

COMPARISON OF BDE-209 CONCENTRATIONS MODELLED IN A DYNAMIC SUBSTANCE FLOW ANALYSIS FOR SWITZERLAND AND FIELD DATA

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Abstract

Predicted environmental concentrations (PEC) of BDE-209 have been estimated based on emissions modelled in a dynamic substance flow analysis for Switzerland. The PECs have been compared to field data from Switzerland and abroad. The outdoor air concentration, the atmospheric deposition and the concentrations in sediment cores modelled are lower than field data. It is concluded that atmospheric emissions might be underestimated based on available literature data.

Introduction

Emissions of PBDEs occur during production, use and disposal of various products and these substances have become ubiquitous environmental contaminants. They are persistent as well as subject to bioaccumulation and long-range transport¹. The dynamic behaviour of the anthropogenic metabolism and emission trends for BDE-209 from anthroposphere to the environment have been determined in a dynamic model for Switzerland during the period of 1980–2020² in order to gain a better knowledge about sources and fate. This knowledge can serve as a base for regulatory and technical measures.

Materials and Methods

The dynamic SFA has been carried out with a model, based on a system of coupled integro-differential equations with (time-dependent) parameter functions using the SIMBOX[®] software. The spatial system boundary is the political border of Switzerland and the temporal period 1980–2020. In order to take into account their different behaviour in the anthroposphere, the use of the selected BFRs has been split up in 4 application areas (E&E, transport, textile/furniture and construction). Time series for the parameter functions (consumption, residence times, transfer coefficients, emission factors) have been estimated based on literature data, industry contacts, measurements and own calculations and assumptions. For a more detailed description of the model, see ref 2.

The uncertainty of the consumption and most transfer coefficients have been estimated as between 20% and 50% (expressed as relative width of a 90% confidence interval). On the other hand, the domains of uncertainty of emission factors and diffuse releases to wastewater are very high. The reasons of these high uncertainties are highly variable or non available laboratory or field data. There are e.g. emission chamber experiments carried out for TVs with PBDEs^{3,4}. The results ranged by one or more orders of magnitude between different runs. Additionally, as no measurements were carried out e.g. for construction materials, assumptions had to be made. The largest proportion of emissions was found on chamber walls, on TV screens and on dust. The proportion of these emissions getting to atmosphere, vacuum cleaner bags, wastewater and washing water had to be estimated as well. Also emission measurements of point sources exhibited a high variance. The emission factors from plastics processing industry measured by the Japanese Ministry of the Environment ranged by two orders of magnitude⁵. These uncertainties do not have a normal, but a right-skewed distribution. The 90% confidence intervals of these parameters have been estimated as $p / 10 < p < p \cdot 10$ (p : best estimate parameter) for all emission factors and diffuse releases in order to achieve a better traceability. Therefore, a lognormal distribution has been expected to be most appropriate. The uncertainty of the substance flows was estimated using a Monte Carlo simulation with @Risk[®] software based on the uncertainty of the individual parameters.

The PECs have been estimated using a simple environmental fate model. The atmospheric emissions modelled have been split in three fractions: (a) the fraction being degraded of photolytic and OH radical reactions, (b) the fraction being deposited by dry and wet deposition and (c) the fraction of the annual emissions residing in the atmosphere at steady-state. These fractions have been derived by estimating the reaction and the deposition rate using the model by Hirai and Sakai⁶ that has been adapted for Switzerland. The atmospheric deposition substance flow has been split up to hydrosphere (5.6%) and soil (94.4%) according to their surface area fraction

in Switzerland. These substance flows have been added to the direct emissions to hydrosphere and soil respectively. The mass remaining in the atmosphere has been estimated for each individual year assuming steady-state throughout the year.

Table 1. Fate of the atmospheric emissions of BDE-209

	Approach based on	Approach based on
	degradation/deposition	sediment flux rates
	mean (range)	range
Fraction degraded in air	2.3% (0.21–20.7%)	99.25–99.79%
Fraction in deposition	97.5% (79.2–99.5%)	
Fraction of annual emissions residing in air at steady-state	0.2% (0.13–0.26%)	0.21–0.75%

These estimates have been compared with total elimination rates estimated from empirical atmospheric half-life distances that were based on dated sediment cores from lakes along a latitudinal transect in North America⁷. The fraction of annual atmospheric emissions that have been estimated to reside in the air at steady-state has been derived from the reverse of the total elimination rates. The lower estimate of the fraction derived in this approach is comparable with the approach above.

The air has been assumed to have a height of 1000 m, which is about the mean height of the atmospheric boundary layer. The atmospheric transport of the chemicals from and to Switzerland has not been included. The export has been assumed to be compensated by the import from adjoining countries. Emissions in these countries have been assumed to be similar and the distance to the sea is only considerably shorter than the atmospheric half-life distances in one of the four main wind directions in Switzerland. For the hydrosphere, the chemical's partitioning at equilibrium into the different compartments water, sediment and aquatic organisms has been modelled for each year using a fugacity model. The sediment has been assumed to cover the area of Swiss surface waters. The sedimentation rate in lakes was found to be approximately 35 mm/year⁸. It has been assumed that the amount released to hydrosphere would partition between the water, the biota and the yearly deposited sediment. No mixing has been supposed and a concentration trend against the depth of the sediment layers has been derived.

There was some data on degradation of BDE-209, but either the type of degradation, the matrix or the temperature was not realistic for lake sediments. The experiments by Gerecke et al.⁹ carried out with digested sewage sludge has been considered to be the most appropriate. A half-life of approximately 2 years was found there. Taking into account that the temperature in the sediments are about 30 °C lower than in the experiment, the microbial community is not the same, the conditions are only partly anaerobic and the fact that the available energy is declining with the age of the sediment, the half-life has been expected to be two orders of magnitude higher than in sludge. A half-life of 200 years has therefore been considered as realistic, but also a half-life of ten years has been included. The concentrations in each sediment layer have been calculated taking into account the degradation rates and the age of the layer with 2006 as the reference year.

Results and Discussion

There was an increase in emissions of BDE-209 until the mid-1990s, followed by a decrease until the late 2000s as illustrated in figure 1a. The emissions have been modelled to stay virtually constant within the next decade, if no ban is assumed. Total emissions estimates at the end of the nineties were about 60 kg/year. Emissions to atmosphere accounted for up to 20 kg/year, emissions to hydrosphere for up to 6 kg/year and emissions to soil for up to 40 kg/year. Wastewater has been the most relevant emission pathway into soil and hydrosphere, especially in the past. As the usage of sewage sludge as fertilizer in agriculture has been declining over the years, the emissions to soil decreased significantly in Switzerland. Figure 1b shows the 90% confidence intervals for the emissions to atmosphere, hydrosphere and soil derived in a Monte Carlo simulation for 2005. The upper boundary of the confidence interval is about one order of magnitude higher than the lower boundary for all compartments. While the maximum values exceed the upper boundary by about one order of magnitude for the

emissions to hydrosphere and soil, the maximum value for atmospheric emission is two orders of magnitude higher than the boundary.

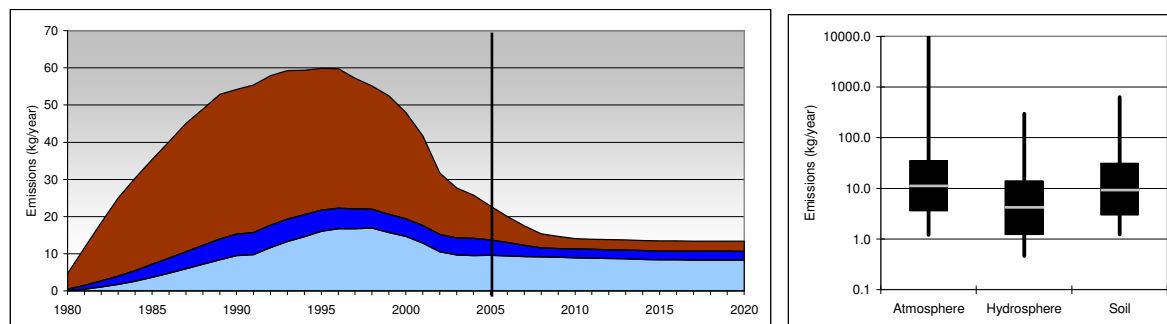


Figure 1. (a) Estimated emission trend of BDE-209 to atmosphere (light blue), hydrosphere (dark blue) and soil (brown). (b) mean, 90% confidence intervals (box), minima and maxima emissions derived with the Monte Carlo simulation for the year 2005.

The outdoor air concentration modelled for the year 2005 is 0.5 pg/m^3 with a lower and upper boundary of 0.1 and 2.3 pg/m^3 as illustrated in figure 2a. The concentrations found in the literature range from 0.05 pg/m^3 (half of detection limit) to 74.5 pg/m^3 in rural and remote regions and from 1.5 to 4200 pg/m^3 in urban areas^{10–13}. The atmospheric deposition modelled is $0.23 \text{ } \mu\text{g/m}^2/\text{year}$ ($0.07\text{--}0.85 \text{ } \mu\text{g/m}^2/\text{year}$). The experimentally determined atmospheric deposition was $1.7 \text{ } \mu\text{g/m}^2/\text{year}$ at the shore of Lake Thun, a pre-alpine lake in the center of Switzerland in summer 2006¹⁴. In Dübendorf, a Swiss municipality close to Zurich, the deposition was $3.6 \text{ } \mu\text{g/m}^2/\text{year}$ in February 2006 (C. Bogdal, personal communication) measured with the same method.

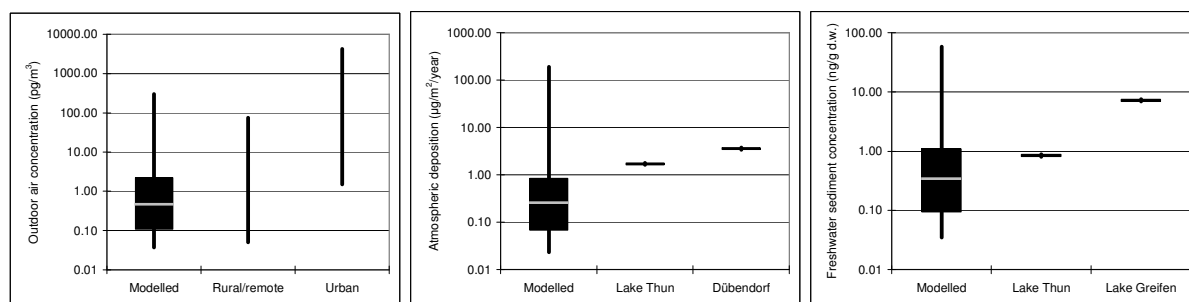


Figure 2. Confidence intervals, minima and maxima emissions derived with the Monte Carlo simulation for the year 2005 compared with measured data: (a) outdoor air concentration, (b) atmospheric deposition and (c) concentration in freshwater sediments.

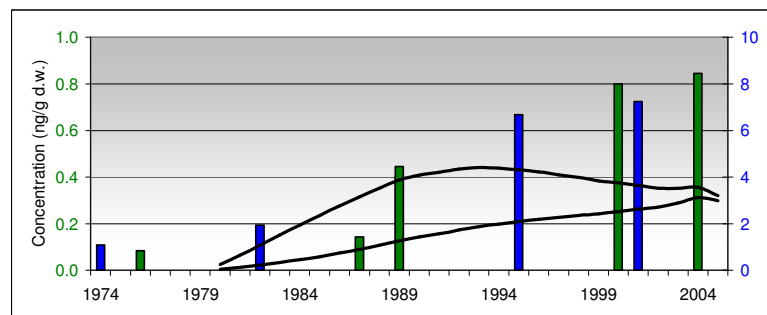


Figure 3. Modelled concentration in sediment layers from different years: half-life of 200 years (upper line), half-life of 10 years (lower line). Concentrations in Lake Thun (green bars) and Lake Greifen (blue bars). Note the different scale on the right hand side for Lake Greifen.

The concentration trends modelled for freshwater sediments cores with half-lives of 200 and 10 years are comparable with the levels found in a data sediment core in Lake Thun. However, the concentrations in Lake Greifen, which is a shallow lake in the urban region of Zurich, are one order of magnitude higher⁸.

The best estimate outdoor air concentrations, atmospheric deposition rates and concentrations in sediment are all predominantly lower compared to the measurements available. It is therefore concluded that the atmospheric emissions might be underestimated based on currently available data on emission factors. The difference in sediment cores is also assumed to mainly result from the too low atmospheric depositions estimates. The emissions to hydrosphere are easier to estimate based on measurements (STP effluents, sewage sludge), which diminishes the risk of a large inaccuracy. Also the high levels found in alpine soils¹⁵ support this hypothesis.

Especially the diffuse emissions from the use phase of products are supposed to be underestimated. Also the emissions from recycling, particularly where waste articles are shredded, could have been underestimated. There are no experimental data on BFR emissions from shredder plants. However, it has been showed that PBDE concentrations in ryegrass cultures placed nearby shredder exceeded background levels by one to three orders of magnitude¹⁶. As BDE-209 has a long-range transport potential, there might also be a net import with the air. Reasons for higher emissions in neighbouring countries could be a higher industrial consumption or a significant difference in waste management legislation and technology. Illegal burning of hazardous waste and frequent fires on illegal dumpsites may be of significance, too. However, these potential foreign sources can not be the only explanations for the differences between modelled values and levels in the environment. Therefore, further research on emissions factors from the use phase and recycling processes is needed.

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