was part of a project to characterize the presence of agricultural pesticides in the atmosphere of the mid-Delmarva Peninsula. Hence, sampling efforts were focused during the main growing season (April–September) and, in general, winter samples (December, January, and February) were not collected. However, one sample each was collected from January, February, and December of 2002 and January of 2003 at Lewes. A total of 240 air samples were collected during the period 2001–2003.

Sample Analysis. PUF plugs and filters were extracted with solvent (details in Supporting Information). PBDE concentrations in PUF and filter extracts were determined using an Agilent (Palo Alto, CA) 6890N gas chromatograph

coupled to an Agilent 5973 mass spectrometer (GC–MS) in selected-ion-monitoring mode using negative chemical ionization (NCI) mass spectrometry (ions m/z : 79, 81, 161, 325, 484, 564, 644). To ascertain if any other BDE congeners were present in the gaseous phase, 20 representative samples from the three sites were sent to an independent laboratory for analysis (Dr. Staci Simonich, Oregon State University). These samples were analyzed for 39 mono- to hepta-BDEs using the isotope dilution technique recently published by Ackerman et al. (10).

Quality Assurance (QA) and Quality Control (QC). Field blanks of PUF plug and filter were obtained monthly from each station by pulling air through the sampling train for ~1 min. In addition, a laboratory blank (a clean PUF plug or filter) and a laboratory spike (a clean PUF/filter spiked with target analytes) were extracted along with each batch of 20 samples to observe any matrix interference or contamination and to determine extraction efficiency, respectively. Method detection limits for the analytes were ascertained as per the U.S. EPA standard methods (11, Supporting Information).

Laboratory spike recoveries ranged from 50 to 80% for PUFs and 70 to 105% for filters (Table 1). Sample concentrations were not corrected for spike recoveries. Since the average spike recovery values for BDE 99 and 100 are 60% and 59%, respectively, air concentrations reported for these congeners may be lower than actual values (BDE 154 was not detected in any PUF samples). The laboratory filter blanks ($n = 18$) did not contain BDEs at concentrations above the

TABLE 1. Selected Physical Constants for Penta-BDE Congeners, Method Detection Limits (MDLs) and Spike Recoveries in Air Samples from This Study

PBDE congener	log K_{ow}^a	ΔH_{oa}^b kJ/mol	ΔH_{vap}^a kJ/mol	method detection limit (MDL) ^c		% spike recovery	
				PUF pg/m ³	filter pg/m ³	PUF (<i>n</i> = 16)	filter (<i>n</i> = 16)
47 (2,2',4,4')	6.19	97	92 ^a –95 ^d	6.0 ^e	1.0	83 ± 17	83 ± 22
99 (2,2',4,4',5)	6.53	91.1	100 ^a –108 ^d	2.6	1.1	60 ± 15	105 ± 31
100 (2,2',4,4',6)	6.86 ^{a,f}	105	102	3.1	1.4	59 ± 13	86 ± 29
154 (2,2',4,4',5,6')	7.39 ^{a,f}	94.4	113	3.3	3.3	47 ± 11	73 ± 28

^a Tittlemier et al. (12). ^b Harner and Shoeib (13). ^c MDLs are based on a sample volume of 720 m³. ^d Wong et al. (14). ^e A higher MDL of 32 pg/m³ was used for air samples from Lewes. ^f Estimated values.

TABLE 2. Summary of Concentration Data for PBDEs in the Air of the Mid-Delmarva Peninsula and Data from Previous Studies (All Concentrations in pg/m³)

	this study ^a						Great Lakes region		
	Lewes		Horn Point		Dover		Chicago ^b	3 remote sites ^b	rural site (Ontario) ^{a,c}
	2001–2003		2001–2003		2002–2003		1997–1999	1997–1999	Jan–June 2002
	(n = 95)		(n = 98)		(n = 47)		(n = 12)	(n = 12)	
	mean ^d	max	mean ^d	max	mean ^d	max	mean ^d	mean ^d	avg
BDE-47	175	671	9.7	26	17	52	33	2.9–8.4	4.6
BDE-99	26	178	5.3	26	7.7	17	16	2.1–5.3	4.3
BDE-100	17	73	5.4	5.4	5.3	5.3	2	0.3–0.8	nd
BDE-154	nd	nd	nd	nd	nd	nd	0.41	0.1–0.2	nd
ΣPBDE	174	912	10	57	19	64	52	5.5–15	

^a Gaseous phase concentrations only. ^b Strandberg et al. (8) (gaseous + particulate phase). ^c Guoin et al. (9). ^d Geometric means.

MDLs except for BDE-47 (in 30% blanks, average concentration ~4.3 pg/m³) and BDE-99 (*n* = 1, concentration 3.7 pg/m³). BDE-99 occurred above the MDL (concentration 6.7 pg/m³) in only one laboratory PUF blank (*n* = 10). Results from samples extracted along with these laboratory blanks which contained BDEs below the amounts present in the lab blanks were not considered in data analyses.

A total of 40 field blanks were collected during this study. PBDEs were not detected in field filter blanks (except BDE-47 in one blank from Lewes, concentration 2.7 pg/m³). Except for some blanks from Lewes which contained BDE-47, BDEs were generally not detected in blank PUFs. An elevated MDL of 32 pg/m³ for BDE-47 was used for samples collected from Lewes (see Supporting Information for details).

Results and Discussion

PBDE Detections in Air. PBDEs were detected in 75% (*n* = 240) of the samples (gaseous + particulate) indicating that these pollutants are ubiquitous and widely dispersed in this region. Among the three sites, Lewes had the highest detection frequency of PBDEs in its atmosphere (98%), followed by Dover (77%), and Horn Point (52%). In the gaseous phase, the detections generally followed the congener pattern 99 > 47 > 100 (Figure SF1) except at Dover, where BDE-47 was detected more frequently than BDE-99. BDE-154 was not detected in gaseous phase samples. BDE-28 was the only other congener present in gas phase in low concentrations (<10 pg/m³) in 25% of the samples (*n* = 20) analyzed by the GC–MS method of Ackerman et al. (10).

PBDEs occurred less frequently on particles; BDEs 47 and 99 occurred in <5% samples from Horn Point and Dover, whereas they occurred in 40–50% samples from Lewes. BDE-47 was the dominant particle-phase congener at Lewes and Dover. BDE-100 and BDE-154 occurred in a few filter samples from Lewes only. The greater frequency of detection of PBDEs

at Lewes, especially in the particle phase, as compared to the other two sites was unanticipated given the land use in this region and its distance from major urban areas.

Spatial and Temporal Variations in Air Concentrations. The three sites differed markedly in terms of occurrence and concentrations of PBDEs in air (Figure SF2 in the Supporting Information). Concentrations were typically highest during the warmer months. Contrary to expectations based on proximity to urban source areas, the frequency of detection and mean concentrations were lowest at Horn Point and highest at Lewes (Table 2). For the three congeners that were detected in the gas phase (47, 99, 100), the concentrations at Lewes were statistically higher (*p* < 0.0001) than those at the other two sites and appear to be increasing over the years (Figure SF2). Concentrations of BDE-47 were higher at Dover (*p* < 0.0001) than at Horn Point, whereas concentrations of BDE-99 were not statistically different between the two sites.

The average ΣPBDE concentrations in air at Horn Point and Dover (10–19 pg/m³) are comparable to the 5–15 pg/m³ reported for the rural and remote locations in the Great Lakes region (8). The mean values for BDE-47 and BDE-99 at Horn Point, in particular, are very similar to what has been reported at a rural location in southern Ontario in 2002 (9). At Dover, the same is true of BDE-99; but the concentrations of BDE-47 are higher (Table 2) than those in rural Ontario. This suggests that Horn Point represents background levels for PBDEs in the air in this region, whereas Dover represents background levels with some local influence.

In contrast, the average ΣPBDE gaseous phase concentration at Lewes (174 pg/m³) is 1–2 orders of magnitude higher than those at the two other sites and is more than three times as high as has been reported for Chicago (52 pg/m³). The elevated levels of PBDEs at Lewes are surprising considering that it is situated in a semi-rural region with no major industry nearby. The deviations in observations from

the other two sites, and the high aerial concentrations combined with much greater detection on particles, indicate the presence of local sources for the sampling site at Lewes.

Influence of Local Meteorological Conditions on Gas-Phase Concentrations. The atmospheric concentrations of semivolatile organic compounds (SVOCs) have been shown to be strongly correlated to atmospheric temperature and may also be influenced by time of year, wind direction, and wind speed. The prevailing wind direction on the Delmarva Peninsula is from west-southwest in summer, while during winter and early spring easterly surface winds frequently result in incursions of relatively "clean" oceanic air. The gas-phase concentrations of BDE congeners were analyzed using a modified form of the Clausius–Clapeyron equation (15)

$$\ln P = a_0 + a_1 \left(\frac{1}{T} \right) + a_2 t + b_1 \cos(WD) + b_2 \sin(WD) + b_3 (\ln WS) \quad (1)$$

This equation accounts for the effect of temperature (T , K) and time (t , relative Julian day) on partial pressure (P , atm) of the compound of interest. The coefficient a_1 ($= -\Delta H/R$) relates to the enthalpy of air-surface exchange (ΔH , kJ) and a_2 is a first-order rate constant. WD and WS are the 24-h averaged wind direction (degrees) and wind speed (mph), respectively. The regressions were performed using the general linear model procedure in SAS (SAS Institute, Inc., Cary, NC).

Regression analyses were performed for the congeners 47, 99 (all three sites), and 100 (Lewes). At Lewes, in particular, the correlations (r^2 : 0.24–0.51) were highly significant ($p < 0.0001$ – 0.0027). Results of the regression analyses (Table ST1) reveal that wind direction governed air concentrations at Horn Point; both temperature and time of year were important at Lewes; whereas, either temperature or time was important at Dover. Wind speed had no significant effect on BDE concentrations.

Temperature dependence of aerial concentrations of semivolatile compounds is often interpreted to imply that local or regional exchange processes control atmospheric levels, whereas nondependence on temperature suggests long-range transport (16). As stated above, PBDE concentrations at Lewes (and at Dover) were correlated with temperature, but those at Horn Point were not. The magnitude of temperature dependence, expressed as the enthalpy of surface exchange (ΔH), is used as an indicator of the dominant exchange process. At Lewes, PBDEs exhibited enthalpies of surface exchange (BDE-47, 53 kJ/mol; BDE-99, 42 kJ/mol; BDE-100, 26 kJ/mol, Table ST1) that are much lower than the laboratory measured values of their enthalpy of vaporization (ΔH_{vap}) and octanol–air exchange (ΔH_{OA}) (Table 1). High dependence on temperature ($p < 0.005$) combined with $\Delta H < \Delta H_{\text{vap}}$ suggests that the sources at Lewes are local but vaporization from surfaces was not the dominant process influencing aerial concentrations during the course of this study. More than one process or some other process with lower heat(s) of exchange could be controlling the aerial concentrations. Dependence on temperature ($p = 0.02$) and the enthalpy of surface exchange for BDE-47 ($= 26$ kJ/mol) at Dover was lower than that at Lewes and indicates a greater distance from source(s).

Results from the regression analysis also provide evidence that concentrations in the Mid-Delmarva atmosphere are increasing over time; however, the rate of increase is not the same for all congeners. Atmospheric doubling times ($t_2 = \ln(2)/a_2$) at Lewes range from 1.1 years for BDE-47 to 1.7 years for BDE-99 and BDE-100.

PBDEs in the Atmosphere at Lewes: Local Sources on Delmarva. As has been discussed earlier, PBDEs were detected most frequently at Lewes (both in gaseous phase

and on particles) and in much higher concentrations than at the other two sites. Concentrations at Lewes were high throughout the year and were significantly correlated with temperature. These observations suggest that Lewes is impacted by continuous, local, terrestrial sources of PBDEs on the Peninsula. This theory is strengthened by the fact that the prevailing wind direction during summer, when the majority of the samples were collected, is from the southwest and that the PBDE concentrations on the Peninsula seem to increase from west to east.

To further investigate the possibility of local sources of PBDEs on the Peninsula, 48-h back trajectories (for 5 starting times over the 24-h sampling period) were acquired using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model available on the website of the National Oceanic and Atmospheric Administration (NOAA) (17). Trajectories were generated for 55% of the air sampling dates for Lewes ($n = 95$) and on selected dates for Horn Point and Dover (10 each).

Lewes consistently exhibited higher PBDE concentrations even though the airmass trajectories for the three sites were similar (Figure SF3). The samples where concentrations at Lewes were low ($\Sigma\text{PBDE} < 25$ pg/m³; $n = 6$) are mostly from March and April and among these (except on 1/3/02) PBDEs were not detected in the particle phase (Figure SF4). In two of these samples airmasses came over the ocean completely bypassing the Peninsula. For the remaining samples, the airmass originated over the Great Lakes and approached the site from northwest completely bypassing the Peninsula on two occasions. Since most of our samples were collected during summer when the temperatures are high and prevailing wind direction is from southwest, influence of wind direction is not always apparent during warmer months. However, there were a few instances where the influence of wind direction at Lewes was seen (Figure 2).

On 4/23/02 and 6/04/02, when PBDE concentrations were low (as compared to the samples collected immediately before and after them), the airmass originated in the north and either bypassed the Peninsula (4/23/02) or approached the site from over the ocean (6/04/02). In contrast when the airmass approached the site from the south and southwest over land (4/16/02, 4/30/02, 5/28/02, and 6/11/02) the concentrations were higher and PBDEs were also associated with particles, which suggests local sources or short-range transport. Hence, results of the back trajectory analysis reveal that Lewes is affected by sources that appear to be located west and south of the site.

Spray Irrigation of Municipal Wastewater: Source of PBDEs in Air. Wastewater treatment facilities generally discharge their effluent to nearby surface waters, but on the Mid-Delmarva Peninsula, spray irrigation is the predominant disposal method. This is due to the availability of open land for disposal, the sandy, well-drained soils, the desire to recharge the shallow surface aquifer, and the increasing legal restrictions on direct surface water discharges (18). In Delaware, total maximum daily loads (TMDLs) for the Inland Bays require that all point sources of nutrient loading (which includes wastewater discharge) to these water bodies must be systematically eliminated (19). In Sussex County (Delaware) alone, more than 5 million gallons of wastewater per day (more than 9 MGD in summer), from 13 municipal and industrial sources, are disposed of by spray irrigation (Figure 1) (20). The scale of spray irrigation operations in Maryland counties on the Peninsula is relatively small; about 2.6 MGD spread over 15 facilities (21).

There are several spray irrigation facilities located south and west of Lewes. Most notable on this list is a large municipal wastewater spray irrigation facility (1.7–4 MGD) located ~6 km SE of the Lewes sampling site. This facility is the largest in Delaware (and on the entire Peninsula). The

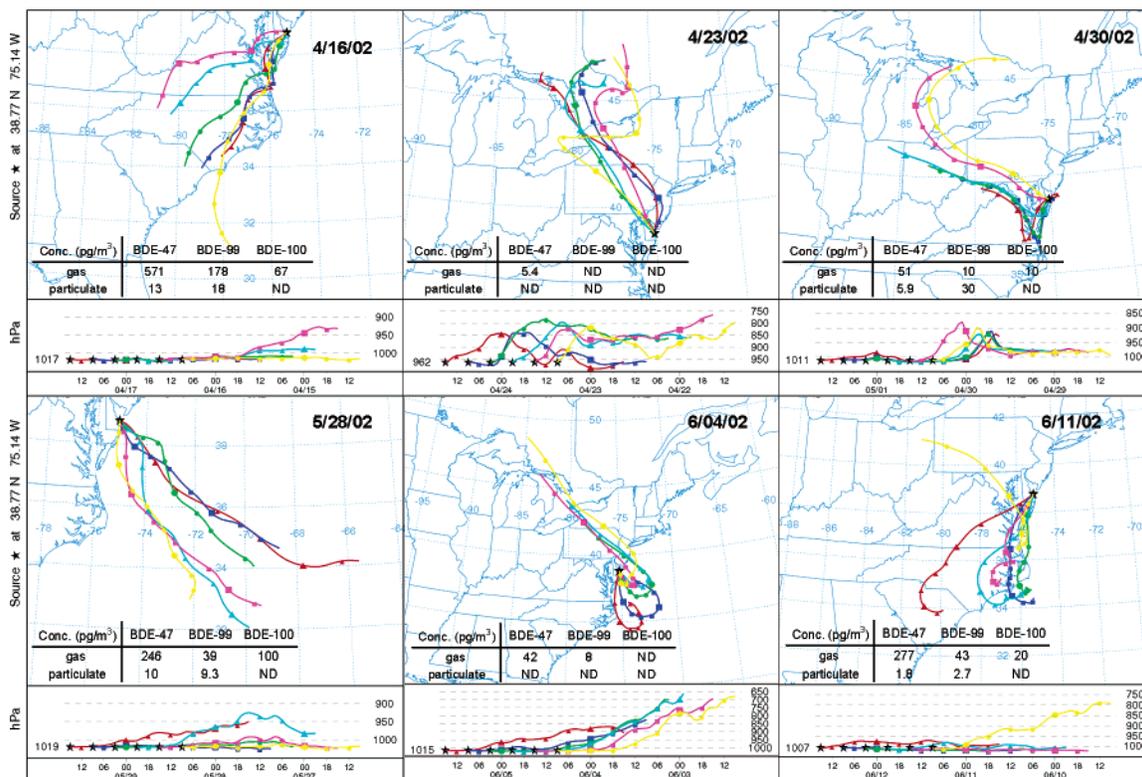


FIGURE 2. Two-day (48-h) back trajectories (at 10 m height) for Lewes acquired from the HYSPLIT transport and dispersion model (NOAA).

wastewater effluent is sprayed onto the fields a minimum of 8 h per day. The influent wastewater is aerated in two large storage lagoons and disinfected before it is released onto the fields using spray irrigators. Several housing communities also operate small spray irrigation facilities located south of Lewes. Some of the nearby facilities are engaged in agricultural processing, so their effluent would not be expected to contain PBDEs. Dover is located downwind of some facilities, while there are no known spray irrigation facilities upwind of Horn Point.

A number of factors governing the timing and volume of wastewater application in the region are consistent with the observed seasonality in PBDE concentrations in air at Lewes (Figure SF2). First, the area in and around Lewes is a popular summer vacation spot; therefore, both the population and the municipal wastewater volume increase during the summer months. Average daily flow at wastewater treatment facilities increases as much as 50% from winter to summer (20). Application is also reduced during the winter months while the ground is frozen. Data from 2004 show that from May to September, the facility southeast of Lewes operated for at least 27 days per month (20) as compared to 3 days in January.

Due to the large surface area of water droplets available during spraying, PBDE loss to the atmosphere during the spray process is likely to be significant. An estimate of the magnitude of this process may be calculated following the approach outlined by Wu et al. (22). Assuming a constant droplet size and ignoring the concentration of PBDEs in the surrounding air, the volatilization rate, J (g/s), from a droplet can be estimated as follows:

$$J = h_m A C_g \quad (2)$$

where h_m (m/s) is the mass transfer coefficient of compound across the concentration boundary layer around a droplet, A is the surface area of the droplet and $C_g (= C_w/K')$ is the concentration in the gas phase at the droplet air interface.

C_w is the concentration in the aqueous phase and K' is the dimensionless Henry's constant.

Assuming PBDE concentrations are similar to those reported by North (5) from a municipal wastewater treatment plant effluent (BDE-47 = 10.5 ng/L, BDE-99 = 11.2 ng/L), a constant droplet size of 0.5 mm, temperature of 25 °C, wind speed of 1.5 m/s (the average wind speed at Lewes), and an exposure time of 1 s, we estimate that at least 22% of BDE-47 and 9% of BDE-99 present in the effluent will be lost during the spray operation. The total loss of PBDEs from the spray irrigation facility is likely to be much larger considering that the aeration lagoon and soil surface (over which the wastewater is being applied) provide additional surfaces for loss of PBDEs. Soils receiving wastewater continuously for many years may be continuing sources of PBDEs or other chemicals to the environment, even after the fields are no longer in use.

Vapor-Particle Partitioning of PBDEs: Potential for Long-Range Transport. The partitioning of semivolatile organic compounds in the atmosphere is an important factor in their fate, transport, and transformation since greater association with particles results in shorter travel distances. For our data from Lewes, we examined the vapor-particle partitioning through the partition coefficient $K_p = (F/TSP)/A$ whose dependence on the sub-cooled liquid vapor pressure of the compound (p_L^0) is described by the linear relationship

$$\log K_p = m_r \log p_L^0 + b_r \quad (3)$$

where F and A are the filter and adsorbent retained PBDE concentrations (pg/m³), respectively, and TSP is the concentration of the total suspended particles in air (μg/m³). For Lewes, summer (April-September) and winter (October-March) TSP values (31.3 and 25.3 μg/m³, respectively) were taken from the measurements of Wolff et al. (23) whose sampling site was located within ~2 km of our site. BDEs did

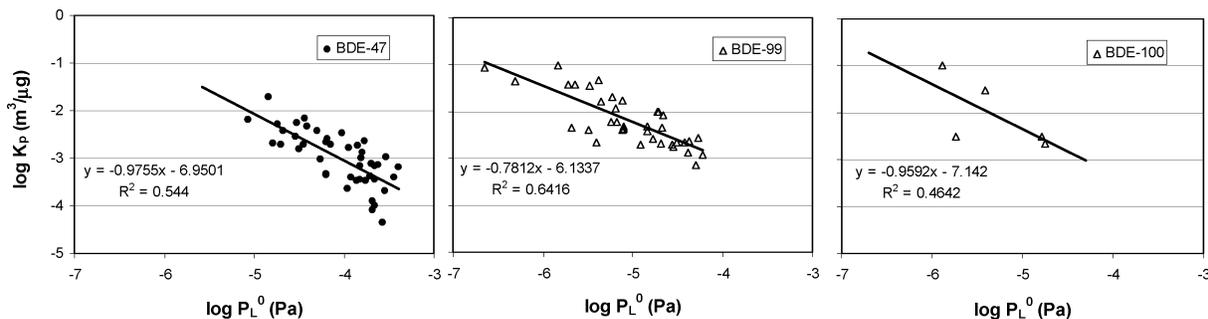


FIGURE 3. Vapor-particle partitioning behavior of PBDEs at Lewes. Temperature-dependent sub-cooled liquid vapor pressure was calculated as $\log p_L^0 = A/T + B$. A and B were taken as averages of values available from references 12 and 14 (BDE-47, $A = -4872.5$, $B = 12.74$; BDE-99, $A = -5435.5$, $B = 13.77$; BDE-100, $A = -5339$, $B = 13.37$).

not occur in sufficient filter samples from the other two sites to permit similar analysis.

Gas-particle partitioning for BDEs 47 and 99 is highly correlated ($r^2 = 0.54-0.64$, $p < 0.0001$) with sub-cooled liquid vapor pressure (Figure 3). Correlation for BDE-100 is not significant ($\alpha = 0.05$) probably due to fewer data points ($n = 5$). Statistically, the slope (m_r) for BDE-47 (-0.98) is not different from -1 (Table ST2) and suggests equilibrium in the vapor-particle partitioning of this compound (24). However, a slope of -1 is not a necessary condition and equilibrium can exist even when the slopes are shallower as has been shown for PCBs in the Great Lakes region (25). In this context, the slope for BDE-99 (-0.75) is close enough to -1 for us to argue that there exists equilibrium for this congener as well. Other meteorological factors such as wind speed and relative humidity were not found to significantly affect partitioning. This finding of equilibrium for both BDE-47 and BDE-99 is not surprising given that the kinetics of gas-particle sorption for SVOCs are fast and a few hours is sufficient to reach equilibrium (26).

Even though equilibrium exists in vapor-particle partitioning, the association of BDEs with the particles is much smaller than has been observed in other studies. At Lewes, for the samples collected when the 24-h average temperature was in the range 25 ± 3 °C, an average of 1.2% of BDE-47 ($n = 9$, range 0.1–3.2%) and 6.0% of BDE-99 ($n = 6$, range 2.2–9.3%) was present in the particulate phase. This is about an order of magnitude less than the predicted association with particles at 25 °C (17% and 45% for BDE-47 and BDE-99, respectively (13)) and observed association at 20 ± 3 °C in Great Lakes region ($\sim 20\%$ for BDE-47 and $\sim 40\%$ for BDE-99 (8)). The discrepancy could reflect the influence of aerosol composition. Since PBDEs are highly hydrophobic (Table 1) the fraction present in the particulate phase will be directly proportional to the organic carbon (OC) content of the aerosol, which is generally higher in urban locations (27). The reported average particulate OC concentrations for the Chesapeake Bay region range from $6.0 \mu\text{g}/\text{m}^3$ (Baltimore, 28) to $4.1 \mu\text{g}/\text{m}^3$ (over the Bay and on the Atlantic coast, 28, 23) with higher concentrations in summertime, both in terms of absolute values (23) and in terms of fraction of TSP (27). The lower OC concentration, in general, at our rural/remote site than in the urban environment combined with still lower OC in wintertime, when the PBDEs would have a greater affinity for the particles, could account for the lower percentage of PBDEs present in the particle phase in our samples.

This study provides evidence for a potentially important source of PBDEs to the atmosphere. Spray field irrigation is an important wastewater management alternative for many regions of the United States where nutrient contamination is degrading the quality of surface waters and their associated ecosystems. However, this practice should be examined

further to determine the magnitude of persistent bioaccumulative chemical emissions to the atmosphere.

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Supporting Information Available

Details of sample collection and analysis, tables for results of regression analyses (eqs 1 and 2), figures for PBDEs detection and observed concentrations in air samples from the three sites, and 48-h back trajectories on selected dates for the three sites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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