

A REVIEW OF CHAMBER EXPERIMENTS FOR DETERMINING EMISSION FACTORS AND INVESTIGATING MIGRATION PATHWAYS OF FLAME RETARDANTS

Rauert C^{1*}, Harrad S¹, Stranger M², Lazarov B²

¹ Division of Environmental Health and Risk Management, Public Health Building, School of Geography, Earth and Environmental Sciences, University of Birmingham; ² Environmental Risk and Health Unit, VITO, Boeretang 200, 2400, Mol, Belgium

Introduction

The widespread use of flame retardants (FRs) in indoor products has led to their ubiquitous distribution within indoor microenvironments with many studies reporting elevated concentrations in indoor air and dust¹. Minimal information is available however on the emission of these compounds to air, particularly the measurement of emission factors (EFs), or the migration pathways leading to dust contamination. Such knowledge gapshamper efforts to develop understanding of human exposure.

Although limited information is available on migration pathways of FRs to indoor dust, proposed hypotheses include: deposition after volatilisation of the more volatile FRs, abrasion of fine particles from treated products through wear-and-tear thus allowing transfer of less volatile FRs, and transfer via direct contact between the treated product and dust, depicted in Figure 1 below.

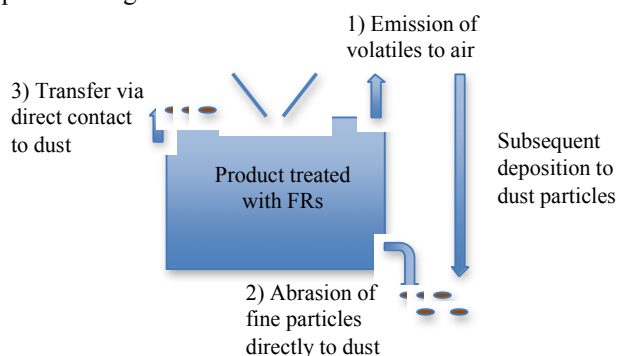


Figure 1: Hypothesised migration pathways of FRs from treated products into indoor air and dust

This review is intended to summarise available published information and highlight information gaps that need to be addressed to further our understanding of human exposure from FRs. The aims of the review are to: 1) summarise the available evidence for the influence of putative sources on indoor contamination with FRs; 2) collate studies using emission chambers to elucidate EFs and mass transfer to dust of FRs; 3) summarise the different chamber configurations/methodological approaches used; 4) identify limitations/difficulties encountered with chamber experiments, and 5) identify knowledge gaps and future research directions.

Materials and methods

The review covers all research published in the open literature up to the end of December 2012 on the use of emission chambers for determining EFs of FRs from flame-retarded products and the subsequent mass transfer to dust. Published EFs for the following FRs, released from treated products, are summarized: polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), tetrabromobisphenol-A (TBBPA), novel brominated flame retardants (NBFRs) and organophosphate flame retardants (PFRs). Published studies that utilize emission chambers for investigations/measurements of mass transfer of FRs or similar compounds to dust are reviewed, discussing the chamber configurations and methods used for these experiments.

Results and discussion

Few published studies are available that report measured EFs of FRs using chamber studies. The available data is summarized in Table 1 below with PBDEs and PFRs the primary FRs studied.

Table 1: Summary of emission factors of various flame retardants determined using chamber studies.

Product	FR	EFs	Reference
<i>Building materials, SERa^a, μg/m².h</i>			
Insulation boards	TCIPP	0.21- 0.60	(2)
	HBCD	0.004 – 0.029	
PUR foams	TCIPP	50 – 140	(3)
Upholstery foam	TCIPP	77	
Wallpaper materials	TCIPP	262.3 – 2166.8	
<i>Electronics</i>			
TV set housing, SERa ^a , ng/m ² .h	BDE-100	0.5	(2)
	BDE-153	1.0	
	BDE-154	0.2	
	BDE-28	0.2	
	BDE-47	6.6	
	BDE-66	0.5	
	BDE-99	1.7	
	ΣHeptaBDE	4.5	
	ΣNonaBDE	0.8	
ΣOctaBDE	1.5		
Printed circuit board, SERu ^b , ng/unit.h	BDE-100	1.3	(2)
	BDE-153	0.04	
	BDE-154	0.1	
	BDE-17	0.6	
	BDE-28	1.9	
	BDE-47	14.2	
	BDE-66	0.6	
	BDE-85	0.1	
	BDE-99	2.6	
	TPHP	496	
PC housing	TBBPA	0.4	(2)
Desktop computer system	TPHP	25 – 85	
Monitors	TCEP	<5 – 34	(4)
	TCIPP	<5 – 2465	
	TDCIPP	<5	
	TNBP	10 – 18	
	TPHP	23- 133	

^a area specific emission rates (SERa); ^b unit specific emission rates (SERu)

To date no published studies have investigated the mass transfer of FRs to dust. Migration of phthalates, similar semi-volatile organic compounds (SVOCs), have been reported in two chamber studies^{5,6}. The issues encountered with studying partitioning to dust of SVOCs in this way were highlighted and can be extrapolated to underline how these experiments may be performed to investigate FRs. The two studies of phthalate migration were conducted in modified chamber experiments to investigate migration from product to dust via: (a) phthalate deposition to dust after volatilisation from the treated material, and (b) transfer via direct contact between the

treated material and dust. Both studies reported significantly increased concentrations in dust samples after these experiments suggesting the validity of both hypothesised migration pathways.

Measurements of mass transfer of SVOCs to dust are shown to be difficult in chamber experiments, with the need for chamber designs to be modified. As reported by Clausen et al.⁵, experiment duration is an important parameter with chamber experiments to allow attainment of equilibrium conditions. Often the extended experiment times needed are not appropriate however as there are few cases where a limited number of days (e.g. less than 50 days) is sufficient to measure time-release behaviour of SVOCs⁷. Another consideration is the different physical compositions of indoor dust samples, particularly organic carbon content. This may lead to different rates of mass transfer, with Schripp et al.⁶ reporting greater mass transfers to particulate matrices with higher organic contents.

Chamber studies have reported inherent problems with test chambers that need to be considered/minimised for conducting experiments. Critical analysis of the literature reveals that the major limitations with utilizing chambers to derive EFs for FRs arise due to the physicochemical properties of FRs. In particular, increased partitioning to particulates due to their lower vapour pressures cause "sink" effects i.e. irreversible loss to chamber surfaces^{2,8}. Methods suggested for minimising this loss include lining the chamber with a Teflon coating or electroplating stainless steel wall surfaces⁹. As yet eliminating total sink effects has not been reported, however investigations of post-experiment recovery of analytes have been published. These methods have included heating the chamber to elevated temperatures with collection of subsequent air emissions, and rinsing the chamber walls with solvent to determine concentrations recovered from the chamber walls^{2,8}.

A standardized method for measuring EFs of FRs in emission chambers is not available and the reported investigations often use very different chamber conditions, making comparisons difficult. Air flow rate has been operated at lower flows (3 mL/min¹⁰) than average indoor scenarios (~20 mL/min¹⁰) to improve LODs. However the standardized methods for testing VOC emissions, require higher air flows for accuracy (100-200 mL/min)¹¹. The stage in the life-cycle of the treated product is an important influence on EFs for the more volatile FRs. Ni et al.³ reported an almost 10 fold decrease in tris(2-chloroisopropyl)phosphate emissions over a 280 day sampling period for wallpaper obtained directly from the manufacturer and tested immediately. Similarly, Carlsson et al.¹² saw a 10 fold decrease in triphenyl phosphate emissions from a computer video display unit over a 183 day sampling period.

Chamber temperature is also of importance as the standardized methods for VOC testing recommend conducting chamber experiments at room temperature (23°C)¹¹. Operating electronics however can reach temperatures of 50°C¹² and chamber experiments with functioning electronics inside have increased chamber temperatures to at least 32°C¹⁰. As such, calculating emissions from products at room temperature may not be relevant for determining total exposure. The operational state of electronics, whilst tested in the emission chamber, is another important parameter. Whether the equipment is idle, in standby mode, partly operational or in full operation for the duration of the test can influence the emissions detected⁹. The ECMA¹¹ standardized method for testing VOCs from computers requires testing whilst tapping keystrokes on the computer, but this will not simulate all systems in action. Underestimations of emissions produced by fully functioning equipment and contamination by fine particle abrasion causing migration to dust may result, with subsequent underestimations of levels of exposure. Enhanced emissions from the product due to the presence of particulates is also a potentially interesting area for research, as mass transfer to particulates (dust) can be an additional emission pathway increasing total emissions of volatiles⁵. Research is required to provide relevant standardized methods, with appropriate experimental parameters specified, to create uniformity in the reported literature.

In summary, the literature reviewed demonstrates how emission chambers have been utilized to generate EFs from products treated with FRs. There are still many research areas that require investigation to improve these experiments and increase knowledge of the migration of FRs into indoor air and dust. Thorough investigations of sink effects and how the different FRs are affected by such effects are needed. For measuring EFs, the most appropriate parameters to test electronic equipment require identification, including the operational state of the equipment during the emission test and the most appropriate chamber temperature. Standardized methods are

needed for chamber tests of FRs that allow determination of EFs that best represent the conditions of indoor environments. Investigations into the migration pathways of FRs to dust are an important area of research and at the time of this review, there were no published chamber experiments that address this area. Appropriate designs for modified chamber experiments are needed so all hypothesized migration pathways can be investigated. The reported difficulties with reaching equilibrium within a realistic experimental time frame for some FRs needs to be addressed, together with considerations of whether mass transfer measurements are relevant if equilibrium conditions inside the chamber are not reached. Standardized methods to handle all these parameters do not yet exist, showing that more research is needed in this area. We conclude that chamber experiments are clearly a useful tool for measuring EFs of FRs and are promising for investigating migration pathways to indoor dust, although more research is required in this area, particularly in the development of standardized methods that facilitate comparisons between reported studies.

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