表 12　テーブルクロスと滑り止めマットからの SVOC 放散速度

放散速度[μg/m²・h]	TB-RS（テーブルクロス）	TB-OR（テーブルクロス）	NSM（滑り止めマット）
2EH	0.5	0.1	0.6
D6	N.D.	0.1	N.D.
BHT	N.D.	N.D.	N.D.
DEP	N.D.	N.D.	0.3
C16	0.1	N.D.	0.1
TBP	N.D.	N.D.	N.D.
TCEP	N.D.	N.D.	N.D.
DBA	N.D.	N.D.	N.D.
DBP	1.2	0.2	0.2
C20	N.D.	N.D.	N.D.
TPP	N.D.	N.D.	N.D.
DOA	N.D.	N.D.	N.D.
DEHP	11.0	7.8	1.0
C16 換算総有機物	119.1	78.1	45.8

表 13　EVA 樹脂タイルからの SVOC 放散速度

放散速度[μg/m²・h]	EV-01	EV-02	EV-03
2EH	4.3	1.0	0.6
D6	N.D.	N.D.	N.D.
BHT	N.D.	N.D.	N.D.
DEP	0.2	N.D.	N.D.
C16	0.3	0.3	0.2
TBP	N.D.	N.D.	N.D.
TCEP	N.D.	N.D.	N.D.
DBA	N.D.	N.D.	N.D.
DBP	3.0	1.4	1.6
C20	N.D.	N.D.	N.D.
TPP	N.D.	N.D.	N.D.
DOA	N.D.	N.D.	N.D.
DEHP	2.2	1.7	2.1
C16 換算総有機物	86.8	66.3	56.8

表 14　PVC シートからの SVOC 放散速度

放散速度[μg/m²・h]	T-1	T2	T-3	T-4
2EH	N.D.	11.8	7.9	0.7
D6	N.D.	N.D.	N.D.	N.D.
BHT	N.D.	N.D.	0.6	N.D.
DEP	0.1	0.1	N.D.	N.D.
C16	1.4	1.3	4.0	1.7
TBP	N.D.	N.D.	N.D.	N.D.
TCEP	N.D.	N.D.	N.D.	N.D.
DBA	N.D.	N.D.	N.D.	N.D.
DBP	1.7	1.4	0.5	1.3
C20	2.4	0.2	1.5	0.3
TPP	N.D.	N.D.	0.1	N.D.
DOA	0.9	0.2	1.4	0.1
DEHP	76.6	7.1	33.1	1.6
BBP	0.1	N.D.	N.D.	N.D.
TBEP	N.D.	N.D.	N.D.	N.D.
DNOP	0.2	N.D.	0.2	N.D.
DINP	3.9	2.7	3.8	6.2
DIDP	0.3	0.4	0.5	1.9
C16 換算総有機物	947.1	150.0	868.2	205.2

表 15　殺虫剤の原液と試験片の表面残量濃度[μg]

化学物質	S-0	S-30	S-60	S-90	S-24h	ORI-1[mg/mL]*
トランスフルスリン	8.5	1.6	1.7	0.8	<0.2	0.36
イミプロトリン	210	60	68	38	16	13
フェノトリン	21	3.0	3.0	1.2	0.3	1.1

＊：殺虫剤の原液濃度

表 16　殺虫剤の再放散試験結果[ng]

化学物質	TA-0	TA-30	TA-60	TA-90
トランスフルスリン	<2.0	<2.0	<2.0	<2.0
イミプロトリン	4.6	<2.0	2.7	<2.0
フェノトリン	<2.0	<2.0	<2.0	<2.0

＜0.2：検出限界以下

表 17　防蟻剤処理した建材からの放散量[ug/mL]

化合物名	TB	A-1	A-3	A-7	B-1	B-3	B-7
ﾎｷｼﾑ	<18	<18	<18	<18	<18	<18	<18
ﾌﾟﾛﾍﾟﾀﾝﾎｽ	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
ﾌｪﾆﾄﾛﾁｵﾝ	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
ｱﾚｽﾘﾝ	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
ｼﾌｪﾉﾄﾘﾝ	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
ﾍﾟﾙﾒﾄﾘﾝ	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

表 18　測定した建材からの各化学物質の放散速度の最小・最大・中央値と検出率

化学物質	最小値[ug/m^2/h]	最大値[ug/m^2/h]	中央値[ug/m^2/h]	検出頻度[%]
2EH	0.1	11.8	4.3	92
D6	0.1	0.2	0.1	8
BHT	0.1	0.6	0.3	8
DEP	0.1	0.3	0.1	21
C16	0.1	4.0	0.3	75
TBP	-	-	-	-
TCEP	-	-	-	-
DBA	-	-	-	-
DBP	0.2	3.8	1.4	100
C20	0.1	2.4	0.3	25
TPP	0.1	0.1	0.1	8
DOA	0.1	1.4	0.5	17
DEHP	0.7	76.6	3.3	100
BBP	0.1	0.1	0.1	50
TBEP	-	-	-	-
DNOP	0.2	0.2	0.2	50
DINP	2.7	6.2	3.8	100
DIDP	0.3	1.9	0.4	100

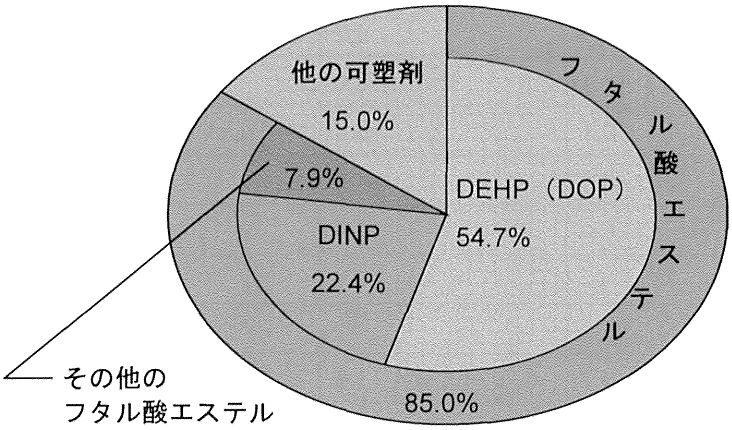


図 1　可塑剤の生産量に占めるフタル酸エステルの割合 [1)]

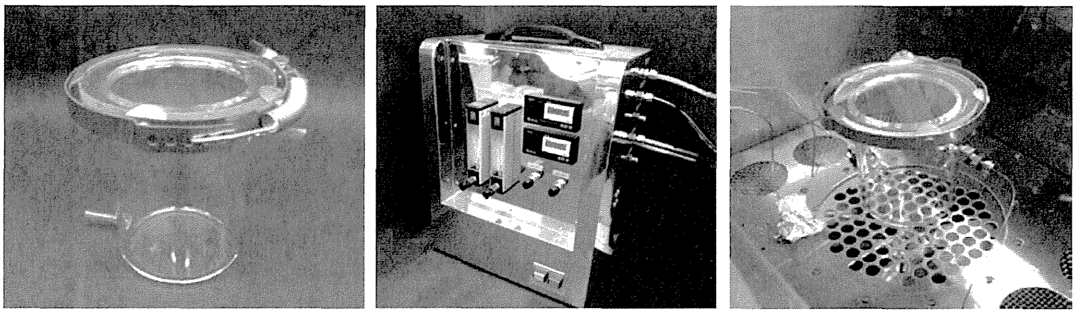


図 2　マイクロチャンバー、清浄空気制御・捕集ポンプ、加熱脱着風景

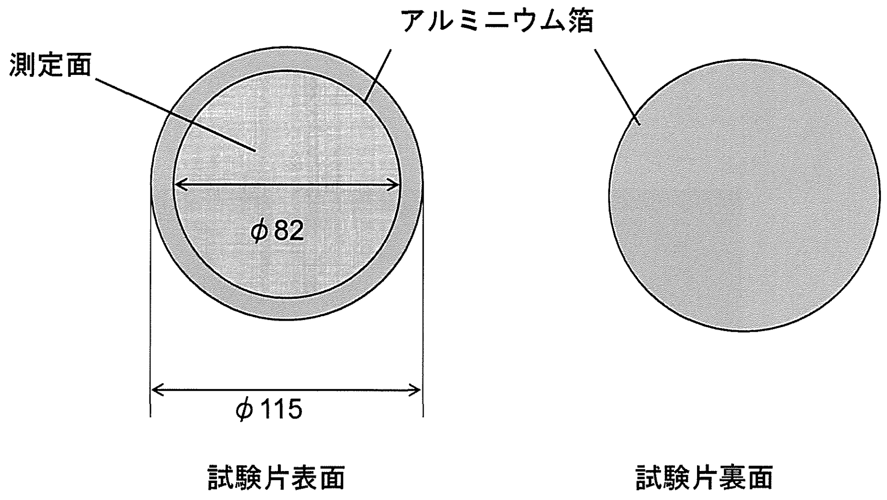


図３　試験片シールの例

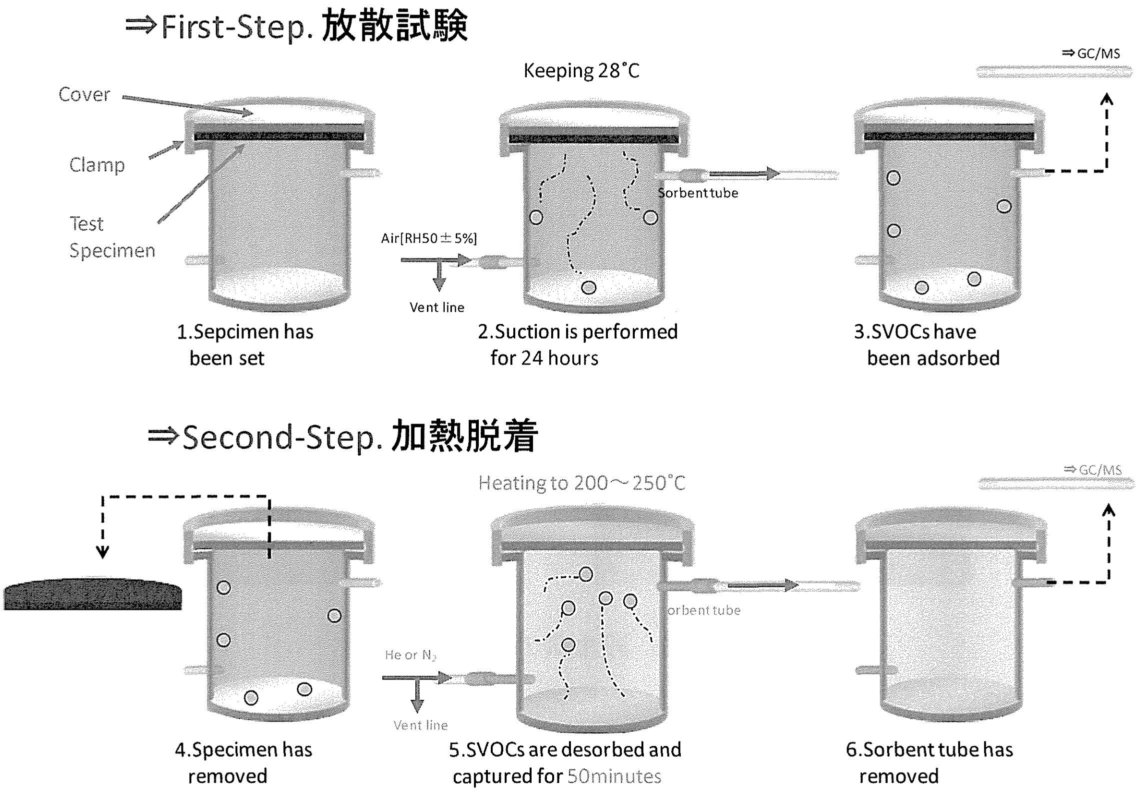


図４　マイクロチャンバー試験の手順（建材放散試験と加熱脱着試験）

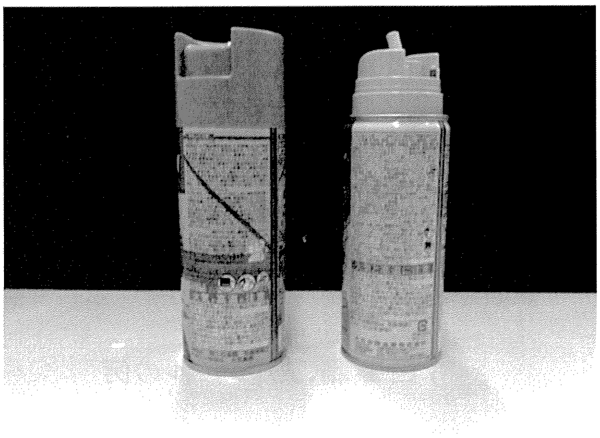


図 5　使用した家庭用殺虫剤

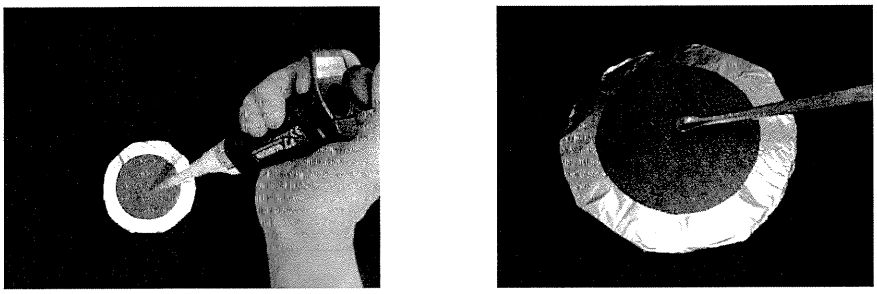


図 6　殺虫剤の塗布風景

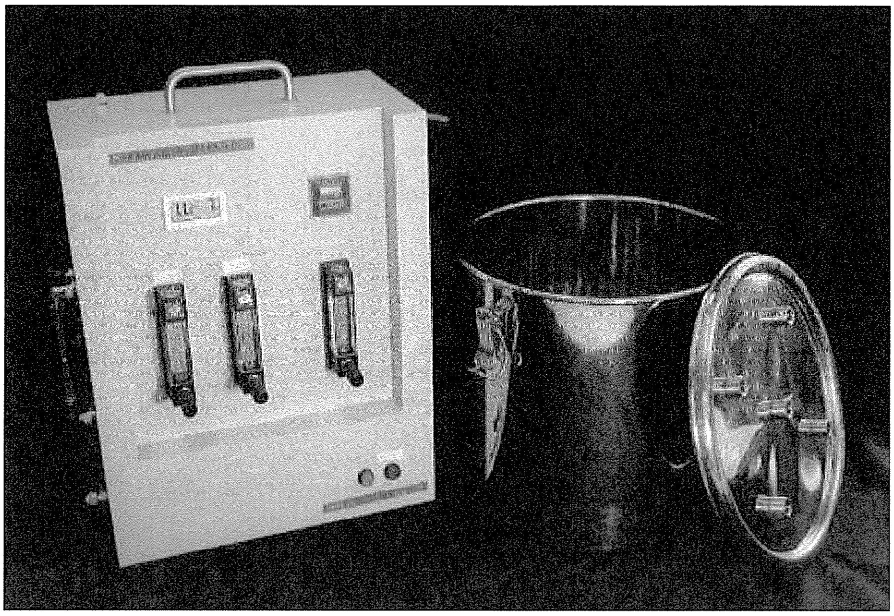


図 7　ADPAC システムと 20L チャンバー

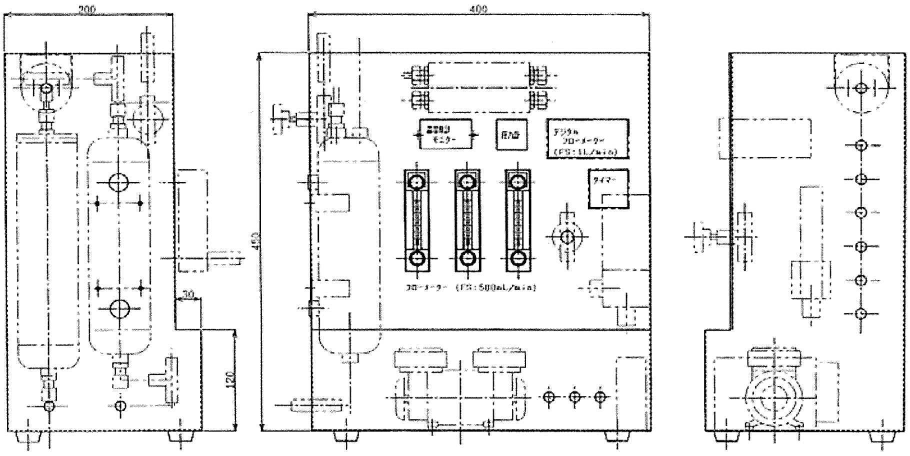
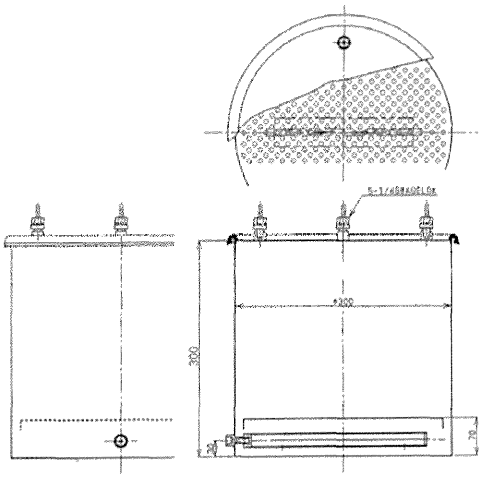


図 8　ADPAC エア制御ユニット詳細



シャワー管穴：	ϕ4mm
シャワー管長さ：	250mm
メッシュ開口面積：	約 40%
シャワー管 Inlet：	ϕ7mm
チャンバーOutlet：	ϕ3mm
（テフロンチューブ）	

図 9　ADPAC20L チャンバー詳細

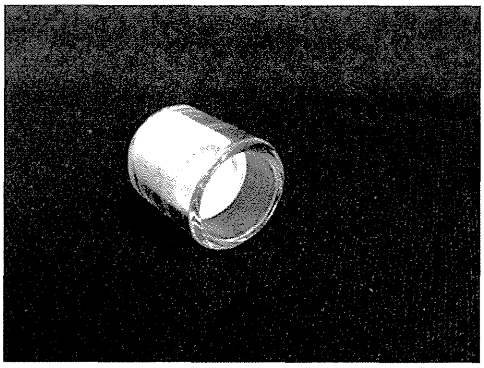


図 10　AERO LE Cartridge SDB 400（GL サイエンス株式会社製）

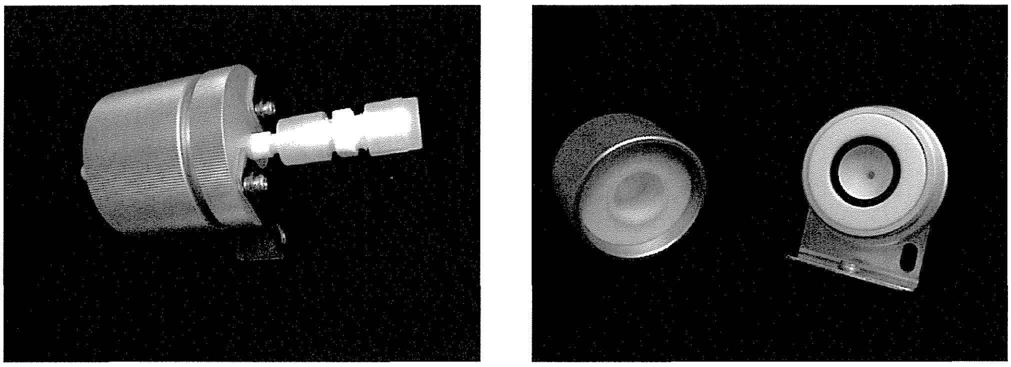


図 11　AERO Holder（GL サイエンス株式会社製）

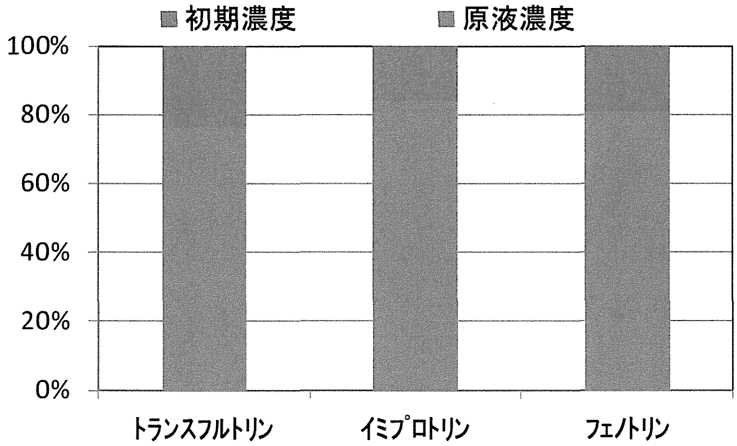


図 12　察収財の原液濃度に対する初期（S-0）試験片の残留量

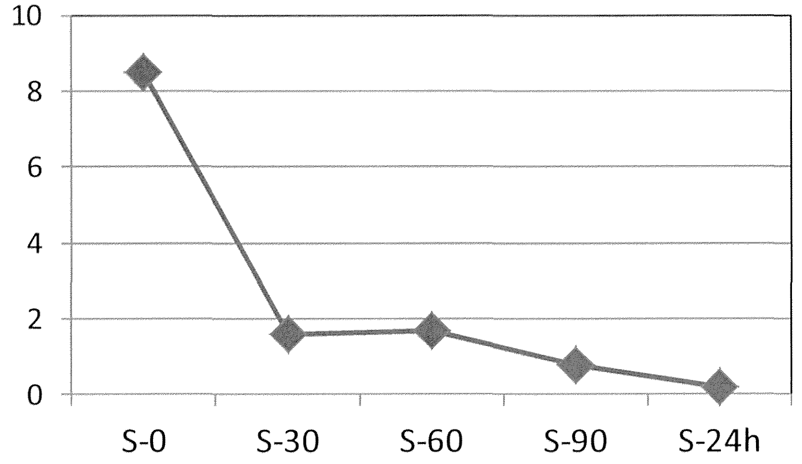


図 13　経時変化によるトランスフルスリンの残留濃度変化

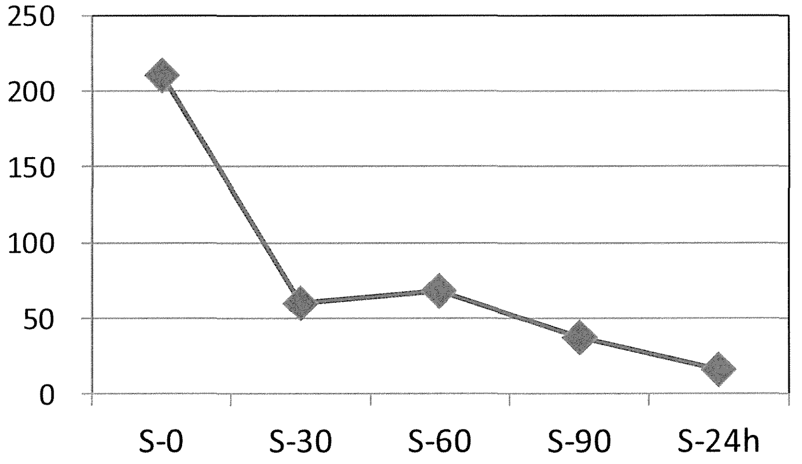


図 14　経時変化によるイミプロトリンの残留濃度変化

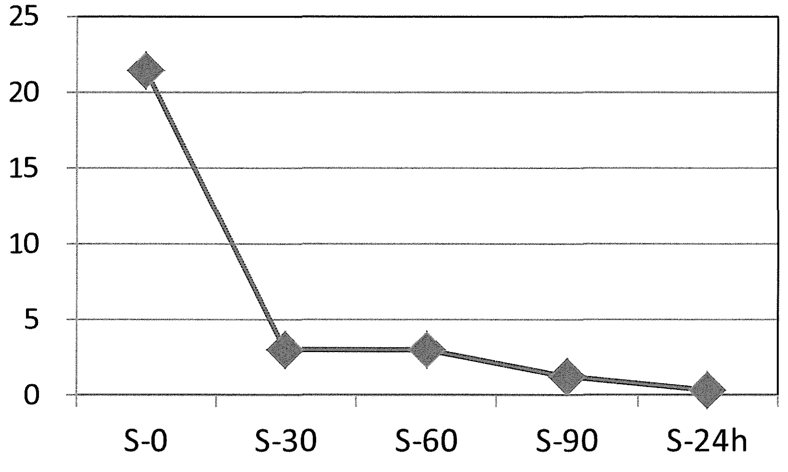


図 15　経時変化によるフェノとリンの残留濃度変化

III. 研究成果の刊行に関する一覧表

研究成果の刊行に関する一覧表

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
Takeuchi S., Kojima H., Saito I., Jin K., Kobayashi S., Tanaka-Kagawa T., Jinno H.	Determination of 34 plasticizers and 25 flame retardants in indoor air from houses in Sapporo, Japan.	*Sci Total Environ*	491-492	28-33	2014

IV. 研究成果の刊行物・別刷

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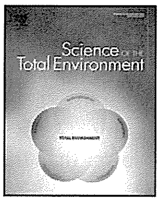

Detection of 34 plasticizers and 25 flame retardants in indoor air from houses in Sapporo, Japan

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HIGHLIGHTS

- 34 semi-volatile organic compounds were detected in the indoor air samples.
- DEHT was detected in indoor air for the first time in Japan.
- Compounds with higher volatility tended to exist in a gaseous phase in indoor air.
- Compounds with lower volatility existed in a particulate phase in indoor air.
- TXIB (20.8 mg/m^3) had the highest concentration among the 34 chemicals detected.

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ABSTRACT

Various plasticizers and flame retardants are contained in building materials and furniture produced for indoor environments. However, some of these material inclusions have been reported to cause endocrine-disrupting and mucosa-irritating effects. Because of the local climate, buildings in Sapporo are better insulated against cold weather than those in many other areas in Japan. In this study, we measured 59 compounds, including plasticizers (phthalates, adipates, and others) and flame retardants (organo-phosphates and brominated compounds), from indoor air samples from six houses in Sapporo. These compounds were measured separately in the gas phase and the particle phase using a two-stage cartridge equipped with a quartz fiber filter (1 μm mesh) and C_{18} solid-phase extraction disk for sampling and analyzed by GC/MS and LC/MS/MS (for the detection of brominated flame retardants). Among the 59 compounds measured in this study, 34 compounds were detected from the indoor air of the six houses. The highest concentration among the 34 compounds found in a newly built house was 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TXIB) at 20.8 μg/m^3. Di(2-ethyl-1-hexyl)terephthalate (DEHT), which has been used in recent years as an alternative to di(2-ethyl-1-hexyl)phthalate (DEHP), was found in all six houses, although at low concentrations ranging from 0.005 to 0.027 μg/m^3. To our knowledge, this is the first report of DEHT in indoor air in Japan. Among the compounds detected in this study, those with lower molecular weights tended to be captured in the C_{18} solid-phase extraction disk rather than in the quartz fiber filter. These results suggest that compounds with higher volatility exist preferentially in the gas phase, whereas compounds with lower volatility exist preferentially in the particulate phase in indoor air.

1. Introduction

The development of new building materials, furnishings, and consumer products in recent decades has resulted in a corresponding increase in new chemicals in indoor environments (Alaee et al., 2003; Rudel and Spengler, 2001; Schossler et al., 2011). Indoor chemical concentrations in the 1990s were higher than those found 50 years prior because of the wider variety of chemicals used and suppression of air exchange rates in buildings to improve their energy efficiency when regulating residential thermal conditions. Health problems suspected to be induced by indoor air polluted with volatile organic chemicals (VOCs) have been observed in Japan, particularly in the 1990s (Seki et al., 2007). However, these problems have generally improved as a result of the Japanese Ministry of Health, Labor and Welfare setting guideline values for 13 compounds between 1997 and 2002. Nevertheless, "non-regulated" chemicals have been used in place of

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the 13 regulated compounds and they have caused sporadic health problems (Kamijima et al., 2002; Kobayashi et al., 2010).

Semi-volatile organic compounds (SVOCs) are a group of chemicals that have higher boiling points than VOCs. As a result of the lower volatility of SVOCs, their concentrations in indoor air are generally much lower than those of VOCs (Kanazawa et al., 2010); however, a number of SVOCs have been detected in indoor dust (Bornehag et al., 2005; Meeker and Stapleton, 2010). In addition, SVOCs, such as pesticides, plasticizers, and flame retardants, have been suggested to cause adverse health effects, including ocular and nasal symptoms and endocrine-disrupting effects (Kojima et al., 2004, 2009, 2013; Rudel and Perovich, 2009; Takeuchi et al., 2005a, 2005b; Wieslander and Norbäck, 2010).

Plasticizers and flame retardants are indispensable because they add strength, plasticity and safety to modern buildings; therefore, large amounts of these chemicals are used in a variety of building materials and furniture. As previously mentioned, these groups contain chemicals categorized as VOCs, SVOCs, and organo-halogen compounds. Although the level of consumption and diversity of these chemicals have been increasing, information on the concentrations of these chemicals in indoor air is limited to only a small number of compounds. Several organo-halogen compounds have been used as flame retardants because of their low cost and relative incombustibility. Brominated flame retardants are one of the main groups of organo-halogen flame retardants used for furniture and in the plastic parts of electrical products (Alaee et al., 2003). The concentrations of these compounds in the indoor air of houses and office buildings in Tokyo have been reported to be relatively low compared to those of organophosphorus flame retardants (Saito et al., 2007); however, they were detected in house dust in both Ottawa and Tokyo (Takigami et al., 2009; Wilford et al., 2005), and their persistence and bioaccumulation are thought to be hazardous to human health (Schecter et al., 2003).

Sapporo is the capital city of Hokkaido, the northernmost prefecture of Japan and a Winter Olympics city. It receives heavy snowfall over the long winter season; therefore, many buildings are well-insulated and people stay indoors for long periods of time. We investigated the concentrations of indoor air chemicals in several buildings in Sapporo, including the houses of patients with sick-building syndrome and/or chemical sensitivity (Takeuchi et al., 2004, 2005b, 2007). In this study, we examined methods for measuring compounds containing newly applied chemicals, such as 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) and Di-2-ethyl-1-hexyl-terephthalate (DEHT), in indoor air samples in both the gas phase and the particulate phase. These methods were applied to indoor air samples from the living rooms and bedrooms of six houses in Sapporo, and a total of 59 chemicals, 34 plasticizers and 25 flame retardants were measured.

2. Materials and methods

2.1. Chemicals

The test chemicals used in this study were of the highest available purity and purchased or provided as analytical standards from the companies listed in Table 1. The chemical names and their abbreviations for every category are also listed in Table 1. Anthracene-d_{10} was purchased from Wako Pure Chemical Industry (Osaka, Japan) and used as an internal control in the GC/MS analysis in this study.

2.2. Sampling and analysis of indoor air chemicals

Air samples were collected from six two-story houses, including one newly built house, in Sapporo. The ages of the houses were approximately two weeks (House 6) and five (House 1), fifteen (Houses 3 and 5), thirty (House 4), and fifty (House 2) years old. Five of the houses were conventional wooden houses, whereas the new house was a brick-built house. Carpets were found in the living rooms of all houses except

Table 1
The 59 compounds measured in this study.

No.	Chemical name	Abbreviation	Supplier
19 phthalates			
1	Dimethyl phthalate	DMP	Wako[a]
2	Diethyl phthalate	DEP	Wako
3	Diisopropyl phthalate	DiPP	TCI[b]
4	Dipropyl phthalate	DPP	Wako
5	Diisobutyl phthalate	DiBP	Wako
6	Dibutyl phthalate	DBP	Wako
7	Dipentyl phthalate	DPeP	Kanto[c]
8	Diisohexyl phthalate	DiHP	Kanto
9	Butyl phthalyl butyl glycolate	BPBG	Wako
10	Dihexyl phthalate	DHP	Wako
11	Butyl benzyl phthalate	BBzP	Kanto
12	Diisoheptyl phthalate	DiHpP	Aldrich[d]
13	Di (2-ethyl-1-hexyl) phthalate	DEHP	Wako
14	Diheptyl phthalate	DHpP	Wako
15	Dicyclohexyl phthalate	DcHP	Wako
16	Diphenyl phthalate	DPhP	Wako
17	Dioctyl phthalate	DOP	Wako
18	Diisononyl phthalate	DiNP	Wako
19	Diisodecyl phthalate	DiDP	Wako
15 non-phthalate plasticizers			
1	1,2-Cyclohexane dicarboxylic acid diisononyl ester	DINCH	Wako
2	Di (2-ethyl-1-hexyl) terephthalate	DEHT	Wako
3	Tris (2-ethyl-1-hexyl) trimellitate	TEHTm	Wako
4	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate	TXIB	Aldrich
5	1-Methyl-2-pyrrolidinone	1M2Pd	Wako
6	Dimethyl adipate	DMA	Wako
7	Diethyl adipate	DEA	Wako
8	Diisopropyl adipate	DiPA	Wako
9	Dibutyl adipate	DBA	Wako
10	Diisobutyl adipate	DiBA	Wako
11	Di (2-ethyl-1-hexyl) adipate	DEHA	Kanto
12	Dibutyl sebacate	DBSb	Wako
13	Di (2-ethyl-1-hexyl) azelate	BEHAz	Wako
14	Dioctyl azelate	DOAz	Wako
15	Bis (2-ethyl-1-hexyl) sebacate	BEHSb	Wako
14 phosphorous flame retardants			
1	Trimethyl phosphate	TMP	Wako
2	Triethyl phosphate	TEP	Wako
3	Tripropyl phosphate	TPrP	Aldrich
4	Tributyl Phosphate	TBP	Wako
5	Tris (2-chloroethyl) phosphate	TCEP	Wako
6	Tris (2-chloro-1-methylethyl) phosphate	TCMEP	Wako
7	Tris (1,3-dichloro-2-propyl) phosphate	TDCPP	Wako
8	Tris (2-butoxyethyl) phosphate	TBEP	Wako
9	Triphenyl phosphate	TPhP	Wako
10	Tri (2-ethyl-1-hexyl) phosphate	TEHP	Wako
11	2-Ethyl-1-hexyl diphenyl phosphate	EHDPhP	TCI
12	Cresyl diphenyl phosphate	CsDPhP	TCI
13	Tricresyl phosphate	TCsP	Wako
14	Trixylenyl phosphate	TXP	DH[e]
11 brominated flame retardants			
1	2,4,4′-Tribromodiphenyl ether	BDE-28	Well
2	2,2′,4,4′-Tetrabromodiphenyl ether	BDE-47	Well
3	2,2′,4,4′,6-Pentabromo diphenyl ether	BDE-100	Well
4	decabromodiphenyl ether	BDE-209	Well
5	2,4,6-Tribromophenol	TBPh	Wako
6	Pentabromophenol	PBPh	Wako
7	hexabromo benzene	HBBz	Wako
8	Hexabromocyclododecane	HBCD	Wako
9	Tetrabromobisphenol A	TBBPA	TCI
10	Tetrabromobisphenol A bis 2,3-Dibromopropylether	TBBPA-BPBE	TCI
11	1,2-Bis pentabromophenyl ethane	BPBPhE	TCI

[a] Wako: Wako Pure Chemical Industry (Osaka, Japan).
[b] TCI: Tokyo Chemical Industry (Tokyo, Japan).
[c] Kanto: Kanto Chemical Co. Inc. (Tokyo, Japan).
[d] Aldrich: Sigma-Aldrich Co. (St. Louis, MO, U.S.A.).
[e] DH: Daihachi Chemical Industry (Osaka, Japan).

for House 4, which had wooden floors, and all living rooms were fitted with a television, sofa, and curtains. All houses except the oldest (House 2) were equipped with forced ventilation systems. The indoor air samples were collected from the living rooms and bedrooms. The air sampling rate was 10 L/min, and the sampling was performed for 12 h during the day in the living rooms and at night in the bedrooms. The sampling was performed during summer (July or August) in 2012 except for in the newly built house, which was sampled in November. An air sampling cartridge with a two-stage filter was used for the isolation of the indoor air chemicals as described elsewhere (Saito et al., 2007; Takeuchi et al., 2004, 2005b, 2007). A quartz fiber filter GMF 150 (1 μm of mesh size) (GL Sciences Inc., Tokyo, Japan) was used as the first stage to catch particulate chemicals larger than 1 μm in diameter, and a solid-phase extraction disk (Empore 2215 FF C_{18} Disk) (3M Company, Saint Paul, MN, U.S.A.) was used as the second stage to catch gaseous chemicals that were not captured by the first-stage filter. The filters, cartridges and all of the glassware tools were rinsed with high-grade acetone (acetone for pesticide residue and polychlorinated biphenyl analysis produced by Wako Pure Chemical Industries Ltd., Osaka, Japan) to remove certain contaminants, such as phthalates and organophosphate flame retardants, prior to use. After indoor air sampling, each stage of the filters was rolled up and placed in 10-mL test tubes along with 10 μL of 100 μg/mL anthracene-d_{10} added as an internal control. Compounds were extracted from the filters by ultrasonication for 15 min with 10 mL of acetone and then concentrated to 1 mL using a rotary evaporator. The concentrated extracts were subjected to GC/MS or LC/MS/MS (for the analysis of brominated chemicals).

2.3. Instruments and analytical conditions

Except for the brominated flame retardants, the analysis of the test compounds was performed using a Shimadzu QP-2010 GC/MS system equipped with a DB-5MS column (30 m × 0.25 mm i.d.). The following parameters were used for quantitative detection in this study: injection volume, 2 μL; carrier gas, helium; and column head pressure, 72 kPa. The GC oven was initially maintained at 40 °C for 2 min, then increased by 25 °C/min to 200 °C and 40 °C/min to 280 °C, where it was maintained for 6 min, and finally increased by 10 °C/min to 320 °C, where it was maintained for 7 min. The analysis of the brominated test compounds was performed using an LC/MS/MS system (Waters ACQITY UPLC and AB SCIEX Triple Quad 5500) in negative atmospheric pressure ionization (APCI) mode with a BEH C_{18} column (2.1 mm i.d. × 50 mm). The injection volume was 10 μL, and the solvent program of the UPLC was initially maintained at 80% methanol in water for 4 min, then gradually changed to 100% methanol over the next 2 min, and finally maintained at 100% methanol for the last 9 min. The flow rate was 0.4 mL/min for the first 10 min and 0.5 mL/min thereafter. The following parameters were used for quantitative detection in this study: temperature, 400 °C; nebulizer gas, 30 psi; nebulizer current, −5A; curtain gas, 15 psi; and collision gas, 12 psi.

2.4. Quality assurance/quality control

The limit of detection (LOD) was defined as the amount of each test compound that yielded S/N = 3 in the analysis. The limits of quantification (LOQ) of the indoor chemicals were calculated from their LODs (except for DEP, DBP, DEHP, TXIB, and TBP, which is described later), the area of the peaks in the analysis of the test compounds extracted from the filters, and air sampling volume (7.2 m^3). Breakthrough testing and recovery studies were performed as part of the setup of the air analysis method. A quartz fiber filter was spiked with 3 μg of each test chemical. The spiked filter was then installed as the first stage of the filter cartridge, and the second and the third stages were fitted with solid-phase extraction disks. Purified indoor air (14.4 m^3) was passed through the cartridge (n = 3). No breakthrough, which was defined by the detection of the spiked test chemicals from the extract of the third-stage filter, was found in this study. The chemicals were extracted from the first- and second-stage filters, and the percentage recoveries were calculated. Reproducibility was also evaluated by collecting duplicate air samples in our laboratory. To check for contamination and pollution by the chemicals during the transport of the sampling materials and air sampling, we used a “travel blank,” which was an additional cartridge equipped with the same type of filters used for the air sampling that traveled together with the sampling materials. The five compounds (DEP, DBP, DEHP, TXIB, and TBP) were detected at low concentrations even in the extracts of the rinsed filters, including those of the travel blanks. Therefore, the LOQs of those compounds were set at the threefold value of the highest concentrations among the travel blanks in this study. The indoor air concentrations of these compounds were calculated by subtracting the travel blank values from the indoor air sample values.

3. Results and discussion

3.1. Phthalates

Table 2 shows the concentrations of the 12 phthalates detected in the indoor air from the six houses, and the compounds in Table 2 are listed by molecular weight in Table 3. DBP at 220 μg/m^3 and DEHP at 120 μg/m^3 are the guideline values that were set by the Japanese Ministry of Health, Labor and Welfare (Committee on Sick House Syndrome: Indoor Air Pollution, 2002); these compounds were detected in the indoor air samples at concentrations less than fifty-fold smaller than the guideline values (Table 2). However, these compounds and their metabolites have been frequently detected in human urine samples (Carlstedt et al., 2013; Bertelsen et al., 2013), which suggest the continuous exposure of humans to DBP and DEHP. Moreover, Carlstedt et al. (2013) reported that polyvinyl chloride flooring, which is known to contain phthalates, is related to phthalate uptake in humans. Although dietary exposure and exposure to indoor dust (presumably through unintentional dust ingestion) are the main exposure routes, phthalates in indoor air should not be ignored as a source of continuous exposure through inhalation and as an indicator of their source.

3.2. Non-phthalates

Table 2 shows the concentrations of the 10 non-phthalate plasticizers detected in the indoor air from the six houses. The concentration of TXIB (20.8 μg/m^3), which was detected in the newly built house, was the highest among the 34 chemicals detected in this study (Table 2). Seven compounds were found at concentrations higher than 1 μg/m^3, and the order of their maximum concentrations was as follows: TXIB > DMA > DiPA > DBP > DBA = 1M2Pd > DEHP. TXIB is used as a plasticizer and solvent and surface stabilizer for water-based paints (Wilke et al., 2004); we previously found TXIB and 1M2Pd at much higher concentrations (maximum concentrations were over 510 μg/m^3 and 1000 μg/m^3, respectively) in the indoor air of a newly built primary school in Hokkaido in which teachers and students had suffered from sick-building syndrome (Kobayashi et al., 2010). Bönisch et al. (2012) reported that exposure to TXIB (32 ± 6 μg/m^3) and 1M2Pd (51 ± 11 μg/m^3) for 5 h/day for 19 days increased the allergic immune response in ovalbumin-sensitized mice, reduced IL-12 production in maturing dendritic cells, and enhanced airway inflammation after adoptive dendritic cell transfer into Balb/c mice. Therefore, the concentrations of chemicals in the indoor air of newly built buildings should be taken into consideration even if water-based paints were used instead of conventional oil-based paints. Moreover, it is desirable to vacate buildings when the concentrations of chemicals are high and to provide adequate ventilation systems to prevent sick-building syndrome.

Table 2
Concentrations of the 34 compounds in the indoor air of the six houses (μg/m^3).

No.	Chemical	House 1		House 2		House 3		House 4		House 5		House 6		
		LR[a]	BR[b]	LR	BR	LR	BR	LR	BR	LR	BR	LR	BR	LOQ[c]
1	1M2Pd	2.8	1.8	–[d]	–	–	–	–	–	0.14	0.53	–	0.20	0.002
2	DMA	3.2	6.1	0.39	0.91	0.88	0.97	0.40	0.074	0.090	0.37	9.8	13.2	0.006
3	TEP	–	–	–	–	–	–	–	–	–	–	0.018	0.019	0.002
4	DMP	0.057	0.076	0.10	0.21	0.068	0.12	0.069	0.16	0.057	0.17	–[e]	–	0.004
5	TXIB	8.8	7.4	10.4	13.7	5.9	7.3	2.9	1.2	0.35	2.2	20.8	10.4	0.02
6	DEP	0.29	0.10	0.23	0.35	0.16	0.26	0.14	0.31	0.14	0.44	0.01	0.02	0.01
7	TPrP	0.054	–	–	–	–	–	–	–	–	–	0.32	0.15	0.001
8	DiPA	–	0.036	0.40	–	6.3	2.5	0.070	0.005	0.50	0.13	–	–	0.003
9	DiBA	0.44	0.41	0.92	0.80	0.46	0.68	0.38	0.027	0.064	0.18	0.34	0.028	0.005
10	DBA	0.73	0.002	1.2	1.2	1.5	2.8	0.80	0.097	0.19	0.15	0.007	0.003	0.001
11	TBP	0.06	0.07	0.08	0.11	0.09	0.08	0.06	0.09	0.04	0.08	0.05	0.04	0.01
12	DiBP	0.17	0.19	0.14	0.22	0.19	0.20	0.094	0.11	0.20	0.062	0.059	0.023	0.004
13	DBP	0.39	0.64	2.7	3.3	2.6	4.0	1.3	3.1	1.3	2.1	0.14	0.10	0.03
14	TCEP	0.037	0.028	0.041	0.060	0.065	0.024	0.025	0.032	–	–	0.013	0.022	0.002
15	BBzP	0.008	0.008	0.008	0.010	0.022	0.072	–	0.032	0.064	0.042	0.004	0.005	0.001
16	DBSb	–	0.079	0.061	0.098	0.092	0.081	0.065	0.061	0.036	0.017	–	0.004	0.002
17	TPhP	–	0.066	0.071	0.074	0.13	0.078	–	–	0.015	0.038	–	–	0.001
18	TCMEP	–	–	0.04	0.08	0.13	0.03	0.06	0.09	–	–	0.01	0.02	0.01
19	DcHP	–	0.004	–	–	0.014	–	–	–	–	–	–	–	0.006
20	TBPh	1.4	1.2	2.1	1.9	1.1	0.9	1.6	1.0	1.1	1.5	0.1	0.2	0.0001
21	DiHpP	–	–	0.021	–	–	–	–	0.012	–	–	–	–	0.002
22	DHpP	0.006	0.011	0.004	–	0.023	0.008	–	–	–	0.013	–	–	0.006
23	EHDPhP	–	–	–	–	–	–	–	–	–	–	–	–	0.03
24	TCsP	–	–	–	0.018	–	–	–	–	–	–	–	–	0.001
25	DEHA	0.04	0.03	0.11	0.42	0.35	0.05	0.04	0.003	0.46	0.59	–	0.009	0.02
26	DEHP	0.80	0.51	0.38	1.1	2.4	1.1	1.4	0.82	1.5	0.77	0.31	0.48	0.02
27	DOP	–	–	–	–	–	0.005	–	–	–	–	–	–	0.001
28	DEHT	0.007	0.006	0.006	0.009	0.006	0.007	0.006	0.006	0.005	0.027	0.005	0.005	0.002
29	TBEP	0.032	–	–	0.040	–	–	0.043	0.032	–	–	–	–	0.006
30	DiNP	0.050	0.13	0.052	0.070	–	0.008	0.29	0.23	0.031	0.36	0.012	0.021	0.006
31	DiDP	0.03	0.06	0.03	–	0.02	–	0.03	0.03	–	0.19	–	0.016	0.02
32	BEHSb	0.094	0.10	0.11	0.13	0.12	0.11	0.098	0.098	0.021	0.073	0.013	0.007	0.001
33	TDCPP	–	–	0.018	–	–	–	–	–	–	–	–	–	0.006
34	HBBz	–	–	–	–	–	–	–	–	–	–	0.3	–	0.0001

[a] LR: living room.
[b] BR: bed-room.
[c] LOQ: limit of quantitation.
[d] Not detected or lower than the LOQ.
[e] Compounds not detected were as follows (LOQ): DiPP (0.001), DPP (0.001), DPeP (0.001), DiHP (0.001), BPBG (0.001), DHP (0.001), DPhP (0.001), DEA (0.002), BEHAz (0.002), DINCH (0.006), DOAz (0.002), TEHTm (0.001), TMP (0.002), TEHP (0.001), EHDPhP (0.03), CsDPhP (0.001), TXP (0.06), BDE-28 (0.0001), BDE-47 (0.0001), BDE-100 (0.0001), BDE-209 (0.0001), BPBPhE (0.0001), HBCD (0.0001), TBBPA (0.0001), TBBPA-BPBE PBPh (0.0001).

DEHT has been used in recent years as an alternative to DEHP (Schossler et al., 2011), and although there have been no previous reports on the indoor air concentrations of DEHT, its detection in house dust samples was reported by Nagorka et al. (2011) in Germany. They reported that DEHT in house dust increased steadily from 1997 to 2009 (Nagorka et al., 2011). In this study, we found DEHT in all six houses, although at low concentrations ranging from 0.005 to 0.027 μg/m^3 (Table 2). This is the first report of DEHT in indoor air samples in Japan. Abe et al. (2012) reported that DEHT was detected in 37% of 101 samples obtained from polyvinyl chloride (PVC) toys for sale on the Japanese market in 2009. Therefore, the use of DEHT may be spreading in Japan, including Sapporo and Germany (Nagorka et al., 2011).

3.3. Organo-phosphorus flame retardants

Table 2 shows the concentrations of the nine organo-phosphorus flame retardants detected in the indoor air from the six houses. Among the 14 organo-phosphorus flame retardants tested, nine compounds were detected in indoor air samples from the six houses (Table 2). Among these nine compounds, four (TPrP, TBP, TPhP, and TCMEP) were detected at concentrations higher than 0.1 μg/m^3. TPrP was detected at the highest concentration (0.32 μg/m^3) among the 14 organo-phosphorus flame retardants tested in this study. However, TPrP was only detected in two houses (Houses 1 and 6). In addition, although the concentration of TPrP in House 6 was greater than 0.1 μg/m^3, it was detected at a low concentration (0.054 μg/m^3) in the living room in House 1 (Table 2). Bergh et al. (2011) measured six phthalates and 11 organophosphates in 30 indoor locations in Stockholm and reported that phthalate esters were more abundant than organophosphates and typically showed ten-fold higher total concentrations. These results suggest that the concentrations of organo-phosphorus flame retardants in indoor air tend to be lower than the concentrations of certain plasticizers, such as DBP and DEHP. However, Kanazawa et al. (2010) reported that TBEP, TCEP, and TCMEP were detected in the floor dust samples from 41 dwellings in Sapporo at high concentrations (5890, 308, and 291 μg/g in the maximum concentrations, respectively). Saito et al. (2007) reported that the use of floor polish agents containing TBEP could affect the concentration of TBEP in indoor air. TBEP was detected in the highest concentration in the living room in House 4, which has wooden flooring (Table 2).

3.4. Brominated flame retardants

Table 2 shows the concentrations of the two brominated flame retardants detected in the indoor air from the six houses. TBPh was detected in the indoor air samples from the six houses at very low concentrations ranging from 0.1 to 2.1 ng/m^3 (Table 2). Saito et al. (2007) indicated that TBPh was vulnerable to oxidative degradation. Based on our previously described recovery test, the recovery rate of TBPh was 54% (TBBPA was 55%), whereas the recovery rates of most of the other compounds were approximately 100% (data not shown). Therefore, the concentrations of TBPh in this study (Table 2) might be underestimated by approximately

Table 3
Proportion of total captured in the quartz fiber disk for the 34 SVOCs detected in this study (%).

No.	Chemicals	MW	House 1		House 2		House 3		House 4		House 5		House 6	
		(g/mol)	LR[a]	BR[b]	LR	BR	LR	BR	LR	BR	LR	BR	LR	BR
1	1M2Pd	99	0	0	0	0	–[c]	–	–	–	0	0	–	0
2	DMA	174	2	1	0	0	0	0	0	0	0	0	0	0
3	TEP	182	–	–	–	–	–	–	–	–	–	–	100	100
4	DMP	194	0	0	0	0	0	0	0	0	0	0	–	–
5	TXIB	216	0	0	0	0	1	0	1	0	0	0	0	0
6	DEP	222	0	0	0	0	1	0	2	0	0	0	0	0
7	TPrP	224	0	–	–	–	0	0	–	–	–	–	0	0
8	DiPA	230	0	0	3	–	2	8	0	0	16	11	0	26
9	DiBA	258	1	5	2	1	8	5	2	8	16	9	11	7
10	DBA	258	8	100	0	0	13	4	24	100	0	0	100	100
11	TBP	266	12	11	36	5	34	23	23	12	0	0	12	20
12	DiBP	278	1	3	3	1	11	8	4	0	14	100	15	18
13	DBP	278	3	10	10	1	23	16	8	2	9	8	63	68
14	TCEP	285	40	50	61	25	100	100	100	39	–	–	100	100
15	BBzP	312	53	55	100	100	100	94	–	55	90	90	100	100
16	DBSb	314	–	100	100	100	100	100	100	100	100	100	–	100
17	TPhP	326	–	100	100	100	100	100	–	–	100	100	–	–
18	TCMEP	327	0	0	100	11	100	100	100	71	100	100	100	100
19	DcHP	330	–	0	–	–	67	–	–	–	–	–	–	–
20	TBPh	330	0	0	0	0	0	0	0	0	0	0	0	0
21	DiHpP	362	–	–	100	–	–	–	–	100	–	–	–	–
22	DHpP	362	52	53	66	–	91	100	–	–	–	65	–	–
23	EHDPhP	362	–	–	–	–	–	100	100	100	–	–	–	–
24	TCsP	368	–	–	–	100	–	–	–	–	–	–	–	–
25	DEHA	370	97	93	100	89	100	96	100	–	100	100	–	–
26	DEHP	390	100	99	99	98	100	100	100	100	100	99	100	100
27	DOP	390	–	–	–	–	–	100	–	–	–	–	–	–
28	DEHTp	390	100	100	100	100	100	100	100	100	100	100	100	100
29	TBEP	397	100	–	–	100	–	–	100	100	–	–	–	–
30	DiNP	418	100	100	100	100	–	100	100	100	100	100	100	100
31	DiDP	446	100	100	100	–	100	–	100	100	–	100	100	100
32	BEHSb	426	100	100	100	100	100	100	100	100	100	83	100	100
33	TDCPP	430	–	–	100	–	–	–	–	–	–	–	–	–
34	HBBz	551	–	–	–	–	–	–	–	–	–	–	0	–

[a] LR: living room.

[b] BR: bed-room.

[c] Not detected or lower than the LOQ (shown in Tables 2).

50% of the actual values, and we are currently conducting an additional study using quartz fiber filters treated with an antioxidant to prevent the oxidative degradation of TBPh. In addition, HBBz was detected at a very low concentration (0.3 ng/m^3) from the living room of House 6 (Table 2). These results are similar to the results reported by Saito et al. (2007) in which they measured TBPh and HBBz in the indoor air of 18 houses in Tokyo. Although brominated flame retardants are widely used in the interiors of houses in Japan, they were only detected at low concentrations in this study, which may have resulted from the low volatility of brominated compounds. Moreover, TBBPA and BDE-209, which are commonly used brominated flame retardants in Japan, were not detected in this study. Further study is required to clarify the trends in concentrations of brominated flame retardants in the indoor air of dwellings across Japan as a whole.

3.5. Phase of the 34 SVOCs detected in this study

The gas and particle phases of the 34 compounds were measured separately using a combination of a solid-phase extraction disk and quartz fiber filter as previously described. These compounds were caught by one or both of the two stages at different rates. Table 3 shows the detection ratios of the 34 compounds from the quartz fiber filter, which was used for the indoor air sampling in the six houses. Similar to Table 2, the compounds in Table 3 are listed by molecular weight, and the compounds with a smaller molecular weight tended to be captured in the C_{18} solid-phase extraction disk. These results suggest that compounds with a higher volatility preferentially exist in the gas phase in indoor air, whereas compounds with lower volatility preferentially exist in the particulate phase. Kanazawa et al. (2010) and Schossler et al. (2011) calculated the logarithm of the octanol-air distribution coefficient (K_{OA}) of 22 and 37 chemicals, respectively, according to the method of Weschler and Nazaroff (2008). The 27 compounds detected in the present study included 19 (seven phthalates, DEHA, and 11 organophosphates) calculated by Kanazawa et al. (2010) and eight (five phthalates, DIBA, DINCH, and TOTM) calculated by Schossler et al. (2011). Among the 27 compounds for which a log K_{OA} value was calculated, TMP had the lowest value (1.4), and TOTM had the highest value (16.24) (Kanazawa et al., 2010; Schossler et al., 2011). The log K_{OA} values of indoor air chemicals, which were captured equally by both stages in this study, were 5.0 (TBP), 8.41 (DiBP), 8.63 (DBP), 9.02 (BBzP), and 11.12 (DHpP) (Kanazawa et al., 2010; Schossler et al., 2011). These results suggest that the border between the two phases was within the range of these log K_{OA} values. A comparison of the values of log K_{OA} and the MWs in Table 3 shows a rough correlation. However, HBBz and TBPh were captured by the C_{18} solid-phase extraction disk at 100%, and these results suggest that HBBz and TBPh exist in a gaseous phase in the indoor air, although other smaller compounds, such as DBSb, TPhP, and TCMEP, mainly existed in a gaseous phase. Bromine atoms in the structures of HBBz and TBPh might affect their phases. Because the indoor air samples in this study were obtained in the summer, the preference for the compounds to exist in a gas phase may have been higher than it would have been in winter.

However, many of these SVOCs have been reported to be endocrine-disrupting chemicals, and the molecular sizes of some of these SVOCs are an appropriate fit for the ligand-binding pockets of certain hormone receptors, such as those of estrogen and androgen. In our previous study, the transcriptional activities of SVOCs via those receptors were investigated using mammalian cell-based reporter gene assays, and