The Story of TCPP Indoors and Outdoors: Sources, Concentrations and Fate

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1. Introduction

Tris(chloropropyl) phosphate or TCPP is one of the most abundant organophosphate ester compounds (OPEs) reported in North American indoor and outdoor air, dust, and surface waters. As a flame retardant, it is added to rigid and flexible polyurethane foam used mainly in upholstered furniture, building insulation and automotive seating. TCPP has been recommended for designation as “toxic” under Canada’s Chemical Management Plan and subject to proposed risk management measures.

TCPP is a mixture comprised of four possible isomers of which one to three are typically found in the technical mixture and in which the tris(2-chloro isopropyl) phosphate (TCiPP) is the dominant isomer. Comparison of literature values is difficult due to inconsistent reporting of TCPP in environmental studies. Problems with comparing reported TCPP concentrations are compounded by its representation by eight CAS numbers.

Here we summarize a series of studies mostly conducted in the Greater Toronto Area in Ontario, Canada which we measured TCPP concentrations in residential indoor air using two types of passive air samplers, residential dust, outdoor urban air, urban rain and streams, and final effluent from waste water treatment plants (WWTP). We used outdoor urban air concentrations to estimate total TCPP emissions to outdoor air and the fate of TCPP in Toronto using the Multimedia Urban Model (MUM) of Diamond et al. (2001).

2. Materials and methods

Indoor measurements were obtained from a study of 51 homes (bedrooms and most used room) in the Greater Toronto and Ottawa areas. Air concentrations were obtained using polyurethane foam (PUF) and polydimethyl siloxane (PDMS) passive air samplers. Dust was collected from the floor by vacuuming into a nylon sock and sieved to <150 µm. Outdoor air was sampled in Toronto using a hi-volume air sampler over 6 months. Bulk water samples were taken from three urban streams during high and low flow periods as grabs. Rainwater was collected at one downtown location (University of Toronto) using a wet-only stainless steel funnel. Samples from three WWTP were collected as hourly grab samples composited over a 24-hour period. In addition, three samples of spray and rigid PUF insulation foam were analyzed for TCPP. All samples were extracted and analyzed by GC-MS using published methods with attention to QA/QC through the use of lab and field blanks and monitoring recoveries.

MUM was parameterized for the City of Toronto using published data. The model was run in “reverse mode” to back-calculate aggregate TCPP emissions to outdoor air based on measured outdoor concentrations (e.g., Diamond et al. 2010).

3. Results and discussion

3.1. TCPP Concentrations in Air, Dust, Surface Waters, Rain and WWTP

TCPP concentrations in indoor air comprised >60% of Σ_6OPEs measured (including TCPP). TCPP concentrations were nearly 400 times higher than Σ_{15}PBDE concentrations measured in the same homes. Indoor dust concentrations of TCPP were also high and dominated total OPE compounds.

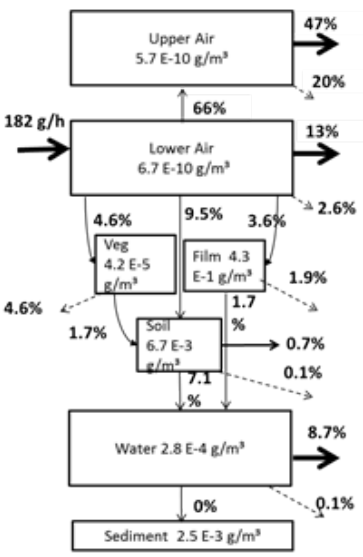
TCiPP was detected in 100, 75 and 100% of stream, rain and WWTP effluent samples. Stream concentrations reached µg/L levels at high flow. Median concentrations were not statistically different at low and high flows nor between the three streams sampled, indicating the diffuse nature of inputs. Rain concentrations, when assessed over the watershed, contributed significantly to stream inputs. Median and maximum concentrations of TCPP in final WWTP effluent were similar to those of streams.

TCPP concentrations in three samples of spray and rigid foam were 2.6% (7-year old rigid foam), 12% (new spray foam) and 26% (new spray foam). Air and dust concentrations from a heavily insulated home were elevated in comparison to the 51 homes sampled here.

Table 1: Concentrations of TCPP in indoor and outdoor air, streams, rain and final wastewater treatment plant effluent (WWTP) sampled in Toronto, Canada.

Medium	n	Median	Minimum	Maximum
Building insulation (%)	3		2.6	26
Indoor Air (pg/m^3)	90	18,000	4,000	105,500
Outdoor Air (pg/m^3)	21	716	165	1522
Streams (ng/L)				
Low flow	22	1000	340	1430
High flow	72	2280	430	5080
Rain	16	110	<DL	920
WWTP	25	2360	1200	4100

3.2. TCPP Fate in City of Toronto



We estimated total aggregate emissions of 180 g/h or ~1600 kg/y to Toronto's air. In comparison, we estimated aggregate emissions of 230 and 28 kg/y of Σ_{88}PCBs and Σ_{28}PBDEs to Toronto in 2009 (Csiszar et al. 2013).

As seen in Fig. 1, 60% of TCPP was estimated to be removed by air advection which less than that of PBDEs and PCBs (70 and 95%, respectively). Total losses due to degradative processes accounted for 30% of inputs. Due to TCPP's high solubility, 9% of total emissions to air were estimated to enter surface waters (streams) from soils, and accumulation and wash-off of surface films on impervious surfaces and vegetation. This input resulted in water concentrations comparable to those measured in this study.

4. Conclusions

TCPP is ubiquitous in all media sampled here, both indoors and outdoors. Sampling in a highly insulated home showed elevated levels of TCPP in air and dust where the insulation was the putative source. The relatively high vapour pressue of TCiPP of 0.035 Pa suggests that it can be released from products into which it is added and thus give rise to its abundance in indoor air.

In turn, indoor losses to outdoors, as well as other potential emissions, support its abundance in outdoor air. Modelling suggests that transfer from urban air is sufficient to supply urban streams with µg/L concentrations that could be of concern to aquatic biota.

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