Effects of Atmospheric Boundary Layer Height on Polybrominated Diphenyl Ether Concentrations in Air

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Introduction

In order to examine the effectiveness of reduction policies on polybrominated diphenyl ethers (PBDEs), the Japan Ministry of the Environment (JMOE) has performed semiannual surveys (in the warm and cold seasons during 2009−2012) on atmospheric PBDE congeners present in the gas plus particle phase concentrations.[1] With the large amount of PBDE data collected across Japan (298 samples), it is essential to apply statistical analysis to determine which factors influence atmospheric PBDE concentrations. It has been widely documented that atmospheric conditions such as temperature and precipitation have a significant effect on PBDE concentrations in air. In addition, the height of the atmospheric boundary layer (ABL) determines the air volume for the dispersion of all atmospheric constituents emitted at the surface of the earth. The Japanese global reanalysis (JRA-55) database, based on four-dimensional variational analysis (latitude, longitude, vertical level, and time), provides high-quality, long-term data (from 1958) relevant to the ABL height.[2] Combining the data from the JRA-55 and the JMOE provides an opportunity to study the relationship between the ABL and atmospheric PBDEs. In this study, the aim was to determine the correlations between the ABL and the behaviors of the atmospheric PBDEs. The research was conducted in two steps, namely, (*i*) estimating the height of the ABL from 50 sites relevant to PBDE sampling, and (*ii*) performing a correlation between the ABL and PBDE air concentrations, along with other predictors such as temperature, rainfall rate, population density, and year.

Materials and methods

Data collection: The atmospheric gas plus particle phases of PBDE congener concentrations and the concurrent site-specific meteorological data (ambient air temperature and rainfall rate) for 50 sites across Japan over four years (2009−2012), have been described in detail in Dien et al. (2016).[3] The sampling was conducted twice a year at each site, namely, in the warm season (approximately August, September, and October) and in the cold season (approximately November, December, and January). In this study, site-specific and time-dependent ABL data (latitude and longitude information and the sampling times) were estimated by using the JRA-55, with the horizontal resolution being approx. 55 km, and vertical levels at the surface and 60 levels up to 0.1 hPa. In the JRA-55 database, model grid data, including model-level analysis fields (*anl_mdl*), surface analysis fields (*anl_surf*), and constant fields (*TL319*), are relevant for estimating the height of the ABL. For *anl_mdl*, we collected data on the geopotential height, u-component of the wind, v-component of the wind, temperature, and the specific humidity. The collection was done every six hours at 9 AM, 3 PM, 9 PM, and 3 AM (Japan time zone, equal to UTC+9) at 60 vertical levels. For *anl_surf*, data on the surface pressure, surface potential temperature, temperature, and specific humidity at the 2 m level were also collected every six hours at (local time) 9 AM, 3 PM, 9 PM, and 3 AM. Furthermore, geopotential and land cover (1=land, 0=sea) information was collected from *TL319*. The data were extracted with the OpenGrADS (version 2.0.2.oga.2), developed by the Center for Ocean-Land-Atmosphere Studies (COLA) and the Institute of Global Environment and Society (IGES). The Python open source program (version 2.7) (Python Software Foundation, Delaware, USA) was used to extract the meteorological data, which are encoded in GRIdded Binary format (GRIB, Edition 1) (World Meteorological Organization [WMO], Commission for Basic System [CBS]).

***Estimating the ABL height*:** Based on the above-mentioned parameters, the height of the ABL was estimated from the maximum value obtained with the parcel method (PM) and the bulk Richardson number (Ri_b) method, as described in Dien et al. (2017).[4] Since atmospheric PBDEs were continuously monitored for three or seven days per sample, the relevant ABL values were estimated as the average for the daytime and nighttime values during a sampling period, and were subsequently used in the regression analysis.

Tobit regression analysis: We performed Tobit regression analysis[3] on atmospheric PBDE concentrations using multiple predictors, including ABL, temperature, rainfall rate, population density, time trend, and spatial variations, as follows:

$$\ln C_{i,y,s} = a + b_1/T_{outdoor\ i,y,s} + b_2 \ln(Ra+1)_{i,y,s} + b_3 \ln(ABL)_{i,y,s} + b_4 \ln(PD+1)_i + b_5 Y_y + \lambda_i + \varepsilon_{i,y,s}$$

where *C* is the concentration of PBDE congeners (pg m^{-3}); $T_{outdoor}$ is the outdoor temperature (K); *Ra* is the rainfall rate ($mm \cdot h^{-1}$); *PD* is the population density ($person \cdot km^{-2}$); *ABL* is the atmospheric boundary layer height (m); *Y* is the year (2009−2012); λ is a random effect of 50 sampling sites across Japan; ε is an error term that follows normal distribution with mean 0 and variance σ^2; *a* is an intercept; b_1, b_2, b_3, b_4, and b_5 are regression coefficients; *i* is the sampling location; *y* is the year; and *s* is the season. The Tobit model was run using the function of panel analysis on the censored model, with the left censoring limit using the Stata 13 software (StataCorp LP, Texas, USA).

Results and discussion

Behavior of the ABL: As the sampling time for the ABL data (corresponding to the PBDE sampling time) was only in early autumn and winter, at specific intervals (three or seven days per sample), the estimated ABLs would probably not show all of the relevant information on the day/night, seasonal, and interannual timescales. Consequently, at first, we analyzed the monthly ABLs over a period of four years for two representative sampling sites on land and sea to determine the trends. The urban air (Tokyo metropolitan) showed a distinct ABL pattern between day and night, being much higher during the daytime, as presented in Figure 1a. On the other hand, no distinct pattern was observed in the marine ABL (the sea around the Okinawa island), as presented in Figure 1b. The contrast between the land (urban) and the sea is attributable to the presence of a large daily exchange of heat and mass between the ABL and the free atmosphere over land, while over sea the mixing occurs primarily by turbulent entrainment. As shown in Figure 1, the seasonal changes in the nighttime ABL (nocturnal boundary layer) are weaker than are those of the daytime ABL (convective mixed layer), particularly for urban sites. We therefore paid attention to the convective daytime ABL for discussing the seasonal pattern. As a result, the ABL height shows differing seasonal trends for the land and marine sites. For the urban sites in Tokyo, the monthly mean of the ABLs during the warm season (spring and late summer) was higher than that during the cold season (winter) (Figure 1a). In contrast, the ABL for the marine sites (Okinawa) was estimated as higher during the cold season (winter) in comparison with the warm season (summer and autumn) (Figure 1b).

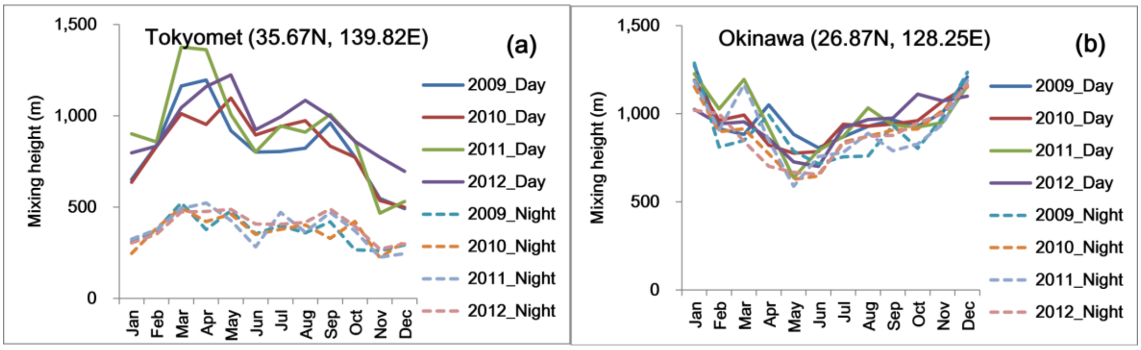

Figure 1 Monthly daytime and nighttime estimates of ABLs (mixing height) during 2009−2012 from two representative locations: (a) Tokyo metropolitan (b) Okinawa sea

Correlation between ABL and PBDEs in air

The results from estimating the site-specific and time-dependent ABL relevant to the PBDE sampling was used for regression analysis. From Figure 2, we found a consistent inverse relationship between the ABL and the concentrations of BDE-47 and -99 in the air (p=0.009 for BDE-47, and p=0.002 for BDE-99). However, interestingly, no significant relationship (p=0.258) was found between the ABL and the concentrations of BDE-209 in the air. These results indicate that higher ABL values produce concentrations of BDE-47 and -99 that are more diluted; however, this does not apply to BDE-209.

Okonski et al. (2014)[5] indicated that most (81% and 90%) of BDE-47 and -99 was found in the fine particles (0.49−3.0 μm), whereas only 65% of BDE-209 was found in these particles. On the other hand, the distribution of BDE-209 was higher (35%) in larger particles (3−10 μm) compared with the distributions of the BDE-47 and -99 (19% and 10%). Zhang et al. (2012)[6], particularly, conducted a study on the particle size distribution of PBDEs at different heights in the urban area of Guangzhou during August and December 2010. These authors found that the distributions of particulate-bound PBDEs (BDE-47, -99, and -209) were bimodal, with a major peak at 0.56−1.0 μm and a minor peak at 3.2−5.6 μm, for heights of 100 and 150 m. However, at the surface (1.5 m above the ground), only the particle size distribution of airborne BDE-209 significantly peaked at a major fraction of 5.6−10 μm and a minor fraction of 0.56−1.0 μm. Consequently, a much higher fraction of BDE-209 was distributed in the large particles in the near-ground air compared with those at heights of 100 and 150 m. These significant differences suggest that the BDE-209 bound to large particles might not be conveyed to high altitudes (e.g., 100 or 150 m). On the other hand, BDE-47 and -99 in the fine particles in both the near-ground and upper air undergo less dry deposition and can be transported to higher altitudes. The findings on the differing behaviors of the PBDE congeners, as discussed above, verify the inverse relationship between the mixing height and the air concentrations of BDE-47 and BDE-99 (being mainly associated with the gas phase and fine particles). The weak relationship between the mixing height and the BDE-209 concentration (with a high fraction in coarse particles) was confirmed by our study.

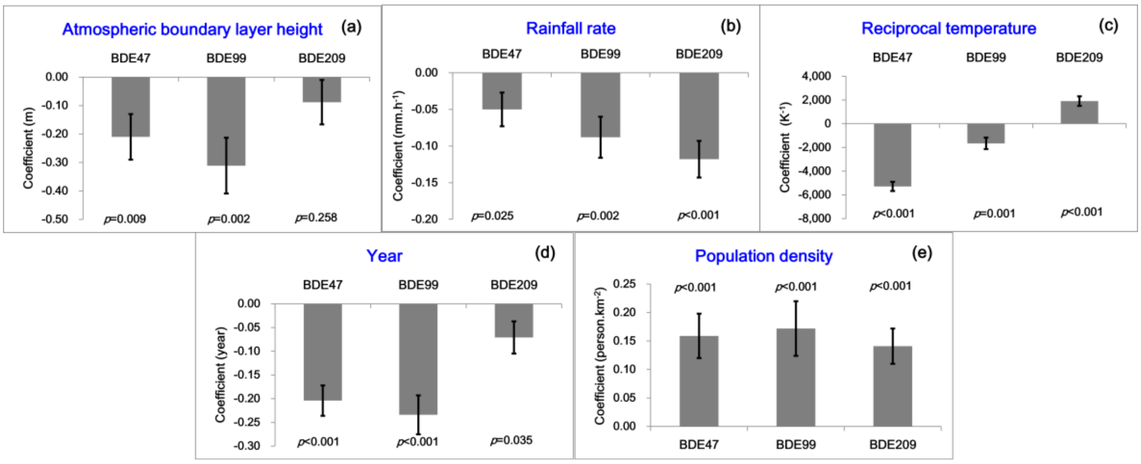

Figure 2 Regression coefficients of the concentrations of PBDE congeners against (a) the atmospheric boundary layer height (m), (b) rainfall rate ($mm \cdot h^{-1}$), (c) reciprocal temperature (K^{-1}), (d) year, and (e) population density ($person \cdot km^{-2}$) across Japan. Notes: The number of data points (n) is 298, the bars represent the coefficient estimates of PBDE congeners, and the error bars show the standard errors (SE)

The Tobit model presented significantly negative slopes against $1/T_{outdoor}$ for the gas plus particle phase concentrations of BDE-47 (Figure 2), with a high regression coefficient (-5290). On the other hand, although the concentrations of BDE-99 and -209 significantly present a relationship with $1/T_{outdoor}$, the regression coefficients (-1660 and 1904, respectively) were low. This result indicates that the temperature has a major effect on BDE-47, but a minor effect on BDE-99 and -209. The effect of the rainfall rate was shown to be greater on the PBDE removal for heavy congeners with particle phase dominance (BDE-209) than for the light congeners with gas phase dominance (BDE-47 and -99). The human population density factor presented a positive correlation with all of the PBDE congener concentrations, and all concentrations exhibited a decrease during 2009−2012.

References

(1) Japan Ministry of Environment (2009−2012). Monitoring Results: http://www.env.go.jp/chemi/kurohon/; **(2)** The Japanese global reanalysis (JRA-55) database: http://jra.kishou.go.jp/JRA-55/index_en.html; **(3)** Dien NT, Hirai Y, Miyazaki T, Sakai S. 2016. Chemosphere 144: 2073–2080; **(4)** Dien NT, Hirai Y, Sakai S. 2017. Environ. Sci. Technol. 51: 356−364; **(5)** Okonski K, Degrendele C et al. 2014. J. Environ. Sci. Technol. 48: 14426–14434; **(6)** Zhang BZ, Zhang K et al. 2012. Environ. Sci. Technol. 46: 7207−7214.