EMISSION LOAD OF HEXABROMOCYCLODODECANE IN JAPAN BASED ON THE SUBSTANCE FLOW ANALYSIS

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Abstract
Atmospheric and aquatic emission load of hexabromocyclododecane (HBCD) for the period 1986-2030 were estimated by substance flow analysis. Through the investigation of quantitative HBCD life cycle, estimated HBCD stock in the use phase shows a continuous increase, indicating that emissions from the materials containing HBCD will be potentially long-term sources of pollutants leaching or volatizing to the environment. In Japan, 571 kg/year and 41 kg/year of HBCD was calculated to emit to the atmospheric and aquatic environment in 2000, respectively. This corresponds to 0.03 % of the consumed HBCD quantity in Japan. These environmental emissions of HBCD were increasing rapidly until 2011. On the other hand, decreasing trend for HBCD were estimated between 2012 and 2030 and the emissions were simulated to be as high as 225 kg/year in 2030. This is due to the scenario that the use of HBCD for textiles would be stopped. The largest component of the emissions is simulated to be into the atmosphere from the consumer product because the stock in the use phase has been growing over the whole period. The source profile of environmental emission would shift from upstream to downstream of product chain. The present study gives an insight to obtain basic information for long term measures toward strategic chemical management considering their life cycle

Introduction
Brominated Flame Retardants (BFRs) are important synthetic additives which are used to reduce the flammability of articles. Despite their benefits, however, the occurrence of BFRs in the environment as contaminants have recently an increasing attention because of the widespread use, high chemical stability and bioaccumulation potential of some BFRs. Among the BFRs, which are available commercially, HBCD has received more interest and has been conducted the risk assessment. Currently, increasing number of reports have shown the environmental distribution of HBCD in Europe [1,2], the U.S.A [3] and Asia [4, 5]. In current risk assessments, however, especially for the calculation of predicted environmental concentrations (PEC) in the environmental exposure assessment, the available dataset in Japan is usually limited. For reliable risk management, the need for identification of its sources and quantification of emissions are growing in importance.
HBCD has been detected in various environmental compartments such as house dust, riverine sediment near the HBCD production plant and sewage sludge from municipal sewage treamtment plant [6]. This implies that emissions of HBCD occur from private use and disposal of flame retarded products, as well as upon production and processing. Identification of emissions covering with the lifecycle (i.e., from production to disporsal) could be of concern for risk assessments. Thus, it is essential to gain knowledge about their behavior in both economic system and environmental system through the lifecycle for chemical substances. Currently, limited research work has focused on the intensive monitoring which is covered with the lifecycle of chemical substance. For the effective risk-reduction strategies of chemical pollutants, the methodology, which can estimate emissions and source of pollutants through their lifecycle, has been needed.
Recently, substance flow analysis (SFA), which is used to describe or analyse the flow of one substance in, out and through a system, have been proposed as a useful tool to evaluate fate of substances quantitatively during all life stages[7]. This includes the evaluation of sources, substance flows and pathways, stocks in private house-holds, industry and waste management. Traditionally, several researchers have employed SFA to support environmental management of heavy metals[8, 9] from the view point of material recycling and resource recovery. On the other hand, only few studies to date have been performed for chemical substances[10-12]. Recenty, Morf et al[13] evaluated the source and environmental emission of some BFRs (Deca BDE and HBCD) through their lifecylce in Switzerland. However, environmental emission and lifecycle of target chemicals vary among countries or areas depending on the application of products and technologies.

In this study, we conducted dynamic (the time series) SFA of HBCD, which is one of the most important BFRs on the market in Japan under several scenarios to obtain basic information for long term measures toward strategic chemical management. The aim of this study was to identify possible emission pathways and determine the environmental occurrence of HBCD in Japan.

Materials and Methods
To estimate environmental emissions of HBCD from past to future during all life stages, the time series substance flow analysis (SFA), which consider the residence times of product, was applied in this study. For the procedure to establish the substance flow of HBCD, we determined the life cycle of HBCD with regard to space, function and time at first. As a next step, the environmental emission, the amount of flow and stock were quantified. The parameter functions for substance flow analysis were estimated based on broad literature data, multiple contacts with research groups, organizations, authorities and industry in Japan, our own analysis and assumptions.

The life cycle of HBCD and Data. The system flow of HBCD in Japan is shown in Fig. 1.The spatial system boundary was defined as the border of Japan. The import of product containing HBCD (e.g., plastic and textile/furniture) and the export of waste have not been included in this study, due to the limitation of available data. Also, we have not considered about the flow after recycling process. In the industrial use stage, the use of HBCD was divided into polystyrene as insulation board and textile. During industrial use of polystyrene, some portion of insulation board was transferred to the use phase and the remaining was recycling. In order to take into account the difference of life time of consumer products during the private use process, the use of insulation board was divided into four applications as end-product (i.e., office building, reinforced concrete house, wooden residential house and tatami mat). On the other hand, the use of textile was divided into interior textile and automobile interior textile. During life time of these consumer products, we have not considered about the degradation loss of HBCD. Finally, the consumer product is distributed after its residence time in the use phase to the waste (landfill or incineration) or recycling processes. In Japan, the product containing HBCD has been disposed to stable type landfill. Therefore, we assume the products are stabilized after one year and release no HBCD. Also, we have considered about the waste containing HBCD, which is generated at each life cycle step (i.e., pre-consumer waste). In this system, the time span was set up 1986-2030 and the time unit was one year.
Based on the life cycle of HBCD, the quantitative data concerning to emissions, flow and stock were gathered as a next step. In each stage, the amount of environmental emission and transfer were calculated by multiplying the input to each sage and emission factor and/or transfer coefficient. The input to a stage corresponds to the amount of transfer from the previous stage. The initial input of HBCD to the system corresponds to the amount of domestic demand, whereas the import HB CD is directly added to the industrial use stage. Emission factors during all the life stages were evaluated or estimated according to EU Risk assessment report of HBCD[14]. To confirm the reliability of factors and whether emission factors from EU can be applied into those of Japan, we have interviewed to the relevant company and committee. Emission factor are defined as constant value from past to future (i.e., 1986-2030), although environmental emission depend heavily on new production and waste management techniques. Transfer coefficients were also defined as constant value. The data were gathered from available literature. These values, in particular management strategies, could be time-dependent. However, due to the limitation of available data, they were defined as constant value through the time period in this study. For the consumption (sum of the amount of domestic demand and import) and application patterns (four application of insulation board and two for textile) of HBCD, the estimated consumption data of HBCD are available from 1986 to 2001in Japan. Based on this data from 1986 to 2001, we extrapolated the consumption to 2030. For this prediction of HBCD consumption, the textile industry association demonstrates that the use of HBCD will be banned until 2013, whereas the use of HBCD for polystyrene as insulation board will be increased. Therefore, this study was incorporated in that scenario. For application patterns, based on the available literature data on relevant industry from 1986 to 2006, we extrapolated the application patterns to 2030. Among application pattern in HBCD, polystyrene as insulation board make up by far the most important component of HBCD consumption (80% in the present year). The application areas, textiles/furniture (20% each) is less important.
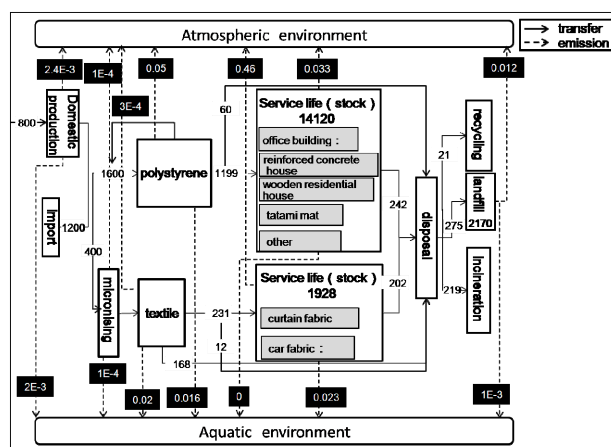
FIGURE 1 HBCD substance flow (tone/year), stock (tone/year) and emission (tone/year) in the anthroposhphere in Japan for 2000. Black square shows the environmental emission from each life stage.

The time series SFA Model. SFA is based on the materials balance, assuming that input mass equals the sum of the mass among the output fractions for each substance. The delay between the input and output was considered in the consumer product of the private use phase (i.e., the residence times of product). In the product, industrial use and disposal stage, the outflow of the substance is given in below.

$$\frac{dM_i(t)}{dt} = I_i(t) - (\Sigma(\alpha+\beta)) \times M_i(t)$$

With $M_i(t)$ is amount of substance, $I_i(t)$ is inflow and α and β is emission rate coefficient and transfer rate coefficient, respectively. When $dM_i(t)/dt = 0$, M(t) can be described as follows:

$$M_i(t) = \frac{1}{\Sigma(\alpha+\beta)} \times I_i(t)$$

Thus, by using emission factor (ef_i) and transfer coefficient (tf_i), environmental emission ($E(t)$) and the amount of transfer ($T(t)$) is

$$E_i(t) = \alpha \times M_i(t) = \frac{\alpha}{\Sigma(\alpha+\beta)} \times I_i(t) = ef_i \times I_i(t)$$

$$T_i(t) = \beta \times M_i(t) = \frac{\beta}{\Sigma(\alpha+\beta)} \times I_i(t) = tf_i \times I_i(t)$$

In the private use stage, the size of future emission can be determined by the inflows in the past and the time characteristics of the stock. In order to investigate the dynamic behavior in the anthroposphere, and to simulate future emissions from the anthroposphere to the environment, a delay model was established. These large residence times induce large delays between the input and output of the use phase, which cannot be described by a stationary model. The dynamic model is based on the method of mathematical material flow analysis, which was extended from material flow analysis by Baccini and Bader for the dynamic case. It is based on a system of coupled integro-differential equations with (time-dependent) parameter functions using the Weibull distribution. Briefly,

$$\frac{dM_i(t)}{dt} = I_i(t) - (\Sigma\alpha) \times M_i(t) - \frac{dw_i(t)}{dt}$$

When the environmental emission ($\Sigma\alpha \times M_i(t)$) will be negligible relative to other parameter, the equation will be as follows:

$$\frac{dM_i(t)}{dt} \approx I_i(t) - \frac{dW_i(t)}{dt}$$

$dWi\ (t)/\ dt$ represents the amount of disposal. The equation for $Wi\ (t)$ can be described

$$W_i(t) = \int [\, I_i(t) \times F\,(t\text{-}i'_i)\,] dt$$

$$F(n) = 1 - exp\,[\,-\,(n/b_i)^{a_n}]$$

By using these equations, environmental emission ($E\ (t)$) can be described as follows:

$$E_i(t) = \alpha \times \int [\, I_i(t) \times (1 - F\,(t\text{-}i)) \,] dt$$

Results and Discussion

Static flow At first, substance flow was established for selected year. This results can yield an overview of flows and stocks in the system investigated. Figure 1 shows an example of the results for Japan in 2000. For this year, HBCD consumption for all application areas was around 2000 tonnes. The polystyrene as insulation board application area accounts for approximately 80 % of the total use at this time. During industrial use of polystyrene, output to the use phase was 75% and the remaining was recycling. For the textile, 58% of HBCD are applied as coatings to textile fibers and the remaing was mainly treated with activated sludge and then disposed to landfill. The stock of HBCD in the use phase was simulated as 16048 tonnes based on the Weibull distribution. Most of this amount is stored in the office building (44% of four end products application) will be released only in many years, when office building are renovated. Some 13 % of the HBCD in disposed of products assumed to be incinerated, 72% to be landfilled. The total stock in landfills related to this application area is almost 2170 tonnes. According to the consumption data of HBCD, the cumulative consumption from 1986 to 2000 was calculated to be 18500 tonnes. On the other hand, the sum of stocks in the use phase and landfill was 18218 tonnes, which was in good agreement with the total consumption until 2000. This indicates our estimation is an almost balanced input-output for all application in 2000 during all life stages.

During all the stages, 571 kg/year of HBCD was emitted to the environment, which was one order of magnitude higher than of those of Switzlerland. This corresponds to 0.03 % of the consumed HBCD quantity in Japan. Morf et al[13] have reported that 0.021 % of HBCD relative to consumption in Switzlerland was annually released to the environment, which is comparable for our results. The relative contribution from all the stages to environmental media indicate that for atmospheric environment, larger contribution (81 % of total emission) was observed from the consumer use stage, whereas industrial use stage (41%) and consumer use stage (40%), which represents mainly washing of textile, was estimated to be a main contributor to aquatic environment.

Dynamic flow Next, the time series substance flow analysis was conducted from 1986 to 2001, and extrapolated to 2030. The estimated consumption data for Japan from 1986 to date, and extrapolated to 2030, were shown for HBCD. The amount of HBCD was estimated to be 2600 tone in 2004. In contrast, an accurate data from Ministry of Economy, Trade and Industry (METI) in 2004 were reported in 3443 tones [15], where there are relatively large gaps. This indicates that the estimated consumption data of HBCD were underestimated. So far, however, an accurate data from METI are available for only three years (i.e., 2004-2006). These less data are not suitable for the prediction of future consumption. Therefore, we applied the estimated consumption data set (1986 to 2001).HBCD represents a typical substance with a steadily increasing consumption rate, which in fact increases over the entire time period investigated. The consumption reached 700 tones/year in the beginning of nineties, and since then has triple (2500 tones/year) up to the present. On the other hand, Japanese textiles/furniture association stated that the use of HBCD for textiles/furniture will stop between 2010 and 2013 and therefore, 90% of Japanese Textiles/furniture company would stop the use. Thus, the consumption of HBCD for textile has been decreasing drastically since 2013. As a result, the future consumption reached 2632 tonnes/year in Japan. Figure 2 shows the simulated stock levels as a function of time for HBCD. HBCD stock in the use phase shows a continuous increase since 1986 and without any ban of polystylene is expected to almost 25 % increase in the next 20 years until 2030, whereas the stock of HBCD for textile were decreased following by stop the use from 2010. As most of the HBCD applications are dedicated to construction materials with a residence time of 30 years or more, measures such as restrictions or a ban on HBCD will have only a highly delayed effect in reducing diffuse emissions from construction materials in buildings. These results indicate that emissions from construction materials will continue for
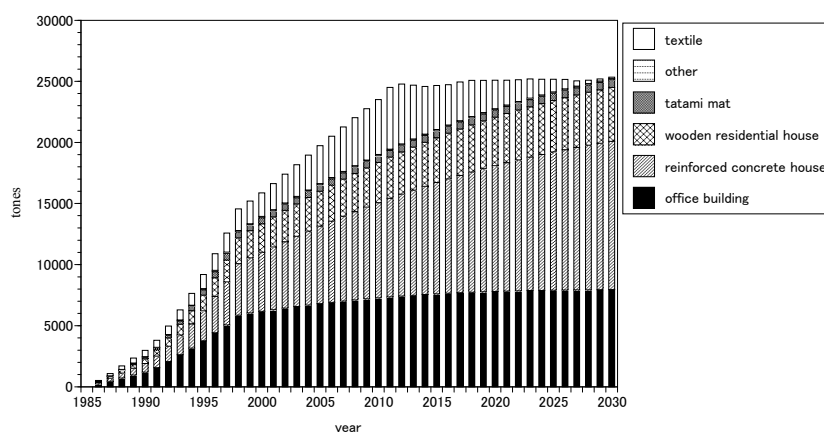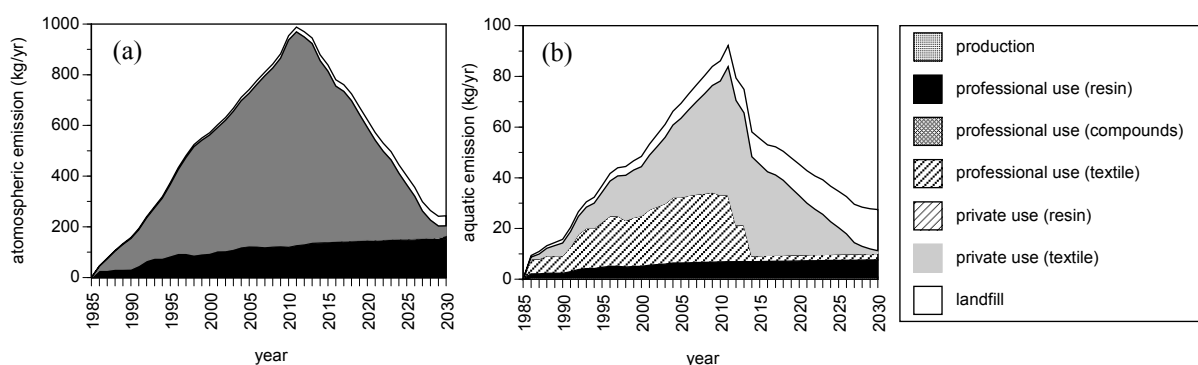
FIGURE 2 Stock of HBCD in the process use

FIGURE 3 Emissions of HBCD to atmosphere (a) and aquatic environment (b)

several decades and be potentially long-term sources of pollutants leaching or volatizing to the environment. Additionally, the increasing HBCD stock seen in Fig. 5 indicates possible problems arising in the recycling of construction materials in the future, when buildings of the present period are renovated or destroyed.

The emissions of HBCD from each stage are shown in Fig.3 (a) and (b). The largest component of the emissions were simulated to be into the atmosphere. Environmental emissions of HBCD are increasing rapidly until 2011. This increasing pattern until 2011 were in good agreement with the environmental concentration data from sediment core [4] and the historical concentration trend in human blood from Japan [16]. On the other hand, decreasing trend for HBCD were estimated between 2012 and 2030. These emissions were simulated to be as high as 225 kg/year in 2030, which has less than half compared to the environmental emission in the year for 2000, in the case that we stop the use of HBCD for textiles. For both atmospheric and aquatic emissions, the change of contribution from each stage was estimated from 1986 to 2030. Among the life stage, atmospheric emissions of HBCD from textile account for more than half of the total emissions from the beginning to 2011. However, as the stock in the use phase for textile has been decreasing from 2011, the significant source to atmospheric environment was estimated to change to industrial use of polystyrene in 2030. For the emission to aquatic environment, the contribution profile of each stage shifted from industrial use and private use for textile to industrial use and landfill.

The use of a dynamic (time-series) substance flow model, combined with more reliable field data, evaluation of historical data and estimates of future developments, have allowed us to improve substantially the quality of the results and identify possible emission pathways. On the other hand, it clearly highlights the need for improved understanding and measurement of the emission factor for HBCD and accurate flow in consumer product after use stage. There are the area of uncertainty in the future construction of the consumption and emission inventory. Further work should focus on the potential for releases from the waste stream.

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