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Empirical and Modeling Evidence of the Long-Range Atmospheric Transport of Decabromodiphenyl Ether

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Understanding of the long-range atmospheric transport (LRT) behavior of decabromodiphenyl ether (BDE-209) is still limited. Most existing model-based approaches to assessing an organic chemical's potential for LRT have assumed invariant environmental conditions, even though many factors impacting on the atmospheric residence time are known to vary considerably over a variety of time scales. Model estimates of LRT also suffer from limited evaluation against observational evidence. Such evidence was sought from dated sediment cores taken from lakes along a latitudinal transect in North America. BDE-209 was generally detected only in recent sediment horizons, and sedimentation fluxes were found to decline exponentially with latitude. The empirical half-distance (EHD) for BDE-209 derived from surface flux data is approximately half that of the Σ PCBs. A dynamic multimedia fate and transport model provides further insight into the temporal variability of processes that control LRT for BDE-209 and PCBs. The variability of precipitation, and in particular, the occurrence of time periods without precipitation coinciding with strong winds, influences the LRT potential of chemicals that combine a sufficiently long atmospheric half-life with very low volatility. Likewise, the forest filter effect may be important for a wider range of chemicals than believed previously, because models assuming constant precipitation fail to account for the impact of differences in dry deposition on days without rain. Chemicals that are both sorbed to particles and potentially persistent in the atmosphere, such as BDE-209, may have a larger potential for LRT than anticipated on the basis of earlier model evaluations. Still, the EHDs illustrate that the model seems to underestimate atmospheric loss processes of potential significance to BDE-209, illustrating the need to critically compare predictions of LRT against observations. Processes that need to be understood better in order to improve

predictions of LRT for BDE-209 include particle dry deposition, precipitation scavenging, and photolysis in the sorbed state.

Introduction

Persistent organic pollutants (POPs) are persistent, bio-accumulative, toxic (PBT), and susceptible to long-range transport (LRT). Recent international agreements are aimed at further reducing environmental exposure to such substances, particularly of indigenous populations living in remote areas (1, 2). To provide scientific support for these conventions, it is important to develop and evaluate criteria and models identifying chemicals with a potential for LRT (e.g., 3–7). A useful and relatively simple measure of chemical mobility in the environment is the characteristic travel distance (L_A), which is defined as the distance over which the initial air concentration of a chemical is reduced to 1/e (~37%) in a plug-flow system (4, 5). Because many POPs have the potential for undergoing reversible deposition to aquatic and terrestrial surfaces, multimedia box models are particularly suited to estimate L_A (5). To gain confidence in the use of such models within a regulatory context, it is imperative that model approaches and predictions are evaluated against observed chemical behavior (8). The determination of historical profiles and concentrations of pollutants in dated sediment cores has provided valuable information on sources, time trends, and current inputs of many POPs (e.g., ref 9). Results from a north–south mid-continental transect of Canadian lakes showed declining deposition rates of POPs in surficial sediments with increasing north latitude (10, 11). For PCBs and Σ DDT, the declining rates with latitude parallel the decline in average annual air concentrations measured at several mid-latitude sites and Arctic locations in the mid-1990s (12). Taken together, these results suggest that lake surficial sediments and sediment cores can provide data on spatial and temporal variability of atmospherically derived inputs of hydrophobic POPs to lakes and terrestrial surfaces over a range of temperature and geological conditions. Sediment data may thus provide information suitable for evaluating model predictions of L_A .

LRT estimations based on L_A have so far mainly been carried out using steady-state models, assuming static environmental conditions. However, recent studies have illustrated that variable environmental conditions, such as temperature and OH radical concentrations (6) as well as intermittent precipitation (8, 13), may have a strong impact on estimates of L_A . In this study, we used a dynamic multimedia fate and transport model to explore in more detail how temporally variable environmental conditions and forest coverage may affect estimates of L_A for various chemicals with divergent partitioning properties. An important goal is to evaluate the validity of approaches to L_A estimation that are based on steady-state model simulations.

Our focus in this study is on the deca-BDE (BDE-209). Polybrominated diphenyl ethers (PBDEs) presumably reach the Arctic environment via long-range atmospheric transport mainly from urban areas in North America, which is a major use area for PBDEs globally (14). Our objective was to examine the fluxes and geographical extent of PBDEs with a focus on BDE-209 along a latitudinal gradient in North America, and to compare the observed and predicted long-range atmospheric transport behavior with that of the polychlorinated biphenyls (PCBs), which are known priority POPs. We were particularly interested in decabromodiphenyl ether (BDE-

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209), because it is the most widely used PBDE mixture, is extremely hydrophobic, has low vapor pressure and high octanol-air partition coefficient and, therefore, is likely to be transported on particles (15). A recent study by Hoh and Hites (16) has also shown that BDE-209 is now relatively abundant in the atmosphere of the east-central United States. Thus it provided an interesting contrast to more volatile, gas-phase contaminants such as PCBs with a more well-characterized long-range atmospheric transport behavior.

Materials and Methods

Sampling and Analysis. Sediment cores were collected from selected lakes along a south-north transect from southern Ontario and upper New York state to Ellesmere Island (Supporting Information (SI), Figure S1). Except for Lake Ontario, all lakes were uninhabited or had a history of very limited human disturbance and are, therefore, referred to as remote or isolated. Collection occurred through holes drilled into the ice or from a small boat between August 1998 and May 2001. A core was collected in western Lake Ontario (station 1007, 43°26'01"N; 79°24'00"W) from the Canadian Coast Guard Ship *Limnos* in June 1998 using a box corer. Cores were extruded on site and slices placed in "WhirlPak" polyethylene bags (cores collected in 1998–2000) or glass "ointment" jars with aluminum foil lined caps (all other cores). The cores were sliced to achieve maximum temporal resolution while obtaining sufficient mass for ^{210}Pb dating and contaminant analysis. All cores from the Arctic were collected with a 6.5 cm diameter corer and sliced at 0.5 cm intervals while most cores from south of 55°N were collected with the 10 cm KB corer and sliced at 1 cm intervals. Sediments were kept in cool dark storage during the field work and then shipped by air freight to the laboratory where they were stored in the dark at 4 °C. Sediment slices were dated using ^{210}Pb and ^{137}Cs and sedimentation rates and dates were estimated using CRS and CIC models (17).

Sub-samples from cores with interpretable ^{210}Pb profiles were analyzed for a suite of halogenated organics following methods of Muir et al. (10, 11) with minor modifications to allow for isolation of PBDEs. All sediment sample extraction and cleanup steps were conducted in a certified clean room at NWRI (positively pressured, HEPA/carbon filtered air) to limit contamination. PBDEs were determined by GC-high-resolution mass spectrometry (MS) in electron ionization (EI) mode (18) using a Micromass Instruments Autospec Ultima. Internal ^{13}C -labeled standards of CDE-128, BDE-47, BDE-77, BDE-100, BDE-99, BDE-126, and BDE-209 (all from Wellington Labs, Guelph ON) were added prior to injection. Further details are provided in the SI.

Laboratory blanks consisting of all reagents were analyzed every six samples. In addition, sediment core slices dated to pre-1900 were analyzed as a further check on background levels. The limit of detection (LOD) for BDE-209 was approximately 10 pg/g (dry wt) based on $3 \times \text{SD}$ of low concentrations standard (19). The method detection limit ($\text{MDL} = \text{blank} + 3 \times \text{SD}$) (20) for BDE-47, 99 and 100 varied with the individual cores, from 10 to 100 ng/g (dw), because of a PBDE background that was more significant in some cores than others. Because blanks for BDE-209 were zero, the LOD was equal to the MDL. MDLs for PCB congeners ranged from 20 to 200 pg/g dw with the median of 40 pg/g dw.

Depositional fluxes of PBDEs were determined by multiplying sedimentation rates for each horizon determined by the CRS model by concentrations and dividing by the sediment focusing factor estimated for each core. Where concentrations were <MDLs, fluxes were expressed as $<1/2 \text{ MDL} \times \text{sedimentation rate}$. Empirical half-distances (EHDs) were calculated using PBDE and PCB results for isolated/

remote lakes by simple linear regression of log surface flux vs latitude. Note, that whereas L_A correspond to a reduction of ~63% in predicted air concentrations, the EHD represents only a 50% decline. Direct comparison is facilitated by estimating an empirical travel distance at 63% reduction (ETD) as $\text{EHD}/\ln(2)$.

Model Description. A detailed description of the model is provided in the SI. In brief, the characteristic travel distance in air (in m) in a model environment which includes multiple environmental surface compartments in contact with the atmosphere, may be expressed as follows:

$$L_A = uM_A/[N_{RA} + \Sigma(N_{ASnet})] \quad (1)$$

where u is the wind speed (m h^{-1}), M_A is the amount of chemical in the atmosphere (moles), N_{RA} is the rate of atmospheric reaction (mol h^{-1}), and $\Sigma(N_{ASnet})$ is the net flux of chemical from the atmosphere to the surface (mol h^{-1}).

L_A was calculated using CoZMo-POP, a non-steady state, nonequilibrium fugacity-based multimedia fate and transport model that has been developed to describe the long-term fate of POP-like substances in a coastal region (21, 22). The original model version includes eight well-mixed compartments, representing the atmosphere, the terrestrial environment (forest canopy, forest soil, agricultural soil), and the aquatic environment (freshwater, freshwater sediment, seawater, and seawater sediments). Chemical fate processes include equilibrium phase partitioning between sub-compartments, advective and diffusive transport between compartments, first-order degradation in each compartment (*2nd order in atmosphere between vapor phase chemical and OH radical*), and sediment burial. In this work, we used a modified version of CoZMo-POP that includes a dynamic water balance (23). Relying on earlier efforts to compile environmental input parameters (24), the model simulation reflects conditions in the Baltic Sea drainage basin. Wind speed, temperatures, atmospheric OH-radical concentration, and precipitation rates (as well as L_A) are assumed to vary on a daily basis in the model but not from year to year. Simulations were carried out for 10 compounds, including seven PCBs (PCB-28, 52, 101, 118, 138, 153, and 180) and three PBDEs (BDE-47, 99, and 209). The required substance-specific properties are listed in Tables S1 and S2 in the SI.

L_A for the 10 chemicals was calculated as a function of season at quasi steady state (QSS), which is obtained by letting the model run with constant emissions to the atmosphere until none of the model results changes by more than 1% during a one-year period (SI 4.3). During the first year of QSS, L_A and selected model outputs were stored at 24-hour intervals. L_A is thus assumed to vary on a daily basis, whereas diurnal variability is ignored. L_A s were calculated for three additional model scenarios to aid in the interpretation of the results. The second scenario is similar to the default scenario, except that the forest and forest soil compartment is removed (with a respective increase in the area of the agricultural soil compartment). The third scenario mimics the output of a steady-state model by assuming that all previously time-variant parameters (OH-radical concentrations, precipitation, temperature, wind speed, parameters associated with the canopy compartment) remain constant at the annual average. The fourth scenario is similar to the third, but without forest (as for the 2nd scenario). The discussion refers to the default scenario unless specified otherwise.

Results and Discussion

Sediment Concentrations and Fluxes. BDE-209 was detectable in recent sediments from all investigated lakes in Ontario, Québec, and northern New York State, but was near or at detection limits in cores collected north of 55°N (Figure 1; SI Table S3). BDE congeners 47, 99, and 100 were also above

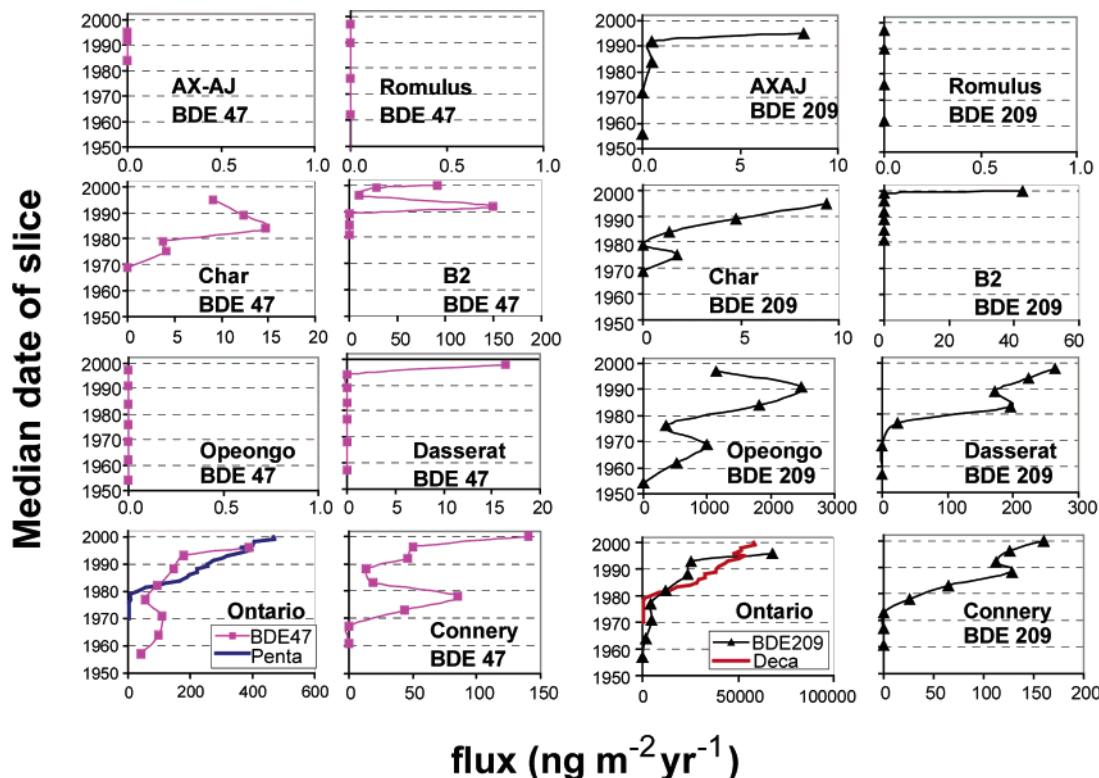


FIGURE 1. Historical flux ($\text{ng m}^{-2} \text{yr}^{-1}$) profiles of BDE-47 and BDE-209 in dated lake sediment cores. Results are organized from north (top) to south (bottom). Lake locations are given in Table 1. Global production estimates (tonnes (t) per yr) for “Penta” and “Deca” BDEs are included with the Lake Ontario results. Penta production figures (t) are divided by 20 in order to use the same scale.

MDLs in most cores although, in some cores, background concentrations resulted in nondetectable levels after blank subtraction. The background may have been introduced by the polyethylene sample bags used for some cores collected in 1997–1998. The bags may have taken up PBDEs from air because, when rinsed with DCM, the solvent residue was found to contain nanogram amounts of BDE-47 and 99. Although this level of contamination was low, it could have contributed to the PBDE levels in the samples. Fewer blank problems were encountered with sediment stored in solvent-rinsed glass jars.

In contrast to the lower-brominated PBDEs, there were essentially no blank problems with BDE-209. Concentrations of BDE-209 in surface sediments ranged from $<10 \text{ pg/g dw}$ in Romulus Lake to $173\,900 \text{ pg/g dw}$ in Lake Ontario (west basin). Concentrations of BDE-47 ranged from $<15 \text{ pg/g dw}$ in Arctic lake sediments to 997 pg/g dw in Lake Ontario sediments. Higher concentrations of all PBDEs were found in surface or near surface horizons of the mid-latitude lakes compared to the Arctic lakes (SI Table S3). Surface fluxes of BDE-209 ranged from <3 to $9.4 \text{ ng m}^{-2} \text{yr}^{-1}$ in the three Arctic lakes, from 43 to $1145 \text{ ng m}^{-2} \text{yr}^{-1}$ in the four mid-latitude lakes, and $67\,800 \text{ ng m}^{-2} \text{yr}^{-1}$ in Lake Ontario (Table 1). Surface fluxes of sum BDE-47, 99, and 100 ranged from <10 to $489 \text{ ng m}^{-2} \text{yr}^{-1}$ in the four mid-latitude lakes and $1036 \text{ ng m}^{-2} \text{yr}^{-1}$ in Lake Ontario. The fluxes of BDE-209 and sum BDE-47, 99, and 100 for the Lake Ontario core agreed well with results of Song et al. (25) who reported surface fluxes of $65\,000 \text{ ng m}^{-2} \text{yr}^{-1}$ and $1950 \text{ ng m}^{-2} \text{yr}^{-1}$, respectively, based on results from a core collected in the central basin.

Historical profiles of BDE-209 and BDE-47 in the eight lakes are shown in Figure 1. BDE-209 was generally detected only in recent horizons, mainly post-1980, including Lake Ontario. Unlike the other lakes, Lake Ontario would receive direct inputs of BDE-209 from municipal waste treatment effluents and other urban sources. The historical profile for BDE-209 and BDE-47 in Lake Ontario closely follows the

estimated global historical production for BDE-209 and “penta” BDE, respectively (26). The other seven lakes do not show as good agreement with the global production figures although all show maxima post-1980 corresponding to the beginning of large scale production of PBDEs. Lake Opeongo is located in Algonquin Park, and Connery Pond is in Adirondack Park; both would likely have received BDE-209 inputs only from atmospheric deposition, although inputs from use of boats and other equipment on the lake cannot be ruled out. BDE-209 was found in deeper slices in Opeongo than in the other lakes. The reason for this is unclear; there may be much more bioturbation in this core than in the others. BDE-209 is highly sorbed to particles and thus susceptible to particle mixing.

The three high Arctic lakes have much lower fluxes consistent with their remote locations. However, Char Lake is located near the Resolute airport and, although it is a protected lake with no boats allowed because it is the village water supply, inputs of PBDEs cannot be ruled out entirely. AX-AJ, on the other hand is completely isolated and was visited only for sediment core sampling. Romulus Lake had a very high sedimentation rate compared to the other Arctic lakes (Table 1), which may explain the nondetectable levels of PBDEs in this core.

Malmquist et al. (27) detected BDE-47 in dated sediment cores from West Greenland. BDE-47 was generally detected in post-1980 horizons although some cores with low sedimentation rates had background concentrations in earlier horizons. Surface fluxes of BDE-47 in Lake G, which had similar temporal resolution to Char Lake and Romulus Lake, were approximately $1.3 \text{ ng m}^{-2} \text{yr}^{-1}$, which is lower than BDE-47 in lakes AX-AJ and Romulus. Stern et al. (28) reported a maximum flux of sum of BDE-47, 99, and 100 of $28.5 \text{ ng m}^{-2} \text{yr}^{-1}$ in a high-resolution core from Devon Island in the Canadian Arctic. This is very similar to the flux estimated for Char Lake but higher than fluxes in lakes G, Romulus, and

TABLE 1. Sediment Core Locations, Sedimentation Rates, and Fluxes (ng m⁻² yr⁻¹) for PBDE and PCB Congeners

location	lake	collection year	latitude/ Longitude	sedi- mentation rate ^a g m ⁻² yr ⁻¹	Flux (ng m ⁻² yr ⁻¹)														
					FF ^b	BDE -47	BDE -100	BDE -99	BDE -209	PCB -31/28	PCB -52	PCB -101	PCB -118	PCB -153	PCB			ΣPCB	
															-138/ 163	-180	-194		
Nunavut (Arctic)	AX-AJ	1998	79°42'N, 87°23'W	110	1.0	<4	<4	1.7	8.3	<1	<1	<1	<1	2.1	5.9	9.3	3.6	292	
Nunavut (Arctic)	Romulus	2001	79°54'N, 85°06'W	820	2.6	<16	<16	<16	<3	200	95	34	12	8.0	6.6	4.5	<1	1152	
Nunavut (Arctic)	Char	1997	74°40'N, 94°50'W	280	2.4	9.1	1.9	9.5	9.4	2.7	4.9	12.4	5.9	6.8	3.0	0.8	<1	112	
northern Québec	B2-1	2000	57°45'N, 76°10'W	160	1.3	92	76	321	43	118	202	146	42	43	10	10	1.1	2242	
western Québec	Dasserat	2000	48°16'N, 79°26'W	470	1.0	16	<16	<16	264	493	346	179	84	79	74	69	26	3954	
northern New Brunswick	Britt Brook	1999	47°55'N, 66°52'W	80	1.0	na ^c	na	na	na	93	132	116	63	48.3	48	14	0.2	2021	
southern Québec	Croche	2001	45°51'N, 74°00'W	140	1.0	na	na	na	na	193	574	215	147	152	168	140	56	5459	
eastern Ontario	Opeongo	1998	45°22'N, 78°22'W	140	1.0	<7	<7	<7	1145	40	<1.4	81	50	54	55	29	18	1201	
upper NY state	Connery	2001	44°20'N, 73°45'W	140	1.0	140	51	161	161	815	590	326	189	179	159	94	31	7548	
Ontario/ NY state	Ontario	1998	43°26'N, 79°24'W	390	1.0	389	117	530	67800	3250	3250	3724	4810	3630	3720	2170	720	92580	

^a Sedimentation rates of the surface slice based on the CRS model. Sedimentation rates of lower horizons are given in Supporting Information Tables S3 and S4. ^b Sediment focusing factor calculated from the average excess ²¹⁰Pb flux rate (pCi·cm⁻²·yr⁻¹) in the core divided by expected ²¹⁰Pb flux rate based on soil cores. ^c Not analyzed for PBDEs.

TABLE 2. Empirical Half-distances and Estimated Annual Average and Median L_A at Quasi Steady-state for the Default Scenario [ln Km].^a

chemicals ^b	empirical half-distances (EHDs) ^c	TaPL3 (L _A) ^a	ELPOS (L _A) ^a	CoZMo-POP (L _A)							
				non-Steady-State environmental conditions					SS environment		
				default Model Scenario (with forest)					no forest	forest	no forest
				L _{A,avg}	L _{A,median}	L _{A,max}	L _{A,min}	years	L _{A,avg}	L _{A,avg}	L _{A,avg}
PCB-28/31	754 ± 324 (1088)	4881	5233	6272	4417	87 070	316	12	8381	5040	8045
PCB-52	895 ± 602 (1291)	7411	9050	7013	3535	162 400	340	18	9484	3929	7164
PCB-101	740 ± 202 (1068)	6337	16 314	5115	2533	90 230	301	48	8591	2621	5488
PCB-118	736 ± 151 (1062)	3463	12 739	1483	1526	4322	188	49	3228	1346	2952
PCB-138/163	878 ± 153 (1267)	2628	18 364	1350	1366	2408	163	60	3224	1229	2970
PCB-153	846 ± 117 (1221)	2843	26 908	1438	1490	3808	181	82	3389	1297	2990
PCB-180	947 ± 281 (1366)	912	6889	1134	1029	1917	128	89	2379	973	2202
BDE-47	1168 ± 942 ^d (1685)	1113	2483	952	778	1827	104	14	1808	758	1470
BDE-99		610	1194	1540	961	3877	118	14	2902	860	1440
BDE-209	566 ± 101 (817)	480	735	9718	4471	48 020	161	14	22 172	2658	3788

^a The daily maximum and minimum values for L_A and the number of years simulated to reach quasi steady-state are also presented for the default scenario. Also given is the estimated annual average L_A at quasi steady-state for (a) a scenario without forest compartment, as well as (b) static environmental conditions (assuming steady-state forest growth and decay, wind speed, precipitation, OH-radical concentrations, and temperatures based on annual average values), and (c) steady state environmental conditions and no forest compartment. ^b Model calculations do only include the first out of two PCB congeners listed in the same row. ^c Details on the calculation of EHDs are provided in SI Table S6. Numbers in parentheses are the ETDs (= EHD/ln(2)). ^d Calculated with 6 lakes, 4 from this study (Table 1) and Lakes DV09 and G from Stern et al. (28) and Malmquist et al. (27), respectively (see SI Table S4). ^e Data from Wania and Dugani (15).

AX-AJ. Similar to Malmquist et al. (27), Stern et al. (28) detected BDE-47 in horizons dated to time periods preceding PBDE manufacture, thus illustrating the challenge of determining low level PBDEs in remote lake sediments.

PCBs were detectable in all lake sediments with higher concentrations and fluxes in cores from temperate lakes. Fluxes for PCBs-28/31, 52, 101, 153, 138/163, 180, and 194 are shown in Table 1, and concentration data are provided in Table S4 (SI). As has been observed previously (11) tri- and tetrachlorobiphenyls generally accounted for a higher proportion of ΣPCB in high Arctic sediments, especially in Lakes Romulus and AX-AJ (SI Table S5).

Empirically Derived Half-Distances and Comparison with Predicted L_As. BDE-209 fluxes declined exponentially

with northern latitude (SI Table S6) corresponding to an empirical half-distance (EHD ± SE) of 566 ± 101 km (Table 2). This was based on results for seven remote lakes and did not include Lake Ontario. EHDs could not be calculated for BDE-47, 99, and 100 with the data for the seven lakes due to high detection limits in three of the lakes. However, combining fluxes derived from reports by Malmquist et al. (27) and Stern et al. (28) with those from Char Lake, Lake B2-1, Dasserat and Connery (N = 6) indicated a declining BDE-47 flux with latitude (not statistically significant), which translated into an EHD (±SE) of 1168 ± 942 km. EHDs for PCB congeners 138/163, 153, and 180 based on nine lakes were significantly greater (P = 0.10) than those for BDE-209 based on paired t-tests of the slopes (SI Table S6). Although

PCB-52 had a longer EHD than more highly chlorinated congeners, the differences were not statistically significant ($P > 0.10$), and no consistent trend was evident with chlorine number. Previous work with larger numbers of sediment cores from isolated lakes ranging from 49 to 82 °N latitude has shown stronger differences between di/tri/tetra-chlorobiphenyls, which did not decline significantly with latitude, and hepta/octa-chlorobiphenyls which did show significant latitudinal trends (11).

The EHD of BDE-209 is smaller but on the same order of magnitude as that of the PCBs (Table 2). Table 2 lists the annual average L_A during the first year of quasi steady-state (QSS) calculated for all four scenarios. For the default scenario the annual average L_A of the 10 chemicals ranges over approximately 1 order of magnitude, with the longest and shortest L_A estimated for BDE-209 (9718 km) and BDE-47 (952 km), respectively. All PCBs investigated using CoZMo-POP fall between these two compounds. The seasonal range of a chemical's L_A , obtained by comparing the maximum and minimum daily L_A , is larger, i.e., between 1 and almost 3 orders of magnitude. This range (along with significant differences in $L_{A,avg}$ and $L_{A,median}$) are particularly notable for PCB-52 and BDE-209, and indicate compounds that may have a tendency to exhibit occasionally elevated levels in the air of remote areas as a result of LRT episodes. Interestingly, Hoh and Hites (16) recently reported significant variability in measured air concentrations of sum of nona-BDEs and BDE-209 at five stations in the east-central United States in comparison to the lower brominated PBDEs. Potential for significant temporal variability in air concentrations thus justifies the use of sampling media representing longer time periods (e.g., sediments) when EHDs for such substances are to be derived.

Still, it is evident that the CoZMo-POP calculations overestimate the observed atmospheric mobility of BDE-209 relative to that of the PCBs (Table 2). This may be caused by processes of potential significance in limiting LRT that are so far not included in the CoZMo-POP model due to lack of quantitative understanding, notably (i) direct or indirect photolytic degradation of BDE-209 sorbed to atmospheric particles (e.g., refs 29, 30) and (ii) snow scavenging of particles, which could be more efficient than rain scavenging (31). Alternatively, it may be caused by problems with the existing parametrization of the model. The following sections, therefore, aim to offer possible mechanistic explanations for the differences in predicted and observed behavior of BDE-209, relative to the PCBs. Using the steady-state models ELPOS (6) and TaPL3 (5), Wania and Dugani (15) had previously predicted L_A s for BDE-209 and BDE-47, which are in better numerical agreement with the EHDs derived here (Table 2). However, calculated L_A s for the PCBs had been up to an order of magnitude higher. A key question is thus also why ELPOS and TaPL3 indicate large differences in L_A between BDE-209 and PCBs, when the EHDs suggest that their mobility is not that different? Since the numerical values of the calculated L_A s should be interpreted with caution, this could be the result of (i) travel distances for the PCBs which are overestimated by ELPOS/TaPL3, relative to BDE-209 (15) or (ii) travel distances for BDE-209 which are underestimated by ELPOS/TaPL3, relative to the PCBs. In summary, whereas the measured data indicate comparable mobility for PCBs and BDE-209, steady-state models suggest that PCBs are much more mobile than BDE-209, and the dynamic CoZMo-POP model predicts higher mobility for BDE-209 than for the PCBs.

Key Processes Controlling L_A . The competing processes of atmospheric reaction and net atmospheric deposition limit L_A at any point of time (eq 1). The results suggest L_A is limited by deposition, rather than reaction, for the heavier PCBs (118 and above) and the PBDEs throughout the year (SI 4.1).

Muir et al. (8) have previously stressed that when assessing LRT of reactive substances it is imperative that the oxidant concentrations apply for the region and time period of interest. This model is parametrized for the Baltic Sea region, which may exhibit lower OH-radical concentrations than the southern reaches of the study region (32). L_A for the lighter PCBs may thus have been overestimated (Table 2; SI Table S7). A larger L_A of the lighter PCBs (Table 2) is in accordance with the prevalence of lighter PCBs found in high Arctic sediments (SI Table S5), if not the EHDs (Table 2).

Intermittent Precipitation. Intuitively, one might expect typical steady-state scenarios with constant precipitation to underestimate the "true" L_A of chemicals that are subject to rain washout (either as vapors or on particles), simply because dry weather is typically more frequent than rain. A comprehensive analysis of the impact of intermittent precipitation on atmospheric transport for 300 different organic chemicals found that the assumption of continuous rain could lead to underestimation of L_A by as much as 3 orders of magnitude (13). At the same time, atmospheric removal processes of α -HCH appeared to be more efficient in a 3-D atmospheric chemistry transport model as compared to the output of a multimedia fate and transport model (33). Comparing scenarios 1 and 3 (Table 2), the annual average L_A for all compounds increases upon introducing temporally variable environmental parameters, most importantly intermittent precipitation. The increase is minor for the PCB congeners 28, 118, 138, 153, and 180 as well as BDE-47 (by a factor of up to 1.3), larger for PCB-52, PCB-101, and BDE-99 (by a factor of 1.8–2.0) and dramatic for BDE-209 (factor of 3.7). BDE-209 is effectively rained out by wet particle scavenging because of its high K_{OA} , and this is also one of the main reasons that BDE-209 shows the largest range in L_A (Table 2, SI 4.2).

Forest Coverage. The observation of enhanced deposition velocities to forest canopies (34) has motivated the development and inclusion of forest canopy compartments in multimedia fate models (35–38), and two studies have previously attempted to investigate how so-called forest filter effect may affect estimates of LRT (37, 38). Scenarios with a forest always yielded lower L_A estimates than scenarios without a forest (Table 2). Comparing first the L_A for the scenarios based on annual averaged environmental conditions (last two columns of Table 2), we find that the effect of including a forest canopy is strongest for those chemicals which physical-chemical properties within a certain window of the chemical partitioning space (35). Specifically, the percentage reduction in annual average L_A (with forest, relative to no forest) is strongest for PCB-138 (59%) and PCB-153 (57%), and limited for BDE-209 (30%). However, the results for the scenarios reflecting non-steady-state environmental conditions (with and without forest) are different. While the forest filter effect is still pronounced for PCB-138 (58%), the reduction in annual average L_A is now of a similar magnitude for BDE-209 (56%). This is due to elevated dry deposition of BDE-209 to the forest canopy on days without rain (SI Figure S6).

Even though they relied on dynamic models, all previous simulations investigating the forest filter effect (35–38) have used the constant precipitation assumption of steady state models. Because wet deposition of a substance is the same to a forested and a nonforested surface, substances that are efficiently washed out ($\log K_{OA} > 11$) did fall outside of the forest filter window established by these simulations. In other words, precipitation scavenging was responsible for the upper K_{OA} threshold of the forest filter window (35). The simulations presented here are the first to combine intermittent rain and forests in a model and reveal that substances beyond these thresholds are still subject to the forest filter effect during dry periods. Based on these results, we suggest that the forest filter effect has the potential to reduce air concentrations of

chemicals that are falling outside the previously identified window of the chemical partitioning space (35).

Dry Deposition. Wania and Dugani (15) used four different models to calculate various indicators (including L_A) of the LRT potential of PBDEs, relative to PCBs. They concluded that the potential for atmospheric long-range transport of BDE-209 is controlled by the atmospheric mobility of the particles to which it is attached, and that the lower-brominated congeners have a LRT comparable to PCBs known to be subject to significant LRT. For this reason, they also suggested that BDE-209 is very likely not subject to significant atmospheric LRT. If we compare our results for PBDEs and PCB-180, we see that both their L_A s are controlled by deposition rather than atmospheric reaction (SI Figure S5), and that the annual average L_A for BDE-209 exceeds that of PCB-180 by almost an order of magnitude. This may appear counterintuitive as BDE-209 in the atmosphere is predicted to sorb entirely (>99.9%) to atmospheric particles ($\log K_{OA} = 15.27$) at the atmospheric temperature range used here, while the percentage sorbed to particles for PCB-180 ($\log K_{OA} = 10.16$) only ranges from 20% (0°C) to 2% (17.4°C) (SI Figure S4).

We offer two explanations for the high estimates of L_A for BDE-209 in this study. The first is our capability to take into account episodes of elevated L_A under dry conditions and elevated wind speed (as discussed). However, this does not explain why our estimates of L_A for BDE-209 are still elevated under the assumption of steady-state environmental conditions. A second explanation, although less significant, is the difference in the dry particle deposition velocities (DDV) in this study as compared to past evaluations (15). As shown above for the forest canopy, the results for BDE-209 are highly sensitive to changes to DDV, whereas PCB-180 is not (see also SI Table S7). The description of dry particulate deposition in this study (24) is based on experimentally determined deposition velocities of semi-volatile organic compounds to forest canopies, bare soils, and grasslands at a location in southern Germany (34, 39). Those dry particle deposition velocities to surface compartments (other than the canopy) are within a range from 0.2 to 1 m/h (24). Past evaluations of LRT used dry deposition velocities an order of magnitude higher (representative of coarse particles found mostly close to sources) and may have overestimated dry deposition velocities of particle bound substances.

Regulatory Relevance. This study illustrates the necessity of comparing model predictions with empirical data in order to better understand and predict the atmospheric mobility of organic chemicals with poorly characterized LRT behavior. Existing approaches to LRT assessment generally assume steady-state (9). The current study suggests that there may be circumstances when these approaches fail to identify potential candidates for further scrutiny. Specifically, the current steady-state models are at risk of underestimating the potential for LRT, not only for water-soluble chemicals that tend to be deposition-controlled (i.e., $L_{AR} < L_{AD}$) as previously recognized (8, 13), but also for chemicals that are strongly sorbed to particles in the atmosphere.

An interesting observation is that the inter-annual variations in predicted L_A is of a larger magnitude as the predicted variation in annual average L_A among the investigated chemicals. Clearly, evaluations of L_A using steady-state models with static environmental conditions may provide relative rankings that may or may not be relevant. A higher tiered approach involving non-steady-state models may thus be desirable in order to capture substances with an episodic transport potential to remote areas (e.g., refs 33, 40). The current study also highlights the need for more research on the LRT behavior of organic chemicals that are strongly sorbed to atmospheric particles. Processes that need to be understood more quantitatively are particulate dry deposition,

precipitation scavenging (including snow scavenging), as well as the direct and indirect photolysis of chemicals sorbed to atmospheric particles.

Acknowledgments

K.B. thanks the Norwegian Research Council and the European Monitoring and Evaluation Program for financial support. PBDEs in Char Lake and AX-AJ Lake cores were analyzed by Axys Analytical Labs, Sidney BC. We thank the following people for sample collection: Camilla Teixeira (Lake Ontario, Lake Opeongo), Mike Mawhinney and Mike Benner (NWRI Research Support, Dasserat Lake, Connery Lake), Reinhard Pienitz and students (Université Laval, Lake B2), John Smol (Queen's University) and Marianne Douglas (University of Toronto) (Char Lake, Lake AX-AJ), Warwick Vincent, C. Belzile and P. van Hove (Université Laval, Romulus Lake), and the reviewers for helpful comments.

Supporting Information Available

Further details on this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review March 28, 2006. Revised manuscript received May 25, 2006. Accepted May 26, 2006.

ES060730S