DETERMINATION OF 34 PLASTICIZERS AND 25 FLAME RETARDANTS IN INDOOR AIR FROM HOUSES IN SAPPORO, JAPAN

Takeuchi S[1*], Kojima H[1], Saito I[2], Jin K[1], Kobayashi S[1], Tanaka-Kagawa T[3], Jinno H[3]

[1] Hokkaido Institute of Public Health, Kita-19, Nishi-12, Kita-ku, Sapporo, Japan; [2] Tokyo Metropolitan Institute of Public Health, Tokyo, Japan; [3]National Institute of Health Sciences, Tokyo, Japan

Introduction

The development of new building materials, furnishings, and consumer products over the past few decades has resulted in a corresponding increase in new chemicals in the indoor environment. Indoor chemical concentrations have increased in comparison to those of 50 years ago because a wider variety of chemicals are now used and air exchange rates in buildings decreased to improve energy efficiency. Health hazard problems suspected to be induced by indoor air pollution with volatile organic chemicals (VOCs) have been observed in Japan, particularly in the 1990s. However, they have generally improved due to the Japanese Ministry of Health, Labor and Welfare setting guideline values against 13 compounds between 1997 and 2002. Nevertheless "non-regulated" chemicals have been used in place of the 13 prescribed compounds and health problems induced by these non-regulated chemicals in indoor air still occur sporadically[1].

Semi-volatile organic compounds (SVOCs) are a group of chemicals having higher boiling points than those of VOCs. Due to the lower volatility of SVOCs, their concentrations in indoor air are generally much lower than those of VOCs. However, some SVOCs, such as pesticides, plasticizers, and flame retardants, have been suggested to have deleterious toxicities, such as endocrine disrupting effects and dioxin-like activity[2,3]. The molecular sizes of many of these SVOCs were thought to fit the ligand-binding pockets of receptors. Therefore, we studied the transcriptional activities of SVOCs via hormone receptors, such as estrogen and androgen receptors, as well as dioxin receptor using reporter gene assays and found several SVOCs possess agonistic and/or antagonistic activities via these receptors[4,5].

Several organo-halogen compounds have been used as flame retardants because of their low cost and low incombustibility. Brominated flame retardants are one of the main groups of organo-halogen flame retardants used for a variety of furniture and plastic parts for electric products. The concentrations of these compounds in indoor air are reported to be relatively low[6], but their persistence and bioaccumulation is speculated to deleterious to human health.

Plasticizers and flame retardants are indispensable to the strength, plasticity and safety of modern buildings, and large amount of these chemicals are used in a variety of building materials and furniture. These groups contain chemicals categorized as VOCs, SVOCs, and organo-halogen compounds, as mentioned above. Although the level of consumption and diversity of these chemicals have been increasing, information on concentrations of these chemicals in indoor air is limited to only small number of compounds.

Sapporo, is the capital city of Hokkaido, the most northern prefecture in Japan, and a winter Olympic city. It receives heavy snowfall in winter so that many buildings are well insulated and people stay indoors for long periods of time, particularly during the long winter season. We have 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[7-9]. In this study, we examined methods with which to measure 34 plasticizers and 25 flame retardants containing recently developed chemicals, such as DINCH and Di 2-ethyl-1-hexyl terephthalate (DEHT), in indoor air samples separately in the gas phase and particulate phase and applied them to measurement of a total of 59 chemicals in indoor air samples from the living rooms and bed rooms of six houses in Sapporo.

Materials and methods

Abbreviations of Chemicals used. 19 Phthalates: Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisopropyl phthalate (DiPP), Dipropyl phthalate (DPP), Diisobutyl phthalate (DiBP), Dibutyl phthalate (DBP), Dipentyl phthalate (DPeP), Diisohexyl phthalate (DiHP), Butyl phthalyl butyl glycolate (BPBG), Dihexyl phthalate (DHP), Butyl benzyl phthalate (BBzP), Diisoheptyl phthalate (DiHpP), Di (2-ethyl-1-hexyl) phthalate (DEHP), Diheptyl phthalate (DHpP), Dicyclohexyl phthalate (DcHP), Diphenyl phthalate (DPhP), Dioctyl

phthalate (DOP), Diisononyl phthalate (DiNP), Diisodecyl phthalate (DiDP). 15 Other plasticizers: 1,2-Cyclohexane dicarboxylic acid diisononyl ester (DINCH), Di (2-ethyl-1-hexyl) terephthalate (DEHT), Tris (2-ehtyl-1-hexyl) trimellitate (TEHTm), Texanol (Txol), 1-Methyl-2-pyrrolidinone (1M2Pd), Dimethyl adipate (DMA), Diethyl adipate (DEA) , Diisopropyl adipate (DiPA), Dibutyl adipate (DBA), Diisobutyl adipate (DiBA), Di (2-ethyl-1-hexyl) adipate (DEHA), Dibutyl sebacate (DBSb), Di (2-ethyl-1-hexyl) azelate (BEHAz), Dioctyl azelate (DOAz), Bis (2-ethyl-1-hexyl) sebacate (BEHSb). 14 Phosphorus flame retardants: Trimethyl phosphate (TMP), Triethyl phosphate (TEP), Tributyl Propyl (TPrP), Tributyl Phosphate (TBP), Tris (2-chloroethyl) phosphate (TCEP), Tris (2-chloro-1-methylethyl) phosphate (TCMEP), Tris (1,3-dichloro-2-propyl) phosphate (TDCPP), Tris (2-butoxyethyl) phosphate (TBEP), Triphenyl phosphate (TPhP), Tri (2-ethyl-1-hexyl) phosphate (TEHP), 2-Ethyl-1-hexyl diphenyl phosphate (EHDPhP), Cresyl diphenyl phosphate (CsDPhP), Tricresyl phosphate (TCsP), Trixylenyl phosphate (TXP). 11 Brominated flame retardants: 2,4,4'-tribromodiphenyl ether (BDE-28), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',6-pentabromo diphenyl ether (BDE-100), decabromodiphenyl ether (BDE-209), 2,4,6-Tribromophenol (TBPh), Pentabromophenol (PBPh), hexabromo benzene (HBB), Hexabromocyclododecane (HBCD), Tetrabromobisphenol A (TBBPA) , Tetrabromobisphenol A bis 2,3-dibromopropylether (TBBPA-BPBE), 1,2-Bis pentabromophenyl ethane (BPBPhE).

Indoor air sampling and analysis. Air samples were collected from six houses, including a newly built house in Sapporo, and the age of the houses were about zero, five, fifteen (two houses), thirty, and fifty years old, respectively. The indoor air samples were collected from the living rooms and bed rooms. Air sampling cartridges with two-stage filters were used for the sampling of indoor air chemicals. A quartz fiber filter was used as the first stage to catch particulate chemicals and a solid-phase extraction disk (Empore^{TM} Disk C_{18}) was used as the second stage to catch gaseous chemicals. These filters were rinsed with acetone to remove some phthalates and other chemicals prior to use. The air sampling rate was 10 L/min for 12h. Compounds were extracted from the filters separately by ultrasonication with 10 mL of acetone and then concentrated to 1 mL using rotary evaporator. The concentrated extracts were subjected to GC/MS or LC/MS/MS (for analysis of brominated chemicals).

Instruments. Analysis of the test compounds was performed by using a Shimadzu QP-2010 GC/MS system equipped with a DB-5MS column (30m x 0.25 mm i.d.). The GC oven was initially maintained at 40°C for 2 min, increased by 25°C/min to 200°C, thereafter increased by 40°C/min to 280°C and maintained for 6 min, and finally increased by 10°C/min to 320°C and maintained for 7 min. Analysis of the brominated test compounds was performed by using LC/MS/MS (Waters ACQITY UPLC and AB SCIEX Triple Quad^{TM} 5500) with a BEH C18 column (2.1mm i.d. x 50 mm). The solvent program of the UPLC was initially maintained at 80% methanol in water for 4 min and then changed to 100% methanol to 15 min. Flow rate was 0.4mL/min for the first 10 min and 0.5mL/min thereafter.

Results and discussion

Of the 59 compounds investigated in this study, 33 compounds were found in the indoor air samples taken from the six houses (Table 1). The concentration of Txol (20.8 μg/m^3) was the highest among the 33 chemicals detected, and it was detected from the newly built house. Seven compounds were found at concentrations over 1 μg/m^3 and the order of their concentrations were as follows, Txol > DMA > DiPA > DBP > DBA = 1M2Pd > DEHP. Txol is used as solvent and surface stabilizer for water-based paint in addition to as a plasticizer, and we previously found Txol at much higher concentrations in the indoor air of a newly built primary school in Hokkaido in which some teachers and students suffered from sick-building syndrome, [1]. Therefore, the concentrations of Txol in the indoor air of newly built houses should be taken into consideration in order to prevent sick-building syndrome.

DBP and DEHP, guideline values for which had been set by the Japanese Ministry of Health, Labor and Welfare at 220 and 120 μg/m^3, respectively, were detected in the indoor air samples at concentrations less than fifty-fold smaller than the guideline values (Table 1). No samples exceeded the indoor air guideline values for DBP and DEHP in Japan. However, these compounds, including their metabolites, were detected at high frequencies from human urine and blood samples, and these facts suggest the continuous exposure of humans to DBP and DEHP. Carlstedt *et al*. reported that polyvinyl chloride flooring, which is known to contain phthalates, is related to phthalate uptake in humans[10]. These results suggest that indoor air concentrations of DBP and DEHP may be an important source of exposure to DBP and DEHP.

Table 1 Indoor air concentrations of 59 chemicals in six houses in Sapporo. (μg/m^3)

No.	Compounds	House 1		House 2		House 3		House 4		House 5		House 6		LOQ
		LR	BR	LR	BR	LR	BR	LR	BR	LR	BR	LR	BR	
1	DMP	0.057	0.076	0.10	0.21	0.068	0.12	0.069	0.16	0.057	0.17			0.004
2	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
3	DiPP													0.001
4	DPP													0.001
5	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
6	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
7	DPeP													0.001
8	DiHP													0.001
9	BPBG													0.001
10	DHP													0.001
11	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
12	DiHpP			0.021					0.012					0.002
13	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
14	DHpP	0.006	0.011	0.004		0.023	0.008				0.013			0.006
15	DcHP		0.004			0.014								0.006
16	DPhP													0.001
17	DOP						0.005							0.001
18	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
19	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
20	DiDP	0.03	0.06	0.03		0.02		0.03	0.03		0.19		0.016	0.02
21	TEHTm													0.001
22	1M2Pd	2.8	1.8							0.14	0.53		0.20	0.002
23	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
24	DEA													0.002
25	TXol	8.8	7.4	10.4	13.7	5.9	7.3	2.9	1.2	0.3	2.2	20.8	10.4	0.020
26	DiPA		0.036	0.40		6.3	2.5	0.070	0.005	0.50	0.13			0.003
27	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
28	DBA	0.73	0.002	1.2	1.2	1.5	2.8	0.80	0.10	0.19	0.15	0.007	0.003	0.001
29	DBSb		0.079	0.061	0.098	0.092	0.081	0.065	0.061	0.036	0.017		0.004	0.002
30	DEHA	0.038	0.029	0.11	0.42	0.35	0.054	0.043		0.46	0.59			0.020
31	BEHAz													0.002
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	DINCH													0.006
34	DOAz													0.002
35	TMP													0.002
36	TEP											0.018	0.019	0.002
37	TPrP	0.054										0.32	0.15	0.001
38	TBP	0.060	0.068	0.078	0.11	0.085	0.084	0.055	0.093	0.036	0.075	0.052	0.039	0.009
39	TCEP	0.037	0.028	0.041	0.060	0.065	0.024	0.025	0.032			0.013	0.022	0.002
40	TCMEP			0.040	0.079	0.135	0.030	0.064	0.086			0.005	0.022	0.008
41	TDCPP			0.018										0.006
42	TBEP	0.032			0.040			0.043	0.032					0.006
43	TPhP		0.066	0.071	0.074	0.127	0.078			0.015	0.038			0.001
44	TEHP													0.001
45	EHDPhP													0.030
46	CsDPhP													0.001
47	TCsP				0.018									0.001
48	TXP													0.063
49	BDE-28													0.0001
50	BDE-47													0.0001
51	BDE-100													0.0001
52	BDE-209													0.0001
53	BPBPhE													0.0001
54	HBBz											0.0003		0.0001
55	HBCD													0.0001
56	TBBPA													0.0001
57	TBBPA-BPBE													0.0001
58	TBPh	0.0014	0.0012	0.0021	0.0019	0.0011	0.0009	0.0016	0.0010	0.0011	0.0015	0.0001	0.0002	0.0001
59	PBPh													0.0001

Notes: LR=living room; BR=bed room; LOQ=limit of quantification

Among the 11 brominated flame retardants tested, TBPh was detected in indoor air samples from the six houses at very low concentrations ranging from 0.1 to 2.1 ng/m^3 (Table 1). In addition, HBBz was detected at a very low concentration (0.3 ng/m^3) from the living room of one of the tested houses (Table 1). Although brominated flame retardants are widely used in the interiors of houses in Japan, they were detected at only very low concentrations in this study. This may be due to the low volatility of the brominated compounds. Moreover, TBBPA and BDE-209, both commonly used brominated flame retardants in Japan, were not detected in this study. Further study is needed to clarify the trends with regards to the concentrations of brominated flame retardants in the indoor air of dwellings across Japan as a whole.

DEHT has been used in recent years as an alternative to DEHP. There have been no previous reports on the indoor air concentrations of DEHT, but house dust samples were studied by Nagorka *et al*. in Germany. They reported that DEHT in house dust increased steadily from 1997 to 2009[11]. 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 1). This is the first report of DEHT in indoor air samples in Japan. Therefore, the usage of DEHT may be spreading to Japan including Sapporo as well as Western countries.

For the 33 compounds detected in this study, the gas and particle phases were measured separately using combination of a quartz fiber filter and a solid-phase extraction disk, respectively, as mentioned in Material and methods. These compounds were caught by the one or both of the two stages at different rates depending on their volatility. These results suggest that compounds with higher volatility prefer to exist in a gas phase, whereas compounds with lower volatility prefer to exist in a particulate phase in indoor air. As the indoor air samples in this study were obtained in summer, the preference for the compounds to exist in a gas phase may have been higher than that in winter.

In this study, we measured 34 plasticizers and 25 flame retardants in indoor air samples from six houses in Sapporo, Japan, and we found 33 compounds, including DEHT, which was found for the first time in indoor air samples in Japan. These results suggest that a variety of plasticizers and flame retardants are used in the indoor environment in houses. These chemicals contribute to increases in the quality and safety of furniture and building materials, and new compounds are continually being added to the list of chemicals. Although the indoor air concentrations of these compounds in this study were much lower than those in cases related to sick-building syndrome in Hokkaido, it is difficult to decide if the concentrations of the chemicals are safe or not, or whether they may increase the risk of sick-house syndrome and/or chemical sensitivity, due to a lack of knowledge regarding the pathogenesis of these conditions. Therefore, further study of indoor air chemicals in buildings such as dwellings and office buildings is required to prevent health problems and to improve the indoor environment in the future.

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