

Global Historical Stocks and Emissions of PBDEs

Golnoush Abbasi,^{*,†} Li Li,[†] and Knut Breivik[‡]

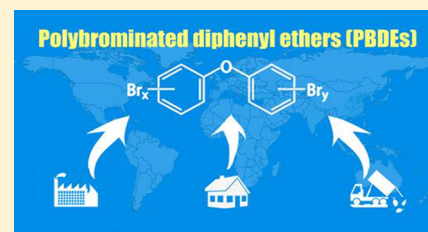
[‡]Norwegian Institute for Air Research, Box 100, NO-2027 Kjeller, Norway

[†]Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4

[‡]Department of Chemistry, University of Oslo, Box 1033, NO-0315 Oslo, Norway

Supporting Information

ABSTRACT: The first spatially and temporally resolved inventory of BDE28, 47, 99, 153, 183, and 209 in the anthroposphere and environment is presented here. The stock and emissions of PBDE congeners were estimated using a dynamic substance flow analysis model, CiP-CAFE. To evaluate our results, the emission estimates were used as input to the BETR-Global model. Estimated concentrations were compared with observed concentrations in air from background areas. The global (a) in-use and (b) waste stocks of \sum_5 BDE(28, 47, 99, 153, 183) and BDE209 are estimated to be (a) ~25 and 400 kt and (b) 13 and 100 kt, respectively, in 2018. A total of 6 (0.3–13) and 10.5 (9–12) kt of \sum_5 BDE and BDE209, respectively, has been emitted to the atmosphere by 2018. More than 70% of PBDE emissions during production and use occurred in the industrialized regions, while more than 70% of the emissions during waste disposal occurred in the less industrialized regions. A total of 70 kt of \sum_5 BDE and BDE209 was recycled within products since 1970. As recycling rates are expected to increase under the circular economy, an additional 45 kt of PBDEs (mainly BDE209) may reappear in new products.



INTRODUCTION

Globalization has connected countries worldwide and facilitated the global flow of resources, goods, and services. Despite all benefits, the environmental impacts due to chemical pollution are recognized as a detrimental aspect of globalization. Since the 1980s, the geographical relocation of heavy polluting industries from more industrialized to less industrialized countries, including chemical manufacturing, has contributed to the decrease of environmental burdens in more industrialized countries and its increase in the less industrialized countries.¹ In the wake of globalization and policy shifts toward a “free market”, the consumption in more industrialized countries is a key driver of pollution, while the less industrialized countries serve as constant suppliers of raw materials and semifinished goods to meet the global demands. Unequal economic integration between industrialized and less industrialized countries has also created an ongoing market for used and waste products (both durable and nondurable) in the less industrialized regions.² Challenges of this trade are intricate when it comes to chemicals in products (CiPs), as some chemicals may not be significantly emitted into the environment before the associated products reach their end of life. Countries lacking stringent regulations and environmentally sound management of waste are therefore at particular risk for enhanced end-of-life emissions. At the international level, these end-of-life products may not be classified as hazardous products and, thus, fall in the loopholes of international treaties on hazardous waste, such as the Basel Convention. The lack of appropriate handling of waste

products represents a potential risk to the environment and human health.^{3,4} Thus, emissions and exposure to harmful chemicals in long-lived products may, therefore, be disconnected in both space and time from the areas where relevant products were initially produced and/or used.

Polybrominated diphenyl ethers (PBDEs), brominated flame retardants used in products to meet the fire safety requirements mostly in North America and Europe,⁵ are an example of CiPs of concern. These compounds have been used since the 1970s, until their harmful characteristics brought them under the radar of environmental authorities (e.g., the European REACH regulation and Stockholm Convention) in the early 2000s,⁶ which led to the termination in the production of the commercial penta and octaBDE mixtures in 2004 and the commercial decaBDE mixture by 2014 in North America.⁷ Penta and octaBDE were listed in Annex A of the Stockholm Convention in 2009, and decaBDE was listed in 2017.⁸ Despite these efforts, differences in spatial and temporal trends of PBDEs in various environmental media^{1,9–12} and biota^{13,14} raise concern regarding the effectiveness of control measures and regulations on a global scale.

Recently, Li and Wania¹⁵ illustrated that the emission profile of most synthetic chemicals follows a bell-shaped curve that rises with increasing production followed by a gradual decline

Received: December 14, 2018

Revised: May 13, 2019

Accepted: May 14, 2019

Published: May 14, 2019

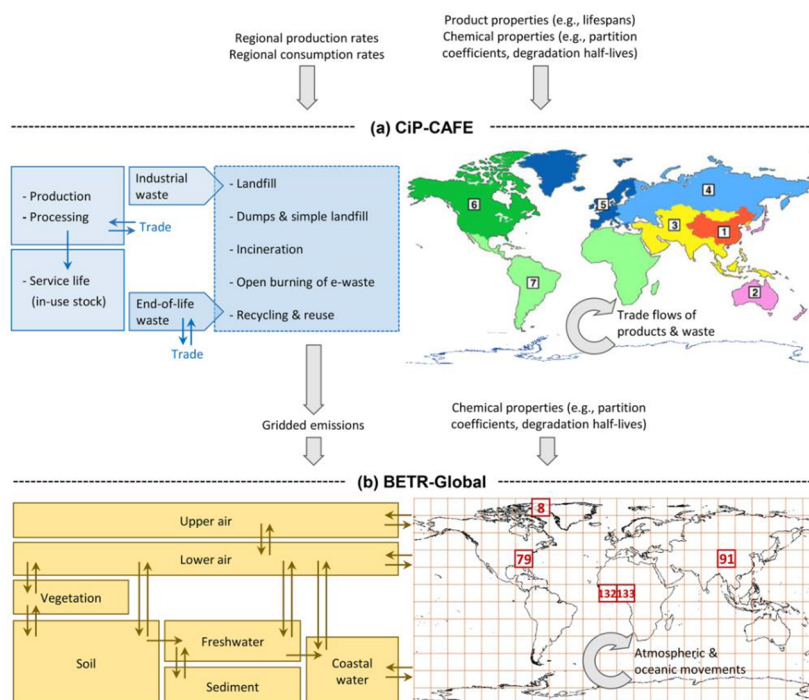


Figure 1. Schematic illustration of employed methodology.

as detrimental effects of chemicals become eminent and their production eventually ceases. The peak in emission could also be influenced by the stock of in-use and/or waste products, depending on the use and properties of chemicals and associated products. Evidently, planning effective measures to reduce emissions of problematic CiPs must consider their entire lifecycle and contribution of each lifecycle stage to their overall global emission. In this attempt, Li and Wania¹⁶ introduced a global-scale dynamic substance flow analysis model, named “Chemical in Products – Comprehensive Anthropospheric Fate Estimation” (CiP-CAFE), to track the long-term fate of CiPs in the global human socioeconomic system (termed “anthroposphere”).¹⁶ By coupling their anthropospheric fate model with a temporally and spatially explicit environmental fate model (e.g., BETR-Global), they provided reliable and comprehensive knowledge on the transport, transformation, and accumulation of selected CiPs in the global physical environment.^{17–19}

The overall goal of this study is to better understand the relationship between emission sources and the environmental occurrence of PBDEs and possible spatial and temporal variation by developing and evaluating a global historical emission inventory of PBDEs. Specifically, feeding the CiP-CAFE model with collected information on annual regional productions of major PBDE congeners (BDE28, 47, 99, 153, 183, and 209), we generate a comprehensive picture of their global fate in the anthroposphere, including in-use and waste stocks and emissions from 1970 to 2050. Emission estimates derived from the CiP-CAFE model were used as inputs to the BETR-Global model to simulate the temporal and spatial variability in the global atmosphere. Predicted atmospheric concentrations of PBDE congeners are compared with literature-reported measurements to evaluate our emission estimates.

METHODS

Stocks and emissions of PBDEs are modeled using the CiP-CAFE model, described in detail by Li and Wania.¹⁶ In summary, CiP-CAFE (Figure S1) splits the world into seven geographic regions (RE1: mainland China, RE2: Japan, South Korea, and Oceania, RE3: rest of Asia, RE4: Russia and Eastern Europe, RE5: Western Europe, RE6: North America, RE7: rest of the world) based on (i) development of chemical industry, (ii) the status of sound management of chemicals and solid waste, and (iii) major international trade of chemical-related products. Each region is further divided into three interconnected phases (i.e., the lifecycle of products containing PBDEs, waste disposal, and the physical environment) to track the movement of CiPs throughout their lifecycle and the environment. The schematic illustration of the methodology is presented in Figure 1.

The starting point of a CiP-CAFE simulation is the annual production rates of the commercial PBDE mixtures in individual regions as well as inter-regional trade of PBDEs as a commercial substance and within PBDE-containing products and waste. In the absence of accurate documented data on the production of PBDEs, a top-down approach based on the production of bromine and market demand of BFR and PBDEs was used to estimate and cross-check the global historical production rates of the commercial PBDE mixtures (Supporting Information (SI) Text S1.1). Regional production rates of the commercial PBDE mixtures were estimated based on the best available data provided by individual countries (SI Text S1.2). A bottom-up approach based on national PBDE consumption for each country provided to the Stockholm Convention was used to estimate the regional consumption of the commercial PBDE mixtures (SI Text S1.3).

Subsequently, estimates of production and consumption of the commercial mixtures were used as indicators to estimate the trade of PBDEs as commercial mixtures between regions (SI Text S1.4). In addition, inter-regional movement of PBDEs

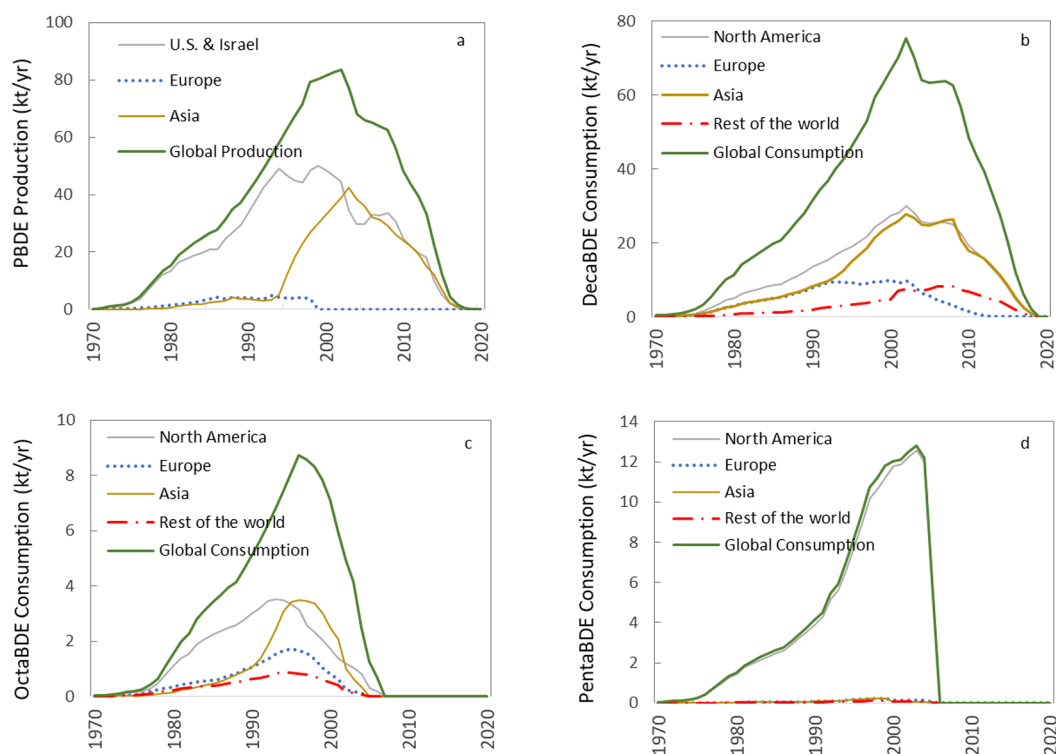


Figure 2. Estimated temporal trends in global and regional production and consumption of PBDE mixtures; (a) total PBDE production, (b) consumption of DecaBDE mixture, (c) consumption of OctaBDE mixture, (d) consumption of PentaBDE.

through the trade of final PBDE-containing products and corresponding waste was estimated based on the fraction of import and export of PBDE-containing products (SI Text S1.4).

To investigate the fate of BDE28, 47, 99, 153, and 183 (hereafter \sum_5 PBDEs) and BDE209, the final estimates of production and trade of the commercial PBDE mixtures are broken down into a congener basis using the mass fraction of each congener in the commercial mixtures (adopted from La Guardia et al.²⁰ and provided in Table S1). On the basis of these data, the sum of BDE47, 99, and 153 accounted for 80% of the commercial pentaBDE mixture, whereas BDE153 and 183 together accounted for 30% of the commercial octaBDE mixture. BDE209 was assumed to account for 100% of the commercial decaBDE mixture in this study.

We consider the distribution of PBDE consumption among five major applications: electronics (AP1), foam and carpet (AP2), construction (AP3), transportation (AP4), and textiles (AP5). Percentages of commercial mixtures of PBDEs used in various applications and the average lifespans of product types are summarized in Table S2. The in-use stock of PBDEs and their flow to waste stream were characterized based on annual consumption and lifespan distribution of each product type for each region. At the end of lifespan, PBDE-containing products are treated as general municipal solid waste (e.g., entering landfills, dumpsites, incineration facilities) except for the fractions subject to inappropriate waste treatment (IWT), such as open burning of e-waste, and environmentally sound management (ESM), such as destruction or irreversible transformation. For definitions and terminologies of the lifecycle stages and waste disposal options, please see Li and Wania.¹⁶ Available data on the treatment of municipal solid waste for different countries were used to account for

differences in waste management practices for each region (SI Text S1.5).

Emission factors for PBDEs from various processes^{21,22} during lifecycle of PBDEs were obtained from the literature (SI Text S1.6). Because empirical emission factors remain scarce, a range of emission factors were explored and used to develop two alternative global historical emission scenarios: a high emission scenario is based on the highest emission factors at each stage, whereas a low emission scenario reflects the lowest available emission factors.

The median estimates of high and low emission scenarios for each year were used to predict time-variant atmospheric concentrations using the BETR-Global model. The BETR-Global model predicts concentrations of chemicals in seven different environmental media in 288 interconnected grid cells ($15 \times 15^\circ$) worldwide based on their emissions within each grid.^{23,24} The CiP-CAFE-derived regional emission estimates are geographically allocated into individual BETR-Global grid cells, using surrogate data including the production capacities and locations of the main BFR producers in the world (for emissions from the production stage), gross domestic product (GDP, for emissions from industrial activities), population density (for emissions from in-use and waste stocks), and the reciprocal GDP per capita (for emissions from inappropriate waste disposal).¹⁶ Other model inputs include partition coefficients between octanol, water, and air phases, and degradation half-lives were taken from Schenker et al.²⁵ The predicted concentrations in air (concentrations based on the high and low emission scenarios and their medians) were compared with available empirical measurements to help assess confidence in the emission scenarios. The model evaluation is deliberately restricted to atmospheric concentrations for the following reasons. First, atmospheric concentrations are likely to be relatively homogeneous and well mixed in background

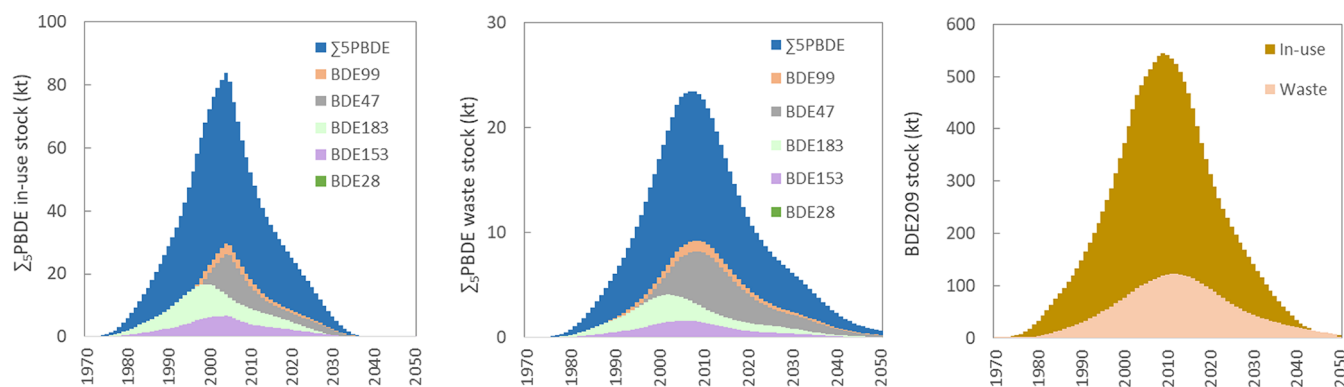


Figure 3. Global in-use and waste stock of PBDEs; (a) in-use stock of Σ_5 PBDEs (BDE28, 47, 99, 153, and 183), (b) waste stock of Σ_5 PBDEs, (c) in-use and waste stocks of BDE209.

air. Second, atmospheric concentrations are likely to respond faster to changes in primary emissions in comparison to other environmental media. Finally, this facilitates an evaluation of potential differences in source–receptor relationships by long-range atmospheric transport versus long-range anthropogenic transports as CiPs.

RESULTS AND DISCUSSION

Production and Consumption of Commercial PBDE Mixtures. Figure 2 demonstrates the estimated temporal trend in the global and regional production (panel a) and consumption (panels b–d) of commercial PBDE mixtures. The cumulative historical productions of commercial penta, octa, and decaBDE mixtures were estimated to be ~175, 130, and 1600 kilotonnes (kt), respectively. The total historical production of commercial mixtures of penta and octaBDE was previously estimated to be around 100 kt each, whereas the historical production of the commercial mixture of decaBDE was reported to be around 1100 kt by 2005.²⁶ The annual production of total PBDEs peaked around 85 kt/yr in 2003 (Figure 2a). Prior to 1995, the US and Israel were the main manufacturers of PBDEs. China started the production of PBDEs (mainly decaBDE) in the 1980s. By 2000, China was one of the main manufacturers of decaBDE. Bans and restrictions on the use of penta and octaBDE in the late 1990s led to a reduction in PBDE production in Japan and Europe, where historical production was less than 10% of the total PBDEs manufactured.

The global historical production of each commercial mixture was assumed to represent the total consumption of PBDEs (Table S3). The global annual consumption of decaBDE peaked at ~75 kt/yr in 2003 with more than 80% of the total decaBDE used in North America and Asia (Figure 2b). The annual consumption of decaBDE declined in Europe and Japan in the late 1990s. The global annual consumption of the commercial octaBDE mixture peaked at ~8.5 kt/yr in 1997 with its primary use in North America followed by Asia (Figure 2c). Because of the higher percentage of octaBDE mixture used in Japan and Europe compared to other PBDE mixtures, the peak in the total consumption of octaBDE occurred earlier than that of other mixtures. The global consumption of the commercial mixture of pentaBDE peaked at ~12 kt/yr in 2003 with its primary use occurring in North America in polyurethane foam (PUF). Thus, the voluntary phase-out of pentaBDE by chemical industries in the U.S. resulted in a sharp decline in global consumption of pentaBDE (Figure 2d).

Fate of PBDEs in the Anthroposphere. Figure 3 demonstrates the estimated temporal evolution in global in-use and waste stocks of PBDE congeners (Σ_5 PBDEs and BDE209). The total in-use stock of Σ_5 PBDEs peaked at ~85 kt in 2004, with BDE47 and 99 being the main constituents of the estimated total stock (Figure 3a). BDE183 (the main congener of the commercial octaBDE mixture) peaked a few years earlier compared to other congeners, which may reflect the shorter overall lifespan of products containing octaBDE (mainly electronics, Table S2) and earlier cessation of octaBDE consumption in Japan and Europe. The regional temporal trends demonstrate the highest stock of Σ_5 PBDEs occurred in more industrialized regions, especially in North America (Figure S5). The global waste stock of Σ_5 PBDEs peaked at ~22 kt in 2009. The in-use stock of Σ_5 PBDEs will dissipate by the mid-2030s; however, the waste stock of Σ_5 PBDEs continues until 2050 (Figure 3b). The global in-use and waste stocks of BDE209 are estimated to have peaked at ~550 and 120 kt in 2010 and 2012, respectively (Figure 3c).

In terms of the geographic distribution, a large portion of the in-use stock of PBDEs historically resided in industrialized regions (RE2, RE5, RE6), whereas the in-use stock in less industrialized regions (RE1, RE3, RE4, and RE7) is anticipated to dominate the global in-use stock in the future. For example, the regional temporal trend of BDE209 stocks demonstrates that the in-use stock of BDE209 started to increase in industrialized regions in the 1980s, while the increase in the in-use stock in less industrialized regions did not occur until late 1990s (Figure S5c). The time lag among regions might be attributed to the discontinuation of PBDE use in new products in more industrialized regions in concert with a growing economy and market demand for electronic products in less industrialized regions in the late 1990s.¹ Following 2030, the in-use stock of BDE209 in less industrialized regions is estimated to account for ~80% of the global in-use stock. By 2050, a total of 5 kt of BDE209 will still be in use, mainly in less industrialized regions. From 1970 to 2018, the regional evolution of Σ_5 PBDEs and BDE209 in waste stock demonstrates that the bulk of the global waste stock accumulated in North America (>60%), followed by the EU (15%) (Figure S6). The global waste stock of six PBDE congeners disposed of in landfills and dumpsites peaked at 140 kt in 2011 with BDE209 accounting for ~120 kt of the total stock. By 2018, about 60% of the global waste stock ended up in controlled landfills in industrialized countries, while 30 and

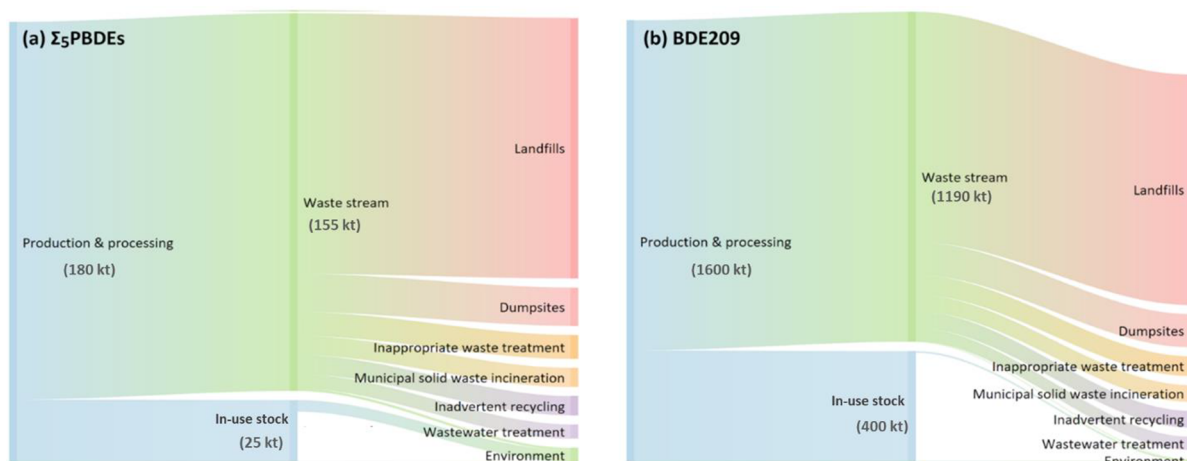


Figure 4. Global anthropogenic fate of (a) Σ_5 PBDEs (BDE28, 47, 99, 153, and 183) and (b) BDE209 as of 2018. Note that the width of the arrows is proportional to the relative importance of pathways in each panel, whereas the total production is different between the panels (180 kt for Σ_5 PBDEs and 1600 kt for BDE209).

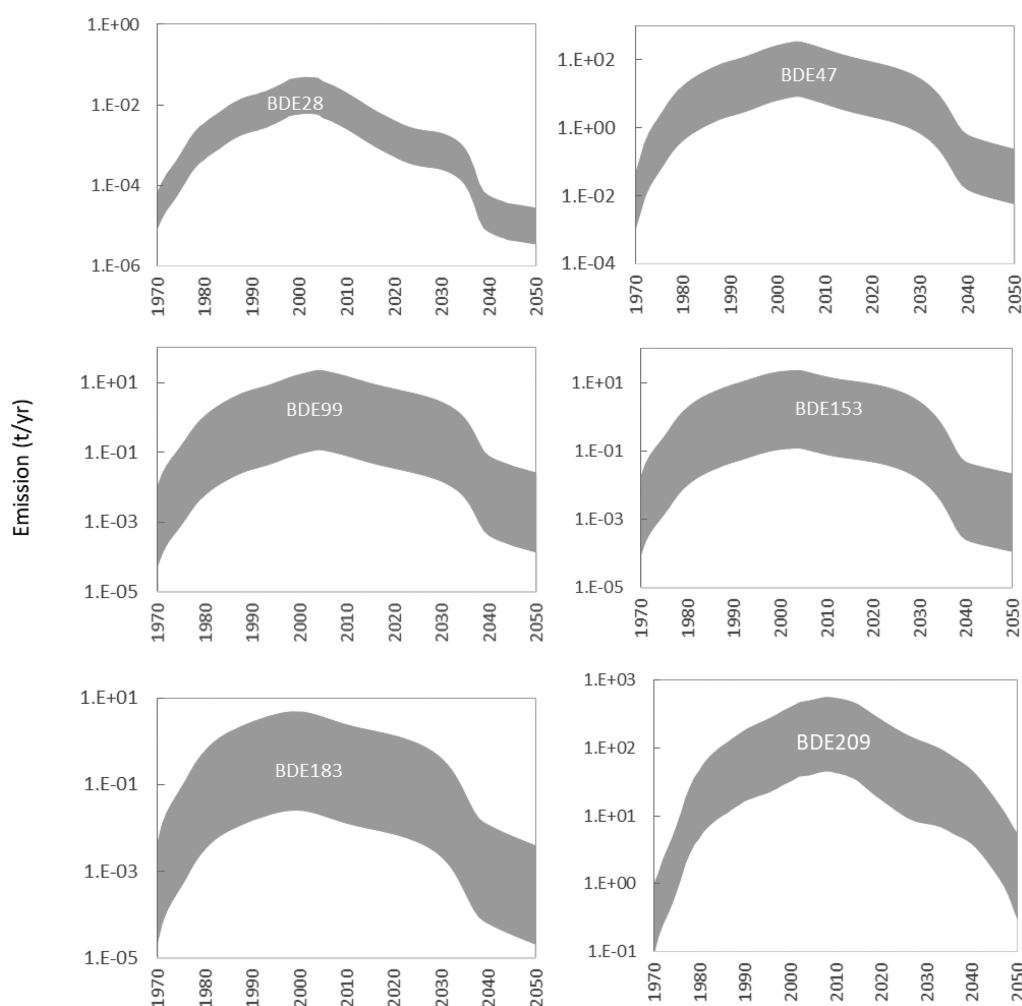


Figure 5. Estimated global temporal trend in atmospheric emissions of PBDE congeners (tonnes/year). The upper and lower bounds of the ranges represent estimates under the high and low emission scenarios, respectively.

10% of the global waste stock in less industrialized countries ended up in simple landfills and dumpsites, respectively.

Our estimates of the in-use stocks in various regions compare favorably with previously estimated regional stocks of PBDEs. The in-use stock of penta and octaBDE mixtures in all

applications except construction materials was previously estimated to peak at ~ 22 kt in North America in 2004.²⁷ Here, the estimated in-use stock of Σ_5 PBDEs peaked at ~ 40 kt in all applications in North America in 2004. The peak in in-use stock of BDE209 was estimated to be at ~ 90 kt in North

America (excluding the stock in the construction materials) in 2017,²⁷ while we estimated the current stock of BDE209 is about 130 kt in all applications. Our estimate of BDE209 stock in Europe in 2017 is ~55 kt, which is within, but closer to, the upper boundary range of 5 to 60 kt estimated by Earnshaw et al.²⁸ Sakai et al.²⁹ estimated the stock of BDE209 to be 60 kt in 2002 in Japan, while we estimated the total of ~70 kt for RE2 in 2002.

The overall global anthropogenic fate of PBDEs up to the year 2018 is presented in Figure 4. From the totals of 180 and 1600 kt of \sum_5 PBDEs and BDE209, respectively, about 25 and 400 kt of \sum_5 PBDEs and BDE209 are still present within the in-use stock, while 155 and 1190 kt entered the waste stream from 1970 to 2018. Globally, about 80% of PBDEs in waste have been destined to both controlled and uncontrolled landfills (dumpsites and simple landfills) accounting for 70 and 10% of the total PBDE in waste, respectively. Approximately, 6 and 5% of the total waste was subject to inappropriate waste treatment and inadvertent recycling, respectively, mainly in less industrialized regions. Minor fractions of PBDEs in waste were destroyed through incineration (5%) and wastewater treatment (4%). If no further control measures are in place by 2050, an additional 40 kt of BDE209 will enter inappropriate waste treatment and recycling processes. As a result of various emission processes, we estimated that in total, up to 6 (0.3–13) kt of \sum_5 PBDEs and 10.5 (9–12) kt of BDE209 have been emitted to the environment by 2018. This accounted for approximately 3 and 0.7% of the cumulative \sum_5 PBDEs and BDE209 productions, respectively.

Environmental Fate of PBDEs. Atmospheric Emissions.

The estimated ranges in global atmospheric emissions for selected PBDE congeners from 1970 to 2050 under high (the upper bound) and low (the lower bound) emission scenarios are shown in Figure 5. The peak in global atmospheric emissions of \sum_5 PBDEs occurred around 2004, dominated by BDE47 (with a peak at ~100 (10–330) t/yr) and BDE99 (with a peak at ~20 (1–30) t/yr). The peak in BDE209 emission occurred at ~145 (50–900) t/yr in 2008.

The regional atmospheric emission profiles of \sum_5 PBDEs and BDE209, from all processes and phases included in this study, are presented in Figure S7. The in-use stock of \sum_5 PBDEs was the main source of \sum_5 PBDEs emissions in all regions. In less industrialized regions, the inappropriate waste treatment was the second largest source of \sum_5 PBDEs emissions, whereas in more industrialized regions where manufacturers were located, the production of \sum_5 PBDEs was the second most important source of emission. For BDE209, the in-use stock was the primary source of emission in all regions except RE1 (China) and RE7. In China, the total BDE209 emission was dominated by the emission during the production phase, possibly because most of BDE209 manufactured in China was subject to export within products to other regions (see SI S1.2). In RE7, the emissions from inappropriate waste treatment were estimated to be the main source of BDE209 emission. On the global scale, the total emission of \sum_5 PBDEs and BDE209 was dominated by the in-use stock, followed by production and then inappropriate waste treatment.

The emission profiles of individual PBDE congeners exhibit a “composite single peak”, which refers to those chemicals that their total emission consists of emissions from individual stages of their lifecycle (production, in-use stock, and waste processes)¹⁵ (Figure S7a). Although the emission profile of

PBDEs shows great variation among congeners in different regions, such a composite single peak was observed in all regions. The regional profile of atmospheric emission reveals that a large portion (>70%) of emissions of PBDEs from production and in-use stock occurred mainly in industrialized regions prior to 2030 (Figure S8a). As the emission declines from dissipation of in-use stock of PBDEs in more industrialized regions, it increases in less industrialized regions mainly because of inappropriate waste treatment (RE1, RE3, and RE7) (Figure S8b).

Since the 1980s, waste containing PBDEs (mainly BDE209 in e-waste and vehicles) from more industrialized regions have been transported to less industrialized regions to be reused or disposed of using extremely primitive techniques (e.g., open burning), which could result in increasing emission of PBDEs and other contaminants in receiving regions, and by extension, in the world.³⁰ To account for the extent of such an increase in emission resulting from the transboundary shipment of waste, we additionally ran the model assuming no waste trade among different regions under the high emission scenario. Our results suggest that, compared with the assumed no-waste-trade scenario, waste trade increased the global annual emission of BDE209 by 20 to 40% from the late 1970s to 2010 and 5 to 15% following 2010 (Figure S9). The increase is particularly notable for RE1 (mainland China). Although no significant changes in BDE209 emission are estimated in industrialized regions, BDE209 emission increased between 20 and 50% in less industrialized regions (RE1 and RE7) as a result of the transboundary movement of waste. These findings are in line with those of Breivik et al.,³ who estimated that the global emission of semivolatile organic contaminants would increase when accounting for the international trade of e-waste.

The estimated emissions in this study are in reasonable agreement with previous estimates of PBDE emissions. For \sum_5 PBDEs, the peak in annual emission of selected pentaBDE congeners (47, 99, 153) in Europe under various emission scenarios was estimated to range between 0.3 and 30 t/yr,³¹ whereas our estimated emission of \sum_5 PBDEs under the default scenario peaked at ~12 (t/yr) (Figure S7). The peak in annual emission of penta and octaBDE mixtures based on the in-use stock was estimated to range from 0.8 to 8 t/yr in the U.S. and Canada.²⁷ We estimated that the emission of \sum_5 PBDEs from in-use stock in RE6 (North America) peaked at ~25 t/yr. The higher estimated emission in our study reflects the inclusion of more applications and of PBDEs that stay in use for a longer period of time (e.g., construction materials).

The emission of BDE209 in Japan (in RE2) from in-use stock and industrial processes was estimated to range between ~0.2 and 2 t/yr in 2002,²⁹ which is smaller than, but close to, the emission in the entire RE2 (~10 t/yr). The emission of BDE209 in China³² was previously estimated to peak at ~30 t/yr, while we estimated that the peak occurred at ~40 t/yr. Earnshaw et al.²⁸ estimated that the peak in the emission of BDE209 occurred at ~10 t/yr in Europe, whereas we estimated a peak in the emission of BDE209 was at ~16 t/yr. Our higher estimated range of BDE209 in North America (10–130 t/yr) in comparison with a previous study (0.35 to 3.5 t/yr)²⁷ reflects the inclusion of more application and emission sources (production and waste) of BDE209 in our study.

From Emission to Concentrations in Air. Since atmospheric concentrations of pollutants are strongly responsive to changes in primary emissions, the estimated emissions of

PBDE congeners to air were used to calculate the atmospheric concentrations of each PBDE congener using the BETR-Global model.²⁴ The BETR-Global model has a coarse spatial resolution (15° latitude \times 15° longitude cells). It is therefore not suitable for resolving concentration gradients from “hot spots” (e.g., urban centers) toward remote background regions. Thus, the comparison between our model predictions and observations is restricted to atmospheric concentrations measured in rural and remote areas. The comparison of predicted and measured values (Table S9) of PBDE congeners at different geographical locations in a specific year of sampling demonstrates that more than 95% of data points fall within 2 orders of magnitude (dashed line) of perfect agreement (solid line) (Figure 6). The predicted values represent the median of

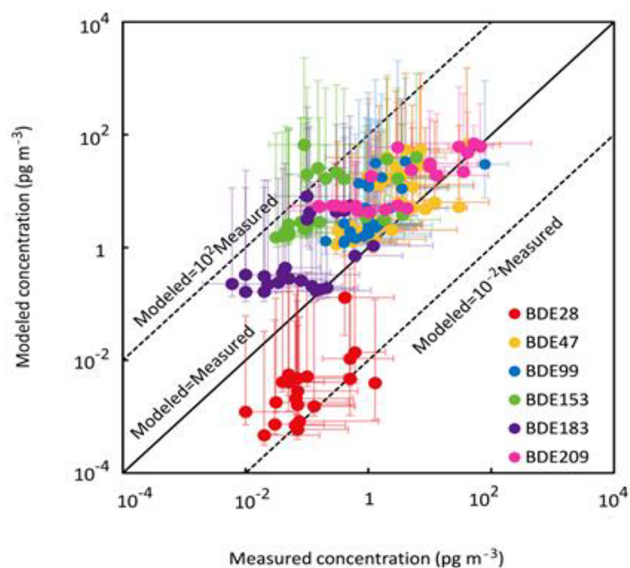


Figure 6. Comparison between estimated modeled and measured concentrations of selected PBDE congeners for a given year in rural or remote regions reported previously in the literature (see Supporting Information for cited references) (Table S9). The dots represent the concentrations under the default emission scenario. The upper and lower caps of the error bars represent the calculated concentrations under the high and low emission scenarios, respectively.

two scenarios with error bars indicating the highest and lowest predicted values under different scenarios. The measured values represent the median values with the minimum and maximum ranges available in the literature. The agreement is generally better for lighter congeners of BDE47 and 99 than BDE153, 183, and 209. A poor agreement for BDE28 could be a result of (i) marginal content of BDE28 in pentaBDE commercial mixture, which could be highly uncertain, (ii) difficulties in chemical analysis of BDE28 because of coelution with BDE33,²⁰ and (iii) degradation of higher brominated congeners to BDE28.²⁵ The fair agreement between modeled and measured values for BDE209 depicts that the model provided realistic results driven by the emission scenarios developed in this study.

To explore which stage of the lifecycle drives the estimated total emission in remote areas within an Arctic zone, we ran the model for BDE209 with emissions separately from industrial processes and in-use stock. Our results demonstrated that the overall atmospheric trend in the Arctic follows the same trend as the emission from the global in-use stock. In

industrial zones (e.g., cells 79 (in RE6) and 91 (in RE1)) where PBDE manufacturers were assumed to be located, the overall air concentration mainly followed the emissions during the production phase while in less industrial zones (e.g., cells 132 and 133 in RE7) where PBDEs in e-waste are inappropriately handled, the emission from waste treatment processes was the contributor to the overall PBDE atmospheric concentrations (Figure S10).

PBDE Emissions and Global Environmental Trends.

Since the first discovery of PBDE congeners in fish in Sweden,³³ their elevated concentrations have been reported widely in various environmental media and biota.^{34–37} Our results suggest that BDE209 concentration in air in the Arctic increased between the 1990s and 2005, with a doubling time of 5 to 10 years (Figure S10). This result is in good agreement with an observation where PBDE concentrations increase with a doubling time of 3.5 years for BDE209 and 6 to 28 years for main congeners of penta and octaBDE mixtures between 1993 and 2006.³⁸ The observed trends in PBDE concentrations in sediment cores across the globe mirror the estimated trends of PBDE stocks and emissions in our study. The concentrations of pentaBDE congeners increased from the early-1970s until the late 1990s in European³⁹ and until the early 2000s in North American sediment cores.⁴⁰ In China, the concentrations of penta and octaBDE congeners in sediment cores increased from the 1960s to 2010, while decaBDE congeners increased sharply from the 1980s to 2010 (the most recently dated sediment samples).¹

We estimated that the global in-use stock of PBDEs in industrialized regions increased with doubling times from 7 to 12 years from the late 1970s to early 2000s. Likewise, a meta-analysis of the total PBDE concentrations in humans from Japan, Europe, and North America demonstrated an exponential increase with a doubling time of \sim 5 years from the 1970s to 2005,^{10,41} corresponding to an increase in human tissues by a factor of 100 over 30 years.⁴² The exponential increase of PBDEs from 1975 to 2000 in Swedish mothers' breast milk⁴³ was an instrumental study for the implementation of regulations on the use of PBDEs, especially in Europe.⁴⁴ Not too long after the phase-out, PBDE concentrations in environmental media and biota declined in North America and Europe.⁴⁵ In Europe, concentrations in air declined up to 50% from 2000 to 2008,⁴⁶ which is in concert with an estimated decline rate of European PBDE in-use stocks in this study (Figure S5). A decreasing trend with estimated half-lives of 2 to 17 years was reported for penta and octaBDE congeners with higher declining rates at sites closer to the urban sites than rural sites adjacent to the Great Lake in Canada by mid-2010s.⁹ The declining trend in biota in urban⁴⁷ and rural areas¹³ seemed to follow declining trends of PBDE stocks and emission. The concentrations of pentaBDE congeners in breast milk had also reached a plateau or started to decrease by 2005 in Europe,^{48–50} whereas BDE209 was still increasing in 2009.⁵⁰ In the US and Canada, following a sharp increase in the 1990s, the total concentrations of PBDEs in the breast milk reached a plateau by 2005.^{51,52}

Conflicting patterns in environmental trends of PBDEs raised concern regarding the management of ongoing sources of PBDEs. Recently, an increasing trend in BDE209 concentration in air was reported in Spain from 2008 to 2015.¹¹ In the US, an increasing trend with a doubling time of 7 to 11 years and/or a leveling off trend was observed for penta and octaBDE congeners at remote sites adjacent to the Great

Lakes.^{12,42} The temporal trend of BDE209 concentration in air was decreasing at one of the urban sites with a halving time of 5.9 years, while no significant changes were observed at other remote sites.⁴² In contrast, Shunthirasingham et al.⁹ found a faster declining trend at remote areas than urban sites in Canada.

In less industrialized regions (e.g., RE1 and RE7), the booming of manufacturing industries, growing economy and higher consumption,¹ and inappropriate waste management practices^{53–56} have caused increasing PBDE concentrations in the environment and human tissues in some Asian and African countries in recent years.^{57–60} In addition, the transboundary movement of e-waste contributes to further emissions of PBDEs and other pollutants in the less industrialized countries and countries in transition.³

Evaluation of Estimates. Our results could successfully portray the overall environmental trends of PBDEs and a lag time in the occurrence of PBDE emissions between the industrialized and less industrialized countries. Yet, the importance of anomalous sources at each region, which might not have been included due to the abstraction and simplification of the model, must be considered to formulate effective control measures. For instance, the high concentrations of decaBDE in Canadian Arctic predatory birds was attributed to the presence of open landfills in Canadian Arctic,¹⁴ or electronic waste recycling in industrialized countries could still act as ongoing emission sources of PBDEs to their surrounding environments.⁶¹

We performed a sensitivity analysis to examine which input parameter(s) are more influential on our model outputs. It shows that our model outputs are sensitive to input parameters in the following order: annual production rate > lifespans of associated products > fraction of regional waste treatment processes > emission factors during use > distribution ratio of the technical PBDE mixtures between applications > emission from inappropriate waste treatment > emission factors during industrial processes. The sensitivity of the model to PBDE production and application data emphasizes the importance of these parameters in understanding the overall fate of PBDEs and therefore devising proper control strategies. Despite the discontinuation of PBDE production “supposedly” by 2014, data on their production and consumption is still scarce. As such, predicting their environmental fate requires extrapolation of these data from available sources, which are subject to large uncertainties. Data on the use and application of PBDEs provided by each country to the Stockholm Convention are inconsistent and bear considerable uncertainty. Moreover, it is still not clear when the total ban on exempted products (e.g., military equipment and medical devices) will occur and whether their productions will be discontinued globally. Given the in-use stock is the main contributor to the overall PBDE emission, more accurate data on the emission factors, usage, and lifespan of PBDE-containing products could significantly improve the reliability of our results. Emission factors from industrial processes at the beginning and end of lifecycles of products bear considerable uncertainty due to the heterogeneous nature of these processes, both locally and globally. For instance, emission factors estimated from recycling facilities in Japan were applied for all regions, which might have resulted in an underestimation of PBDE emissions through these processes on the global scale. It should also be mentioned that despite the applied range of emission factors, emissions from products could be influenced by various environmental

and anthropogenic factors that might not be taken into consideration in our estimates. As such, we defined high and low emission scenarios to account for inevitable uncertainties in our assumptions. As a result of limited data and information on the fate of associated products and possible waste management processes in less industrialized countries, any available data for a few countries were extrapolated to describe the entire regions. Given the anticipated transition in emissions toward such regions in time, further research associated with emission from informal waste and recycling processes may be informative. In addition, estimating the quantity of PBDEs in waste vehicles, electronics, and textiles that have been transported to less industrialized countries remains uncertain, largely because of the illicit nature of transboundary movements of waste products. Finally, the unintentional formation of PBDEs from various industrial processes was not included here, as this study was deliberately restricted to CiPs.

Implications and Future Perspectives. This study presented the first spatially and temporally resolved overview of the fates of PBDE congeners in both the anthroposphere and the environment. Our results demonstrated that the long residence of PBDEs in the anthroposphere leads to continuous emission of PBDEs to the environment, despite restrictions on their new use in the past decade, especially in more industrialized countries. In addition, a thorough examination of the fate of PBDEs on a regional scale provides a comprehensive overview of their global fate. The fire safety requirements mainly in North America and Europe resulted in the ubiquitous presence of PBDEs. As the demand of PBDE-containing products declined in more industrialized countries, their use increased in the less industrialized countries because of economic growth. Moreover, the export of associated waste products to less industrialized countries or countries in transition contributed to their global emissions. This will also be applicable for other flame retardants and CiPs, which emphasizes the need for holistic approaches to better investigate the unequal flows of contaminants between industrialized and less industrialized regions.

While our emission scenarios are subject to uncertainties, the fair agreement between model predictions and observations suggests that the emission inventory may serve as a valuable starting point to help decipher the spatial and temporal trends of PBDEs in both the anthroposphere and the environment. In particular, the established trends of PBDE stocks and emissions in this study systematically portray the existing lags in time and space in current chemical management practices. On the one hand, despite the phase-out of PBDEs, the emission of PBDEs from in-use and waste stocks will continue until 2050. Such a delay between the discontinued production and emission reflects a “time lag”. As demonstrated here, PBDE emissions from production declined in immediate response to restrictions on the production and new use of PBDEs in regions where the production took place. However, emission from the widespread stock of PBDEs continued for a longer period of time. In fact, atmospheric concentrations of PBDE in the Arctic and other remote regions appear largely dictated by the temporal trends in emissions from in-use stock. Moreover, such a decadal time lag between the discontinued production and emission seems common for a wide array of chemicals in products, such as polychlorinated biphenyls,⁶² hexabromocyclododecane,¹⁹ perfluoroalkyl substances,⁶³ and short-chain chlorinated paraffins.⁶⁴ As such, future chemical management

policies should regulate not only the production and new use of these chemicals but also possible future emissions from their long-term in-use and waste stocks.

On the other hand, the transition of emission sources from one region to the other has also created a “space lag”. The global market demand for PBDEs doubled in the 1990s because of the enforcement of fire safety codes and increasing demand for associated products in North America and Europe. Almost 20 years later when PBDEs have been recognized as ubiquitous environmental contaminants in more industrialized regions, their consumption peaked in less industrialized countries and/or countries in transition. In particular, the trade of waste containing PBDEs resulted in minor changes in their emission in the industrialized countries, while it resulted in a significant increase in the less industrialized countries. Consequently, PBDE contaminations in less industrialized countries are becoming a pressing environmental problem. As it was also illustrated previously by Breivik et al.,³ the export of e-waste to warmer regions could preclude the objective of emission reduction strategies of the Stockholm Convention at the global scale because of enhanced emission of semivolatile organic contaminants from informal waste and disposal activities.

In the context of the global environment, our work confirms that stopping production of CiPs, after decades of use, will not adequately address and quickly solve their long-term environmental impacts.^{17,65,66} Additionally, we estimated that a significant amount of PBDEs (about 70 kt) was subject to inadvertent recycling, which could lead to undesirable reappearance of PBDEs and possibly other legacy contaminants in new products including children toys.⁶⁷ In the context of the circular economy, if no further efforts will be taken to efficiently divert PBDEs from the waste stream, an additional 45 kt of PBDEs are expected to be recycled and reappear in plastic products. In the context of the “Clean Planet, Healthy People” that aims to achieve global health for people and the environment, regulations must provide more stringent guidelines on the new use of alternative chemicals prior to their application in consumer products to prevent their wide distribution and the potential long-term risk of harmful CiPs to environmental and human health on a global scale.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.8b07032](https://doi.org/10.1021/acs.est.8b07032).

Details on input parameters, estimation of PBDE production and consumption, emission factors, and sensitivity analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +47 63 89 80 57; e-mail: goa@nilu.no. (G.A.)

ORCID

Golnoush Abbasi: [0000-0002-0486-8363](https://orcid.org/0000-0002-0486-8363)

Li Li: [0000-0002-5157-7366](https://orcid.org/0000-0002-5157-7366)

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was financed by the Research Council of Norway (213577 and 244298). L.L. acknowledges support through a MITACS Elevate postdoctoral fellowship. The authors thank Dr. Hayley Hung (Environment Canada and Climate Change) for providing PBDE concentrations in air from Alert station in the Arctic.

■ REFERENCES

- (1) Li, Y.; Lin, T.; Hu, L.; Feng, J.; Guo, Z. Time trends of polybrominated diphenyl ethers in East China Seas: Response to the booming of PBDE pollution industry in China. *Environ. Int.* **2016**, *92*–93, 507–14.
- (2) Hoorweg, D.; Bhada-Tata, P. *What a waste: a global review of solid waste management*; Urban Development Series Knowledge Papers; World Bank: Washington, D.C., 2012, No. 15.
- (3) Breivik, K.; Armitage, J. M.; Wania, F.; Sweetman, A. J.; Jones, K. C. Tracking the Global Distribution of Persistent Organic Pollutants Accounting for E-Waste Exports to Developing Regions. *Environ. Sci. Technol.* **2016**, *50* (2), 798–805.
- (4) Nøst, T. H.; Halse, A. K.; Randall, S.; Borgen, A. R.; Schlabach, M.; Paul, A.; Rahman, A.; Breivik, K. High Concentrations of Organic Contaminants in Air from Ship Breaking Activities in Chittagong, Bangladesh. *Environ. Sci. Technol.* **2015**, *49* (19), 11372–11380.
- (5) Betts, K. S. Hand-Me-Down Hazard: Flame Retardants in Discarded Foam Products. *Environ. Health Perspect.* **2015**, *123* (3), 56–63.
- (6) Stockholm Convention. *The Stockholm Convention on Persistent Organic Pollutants (POPs)*; 2001; <http://chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx>.
- (7) US EPA. *An alternative assessment for the flame retardant Decabromodiphenyl ether (DecaBDE)*; 2014; https://www.epa.gov/sites/production/files/2014-05/documents/decabde_final.pdf.
- (8) European Commission. *Proposal for a COUNCIL DECISION: on the position to be adopted, on behalf of the European Union, at the Eighth Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants regarding the proposals for amendments of Annexes A and C*; 2017/0058 (NLE); 2017.
- (9) Shunthirasingham, C.; Alexandrou, N.; Brice, K. A.; Dryfhout-Clark, H.; Su, K.; Shin, C.; Park, R.; Pajda, A.; Noronha, R.; Hung, H. Temporal trends of halogenated flame retardants in the atmosphere of the Canadian Great Lakes Basin (2005–2014). *Environ. Sci. Process. Impacts* **2018**, *20* (3), 469–479.
- (10) Venier, M.; Salamova, A.; Hites, R. A. Halogenated flame retardants in the Great Lakes environment. *Acc. Chem. Res.* **2015**, *48* (7), 1853–61.
- (11) Roscales, J. L.; Munoz-Arnanz, J.; Ros, M.; Vicente, A.; Barrios, L.; Jimenez, B. Assessment of POPs in air from Spain using passive sampling from 2008 to 2015. Part I: Spatial and temporal observations of PBDEs. *Sci. Total Environ.* **2018**, *634*, 1657–1668.
- (12) Ma, Y.; Salamova, A.; Venier, M.; Hites, R. A. Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2013**, *47* (20), 11457–64.
- (13) Bjurlid, F.; Dam, M.; Hoydal, K.; Hagberg, J. Occurrence of polybrominated dibenzo-p-dioxins, dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs) in pilot whales (*Globicephala melas*) caught around the Faroe Islands. *Chemosphere* **2018**, *195*, 11–20.
- (14) Verreault, J.; Letcher, R. J.; Gentes, M. L.; Braune, B. M. Unusually high Deca-BDE concentrations and new flame retardants in a Canadian Arctic top predator, the glaucous gull. *Sci. Total Environ.* **2018**, *639*, 977–987.
- (15) Li, L.; Wania, F. Occurrence of Single- and Double-Peaked Emission Profiles of Synthetic Chemicals. *Environ. Sci. Technol.* **2018**, *52* (8), 4684–4693.

- (16) Li, L.; Wania, F. Tracking chemicals in products around the world: introduction of a dynamic substance flow analysis model and application to PCBs. *Environ. Int.* **2016**, *94*, 674–86.
- (17) Li, L.; Liu, J. G.; Hu, J. X.; Wania, F. Degradation of Fluorotelomer-Based Polymers Contributes to the Global Occurrence of Fluorotelomer Alcohol and Perfluoroalkyl Carboxylates: A Combined Dynamic Substance Flow and Environmental Fate Modeling Analysis. *Environ. Sci. Technol.* **2017**, *51* (8), 4461–4470.
- (18) Li, L.; Arnot, J. A.; Wania, F. Towards a systematic understanding of the dynamic fate of polychlorinated biphenyls in indoor, urban and rural environments. *Environ. Int.* **2018**, *117*, 57–68.
- (19) Li, L.; Wania, F. Elucidating the Variability in the Hexabromocyclododecane Diastereomer Profile in the Global Environment. *Environ. Sci. Technol.* **2018**, *52* (18), 10532–10542.
- (20) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254.
- (21) Redfern, F. M.; Lee, W. J.; Yan, P.; Mwangi, J. K.; Wang, L. C.; Shih, C. H. Overview and Perspectives on Emissions of Polybrominated Diphenyl Ethers on a Global Basis: Evaporative and Fugitive Releases from Commercial PBDE Mixtures and Emissions from Combustion Sources. *Aerosol Air Qual. Res.* **2017**, *17* (5), 1117–1131.
- (22) Li, T. Y.; Zhou, J. F.; Wu, C. C.; Bao, L. J.; Shi, L.; Zeng, E. Y. Characteristics of Polybrominated Diphenyl Ethers Released from Thermal Treatment and Open Burning of E-Waste. *Environ. Sci. Technol.* **2018**, *52* (8), 4650–4657.
- (23) Macleod, M.; McKone, T. E.; Mackay, D. Assessing the influence of climate variability on atmospheric concentrations of polychlorinated biphenyls using a global scale mass balance model (BETR-Global). *Environ. Sci. Technol.* **2005**, *39* (17), 6749–6756.
- (24) MacLeod, M.; von Waldow, H.; Tay, P.; Armitage, J. M.; Wohnschimmel, H.; Riley, W. J.; McKone, T. E.; Hungerbühler, K. BETR global - A geographically-explicit global-scale multimedia contaminant fate model. *Environ. Pollut.* **2011**, *159* (5), 1442–1445.
- (25) Schenker, U.; Soltermann, F.; Scheringer, M.; Hungerbühler, K. Modeling the environmental fate of Polybrominated Diphenyl Ethers (PBDEs): The importance of photolysis for the formation of lighter PBDEs. *Environ. Sci. Technol.* **2008**, *42* (24), 9244–9249.
- (26) UNEP. *Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants*; 2012; <http://chm.pops.int/Implementation/NIPs/GuidancefortheinventoryofPBDEs/tabid/3171/Default.aspx>.
- (27) Abbasi, G.; Buser, A. M.; Soehl, A.; Murray, M. W.; Diamond, M. L. Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020. *Environ. Sci. Technol.* **2015**, *49* (3), 1521–8.
- (28) Earnshaw, M. R.; Jones, K. C.; Sweetman, A. J. Estimating European historical production, consumption and atmospheric emissions of decabromodiphenyl ether. *Sci. Total Environ.* **2013**, *447*, 133–142.
- (29) Sakai, S.-i.; Hirai, Y.; Aizawa, H.; Ota, S.; Muroishi, Y. Emission inventory of deca-brominated diphenyl ether (DBDE) in Japan. *J. Mater. Cycles Waste Manage.* **2006**, *8* (1), 56–62.
- (30) Breivik, K.; Armitage, J. M.; Wania, F.; Jones, K. C. Tracking the global generation and exports of e-waste. Do existing estimates add up? *Environ. Sci. Technol.* **2014**, *48* (15), 8735–8743.
- (31) Prevedouros, K.; Jones, K. C.; Sweetman, A. J. Estimation of the production, consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe between 1970 and 2000. *Environ. Sci. Technol.* **2004**, *38* (12), 3224–3231.
- (32) Zhang, B.; Zhao, B.; Yu, M.; Zhang, J. Emission inventory and environmental distribution of decabromodiphenyl ether in China. *Sci. Total Environ.* **2017**, 599–600, 1073–1081.
- (33) Andersson, O.; Blomkvist, G. Polybrominated aromatic pollutants found in fish in Sweden. *Chemosphere* **1981**, *10* (9), 1051–1060.
- (34) Law, R. J.; Allchin, C. R.; de Boer, J.; Covaci, A.; Herzke, D.; Lepom, P.; Morris, S.; Tronczynski, J.; de Wit, C. A. Levels and trends of brominated flame retardants in the European environment. Proceedings of the 3rd International Workshop on Brominated Flame Retardants, Toronto, Canada, June 6–9, 2004; pp 187–208.
- (35) Law, R. J.; Allchin, C. R.; de Boer, J.; Covaci, A.; Herzke, D.; Lepom, P.; Morris, S.; Tronczynski, J.; de Wit, C. A. Levels and trends of brominated flame retardants in the European environment. *Chemosphere* **2006**, *64* (2), 187–208.
- (36) Law, R. J.; Herzke, D.; Harrad, S.; Morris, S.; Bersuder, P.; Allchin, C. R. Levels and trends of HBCD and BDEs in the European and Asian environments, with some information for other BFRs. *Chemosphere* **2008**, *73* (2), 223–41.
- (37) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46* (5), 583–624.
- (38) Hung, H.; Kallenborn, R.; Breivik, K.; Su, Y. S.; Brorstrom-Lunden, E.; Olafsdottir, K.; Thorlacius, J. M.; Leppanen, S.; Bossi, R.; Skov, H.; Mano, S.; Patton, G. W.; Stern, G.; Sverko, E.; Fellin, P. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.* **2010**, *408* (15), 2854–2873.
- (39) Zegers, B. N.; Lewis, W. E.; Booi, K.; Smittenberg, R. H.; Boer, W.; de Boer, J.; Boon, J. P. Levels of polybrominated diphenyl ether flame retardants in sediment cores from Western Europe. *Environ. Sci. Technol.* **2003**, *37* (17), 3803–7.
- (40) Qiu, X.; Marvin, C. H.; Hites, R. A. Dechlorane Plus and Other Flame Retardants in a Sediment Core from Lake Ontario. *Environ. Sci. Technol.* **2007**, *41* (17), 6014–6019.
- (41) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38* (4), 945–956.
- (42) Venier, M.; Salamova, A.; Hites, R. A. Halogenated Flame Retardants in the Great Lakes Environment. *Acc. Chem. Res.* **2015**, *48*, 1853.
- (43) Noren, K.; Meironyte, D. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20–30 years. *Chemosphere* **2000**, *40*, 1111–1123.
- (44) Betts, K. S. Rapidly rising PBDE levels in North America. *Environ. Sci. Technol.* **2002**, *36* (3), 50A–52A.
- (45) Law, R. J.; Covaci, A.; Harrad, S.; Herzke, D.; Abdallah, M. A.; Fernie, K.; Toms, L. M.; Takigami, H. Levels and trends of PBDEs and HBCDs in the global environment: status at the end of 2012. *Environ. Int.* **2014**, *65*, 147–58.
- (46) Schuster, J. K.; Gioia, R.; Breivik, K.; Steinnes, E.; Scheringer, M.; Jones, K. C. Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs. *Environ. Sci. Technol.* **2010**, *44* (17), 6760–6766.
- (47) Crimmins, B. S.; Pagano, J. J.; Xia, X.; Hopke, P. K.; Milligan, M. S.; Holsen, T. M. Polybrominated diphenyl ethers (PBDEs): turning the corner in Great Lakes trout 1980–2009. *Environ. Sci. Technol.* **2012**, *46* (18), 9890–7.
- (48) Alivernini, S.; Battistelli, C. L.; Turrio-Baldassarri, L. Human milk as a vector and an indicator of exposure to PCBs and PBDEs: temporal trend of samples collected in Rome. *Bull. Environ. Contam. Toxicol.* **2011**, *87* (1), 21–5.
- (49) Hoopmann, M.; Albrecht, U. V.; Gierden, E.; Huppmann, R.; Suchenwirth, R. Time trends and individual characteristics associated with polybrominated diphenyl ethers in breast milk samples 2006–2009 in Lower Saxony, Germany. *Int. J. Hyg. Environ. Health* **2012**, *215* (3), 352–9.
- (50) Link, B.; Gabrio, T.; Mann, V.; Schilling, B.; Maisner, V.; Konig, M.; Flicker-Klein, A.; Zollner, I.; Fischer, G. Polybrominated diphenyl ethers (PBDE) in blood of children in Baden-Württemberg between 2002/03 and 2008/09. *Int. J. Hyg. Environ. Health* **2012**, *215* (2), 224–8.
- (51) Ryan, J. J.; Rawn, D. F. The brominated flame retardants, PBDEs and HBCD, in Canadian human milk samples collected from 1992 to 2005; concentrations and trends. *Environ. Int.* **2014**, *70*, 1–8.

(52) Turyk, M. E.; Anderson, H. A.; Steenport, D.; Buelow, C.; Imm, P.; Knobeloch, L. Longitudinal biomonitoring for polybrominated diphenyl ethers (PBDEs) in residents of the Great Lakes basin. *Chemosphere* **2010**, *81* (4), 517–22.

(53) Wang, J.; Ma, Y. J.; Chen, S. J.; Tian, M.; Luo, X. J.; Mai, B. X. Brominated flame retardants in house dust from e-waste recycling and urban areas in South China: Implications on human exposure. *Environ. Int.* **2010**, *36* (6), 535–541.

(54) Wang, L. C.; Lee, W. J.; Lee, W. S.; Chang-Chien, G. P. Emission estimation and congener-specific characterization of polybrominated diphenyl ethers from various stationary and mobile sources. *Environ. Pollut.* **2010**, *158* (10), 3108–15.

(55) Wang, T. E-waste creates hot spots for POPs. *Environ. Sci. Technol.* **2007**, *41* (8), 2655–2656.

(56) Yang, Q. Y.; Qiu, X. H.; Li, R.; Liu, S. S.; Li, K. Q.; Wang, F. F.; Zhu, P.; Li, G.; Zhu, T. Exposure to typical persistent organic pollutants from an electronic waste recycling site in Northern China. *Chemosphere* **2013**, *91* (2), 205–211.

(57) Tang, J.; Zhai, J. X. Distribution of polybrominated diphenyl ethers in breast milk, cord blood and placentas: a systematic review. *Environ. Sci. Pollut. Res.* **2017**, *24* (27), 21548–21573.

(58) Asante, K. A.; Adu-Kumi, S.; Nakahiro, K.; Takahashi, S.; Isobe, T.; Sudaryanto, A.; Devanathan, G.; Clarke, E.; Ansa-Asare, O. D.; Dapaah-Siakwan, S.; Tanabe, S. Human exposure to PCBs, PBDEs and HBCDs in Ghana: Temporal variation, sources of exposure and estimation of daily intakes by infants. *Environ. Int.* **2011**, *37* (5), 921–928.

(59) Linderholm, L.; Biague, A.; Mansson, F.; Norrgren, H.; Bergman, A.; Jakobsson, K. Human exposure to persistent organic pollutants in West Africa—a temporal trend study from Guinea-Bissau. *Environ. Int.* **2010**, *36* (7), 675–82.

(60) Devanathan, G.; Subramanian, A.; Sudaryanto, A.; Takahashi, S.; Isobe, T.; Tanabe, S. Brominated flame retardants and polychlorinated biphenyls in human breast milk from several locations in India: potential contaminant sources in a municipal dumping site. *Environ. Int.* **2012**, *39* (1), 87–95.

(61) McGrath, T. J.; Morrison, P. D.; Ball, A. S.; Clarke, B. O. Spatial Distribution of Novel and Legacy Brominated Flame Retardants in Soils Surrounding Two Australian Electronic Waste Recycling Facilities. *Environ. Sci. Technol.* **2018**, *52* (15), 8194–8204.

(62) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 3. An update. *Sci. Total Environ.* **2007**, *377* (2–3), 296–307.

(63) Wang, Z.; Cousins, I. T.; Scheringer, M.; Buck, R. C.; Hungerbühler, K. Global emission inventories for C4–C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, Part I: production and emissions from quantifiable sources. *Environ. Int.* **2014**, *70*, 62–75.

(64) Glüge, J.; Wang, Z.; Bogdal, C.; Scheringer, M.; Hungerbühler, K. Global production, use, and emission volumes of short-chain chlorinated paraffins—A minimum scenario. *Sci. Total Environ.* **2016**, *573*, 1132–1146.

(65) Li, L.; Liu, J.; Hu, J. Global inventory, long-range transport and environmental distribution of dicofol. *Environ. Sci. Technol.* **2015**, *49* (1), 212–22.

(66) Li, L.; Weber, R.; Liu, J.; Hu, J. Long-term emissions of hexabromocyclododecane as a chemical of concern in products in China. *Environ. Int.* **2016**, *91*, 291–300.

(67) Ionas, A. C.; Dirtu, A. C.; Anthonissen, T.; Neels, H.; Covaci, A. Downsides of the recycling process: harmful organic chemicals in children's toys. *Environ. Int.* **2014**, *65*, 54–62.