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COMPLEMENTING DOCUMENT TO THE EMISSION SCENARIO DOCUMENT ON PLASTIC ADDITIVES: PLASTIC ADDITIVES DURING THE USE OF END PRODUCTS

Series on Emission Scenario Documents
No. 38

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OECD Environment, Health and Safety Publications
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IOMC
INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD

Environment Directorate
ORGANISATION FOR ECONOMIC COOPERATION AND DEVELOPMENT
Paris 2019

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Explanatory Notes

Purpose and background

This OECD Emission Scenario Document (ESD) is intended as a complement to the "Emission Scenario Document on Plastic Additives" (OECD, 2008[1]) and provides information on the sources, use patterns and release pathways of chemicals used as additives in plastics to assist in the estimation of releases of chemicals into the environment.

The series of ESDs should be seen as 'living' documents which provide the latest information available. As such, this ESD may be updated to take account of any changes and new information in relevant industries (e.g. plastic and chemical industries). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division (env.riskassessment@oecd.org). The comments received will be forwarded to the OECD Working Party on Exposure Assessment (WPEA), which will review the comments every two years so that the lead country, i.e. Japan, can update the document. The submitted information will also be made available to users via the OECD website (www.oecd.org/env/riskassessment).

How to use this document

The user of this ESD needs to have information on the physical-chemical properties of each additive being assessed, the usage of resulting products and other relevant environmental conditions which may affect the emission routes.

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available, it should be used in preference to the defaults.

Coverage and methodology

The original ESD on Plastics Additives (OECD, 2004[2]) was proposing Emission Factors (EFs) for different life cycle stages of plastic additives, including processing, consumption and disposal but failed to take into account differences in physical-chemical properties of different substances. The revised ESD on Plastics Additives (OECD, 2008[1]), in turn, provides a formula which estimates EFs taking into account the unique physical-chemical properties of different substances.

This complementary document describes an alternative approach to estimate releases from a chamber wall collected through a sorbent tube, such as the Micro Chamber Method developed by Japan.

The vapour pressure of a substance is influential in determining its EF and Annex B illustrates how vapour pressure is incorporated into calculating such EFs. Further, results from using the ESD on Plastic Additives (OECD, 2008[1]) and results by Yaws (1997[3]) were also documented to illustrate which method is more suitable to be used for particular

environmental conditions. In Annex C, the mechanisms of volatilization from the surface of resin and the concept of activation energy is explained.

This ESD is providing a number of guiding principles, insights and potential limitations for using estimation and testing methods of EFs.

How this document was developed

This document was developed mainly by Japan based on multiple sources of reports including the ESD on Plastic Additives (OECD, 2008[1]). In addition, the results from a newly developed chamber testing method (Japanese Standards Association, 2008[4]) as documented in Annex B were used to develop this report. It was prepared under the supervision of the WPEA.

This document is published under the responsibility of the Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology of the OECD.

Abbreviations and Acronyms

ABS	Acrylonitrile Butadiene Styrene
AIST	National Institute of Advanced Industrial Science and Technology
BDP	Bisphenol A bis(Diphenyl Phosphate)
CDP	Cresyl Diphenyl Phosphate
DBP	Di-*n*-Butyl Phthalate
deca-BDE	Decabromodiphenyl Ether
DEHP	Di(2-ethylhexyl) Phthalate
DIDP	Diisodecyl Phthalate
DINP	Diisononyl Phthalate
EBPBP	Bis(pentabromophenyl) Ethane
EF	Emission Factor
ESD	Emission Scenario Document
EURAR	European Union Risk Assessment Report
GC	Gas Chromatography
HBCD	Hexabromocyclododecane
HIPS	High-Impact Polystyrene
ISO	International Organization for Standardization
JIS	Japanese Industrial Standards
MS	Mass Spectrometry
PC	Polycarbonate
PC/ABS	Polycarbonate/Acrylonitrile Butadiene Styrene
PVC	Polyvinyl Chloride
RDP	Resorcinol bis(Diphenyl Phosphate)
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RoHS	Restriction on the Use of Certain Hazardous Substances
SVOC	Semi-Volatile Organic Compound
TBBA	Tetrabromo Bisphenol A
TCP	Tricresyl Phosphate
TGA	Thermo-Gravimetric Analysis
TPP	Triphenyl Phosphate
TXP	Trixylenyl Phosphate
UV	Ultraviolet
VOC	Volatile Organic Compound

Table of contents

OECD Environment, Health and Safety Publications **3**

Series on Emission Scenario Documents **3**

No. 38 ..... **3**

COMPLEMENTING DOCUMENT TO THE EMISSION SCENARIO DOCUMENT ON PLASTIC ADDITIVES: PLASTIC ADDITIVES DURING THE USE OF END PRODUCTS..... 3

Explanatory Notes **6**

Abbreviations and Acronyms **8**

1. Purpose and Coverage **13**

1.1. Purpose..... 13
1.2. Scope..... 13

2. Outlines of major plastic additives **15**

2.1. Outline of functions 15
2.3. Duration of the service life 16

3. Emission Factor Estimation **17**

3.1. Determination of emission factors (EFs) 17
3.2. Estimation of emissions 20
3.3. Example of an estimation..... 23

References **25**

Annex A. Estimation of Vapour Pressures **27**

1. Estimation equation proposed in the ESD 27
2. The Yaws estimation equation..... 27
3. Comparison of vapour pressure estimation equations 28

Annex B. Measurement of Emissions from End Products **30**

1. Outline of the Micro Chamber Method..... 30
2. Measurements of emission rates for plasticizers..... 32
3. Measurement of emission rates for flame retardants 34
4. Discussion..... 37

Annex C. Examining the Estimation of Emission Factors **40**

1. Requirements 40
2. Determination of EFs based on vapour pressure 40
3. Determination of EFs using activation energy..... 40
4. Determination of EFs using heating loss 44

Annex D. Calculation of In-use Stock **47**

1. Determining the duration of the service life of final products 47
2. Examples of calculation of in-use stock 51

Annex E. Thickness of Plastic Plates **53**

Annex F. In-service use of products..... 54
Annex G. Emission rates, Emission Factors or Emission Coefficients found in the Literature... 55

Tables

Table 1. Outline of the functions of plastic additives 15
Table 2. Duration of service life of plastic products 16
Table 3. Emission factors for plasticizers 18
Table 4. Emission factors for flame retardants 18
Table 5. Emission factors for antioxidants 19
Table 6. Emission factors for absorbing agents 19
Table 7. Emission factors for PVC stabilizers 20
Table 8. Plastic density (g/cm^3) 22
Table 9. Parameters used in Formula 4-1 to estimate emissions of deca-BDE 23
Table 10. Parameters used in Formula 4-2 to estimate emissions of deca-BDE 23

Table A.1. The coefficient data of Yaws equation on the characteristics of plastic additives 28
Table B.1. SVOCs loaded into the micro-chamber (ng) and recovery rates (%) 32
Table B.2. Emission rates from PVC product samples 32
Table B.3. Conditions for preparation of test samples for emission test 33
Table B.4. Emission-collection conditions 33
Table B.5. Vinyl chloride products used as samples in micro chamber method testing, and emission rates for flame retardants 35
Table B.6. Home appliance products used as samples in micro chamber technique testing, and rates for release flame retardants 35
Table B.7. Emission rates (μg/m^2/h) for flame retardants from samples of home appliances 36
Table B.8. Preparation of test samples used for emission testing of flame retardants 36
Table B.9. Emission rates (μg/m^2/h) for flame retardants from test samples 37
Table C.1. Loss constants of plastic additives at various temperatures 41
Table C.2. Activation energies of plastic additives at various temperature ranges 43
Table C.3. Heating losses of phosphate esters 45
Table C.4. Heating losses of phthalate esters 46
Table D.1. Product lifetimes 47
Table D.2. Technical lifetimes of products including DEHP 48
Table D.3. Product lifetimes as reported by Nakai et al. (2000) 49
Table D.4. Product lifetimes, as revealed by an interview survey conducted by the Study Group for Risk Assessment and Management of Phthalates 50
Table D.5. Duration of the service life of final products (housing and other electrical and electronic products) and parameters of the Weibull distribution 52
Table E.1. Measured thicknesses of plastic products (mm) 53
Table F.1. In-service use of home appliances in the living room 54
Table G.1. Emission rates, emission factors or emission coefficients found in the literature 56

Figures

Figure 1. Emissions of deca-BDE from in-use stock into the air 24

Figure A.1. Comparison of measured and estimated vapour pressures of the plasticizers DEHP and DIDP as examples 28
Figure A.2. Comparison of measured and estimated vapour pressures of the flame retardants TCP and TPP as examples 29
Figure B.1. Micro-chamber method 31

Figure B.2. Emissions of plasticizers from PVC products (using sample thickness and concentration as parameters) 34
Figure B.3. Emissions of plasticizers from PVC products (using temperature and flow rate as parameters) 34
Figure B.4. Relationship between plasticizer emission rate and vapour pressure (measured values)... 37
Figure B.5. Relationship between plasticizer emission rate and vapour pressure (ESD equation) 38
Figure B.6. Relationship between plasticizer emission rate and vapour pressure (Yaws' equation) 38
Figure C.1. Arrhenius plots of loss constant of substances in PVC against 1/temperature..... 42
Figure C.2. Relationship between EFs estimated by using activation energy and measured EFs (for DEHP, DINP, DIDP, and TCP)..... 44
Figure C.3. TGA curves of condensed phosphate esters RDP and BDP..... 45
Figure C.4. Comparison between estimated and measured EFs based on heating losses (for DEHP, DINP, DIDP, and TPP) 46
Figure D.1. Domestic demand for deca-BDE..... 52
Figure D.2. Ratio of domestic demand to domestic shipping of home appliances..... 52
Figure D.3. Estimation of the in-use stock of deca-BDE 53

1. Purpose and Coverage

1.1. Purpose

Plastic additives are widely used in, for example, construction materials and electrical and electronic products with a long life expectancy. Therefore, a large proportion of the emission of plastic additives is attributed to their in-service phase. This emission scenario document (ESD) provides emission factors (EFs) for plastic additives during the use of end products.

1.2. Scope

The original OECD ESD on Plastics Additives published in 2004 [ENV/JM/MONO(2004)8] (OECD, 2004[2]) presents EFs for the life cycle stages of plastic additives, including processing, consumption, and disposal. However, the EF for emissions into the air and water is assumed to be 0.05% during the entire service life of the final products regardless of their physical-chemical properties. Therefore, these coefficients cannot be used for assessing risk trade-offs or for alternatives assessment with the aim of substitution.

The revised ESD on Plastics Additives published in 2008 [ENV/JM/MONO(2004)8/REV1] (OECD, 2008[1]) provides an equation for estimating EFs for plasticizers based on vapour pressure. However, in general, plastic additives have a very low vapour pressure, resulting in highly uncertain emission results. It is therefore necessary to examine the equation by using measured emission rates. Unfortunately, semi-volatile organic compounds (SVOCs) such as plastic additives are emitted from the surface of plastics very slowly and are easily adsorbed onto the inner surface of the measurement chamber, preventing the emission determination using standard methods for measuring volatile organic compounds (VOCs).

The emission of plastic additives in a given year during the service life of end products can be estimated by multiplying the in-use stock of the additives in the year by the EF. However, the ESD does not consider the service period of end products when investigating changes in the in-use stock and emissions over time. In addition, no existing ESD includes a method for determining the in-use stock for a given year. Nevertheless, the in-use stock of additives used in end products should be calculated so that changes in emissions over time can be estimated.

In this document, an equation is proposed for estimating the EFs for additives that are emitted from plastic products into the atmosphere, using emission rates measured by a micro-chamber method that can measure the emission of low-volatility additives with high precision. The methodology and results of the material flow analysis are described in Annex B.

Then a method is proposed to determine the emission of plastic additives during the service life of the final products. The emission of a flame retardant is calculated as an example.

Indoor emission from the surface of plastics products is probably common throughout the world. Although there is a large difference in indoor emission into water between Western and Eastern countries because of their practice of wearing or not wearing shoes in the home, this ESD does not include emission into water.

In recent years, in compliance with new legislations, many substances that pose potential risks have been substituted by alternatives. In many cases, difficulties in estimating emissions make exposure analysis difficult in investigating potential risks posed by substitutes. This document may enable better alternatives assessments.

2. Outlines of major plastic additives

2.1. Outline of functions

Plastics are used for various purposes, owing to their lightness, moldability, clarity of colour, electrical non-conductivity, or chemical, water, and oil resistance. However, polymers alone cannot satisfy all the functions demanded in various uses. Various types of additives are used to improve processability, to ensure stability against deterioration due to heat during processing and to visible and ultraviolet (UV) light during use, to prevent fire and for other functions of plastics. Table 1 summarises the functions of plastic additives.

Table 1. Outline of the functions of plastic additives

Additive classification	Additive sub-classification	Description
Additives for processability	Plasticizers	Plasticizers improve the fluidity of plastics during processing and flexibility at room temperature. Used extensively in polyvinyl chloride (PVC) molding.
	Lubricants	Lubricants help prevent the adhesion of plastics to the surface of metal molds and to each other, improve the fluidity of plastics, and reduce friction during melting and molding plastics.
	Blowing agents	Blowing agents, used in foam molding, decompose through heat and compression to produce carbon dioxide, water, nitrogen, and other gases.
Surface protector/ modifier	Antistatic agents	Antistatic agents prevent static electrification of electrical insulators. Classified into coating agents and blending agents. Surfactants are used.
	Antifriction agents	Antifriction agents reduce the surface friction coefficient.
	Adhesion-improving agents	Adhesion-improving agents improve the adhesiveness of the surface of plastics.
	Anti-fog additives	Hydrophobic surfaces permit condensation, leading to loss of translucency. Surfactants prevent fogging.
Material protectants	Antioxidants	Some plastics produce radicals in response to heat and/or light. Antioxidants prevent oxidation and deterioration caused by heat during processing.
	Light stabilizers	Light stabilizers prevent oxidation caused by light during the service life of a plastic product.
	Ultraviolet-absorbing agents	UV-absorbing agents prevent the breakage of molecular bonds by UV light and the generation of radicals.
	Thermostabilizers	Thermostabilizers inhibit discoloration caused by the HCl produced from vinyl chloride resin because of heat during processing.
Physical-chemical property improvers	Flame retardants	Added to combustible plastics.
	Fillers/reinforcement materials	Various fibers and powders improve the strength of plastics.
Functionalization agents	Coloring agents	Organic or inorganic pigments add color and make plastics light resistant.

2.3. Duration of the service life

To estimate the total amounts of plastic additives in use, it is necessary to know the duration of the service life of the different types of plastic products. Table 2 lists these durations as derived from published reports and responses to interviews with industry organizations.

Table 2. Duration of service life of plastic products

Product	Duration (years)
Film and sheet	1-5
Board	5-20
Synthetic leather	5-10
Pipes and joints	10-50
Mechanical parts and electrical and electronic appliances	5-15
Daily commodities and groceries	1-5
Containers	1
Construction materials	5-20
Foam products	1-20
Reinforcement products (other than mechanical parts)	5-20
Other	1-10

3. Emission Factor Estimation

3.1. Determination of emission factors (EFs)

The EFs for plastic additives into the air per year can be estimated according to the following methods:

1. The EF is estimated from the emission rate determined in accordance with International Organization for Standardization (ISO) standard 16000-25 (ISO, 2009[5]) (Annex B).
2. The EF is estimated by using the activation energy determined from the heating losses of plastic additives from resin at high temperature. The EFs for flame retardants can be estimated from thermo-gravimetric analysis (TGA) curves (Annex C).
3. In the absence of any data for estimating the EF for a substance, the emission rate is determined in accordance with its properties (especially its molecular weight and vapor pressure) by using another substance with a known emission rate as a reference, assuming that the emission rate is proportional to vapor pressure and inversely proportional to molecular weight (Annex B).

In terms of accuracy, (i) is deemed as the most accurate and (ii) and (iii) are equivalent. In the following sections, the emission rate R_{air} ($\mu g/m^2/h$) of plastic additives emitted to air per unit area of plastic resin or the emission factor $F_{air,y}$ (-) in year *y* of plastic additives emitted to air from end products in a certain year are outlined in accordance with the procedures above. The outlined EFs are applicable to in-service use of plastic products.

3.1.1. Emission factors for Plasticizers

1. Measured emission rates from Polyvinyl Chloride (PVC) are available for di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), triphenyl phosphate (TPP) and tricresyl phosphate (TCP).
2. The heating losses of DEHP, DIDP, TPP, and TCP are not taken into consideration, because measured values are available.
3. Emission rates for the phosphate esters, cresyl diphenyl phosphate (CDP) and trixylenyl phosphate (TXP) are estimated by using the measured emission rate for TCP as a reference.

The resulting EFs for plasticizers is shown in Table 3. The emission rates were converted to EFs by using a plate thickness of 0.5 mm and resin specific gravity of 1.23 (PVC). DBP was excluded because it has a high vapor pressure and therefore diffusion within the resin will be the rate-determining factor.

Table 3. Emission factors for plasticizers

Substance	CAS number	(i) Measured values		*(ii) Value estimated from heating loss*	*(iii) Values estimated from physical properties*	
		R_{air}(µg/m²/h)	$F_{air,y}$(-)	$F_{air,y}$(-)	R_{air}(µg/m²/h)	$F_{air,y}$(-)
Di(2-ethylhexyl) phthalate(DEHP)	117-81-7	4.1	2×10^{-4}			
Diisononyl phthalate(DINP)	28553-12-0	0.6	2×10^{-5}			
Diisodecyl phthalate(DIDP)	26761-40-0	0.3	1×10^{-5}			
Triphenyl phosphate (TPP)	115-86-6	4.9	4×10^{-4}			
Tricresyl phosphate (TCP)	1330-78-5	0.75	9×10^{-5}			
Cresyl diphenyl phosphate (CDP)	26444-49-5				6.8	8×10^{-4}
Trixylenyl phosphate (TXP)	25155-23-1				0.06	7×10^{-6}

Source: Annex B

3.1.2. Emission factors for Flame retardants

1. Measured emission rates are available for decabromodiphenyl ether (deca-BDE) and bisphenol A bis(diphenyl phosphate) (BDP).
2. EFs are estimated from the heating losses for resorcinol bis(diphenyl phosphate) (RDP) and BDP using the common activation energy of 30.8 kcal/mol.
3. Emission rates for brominated flame retardants are estimated from the measured emission rate for deca-BDE from High-impact polystyrene (HIPS) as a reference. The emission rates for phosphorous flame retardants are estimated from the measured emission rate for BDP from polycarbonate/acrylonitrile butadiene styrene (PC/ABS).

The resulting EFs for flame retardants is shown in Table 4. These data apply to electrical and electronic products at an in-service temperature of 60 °C. The emission rates were converted to EFs by using a plate thickness of 3 mm and a resin specific gravity of 1.2 (HIPS and PC/ABS) and an in-service use time of 5 h/day.

Table 4. Emission factors for flame retardants

Substance	CAS number	(i) Measured values		*(ii) Value estimated from heating loss*	*(iii) Values estimated from physical properties*	
		R_{air}(µg/m²/h)	$F_{air,y}$(-)	$F_{air,y}$(-)	R_{air}(µg/m²/h)	$F_{air,y}$(-)
Tetrabromo bisphenol A (TBBA)	79-94-7				(3×10^{-5})	(9×10^{-11})
Decabromodiphenyl ether (deca-BDE)	1163-19-5	<0.5 (0.03)	$<2 \times 10^{-6}$ (1×10^{-7})			
Hexabromocyclododecane (HBCD)	3194-55-6				(1.9)	(6×10^{-6})
Bis(pentabromophenyl) ethane (EBPBP)	84852-53-9				(2×10^{-7})	(5×10^{-13})
Resorcinol bis(diphenyl phosphate) (RDP)	57583-54-7			1×10^{-6}	<0.06	$<2 \times 10^{-7}$
Bisphenol A bis(diphenyl phosphate) (BDP)	5945-33-5	<0.05	$<2 \times 10^{-7}$	8×10^{-7}		

Source: Annex B and Annex C

3.1.3. Emission factors for Antioxidants

1. There are no available measured emission rates.
2. There are no available measured or estimated heating losses.
3. Emission rates are estimated from the measured emission rate for TCP from PVC as a reference.

The resulting EFs for antioxidants is shown in Table 5. The emission rates were converted to EFs by using a plate thickness of 0.5 mm and a resin specific gravity of 1.23 (PVC). 2,6-Di-*tert*-butyl-4-methyl-phenol (BHT) was excluded because it has a higher vapour pressure than other substances and therefore diffusion within the resin is a rate-determining factor.

Table 5. Emission factors for antioxidants

Substance	CAS number	(i) Measured values		*(ii) Value estimated from heating loss*	*(iii) Values estimated from physical properties*	
		R_{air}(μg/m²/h)	$F_{air,y}$(-)	$F_{air,y}$(-)	R_{air}(μg/m²/h)	$F_{air,y}$(-)
Tris(2,4-di-t-butylphenyl) phosphite	31570-04-4				4×10^{-8}	4×10^{-12}
Didodecyl 3,3′-thiodipropionate	123-28-4				4×10^{-4}	4×10^{-8}

Source: Annex B

3.1.4. Emission factors for Ultraviolet-absorbing agents

1. There are no available measured emission rates.
2. There are no available measured or estimated heating losses.
3. Emission rates are estimated from the measured emission rate for TCP from PVC as a reference.

The resulting EFs for absorbing agents are shown in Table 6. The emission rates were converted to EFs by using a plate thickness of 0.5 mm and a resin specific gravity of 1.23 (PVC).

Table 6. Emission factors for absorbing agents

Substance	CAS number	(i) Measured values		*(ii) Value estimated from heating loss*	*(iii) Values estimated from physical properties*	
		R_{air}(μg/m²/h)	$F_{air,y}$(-)	$F_{air,y}$(-)	R_{air}(μg/m²/h)	$F_{air,y}$(-)
2-(2-Hydroxy-5-methylphenyl)-2H-benzotriazole	2440-22-4				0.17	2×10^{-5}
2,4-Dihydroxybenzophenone	131-56-6				0.32	4×10^{-5}
Sebacic acid bis(2,2,6,6-tetra-methyl-4-piperidinyl) ester	52829-07-9				4×10^{-4}	4×10^{-8}

Source: Annex B

3.1.5. Emission factors for PVC stabilizers

1. There are no available measured emission rates.
2. There are no available measured or estimated heating losses.
3. The emission rates for antioxidants are estimated from the measured emission rate for TCP from PVC as a reference.

The resulting EFs for stabilizers is shown in Table 7. The emission rates were converted to EFs by using a plate thickness of 0.5 mm and a resin specific gravity of 1.23 (PVC).

Table 7. Emission factors for PVC stabilizers

Substance	CAS number	(i) Measured values		*(ii) Value estimated from heating loss*	*(iii) Values estimated from physical properties*	
		R_{air}(μg/m²/h)	$F_{air,y}$(-)	$F_{air,y}$(-)	R_{air}(μg/m²/h)	$F_{air,y}$(-)
Bisstearic acid lead	1072-35-1				1×10^{-6}	6×10^{-11}
Zinc stearate	557-05-1				7×10^{-8}	3×10^{-12}
Octadecanoic acid, barium salt	6865-35-6				2×10^{-6}	7×10^{-11}
Dimethyltin bis(isooctyl thio-glycolate)	26636-01-1				0.37	1×10^{-5}

Source: Annex B

3.2. Estimation of emissions

This section focuses on indoor emissions from end products into the air. First, an equation is presented for estimating emissions. Next, each parameter of the equation is described. Finally, the estimation of the emission of flame retardants is described as an example.

3.2.1. Equation for the estimation

Many indoor products containing plastics are used for many years. Therefore, the plastic additives may be emitted from plastics at very low and constant rates for many years. The total indoor emission of a plastic additive from an end product in a certain year can be calculated as:

$$E_{air}(y) = Stock(y) \times \frac{10^{-3}}{C_0 dt} \times T_{product} \times 365 \times R_{air} \qquad \text{(Formula 4-1)}$$

where:

- $E_{air}(y)$ is the emission of the plastic additive into the air (kg/year) in the year y;
- $Stock(y)$ is the in-use stock (tonnes) in the year y;
- C_0 is the initial concentration (wt%) of the additive in the end product;
- d is the plastic density (g/cm^3);
- t is the thickness of plastic board (mm);

- $T_{product}$ is the in-service use time (h/day) of the end product; and
- R_{air} is the emission rate into the air (μg/m²/h) of the plastic additive.

Alternatively, E_{air} can be calculated using the $F_{air,y}$ (-) calculated in Section 3 and the following method:

$$E_{air}(y) = Stock(y) \times 10^{-3} \times F_{air} \quad \text{(Formula 4-2)}$$

The calculation of in-use stock is described below. In addition, Annex E and Annex F provide information on board thickness and in-service use time.

(1) In-use stock

Most plastic additives are distributed within the plastic parts of final products, retained throughout the lifetime of the products, and discarded together with the products. The in-use stock of plastic additives in final products can be calculated as:

$$Stock(y) = \int_{y'=0}^{y} I(y') \times (1 - W(n)) dy' \quad \text{(Formula 4-3)}$$

where:

- $Stock(y)$ is the in-use stock (tonnes) of plastic additives;
- y is the investigational year;
- y' is the shipping year of final products to calculate cumulative in-use stock of plastic additives shipped from the past up until the investigational year;
- $I(y')$ is the amount of additive (tonnes) contained in final products in shipping year y';
- $W(n)$ is a function of waste ratio; and
- n (= y - y') is the number of years since the shipping of final products (Annex D).

(2) Waste ratio

To determine the longevity of consumer durables, the Weibull distribution is commonly used as a distribution of the cumulative age of service. $W(n)$ is expressed as:

$$W(n) = 1 - \exp\left\{-\left(\frac{n}{b}\right)^{a}\right\} \quad \text{(Formula 4-4)}$$

where a is a shape parameter and b is a scale parameter of the Weibull distribution. A shape parameter of 3 approximates a normal curve, and a parameter between 2 and 4 also results in an approximately normal curve. A lower value for the parameter, e.g. 1.25, results in a right-skewed curve, whereas a higher value, e.g. 10, results in a left-skewed curve.

A scale parameter stretches or contracts the distribution curve along the age of service axis. From the formula 4-4, when the age of service n is equal to the scale parameter b, the resulting value for $W(n)$ will be approximately 63% (i.e. 63% of the final products are discarded by the end of their assumed service life).

In this ESD, parameters *a* and *b* were determined by assuming that 90% of total final products are discarded by the end of their assumed service life (Annex D).

3.2.2. Parameters used for the estimation

(1) Plastic density

In accordance with the findings of several handbooks etc. on physical properties of plastics in Japan, representative values for plastic density are listed in Table 8.

Table 8. Plastic density (g/cm^3)

Resin	Abbreviation	Minimum	Maximum	Representative
Low density polyethylene	LDPE	0.91	0.97	0.92
Medium density polyethylene	MDPE	0.926	0.94	0.93
High-density polyethylene	HDPE	0.92	0.97	0.96
Polypropylene	PP	0.9	1.33	0.9
Polystyrene	PS	1.02	1.33	1.05
(High impact polystyrene)	(HIPS)			
Polyvinyl chloride	PVC	1.3	1.6	1.4
Vinylidene polychloride	PVdC	1.65	1.72	1.7
Polyethylene terephthalate	PET	1.38	1.6	1.38
Acrylonitrile Butadiene Styrene resin	ABS	0.99	1.36	1.07
Phenolic resin	PF	1.21	2	1.5
Methacryl resin	PMMA	1.17	1.2	1.19
Modified acryl	MS	1.08	1.16	
Polyamide	PA	1.12	1.425	1.14
Polyacetal	POM	1.41	1.425	1.41
Polycarbonate	PC	1.19	1.52	1.2
Polybutylene terephthalate	PBT	1.31	1.52	1.31
Epoxy resin	EP	0.75	2	1.6
Polyvinyl alcohol	PVA	1.21	1.31	
Styrene-acrylonitrile copolymer	AS	1.08	1.1	
Ethylene-vinyl acetate copolymer	EVA	0.92	0.95	
Cellulose acetate	CA	1.23	1.34	
Polyurethane	PU			1.2

Source: Several handbooks etc. on physical properties of plastics in Japan

(2) Thickness of plastic plates

The following default values can be used (Annex E):

- Film and sheet: 0.5mm
- Board: 2mm
- Pipes and joints: 5mm
- Mechanical parts: 2.5mm
- Daily commodities and groceries: 2mm
- Containers: 1.5mm

- Construction materials: 4mm
- Foam products: 20mm
- Reinforcement products: 3mm
- Other: 2mm as the representative thicknesses of commercially available plastic products.

(3) In-service use time for products

Products containing plasticizers are used mostly at room temperature indoors; therefore, changes in temperature do not need to be taken into consideration. Outdoors, temperature may increase under direct sunlight; therefore, emissions should be estimated on the assumption that products are used at 40 °C in daylight.

Emissions of flame retardants may vary widely, depending on the in-service use of electrical and electronic products. 5 h/day—the mean number of in-service hours of TVs and personal computers—is used in estimating the emissions of flame retardants from products (Annex F).

3.3. Example of an estimation

The formulas in Section 3.2.1 are used to estimate emissions of the flame retardant deca-BDE in Japan. The parameters used in Formula 4-1 are shown in Table 9.

Table 9. Parameters used in Formula 4-1 to estimate emissions of deca-BDE

Parameter	Value	Units	Reference
In-use stock (y)	Annual data	tonne	Section 3.2 and Annex D
Plastic density d	1.05	g/cm^3	Polystyrene
Plastic thickness t	2.5	mm	Mechanical parts
Initial concentration C_0 of additives	16	wt%	Data used in the emission tests in Annex B
In-service hours of products $T_{product}$	5	h/day	Mean values for appliances such as TVs and PCs
Emission rate R_{air}	0.03	µg/m^2/h	Measured (detected) value in Annex B

The parameters used in Formula 4-2 are shown in Table 10.

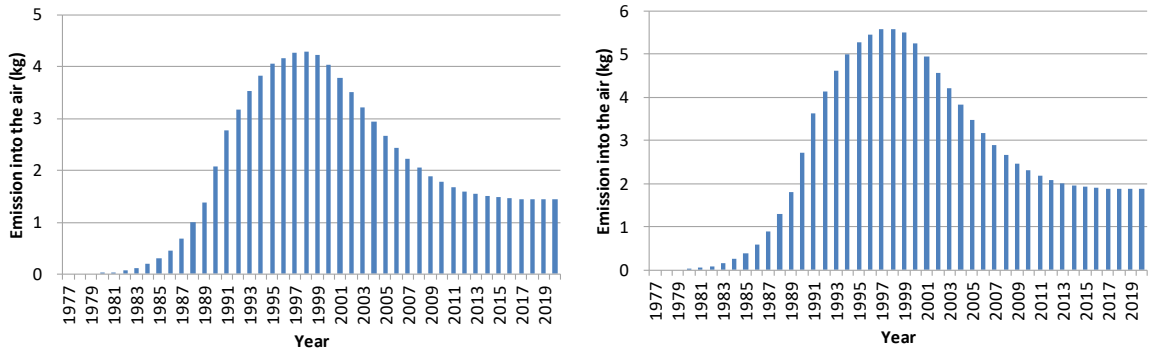
Table 10. Parameters used in Formula 4-2 to estimate emissions of deca-BDE

Parameter	Value	Units	Reference
In-use stock $Stock(y)$	Annual data	tonne	Section 3.2 and Annex D
Emission factor $F_{air,y}$	1×10^{-7}	-	Section 3.1

Figure 1 shows the results. There are some differences in results between Formulas 4-1 and 4-2, but the estimated values are comparable. In addition, Figure D.1 shows the results of the calculation for the amount of deca-BDE in the final products put on the market each year, and Figure D.3 shows the estimation of the in-use stock of deca-BDE.

Figure 1. Emissions of deca-BDE from in-use stock into the air

Calculations using Formula 4-1 (left) and Formula 4-2 (right)



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Annex A. Estimation of Vapour Pressures

The vapour pressure of a substance is an important parameter that can have a great influence on the emission rate for the substance. There are very few reliable data on the vapour pressures of plastic additives, which are very low compared with those of volatile organic substances. Therefore, the pre-existing equation below was used to estimate vapour pressure.

1. Estimation equation proposed in the ESD

In the appendices of ESD of 2008 (OECD, 2008[1]), the formula based on the Miles experiment (Miles, 1943[6]) is applicable, if it is appropriately modified, to estimate vapour pressures of substances that are used in liquid form for the plasticization of PVC.

The following equation is proposed for the estimation of the vapour pressure at 150°C (423 K):

$\log P = 0.4M^{0.5}(1 - Tb/423)$

where, P = vapour pressure in the air (atm)

M = molecular weight

Tb = normal boiling point (K)

By using the equation above, an equation for estimating vapour pressure at a given temperature can be expressed as follows:

$\log P = 0.4M^{0.5}(1 - Tb/T)$

where, T = a given temperature (K).

2. The Yaws estimation equation

Yaws (1997[3]) provided the following equation for estimating the vapour pressures of various substances:

$\log_{10}P = A + B/T + C \times \log_{10}T + D \times T + E \times T^2$

where, P = vapour pressure [mm Hg]

T = temperature [K]

and A, B, C, D, and E are coefficients

Table A.1 lists the coefficients for a number of plastic additives.

Table A.1. The coefficient data of Yaws equation on the characteristics of plastic additives

Substance	Dibutyl phtalate (DBP)	Bis(2-ethylhexyl) phtalate (DEHP)	Diisodecyl phtalate (DIDP)	Diisononyl phtalate (DINP)	Dimethyl phtalate (DMP)	Diethyl phtalate (DEP)	Triphenyl phosphate (TPP)	Tricresyl phosphate (TCP)	Trimethyl phosphate (TMOP)	2.6-Di-tert-butyl-4-methylphenol (BHT)
Formula	$C_{16}H_{22}O_4$	$C_{24}H_{38}O_4$	$C_{28}H_{46}O_4$	$C_{26}H_{42}O_4$	$C_{10}H_{10}O_4$	$C_{12}H_{14}O_4$	$C_{18}H_{15}O_4P$	$C_{21}H_{21}O_4P$	$C_3H_9O_4P$	$C_{15}H_{24}O$
Molecular weight	278.34	390.56	446.66	418.61	194.18	222.24	326.28	368.36	140.08	220.35
A	152.6750	27.8473	81.7895	-93.73	12.6974	72.1438	28.0972	21.1624	72.2176	69.7769
B	-1.0754E+04	-7.6834E+03	-7.4225E+03	-4049	-4.20E+03	-7.07E+03	-5.6684E+03	-5.2756E+03	-4.5518E+03	-6.57E+03
C	-5.1170E+01	-2.1134E+00	-2.6916E+01	17.3	3.46E-01	-2.10E+01	-5.9768E+00	-3.3565E+00	-2.4613E+01	-2.04E+01
D	1.6933E-02	-1.5234E-02	1.1502E-02		-7.6524E-03	-3.2404E-10	-3.1567E-09	8.6660E-06	1.3118E-02	4.0687E-09
E	2.4948E-14	6.2365E-06	-4.3530E-14		3.3490E-06	3.4691E-06	1.0751E-12	-2.9202E-09	-4.7970E-14	3.5418E-06
Temperature lower limit (K)	238	298	233		272	269	323	428	227	344
Temperature upper limit (K)	781	806	723		766	757	687	566	764	720

3. Comparison of vapour pressure estimation equations

Figure A.1 compares measured vapour pressures of plasticizers and vapour pressures estimated using the two equations above. This figure shows that the vapour pressures estimated in accordance with the ESD proposal are more similar to the measured ones than the Yaws (1997[3]) estimations within a range of normal temperatures for DEHP. The ESD estimation also indicates that the vapour pressure of DEHP is larger than that of DIDP. In contrast, Yaws' estimates are more similar to the measurements within a range of temperatures of 200 °C or higher for DEHP.

Figure A.1. Comparison of measured and estimated vapour pressures of the plasticizers DEHP and DIDP as examples

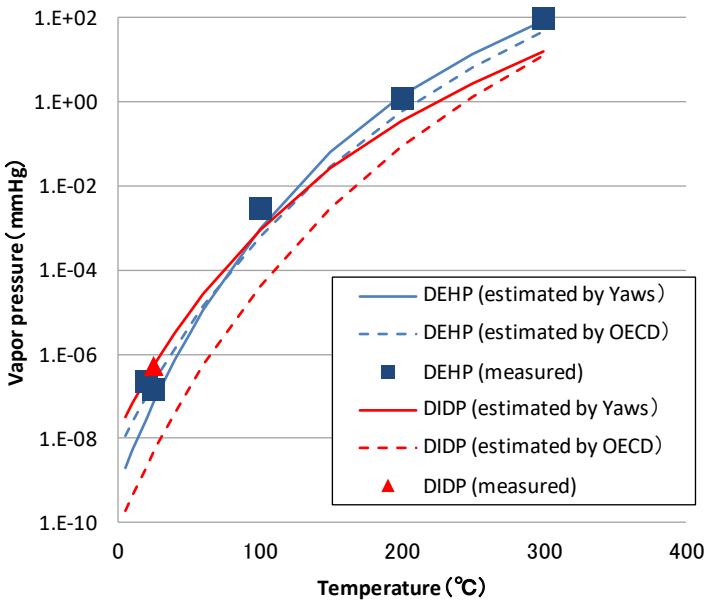
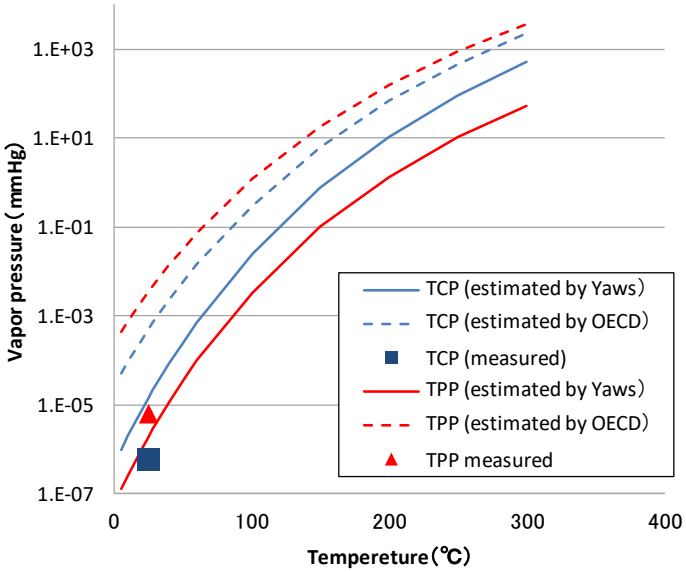


Figure A.2 compares the measured and estimated vapour pressures of flame retardants. This figure shows that Yaws' (1997[3]) estimated vapour pressures are more similar to the measured ones within a range of normal temperatures. Vapour pressures estimated in accordance with the ESD proposal were three orders of magnitude higher than the measured ones.

Figure A.2. Comparison of measured and estimated vapour pressures of the flame retardants TCP and TPP as examples



Therefore, estimation in accordance with the ESD proposal is valid only for limited plasticizers. Yaws' (1997[3]) estimation equation might be applicable to a wider spectrum of both plasticizers and flame retardants than is the ESD proposal. However, Yaws' estimation equation still covers only several substances and cannot be applicable to many plastic additives. Therefore, it is impractical to use a single equation to estimate the vapour pressures of all plastic additives.

Annex B. Measurement of Emissions from End Products

This section describes a newly developed micro-chamber method by which the emission rate for SVOCs can be determined. The measured results for plasticizers and flame retardants are also shown.

1. Outline of the Micro Chamber Method

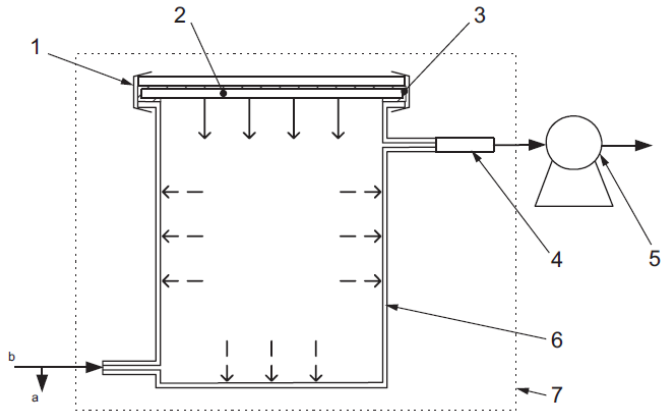
Many plastic additives, being SVOCs, are difficult to analyse by methods for measuring VOCs, as substances are adsorbed to the inner surface of the measurement chamber. ISO standard 16000-25 (ISO, 2009[5]) defines a method newly developed for SVOCs:

1. In the emission-collection process, SVOCs are released into the chamber from a sample, collected in the sorbent tube, and then quantified by gas chromatography-mass spectrometry (GC/MS) Figure B.1). Within the micro-chamber, the temperature and humidity are 28 °C and 50%.
2. In the heating-desorption-collection process, the sample is removed from the chamber, and the chamber is heated in an oven at 200-220 °C for about 40 min. SVOCs adsorbed to the chamber wall are vaporized in the presence of an inert gas (He or N2) and collected. After quantification by GC/MS, the results of (1) and (2) are summed as the emission.

Figure B.1. Micro-chamber method

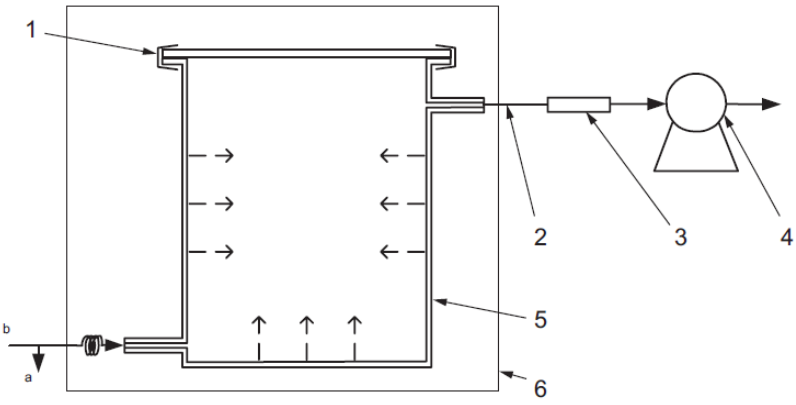
ISO16000-25, Part 25: Determination of the emission of semi volatile organic compounds by building products — Micro-chamber method (ISO, 2009[5])

Emission test (first step test)



1 clamp
2 test specimen
3 sealing material
4 sorbent tube (sampling of air in chamber)
5 sampling pump
6 micro-chamber
7 thermostatic oven
a Vent line.
b Humidity-controlled clean air [(50 ± 5) % RH] inlet.

Desorption test (second step test)



1 clamp
2 transfer line (holding temperature of 200 °C to 220 °C or higher is maintained at all times)
3 sorbent tube (sampling of SVOC thermally desorbed from chamber inner walls)
4 sampling pump
5 micro-chamber
6 chamber heating device (200 °C to 220 °C)
a Vent line.
b Inert gas (He or N_2) inlet.

The World Health Organization (WHO) defines SVOCs as organic compounds with boiling points ranging from 240-260 °C to 380-400 °C (WHO, 1989[7]). However, as the micro-chamber method determines SVOCs by GC, this document defines SVOCs as organic compounds from n-tridecane (n-C13, boiling point 234 °C) to n-hexacosane (n-C26, boiling point 399.8 °C) eluted under GC via a non-polar column.

Table B.1 summarizes SVOCs within that range that were loaded in the micro-chamber (100, 200, 500, and 1000 ng) and their recovery rates. The SVOCs were recovered at rates of 80% or more at all loading rates except for tri-n-butyl phosphate (TBP). About 100 to 1000 ng DEHP from construction materials in which plasticizers were used was adsorbed to the micro-chamber (Japanese Standards Association, 2008). Precise measurement can be done by knowing the recovery within this range.

Table B.1. SVOCs loaded into the micro-chamber (ng) and recovery rates (%)

Compound	100 ng	200 ng	500 ng	1000 ng
Dodecamethylcyclohexasiloxane (D6)	88	89	101	102
2,6-Di-*tert*-butyl-4-methyl-phenol (BHT)	93	92	99	100
Diethyl phthalate (DEP)	96	91	103	101
Tri-*n*-butyl phosphate (TBP)	52	68	94	94
Trichloroethyl phosphate (TCEP)	85	84	97	97
Di-*n*-butyl adipate (DBA)	94	90	101	99
Di-*n*-butyl phthalate (DBP)	92	85	97	107
Triphenyl phosphate (TPP)	92	85	97	107
Di(2-ethylhexyl) adipate (DEHA)	90	87	98	98
Di(2-ethylhexyl) phthalate (DEHP)	90	89	99	100

Source: Japanese Standards Association, 2008.

The micro-chamber method was developed by the Japan Petroleum Energy Center, reviewed over 3 years by the Japan Testing Center for Construction Materials, reviewed by the Japanese Industrial Standards Committee of the Ministry of Economy, Trade and Industry, and published as JIS A 1904 in 2008 (Japanese Standards Association, 2008[4]). This method was standardized as an ISO standard 16000-25 in 2009 (ISO, 2009[5]).

2. Measurements of emission rates for plasticizers

2.1 Emission rates from PVC products

Following JIS A 1904 (Japanese Standards Association, 2008[4]), emission data was collected for 24 hour in a micro-chamber at an input flow rate of 20 mL/min (one cycle of ventilation every 2 h). After heating-desorption-collection, the results were quantified by GC/MS (Table B.2). Emissions during the emission-collection process fell below the limit of detection in almost all samples but were higher during the subsequent thermal desorption process. Emission rates were influenced mainly by plasticizer and less by product or concentration of plasticizers.

The emission rates might reflect the physical-chemical properties, such as vapour pressure, molecular weight, and boiling point.

Table B.2. Emission rates from PVC product samples

Substances	Number of Samples	Emission rate (μg/m²/h)		
		Mean	Minimum	Maximum
DEHP	14	4.1	3.1	5.7
DINP	16	0.6	0.2	1.4
DIDP	3	0.3	0.0	0.7

2.2 Measured results of emission rates for test samples

(1) Methods

With support from industry, pressed sheets were prepared containing DEHP, DINP, or DIDP as a plasticizer. In general, 50 to 60 parts of plasticizer are added to 100 parts of PVC to prepare general-purpose film. 30, 60, and 90 parts of DEHP were blended to prepare test

samples. The plasticizing efficiencies of DINP and DIDP, which are expressed as substitution factors (SFs) compared to DEHP, are 1.02 and 1.12 respectively, thus the ratios were adjusted accordingly. The plasticizers were added during compounding at 125 to 175 °C (Table B.3). Test samples were formed in a pressing machine to 130 mm × 160 mm by 0.5-2.0 mm. DEHP-2 represents a standard film.

Table B.3. Conditions for preparation of test samples for emission test

Sample No. (substances)		DEHP-1	DEHP-2	DEHP-3	DEHP-4	DEHP-5	DINP-1	DIDP-1
Blending (parts)	PVC	100	100	100	100	100	100	100
	Plasticizers	30	60	90	60	60	61.2	67.2
	Ba-Zn stabilizers	3	3	3	3	3	3	3
Temperature during compounding (°C)		175	145	125	145	145	145	145
Thickness (mm)		0.5	0.5	0.5	1.0	2.0	0.5	0.5

Emissions from these samples were tested according to JIS A 1904 (Japanese Standards Association, 2008[4]). Then samples DEHP-2, DINP-1, and DIDP-1 were tested at 40 and 60 °C. Finally, sample DEHP-2 was tested at input flow rates of 40 and 60 mL/min (Table B.4).

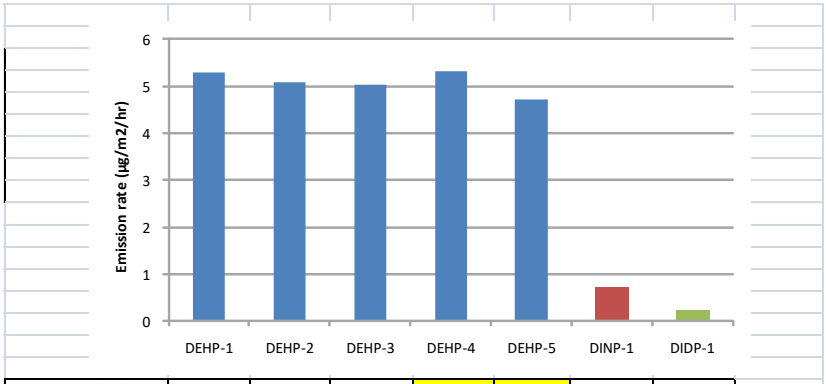
Table B.4. Emission-collection conditions

Sample No.	Emission-collection 1		Emission-collection 2		Emission-collection 3	
	Temp. (°C)	Flow rate (mL/min)	Temp. (°C)	Flow rate (mL/min)	Temp. (°C)	Flow rate (mL/min)
DEHP-1	28	20				
DEHP-2	28	20	40, 60	20	28	40, 60
DEHP-3	28	20				
DEHP-4	28	20				
DEHP-5	28	20				
DINP-1	28	20	40	20		
DIDP-1	28	20	40	20		

(2) Results

Figure B.2 shows the results from emission-collection 1 in Table B.4. As in the emission test of PVC product samples, the emissions of plasticizers were below the detection limit during the emission-collection process, and higher during the subsequent thermal desorption process. The emission rates fell within the range of the PVC product samples, indicating the validity of the results. Sample thickness and plasticizer ratio had limited effects on emission rates.

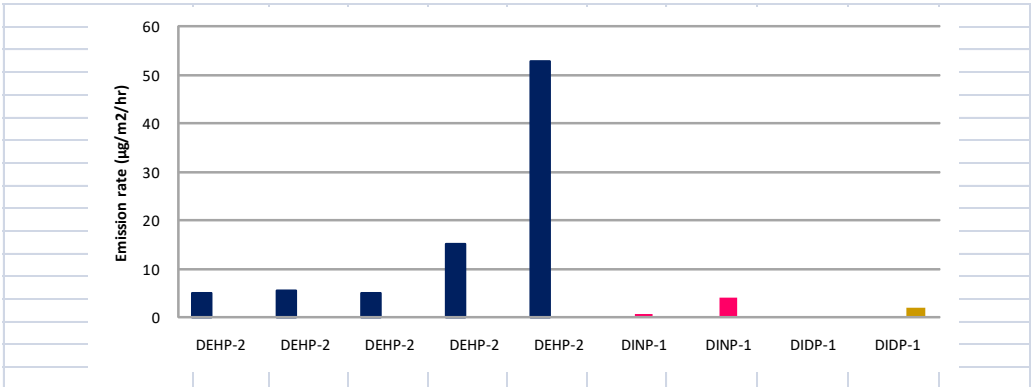
Figure B.2. Emissions of plasticizers from PVC products (using sample thickness and concentration as parameters)



Thickness (mm)	0.5	0.5	0.5	1.0	2.0	0.5	0.5
Blending (parts /PVC resin)	30	60	90	60	60	61.2	67.2

Input flow rate had no effect on emission rates, but the rates increased with temperature (Figure B.3), possibly because of an increase in vapour pressure.

Figure B.3. Emissions of plasticizers from PVC products (using temperature and flow rate as parameters)



Flow rate (mL/min)	20	40	60	20	20	20	20	20	20
Temperature (℃)	28	28	28	40	60	28	40	28	40

3. Measurement of emission rates for flame retardants

3.1 Emission rates from product samples

Table B.5 shows the emission rates for flame retardants from vinyl chloride products containing phosphorus flame retardants, as investigated by the Japan Vinyl Goods Manufacturers Association (2009[8]).

Table B.5. Vinyl chloride products used as samples in micro chamber method testing, and emission rates for flame retardants

Substances	Number of samples	Emission rate (μg/m²/h)		
		Mean	Minimum	Maximum
TCP	8	0.47	0.06	0.9
TPP	6	5.0	3.7	6.0
TXP	2	0.1	0.1	0.1

To determine the emission rate for flame retardants during the product service life, plastic samples from the housings of home appliances were used for flame retardants emission testing in accordance with JIS A 1904 (Japanese Standards Association, 2008[4]) at National Institute of Advanced Industrial Science and Technology (AIST). A second-hand television manufactured in about 1990 was used as a product sample. In addition, housings of desktop or laptop computers were obtained. The emissions were determined for four substances: substituted deca-BDE, substituted BDP, antimony trioxide (Sb2O3) used in combination with deca-BDE, and BDPs containing TPP impurities (Table B.6).

Table B.6. Home appliance products used as samples in micro chamber technique testing, and rates for release flame retardants

Product	Part	Resin	Flame retardant	Remarks
Tube from television manufactured in 1989	Side of housing	Unknown	Unknown	Depending on year of manufacture, deca-BDE is presumably present
Desktop personal computer	Panel on face	ABS	Brominated	Brominated compound as a possible substitute for deca-BDE
Laptop computer A	Top, gray	PC/ABS	Phosphorus	BDP is presumably used
Laptop computer B	Inside, black	PC/ABS	Phosphorus	Ditto
Laptop computer C	Inside, black	PC/ABS	Phosphorus	Ditto
Laptop computer D	Inside, black	PC/ABS	Phosphorus	Ditto

When these products are in service, their housings are heated to 40 to 80 °C. The 24-h emission-collection process was conducted at 60 °C as in Annex B. It was then repeated at 40 and 28 °C for compounds that were detected at 60 °C. It was not repeated at the lower temperatures for compounds not detected at 60 °C, which are likely not to be detected at lower temperatures.

The emissions of compounds did not exceed the detection level in almost all samples during the emission-collection process, and emission was increased during the subsequent thermal desorption process (Table B.7). At 60 °C, deca-BDE was not detected in any sample. Except for BDP, which was detected in one sample at an estimated release rate of 0.05 μg/m²/h, no compound exceeded the detection limit. Although TPP, one of the impurities of BDP, was detected at a higher rate than BDP, possibly because its vapour pressure is higher than that of BDP, its emission rates varied from <0.2 to 14 μg/m²/h among samples. The emission rate was higher in samples of a single product. This may mean that the aromatic phosphate ester TPP, not the condensed phosphate ester BDP, was used to make the product. TPP emission testing using the same samples at 40 and 28 °C revealed that the emission rates were lower at lower temperatures.

Table B.7. Emission rates (µg/m²/h) for flame retardants from samples of home appliances

Products	Deca-BDE	Sb_2O_3	BDP	TPP
Tube from television manufactured in 1989	<0.5 (60 °C)	–	–	–
Desktop personal computer	<0.5 (60 °C)	–	–	<0.2 (60 °C)
Laptop computer A	<0.5 (60 °C)	–	<0.05 (60 °C)	14 (60 °C), 3.7 (40 °C), <0.2 (28 °C)
Laptop computer B	<0.5 (60 °C)	–	<0.05 (60 °C)	1.4 (60 °C)
Laptop computer C	<0.5 (60 °C)	–	0.05 (60 °C)	1.3 (60 °C)
Laptop computer D	<0.5 (60 °C)	–	<0.05 (60 °C)	0.8 (60 °C)

3.2 Measured results of emission rates for test samples

(1) Methods

With support from industry, molded resins were prepared that contained deca-BDE or BDP. HIPS was used with deca-BDE, a brominated flame retardant, and PC/ABS was used with the phosphorus flame retardant. The flame retardants were mixed into the respective compounds. Plates of the resulting mixture were shaped by injection molding and then pressed into a size of 120 mm × 120 mm × 3 mm to use as test samples (Table B.8).

Table B.8. Preparation of test samples used for emission testing of flame retardants

Sample (resin)		HIPS	PC/ABS
Composition (parts)	Resins	100	100 (PC 80, ABS 20)
	Flame retardants	20 (deca-BDE)	15 (BDP)
	Flame retardant enhancers (Sb2O3)	5	None
Extrusion/injection temperature (°C)		180-200	260-280
Molding temperature (°C)		35	80
Press molding temperature (°C)		190	290
Thickness (mm)		3	3

Release testing was conducted in accordance with JIS A 1904 (Japanese Standards Association, 2008[4]). For all samples, the emission-collection process was conducted at 60 °C, representing the product use temperature, and at 40 or 28 °C for samples from which any of the target compounds was detected. The inlet flow rate was 20 mL/min.

(2) Results

The emission rates for deca-BDE, Sb2O3, and BDP fell below the detection limit in all samples (Table B.9). The respective emission rates for deca-BDE and Sb2O3 were 0 to 0.03 and 0.03 to 0.32 µg/m²/h when distinguishable peaks lower than the detection limit are counted. Therefore, deca-BDE and Sb2O3 were estimated to be emitted at about 0.01 to 0.03 and 0.2 µg/m²/h, respectively. The emission rate for TPP was estimated to be 0.2 to 0.3 µg/m²/h at 60 °C. In all samples, these substances could not be detected at 40 °C, and their emission rates were estimated to be <0.2 µg/m²/h at this temperature. The results of the emission testing of the samples are valid because the emission rate was similar between BDP and TPP in the test samples.

Table B.9. Emission rates (µg/m²/h) for flame retardants from test samples

Test sample	Deca-BDE	Sb_2O_3	BDP	TPP
HIPS resin (n = 3)	<0.5 in all samples [h 0.03 in one sample] (60 °C)	<0.8 in all samples [0.03-0.32] (60 °C)	<0.05 in all samples (60 °C)	–
PC/ABS resin (n = 3)	<0.5 in all samples (60 °C)	–	<0.05 in all samples (60 °C)	0.2, 0.3, 0.3 (60 °C) <0.2 (40 °C) in all samples

Note: Reference values, below the detection limit, are shown in brackets.

4. Discussion

Emission rates tended to be inversely proportional to molecular weight and boiling point and to be proportional to vapour pressure. The vapour pressures were estimated with the ESD equation (Annex A). However, measured rates and values estimated with Yaws' equation (Yaws, 1997[3]) correlated inversely (Figure B.4, Figure B.5 and Figure B.6). This shows that vapour pressure data must be highly reliable.

Figure B.4. Relationship between plasticizer emission rate and vapour pressure (measured values)

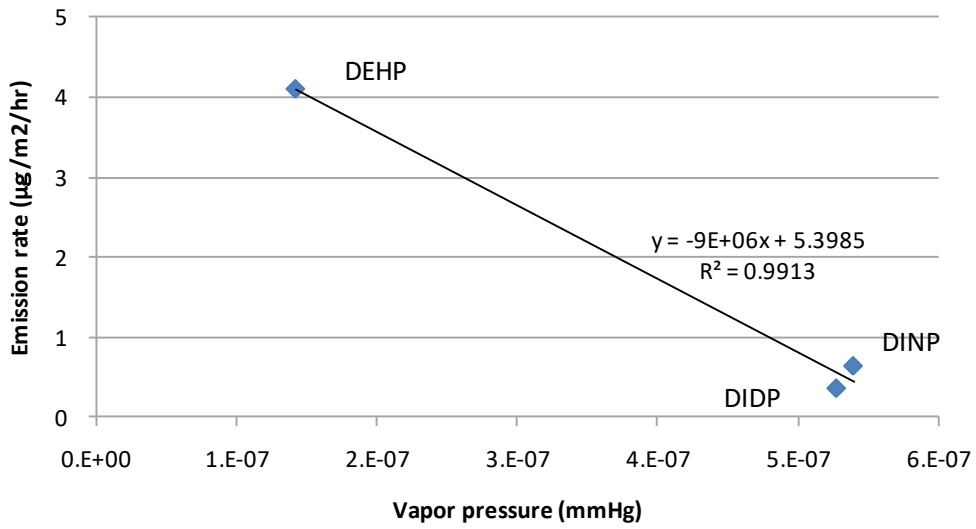


Figure B.5. Relationship between plasticizer emission rate and vapour pressure (ESD equation)

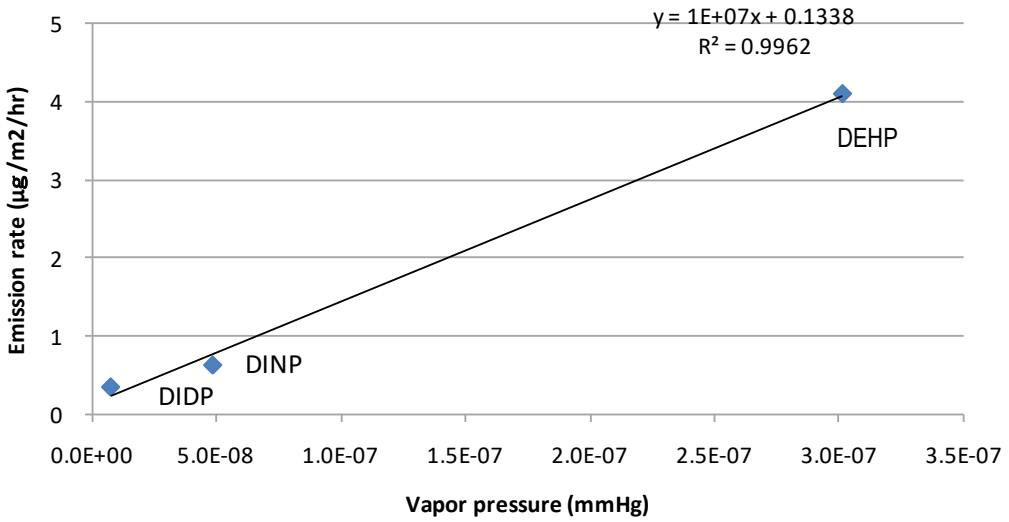
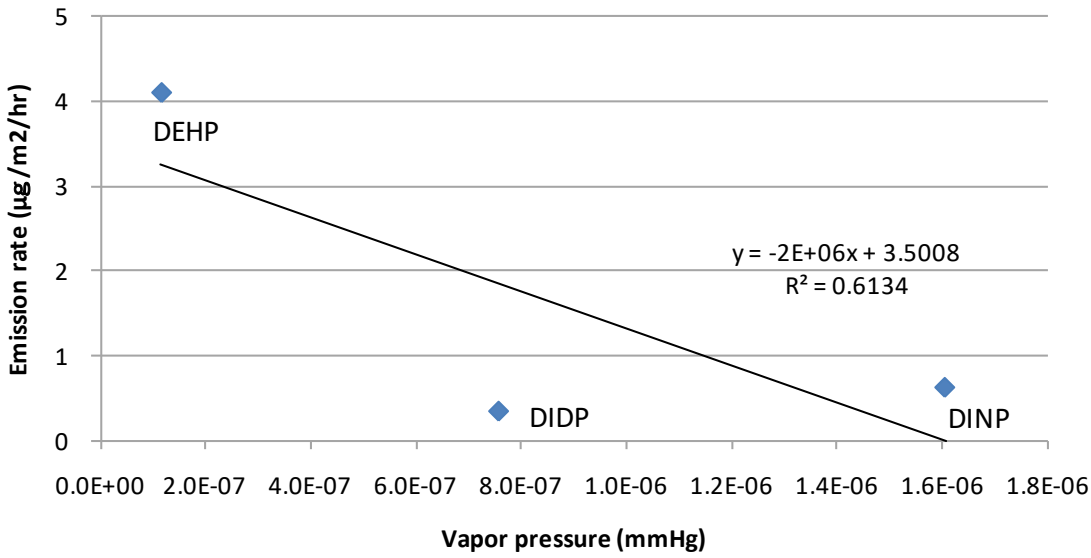


Figure B.6. Relationship between plasticizer emission rate and vapour pressure (Yaws' equation)



Three different techniques proposed for estimating the emission rates for the plasticizer DEHP (ENVIRON, 1988[9]) were used, either at a particular rate of airflow above a vinyl sheet or by allowing for diffusion either in the air or via ventilation. The emission rate for DEHP was increased under forced ventilation. However, the above results showed almost no change in emission rate with different airflow rates; therefore, the relationship between emission and airflow rates seems not to be important.

No plasticizer was detected during the emission-collection process, but much was detected during the thermal desorption process. Therefore, during use, it can be assumed that, after its emission from the surface of the plastic, most of the plasticizer adheres to the dust attached to the surface and is not diffused in the air. The plasticizer/dust can then be airborne by ventilation, removed by vacuuming or transferred through surface cleaning into water. Oral exposure to these compounds among children is possible through inhalation or ingestion of dust.

DEHP, DINP, and DIDP were estimated to be emitted at 4.1, 0.6, and 0.3 $\mu g/m^2/h$, respectively, at normal temperatures.

The emission test of flame retardants revealed that, similar to plasticizers, flame retardants could not be detected during the emission-collection process. Therefore, flame retardants may behave similarly to plasticizers after their emission. Oral exposure to such compounds can occur among children. The emission rate for flame retardants may vary widely between electrical and electronic products that are in and out of service; therefore, emission estimations should take the in-service duration of the product into account.

The emission rate for deca-BDE, a brominated flame retardant, was $<0.5\ \mu g/m^2/h$ at about 60 °C during the in-service phase, or an estimated 0.01 to 0.03 $\mu g/m^2/h$. The emission rate for Sb_2O_3, which is used in combination with deca-BDE, was estimated to be around 0.2 $\mu g/m^2/h$. BDP, a phosphorus flame retardant, was emitted from both product and test samples at $<0.05\ \mu g/m^2/h$ at 60 °C, suggesting that its actual emission rate is smaller than that of deca-BDE. TPP, an impurity in BDP, was estimated to be emitted at 0.2 to 0.3 $\mu g/m^2/h$—higher than that of BDP.

Annex C. Examining the Estimation of Emission Factors

1. Requirements

Plastic additives are meant to be retained in the polymeric resin for a prolonged period of time. Anti-volatility and transfer resistance are important for their retention. Anti-volatility refers to the limited volatility of plastic additives from the surfaces of molded articles during processing and service life. Transfer resistance refers to the limited transfer of plastic additives within a compound through diffusion. In general, plastic additives are less volatile in compounds with higher molecular weight, or if they are highly miscible with the resin. Plastic additives cannot easily diffuse within a compound with a bulky functional group. Therefore, most plastic additives have a low vapour pressure and are SVOCs.

The mechanisms of volatilization from the surface of the resin and of transfer within the resin are highly complicated. Therefore, some major simplifications are required to estimate EFs. One assumption is that the molecular movement is faster than the release from the surface of a resin under the conditions of usual product use, and that the release of a substance from the surface of the resin is a rate-determining factor. Diffusion of plastic additives within the resin on the surface is a rate-determining factor for very low concentrations of plastic additives or high volatility of the additives. These conditions are not covered in this ESD.

2. Determination of EFs based on vapour pressure

Based on the emission rates for PVC shown in Annex B, the emission rate $F_{air,y}$ (-) of plasticizer X can be calculated by using the following equation, assuming that it is proportional to the vapour pressure P_T of the substance at temperature T (K):

$$F_{airx,y} = 1 \times 10^7 \times P_T + 0.1338$$

In addition, based on the emission rates for DEHP and TCP, the emission rates for most plastic additives could be appropriately assumed to be proportional to their vapour pressures and inversely proportional to their molecular weights. For example, the following equation can be used to calculate their emission rates:

$$F_{airxb,y} = F_{airDEHP,y} \times P/M/(P_{DEHP}/M_{DEHP})$$

Where, P is the vapour pressure at 25°C, and M is the molecular weight. This equation can be used only for substances with known vapour pressures. As shown in Annex A, the vapour pressures of plastic additives are very low and, in general, measured values are highly variable and may not be reliable. Therefore, another method is introduced below, independent of the data on vapour pressure.

3. Determination of EFs using activation energy

The activation energy generated during the emission of plastic additives from the surface of resins into the air was examined. The heating loss of plastic additives, including plasticizers and flame retardants, from resin increases exponentially over time at increased temperatures (Takano, 2008[10]). The rate of loss of a substance from a resin by volatilization, assuming that it is proportional to the concentration of plastic additive at that time, can be expressed as:

$$-dC/dt = kC$$

where C is the concentration of plastic additive in the resin and k is the loss constant.

The equation can be integrated into the following equation:

$$-\ln C = kt + \text{const.}$$

When the initial concentration of plastic additive in resin is C_0, the following equations hold true at $t = 0$:

$$-\ln C_0 = \text{const.}$$

$$kt = \ln C_0 - \ln C = -\ln(C/C_0)$$

$$k = -\ln(C/C_0)/t$$

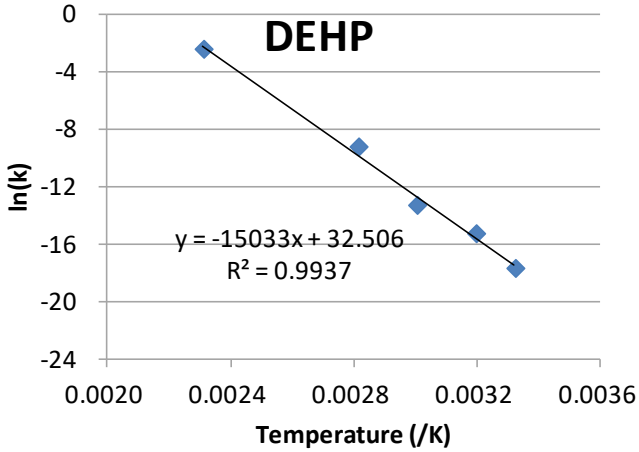
Table C.1 shows the results of calculations of loss constants of some plasticizers, in addition to the data on emission tests shown in Annex B and on heating loss, indicating the relationship between resin heating time and loss of volatiles.

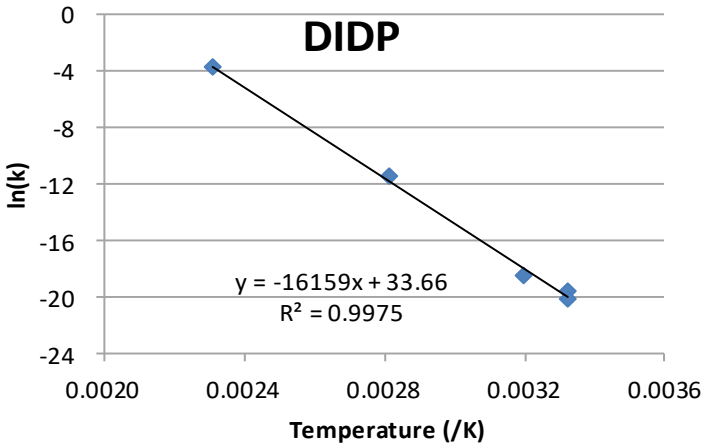
Table C.1. Loss constants of plastic additives at various temperatures

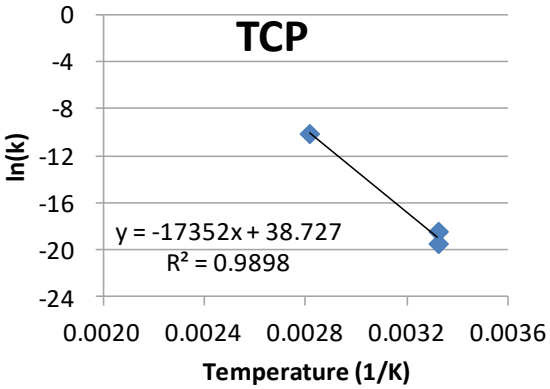
Substance	Resin	Initial conc. %	Temperature °C	Heating loss %/h	Emission rate μg/m²/h	Reference	Loss constant k
DEHP	PVC	36.8	28	–	4.1	(Tsunemi and Kawamoto, 2011[11])	2.2×10^{-8}
DEHP	PVC	36.8	40	–	46	(Hoshino, Kato and Ataka, 2007[12])	2.5×10^{-7}
DEHP	PVC	36.8	60	–	330	(Hoshino, Kato and Ataka, 2007[12])	1.8×10^{-6}
DEHP	PVC	29.5	82.5	0.01	–	(Kawahara and Imoto, 1987[13])	1.0×10^{-4}
DEHP	PVC	33.3	160	9.2	–	(Kawahara and Imoto, 1987[13])	9.3×10^{-2}
DIDP	PVC	20.0	28	–	0.05	(Japan Vinyl Goods Manufactures Association, 2009[8])	2.9×10^{-9}
DIDP	PVC	39.5	28	–	0.3	(Tsunemi and Kawamoto, 2011[11])	1.7×10^{-9}
DIDP	PVC	39.5	40	–	19	(Tsunemi and Kawamoto, 2011[11])	9.9×10^{-9}
DIDP	PVC	36.8	82.5	0.01	–	(Kawahara and Imoto, 1987[13])	1.0×10^{-5}
DIDP	PVC	33.3	160	2.3	–	(Kawahara and Imoto, 1987[13])	2.3×10^{-2}
TCP	PVC	5.0	28	–	0.07	(Japan Vinyl Goods Manufactures Association, 2009[8])	3.6×10^{-9}
TCP	PVC	20.0	28	–	0.75	(Japan Vinyl Goods Manufactures Association, 2009[8])	1.0×10^{-8}
TCP	PVC	29.5	82.5	0.004	–	(Kawahara and Imoto, 1987[13])	4.2×10^{-5}

Arrhenius plots of the log of the loss constant associated with volatilization of these substances with the reciprocal of absolute temperature indicate a linear relationship (Figure C.1). This means that the loss constant changes with the activation energy in accordance with the Arrhenius equation.

Figure C.1. Arrhenius plots of loss constant of substances in PVC against 1/temperature







Therefore, the loss constant k and activation energy E generated by volatilization of substances can be expressed as:

$$k = Ze^{-E/RT}$$

where Z is a constant factor and R is the gas constant (0.082 atm L/K/mol). This equation can be transformed into the following equation:

$$\ln(k) = -E/RT + \ln(Z)$$

This supports the Arrhenius relationship, as shown in Figure C.1. The activation energy E involved in the loss due to volatilization can be calculated from the gradient of the lines at various ranges of temperature (Table C.2).

Table C.2. Activation energies of plastic additives at various temperature ranges

Substance	Resin	Range of temperature (°C)	Activation energy (kcal/ mol)
DEHP	PVC	28-60	26.7
		28-160	29.8
DIDP	PVC	28-60	26.8
		28-160	32.1
TCP	PVC	28-82.5	32.4

These results show slight differences between the lower range of temperature (28-60 °C) and the higher ranges of temperature (28-160 °C: molding temperature). To estimate emissions during the service life, one calculation was examined using the mean activation energy of 27.5 kcal/mol at 28 to 60 °C as a common value, and another using the mean activation energy of 30.8 kcal/mol at 28 to 160 °C as a common value.

Application of the above common activation energy E (kcal/mol) to substances enables the calculation of the constant factor $\ln(Z_x)$ specific to substance X when there is a known residual proportion C_a/C_0 after the loss of substance X after period t_a (h) at temperature T_a (K). It therefore enables calculation of an annual EF $F_{airxb,y}$ at a given temperature T_b (K) as:

From $k_a = -\ln(C_a/C_0)/t_a$ the resulting equation is $\ln(Z_x) = \ln(k_a) + E/RT_a$

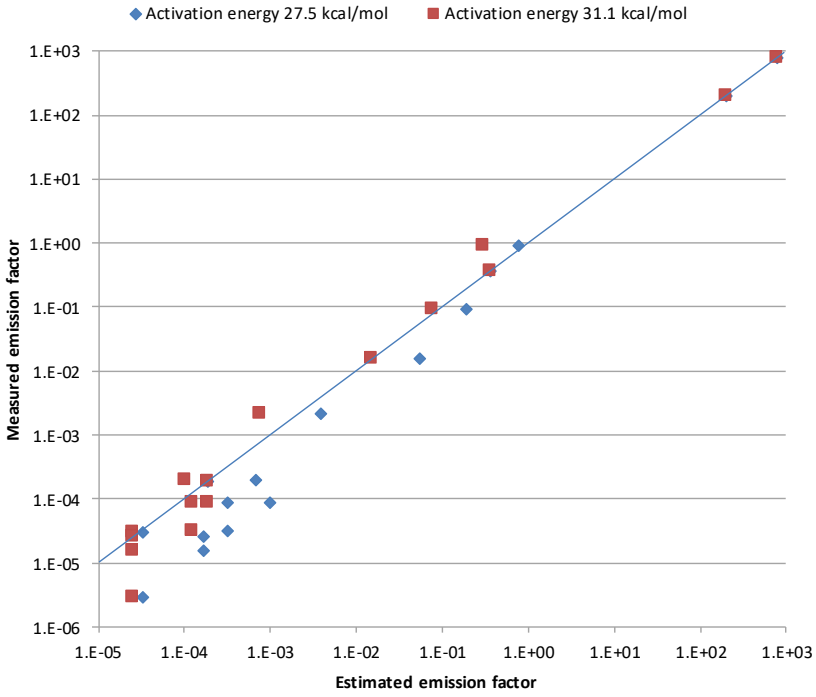
From $\ln(k_b) = \ln(Z_x) - E/RT_b$ the resulting equation is $k_b = Z_x \exp(-E/RT_b)$

Finally, the emission factor can be calculated by $F_{airxb,y} = \{1 - \exp(-k_b)\} \times 365 \times 24$

Figure C.2 compares EFs estimated by the above calculation by using loss constants of DEHP, DINP, DIDP, and TCP at the highest temperature and those obtained based on the measured emission rates for these substances. The estimated values tend to exceed the measured ones at an activation energy of 27.5 kcal/mol, are similar to the latter at higher EFs, and are higher than the latter at lower EFs and an activation energy of 30.8 kcal/mol. Thus, 30.8 kcal/mol—the mean activation energy at the higher range of temperature—was the appropriate choice as a common value.

Therefore, if there are data on heating loss constant of a certain substance in resin at a higher range of temperature, then EFs within the normal or lower range of temperature can be calculated at a mean activation energy of 30.8 kcal/mol as a common value by using the equations above.

Figure C.2. Relationship between EFs estimated by using activation energy and measured EFs (for DEHP, DINP, DIDP, and TCP)

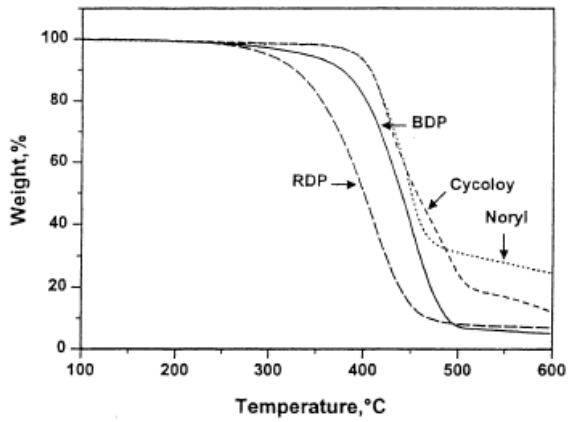


4. Determination of EFs using heating loss

Section 3 included the emission rates for plasticizers and flame retardants contained in resin; these rates were obtained through emission testing and could not be widely extrapolated to other substances. Therefore, attempts were made to use data obtained from heating-loss tests—especially of flame retardants—conducted internally by manufacturers.

Unique thermal decomposition curves have been determined by using thermogravimetric analysis (TGA) to identify the thermal decomposition and combustion points of flame retardants. Figure C.3 shows TGA curves of the condensed phosphate esters, RDP and BDP.

Figure C.3. TGA curves of condensed phosphate esters RDP and BDP



Source: tests supervised by (Nishizawa et al., 2002[14])

The TGA curve up to the kick-off point of a flame retardant represents the volatility of the substance and, therefore, can be considered to give the heating loss of the substance at a certain temperature. Table C.3 shows the heating losses of phosphate esters at 250 and 300 °C. Although the heating losses are very low at the lower range of temperatures that these data cannot be used for estimating EFs, those between 200 and 300 °C are high enough.

Table C.3. Heating losses of phosphate esters

Substance	Heating temperature °C	Heating loss wt%
TPP	250	12.8
TPP	300	85
RDP	250	0.7
RDP	300	2.6
BDP	250	0.8
BDP	300	1.9

Source: Technical Information Institute, 2008

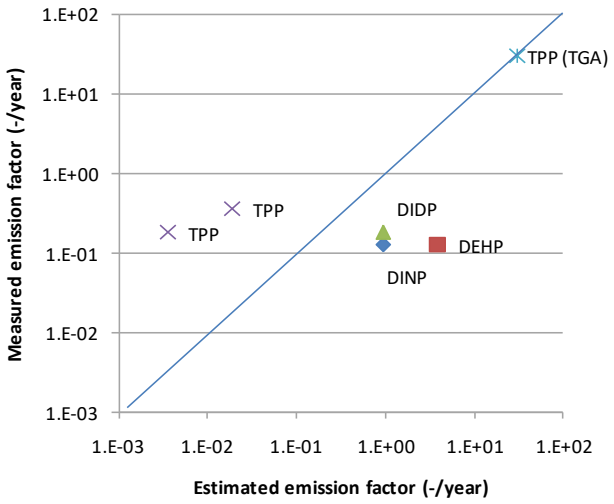
JIS K 6751-4 (Japanese Standards Association, 1999[15]) describes the measurement of heating losses of phthalate esters. About 30 g of sample is put into a drying oven and heated at 125 ± 3 °C for 3 h; the loss is then measured. Publically available results are listed in Table C.4.

Table C.4. Heating losses of phthalate esters

Substance	Test	Heating temperature (°C)	Duration of heating (h)	Heating loss (wt%)	References
DEHP	JIS K 6751	125	3	<0.07 <0.1	Website of Nichibi Trading Co., Ltd. Website of Showa-Ether
DINP	JIS K 6751	125	3	<0.07	Website of Nichibi Trading Co., Ltd. and Showa-Ether HP
DIDP		125	3	<0.1	Website of Showa-Ether
DBP	JIS K 6751	125	3	<0.5	Website of Nichibi Trading Co., Ltd. and Showa-Ether
DOA	JIS K 6751	125	3	<0.1	Website of Showa-Ether
TCP	–	Unknown	Unknown	0.1	Website of J-plus Co., Ltd
TPP	–	115 100	3 3	<0.2 <0.1	Website of Showa-Ether Website of Ajinomoto Fine-Techno Co., Inc.

Figure C.4 compares the EFs (values below the detection limit were assumed to be half the limit) estimated from the common activation energy under Section 2 in Annex C and those determined from measured emission rates in Annex B based on the heating losses in Table C.4. Despite the limited accuracy of the EFs estimated in accordance with JIS K 6751-4 (Japanese Standards Association, 1999[15]), the TPP EF estimated from the TGA curve was similar to the measured one. Most of the heating losses of plasticizers determined in accordance with JIS K 6751-4 were below the detection limit and thus unusable. Data held by manufacturers could be used to estimate EFs by using heating losses determined from TGA curves, although further testing of the estimates would be required for other substances. Similar testing of other substances could show that the emission rates for such substances from the resin surface could depend on the volatility of the substances.

Figure C.4. Comparison between estimated and measured EFs based on heating losses (for DEHP, DINP, DIDP, and TPP)



Annex D. Calculation of In-use Stock

This section shows how to calculate the in-use stock for each year in accordance with changes over time in domestic demand for plastic additives. Then it provides a list of longevities for each use. Finally, it describes examples of calculations of the in-use stock of flame retardants.

1. Determining the duration of the service life of final products

In this section, the duration of the service life of each type of goods is taken from published reports, which is needed for determining the parameters of the Weibull distribution (Table D.1).

Table D.1. Product lifetimes

Life	Examples of product types	Lifetime of product
Short	Packaging, medical applications, office supplies	<2 years
Medium	Wall coverings, flooring materials, footwear	2-10 years
Long	Flooring, wires/cables, furniture, automobiles	10-20 years
Very long	Pipes, window profiles, cables, roofing liners	>20 years

Source: (European Commission DGXI Unit E3, 2000[16]).

In the EU Risk Assessment Report (2008[17]) for DEHP, products are classified into indoor and outdoor uses, and durations of the service life are reported for various types of polymer and non-polymer products (Table D.2).

Table D.2. Technical lifetimes of products including DEHP

	Use	Technical lifetime				
		ECPI [1]	Industry Co. [2]	Miljöstyrelsen [3]	Others	EU Risk Assessment Report [7]
Indoor use	Coated products	7	–	–	–	7
	Films/sheets	7	–	1-5 [4]	–	7
	Hoses/profiles	10 [5]	–	1-10	–	10
	Floors	10	–	–	20 [6]	20
	Sealants, adhesives	–	–	–	–	20
	Cables	30	–	30-50	–	30
	Lacquers and paints	–	–	–	–	7
	Printing inks	–	–	–	–	1
Outdoor use	Roofing materials	–	20	–	–	20
	Roofing (coil coating)	–	10	–	–	10
	Cables	–	10-30	30-50	–	30
	Coated fabrics	–	10	–	–	10
	Hoses/profiles	–	10	–	–	10
	Car under-coatings	–	12	16	–	12
	Shoe soles	–	5	–	–	5
	Sealants, adhesives	–	–	–	–	20
	Lacquers and paints	–	–	–	–	7

Source: 1) European Council for Plasticisers and Intermediates 1996
2) Industry, 1999 survey
3) Miljöstyrelsen 1996 (Denmark)
4) PVC foil
5) Assumed to be the same as flooring material
6) Estimated average; Tarkket-Sommer, 1999 survey
7) (EURAR, 2008[17])

Nakai et al. (2000[18]) reported that the useful lifetime was 38.7 years for construction materials, 50 years for PVC pipes, 9.1 to 38.7 years for wire coverings, 7.15 to 12.74 years for automobiles, and 8.7 to 12.85 years for home electrical appliances (Table D.3).

Table D.3. Product lifetimes as reported by Nakai et al. (2000)

Use	Item	Useful lifetime (years)
1 Construction		38.7
2 Civil engineering (PVC pipe)		50.0
3 Wire covering	3.1 Winding wire	9.18
	3.2 Electrical wire for electrical equipment	9.18
	3.3 Electrical wire for transport equipment	9.1
	3.4 Power and communication cables	20.0
	3.5 Other insulated electrical wires	38.7
4 Agriculture	4.1 Film for greenhouses	2.5
	4.2 Film for tunnel culture	Consumer non-durables
	4.3 Film for mulching	Consumer non-durables
	4.4 Other agricultural materials	Consumer non-durables
5Automobiles	5.1 Passenger cars	9.9
	5.2 Trucks	10.02
	5.3 Buses	12.74
	5.4 Motorbikes	7.15
6 Home electrical appliances	6.1 Color TVs	10.15
	6.2 Refrigerators	11.85
	6.3 Washing machines	8.7
	6.4 Vacuum cleaners	8.7
	6.5 Room air-conditioners	12.85
	6.6 Other home electrical appliances	9.18
7 Medical use		Consumer non-durables
8 Container packaging		Consumer non-durables
9 Household supplies		Consumer non-durables

Consumer non-durables include agricultural materials, medical applications, containers and packaging, and household supplies.

The Study Group for Risk Assessment and Management of Phthalates (2003[19]) found useful lifetimes ranging from 0.5 years to 20 years for various products (Table D.4).

Table D.4. Product lifetimes, as revealed by an interview survey conducted by the Study Group for Risk Assessment and Management of Phthalates

Name of industry	Product using DEHP	Product useful lifetime (years)
Synthetic Resin Manufacturers' Association	Film, sheet, plasticizer, hardener, urethane resin, emulsion resin, phenol resin	1-10
Japan Vinyl Goods Manufacturers' Association	General-purpose film	1-15
	PVC films for agriculture	2
	Fake leather	5-20
	Compound	5-20
	Wallpaper	5-20
	Others	0.3-25
Japan Rubber Footwear Manufacturers' Association	PVC injection-molded boots, PVC injection molded cloth shoes, sandals, shoe soles	0.5-5
Japan Vinyl Hose Manufacturers' Association	Hoses (for gardening, agriculture and industry), compounds for use in packing materials	3-10
Japan Rubber Vinyl Gloves Industrial Association	Vinyl gloves (for medical, food service, and general uses)	1-3 (medical use is disposable)
Foamed Styrene Manufacturers' Association	Cushion packaging materials	0.5-3
Japan Urethane Raw Materials Association	Urethane resin for construction and building, sealant for civil engineering works, binders, insulation for home electrical appliances, urethane resins for paint, urethane elastomers	10-20
Japan Plastic Manufacturers' Co-operative Association (Kanto)	Plastic covers, corrugated plates	5
Japan Plastic Toy Manufacturers' Co-operative Association	Vinyl balls, beach inner tubes, small swimming pools, floats, dolls	2-6
Japan Inflatable Vinyl Products Manufacturers' Association	Small swimming pools, inner tubes, beach balls, surf mats, blow-up boats, dolls	2-6
Japanese Electrical Wire and Cable Makers' Association	Insulating sheath material for electrical wire cables, electrical wires, sealants	10-30
Japan Printing Ink Association	Inks for gravure, building, electrical wire covering, adhesives, ink jet sheets, and printed circuit boards	10-20
Japan Paint Manufacturers' Association	Paint for construction sites (vinyl resins, chlorinated rubbers, water emulsion paints)	10 (3-5 depending on user)
Interior Floor Industrial Association	PVC sheet flooring, PVC tiles, cushioned vinyl flooring	5-20 (5 for fashion ones)
Japan Carpet Industry Association	Carpet tiles	5-10
Plastic Resin-Coated Steel Sheets Association	Building materials (exterior and interior), home electrical appliances, steel furniture, vehicles, sundries	10-20
Synthetic Polymeric Roofing Sheet Manufacturers' Association	Riveted roofs, waterproof sheets	15-20
Japan Medical Devices Manufacturers' Association	Blood circuits for artificial kidney and heart-lung machines, blood transfusion sets, tubing, blood collecting devices, blood bags, gloves	3-5 (mostly disposable)

2. Examples of calculation of in-use stock

Based on domestic demand for the flame retardant deca-BDE in Japan, annual in-use stock between 1977 and 2020 was estimated by using a longevity function. Data reported by *The Chemical Daily* was used as the domestic demand between 1986 and 2005. Domestic demand before 1985 was estimated by using an exponential function from which demand over time in accordance with reported values was extrapolated (Tokai et al., 2008[20]). Demand between 2006 and 2020 was estimated by assuming that demand in 2005 will continue. Global demand for deca-BDE is expected to become zero in future as it was listed as a chemical targeted for elimination under Annex A in the Stockholm Convention in 2017 (Stockholm Convention, 2017[21]), but this estimation does not take into account of this trend toward zero demand. The total demand for deca-BDE was divided in accordance with the chemical's uses—resins and fibers—to plot them. The ratio of resins to fibers was 6:4 (Tokai et al., 2008[20]) . Figure D.1 shows the domestic demand for deca-BDE.

Because deca-BDE is used for resin and fiber, the demand for its use in resin was included in the domestic demand. The ratio of the demand for its use in resin to that in fiber was assumed to be 6:4 (Tokai et al., 2008[20]) in 2005. The total demand was 1800 t in 2005; therefore, 1080 t was used for resin and 720 t was used for fiber. Then, on the assumption that demand for use in fiber was constant between 1986 and 2005, the remainder after subtraction of 720 t was considered to be the demand for use in resin. Because of the many uncertainties in data up to 1985, demand for use in resin was assumed to have been 76% of the total domestic demand, in accordance with the fact that 720 t (24%) of the total domestic demand in a year is used for fiber.

To estimate emissions from products by using domestic demand data, imported or exported final products should be counted in addition to products manufactured in Japan. Therefore, the final domestic demand in which the import and export are counted was calculated based on the ratio obtained by dividing the domestic demand for home appliances in which deca-BDE is used by the domestic production (Figure D.2). The domestic final demand obtained was used to estimate the in-use stock of deca-BDE, taking the duration of the service life for respective uses into consideration, by using the Weibull distribution formula in Section 3.2.1. In this estimation, parameters a and b were defined by assuming that 90% of total final products are discarded within their service life. Table D.5 shows the duration of the service life of final products and parameters of the Weibull distribution. Figure D.3 shows the calculated in-use stock. Domestic demand for deca-BDE peaked in about 1990. The in-use stock peaked at approximately 50 000 t several years later, in about 1998. In recent years, the reduction in domestic demand has lowered the in-use stock.

In a risk assessment of a chemical substance in a certain year, the emissions of the substance from in-use stock in that year can be calculated by multiplying the in-use stock obtained as above by the EF. The emissions of plastic additives during the in-stock use are likely to exceed the emissions during other life stages because they exist as in-use stock for long periods.

Figure D.1. Domestic demand for deca-BDE

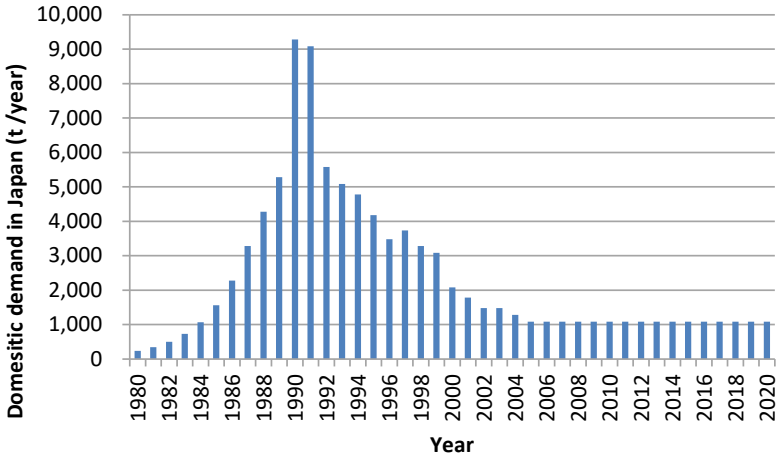


Figure D.2. Ratio of domestic demand to domestic shipping of home appliances

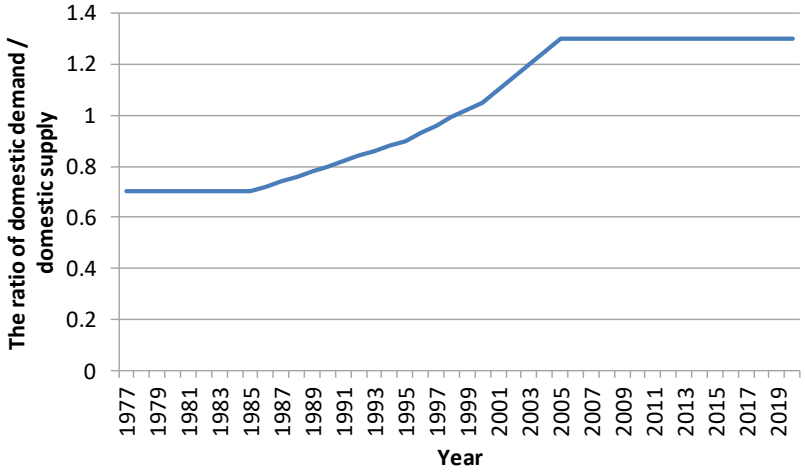
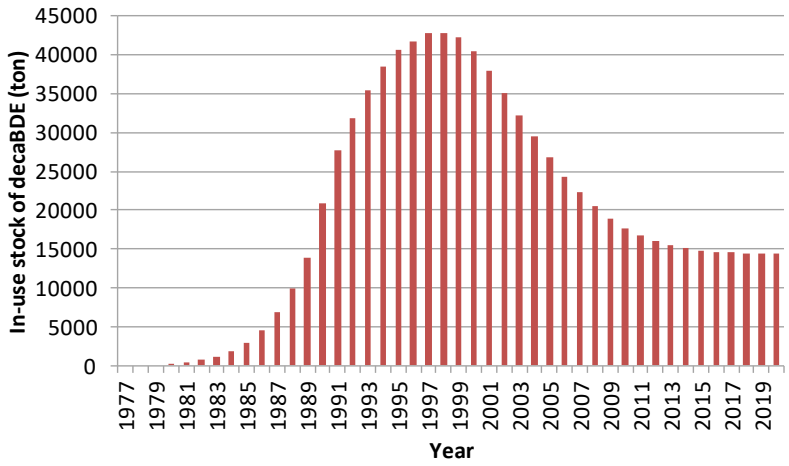


Table D.5. Duration of the service life of final products (housing and other electrical and electronic products) and parameters of the Weibull distribution

Parameter	Value
Duration of the service life [years]	5-15
a [-]	3.70
b [-]	11.2

Figure D.3. Estimation of the in-use stock of deca-BDE



Annex E. Thickness of Plastic Plates

This section provides measured thicknesses of commercially available plastic products available from do-it-yourself stores or in common use with a micrometer (Digimatic Micrometer MDC-25MJ, Mitutoyo). Representative values were chosen for each product group as shown in Table E.1.

Table E.1. Measured thicknesses of plastic products (mm)

	N	Minimum	Mean	Maximum	Representative
Total	179	0.02	5.215	100	
Film and sheet	20	0.02	0.349	3	0.5
Board	17	0.5	1.967	5	2
Pipes and joints	7	1.721	4.810	10.883	5
Mechanical parts	35	1.471	2.549	3.888	2.5
Daily commodities and groceries	50	0.201	2.095	5	2
Containers	13	0.114	1.398	3.192	1.5
Construction materials	7	1.197	3.818	8.928	4
Foam products	21	1.968	28.519	100	20
Reinforcement products	4	1.06	2.848	4.697	3
Other	5	1.176	2.035	3	2

Annex F. In-service use of products

Products containing plasticizers are used mostly at room temperature indoors; therefore, changes in temperature do not need to be taken into consideration. Outdoors, temperature may increase under direct sunlight; therefore, emissions should be estimated on the assumption that products are used at 40 °C in daylight.

Emissions of flame retardants may vary widely, depending on the in-service use of electrical and electronic products. Table F.1 shows the daily in-service hours of representative products used in the home. 5 h/day—the mean number of in-service hours of TVs and personal computers—was used in estimating the emissions of flame retardants from products.

Table F.1. In-service use of home appliances in the living room

	No. of items	Number of in-service hours				
		10th percentile	Median	90th percentile	Mean	SD
TVs	262	1.5	5.0	10.0	5.4	3.7
AV equipment	181	0.5	1.0	3.0	1.6	2.1
Personal computers	169	1.0	3.0	10.0	4.2	4.1
Printers	95	0.5	0.5	1.0	0.9	2.4

Source: (AIST, n.d.[22])

Annex G. Emission rates, Emission Factors or Emission Coefficients found in the Literature

Table G.1 provides emission rates, emission factors and emission coefficients found in the literature. In this table, the unit of data is same as the original literature.

Table G.1. Emission rates, emission factors or emission coefficients found in the literature

Chemical Name	Material	Emission rate, emission factor, emission coefficient	Unit	Other	Reference	Cited reference
DEHP	DEHP-containing vinyl flooring	1.6×10^{-4}- 5.4×10^{-4}	$\mu g/m^2 \cdot s$	Emission rate per surface area of Flooring	Benning et al, 2013	
RDP	personal computers	2	$ng\ h^{-1}unit^{-1}$	Desktop PCs in operation	Destaillats et al, 2008	Kemmlein et al, 2003, Carlsson et al, 2000
BDP	personal computers	44				
TCPP	personal computers	24				
TPP	personal computers	25				
DBP	personal computers	110-650		Notebook computer		Hoshino et al, 2003
DEHP	vinyl flooring	0.22±0.09	$\mu g/(m^2h)$	The calculated initial specific area emission rate (SER) of DEHP from vinyl flooring was 0.22±0.09 $\mu g/(m^2h)$, which is in accordance with CLIMPAQ measurements for DEHP of 0.2 to 0.4 $\mu g/(m^2h)$.	Holmgren et al, 2012	Clausen et al, 2004

TCPP	IB: Insulating board (80gl^{-1})	0.35	µgm^{-2} h^{-1}	Calculated from: mtot/(ttot*A); mtot(µg): integrated emission concentration+total mass on chamber walls; ttot(h): totaltest period; A(m^2): sample surface area.	Kemmlein et al, 2003	
	AF: assembly foam (rough, new)	—				
	AF: assembly foam (smooth, new)	—				
	Upholstery stool	28				
	Mattress	—				
	IB: Insulating board (80gl^{-1})	0.21		Calculated from: ceq*q; ceq(µgm^{-3}): estimated equilibrium concentration; q (m^{3}m^{-2}h^{-1}): area-specific air flow rate.		
	AF: assembly foam (rough, new)	70				
	AF: assembly foam (smooth, new)	50				
	Upholstery stool	36				
	Mattress	0.012				
	IB: Insulating board (30gl^{-1})	0.7		Calculated from: mtot/(ttot*A); mtot(µg): integrated emission concentration+total mass on chamber walls; ttot(h): totaltest period; A(m^2): sample surface area.		
	AF (rough, stored)	130				
	AF (smooth, stored)	70				
	upholstery foam	—				

TCPP	IB: Insulating board (30gl^{-1})	0.6	µgm^{-2} h^{-1}	Calculated from: ceq*q; ceq(µgm^{-3}): estimated equilibrium concentration; q (m^{3}m^{-2}h^{-1}): area-specific air flow rate.	Kemmlein et al, 2003	
	AF (rough, stored)	140				
	AF (smooth, stored)	50				
	upholstery foam	77				
HBCD	EPS (Expandable polystyrene, 0.02m^3)	4	ngm^{-2} h^{-1}	Calculated from: mtot/(ttot*A); mtot(ng): total content on the chamber walls; ttot(h): total test period; A(m^2): sample surface area.		
	EPS (Expandable polystyrene, 0.001m^3)	1				
	XPS(Extruded polystyrene, 0.02m^3)	29				
	XPS(Extruded polystyrene, 0.001m^3)	0.1				
1, 3, 5, 10, 20%-TCPP	Wallpaper materials	Mean 262.3 (SD 29.3)	µgm^{-2} h^{-1}	TCPP (1w/w% content), 25℃	Kumagai and Yanagisawa, 2007	
		Mean 452.6 (SD 60.6)		TCPP (3 w/w% content), 25℃		
		Mean 644.8 (SD 94.2)		TCPP (5 w/w% content), 25℃		
		Mean 1119.1 (SD 1119.1)		TCPP (10 w/w% content) , 25℃		
		Mean 2166.8 (SD 2166.8)		TCPP (20 w/w% content) , 25℃		
5%-TCPP		1135.7		40 ℃		
		2841.2		60 ℃		

DnBP	Vinyl flooring	7.8	µg/m^{2}h		Liang and Xu, 2014	
Iso-DEHP		0.06				
PBDEs	TV set dismantling area	8.67×10^{-10}	g/g		Park et al, 2014	KECO, 2008
		8.10×10^{-9}				
		1.18×10^{-9}				
		2.69×10^{-6}				
		1.99×10^{-7}				
		2.74×10^{-9}				
	Crushing Area	9.48×10^{-11}				
		8.85×10^{-10}				
		1.29×10^{-10}				
		2.94×10^{-7}				
		2.17×10^{-8}				
		2.99×10^{-10}				
	Open Air yard	2.68×10^{-10}				
		2.50×10^{-9}				
		3.66×10^{-10}				
		8.31×10^{-7}				
		6.13×10^{-8}				
		8.46×10^{-10}				
	Crushing Area	6.97×10^{-8}				
	Open Air yard	1.04×10^{-8}				

TCIPP	Insulation boards	0.21～0.60	μg/m^{2}h	Building Materials	Rauert et al, 2014	Kemmlein et al, 2003
HBCD		0.004～0.029				
TCIPP	PUR foams	50-140				
TCIPP	Upholstry foam	77				
TCIPP	Wallpaper materials	262.3～2166.8				Ni et al., 2003
BDE-100	TV set housing	0.5	ngm^{-2} h^{-1}	Area specific emission rate		Kemmlein et al, 2003
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				
ΣHeptaBDE		1.5				
BDE-100	Printed Circuit Board	1.3	ng unit^{-1}h^{-1}	Unit specific emission rate		
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				
TBBPA	PC Housing	0.4				
TPHP	Desktop Computer System	25-85				
TCEP	Monitors	<5-34				Wensing, 2004
TCIPP		<5-2465				
TDCIPP		<5				
TNBP		10～18				
TPHP		23～133				

PBDEs / SER	Computers	5.4～35	ng unit^{-1} h^{-1}	(or 25～175 ng m^{-2} h^{-1})	Rauert et al, 2014	Zhang et al. (2009)
	TV housing	11	ng m^{-2} h^{-1}	Aea specific emission rates		Kemmlein_et_al_2003
	Printed circuit board	21	ng unit^{-1} h^{-1}			
TCIPP	Assembly foam with rough surface	21-140	ng m^{-2} h^{-1}	Aea specific emission rates		
Σ HBCD	polystyrene insulating boards	0.1 ～ 29	ng m^{-2} h^{-1}	Aea specific emission rates		Clausen et al., 2010
BDE-209	Flue gas	3.9 E-08	g/g	Plastics processing, Emission factor	Sakai et al, 2006	
BDE-209		8.3 E-08				
BDE-209		5.0 E-09				
BDE-209		1.4 E-07				
BDE-209		1.6 E-09				
BDE-209	Flue gas in the e-waste recycling facility	7.7 E-09	g/g	Dismantling and crushing, Emission factor		
		3.1 E-08				
		1.3 E-08				
		4.5 E-08				
		3.5 E-07				
		4.5 E-06				
		1.4 E-08				
PBDEs	Combustible waste+ waste TV housing	1.0 E-07	g/g	Incineration, Emission factor		Japan Waste Research Foundation (2001)
		1.2 E-06				
	Incineration residue+ shredded e-waste	1.8 E-06				Tamade et al., (2002)
BDE-209	Production of DBDE	7.0 E-05	g/g	Emission factor		EC (1993)
	Textile processing	9.0 E-07				This study
	Plastics processing	1.4 E-07				
		5.0 E-04				TGD (1996)
	Dismantling and crushing	5.0 E-06				This study
		2.0 E-05				ECB (2000)
	Incineration	1.8 E-06				This study

TCPP	Insulation board (80 g l^{-1})	0.21	µg/(m^2 h^{-1})		Wensing et al, 2005	Kemmlein et al., 2003
	Insulation board (30 g l^{-1})	0.60				
	PUR foam (porous surface, new)	70				
	PUR foam (porous surface, old)	140				
	PUR foam (smooth surface, new)	50				
	PUR foam (smooth surface, old)	50				
	Upholstery foam	77				
DINP	PVC floor 1 (13 ± 1.1% (w w^{-1}))	9.05×10^{-4}	hm^b (ms^{-1})	*[b] hm was calculated as described in Holmgren et al. (2012), using the chamber airflow of 8 Lmin−1.	Cousins et al, 2014	
	PVC floor 2 (13 ± 1.1% (w w^{-1}))	7.88×10^{-4}				
	PVC wall cover	9.05×10^{-4}				
PBDEs	Sinter plants	0.0907	mg/tonne-productb	Important PCDD/F Emission Sources, Emission factor	Wang et al, 2010	
	EAFs	0.207	mg/tonne-productc			
	Power plants (coal)	0.407	mg/tonne-coald			
	Power plants (fuel)	0.348	mg/tonne-fuele			
	Secondary ALSs	0.544	mg/tonne-feedstock			
	Road transport	92.3	ng/kmf			
	MSWIs	0.153	mg/tonne-waste			
	Ferrous foundries	0.663	mg/tonne-feedstockg			
	IWIs	0.0844	mg/tonne-waste			
	MWIs	0.103	mg/tonne-waste			
	Fly ash treatment plants	0.428	mg/tonne-feedstockh			
	Batch MSWIs	1.77	mg/tonne-waste			