Measurement and modeling of urban atmospheric PCB concentrations on a small (8 km) spatial scale

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Abstract

Atmospheric transport and deposition of polychlorinated biphenyls (PCBs) is an important problem for ecosystems around the world. Data from several monitoring networks demonstrate that atmospheric PCB concentrations are dramatically elevated in urban areas compared to rural or background regions, such that these urban emissions of PCBs support the regional and global transport and deposition of PCBs to more remote areas. Identifying and controlling the sources of urban atmospheric PCBs is thus essential in minimizing the regional and global transport and deposition of these compounds. From December 1999 to November 2000, gas-phase PCB concentrations were measured at two monitoring locations, 8 km apart, within the New York City metropolitan area, at Jersey City and Bayonne, NJ. Concentrations, congener patterns, and temporal patterns of PCBs differ dramatically at the two sites, suggesting that a significant source of atmospheric PCBs exists within 8 km of the Bayonne site, resulting in spikes in gas-phase PCB concentration at Bayonne that are not observed at Jersey City. The Regional Atmospheric Model System (RAMS) coupled with the Hybrid Particle and Concentration Transport model (HYPACT) was used to estimate that the PCB source near Bayonne emits a flux of $\Sigma$PCBs on the order of 100 g d$^{-1}$. Extrapolation of this source magnitude to the area of New York City suggests that this urban area emits at least 300 kg yr$^{-1}$ $\Sigma$PCBs to the regional atmosphere, similar in magnitude to the flow of $\Sigma$PCB out of the Upper Hudson River into the New York/New Jersey Harbor.

Keywords: RAMS; HYPACT; Transport modeling; Persistent organic pollutants; New York; New Jersey; Harbor

1. Introduction

Measurement of atmospheric polychlorinated biphenyls (PCB) concentrations has been conducted in the east coast of the US and the Great Lakes primarily for the purpose of estimating atmospheric inputs to coastal waters (Baker et al., 1997; Buehler et al., 2001; Totten et al., 2004). The New Jersey Atmospheric Deposition Network (NJADN) was established for this reason and data from this...
project has been used to estimate atmospheric deposition fluxes to the NY/NJ Harbor Estuary and the tidal Delaware River. NJADN as well as the Integrated Atmospheric Deposition Network (IADN), the Chesapeake Bay Atmospheric Deposition Study (CBADS), and other studies have demonstrated that atmospheric deposition can be an important and sometimes dominant source of PCBs to coastal waters, and that atmospheric PCB concentrations are generally greater in urban areas than in rural or suburban areas (Baker et al., 1997; Buehler et al., 2001; Totten et al., 2004). This observation suggests that urban emissions of PCBs support the regional background concentrations observed in rural areas and control the atmospheric deposition of these compounds. Thus it is important to understand the sources of urban PCBs so that they can be effectively controlled (Gingrich and Diamond, 2001; Harner et al., 2004).

A further impetus for understanding urban PCB sources comes from the requirement for total maximum daily loads (TMDLs) in many aquatic systems in the US. For example, the Delaware River TMDL model, using NJADN data, estimates that the atmospheric load of $\Sigma$PCBs is $\sim4000$ g day$^{-1}$ (Fikslin and Suk, 2003), exceeding the TMDL by an order of magnitude.

The cost and logistics of maintaining atmospheric deposition networks such as NJADN and IADN typically limit the scope of the project to a small number of monitoring sites, mostly located at regional sites and tens to hundreds of kilometer apart. For example, the IADN was originally designed to have one remote site for each of the Great Lakes and was later expanded to include two urban sites in Chicago at the Illinois Institute of Technology (IIT) and the University of Illinois at Chicago (UIC). Concentrations of PCBs at UIC were found to be about twice those at IIT, although congener patterns at the two sites were virtually identical (Basu et al., 2004). The NJADN included at various times 13 monitoring locations in New Jersey, eastern Pennsylvania, and Delaware. Even so, the NJADN spaced monitoring locations as far apart as possible. When only one monitoring station is placed in each city, the tacit assumption is made that this single station accurately characterizes the atmospheric concentrations of PCBs for the whole city.

From December 1999 to November 2000, atmospheric PCBs were measured at two monitoring locations about 8 km apart within the New York City metropolitan area (Fig. 1): Jersey City and Bayonne. The Bayonne monitoring site was established to determine the background atmospheric concentrations of PCBs in Bayonne prior to disposal of stabilized dredge material from the Hudson River at a landfill in Bayonne, NJ (Korfiatis et al., 2003). This paper examines the similarities and differences in PCB concentrations and patterns at these two sites in order to improve our understanding of urban sources of atmospheric PCBs. In order to assess the emissions required to produce the measured concentrations, the Regional Atmospheric Model System (RAMS) was used to generate local meteorology simulations, and the Hybrid Particle And Concentration Transport model (HYPACT) was used to model transport of the emitted PCBs. This represents the first report of the use of the RAMS/HYPACT model system to examine atmospheric concentrations of persistent organic pollutants (POPs).

2. Experimental section

2.1. Site characterization

Bayonne and Jersey City lie on a peninsula separating Newark Bay from the Upper New York Bay and Hudson River (Fig. 1). The Jersey City site was operated on the grounds of the Liberty Science Center, in a grassy area less than $\sim30$ m from the Hudson River. The Bayonne site was located on top of an air monitoring trailer operated by the NJ Department of Environmental Protection, parked at the edge of the football stadium of Bayonne High School, within $\sim30$ m of Newark Bay.

The entire peninsula is heavily urbanized and industrialized (Fig. 1). Due west lies the city of Newark, home to the Port of Newark, Newark Airport, and a major incinerator. Just north of Newark lies the New Jersey Meadowlands, home to more than 10 current or former landfills. Newark Bay represents the confluence of the Passaic and Hackensack Rivers and receives effluent from at least four paper mills. Newark Bay and the Hudson River are hydraulically linked and tidally mixed. The waters surrounding the peninsula contain about 10–20 ng L$^{-1}$ $\Sigma$PCBs (dissolved plus particulate) (Litten, 2003) and are therefore potential sources of atmospheric PCBs (Totten et al., 2001). The rivers feeding this area (the Hudson, Passaic, and Hackensack Rivers) all contain similar levels of PCBs.
2.2. Sampling

Details of sample collection, preparation, extraction and analysis can be found elsewhere (Totten et al., 2001, 2004; Brunciak et al., 2001) and will be summarized here. Air samples (24 h) were collected at 12 day frequencies using a modified high volume air sampler (Tisch Environmental, Village of Cleves, OH, USA) with a calibrated airflow of $\frac{0.5}{24} \text{ m}^3 \text{ min}^{-1}$. Quartz fiber filters (QFFs; Whatman) were used to capture the particulate phase and polyurethane foam plugs (PUFs) were used to capture the gaseous phase. Particle-phase PCBs were not quantified at Bayonne because it was assumed that any PCBs emitted from the stabilized sediment would be emitted into the gas phase, and because the particle phase typically contains <10% of the atmospheric PCB burden. The samples were extracted using a Soxhlet apparatus, cleaned up using 3% deactivated alumina, and analyzed for PCBs by electron capture detection (ECD). Sixty peaks representing 93 PCB congeners were quantified and summed to yield “ΣPCBs”. Three surrogates were used to quantify the recovery of PCBs: PCBs 23, 65, and 166. Surrogate recoveries were used to correct PCB concentrations, averaged
better than 80%, and were never below 50% at both sites.

2.3. RAMS/HYPACT modeling

RAMS version 4.3 was used to downscale the Eta Weather Prediction Model forecast (Mesinger et al., 1988; Rogers et al., 1996) conducted with spatial resolution of about 32 km. The downcaled meteorological fields were used in the HYPACT model for fine grid transport and deposition calculations. To account for a multiscale structure of the transport here we conducted calculations in three nested domains centered on the Bayonne peninsula (Figs. 1 and 2). The large parent domain is necessary to accommodate mesoscale structures to be downscaled in two smaller nested domains centered at the same central point covering areas of 54 km × 54 km and 10.5 km × 10.5 km, respectively (Fig. 2). The spatial resolution of Grids 1, 2, and 3 is, respectively, 4 km × 4 km, 1 km × 1 km, and 0.25 km × 0.25 km and number of grid points are 75 × 75, 54 × 54, and 42 × 42. The vertical grid is non-uniform, contains 39 levels starting from 10 m surface layer and reaching 1700 m at the top of the domain at the altitude of 16 km.

The original RAMS land elevation and vegetation cover data sets are of 1-km resolution that is sufficient for calculations of mesoscale circulation but is not enough for our application. To conduct finer-resolution simulations in the metropolitan area we adopted high-resolution National Land Cover Dataset (NLCD) and National Elevation Data (NED) from the United States Geological Survey (USGS) (http://edcwww.cr.usgs.gov/doc/edchome/ndcldb/ndcldb.html). NED has a resolution of 2
1 arc-second or about 30 m for conterminous United States.

NLCD is a multilayer and multisource database that contains 30-m resolution 21-class land classification for territory of the United States in the form of visual images. The Visual Basic script was used to read pixel values and to produce a digital data file. Further we converted the NLCD classes to Olson type classes (http://edcdaac.usgs.gov/glcc/globdoc1_2.html) and then produced a LEAF2 database for RAMS.

The original RAMS sea surface temperature (SST) is based on climatologically averaged monthly mean 1° × 1° resolution data set of Reynolds et al. (2002). However, fine-scale transport of pollutants in this area is almost certainly affected by sea breezes initiated by the actual land/sea temperature contrast. Therefore in our simulations we have used real-time SST with better spatial resolution. For this purpose we acquired 1 km resolution multichannel Advanced Very High Resolution Radiometer satellite retrievals (Bernstein, 1982) from the Marine Remote Sensing Laboratory of the Rutgers Institute for Marine and Coastal Sciences. These data were processed to remove the effect of clouds seen in the instantaneous retrievals and produce the 3-day SST composites.

The meteorology simulations are driven by the initial and boundary conditions that we developed using the objective analysis package belonging to RAMS. These objectively analyzed fields are calculated using 3-h Eta model operational analysis (Mesinger et al., 1988; Rogers et al., 1996). The Eta model data were provided by the National Center for Environmental Prediction (NCEP) in gridded binary (GRIB) format on a horizontal grid with the spatial resolution of 32 km. The objectively analyzed 3-h fields are used to constrain the flow near the boundaries of the grid 1 domain using nudging type Davies (1976) boundary conditions with the nudging time of 30 min at the 5-grid-cell boundary belt. In addition, to keep the flow close to observation during the entire period of simulations we nudged horizontal velocity, potential temperature, and Exner function in the interior of the domain with much larger nudging time of 12 h to let small-scale high-frequency disturbances to develop. The RAMS simulations were conducted using radiative scheme of Harrington (1997), turbulent closure of Mellor and Yamada (1982), and driving fields calculated using Eta fields. The meteorological fields were saved every 30 min. Transport of pollutants was calculated off line using the Lagrangian model HYPACT version 1.2 that utilizes RAMS output.

3. Results and discussion

The results from several years of measurements at the Jersey City site were presented in Totten et al. (2004). During the year of simultaneous sampling, average (± standard deviation) gas-phase ΣPCB concentrations were 1600 ± 880 pg m⁻³ at Bayonne and 930 ± 460 pg m⁻³ at Jersey City. These concentrations are typical of those measured over a longer time period at Jersey City (averaging 1260 pg m⁻³ from October 1998 to January 2001). They are significantly higher than the concentrations measured at more remote regions of New Jersey, where gas-phase ΣPCBs typically average 150–220 pg m⁻³ (Totten et al., 2004). ΣPCB concentrations were more variable at Bayonne (Fig. 3). At Bayonne, the ΣPCB concentrations are similar (the ratio of the Bayonne to the Jersey City concentration is between 0.5 and 2) on 15 of the 25 simultaneous sampling days, and dissimilar (Bayonne/Jersey City > 2) on 10 days. These periodic spikes in concentration raise the PCB levels at Bayonne on average by about 1500 pg m⁻³.

Congener patterns at the two sites were usually similar with an $R^2$ greater than 0.7 for 20 of the 25 paired samples. Very dissimilar congener patterns did not necessarily occur on days when the absolute ΣPCB concentrations were also very different. For example, on 5/24/2000, the ΣPCB concentrations were virtually identical, but the correlation ($R^2$) between the congener patterns was 0.56. This suggests that differences in congener patterns do not necessarily lead to differences in ΣPCB concentrations. There was no clear correlation between low correlation coefficients or spikes in concentration at Bayonne (Table 1) and any natural phenomena, including wind directions, back trajectory endpoints (NOAA HYSPLIT), precipitation patterns, or tidal cycles (neap vs. spring tides). The only meteorological variable to display a significant ($R^2 = 0.19, p = 0.028$) correlation with the Bayonne/Jersey City PCB ratio was the average wind speed, with the ratio being higher when wind speeds were greater. The absolute concentrations at Bayonne were not correlated with wind speed, although at Jersey City, ΣPCB concentrations decreased when wind speeds increased ($R^2 = 0.24, p = 0.01$), possibly due to dilution.
The temperature ($T$ in Kelvin) dependence of the gas-phase PCB partial pressures ($p$ in atm) was investigated by application of the Clausius–Clapeyron equation

$$\ln p = \frac{a}{T} + b,$$

(1)

where $a$ and $b$ are constants. This approach has been used by many researchers, with steeper slopes thought to indicate closer sources (see Wania et al., 1998; Carlson and Hites, 2005 for reviews). Carlson and Hites (2005) suggest that the ~25 data points used here are insufficient to accurately determine the temperature dependence of PCBs over the long term at these sites. The goal of this analysis, however, is not to determine long-term differences in PCB dynamics, but to assess short-term differences in PCB behavior. For this purpose, 25 data points are sufficient to reveal significant differences in PCB dynamics.

At Jersey City, the Clausius–Clapeyron regressions were significant ($p < 0.05$) for all PCB congeners and co-eluting congener groups, with $R^2$ values ranging from 0.30 to 0.89. The slopes ($a$ values) derived displayed a stronger correlation ($p < 10^{-5}$; $R^2 = 0.35$) with the log of the hypothetical sub-cooled liquid vapor pressure (log of $p_L$ from Falconer and Bidleman, 1994) than the slopes at Bayonne. In contrast, the Clausius–Clapeyron regressions were not significant ($p > 0.05$) for four congener groups at Bayonne, and the $R^2$ values, even for the regressions that were significant, were generally weaker than at Jersey City and weakest for congeners with log vapor pressures ranging from $-2.2$ to $-3.5$ Pa (i.e. PCBs eluted between and including PCBs 66 + 95 and PCB 185 and containing 3–6 chlorines). Data from Bayonne for days with no observed PCB spike displayed higher Clausius–Clapeyron correlation coefficients for the congeners between 66 + 95 and 185 than the “spike” days. This indicates that the “background” PCB concentrations are primarily driven by processes that are correlated with temperature, such as passive volatilization from contaminated land, vegetation, or water surfaces, but the process that is driving the PCB spikes at Bayonne is not driven by temperature. Days with PCB spikes at Bayonne generally did not display positive residuals for the Clausius–Clapeyron regressions at Jersey City, indicating that the spike at Bayonne did not elevate the concentration at Jersey City significantly above the concentration that would be predicted by temperature.

A chemical mass balance model was applied to the PCB concentration data to elucidate the Aroclor pattern of the atmospheric PCBs and to determine whether the PCB spikes were due to emissions of an identifiable Aroclor. The congener compositions

![Fig. 3. Gas-phase ΣPCB concentrations at Bayonne and Jersey City from December 1999 to November 2000.](image_url)
from Frame et al. (1996) of the four Aroclors produced in highest volumes (Brown, 1994) were multiplied by their sub-cooled liquid vapor pressures (Falconer and Bidleman, 1994) to convert them to the congener profile expected in the atmosphere, and then expressed as a percent of the total composition. Aroclor 1016 was not used in this model because it represents a distillation of Aroclor 1242. These congener patterns were then fit via a least-squares regression to the congener pattern of each sample (again expressed as a percent of total), with the constraint that the coefficients $a$, $b$, $c$, and $d$ must be greater than or equal to zero

$$C_i = aC_{1242} + bC_{1248} + cC_{1254} + dC_{1260},$$  \(2\)

where $C_i$ is the normalized concentration of congener $i$ in the atmospheric sample, and $C_{12xx}$ is the normalized concentration of congener $i$ in Aroclor number 12xx. Aroclors patterns 1248b and 1254b (Frame et al., 1996) were used in the analysis because they consistently gave better fits to the data than the alternative samples of the same Aroclor. Aroclor 1242 was usually present, and the other Aroclors were always present in the samples. The average Aroclor profiles of the two sites were similar, with the percentages of Aroclors 1242, 1248, 1254, and 1260 respectively being 10%, 44%, 21%, and 14% at Jersey City and 14%, 28%, 26%, and 15% at Bayonne. The residual (that part of the congener pattern not described by the Aroclors) averaged 10% at Jersey City and 17% at Bayonne.

There were no obvious differences in Aroclor composition between the days with PCBs spikes at Bayonne and the days without, nor between the Bayonne Aroclor composition and the Jersey City composition on the days with spikes. This suggests

<table>
<thead>
<tr>
<th>Date</th>
<th>$\Sigma$PCBs (pg m$^{-3}$)</th>
<th>BA/JC ratio</th>
<th>Wind direction (deg)</th>
<th>Average wind speed (m s$^{-1}$)</th>
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that the source of the PCBs spikes at Bayonne does not consist of a single Aroclor, but is a mixture of several Aroclors.

This analysis has suggested that one or more active sources of PCBs existed near the Bayonne site during 1999–2000 and may still exist. It also provides some information as to the type and location of the source. The source is probably within ~8 km of the Bayonne monitoring site, since 8 km away at Jersey City, the signal from this source is not measurable. In addition, it is logical to assume that the source is closer to the Bayonne site than the Jersey City site. Because there is no correlation between PCB spikes at Bayonne and any natural phenomenon (temperature, tides, precipitation), the PCB spikes are thought to arise from anthropogenic activities that could include periodic disposal or trans-shipment of PCB-contaminated waste, and illegal disposal of PCB-containing materials. Finally, the analysis of congener patterns suggests that the source contains a mixture of PCBs, as opposed to being comprised of a single Aroclor. Unfortunately the area around Bayonne contains dozens of sites fitting this description, and additional data collection would be needed to determine which of the many suspect is responsible for the PCB spikes at Bayonne.

The dredging of NY/NJ Harbor Estuary to maintain, and in some cases deepen, the shipping channels is of enormous economic importance to the region, and is environmentally problematic due to the relatively high levels of PCBs and other contaminants in the surficial sediments of the Harbor (Adams et al., 1998). During the period of sample collection, the confined disposal facility (CDF) in Newark Bay was the only disposal option for this dredge material. For this reason, dredging and disposal records provided by the NJ Office of Maritime Resources were examined to determine whether the CDF could be a source of atmospheric PCBs to Bayonne. The records indicate that neither dredging nor disposal occurred in this region during the first half of 2000, suggesting that the CDF is not the source of the PCB spikes observed at Bayonne.

How large must the emissions of PCBs be to support the atmospheric concentrations of PCBs observed at Bayonne? To answer this question, a RAMS/HYPACT modeling exercise was conducted in which three possible sources of PCBs were examined, the CDF, New York City (NYC) and the landfill where sediment dredge material (SDM) from the Hudson River was disposed. These models were recently applied by the authors to an investigation of the fate of the plume of contamination emanating from the World Trade Center in lower Manhattan resulting from the terrorist attacks of 11 September 2001 (Stenchikov et al., 2005a, b).

Three unit PCB sources emitting in the 1-m surface layer were included in calculations of PCBs at the SDM landfill, the CDF, and NYC. The CDF location was chosen because it possessed the characteristics attributed to the PCB source: it is within 8 km of the Bayonne trailer and is closer to the Bayonne site than the Jersey City site. The NYC site was chosen because it is reasonable to assume that NYC emits significant quantities of gas-phase PCBs. To distinguish the effects of all these three sources their emissions were treated as different tracers. PCBs at the Bayonne SDM landfill and the CDF were emitted from a square area of 500 m × 500 m. The source in NYC has a rectangular shape of 4 × 10 km covering the lower part of Manhattan. The magnitude of these sources is not known, therefore we conducted calculations with unit sources of 1 g s⁻¹ and later scaled the emission to fit the observed concentrations, assuming a linear relationship between emission and measured concentration. For this initial modeling effort, PCBs were assumed to exist in the gas phase only and were not subjected to hydroxyl radical reactions. This is reasonable considering the short distances involved, which imply travel times of a few hours at most. Also, these assumptions provide the highest, or worst-case scenario, estimates of atmospheric PCB concentrations.

HYPACT simulations were conducted for six periods during which intensive sampling of atmospheric PCBs was conducted at three locations within the landfill and at the NJDEP trailer during placement of SDM at the landfill in Bayonne (Korfiatis et al., 2003). For purposes of calculating the emissions necessary to produce the observed concentrations at the Bayonne trailer, we used results obtained for 23–26 October 2001. The meteorology during this period was representative of the typical airflow patterns in this region, and therefore is sufficient for the purpose of estimating the source intensity.

Observed wind series measured by Automated Surface Observation Stations (ASOS) at the JFK and Newark airports available from National Climate Data Center (NCDC) (http://www4.ncdc.noaa.gov/cgi-win/wwcgi.dll?wwdi~ASOSPhotos) were compared with
RAMS output to assess model accuracy (Fig. 4). The simulations captured time variations of wind directions and magnitude fairly accurately at both locations.

Fig. 5 depicts observed and simulated $\Sigma$PCB concentrations at the SDM and trailer sites for the October 2001 model period. In interpreting this figure it is important to remember that the measured concentrations represent integrated 4-h measurements, while the lines are instantaneous predicted concentrations. PCB concentrations predicted at two locations (SMD landfill and trailer) are shown as they are produced by three different sources located at SDM landfill, CDF, and NYC, as was discussed above. The magnitude of each source needed to produce concentrations of the same magnitude as observed at a particular location was estimated. To our knowledge, this is the first time RAMS/HYPACT or similar atmospheric model has been used to examine emissions of persistent organic pollutants on a local scale, and the results provide powerful insights into the magnitude of emissions necessary to produce the PCB levels routinely measured in urban areas.

At the sediment site we have shown only concentrations transported from the local SDM landfill source (green curve). The magnitude of PCB emissions at the SDM landfill that produces concentrations of 4000–7000 pg m$^{-3}$ as observed at the SDM site (open circles; see Korfiatis et al., 2003) is $10^{-4}$ g s$^{-1}$ or about 3 kg yr$^{-1}$. Dividing this emission rate by the surface area over which sediment was spread on that particular day yields a surface flux equal to 400 pg m$^{-2}$ s$^{-1}$. This value is in good agreement with a separate investigation of the PCB emissions from the SDM based on measurements of gas-phase PCB concentrations at two heights above the SDM, which calculated an average flux of about 570 pg m$^{-2}$ s$^{-1}$ (Korfiatis et al., 2003). The transport of PCB emissions of this magnitude from the SDM source could produce concentration spikes of 100–200 pg m$^{-3}$ at the Bayonne trailer (red curve). These instantaneous levels are well below observed 4-h integrated concentrations at this site that range from 400 to 2000 pg m$^{-3}$ (closed squares), suggesting that the emissions from the SDM landfill have a small effect on the overall levels of PCBs measured at the Bayonne trailer. That a source of 3 kg of PCBs per year produces a minimal PCB signal 8 km away suggests that the levels of PCBs routinely measured in urban areas are produced by emissions that are orders of magnitude greater. Also, it suggest that the emissions which produced the PCB spikes at Bayonne are either much greater than 3 kg yr$^{-1}$ or that the source is much closer than 8 km.

It is useful to examine the impact that emissions from NYC have on the PCB levels measured at Bayonne, because although we do not know the magnitude of emissions from NYC, it is safe to assume that such emissions do exist. Of course, NYC cannot be the source of the PCB spikes measured at Bayonne because, due to its location, its emissions would have a greater impact at the Jersey City site than at the Bayonne site. Nevertheless, Fig. 5 indicates that PCB emissions from NYC on the order of 32 kg yr$^{-1}$ are not observable at the Bayonne site most of the time. Only on the relatively rare occasions when the winds blow directly from NYC to Bayonne (for example,
23 October at noon) can this level of emissions produce a measurable PCB concentration at Bayonne.

Could emissions from the CDF explain the PCB spikes measured at the trailer? PCB concentrations resulting at the trailer site from the CDF (orange curve) are also shown in Fig. 5. The magnitude of the CDF source needed to produce short-term spikes in PCB concentrations that are similar in magnitude to those observed at the trailer is about $10^{-3} \text{ g s}^{-1}$. Are these emissions plausible? For the CDF, the emissions represent some fraction of the total mass of PCBs deposited to the CDF during the measurement period. During the second half of 2000, approximately 160,000 cubic yards of dredge material were placed into the CDF. If the density of this material is assumed to be 500 kg m$^{-3}$ and the PCB concentration is assumed to equal that of Newark Bay surficial sediments ($\sim 750$ ppb, Adams et al., 1998), then about 45 kg of PCBs were placed into the CDF during this 6-month period. At $10^{-3} \text{ g s}^{-1}$, about 16 kg of PCBs would have volatilized out of the CDF during this period, or one-third of the PCB inventory in the sediments placed in the CDF. This seems unreasonably high. This calculation supports the conclusion that the CDF cannot be the source of the PCB spikes observed at Bayonne.

In addition to horizontal concentrations, it is useful to examine the vertical distribution of PCBs (Fig. 6). Vertical concentration profiles of unreactive contaminants are determined by three factors: the height of the emissions, the distance from the source, and the structure of the boundary layer. For PCBs, we assume that all emissions occur at ground level. The relatively low temperatures during the period of the modeling (October) will tend to create stable boundary conditions, trapping the ground
level emissions below the boundary layer. During hotter months when the boundary layer is less stable or during front passage or convective events, greater turbulent mixing will facilitate the transport of PCBs above the boundary layer, where they will have greater potential for long-range transport (Stenchikov et al., 2005a, b). Maximum PCB concentrations occur at ground level only when the receptor (monitoring site) is directly above the emission point (in our scenario, at the SDM). When the receptor is removed from the source by a few km (NYC or CDF), the PCB concentrations reach a maximum 15–45 km above ground level. Farrar et al. (2005) measured the vertical distribution of PCBs in the urban atmosphere of Toronto up to 360 m. These researchers noted a profile characteristic of ground level emissions and a stable boundary layer (concentrations are highest at ground level and decrease with height) for some PCB congeners, but $\Sigma$PCBs were generally well mixed up to 360 m. These observations are in good agreement with our model results, which indicate that PCB concentrations do not necessarily display obvious vertical gradients below the urban boundary layer, which is generally above 400 m, unless the receptor is immediately above the emissions source.

Our modeling indicates that PCB concentrations drop to zero at $\sim$100 m, whereas Farrar et al. (2005) measured significant PCB levels at 360 m. This discrepancy results from at least two factors: the stability of the October boundary layer, and the small number and relatively low intensity of the PCB sources in the model. Instability in the boundary layer would lead to a concentration...
profile that is relatively constant with height. Additional sources added to the RAMS/HYPACT model, especially sources located farther from the receptor, would increase PCB concentrations at heights above 100 m. This fact, coupled with the observations of Farrar et al. (2005), suggest that urban areas such as NYC and Toronto probably emit far more PCBs to the atmosphere than the $\sim 70$ kg yr$^{-1}$ used in our model.

How big might the urban emissions of PCBs be? The model results can be used to calculate the minimum total PCB emissions necessary to maintain the concentrations measured at the Bayonne trailer and at the nearby Jersey City NJADN site. The modeled flux of $10^{-3}$ g s$^{-1}$ from the CDF represents a load of about 32 kg yr$^{-1}$ to the atmosphere of the region. This is similar to the load of PCBs emitted to the water from all of the wastewater treatment plants in the NY/NJ Harbor (Totten, 2005). This calculated emission is only that required to generate the PCB concentrations observed at the Bayonne trailer. Since the model also indicates that these emissions from the CDF would be barely observable at the Jersey City site (8 km away), it follows that a source of this magnitude is sufficient to contaminate the air in about a 6 km radius, or about 100 km$^2$. If a source of this magnitude is located within every 100 km$^2$ block of NYC (785 km$^2$), they would generate a relatively constant gas-phase PCB concentration of about 1000 pg m$^{-3}$ at ground level throughout the City, similar to the levels observed at the Bayonne trailer and the Jersey City NJADN site. This PCB concentration is reasonable given that it is similar to the average gas-phase PCB concentrations measured in urban areas such as Camden, NJ (Totten et al., 2004) and Chicago, IL (Basu et al., 2004). This corresponds to PCB emissions on the order of $\sim 800$ g d$^{-1}$ or $\sim 300$ kg yr$^{-1}$. For comparison, the largest single source of PCBs to the water column, the Hudson River, is estimated to contribute about 300 kg yr$^{-1}$ to the NY/NJ Harbor (Farley et al., 1999). This represents a minimum estimate because it does not consider the removal of PCBs from the lower atmosphere due to dry deposition and hydroxyl radical reactions. Thus our RAMS/HYPACT modeling of the Bayonne emissions allows us to calculate that while the Upper Hudson River releases 300 kg yr$^{-1}$ of PCBs to the Harbor each year, it is possible that a similar amount volatilizes off contaminated surfaces in NYC alone (not including neighboring cities and outlying suburbs) each year. Additional RAMS/HYPACT modeling by our group suggests that during periods of turbulent mixing and unstable boundary conditions, a significant fraction of these ground level emissions will be transported to the middle troposphere, where they will become available for long-range transport (Stenchikov et al., 2005a, b). Thus urban areas emit hundreds of kilograms of PCBs to the atmosphere each year, a substantial fraction of which may undergo long-range transport to the arctic.

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