ppLFER-MUM: An Updated Multimedia Urban Model (MUM) used for Estimating Organophosphate Ester (OPE) Transport, Fate and Emissions in Toronto, Canada

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Introduction

Organophosphate esters (OPEs) are widely employed as flame-retardants and plasticizers, with usage increasing following the listing of penta- and octa-BDEs as persistent organic pollutants (POPs) under the Stockholm Convention. Measured concentrations of OPEs in indoor and outdoor air are in the range of $\mu g/m^3$ and high pg/m^3 to low $\mu g/m^3$, respectively, in Toronto, Canada[1]. OPE concentrations in Toronto tributaries reach $\mu g/L$ levels at high flow[2]. These levels in river water occur in the absence of releases of OPEs from wastewater treatment plants. The higher concentrations in river water could pose a risk to aquatic biota.

In this study, we modified the Multimedia Urban Model (MUM) of Diamond and co-workers using polyparameter linear free energy relationships (ppLFERs) to estimate the emissions, fate, and transport of three chlorinated (Cl-OPEs) and three non-chlorinated OPEs (non-Cl-OPEs) in Toronto, Canada. In particular, we wondered whether the measured river water concentrations were reflecting direct emissions such as wastewater inputs, or if those river water concentrations could be attributed to air emissions.

Materials and Methods

MUM is a seven compartment, fugacity-based multimedia model run for steady-state conditions[3]. The model was modified by adding ppLFERs, first proposed by Abraham and co-workers[4], describing partitioning between aerosol-air[5], organic carbon-water[6], and storage lipid-water[7] phases, using the thermodynamic cycle to derive others as required. We used these equations to derive the fugacity capacities for the aerosol, sediment, soil organic carbon, vegetation, and surface film compartments. These relationships replaced previous single-parameter relationships, such as those based on K_{OW}, as ppLFER-based relationships are more accurate when describing polar chemicals, especially when experimental data are sparse or unreliable[8]. The ppLFER equations are based on Abrahams solvation parameters[4], which allow for a more mechanistic understanding of partitioning, and therefore of fate.

We parameterized ppLFER-MUM for Toronto, using the values of Csiszar and co-workers[9]. The three Cl-OPEs modelled were TCPP, TCEP and TDCPP. The three non-Cl-OPEs modelled were EHDPP, TBEP and TPhP. Aggregate emissions to air (0-50 m elevation) were estimated by back-calculating from outdoor air concentrations measured in 2010[1]. As air concentrations of TBEP for Toronto were unavailable, we used measured air concentrations taken in Lake Ontario (also for 2010) and an urban-rural scaling factor[10] based on the observed ratio of air concentrations at Toronto urban sites to Lake Ontario sites for the other five OPEs in the data set[9]. Model results were evaluated against river water concentrations measured in Toronto for one year in 2010-11[2]. Model results were also compared to those of PCBs and PBDEs based on air measurements made in 2008[9].

Results and discussion

Based on modelled emissions to air, modelled water concentrations were within an order of magnitude of the measured values; these range from 88% below for TCPP to 1400% above for TPhP, with an RMSE/mean of 4.0. With the exception of TCPP, the model tended to over-estimate water concentrations. Since the water concentrations were taken independently of the air concentrations, these results give some credence to the model estimates and show that the emissions estimates are accurate to approximately an order of magnitude. This indicates that aggregate air emissions are a major source of OPEs to the urban environment, including surface waters. In addition, surface waters receive loadings from wastewater treatment plants.

Estimated aggregate emissions to outdoor Toronto air of OPEs for 2010 ranged from 540 (EHDPP) to 7,900 (TPhP) kg/y and were significantly higher than emissions of Σ_5PCBs (240 kg/y) and Σ_5PBDEs (4 kg/y) for 2008, calculated using the same model (Table 1).

Table 1: Emissions to Toronto air of OPEs (2010), Σ_5PBDEs (-28, -47, -100, -154, -183, 2008) and Σ_5PCBs (-28, -52, -101, -153, -183, 2008) calculated from measured air concentrations using MUM. Emissions are shown per modelled area and per capita for the city of Toronto, as well as per year.

Compound	Emissions (kg/yr)	Emissions (mg/m²/yr)	Emissions (mg/ca/yr)[11]
TCPP	1,600	3	590
TCEP	2,300	4	820
TDCPP	1,000	2	370
EHDPP	540	1	200
TBEP	7,900	12	2,900
TPhP	2,300	4	850
Σ_6OPEs	15,700	25	5,700
Σ_5PBDEs	4	6.2E-03	1
Σ_5PCBs	230	3.6E-01	85

The high emissions of OPEs relative to PBDEs and PCBs are supported by the comparatively high levels of OPEs sampled in surface wipes of consumer products by Yang and co-workers[12]. Their work also showed that TBEP concentrations were significantly higher than those of other OPEs, which is consistent with the emission estimates.

We found that generally, Cl-OPEs with their high water solubility, were transferred from air to river water via rain washout and film washoff through storm water, followed by loss from water export (e.g., to Lake Ontario) with minimal accumulation in soils or sediment. In comparison, the less soluble non-Cl-OPEs, with the exception of TBEP, were estimated to be mainly lost via air advection. For example, 67% of total TPhP emissions to air were lost by air advection, with transformation being the next most important loss mechanism (Figure 1). By contrast, approximately 95 and 70% of total emissions to air of PCBs and PBDEs were previously estimated to be lost by air advection[6].
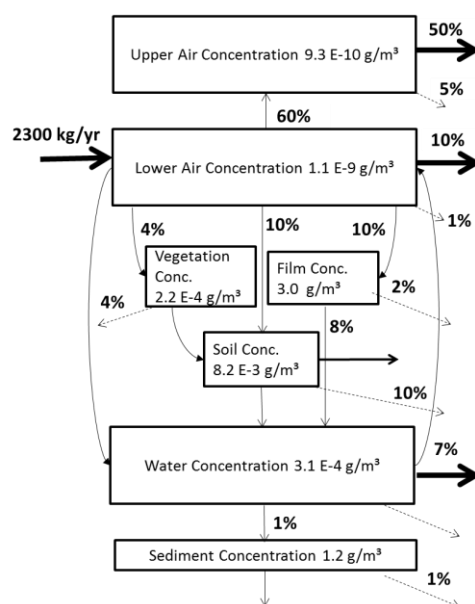

Figure 1: Emissions, distribution and fate of TPhP in Toronto, Ontario. All percentages are given as a percent of the total emissions (2,300 kg/yr). Degradation processes are shown as dashed lines.

OPEs proved to be more susceptible to transformation than PCBs or PBDEs. For OPEs, steady-state primary transformation ranged from 26 to 88 % of emissions for TPhP and TBEP, respectively, while for PCBs and PBDEs the maximum primary transformation was 2% of emissions. It is important to note that once transferred to water, OPE transformation was heavily curtailed, with less than 1% occurring in the water phase for any of the studied compounds.

These model estimates provide evidence of relatively high emission rates to air and, by showing OPE mobility in water, lend credence to the hypothesis of long-range transport of Cl-OPEs by rivers[9]. The major route of transfer for Cl-OPEs to surface water systems is through stormwater runoff, either through film or soil wash-off. Reduction of Cl-OPE inputs to surface water may be possible using control mechanisms enhancing infiltration or retention of storm water.

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