SELECTED BROMINATED FLAME RETARDANTS: SOURCES, SINKS IN THE ANTHROPOSPHERE AND EMISSIONS TO THE ENVIRONMENT

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Introduction

Most studies and investigations on potentially hazardous substances are focused on aspects about their occurrence and fate in the environment (monitoring and modelling studies). This information is useful to estimate the environment impact and the potential exposure of human. In order to early recognize future environmental impacts and establish effective chemicals management measures, it is essential to know their anthropogenic metabolism, too. To get an overview about sources and final sinks for four selected brominated flame retardants (BFR) a substance flow analysis (SFA) was elaborated in 2003 for Switzerland.[1] The substances selected were pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE), decabromodiphenyl ether (DecaBDE), and tetrabromobisphenol-A (TBBPA). The SFA was based exclusively on data from the literature, and it examined the anthropogenic metabolism of these BFRs in Switzerland in the late 1990s. Based on the import of semi-finished and finished products treated with these BFR, accumulated stocks in the anthroposphere, annual flows through export, waste management and emissions into the environment were estimated.

Even though bans on PentaBDE and OctaBDE came into force in 2004, substantial amounts of these compounds remain in the anthroposphere for many years. Other high volume production volume BFRs are still in use despite of some controversial discussions (DecaBDE, TBBPA, HBCD). A better knowledge of the quantities of the flows and emissions from the use and waste management processes and their temporal behaviour is essential for effective risk reduction measures and chemical management, particularly during the disposal and reuse phases. Due to these facts and because there exists also substantial evidence that representatives of BFR are potential endocrine disrupters, a project to investigate the temporal behaviour of the anthropogenic metabolism in more detail, started at the beginning of this year. The project is called 'Dynamic substance flow analysis model for selected brominated flame retardants as a base for decision making on risk reduction measures'. In this project time trends of emissions into the environment as well as stock changes in the anthroposphere are estimated with a dynamic mathematical model. Additionally to the four substances mentioned above, hexabromocyclododecane (HBCD) is included. In combination with outcomes of other studies, the results will serve as a base for recommendations for future regulatory and technical measures regarding the use and disposal of the selected BFR.[2,3] In this paper, an overview about the results of the first part of the investigation and a short outlook for the second part of the running study are presented.

Materials and Methods

The method adopted in the 2003 study consisted of the determination of the flows of substances in subordinate systems and the following aggregation to form the whole system. The method of substance flow analysis was used to model processes and calculate flows. The physical boundary of the system was the political border of Switzerland. The temporal system boundary was fixed at one year in order to draw a rough picture of the situation in Switzerland at the end of the 1990s. The system comprised the transport processes of PentaBDE, OctaBDE, DecaBDE, and TBBPA in Switzerland at the end of the 1990s. The flame retardants under study, being commercial products, were not pure substances but technical congener mixtures. In order to balance the quantities, the values for commercial BFR were expressed in terms of chemical substances. For commercial PentaBDE, the concentration was set at 59% and for commercial OctaBDE at 34%. As a first approximation, it was assumed that commercial DecaBDE and TBBPA were present as pure substances.

The system was divided into three separate subsystems comprising the following processes: 'trade in products' (production, trade, consumption), 'waste management' (reuse, waste water treatment, incineration, dumping in landfills), and 'environment' (atmosphere, hydrosphere, pedosphere/lithosphere, biota). In the subsystem 'trade in products', the substance flows were calculated from the flow of goods and the concentrations (percentage of plastics, BFR applied and BFR concentrations) of the four substances under study. The data were gathered from market analyses for Switzerland and other European countries and from literature. The concentration of flame retardants in plastics was determined from information obtained from BFR manufacturers and the plastics industry, and was also based on analyses of used and new EE appliances.[4] The estimation of stocks in the process 'trade in products' was based on the average life cycle of consumer products. To determine the input flows to 'waste management', data from the process 'trade in products' were used. The substance flows were assigned to the treatment processes in waste management based on their product-related uses, taking into account the disposal situation in Switzerland. The flows between the various processes of waste management and among the products of disposal processes were calculated using transfer coefficients. For the subsystem 'environment', inputs from the subsystems 'trade in products' and 'waste management' were used. The derived flows and stocks were compared with rough estimations based on concentration measurements made outside Switzerland as given in the literature.[5,6] In Switzerland, no measurements of the four substances under study were available in environmental compartments at that time.

Results and Discussion

About 1,700 tonnes of the four BFRs studied came into Switzerland annually by the end of the 1990s, in semi-finished and finished products. About 46 percent of this was re-exported in finished products, and the remainder was consumed in Switzerland. Over the past twenty years, the consumption of flame-protected products in Switzerland had led to the accumulation of about 12,000 tonnes of the BFRs studied. By the end of the 1990s, the stocks of PentaBDE and OctaBDE were being reduced, whereas the amount of stored TBBPA was increasing, and that of DecaBDE was virtually stable. Each year, approximately 900 tonnes of BFRs left storage. Nearly all of this quantity was disposed of as solid waste. The BFRs in solid waste were mainly disposed of by thermal treatment in controlled incineration processes (65 to 85 percent, depending which BFR, except for PentaBDE, where the figure was 23 percent), and they were almost completely destroyed in this way. In addition to storage in consumption, over recent decades, a tenfold lesser storage of 1,500 tonnes of BFRs had accumulated in Swiss landfill sites. This stock increased by about 130 tonnes per year. The following sections include brief summaries for the most important results for each of the selected substances. Figure 1 shows the aggregated results for each substance in an overview for the whole system.

PentaBDE

In the late 1990s, the quantities of products treated with PentaBDE flame retardants imported into Switzerland were low compared with figures for other flame retardants. About 1.9 tonnes of PentaBDE were imported into Switzerland annually in finished products, and of this, about 1.5 tonnes per year were consumed. The majority of PentaBDE-treated consumer goods were in PU foam of upholstery materials, textiles and plastics for motor vehicles. The amounts of PentaBDE were about tenfold to thousand fold lower than for the other BFRs. Over the past two decades, as a result of the various uses of PentaBDE, about 500 tonnes had accumulated in storage in consumption, and 91 percent of this consisted of construction materials. This stock was decreasing by about 30 tonnes per year at that time. It was estimated that if this trend was to continue over the next few years, then in 7 to 10 years time, the amount stored in waste management would represent the most important anthropogenic stock, of about 280 tonnes. About 30 tonnes of PentaBDE per year were treated as waste, most of which (72 percent) went to landfill sites, and about 20 percent of which was destroyed by incineration. A small remainder (1 tonne per year, 3 percent) was exported. Every year, about 1.9 tonnes emitted from its storage in consumption. Annual emissions of PentaBDE were considerably greater than those for OctaBDE and TBBPA.

OctaBDE

About 41 tonnes of OctaBDE were imported into Switzerland annually as flame retardants in products, and about 22 tonnes of this was consumed, whereas the remainder was exported. About two third of the OctaBDE was in EE appliances, and about one third in motor vehicles. Over the past two decades, about 680 tonnes of OctaBDE had accumulated in storage in consumption, comprising 69 percent EE appliances, 21 percent motor vehicles and 10 percent construction materials. This stock was being reduced by about 40 tonnes per year by the end of 1990s. If this trend was to continue over the next few years, in about 13 to 18 years time, the largest anthropogenic stock (about 160 tonnes) would be in the waste management. Waste from consumption contains about 62 tonnes of OctaBDE per year, almost all of which (87 percent) was destroyed in incineration plant, with 10 percent stored in landfill sites. The remainder (about 3 percent) was exported. About 0.4 tonnes per year of OctaBDE emitted from storage in consumption.

DecaBDE
In the late 1990s, 550 tonnes of DecaBDE flame retardants were imported into Switzerland annually in semi-finished and finished products. Of this, about 320 tonnes per year were consumed and the remainder was re-exported. About 45 percent of DecaBDE consumed in Switzerland were in EE appliances (EDP and office equipment), about 30 percent was in imported motor vehicles, and about 25 percent in construction materials (PE sheets). The storage of DecaBDE in consumed products amounted to approximately 5,600 tonnes, and was approximately in a steady state. This means that approximately the same amounts of DecaBDE were consumed as were disposed of as waste. Of the approximately 370 tonnes per year of DecaBDE in waste, the great majority (about 80 percent) was destroyed in incineration plants. About 9 percent was exported, and about 13 percent was disposed of in landfill sites. If this situation was to continue, in the next 20 years, storage in consumption would remain the largest stock, in comparison with storage in landfill sites and in the environment. Stocks of DecaBDE in consumption comprised 40 percent in EE appliances and 30 percent in construction materials and motor vehicles. About 2.1 tonnes of DecaBDE from this stock emitted into the environment annually. It is noteworthy that despite the relatively large stock of DecaBDE, the annual diffuse emission to the environment is about the same as that for PentaBDE.

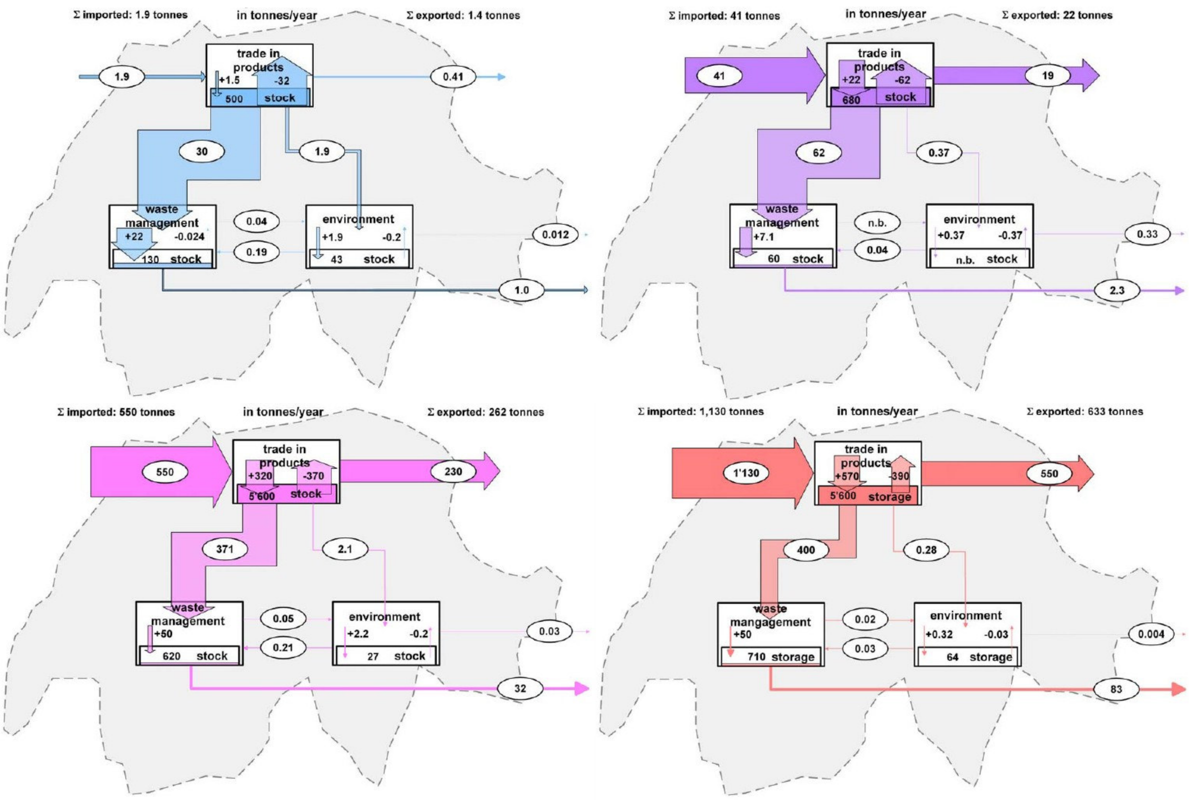

Figure 1 PentaBDE, OctaBDE, DecaBDE and TBBPA flows in Switzerland at the end of the 1990s

TBBPA

In the late 1990s, 1,130 tonnes of TBBPA flame retardants were imported into Switzerland annually as semi-finished and finished products. About 570 tonnes of this were consumed annually, and the remainder was re-exported. Almost all the TBBPA consumed were in EE appliances, with about 83 percent in computers, and about 11 percent in consumer electronic equipment. The amounts of TBBPA traded and consumed were larger than for other BFRs. The stocks of TBBPA in consumer products accounted for about 5,600 tonnes, and consisted predominantly (59 percent) of EE appliances and to a lesser extent (20 percent each) of construction materials and motor vehicles. Although the amount of TBBPA consumed annually was about double that for DecaBDE, the amount of both in stock was similar. This was a result of the fact that most products containing TBBPA have a shorter lifetime than products containing DecaBDE. Storage in consumption was increasing by about 180 tonnes per year. Waste from consumption contained about 400 tonnes of TBBPA per year. Of this, about 68 percent was destroyed in incineration plants, about 11 percent was disposed of in landfill sites, and about 21 percent was exported. Approximately 0.3 tonnes of TBBPA per year emitted from storage in consumption into the environment. Despite the fact that there was greater storage of TBBPA than of the other BFRs studied, this was the lowest diffuse emission.

Discussion

The study of the anthropogenic metabolism in 2003 showed that there is only scant information available at present on the global distribution of BFR. But it was possible to draw a first picture about the flows and stocks of the selected BFR in Switzerland at the end of the 20th century. It was possible to show the different characteristics of the use patterns and relevance of flows and stocks for the four BFR in the anthroposphere. E.g. for PentaBDE the stock and waste management control is of most importance. For DecaBDE and TBBPA with a still strong increase of the use figures the topic of emissions during different use applications is of large interest, too. First field measurements in relevant anthropogenic flows allow comparison with the study.[7,8] For example for Octa- and DecaBDE values in electronic waste are in good agreement. PentaBDE analysis disagrees with the results of the first study. First results from the running project demonstrate that (a) compared to the existing SFA more but still rather limited information about production volumes and use time trends is available and (b) the data base required to proper estimate emission factors is still limited and sometimes controversial.[9] As a consequence future measures are more difficult to be defined efficiently, due to required scenario technique modelling with higher data uncertainty.

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