PBDE Fate and Transport in an Urban Centre: Application of the Multimedia Urban Model

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Introduction

Since PBDEs are emitted from a wide range of consumer products, it is logical that urban areas should be the geographic source of these compounds to the surrounding region[1]. Analogously, PCBs have in the past and are continuing to be released from cities[2] despite their discontinued production in the 1970s. The physical environment of cities, notably the dominance of impervious surfaces and highly disturbed vegetation and hydrologic regime, has been hypothesized to increase contaminant mobility relative to natural, forested areas[3]. However, what remains unclear is the magnitude of emissions from the city as a whole and how these emissions partition among media within the city versus export from the city. The goal of this paper is to approximate emissions from a typical North American city, namely Toronto, Canada, and to evaluate the mobility of the emitted PBDEs. We approach this goal by using the Multimedia Urban Model or MUM-Fate.

Methods

MUM-Fate is a steady-state (Level III), non-equilibrium, fugacity-based multimedia chemical fate model which considers six compartments (i.e., air, soil, vegetation, surface film, water and sediment)[3]. Full details of the model application and assumptions are discussed by Jones-Otazo et al.[1]. The model was parameterized for a 470 km^2 area centered on Toronto and with a population of 1.3 million people within this area. The area has 60% impervious surfaces with an Impervious Surface Index of 2.3and 10% coverage by vegetation with a Leaf Area Index of 1.6. The water compartment is considered to be nearshore Lake Ontario that extends to 30% of the modelled domain. The previous version of MUM-Fate has been adapted to include lower (0 to 50 m) and upper (50 to 500 m) air compartments and distinguishes emissions from sources within the domain (e.g., from indoor sources or industrial uses), from those advected from upwind sources. The 50 m lower mixing height was based on the thickness of the well-mixed layer for compact residential, industrial and <10 story commercial land-use categories with an exchange rate of 0.5 m/s beween upper – lower air boxes, which is consistent with vertical wind speeds estimated for urban canyons, with an average horizontal wind speed of approximately 4 m/s.

We considered a summer scenario at 25^{o}C using an average rain rate. The model was run for each of 10 PBDE congeners and the results summed to yield ∑PBDE. Although BDE-209 is explicitly excluded from the estimates, some BDE-209 is implicitly included through debromination to lower brominated congeners.

Physical-chemical data for the PBDE congeners were taken from Wania and Dugani[4]. Qualitative environmental degradation half-lives in all media were obtained by the U.S. EPA's AOPWIN and BIOWIN programs but this approach does not explicitly account for the formation of lower brominated congeners due to debromination of higher brominated congeners nor the increased degradation rates with increasing bromination.

We estimated advective inputs of each PBDE congener from gas-phase concentrations obtained from sampler deployed in Toronto Harner *et al.*[5] and corresponding particle-phase concentrations. Gas- and particulate-phase concentrations were summed for the estimate of total input air concentrations assuming a rural total suspended particulate concentration of 15 μg/m^3. Total urban air concentrations were calculated similarly, using data[5] from five Toronto urban sites and assuming an urban total suspended particulate concentration of 80 μg/m^3. We calculated a range of likely emissions within the 470 km^2 area which, in addition to the rural/suburban advection, to equal an advected air output equivalent to the Toronto urban air concentrations[5]. We considered six emission scenarios which were derived from three advection scenarios and two urban air output scenarios. The ranges of modelled concentrations in soil and film were compared with literature values to evaluate model efficacy[1].

Results and Discussion

Emissions to the 470 km^2 area obtained from MUM-Fate results during this summer scenario are 100-422 g/day of ΣPBDEs. This compares with an average of 74-207 g/day of PBDEs from upwind sources (Fig. 1). These estimated emission rates result in media concentrations that are within an order-of-magnitude of literature values. Soil concentrations are within the measured range reported, however these measured values were downwind of a polyurethane foam manufacturer, and span a range from below a detection limit of an order of magnitude below modelled concentrations, to an orders of magnitude above modelled concentrations. Water, as a mobile medium, was assumed to have an input at a concentration of zero, thus the modelled concentrations represent net increase above urban background. Although there is substantial uncertainty in estimates of total emissions, the result that 57-85% of ΣPBDE originate from within Toronto (rather than advection from regional inputs) is consistent with the congregation of likely residential and small industrial emission sources within the city. The range of emissions derived for BDE-47 and -99 for Toronto corresponds to -19-82 mg/capita/year in the modelled area, which are ~3-12 times greater than the 7.0 mg/capita/year for Swedish citizens estimated by Palm[1] based on a Substance Flow Analysis for Denmark. Given that North American concentrations are 20-fold higher than those of Europe and that the estimates from Palm and this paper were obtained using very different methods, the difference in estimates is not surprising.

Over 95% of ΣPBDE entering the model domain are lost through air advection. The remaining emissions undergo either degradation or multi-media partitioning and result in increased urban media concentrations (Fig. 2). Approximately 5% (8-17 g/day) of emissions are transferred to films on impervious surfaces that achieve the highest concentration among media of 121-292 ng/g or 7.2-17 ng/m^2. In turn, 1.5-3 g/day volatilizes from the films and 6-13 g/d is transferred to surface water (near-shore Lake Ontario), resulting in concentrations of up to 2 pg/L, where it is available for uptake into the aquatic food web. Modelled concentrations of the various congeners in the upper air box (50-500 m) varied from 27-81% of the lower air box (0- 50 m) values, which agrees reasonably with the data presented by Harner *et al.*[5] from passive samplers deployed at Toronto's CN tower where they found congener concentrations at 300 m were 14-54% of the 30 m congener concentrations.

There are numerous sources of uncertainty associated with estimates of emissions and fate. Specific to this application, the major uncertainties are exclusion of BDE-209 from the calculations, process rates in general, and the back-calculation of within city emissions from regional air inputs. The uncertainty in the latter is, in part, attributable to variations of 3-4 times within each of the urban and the suburban/rural samples, and that while urban concentrations are on average 2-3 times higher than suburban/rural measurement from the same time frame, periodically a congener in the urban environment can be at a lower concentration than in the suburban/rural environment. Degradation rates and the potential for transformation of higher into lower brominated congeners are also major uncertainties in the model, particularly since the rates used were estimated and not measured values, with congener-specific reaction rates decreasing with increasing bromination. Due to the steady-state nature of the model, we have ignored seasonal and diurnal variations in degradation and transport rates (e.g., temperature, wind speed and direction, precipitation, atmospheric mixing height etc.). As illustration of this effect, considering a temperature of 0 rather than 25°C increases partitioning to solid phases, such as soils and surface waters (e.g., increasing BDE-99 concentrations 2.5 times in water and 24 times in soil).

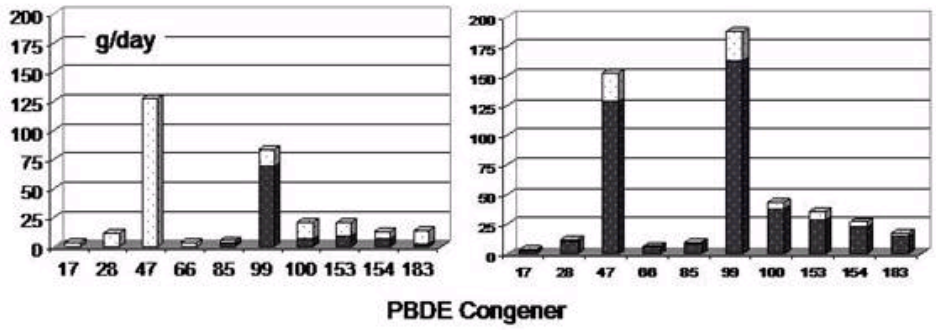

Figure 1. Model estimated ΣPBDE emissions advected into Toronto (light bars) and released within a 470 km^2 area

of Toronto (dark bars), Canada.

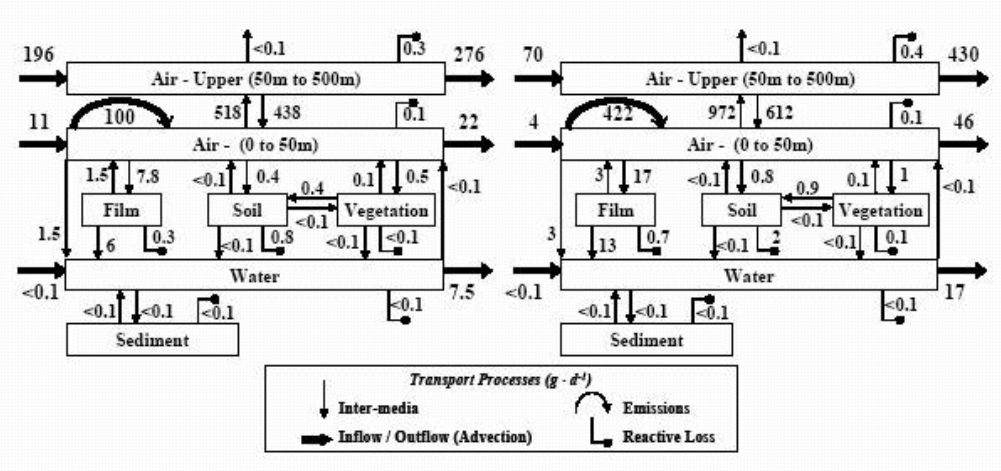

Figure 2. Results of Multimedia Urban Model (MUM-Fate) for ΣPBDEs in a 470 km^2 area of Toronto, Canada. Two simulation illustrate range of estimated inputs where a. is maximum advective inputs and b. is maximum "within Toronto" inputs. Model results for 25^0C.

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References

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