

Exposure Workflows: Conceptual Workflow for PBDEs in Electronic Cases

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Context

We have been asked to develop a workflow for a chemical-product system that is data-rich and that can be used as a case study from which to learn how to advance exposure modelling methods. The context of the workflow development is two-fold. The first motivation for the work is to meet the needs of estimating exposures of chemicals of concern to which the public is exposed. A prime example here is of PFOS and PFOA and other long-chained PFAS that are known health hazards and to which human exposure is widespread. The second motivation is to advance methods used in Alternatives Assessment whereby alternatives are sought to reduce exposure to a chemical of concern in a product. The framework for Alternatives Assessment is provided by California's Safer Consumer Products Alternatives Analysis Guide (2017).

What product-chemical combination is considered?

The chemical-product system we have chosen is polybrominated diphenyl ethers (PBDEs) that were added to the exterior cases of electronic devices such as desktop and laptop computers. For the purpose of taking a Life Cycle Risk Assessment approach (Aissani et al. 2012), we have further narrowed the case study to PBDEs in external computer cases.

We have chosen this as a case study because of the availability of information across the life cycle and across the emission-to-exposure pathway. The case study considers multiple exposure pathways are included, from direct contact of hands touching casings, through to exposure via indoor air and dust, and far field exposure through diet. Across the product life cycle, the case study considers the use and End-of-Life (EoL) phases (although we are not aware of data pertinent to the manufacturing life cycle stage). Considerations at the EoL stage intersect with the large and vexing issue of e-waste handling. The EoL stage also presents the interesting situation of where PBDEs that may have been used in electronic cases have ended up in new products manufactured from recycled plastic, e.g., some food contact containers, toys, Samsonite and Puype 2015, Ionas et al. 2014). This situation opens the door to consider the linear vs circular economy, which is beyond the remit of this project, but should not be forgotten.

Finally, the case study is relevant to exposure across the human life cycle spanning fetal exposure from the mother who has been exposed, toddlers exposed by direct contact with electronic devices, mouthing activities of PBDE-containing objects and from the indoor environment, through to children and closing the circle with adults.

Goal: To develop a workflow to estimate external human exposure across age classes (the human life cycle), to PBDEs (all congeners) originating from use in external computer cases across the product life cycle.

What aspects of the decision context are emphasized in this example?

This case study is applicable to both Risk Assessment and an extended Life Cycle-Near and Far Field Assessment (Csiszar et al. 2016) or Life Cycle Risk Assessment (LCRA, Aissani et al. 2012) that can be used in the context of Alternatives Assessment. In terms of Risk Assessment, we present a detailed description of the product-emission-fate-exposure pathway that would allow for estimating exposures and applicable across the product life cycle from the use of EoL life cycle stages and for human age classes. For LCRA, the case study is relevant to numerous flame retardants and other additives to plastic polymers used in exterior plastic cases and covers of durable consumer goods, e.g., antioxidants, plasticizers. The case study could be applicable to reactive chemical additives to plastic polymers as well, e.g., tetrabromobisphenol A (TBBPA) which is the highest production volume flame retardant for use in electronics.

More broadly, the case study is useful for both Risk Assessment and Alternatives Assessment for considering neutral semi-volatile organic compounds (SVOCs) employed as additives to plastic polymers in consumer products used indoors.

Selected Chemical/Product: PBDEs in External Computer Cases - Background

Polybrominated diphenyl ethers or PBDEs, were produced as additive flame retardants for a wide variety of uses. All PBDE formulations saw the greatest use in North America. Penta-BDE was used most in polyurethane foam used in upholstered furniture, but also saw use (2% of total use) in electrical and electronic products including cases of consumer electronic products, e.g., laptops, desktop computers (Abbasi et al. 2015). About 35% of Deca-BDE, the formulation with the greatest total production, was used in electrical and electronic casings. Due to the ubiquitous distribution of all PBDEs in virtually all media at a global scale, and mounting evidence of their ability to harm human health, Penta- and Octa-BDEs were phased out of use in 2004 in the US followed by Canada, and Deca-BDE was phased out in the US in 2009 (Blum et al. 2019). The strongest evidence for harm is for BDE-47 (US NAS 2017), the major congener of the Penta formulation, but even the high molecular weight BDE-209 in Deca-BDE has been shown to cross the placental barrier.

Although the use of these chemicals has been restricted in *new* products, PBDE-containing products continue to be used in homes and workplaces as a function of the life-span of that product, e.g., desktop computers have an average lifespan of 12.5 years (US EPA 2011). Environmental levels of PBDEs have declined, but they continue to be found globally in air, water and the food supply. Indoors, PBDEs continue to be measured at high levels relative to the replacement brominated flame retardants (Yang and Jilkova et al. in review, *inter alia*). Biomonitoring studies show that levels, particularly of Penta-BDE, have declined considerably since peak usage, but are still widely measured in the general population (Sjödin et al. 2019). Whereas exposures to the general population have decreased, e-waste dismantlers are currently

exposed to relatively high levels of PBDEs and will continue to be exposed for many years (Nguyen et al. 2019 *inter alia*).

Numerous studies have documented diverse aspects of PBDEs, from occurrence (including temporal and geographic trends), to fate processes indoors and outdoors, presence in diet, human exposure in terms of estimated external dose, and measured internal dose from biomonitoring studies (e.g., Blum et al. 2019 *inter alia*). The physical-chemical properties of PBDEs are relatively well known. The stocks and flows of PBDEs in North America have also been estimated (Abbasi et al. 2015). Emission estimates have been made from measurements and modelling, from the scale of products (Zhang et al. 2009; Rauert et al. 2015) to emissions at a city-wide scale (Csiszar et al. 2013a, b).

PBDEs can be considered as a compound class for the purpose of developing a workflow. However modelling PBDEs requires that specific congeners be considered because they span a wide range of physical-chemical properties and thus fate pathways, and also vary in toxicity. Briefly, the higher congeners (e.g., BDE-28) in Penta-BDE are found mostly in the gas phase whereas BDE-209, the main constituent of Deca-BDE, is found almost entirely in condensed phases.

Life Cycle Risk Assessment Approach

Life-cycle Segments and Exposure Potential

Figure 1 illustrates the considered life-cycle stages from product manufacturing to EoL, as well as the exposure pathways and affected populations. We have not included packaging, transportation, and distribution life cycle stages because these segments are not expected to influence the outcome. We assume that the case study takes place in North America.

At this stage we have focused on adult exposure. A more complete assessment needs to include exposures across all age classes to account for the greater vulnerability during fetal exposure and higher exposures to toddlers.

Manufacturing of PBDEs and their incorporation into computer cases can result in releases of these compounds to indoor air and outdoor ambient air, followed by multimedia partitioning. During the manufacturing phase, workers and surrounding communities would be at risk of exposure. For the latter population, exposure potential will be largely location-dependent.

Most information is available for the *use phase*. We assume, but have not tested the assumption, that the product use phase dominates the life cycle impacts of PBDEs in computer cases because of the ~decade long life span of these products (US EPA 2011). Further, these products may “hibernate” in the home before entering the EoL phase, bring the total span within the home of perhaps 10-20 years. The longevity of PBDEs in computer cases is accentuated by the high K_{OA} which implies that they largely partition to condensed-phase reservoirs, such as polyurethane foam or textiles, from which they can be re-emitted after source removal (Zhang et al. 2009).

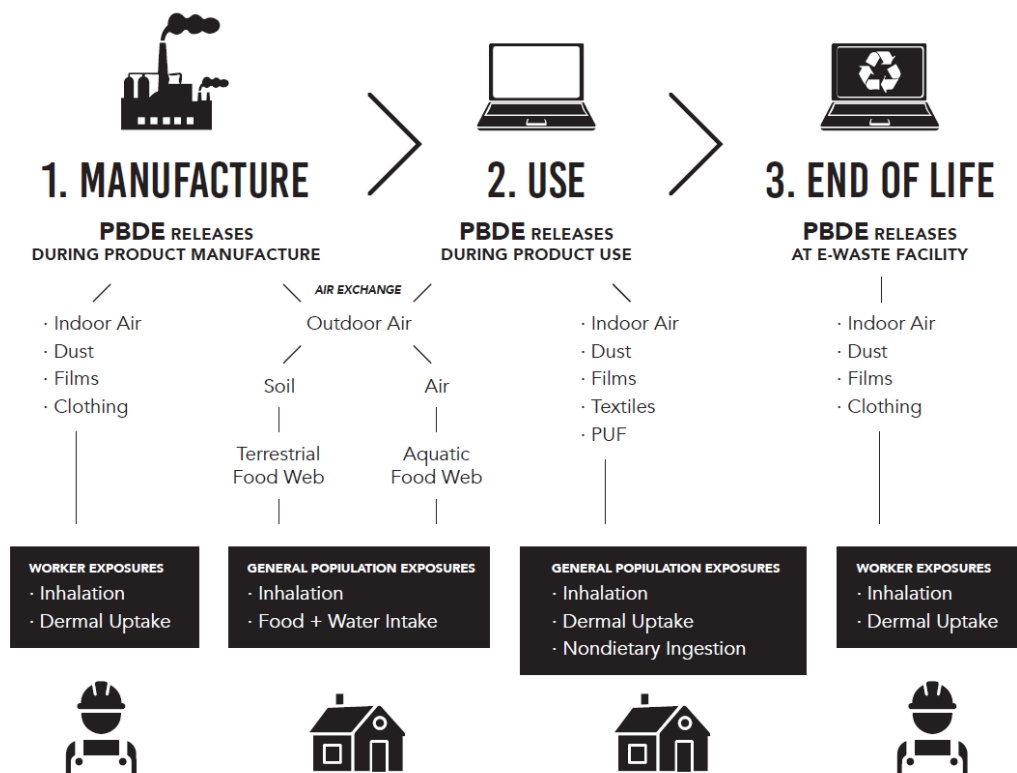


Figure 1. PBDE exposure pathways across the life cycle for a computer product assuming an adult receptor.

The general population throughout the human life cycle, including office workers, would be subject to exposure during this phase. Exposure levels will depend on consumer purchasing habits, indoor human activities, and/or housing characteristics (e.g., air-exchange rate). Therefore, exposure variability will be important to characterize using probabilistic methods.

At *EoL*, occupational exposures of e-waste recyclers would be of concern. Abassi et al. (2015) estimated that 10,000 tonnes of PBDEs entered the *EoL* phase between 2005 and 2008 and would decline at 4-12% annual until 2020, the end of their simulation period. Nguyen et al. (2019) found that BDE-209 had the highest air and dust concentrations of a range of brominated and organophosphate flame retardants in an Ontario e-waste facility and thus contributed most to total exposure.

EoL also presents opportunities for PBDE release to the environment and hence far field exposure from electronics improperly disposed of in landfills (Stubbings and Harrad 2016) and from informal e-waste dismantling (e.g., Someya et al. 2016).

Proposed Workflow for Life Cycle Risk Assessment Approach

Figure 2 illustrates the conceptual workflow for estimating human exposure across the life cycle through modeling. PBDEs are no longer used in external casings of computers and as far as we know, and Penta- and Octa-BDE mixtures are no longer produced. However, we have kept the workflow comprehensive so that it can be used for “current use” plastic additives, i.e., we have kept the manufacturing life cycle stage. The other reason to include the manufacturing stage is that locations of PBDE manufacturing have or may be contaminated as a legacy to part production and part of today’s environment burden can be attributed to past manufacturing. The issue of legacy contamination from past manufacturing is of great importance for PFOS, PFOA and, to go further back into history, PCBs and now-banned legacy pesticides.

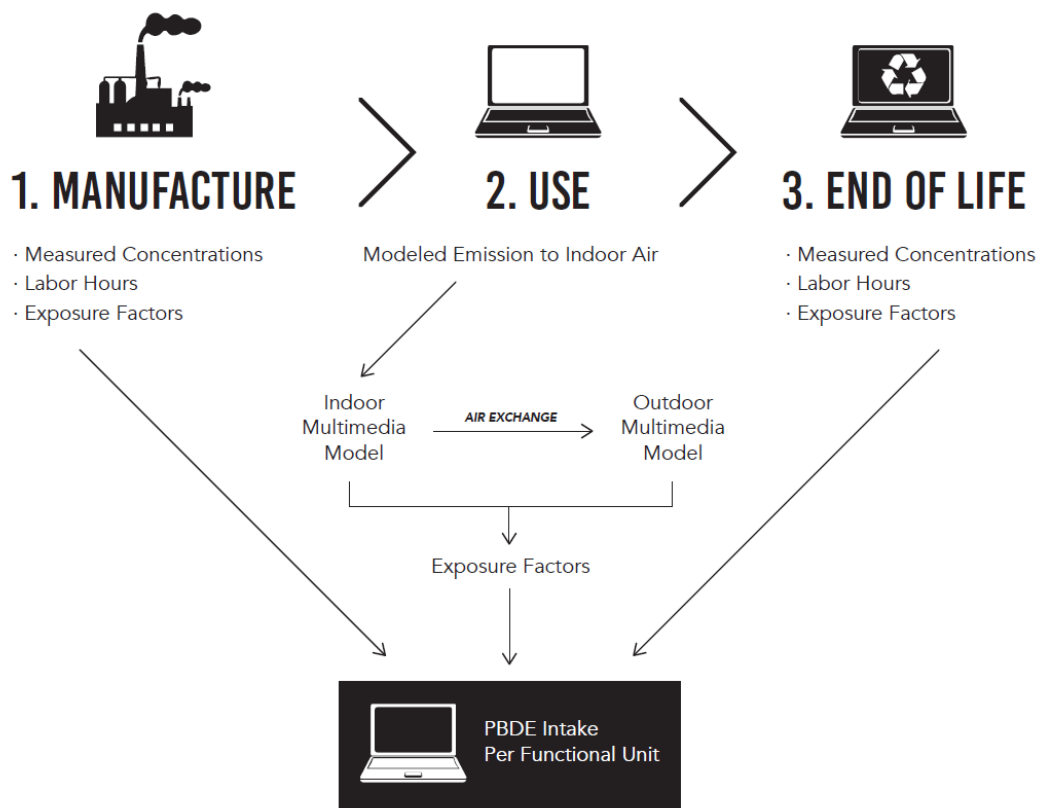


Figure 2. Scientific workflow for estimating human exposure to PBDEs per functional unit across the product life cycle and assuming an adult receptor.

To facilitate comparing exposures in the context of LCRA and Chemical Alternatives Assessment, we will adopt a product-oriented approach, as opposed to a receptor-oriented approach that would be more suitable for risk-assessment applications. From this perspective, we will quantify human exposure to the chemicals of interest per a defined unit of product function. We define this “functional unit” as one computer used over five years, based on the average lifespan of consumer desktop PCs in the United States (Statistica 2020, US EPA 2011). This approach assumes that the production rate of computers would remain constant between chemical alternatives.

The final stage of the workflow is converting external exposure to internal exposure and doing this across age classes from fetal exposure to toddler, children and adults. The workflow would thus include a simple pharmacokinetic model to account for differing half-lives of PBDE congeners (e.g., Wong et al. 2013, Gyalpo et al. 2015).

We present a two-tiered exposure assessment. The goal of Tier I is to obtain order-of-magnitude estimates of exposure potential across the product life cycle, from manufacture to EoL phases. Results from Tier I will help us focus our efforts on the most important life-cycle segments in a more-detailed Tier II assessment.

Tier I Exposure Assessment

Manufacture phase. The manufacturing of thermoplastics, such as acrylonitrile butadiene styrene (ABS) used for computer casings, consists of three phases: manufacturing polymers and chemical additives, compounding polymer resins and chemical additives, and converting the compounded plastic into finished products (US EPA 2014a; 2014b). We are aware of one study in which Deca-BDE levels were measured in air and workers serum and urine in a chemical plant that manufactured 5000 tons of Deca-BDE annually in China (Wang D et al. 2019).

Emission factors for specific manufacturing processes are generally unknown, and work environments are largely heterogeneous with respect to characteristic parameters such as ventilation rate and geometry. Therefore, we propose to adopt an approach presented by Kijko et al. (2015; 2016) that uses measured (as opposed to modelled) concentrations as a point of departure for estimating occupational exposures, coupled with labour hours per functional unit.

Data on measured concentrations for hundreds of chemicals and sectors are routinely made available by the US Occupational Safety & Health Administration (OSHA 2020).

We will estimate labour hours and other exposure factors based on information provided in two reports drafted by US EPA (2014a; 2014b). These reports include manufacturing process descriptions, typical weight fractions of flame-retardant additives in ABS, the number of workers potentially exposed, and other relevant exposure factors. This information is suitable for deriving conservative, screening-level assessments of occupational exposures for the thermoplastics manufacturing industry. The resulting estimates of chemical intake per functional unit can then be compared with other life-cycle segments.

Use phase. We will use an integrated modeling approach to estimate near-field and far-field exposures throughout the use phase of the product. This approach will involve combining two fugacity-based, multimedia mass-balance models. Some physical-chemical properties (e.g., equilibrium partition coefficients, vapour pressure, molecular weight) will be obtained from the CompTox Chemicals Dashboard (US EPA 2020), while others (e.g., half-lives) from estimation programs such as CATALOGIC. Half-lives for PBDE congeners in humans can be taken from the literature (e.g., Wong et al. 2013).

The first model, known as ICECRM (Zhang et al., 2014), is parameterized to represent a single-room North American residence, and includes a human adult in the mass balance. We will apply a steady-state emission rate from the product to the indoor air compartment. PBDEs are emitted

from computer cases according to three main processes as discussed below (Rauert et al. 2015). We will use the parameterized ICECRM model to estimate human exposure, integrated over five years, through inhalation, dermal uptake, and nondietary ingestion. We suggest extending model estimates to consider external exposure across human age classes.

The product of the steady-state chemical fugacity in indoor air and the air-exchange rate will then be used to assess chemical transport and fate in an outdoor evaluative environment, including bioaccumulation and biomagnification in aquatic, terrestrial and agricultural food webs. For this, we will employ the RAIDAR model to estimate human exposure, integrated over five years, from consumption of drinking water and contaminated food, and inhalation of outdoor, air, e.g., Arnot et al. (2010), Li et al. (2018).

End-of-life phase. We will use a similar approach to estimate occupational exposures during the end-of-life phase as for the manufacture phase. For this, we propose to use data on measured workplace concentrations and labour hours per functional unit from studies that we have conducted in Ontario and Quebec, Canada (Nguyen et al. 2019; Nguyen et al., in-prep). Estill et al. (2020) have published data on worker exposure to PBDEs in a US facility. Assumptions will be required to translate measured PBDE levels in e-waste dismantling facilities according to the functional unit considered here which is one computer.

We have not considered far field exposure arising from PBDE emissions from the recycling process. We have estimated the release of a total of 79 flame retardants from the Ontario recycling facility mentioned above of 140 and 310 ng kg⁻¹ day⁻¹ to the air and 9400 to 25,000 ng kg⁻¹ day⁻¹ to the dust. This amounts to a total mass released to air of 4 ± 1 mg day⁻¹ and 270 ± 91 mg day⁻¹ released to dust where the latter is deposited in landfill (Stubbings et al. 2019). Without question, releases of PBDEs from informal e-waste facilities located in low and middle-income countries is a source of local to regional contamination of the environment and food supply (e.g., Labunska et al. 2014).

Tier II Exposure Assessment

Results from the Tier I exposure assessment will inform the choice of which life-cycle stage(s) to further evaluate using more-detailed methods. Tier I exposure assessment is also useful for obtaining the central tendency and a measure of dispersion based on ranges of parameter values.

Recent evidence suggests that typical occupant activities can induce short-term variation in exposure to SVOCs (Wu et al., 2018; Lunderberg et al., 2019). Such variation would not be adequately captured by time-averaged and/or steady-state modeling approaches (Kvasnicka et al., in prep). Variations that lead to particularly high exposures may also not be captured. Therefore, improvements under the Tier II assessment would include the use of dynamic modeling with probabilistic (Monte Carlo) methods to characterize intra- and interindividual variability of occupant exposures.

The model that we would use for this assessment is known as the Activity-Based Indoor Chemical Assessment Model (ABICAM). This model extends the ICECRM framework by numerically integrating mass-balance equations that are parameterized as functions of time-dependent activities (Kvasnicka et al., in prep). The primary additional data requirement of

ABICAM are occupant activities in the form of a schedule or “activity diary.” Brandon et al., developed an agent-based model to simulate longitudinal (year-long) patterns of occupant activities (Brandon et al., 2018). However, their model evaluation suggested that the longitudinal component did not significantly contribute additional variance for a general set of activities (Brandon et al., 2019). Therefore, we would consider shorter (24-hour) periods by randomly sampling activity diaries from existing data bases (e.g., Consolidated Human Activities Database; American Time Use Survey) and comparing weekends vs. weekdays, and different seasons.

We would also leverage the Residential Population Generator (RPGen) module, which was developed by US EPA in the R programming language (www.r-project.org) as part of the Human Exposure Model (Dionisio et al., 2018). Specifically, we would use RPGen to produce a random sample of occupant and housing characteristics (e.g., age and sex of occupant, square footage of residence, number of computers used, etc.). These samples would then be used as inputs to ABICAM to simulate a distribution of PBDE intakes during the use phase. Including such variability would allow us to consider the upper tails of population exposure distributions where health risks may be most important.

ABICAM would be applied to predict external exposure across the human life cycle. In fact, here ABICAM is particularly useful for mechanistically accounting for increased exposure of toddlers due to specific behaviours. For example, Ionas et al. (2016) have estimated PBDE exposure from toddlers mouthing PBDE-containing toys.

Finally, a pharmacokinetic model needs to be added to this workflow to translate external to internal dose. Estimated internal doses cannot be used for model evaluation against biomonitoring data given the problem formulation according to a functional unit. However, well vetted pharmacokinetic models could be employed (e.g., Verner et al. 2015).

Application of the Life Cycle Risk Assessment for PBDEs in Computer Cases

Table 1 summarizes the data needed and models that could be used in the workflow. Prior to embarking on the workflow, decisions need to be made to bound the model domain temporally and geographically for near field and far field estimates. We recommend applying the model to the Great Lakes basin given the abundance of data.

Diet can be considered by modelling, as done by Li et al. (2020). Alternatively, measured levels of PBDEs in foods (Boucher et al. 2018), as done in some exposure assessments (e.g., Jones-Otazo et al. 2005, Johnson-Restrepo and Kannan 2009). The advantage of using measured food concentrations is obtaining a more realistic assessment of dietary exposure that includes PBDEs entering the food supply from the agricultural system and food handling. But taking the latter approach would “disconnect” the dietary intake from the LCRA approach that considers incremental exposure from the functional unit.

Proposed Workflow for Risk Assessment Approach

Considering chemical exposure according to a functional unit allows consideration of chemical alternatives and understanding the key life cycle stages and processes that should be considered. However, taking such an approach misses the importance of the growth of the stock of the

chemical over time in both products and the environment, where the latter is especially important for persistent compounds that accumulate in the environment. Harrad and Diamond (2006) hypothesized that the importance of considering time trends is that the relative importance and magnitude of exposures from near vs far field change over time for a persistent compound. Bramewell et al. (2016) found support for this hypothesis by reviewing the literature and Li et al. (2020) showed the shift from near to far-field exposure to PBDEs over time using the model PROTEX (PROduction to Exposure) model.

Figure 3 provides a conceptual diagram for taking a risk assessment approach that threads together the life cycle stages and dimensions of time and space for PBDEs in all computer cases. Here the domain could be all of North America or the Great Lakes basin (e.g., Abbasi et al. 2015).

The problem formulation can be simplified by considering the total mass or stock of PBDEs in computer cases at each product life cycle stage as a snap-shot in time, e.g., total stock of PBDEs in the use phase in 2020. A more complex solution considers changes over time where the stock reflects changes in chemical production, chemical usage in that product, product usage and movement of the product from the use to EoL phase.

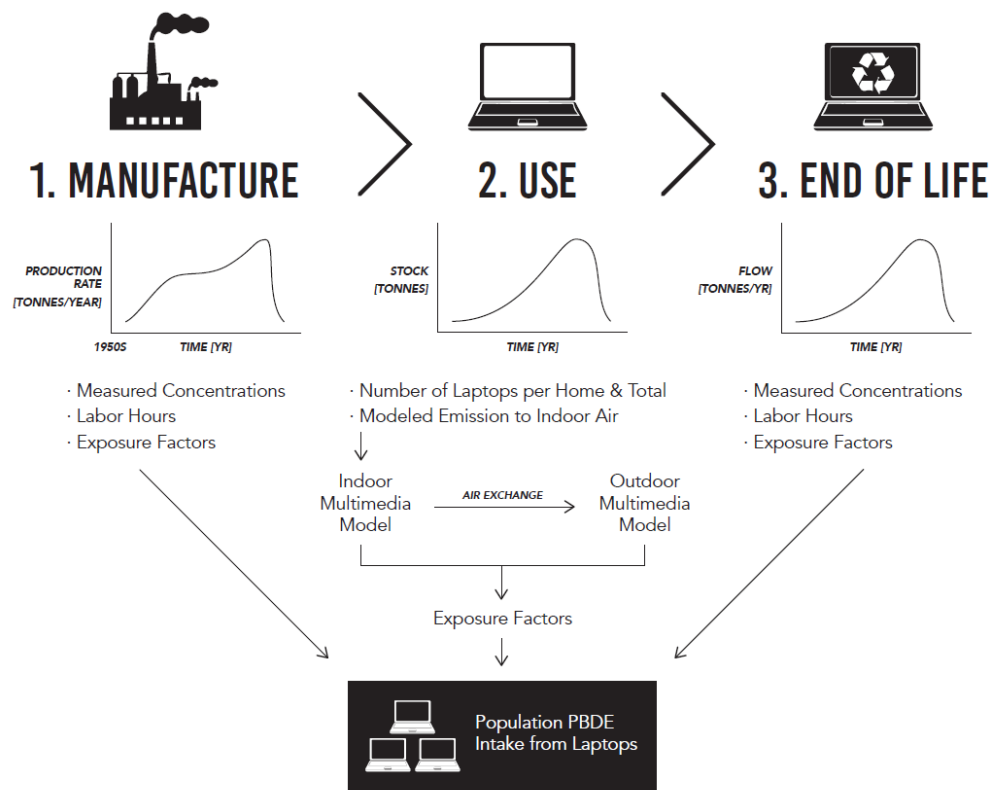


Figure 3. Scientific workflow for estimating population PBDE intake across the product life cycle.

We note that within the use phase, the stock of PBDEs in computer cases grows and declines at an aggregate societal scale, but also at the scale of individual homes and workplaces, as discussed by Ryen et al. (2015). They quantified the accumulation over time of in-use and “hibernating” electronic products within households with implications for resource use.

Space, or the geographic dimension, could be considered for completeness. Electronic supply chains are characterized by complex networks. Raw materials and flame retardant production may happen in Country A, electronic device assembly in Country B, use in Country C, and EoL of products from Country C may occur in Countries C, D and F.

Another important facet of this analysis comes in better accounting for age-specific exposure. For example, mother’s exposure controls fetal exposure with important implications for toxicological outcomes. Infants can receive the greatest exposure of all age classes (per kg body weight) as a result breast feeding. Toddlers receive elevated exposures due to increased inhalation of airborne PBDEs due to crawling, increased exposure from hand-to-mouth transfer and from mouthing PBDE-containing toys and textiles. The magnitude of all these exposures is, of course, a product of indoor levels that change over time, and the prevalence of PBDE-containing products.

Li et al. (2020) provide a workflow for considering this case study (**Figure 4**). Their workflow considers PBDEs in electrical and electronic equipment, polyurethane foams, textiles, automobiles, and construction materials in southern Ontario. They modelled BDE-47, -99, -153, and -209.

Model estimates along the workflow can be evaluated against measured data that vary according to date of collection and location.

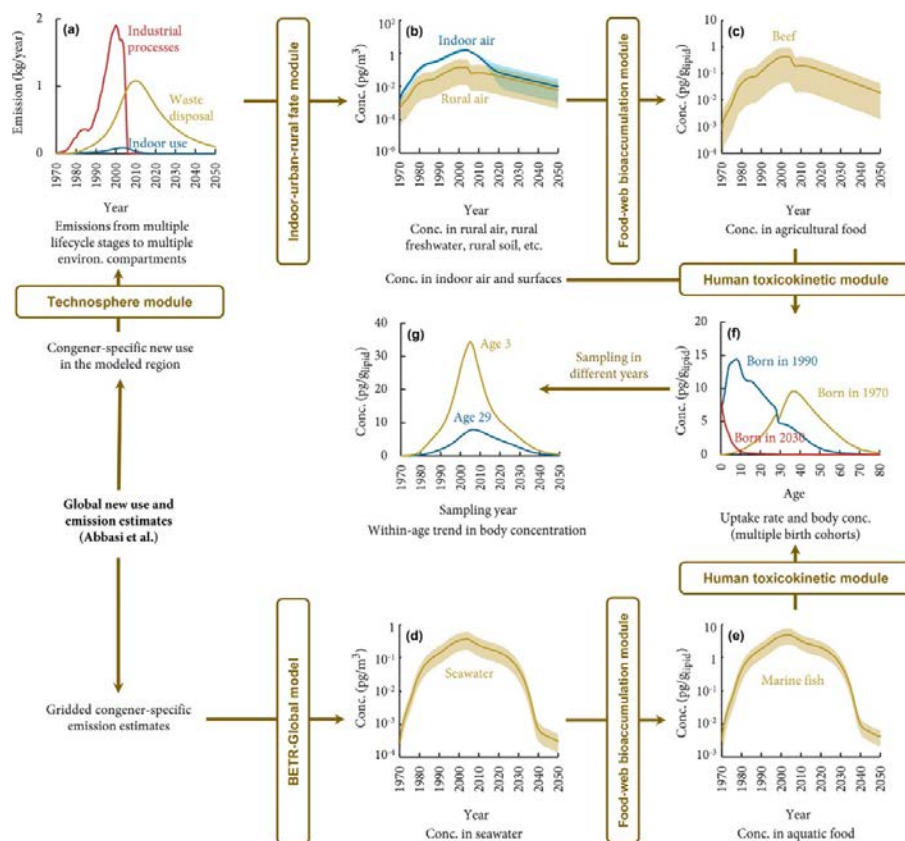


Figure 4. Conceptual diagram showing the components of the PROTEx model as applied here to BDE-153. Taken from Li et al. (2020). The model produces time-dependent emissions from a “technosphere” model (e.g., material flow of PBDEs in products), a nested indoor-urban-rural fate model to estimate indoor and far field concentrations, a food web model to estimate concentrations in agricultural and aquatic food webs, and a toxicokinetic module that calculates the lifetime uptake rates and body concentrations of individuals according to specific birth cohorts.

Identification of Relevant Factors

The following factors should be considered based on their likelihood of making a material contribution to human exposure and having a material difference on such exposure from the PBDEs in computer cases scenario:

- **Physical-chemical properties** have been shown to largely govern the behaviour of SVOCs in general, and PBDEs specifically, once released into the environment and as such, exposure pathways indoors, outdoors and through diet.
- **Product life cycle stages** where each life cycle stage may take place in a different geographic location and where PBDE mobility might differ.
- **Product performance / lifespan** for the use stage controls the rate at which products containing PBDEs transition from the use phase to EoL phase and the length of time expected for exposure in both life cycle stages.

- **Environmental fate** indoors and outdoors will be determined by physical-chemical properties, transport and transformation pathways, and characteristics of the receiving environment. Environmental fate outdoors, along with persistence, influence the incorporation of PBDEs into the food supply through bioaccumulation.
- **Environmental persistence** leading to accumulation and losses over time from all relevant environmental compartments. Here we need to consider persistence indoors after the PBDE-containing computer is removed. We also need to consider persistence outdoors which influences the time-course of PBDEs in the food supply.
- **Bioaccumulative potential** which influences the accumulation of PBDEs in various trophic levels of the agricultural food web, including livestock. We also need to consider PBDE accumulation in wild populations as well, since they are food sources for some indigenous people who constitute a vulnerable population.
- **Product use scenarios** that control whether and which human receptor comes in direct contact with the product or not, where we consider age classes and non-occupational and occupational exposure. For example, children and adults come in direct contact with a computer during the use phase and occupational workers are in direct contact with all these products during manufacturing and dismantling. Each age class-life cycle stage combination can emphasize different exposure pathways.
- **Flammability Standards** dictate the use of flame retardants in external electronic cases. The standards do not specify which flame retardant can be used, but rather specify a performance standard. Some flammability standards are written into legislation and are legally binding whereas others are subject to manufacturers' voluntary compliance. We do not go into this further but note that the banning of the use of halogenated flame retardants in newly manufactured external electronic cases is moving forward in the US through the U.S. Consumer Product Safety Commission's decision in 2017 and the European Union in 2018 (came into force in 2019) (Blum et al. 2019).

A note about Exposure and Emissions

Detailed information is available to inform our understanding of exposure mechanisms and the relevant emissions. Emission rates are usually the most difficult data to obtain. Below we review exposure pathways as related to data needs.

1. *Exposure from direct contact with the PBDE-containing e-case.* We are not aware of studies that show this directly other than an estimate of children mouthing PBDE-containing toys (Ionas et al. 2016). We do know that PBDEs are easily removed from surface wipes of computer cases. Abbasi et al. (2016) discussed this with respect to exposure potential. Yang et al. (2019) found a correlation between concentrations of abundant organophosphate ester metabolites wiped from mobile phone cases and the corresponding urinary metabolite of the mobile phone owner, where hand-to-mouth and dermal transfer are the putative mechanism. By analogy, we hypothesize that PBDE exposure could be from the product casing to hands. Watkins et al. (2011) showed a significant relationship between PBDEs on hands and biomonitoring levels. *We are not aware of a factor or emission rate for direct transfer.*

2. *Exposure via indoor air and dust.* Relevant emission rates here are either product-specific (LCRA) or aggregate to indoor environment (Risk Assessment).

Indoor air contributes minimally to PBDE exposure because of low levels in the air phase. The latter is because of their low vapour pressures/ K_{OA} and because of low levels of inhalable particles indoors.

Dust can contribute to exposure by adherence on skin followed by dermal transfer. Exposure also occurs through dust ingestion. PBDEs in dust originate from three mechanisms listed here in terms of relative importance as summarized by Rauert et al. (2015a):

a. PBDE transfer via direct contact with dust either on the surface of the product or in the interior that is expelled from a computer when the fan runs (e.g., Suzuki et al. 2009, Takagami et al. 2008, Rauert et al. 2014, 2015a) noting that dust coming from within a computer can be highly contaminated. The process of surface-to-dust transfer can be modelled based on knowledge of PBDE concentration on the surface of the product (Abbasi et al. 2016, Yang and Jilkova et al., in review) and dust characteristics.

b. Abrasion of fine particles containing PBDEs from the surface of the casing (Webster et al. 2009) noting that although levels could be high, the PBDEs may not be bioaccessible because of occlusion within the polymer matrix. We are not aware of emissions data for this mechanism.

c. Volatilization of PBDEs from the polymer surface followed by partitioning to dust (Rauert et al. 2014, 2015) where those PBDEs would presumably have high bioaccessibility. Kemmelein et al. (2003) measured emissions (specific emission rates or SER_a , $ng\ m^{-2}\ h^{-1}$) of PBDEs from a TV housing and printed circuit board using a chamber. Emissions from the printed circuit board did not decrease over 115 days.

Another approach to estimate volatilization emissions would be from the estimated concentration of the chemical in the air immediately adjacent to the product surface. We could be derived from the estimated concentration or weight fraction of the chemical in the product (e.g., Abbasi et al. 2015), assuming it is constant and homogeneously-distributed, and the product-air partition coefficient (Li et al., 2018). However, this assumption is questionable. Surface wipes of electronic devices indicate low levels of a wide variety of flame retardants and plasticizers suggesting, a. depletion of the plastic additive from the surface of older electronic cases, and b. accumulation of flame retardants and other chemicals from other indoor sources (Yang et al. 2019, Yang and Jilkova et al., in review).

Zhang et al. (2009) estimated emission rates for Penta-BDE congeners in Stuart Harrad's office at the University of Birmingham, where concentrations he measured a 80% decrease after he switched out his Mac laptop for a newer version. Zhang et al. derived the emission rates using the Multimedia Indoor Model, back-calculating from measured air concentrations, while accounting for PBDEs in the carpet and PUF cushions of Stuart's decrepit office chairs. Others such as Batterman et al. have also approximated aggregate indoor emissions.

Exposure can also occur via PBDE-contaminated clothing where the PBDEs would originate from ambient air and dust levels (PBDEs were not intentionally added to clothing textiles).

Although cotton and polyester accumulate PBDEs (Saini et al. 2016 a,b) and they are poorly removed by laundering (Saini et al. 2016c), dermal transfer is low (Abdallah et al. 2015). Dermal contact with PBDE-treated textiles covering upholstered furniture could be a source of exposure (e.g., Abdallah and Harrad 2018).

3. *Emissions to the outdoor urban environment.* Emissions to the outdoor environment also have been using reverse modelling methods. Csiszar et al. (2013) reported congeners specific aggregate emissions to the air of the City of Toronto of $\Sigma 26$ PBDEs were 28 (6–63) kg y⁻¹, 34 (7–77) g y⁻¹ km⁻², or 11 (2–25) mg y⁻¹ capita⁻¹. They also approximated emissions at 0.01% of the PBDE inventory of Toronto, acknowledging that this inventory was incomplete. However, that emission rate is close to that of PCBs of 0.04% of the PCB inventory where the latter was relatively complete.

Guidelines for selecting data

First, we acknowledge that information must be reliable where this has been discussed by US EPA (1999) and will not be covered here.

We suggest the following criteria to guide data selection:

1. Measurements of PBDEs in various media for use in model evaluation.

a. Sound QA/QC. Early measurements of PBDEs suffered from analytical uncertainties, especially for deca-BDE congeners. To decide on the use of measured data, the study needs to be reviewed for the use of QA/QC procedures such as clear methods for taking lab and field blanks, lab correction, recovery correction, etc.

b. Review of detection limits and handling of “no detect’s”.

2. Data used for model parameterization. Examples:

- PBDE-specific data, e.g., PBDE concentrations in computer cases, PBDE emissions, physical-chemical properties.
- Generic data, e.g., environmental and receptor characteristics, mass transfer coefficients, rates of advection, deposition.

Clearly, well vetted data need to be used in all cases. Models used within the proposed workflows contain generic data that would need to be reviewed for their appropriateness to the workflow goals.

What to do about data gaps, uncertainties and incongruences

This case study was chosen because it is data-rich. For example, physical-chemical properties, both measured and modelled, are known with high confidence. However many data gaps exist. General guidance documents exist for dealing with data uncertainties, e.g., IPSC (2008). Gaps need to be filled using vetted methods such as extrapolation or interpolation from other data and ultimately, the use of a lot of professional judgement. Assessing whether the assumed data are reasonable requires model evaluation against measured data and sensitivity and uncertainty analyses.

Filling data gaps needs to be prioritized according to the sensitivity of the outcome to the missing data. The process used to fill the gaps will depend on the type of data missing and the congener considered, i.e., more volatile congeners will be more sensitive to parameters that influence gas-phase concentrations. Here we discuss the sensitivity of the indoor, near field fate model in terms of its sensitivity.

Zhang et al. (2009) conducted a sensitivity analysis for the fate of PBDEs indoors. They found that model estimates were most sensitive to (in descending order of importance):

- Emissions
- Temperature with its effects on vapour pressure and hence gas-particle partitioning
- Particle concentrations indoors
- Vertical particle deposition rate
- K_{OA}

The model was also sensitive to (again in decreasing order of sensitivity): air exchange rate, resuspension rate, fraction of organic carbon in particles, particle-air partition coefficient, vapour pressure, carpet-air partition coefficient and area of PUF. Most of these data are relatively well known, with the exceptions of emissions and carpet-air partition coefficient. We have discussed sources of emission data herein.

And while on the topic of model sensitivity, the indoor fate model is also sensitive to the assumption of instantaneous equilibrium between gas and condensed phases, especially for congeners with values of $K_{OA} > 12$ (Weschler and Nazaroff 2010). Here, the data gap is the kinetics of gas-particle partition, however inclusion of this as a submodel significantly increases model complexity and data demands.

Approaches for using home dust data

Many studies have reported levels of PBDEs in indoor dust in North America and globally, starting with Wilford et al. (2005) for Ontario, Canada. PBDE concentrations in dust have been directly related to biomonitoring levels (e.g., Stapleton et al. 2008).

Levels of PBDEs in indoor dust can be used to:

- a. Estimate exposure directly from dust ingestion and adherence of dust to skin followed by dermal transfer using methods summarized by US EPA. Numerous authors have done this for residential settings (e.g., Jones-Otazo et al. 2005 and more) and Nguyen et al. (2019) have done this for PBDE exposure to e-waste dismantlers in Ontario.
- b. Estimate air concentrations and overall indoor fate from which all indoor exposure routes can be considered (e.g., partitioning from air-to-skin, inhalation). Here it is important to consider that whereas dust/air (gas phase) follows expectations of partitioning according to vapour pressure or K_{OA} this holds only until $\sim \log K_{OA} 11$, after which empirically derived dust/air distribution

coefficients level off (Zhang et al. 2011). We also note that air-to-skin and inhalation present minor exposure routes.

Generalizing the Workflow.

We have presented a workflow specific to PBDE in computer cases but that can be generalized for SVOC additives to plastic polymers used in consumer products. Applications SVOCs other than PBDEs in computer cases would differ by data sources and physical-chemical properties.

The proposed framework would leverage existing models to evaluate human exposures across the product life cycle, using a common functional unit for comparison between chemical alternatives. The use of mechanistic, as opposed to empirical models, can allow for a generalizable framework that can be adapted to different decision contexts. We propose two ideas to further generalize the proposed framework.

Many multimedia-based environmental models have been developed and made publicly available by various organizations for different purposes, yet have similar, and in some cases overlapping, data requirements and modeling components. One idea is to reach consensus on and merge existing modeling components across these models into a common library in an open-source, object-oriented programming (OOP) language, such as Python (www.python.org). Such a library can incorporate organizational features of OOP (e.g., classes and inheritance) by wrapping the smallest units of employable code into individual functions that can be rapidly implemented for different decision contexts, based on a set of user-defined conditions. One potential challenge of this approach, however, is that individuals may have different preferences for models, which would make it difficult to reach consensus on a harmonized library.

An alternative approach would be to combine the predictions of multiple models together to make more-defendable modeling predictions. For instance, one could create a wrapper in Python that can load individual models from their original languages (e.g., Visual Basic for Applications), and then run all models in aggregate with a common set of input parameterization to produce a distribution of outputs. This approach is analogous to the concept of “bagging” in the machine-learning literature (Breiman 1996). In theory, by capturing *model* uncertainty, this distribution would represent the current scientific understanding among the environmental-modeling community. A central tendency (e.g., a median) of such a distribution may be a more-justifiable basis for decision-making, as opposed to the output of any individual model. Furthermore, if a more-complex distribution shape (e.g., bimodal) is observed, it would be worth investigating the reasons for such a shape.

Table 1. Summary of data needed, data sources and models that could be used to execute the workflow for PBDEs in computer cases.

Part of Workflow	Data needed	Data and/or models	Notes
All mechanistic chemical models	Physical-chemical properties	<ul style="list-style-type: none"> • CompTox Chemicals Dashboard (U.S. EPA) • Measured data 	Preference for measured vs predicted depends on use of data. Preference for “Final Adjusted Values” for use in models, especially for nona- and deca-BDE congeners for which measured VP, Koa, Kow etc are uncertain
Manufacturing, far field	Manufacturing facility releases to air, water, land	<ul style="list-style-type: none"> • Not aware of measured data for either PBDE synthesis or computer case manufacturing • Use model such as US EPA’s ChemSTEER? 	Estimates needed as inputs (emissions) to model of outdoor environmental fate
Manufacturing, near field	Releases to indoor occupational environment	<ul style="list-style-type: none"> • Measured data for DecaBDE chemical synthesis (Wang D. et al. 2019) • See above. 	To estimate exposure to workers manufacturing and assembling external electronic cases. Most activity occurs “off shore”
Use stage, far field	Total time-dependent stock of PBDE-e-cases	<ul style="list-style-type: none"> • Material flow analysis of 1. Computer products, 2. PBDEs in computer products • See Abbasi et al. 2015 	Used to estimate aggregate time-dependent emissions to environment Also used to estimate flow of e-products to EoL
	Aggregate emissions to environment	<ul style="list-style-type: none"> • Multimedia Urban Model • See Jones-Otazo et al. 2005; Csiszar et al. 2013a,b for total PBDE emissions, all sources 	Use multimedia model in “reverse” to back-calculate aggregate PBDE emissions based on outdoor air concentrations. <i>For all PBDE-containing products and waste, not just computer cases.</i>

	Emissions from computer cases only	<ul style="list-style-type: none"> • Scale down from aggregate emissions (see above) OR • Emissions estimated from indoor model 	Obtain very rough approximation from the product of aggregate emissions and the fraction of PBDE inventory comprised of computer cases (Abbasi et al. 2015)
	Characteristics of receiving environment	<ul style="list-style-type: none"> • Yes, data depending on domain chosen. • Recommend Great Lakes basin because of abundant data 	Needed to estimate PBDE concentrations in air, water, soil, sediment, etc in receiving environment.
	Environmental fate in receiving outdoor environment	<ul style="list-style-type: none"> • USETox, RAIDAR, BETR 	Less-detailed (steady-state), general model for outdoors, because of low exposure potential from air, soil, etc.
Use stage, near field	Demographic and housing characteristics	<ul style="list-style-type: none"> • RPGen module (U.S. EPA) 	Generate probability distribution of housing stock and demographics
	Workplace characteristics	???	Characteristics of archetypal workplace settings, e.g., white collar, where PBDE-containing computers would have been used
	Number and types of products per residence/workplace	<ul style="list-style-type: none"> • See Ryen et al. 2015 • Possible to construct MFA on a household basis. 	Static vs dynamic. Not necessarily harmonized with region-wide MFA.
	Emissions from computer cases only	<ul style="list-style-type: none"> • Kemmelein et al. 2003 • Rauert et al. 2014, 2015a,b • Model emissions due to volatilization and direct transfer to dust 	Estimates from chamber studies and model estimates.
	Human activities	<ul style="list-style-type: none"> • Consolidated Human Activities Database (U.S. EPA) • American Time Use Survey (U.S. BLS) 	Hours at home vs. work, activities indoors influence multimedia distribution and exposure

	Environmental fate in indoor residential settings	<ul style="list-style-type: none"> Activity-Based Indoor Chemical Assessment Model (Kvasnicka et al. <i>in prep</i>) 	Detailed model feasible for this non-high-throughput application and warranted for this case study. However, some development would be needed to use stochastic parameter values.
	Indoor fate in indoor workplace settings	<ul style="list-style-type: none"> Adapt ABICAM or simpler multimedia indoor model 	
	Indoor transformation rates	<ul style="list-style-type: none"> Half-lives of PBDEs reactions with ozone, hydroxyl radical and other radicals produced indoors. Affects life-time of gas- and condensed phases, e.g., Shiraiwa et al. 2019, Won et al. 2019. 	Not aware of any data on this but could extrapolate from radical concentration data.
	Exposure calculations	<ul style="list-style-type: none"> US EPA guidance Empirical measurements, e.g., Ionas et al. 2016 for mouthing PBDE-containing toys, and for hand wipe data Stapleton et al. 2008, Yang and Jilkova et al., in review 	Need to consider: <ul style="list-style-type: none"> Direct contact with product Inhalation Dust ingestion Dermal transfer to skin covered and not by clothing Hand-to-mouth transfer Toddlers Mouthing textiles and other stuff
	Exposure factors	<ul style="list-style-type: none"> Exposure Factors Handbook (U.S. EPA) 	Parameters such as body weight, skin-surface area.
Manufacturing & Use stages, Dietary exposure	Food web transfer: Characteristics of food web pertinent to dietary exposure	<ul style="list-style-type: none"> Food web model, e.g., in RAIDAR (Arnot et al. 2006) 	To estimate, for example, fish concentrations.
	PBDEs measured in food	<ul style="list-style-type: none"> Boucher et al. 2018 	Empirical data to give more realistic estimate of total dietary exposure but cannot be linked to functional unit.

			Accounts for PBDEs that enter foods from agricultural system and food processing activities
	Food-specific intake rates	<ul style="list-style-type: none"> • US food consumption rates 	
EoL, far field	E-waste handling facility releases to air, water, land	<ul style="list-style-type: none"> • Literature sources, e.g., Stubbings et al. 2019 	
EoL, near field	Total time-dependent stock of PBDE-e-cases entering EoL stage	<ul style="list-style-type: none"> • Material flow analysis of 1. Computer products, 2. PBDEs in computer products See Abbasi et al. 2015 	Used to estimate flow of e-products to EoL
	E-waste dismantler exposure	<ul style="list-style-type: none"> • Empirical data on current exposure of e-waste workers in Ontario 	See Nguyen et al. (2019) for exposures to e-waste workers in Ontario, Nguyen et al. in prep for exposures in Quebec facilities, Estill et al. (2020) for exposures to e-waste workers in US
Use and EoL	Internal body burdens, including human age classes	<ul style="list-style-type: none"> • Pharmacokinetic model, e.g., Wong et al. 2013, Gyalpo et al. 2015, Verner et al. 2015 	Can vary from simple 1-compartment model to multi-compartment PBPK models, specific for age class.
Use and EoL, far field, model evaluation	PBDE concentrations in ambient outdoor media, e.g., air, sediment, fish	<ul style="list-style-type: none"> • For example, Great Lakes basin: IADN, GLNPO water, sediment & fish data, https://binational.net/wp-content/uploads/2018/04/PBDE-Strategy-Draft_Apr-5-CLEAN-for-public-review.pdf 	Need to account for year of sample collection
Use, near field model evaluation	PBDE concentrations in indoor environments	<ul style="list-style-type: none"> • Many studies including our own for which we have data collected from 2006, 2013 and 2015 (e.g., Zhang et al. 2011, Venier et al. 2016, Yang and Jilkova et al. in review) 	Need to account for year of sample collection
Use, near field internal body burden evaluation	Assess across human life cycle stages using human biomonitoring data	<ul style="list-style-type: none"> • Biomonitoring data, e.g., Sjodin et al. 2019, Drage et al. 2019 	Need to account for year of sample collection

Adaptation of Workflow to PFAS

PFAS represent a large class of ~4700 compounds as well as transformation and degradation products (e.g., perfluorinated side-chains from the now widely used polymeric formulations) (Wang et al. 2014). Up to ~100 of these compounds have been identified using speciated chemical analysis. A very much smaller subset yet are well characterized, e.g., physical-chemical properties, degradation rates.

The challenges with applying the existing workflow to PFAS include the following:

- Some of compounds, such as the carboxylic acids, can ionize and thus require consideration of neutral and ionized species.
- Some of the compounds can undergo conversion to other species, e.g., PFOA and PFOS can be produced by transformation of PFAS precursors (Dinglasan et al. 2004, Schenker et al. 2008, Washington and Jenkins 2015) .
- Physical-chemical properties are well known for only a small fraction of total PFAS compounds (Gomis et al. 2015).
- Exposure assessments have largely relied on measured intake values rather than model estimates (e.g., Vestergren and Cousins 2009, Pootong et al. 2020)

On the positive side, the development of a PFAS-specific workflow can build off of several excellent studies. For example, the CliMoChem model has been used to estimate the global fate of parent and transformation products globally (Armitage et al. 2009). Boucher et al. (2019) has estimated emissions for C-4 to C-10 chain length perfluoroalkanesulfonic acids and related precursors. Numerous studies have reported ambient levels of PFAS outdoors and indoors (e.g., Gewurtz et al. 2013, Karaskova et al. 2016), noting that sampling artefacts can affect the interpretation of some air measurements (Ahrens et al. 2012).

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