MODELING THE CONTRIBUTION OF DECA-BDE TO LEVELS OF LIGHT PBDES IN THE ENVIRONMENT: THE IMPORTANCE OF DIRECT PHOTOLYSIS

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Introduction

Polybrominated diphenylethers (PBDEs) are frequently used as flame retardants in textiles and polymeric materials. Recently, PBDEs have been found in remote areas[1] where they have not been used in significant amounts. Measurement studies find light PBDEs more often in remote locations such as the Arctic[2], whereas heavy PBDEs are only rarely detected far from the source areas. One reason for this is the very low vapor pressure of heavy PBDEs, which efficiently prevents their evaporation and thus their ability for atmospheric long-range transport. In some modeling studies, this finding is confirmed, because light PBDEs were shown to have a higher long-range transport potential[3] than the heavy homologues. PBDE concentrations in human milk have increased exponentially between 1972 and 1997[4]. Studies on toxicity of different PBDE homologues have furthermore shown that light PBDEs are more toxic than the heavy homologues[5]. Therefore, the commercial octa- and penta-BDE mixtures have recently been phased-out in the European Union[6]. The commercial deca-BDE mixture, which contains mainly the deca-BDE homologue, remains still in use. Because of its low vapor pressure and toxicity, deca-BDE is believed to be less of a concern.

Recently, evidence has risen that heavy PBDEs, in particular deca-BDE, might be degraded into light PBDEs: deca-BDE in organic solvents or absorbed on mineral surfaces that was exposed to sunlight has been shown to degrade quickly into lower brominated PBDEs[7-10]. This would suggest that heavy PBDEs might be similarly problematic for the environment and human health as light PBDEs. However, because these processes were identified under controlled laboratory conditions only, it has been questioned whether they are relevant in the environment[11]. In particular, it is unclear to which extent heavy PBDEs are exposed to sunlight, because their low vapor pressure efficiently prevents their evaporation. Model predictions suggest that a large fraction of the mass of heavy PBDEs is sorbed to sediments and soils and is not reached by sunlight[12, 13].

Environmental fate models can be used to predict the behavior of chemicals in the environment. PBDEs have been investigated using environmental fate models in the past[3, 13, 14], but these studies focus on the environmental fate of different PBDE homologues. To our knowledge, the importance of degradation of heavy PBDEs into lighter ones in the environment has hitherto not been assessed with environmental fate models. Furthermore, the relevance of direct photolytic degradation for the fate of different PBDE homologues has, to our knowledge, only been assessed on a local scale for the Great Lakes area in North America[15], and the implications of this process on a global scale remain unclear.

Here we use the global environmental fate model CliMoChem to characterize the behavior of different PBDE homologues. For the first time, direct photolysis is taken into account on a global scale, and its importance for long-range transport of different PBDE homologues is described. We estimate degradation yields for heavy PBDEs into light PBDEs. Using a realistic emission inventory of the different commercial mixtures of PBDEs, we then characterize the relative contributions of direct emissions of light PBDEs and environmental degradation of heavy PBDEs.

Material and Methods

We have used the environmental fate model CliMoChem[16, 17] to describe the fate of PBDEs in the environment. CliMoChem is a global multi-media box model and assembles ten zones in the north-south direction within which concentrations are assumed to be homogeneous in the east-west direction. Each zone is composed of ocean-water, bare soil, vegetation-covered soil, vegetation, and atmosphere. Environmental exchange and degradation processes (such as rain washout, wind, or microbial degradation) are calculated individually for each zone, assuming zone-specific environmental parameters (such as rain rates, wind speed, or organic matter content of soils). The current version of the model is capable of calculating several substances simultaneously, and makes it possible to take into account that one substance is degraded into others, using different transformation yields for different environmental media.

To include direct photolysis in the model, a new degradation process was introduced into CliMoChem: direct photolysis is a function of the intensity of sunlight, which is in turn dependent on the latitudinal zone and the season of the year. We use light intensity data from a global meteorological model[18] that takes into account variable degrees of cloud cover and day-length variations. Furthermore, we have introduced shielding factors that take into account that PBDEs are shielded from sunlight when absorbed to aerosols, soils, or ocean water.

We have compiled partitioning data for different PBDE homologues from previous compilations[14] and newly published measurements. Degradation rate constants for PBDEs in surface media and OH radical reaction rates have been estimated with QSPR software[19]. To calculate direct photolytic degradation rates, measurements in organic solvents and mineral surfaces[7-9, 15] have been extrapolated to the gas-phase. Our photolysis rate constants compare well with those from a recent study on direct photolysis of PBDEs on a local scale[15].

Realistic emissions of different PBDE homologues are calculated based on estimated production data[20] for PBDEs. We cover emissions of PBDEs during production, in the use phase (evaporation and wash-out from polymeric materials and textiles), and emissions of PBDEs during the waste management process (as leakage from landfills, during controlled incineration, and from accidental or intentional open burnings of waste). Higher emission factors are obtained for the relatively volatile light PBDEs as compared to the relatively non-volatile heavy PBDEs.

Results and Discussion

Direct photolysis is the dominant degradation pathway for heavy PBDEs (see Figure 1). Compared to OH radical reactions in the gas phase, direct photolysis is about 1000 times faster for deca-BDE, whereas direct photolysis and OH radical reactions have a comparable rate constant for penta-BDE. The overall atmospheric degradation half-life for deca-BDE is about 100 times below that of penta-BDE, because direct photolysis is an efficient degradation pathway. These results are very similar to the ones presented previously[15] and confirm that direct photolysis should be taken into account when the environmental fate of PBDEs is modeled.

The influence of direct photolysis on the fate of PBDEs in a global model can be seen in Table 1, where indicators of environmental persistence and long-range transport are given for penta-BDE and deca-BDE, with and
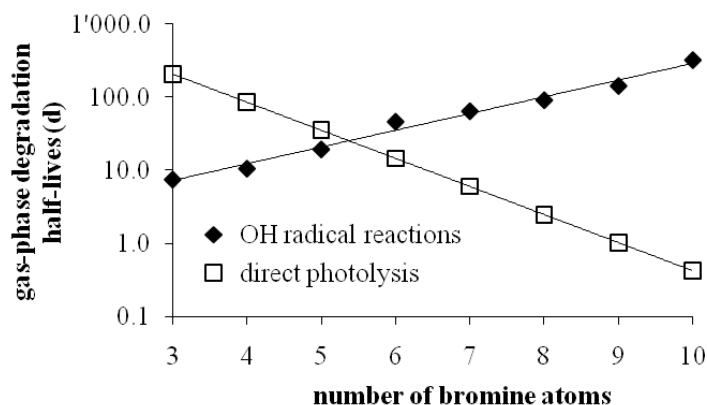

Figure 1 Atmospheric degradation half-lives of different PBDE homologues for OH radical reactions and direct photolysis. OH radical concentrations and light intensity are representative of the northern temperate zone.

without the inclusion of direct photolytic degradation processes. Direct photolysis reduces the overall persistence (an indicator for the residence time of chemicals in the environment[21]), the spatial range[21], and the arctic contamination potential[22] (both indicators for the long-range transport potential of chemicals). The importance of direct photolytic degradation can be seen most clearly for the overall persistence, which decreases by almost a factor of 10 in the case of deca-BDE, and a factor of 5 in the case of penta-BDE. The spatial range and the arctic contamination potential are influenced less strongly by photolysis. The arctic contamination potential, for example, decreases by a factor of five for deca-BDE, and by about a factor of two for penta-BDE. It can also be seen that deca-BDE is generally more strongly influenced by direct photolytic degradation than penta-BDE, because direct photolytic degradation is less important for penta-BDE than for deca-BDE (as shown in Figure 1). Finally, Table 1 also indicates that the long-range transport potential (expressed as the spatial range or the arctic contamination potential) of penta-BDE is considerably greater than that of deca-BDE if photolysis is taken into account, consistent with findings from field data[2, 3]. If photolysis is not taken into account, in contrast, the long-range transport potentials of deca- and penta-BDE are very similar, which is against evidence from the above mentioned field data.

Table 1: Overall persistence (in days), spatial range (in percent), and arctic contamination potential (eACP-10, in percent) of different PBDE homologues, with and without the inclusion of direct photolysis.

	photolysis	persistence (d)	spatial range (%)	eACP-10 (%)
penta-BDE	yes	70	15	0.74
	no	355	32	1.97
deca-BDE	yes	183	10	0.38
	no	1552	30	1.78

The contribution of the different commercial PBDE mixtures to PBDE levels in the environment are shown in Figure 2. Whereas the levels of heavy PBDEs (such as hexa-BDE, right pie-chart in Figure 2) are strongly influenced by emissions and degradation of the commercial deca-BDE and octa-BDE mixtures, levels of lighter PBDEs are mainly determined by direct emissions of penta-BDE. For instance, 88% of the penta-BDE in ocean water is due to emissions of the commercial penta-BDE mixture, and only 12% due to the degradation of the deca- and octa-BDE mixtures. These results are similar in other environmental media and other latitudinal zones. For lighter homologues than penta-BDE, the importance of the deca-BDE mixture is even lower, whereas for heavier PBDEs than hexa-BDE, the importance of the deca-BDE mixture is higher.
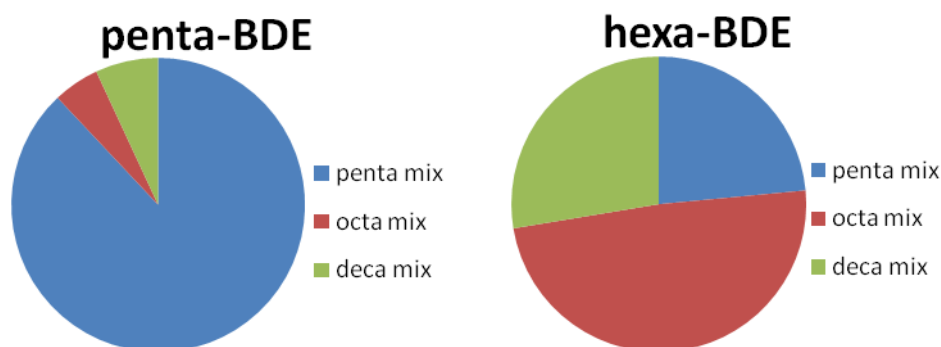

Figure 2 The relative contributions of the emissions of different commercial PBDE mixtures to levels of penta- (left side) and hexa-BDE (right side) in ocean water of the northern temperate zone in the year 2005.

There are considerable uncertainties associated with the above calculations. Emission factors for the different PBDE homologues from the use phase and the waste management process are highly uncertain and have considerable influence on the model results. On the other hand, the debromination yields of the photolytic degradation processes are relatively uncertain, too. Often, debromination has only been measured in organic solvents, and it is unclear whether the measured debromination yields may be extrapolated to the environment. By comparing the model results with field data, we have tried to reduce the influence of these uncertainties on our model results. In particular, we have compared the ratio of penta- to deca-BDE in the model and in field data. We find that this ratio is relatively similar, which suggests that the relative importance of emissions of the commercial deca- and penta-BDE mixtures is approximately correct in our assumption. Furthermore, we varied the debromination yields and compare the ratio of tri- to penta-BDE in the model with field data. We find that a reduced debromination yield in the model leads to a ratio of tri- to penta-BDE that is considerably below the ratio found in field data. This suggests that debromination is a relevant degradation process for lower brominated BDEs, too.

Our model results suggest that the main contributor for levels of light PBDEs in the environment is the commercial penta-BDE mixture. Thus, if the environmental risk from the toxic and mobile light PBDEs is to be decreased, a ban of the commercial penta-BDE mixture (and possibly also the octa-BDE mixture) is an efficient measure. However, if the commercial deca-BDE mixture remains in use, levels of penta-BDE in the environment will only decrease by about a factor of ten, because penta-BDE is continuously regenerated in the environment by degradation of heavier PBDEs. If a stronger reduction of the levels of light PBDEs in the environment is required, the emissions of deca-BDE have to be reduced, too. To reduce uncertainties in our results, we suggest

to better characterize debromination yields of PBDE in the environment, and to improve emission estimates of PBDEs.

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