Environmental Pollution 177 (2013) 116–124

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Atmospheric concentrations and potential sources of PCBs, PBDEs, and pesticides to Acadia National Park

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ARTICLE INFO

Article history:
Received 4 October 2012
Received in revised form
28 January 2013
Accepted 8 February 2013

Keywords:
POPs
Back-trajectory
PSCF
Long-range transport
Acadia National Park

ABSTRACT

This study assessed concentrations and investigated potential source regions for PCBs, PBDEs, and organochlorine pesticides in Acadia National Park, Maine, USA. Back-trajectories and potential source contribution function (PSCF) values were used to map potential source areas for total-PCBs, BDE-47, and 10 organochlorine pesticides. The constructed PSCF maps showed that ANP receives high pollutant concentrations in air masses that travel along four main pathways: (1) from the SW along the eastern Atlantic seaboard, (2) from the WSW over St. Louis, and Columbus regions, (3) from the west over Chicago, and Toronto regions, and (4) from WNW to NNW over the Great Lakes, and Quebec regions. Transport of all studied pollutants were equally distributed between the first three pathways, with only minor contributions from the last pathway. This study concludes that the high-pollutant concentrations arriving at ANP do not exclusively originate from the major urban centers along the eastern Atlantic seaboard.

1. Introduction

Persistent organic pollutants include a wide range of chemical groups such as polychlorinated biphenyls (PCBs), polybrominated ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs). These chemicals are resistant to degradation, have a tendency to bioaccumulate in fatty tissues, and many are considered to be endocrine disruptors (Jones and de Voogt, 1999). The production and usage of many of these chemicals (PCBs and OCPs) were banned almost two decades ago, while two of the PBDE technical formulations (penta- and octa-BDE) were banned in the European Union and in ten states of the USA in 2004 (Frederiksen et al., 2009).

Pesticide source regions are generally widespread because of historical and current use. For example dieldrin, DDT, and total chlordane (consisting of *cis*- and *trans*-chlordane, and *trans*-nonachlor) were found to be transported to the Great Lakes region from the south, whereas hexachlorocyclohexanes were transported from much of the US and Canada, and endosulfans originated from mainly in the northern U.S. states (Hafner and Hites, 2003). Previous studies have shown that urban areas have higher concentrations of PCBs compared to nonurban areas (Hafner and Hites, 2003; Hsu et al., 2003) as urban areas are thought to be ubiquitous PCB sources due to past use. Urban areas may also have specific sources that may include sludge drying beds, landfills, and transformer storage yards (Hsu et al., 2003). Urban–rural concentration gradients correlate with local population densities (Schuster et al., 2010b). Jamshidi et al. (2007) presented evidence that ventilation of indoor air is most probably responsible for the urban pulse, not volatilization from soil on a rural–urban transect. On a global scale, estimated spatial patterns (Breivik et al., 2007) were found to be in accordance with surface soil concentrations measured by Meijer et al. (2002). In addition to soils, PCBs may be emitted from hot spot areas (Kaya et al., 2012; Odabasi et al., 2009; Ruzickova et al., 2007) or volatilized from contaminated waters and shelf seas (Ilyina et al., 2008). Mobilization of strongly retained POPs from soils and riverine sediments may be possible due to flooding (Dvorska et al., 2009).

A review of global PCB data (Li et al., 2009) showed that primary sources dominate where previously deposited PCBs are not available for re-volatilization because they are strongly retained in soil for compounds with soil–air fugacity fractions well below 0.5. Secondary sources become important for compounds with soil–air fugacity fractions above 0.5, because they are available for air–soil exchange, and therefore “grasshopping”. The dominance of primary sources, which is shown to be the case in Europe (Schuster et al.,

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http://dx.doi.org/10.1016/j.envpol.2013.02.015

2010a,b), results in the primary fractionation (absolute amounts of individual congeners decrease with increasing distance from the source area while the fraction of more volatile ones increases). A dominance of secondary sources would result in the secondary fractionation which is controlled by surface–air partition coefficients that depend on temperature and soil organic matter content. Although this is a long-term scenario because it is a slower process, both of the processes are thought to be at work today (Li et al., 2009). Wohrnschimmel et al. (2012) estimated that secondary sources of PCB-28 would start to take over after 2030 in North America, whereas >50% of ambient air concentrations would be accounted by primary sources until 2020s.

Trajectory statistical methods have been used to determine source areas to receptor sites. There are two main groups of trajectory statistical methods (Scheifinger and Kaiser, 2007): Potential Source Contribution Function (PSCF) (Ashbaugh et al., 1985; Zeng and Hopke, 1989) and concentration field (CF) (Seibert et al., 1994) methods. Stohl (1996) improved the CF method by reweighting of concentrations along a trajectory, termed Concentration Weighted Trajectory (CWT), to extract more information from the data. These methods were compared using idealized conditions with virtual and real sources, and real world situations (Scheifinger and Kaiser, 2007). The CF and CWT methods performed better under idealized conditions (the best common spatial variance of 78% with the CWT method), whereas the PSCF method resulted in the highest common spatial variance of 33%. The European Monitoring and Evaluation Program SO_2 inventory was used in these experiments. Kabashnikov et al. (2011) compared the three trajectory statistical methods using a species-independent, accuracy estimation statistic: Spearman's rank order correlation between virtual and reconstructed source distributions. The correlation levels were similar for all three methods, especially for substances with long decay times (240 h vs. 12 h).

In light of the studies by Scheifinger and Kaiser (2007) and Kabashnikov et al. (2011), the PSCF was the method of choice in this study. The PSCF is a probabilistic model that identifies possible source areas for a pollutant using air mass trajectories and concentrations measured at a receptor site (Ashbaugh et al., 1985; Zeng and Hopke, 1989). It has been used to determine source areas of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs) around the globe (Dvorska et al., 2008; Peng et al., 2007; Xu et al., 2011) and in North America (Choi et al., 2010; Du and Rodenburg, 2007; Hafner and Hites, 2003). Compound specific atmospheric pressures are often correlated with ambient temperature by the use of the Clausius–Clapeyron (C–C) equation that relates an increase in natural logarithm vapor pressure to increasing temperature. The use of this approach as a criterion to define "high" concentrations for use in PSCF modeling has been found to facilitate an assessment of source regions (Choi et al., 2010; Hoh and Hites, 2004).

Acadia National Park (ANP) is located on Mt. Desert Island in the State of Maine on the northeastern coast of the United States. It is far from major pollution sources and urban and agricultural areas. However prevailing winds make it downwind of much of the continental US so it can be used to determine the extent of POPs' transport in North America. Previous studies conducted in ANP have focused on ozone (Bartholomay et al., 1997; Ray et al., 1996) and mercury (Bank et al., 2007; Johnson et al., 2007). The majority of POPs related studies conducted in the region (Maine, USA, Nova Scotia and New Brunswick, Canada) have investigated levels in the marine environment and biota from as early as 1980s (Larsen et al., 1984, 1983) all the way to the present (Apeti et al., 2010; Park et al., 2009; Wade et al., 2008). However, atmospheric studies are scarce. Bidleman et al. (1992) pointed to the importance of atmospheric transport to Sable Island, Nova Scotia in 1992. More recently, Brun et al. (2008) reported a decreasing trend for wet deposition of α-HCH from 1980 to 2000 whereas relatively stable levels were observed for γ-HCH, (α + β)-endosulfan, atrazine, and pentachlorophenol at sites in Atlantic Canada. Since there have been no atmospheric POPs research in ANP, and no source assessment studies in the region, this study assessed concentrations in ANP, investigated potential source regions for PCBs, PBDEs, and organochlorine pesticides using back-trajectories, and calculated PSCF values to map potential source areas for total-PCBs, BDE-47, and 10 OCPs (*cis*-chlordane, *trans*-chlordane, oxychlordane, *p*,*p*′-DDE, *p*,*p*′-DDT, dieldrin, endosulfan-I, endosulfan-II, endrin, and *trans*-nonachlor).

The purpose of this study was to provide baseline seasonal ambient air concentrations for a suite of POPs, and to identify their potential source regions to Acadia National Park. The measurement and determination of the scope of long-range POPs transport to the ANP environment is of interest to park resource managers and government officials in order to assess the impact of these contaminants on threatened and endangered natural and wildlife resources.

2. Experimental section

2.1. Sampling

Air samples were collected at the McFarland Hill class I air station at Acadia National Park near Bar Harbor, ME (44.37°N, 68.26°W). A total of 110 vapor-phase air samples were collected on polyurethane foam (PUF) cartridges and glass fiber filters (GFF) using a modified hi-volume sampler (Tisch Environmental, Inc., Cleves, OH) between June 26, 2007 and August 17, 2010. Each air sample was collected for a 24-h period, with an average volume of approximately 1200 m^3. A complete description of air sampler operation, procedures, and calibrations is included in the Great Lakes Commission approved Quality Assurance Project Plans (Pagano, 2005). Because the majority of GFF sample analytes were not detected or were too close to the method detection limits to be reliably used in this study, only gas phase samples were considered.

2.2. Sample extraction and cleanup

PUF cartridges were cleaned and extracted according to analytical methods described in detail in the Great Lakes Commission Approved Quality Assurance Project Plan (Pagano, 2005) and is briefly described below. Surrogate standards (IUPAC PCB-014, PCB-065, PCB-166, and PCT-05) were added to all samples prior to PUF extraction. PUFs were extracted in a Soxhlet apparatus for 24 h using hexane. Samples were subjected to silica gel column cleanup (5.5 g of 4% deactivated silica – Sigma–Aldrich, grade 923, 100–200 mesh) in order to separate PCBs (fraction 1) and OCPs/PBDEs (fraction 2) from other interferences. The sample extract was sequentially eluted with 25 mL of hexane in fraction 1 (F1) and 25 mL hexane: dichloromethane in fraction 2 (1:1, v/v, F2). Each fraction was concentrated in a TurboVap II to 2 mL for gas chromatographic analysis. Surrogate standard PCT-05 which elutes exclusively in Fraction 2 was used to check the effectiveness of the F1 and F2 silica separation, and recoveries of OCPs/PBDEs.

2.3. Chemical analysis

Congener-specific PCB, PBDE, and OCP analyzes were conducted based on dual-column capillary procedures previously described (Chiarenzelli et al., 2001; Pagano et al., 1999; Stewart et al., 2008). Analytical instruments were recalibrated every five samples, and included at least one mid-level calibration check. An Agilent Model 7890A GC with an electron capture detector (ECD–Ni^{63}) and autosampler were used. The capillary column used was a J&W 60 m DB-XLB with 0.25 mm id and 0.25 μm film thickness. The calibration standard used was a 1:1:1:1:1 mixture of congener sets C-CSQ-SET 1–5; 10 pg/μL per individual congener (AccuStandard, Inc., New Haven, CT) (Frame et al., 1996). PCB analyzes were confirmed with Agilent Model 7890A GC with ECD–Ni^{63} and autosampler. The capillary column utilized was Agilent Ultra II, 25 m with 0.22 mm id and 0.33 μm film thickness. The calibration standard used was a 1:1:1:1 mixture of Aroclors 1221, 1016, 1254, and 1260 each at 200 pg/μL, hexachlorobenzene (HCB) at 5 pg/μL, and *p*,*p*′-DDE and Mirex each at 10 pg/μL (Custom Mixed Fraction #3, AccuStandard, Inc.). Internal standard (IUPAC PCB-030) was added prior to analysis by GC-ECD. Total-PCBs were calculated by the summation of all 92 congeners and coeluters listed in Supporting Information-1 (SI-1). The correlation between the total-PCBs calculated from the analysis of the dual-columns was strong ($r = 0.975$, $p < 0.001$), with a mean relative percent difference (RPD) of 8.7% on a mass/volume basis. Additionally, a congener-specific PCB mass calculation of average number of chlorines per biphenyl (AVG-ClBP) for the two different column stationary phases (4.41 vs. 4.49 AVG-ClBP, RPD 1.7%) provides further validation of the two column confirmation system used for this work.

Congener-specific PBDE and organochlorine analyzes were conducted with Agilent Model 7890A GC with ECD–Ni^{63} and autosampler using a 60 m DB-XLB capillary column with 0.25 mm id and 0.25 μm film thickness. The PBDE calibration standard used was a 1:1:1:1:1 mixture of BDE-047, BDE-099, BDE-100, BDE-153, and BDE-154 at 50 pg/μL per individual congener (AccuStandard, Inc., New Haven, CT). Select organochlorine pesticides were measured based on Method 8081A (Organochlorine Pesticides by Gas Chromatography) described in USEPA protocols (USEPA, 1997). Single instrument/column detection was used for quantitation (DB-XLB). The calibration standard used was a 100 pg/uL composite mixture (Single-Column Analyte Mix, M-8081-SC, AccuStandard, Inc.) of USEPA 8081A standard analytes. PCB, OCP, and PBDE identification in air samples were confirmed by mass spectrometry, using Agilent Model 7890A GC with Agilent 5975C Inert XL EI/CI MSD with multi-mode inlet. PCB, PBDE, and OCP analytical data was processed utilizing Agilent ChemStation, SPSS Statistics 17.0, and Microsoft Excel software.

2.4. Quality assurance

Laboratory Quality Assurance/Quality Control at the SUNY Oswego ERC is based on a program developed from USEPA protocols (USEPA, 1997). The program consists of replicate analyzes, surrogate/internal standard analyte recoveries (IUPAC PCB-014, PCB-30 IS, PCB-065, PCB-166, and PCT-05), matrix spikes/matrix spike duplicates, method, reagent and system blanks at prescribed intervals. A summary of all QC requirements and sample acceptance criteria for PCB analyzes can be found in the Great Lakes Commission approved Quality Assurance Project Plan (Pagano, 2005). Project surrogate recoveries for all air samples and method/field blanks can be found in SI-2. Method blanks ($N = 23$) were measured for every batch of samples shipped to the ERC throughout the three year sampling period and averaged 30.9 pg m^{-3} with a standard deviation of 12.9 pg m^{-3} for total-PCBs. Field blanks ($N = 6$) were randomly selected from PUFs ready for sampling, opened in the field, installed on the air sampler, immediately removed, and stored with project samples until shipped. No significant difference was noted between the means of the field blanks (31.9 pg m^{-3}) and method blanks (30.9 pg m^{-3}).

2.5. Statistical analysis

Statistical analyzes were performed using SPSS (Release-12). The Kruskal–Wallis test was used to compare more than two groups of data. The null hypothesis was that all the groups had identical distribution functions against the alternative hypothesis, that at least two of the samples differed with respect to location (median), if at all. The Mann–Whitney Test was used to test for difference between the medians of two groups. A significance level of 0.05 was considered as significantly different between the compared groups. Factor analysis was applied to infer pollution source contributions using varimax rotated principal component analysis. Eigen values >1 and loadings >0.45 were regarded as significant for interpretation of factors.

2.6. Back trajectory modeling

The trajectories of the air masses transported to the sampling site (i.e., the receptor site) were estimated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model Version 4.8 (Draxler and Hess, 2005). Back trajectories of 120 h were calculated with Eta Data Assimilation System (EDAS) (40 km grid) from Gridded Meteorological Data Archives by the National Oceanic and Atmospheric Administration–Air Resources Laboratory (NOAA–ARL). The arrival height of the back trajectories was selected as 500 m based on previous PSCF modeling results (Choi et al., 2008; Han, 2003). A back trajectory was calculated for every six hours for each 24-h sample.

2.7. Potential source contribution function (PSCF)

The following description of the method is mainly from Choi et al. (2008). PSCF is the probability that an air mass with a pollutant concentration above a criterion value arrived at the sampling site after having passed through a specific geographical area (or cell). Since this approach does not consider chemical transformations, all modeled contaminants are assumed to be conservative species. The conditional probability function, PSCF, can identify the source areas that have a potential to contribute to the high concentrations of contaminants observed at the sampling site because cells containing pollutant sources would have high conditional probabilities (Ashbaugh et al., 1985; Zeng and Hopke, 1989). The time segment end point is defined for each back trajectory by the time interval of the back trajectory calculation. Each trajectory segment end point estimated via back trajectory analysis that terminates within that grid cell is counted by the PSCF model algorithm. The possible source region (the geographic area covered by the trajectories) is subdivided into a gridded i by j array. If N is the total number of trajectory segment end points over the study period, T, and if n segment trajectory end points fall into the ij-th cell, the probability of this event, A_{ij}, is given by $P[A_{ij}] = n_{ij}/N$. If there are m_{ij} end points that correspond to the trajectories that arrived at a sampling site with pollutant concentrations higher than some criterion, the C–C regression line in this study, then the probability of this high concentration event, B_{ij}, is given by, $P[B_{ij}] = m_{ij}/N$. The probability of high concentration events ($P[A_{ij}]$) divided by the probability of total events in a fixed grid cell ($P[B_{ij}]$) defines the PSCF value. $\mathrm{PSCF}_{ij} = P[B_{ij}]/P[A_{ij}] = m_{ij}/n_{ij}$. A detailed description of this approach can be found in SI-3. Due to plume dispersion, and inherent trajectory inaccuracies, PSCF results generally show possible source areas rather than indicating individual sources. In addition, a trailing effect occurs because a constant weight along the path of the trajectories is assumed. As a result, areas upwind and downwind of actual sources may be identified as possible source areas.

In this study back-trajectory analysis showed that some of the air masses traveled over the ocean before reaching ANP, which resulted in nearshore marine potential source areas in the PSCF maps. Identifying the ocean as a potential source area may be an artifact of the aforementioned disadvantages. However the ocean may be a real source as contaminated sediments/waters are generally sinks for POPs, although in special circumstances they may act as a source (Dvorska et al., 2009; Ilyina et al., 2008).

3. Results and discussion

3.1. POP concentrations

Overall total-PCBs concentrations ranged from 30 to 510 pg m^{-3} with a median and a mean of 153 and 169 pg m^{-3}, respectively. Box plots that show the 5th to 95th percentile variation are shown in Fig. 1 for compounds with at least a 50% detection rate. BDE-47 concentrations, which constituted about 95% of the total BDEs,

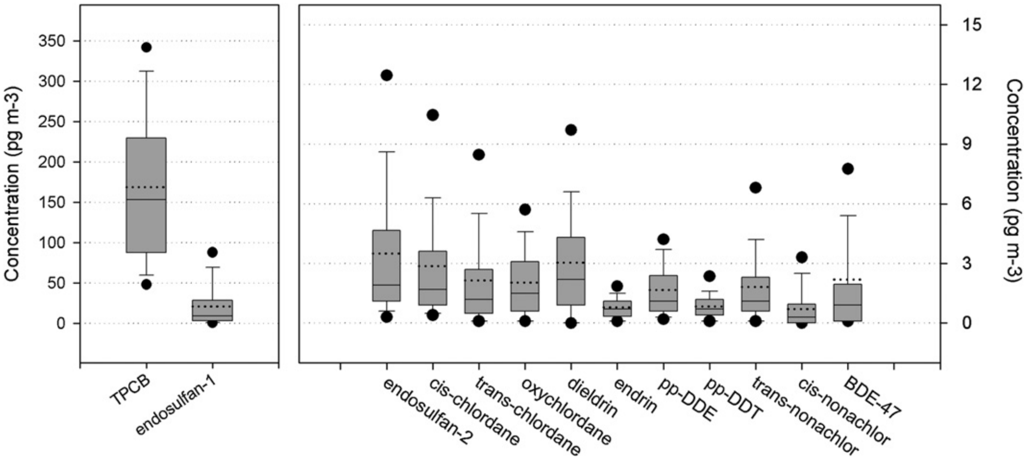

Fig. 1. Box plots of POP concentrations (endpoints show 5th and 95th percentiles, solid and dashed lines show median and mean, respectively).

were two orders of magnitude lower than total-PCBs with a median and a mean of 0.9 and 2.2 pg m^{-3}, respectively. BDE-47 levels were similar to the OCPs except for endosulfan-I which had a median and a mean value of 9.1 and 21 pg m^{-3}, respectively. Levels of the remaining OCPs ranged from 0.3 pg m^{-3} to 2.2 pg m^{-3} (median concentrations for *cis*-nonachlor and dieldrin, respectively).

In general, higher concentrations were measured in summer followed by spring, fall, and winter (Fig. 2). The Kruskal–Wallis test showed that there was at least one season in which concentrations were significantly different from the other seasons. Further testing using the Mann–Whitney test showed that summer concentrations were significantly higher than those of winter and fall for all measured POPs, whereas summer concentrations were higher than those of spring for all measured POPs except for BDE-47, *cis*-nonachlor, endrin, and *p,p*′-DDT. The concentrations in spring were significantly higher than those of winter and fall except for just one instance (fall BDE-47). Fall and winter concentrations were similar for BDE-47, endosulfan-II, endrin, and *p,p*′-DDT, however, *cis*-chlordane, *trans*-chlordane, dieldrin, endosulfan-I, *cis*-nonachlor, *trans*-nonachlor, oxychlordane, *p,p*′-DDE, and total-PCBs concentrations were significantly lower in fall and winter.

Summertime application of the technical formulation of endosulfan-I to Maine's major agricultural products such as blueberries, apples, and potatoes is likely to have caused elevated endosulfan-I summer concentrations. Endosulfan-II is a breakdown product of endosulfan-I and had a concomitant increase in summertime concentrations.

It is well established that re-volatilization is a major source for POPs that are no longer in use and that their concentrations are elevated in summer due to the relationship between temperature and vapor pressure. Modeling with the C–C equation, which relates contaminant partial pressure to temperature was used with the POPs that were detected in at least 75% of the samples. According to the results of regression modeling, concentrations were well correlated with temperature (see Table 1). The regression output for BDE-47 was not as strong as the others with a lower *R*-square and a higher *p*-value. This may be because BDE-47 production was only recently curtailed.

OCP concentrations measured in this study were found to be generally lower than those measured in long-term monitoring programs of the Integrated Atmospheric Deposition Network, the New Jersey Atmospheric Deposition Network, and the Lake Ontario Atmospheric Deposition Study (see Table 2)(Pagano, 2005; Sun et al., 2007; Totten et al., 2006). Acadia National Park's distance from large-scale current or historical use of agricultural pesticides in comparison to other site locations may explain the relatively low contaminant levels reported in this study. Total-PCBs and BDE-47 concentrations are at similar levels to rural/remote sites, while they are relatively lower than those measured in urban/industrial areas where they had or have been manufactured and utilized in large quantities as chemical flame retardants (Venier and Hites, 2008).

Concentrations of the 12 POPs listed in Table 1 were analyzed using the Pearson correlation matrix and factor analysis to assess PSCF modeling results, as correlations and commonalities of the contaminants may help infer common source regions. (The Pearson correlation matrix is presented in SI-4.) The correlation between almost all of the POPs were significant at $\alpha = 0.01$ level, except for

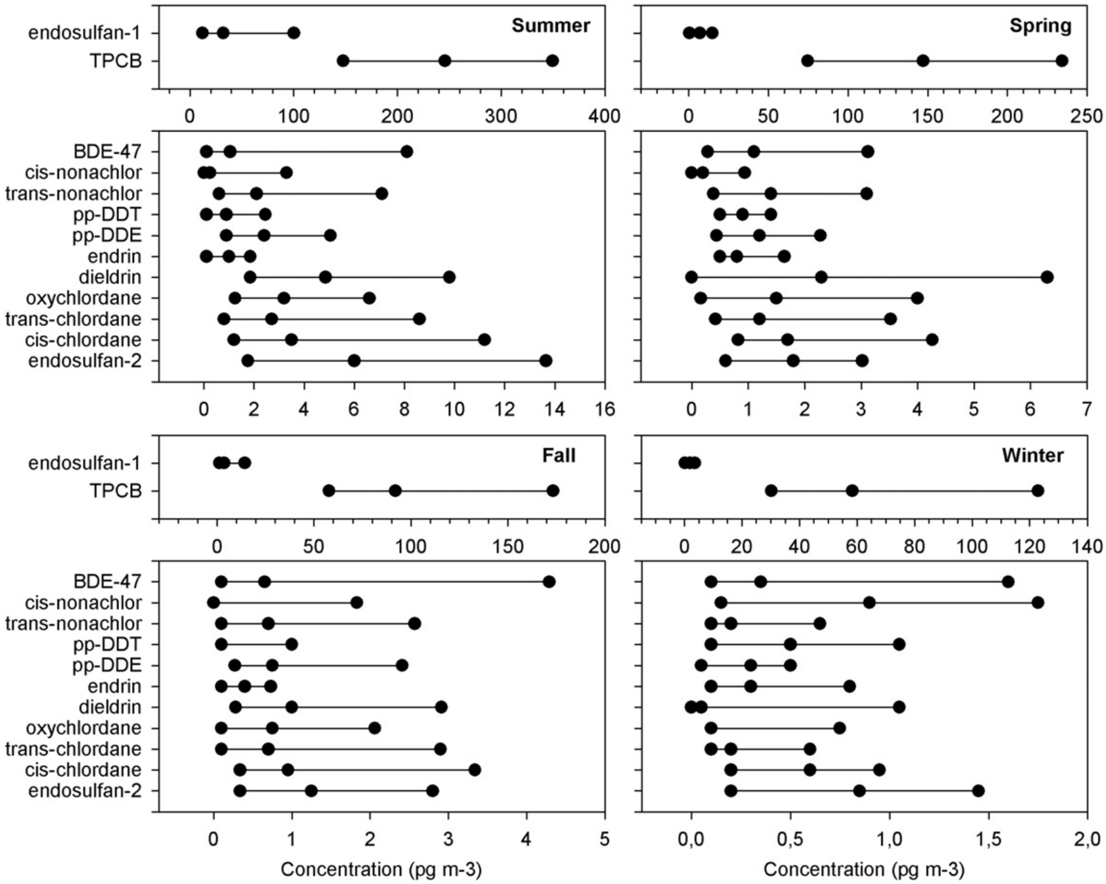

Fig. 2. Seasonal variation in the measured POP concentrations (from left to right points denote 10th, 50th, and 90th percentiles; sample sizes were 44, 25, 26, and 14 for summer, spring, fall, and winter, respectively.).

Table 1
Performance of simple linear regression of Clausius–Clapeyron equation.

	$\ln P = (a/T) + b$	R^2	p-value
Total-PCBs	$a = -4020$	0.52	<0.001
	$b = -11.1$		
Endosulfan-I	$a = -8869$	0.50	<0.001
	$b = 2.93$		
Endosulfan-II	$a = -5144$	0.39	<0.001
	$b = -11.5$		
cis-Chlordane	$a = -5480$	0.41	<0.001
	$b = -10.6$		
trans-Chlordane	$a = -5942$	0.32	<0.001
	$b = -9.34$		
Oxychlordane	$a = -5986$	0.35	<0.001
	$b = -9.09$		
Dieldrin	$a = -7008$	0.50	<0.001
	$b = -5.01$		
Endrin	$a = -2987$	0.30	<0.001
	$b = -20.1$		
p,p′-DDE	$a = -6444$	0.55	<0.001
	$b = -7.47$		
p,p′-DDT	$a = -2614$	0.26	<0.001
	$b = -21.3$		
trans-Nonachlor	$a = -5110$	0.30	<0.001
	$b = -12.4$		
BDE-47	$a = -3304$	0.11	0.003
	$b = -18.7$		

P: partial vapor pressure (atm), T: temperature (K).

BDE-47 and oxychlordane, *p,p′*-DDE, total-PCBs, and endosulfan-II. R^2 values for the significant correlations ranged from 0.23 to 0.97. The lowest ones (<0.30) were between BDE-47 and others. The majority ($n = 42$, 64%) of R^2 values were >0.50. The strongest ($R^2 > 0.85$) relationships were among chlordanes. Correlations of a suit of individual PCB congeners to the OCPs and BDE-47 were also investigated. The correlations were similar to that of total-PCBs and the remaining POPs (see SI-4). The generally poor correlation with BDE-47 and most compounds is probably due to analytical uncertainties resulting from low atmospheric concentrations of BDE-47, in addition to the fact that it may be originating from active sources compared to most other compounds having passive sources. This finding of potentially active sources is supported by the poor C–C modeling fit for BDE-47.

Factor analysis (FA) resulted in three factors explaining 83% of the variation (see SI-4). OCPs, except for endrin, formed Factor-1 which explained 65% of the variation. Endrin and total-PCBs formed Factor-2, whereas only BDE-47 was in Factor-3. Factors-2 and -3 explained nine and eight percent of the variation, respectively. The variation in the strength of the correlations and the grouping in the factor analysis is probably due to similarity and differences in source regions and variable dependence of atmospheric partial pressures on temperature. The source regions are discussed in the next section.

3.2. PSCF modeling

PSCF results are presented in Figs. 3–5. The maps include American cities with >350,000 population and major Canadian cities. Fig. 3 shows PSCF maps for OCPs that were grouped as Factor-1. Figs. 4 and 5 present total-PCBs (Factor-2) and BDE-47 (Factor-3), respectively. The constructed PSCF maps showed that ANP receives high pollutant concentrations in air masses that travel along four main pathways: (1) from the SW over Washington, DC, Baltimore, New York City, and Boston regions, (2) from the WSW over St. Louis, Indianapolis, Cincinnati, and Columbus regions, (3) from the west over Chicago, Detroit, Cleveland, and Toronto regions, and (4) from WNW to NNW over the northern Great Lakes, Ottawa, Montreal, and Quebec regions. All factors were mainly associated with pathways 1, 2, and 3.

Factor-1 consists of OCPs that are of both current (endosulfans) and legacy contaminants (the remaining seven). Overall, Factor-1 is mainly associated with all four pathways. The difference between Factor-1 and the other factors that also included pathway 1, is that it ran deeper into the south covering some of the southern agricultural lands. In terms of pathway 4, while the WNW component was apparent for all OCPs, only oxychlordane, *p,p′*-DDE, and *p,p′*-DDT showed a more northerly component.

As an overall assessment, modeled OCPs in this study have southern, midwestern, and eastern US source regions that were not limited to current or past agricultural areas but included areas where OCPs (*cis-* and *trans*-chlordane, *trans*-nonachlor, and dieldrin) were used as termites to treat wooden house foundations (Hafner and Hites, 2003; Shen et al., 2004). Relatively higher concentrations, ratios of *trans-* to *cis*-chlordane, and chiral analysis of ambient air samples obtained at Point Petre, Toronto, the southeastern US, and Belize (Shen et al., 2004), and of indoor samples (Leone et al., 2001)

Table 2
Comparison of the mean OCP concentrations (pg m^{-3}) across several program monitoring sites.

	Point Petre, ON	Sturgeon point, NY	Sandy Hook, NJ	Sterling, NY	ANP, ME
	IADN[a]	IADN[a]	NJADN[b]	LOADS[c]	This study
Sampling period	1992–2003	1991–2003	2000–2001	2005–2006	2007–2010
Dieldrin	13	26	9.7	9.8	3.0
Endosulfan-I	110	110	15	258	21
Endosulfan-II	24	9.5	2	51	3.5
Endrin	1.3	4.6	NR[d]	2.3	0.8
p,p′-DDT	2.8	9	NR	3.5	0.8
p,p′-DDE	11	17	NR	19	1.7
p,p′-DDD	0.4	3.5	NR	0.4	ND[e]
$\sum$DDT	14	30	53	23	2.5
cis-chlordane	3.9	11	NR	4.2	2.9
trans-chlordane	3.6	10	NR	4.2	2.1
trans-Nonachlor	4	7.7	NR	4.1	1.8
$\sum$chlordanes[f]	12	29	83	13	6.8

[a] Sun et al. (2006).
[b] Gioia et al. (2005).
[c] Pagano (2005).
[d] Not reported.
[e] Not detected.
[f] Sum of chlordanes (*cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor).

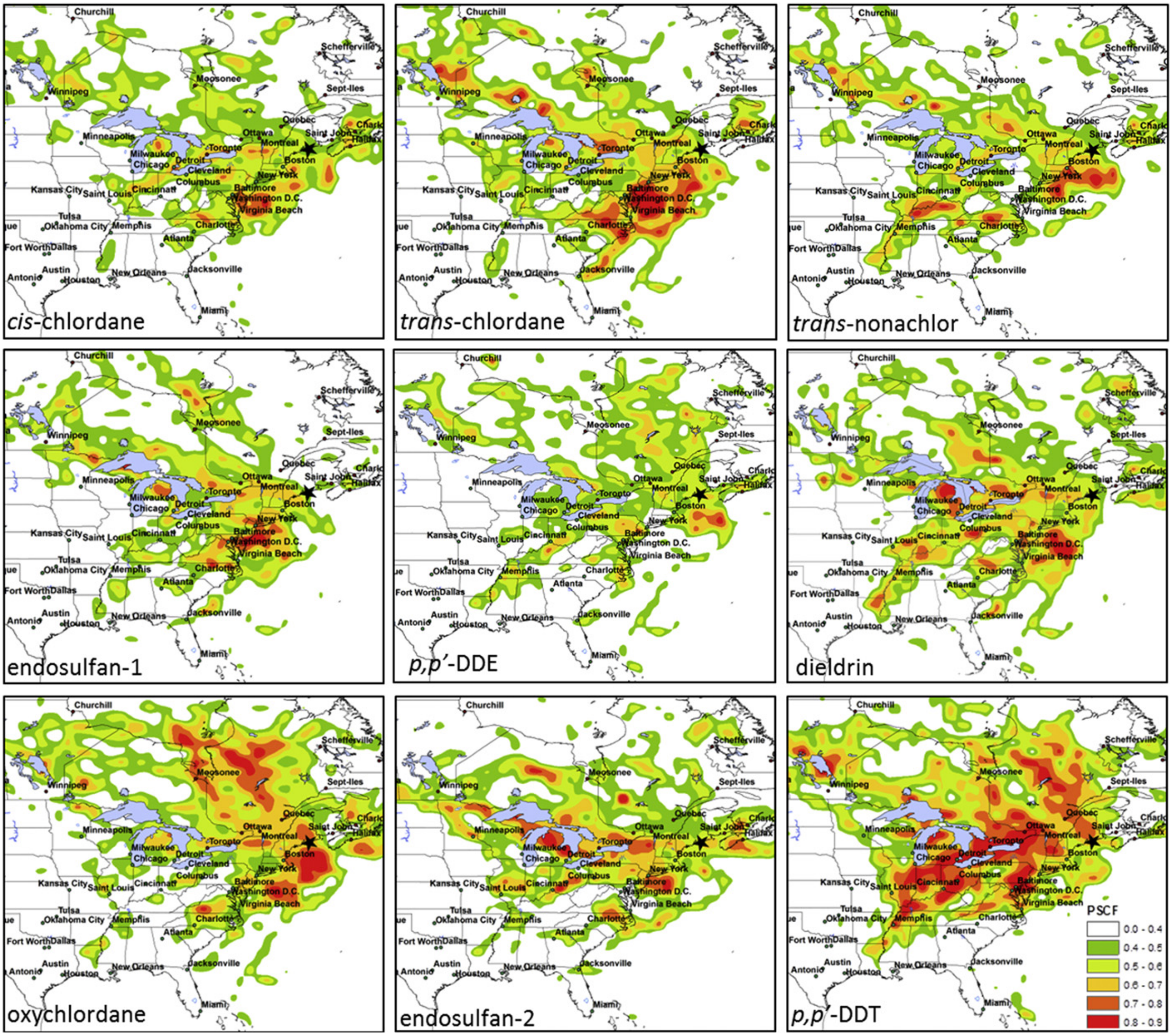

Fig. 3. Potential source contribution function results for organochlorine pesticides.

indicated that the midwestern US probably also has termite-treated house foundations as active sources (Shen et al., 2004).

In general, chlordane potential source regions extend across the eastern, midwestern, and southeastern US (Hafner and Hites, 2003; Shen et al., 2004). In addition, PSCF modeling for Great Lakes pointed to Iowa and the Wisconsin region as potential source areas (Shen et al., 2004), although their data suggested that the main source regions for dieldrin are in the southern US as its concentrations in Alabama were about 1.5–3 times higher than those in Great Lakes. It has been shown that DDT may still have been in use for malaria vector control in Central America and there may be an "aged" source of past use in Canada (Shen et al., 2004). The p,p'-DDE > p,p'-DDT > p,p'-DDD concentration profile is similar to what is seen at the IADN sites (see Table 1). Correlations of $\ln P$ vs. $1/T$ are similar to those reported by Gioia et al. (2005) for Camden and New Brunswick, New Jersey. DDE correlates better compared to DDT, indicating that their source regions may be different because their emissions may be controlled by different mechanisms.

Hafner and Hites (2003) suggest that the Great Lakes are affected by short-range transport of endosulfan from source regions in Michigan and New York where it is used widely, and to a lesser extend in Pennsylvania. Hoh and Hites (2004) appended the region of Kentucky to Florida to the above northern potential source regions. Shen et al. (2004) measured annual average concentrations using passive samplers and found that endosulfan concentrations were relatively high at Canadian sites in British Columbia, Manitoba, and New Brunswick, and associated with fruit groves and agriculture. The last site is about 650 km northwest of ANP. The annual average endosulfan-I concentration measured in New Brunswick (about 115 pg m^{-3}) is close to the maximum 24-h average concentration measured at ANP (136 pg m^{-3}) while the median and mean 24-h average concentrations at ANP were 9 and 21 pg m^{-3}, respectively. This difference may indicate that short-range transport could be significant for this pesticide, therefore the use of conditional probability function instead of back-trajectory statistics would be preferred.

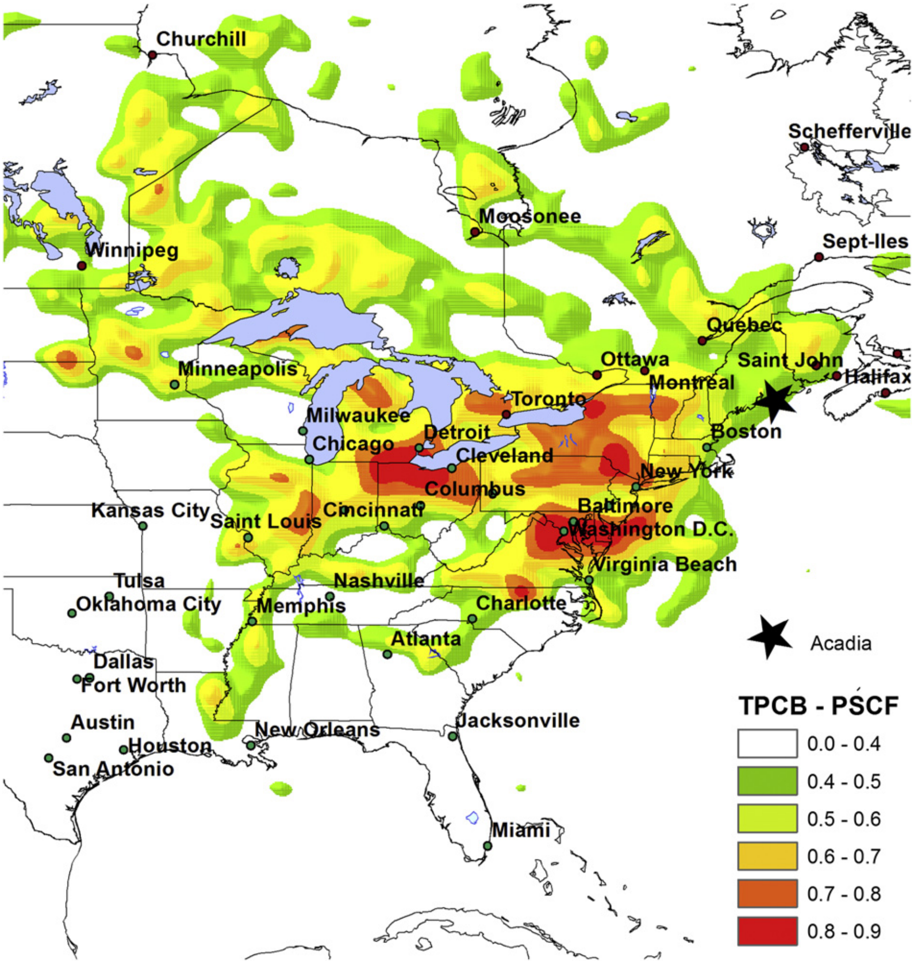

Fig. 4. Potential source contribution function results for total polychlorinated biphenyls.

Factor-2 consists of endrin and total-PCBs for which high PSCF values were primarily found on pathways 1, 2, and 3, again coinciding with the major urban areas of Chicago, Detroit, Toronto, Cleveland, St. Louis, Indianapolis, Cincinnati, and Columbus, Washington, DC, New York City, and Boston for total-PCBs. The difference from BDE-47 is that pathway 4 was not significant for total-PCBs. Endrin, however, showed a more northerly pathway. Previous studies have shown that urban areas have higher concentrations of PCBs compared to nonurban areas (Hafner and Hites, 2003; Hsu et al., 2003) as urban areas are thought to be ubiquitous PCB sources due to past use. Urban areas may also have unique sources that may include sludge drying beds, landfills, and transformer storage yards (Hsu et al., 2003). In addition, many buildings constructed during 1960s and 1970s used PCB-containing materials, such as caulking, grouts, paints, sealants, ceiling tiles (Heinzow et al., 2007) in addition to other urban sources like transformers, capacitors, heat transfer and hydraulic fluids, lubricating and cutting oils, and adhesives (Godish, 2001).

Since BDE-47 (Factor-3) has active sources that are mainly urban areas, all metropolitan areas in all of the pathways, namely Canadian cities of Montreal, Ottawa, and Quebec in addition to the above listed for total-PCBs, could be the major source areas that impact ANP. Production, use, and disposal of flame retardant – treated polyurethane foam which is used extensively in a wide range of everyday products such as vehicles, furniture, carpets, bedding, etc. has been implicated as the major source of BDE-47 and other four to six brominated congeners (Alcock et al., 2003; Hale et al., 2002).

The majority of the Top-10 events (the highest vapor pressure samples compared to C–C regression line) were summer samples (from 6 of 10 for total-PCBs and oxychlordane to 9 of 10 for *p*,*p*′-DDT, endosulfan-I and II). For the Top-10 total-PCBs events, 26%, 35%, and 37% were associated with pathways 1, 2, and 3, respectively. The average (and range) of the values for the OCPs were 30 (13–45)%, 33 (22–41)%, and 32 (15–52)% for pathways 1, 2, and 3, respectively. Pathway 4 was associated with $<10\%$ of the events for total-PCBs (2%) and OCPs (0–9%). For the Top-10 BDE-47 mass concentration events (nine of which were summer samples) 23%, 16%, and 45% were associated with pathways 1, 2, and 3, respectively. The contribution of pathway 4 (16%) was similar to pathway 2, and higher compared to total-PCBs and OCPs. Trajectory frequency plots that show seasonal differences are presented as supporting information (SI-5).

4. Summary and conclusion

PCB, PBDE, and OCP concentrations were measured in Acadia National Park (ANP) in Maine, USA and potential source areas for the region were investigated for the first time. POPs concentrations were lower than those typically measured in and around urban locations, with median values ranging from $0.3\ \mathrm{pg\ m^{-3}}$ for *cis*-nonachlor to $153\ \mathrm{pg\ m^{-3}}$ for total-PCBs. Highest concentrations were measured in summer followed by spring, fall, and winter. Correlations among measured compound concentrations and good correlation between temperature and concentrations point out that

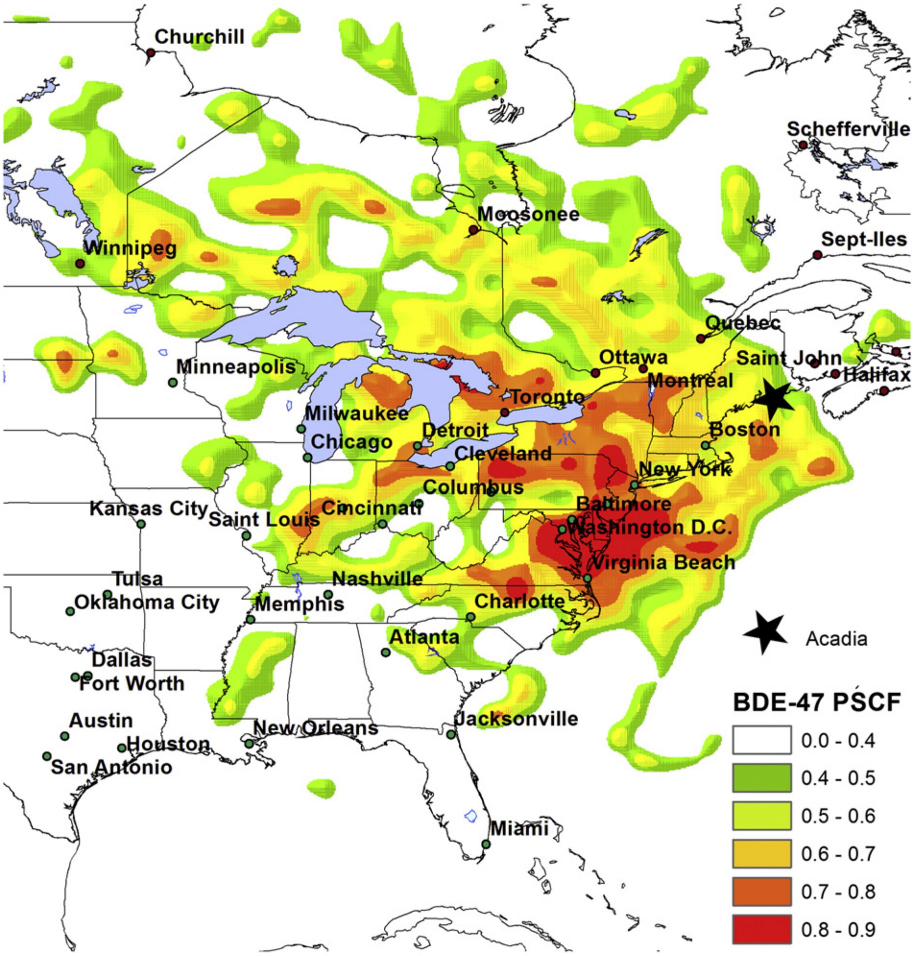

Fig. 5. Potential source contribution function results for brominated diphenylether-47.

re-volatilization was probably the dominant source except for BDE-47. PSCF maps showed that elevated concentrations in ANP occurred when arriving air mass had traveled through four pathways: (1) from the SW over Washington, DC, Baltimore, New York City, and Boston regions, (2) from the WSW over St. Louis, Indianapolis, Cincinnati, and Columbus regions, (3) from the west over Chicago, Detroit, Cleveland, and Toronto regions, and (4) from WNW to NNW over the northern Great Lakes, Ottawa, Montreal, and Quebec regions. The results suggest that OCP source regions were not limited to current or past agricultural areas but included areas where OCPs were used for the control of termites. The pathways for high concentration PCB and BDE-47 events coincided with major urban areas, including Chicago, Detroit, Toronto, Cleveland, St. Louis, Indianapolis, Cincinnati, Columbus, Washington, DC, New York City, and Boston, suggested urban areas were the major sources. This study concludes that the high-pollutant concentrations arriving at ANP do not exclusively originate from the major urban centers along the eastern Atlantic seaboard.

Conflict of interest

The authors declare that there are no conflicts of interest.

Acknowledgments

The authors acknowledge the Maine Department of Environmental Protection for use of meteorological data, and Bill Gawley and David Manski at Acadia National Park Resource Management for technical assistance and sample collection. In addition they would like to thank Prof. Philip Hopke for his assistance in PSCF modeling. This project was funded in part by a Faculty Collaborative Challenge Grant from SUNY Oswego, and from in-kind technical and analytical services provided by the Acadia National Park, Clarkson University, and SUNY Oswego.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.02.015.

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