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Report

Simultaneous Analysis of Insecticides and Phthalates in Residential Buildings Based on Japan's Indoor Air Quality Guidelines

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The Ministry of Health, Labour and Welfare, Japan, had set guidelines for concentrations of indoor air pollutants such as di-*n*-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) and the insecticides fenobucarb, diazinon, and chlorpyrifos, which are semi-volatile pollutants in indoor air. The Committee on Indoor Air Pollution, Japan, is reviewing the 20-year old indoor air quality guidelines. Therefore, the current levels of semi-volatile pollutants in indoor air must be established. Insecticides and phthalates are estimated separately, necessitating more efficient analytical methods. We developed a gas chromatography-mass spectrometry for simultaneous analysis of insecticides and phthalates using a cartridge composed of a quartz filter and a styrene divinylbenzene copolymer and applied it to a field survey. The recovery and relative standard deviations (RSD) for the insecticides' were 97.4–103% and 3.58–9.65%, and those for phthalates were 87.4–102% and 1.35–8.22%, respectively. The limits of quantitation (LOQ) for chlorpyrifos, diazinon, and fenobucarb were less than 1/10 of guideline values at 0.0128, 0.0201, and 0.00667 μg/m³, respectively. The LOQs of phthalates were 0.0882 μg/m³ for DBP and 0.107 μg/m³ for DEHP, each less than 1/193 and 1/935 of guideline values, respectively. The simultaneous analysis method was used to survey residential houses. Insecticides were not detected in the indoor air of residential houses. In contrast, phthalates, diethyl phthalate (DEP), DBP, and DEHP were detected, and their concentration distributions decreased from those found in the 2000s.

Key words indoor air, semi-volatile organic compounds, insecticides, phthalates, field survey

INTRODUCTION

Semi-volatile organic compounds (SVOCs) have boiling points ranging from 240 to 400°C, are emitted from plasticizers, flame retardants, and insecticides in furniture, building materials, and household products.[1] The SVOCs are causative agents of "sick building syndrome," and Japan's Ministry of Health, Labour, and Welfare (MHLW) has established guideline values for indoor air concentrations for 13 compounds, including volatile organic compounds (VOCs) and SVOCs. The SVOCs for which guideline values were established include three insecticides, fenobucarb, diazinon, and chlorpyrifos, and two phthalates, di-*n*-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP). However, more than 20 years after the establishment of the guideline values for indoor air concentrations, they are being reviewed by the Committee on Indoor Air Pollution. The review process necessitates a thorough risk assessment of candidate substances and an accurate survey of indoor air quality.

We have recently reported an analytical method based on solid-phase adsorption/solvent extraction to quantify insecticides according to the established guidelines.[2] Tanaka-Kagawa *et al*. also demonstrated that the same method can analyze phthalates.[3] The technique uses a cartridge composed of a quartz filter and a styrene divinylbenzene copolymer. The cartridge method does not require any pretreatment, and analysis can proceed after extraction with acetone.[2–4] However, simultaneous analysis of insecticides and phthalates using this technique has not yet been considered.

In actual indoor air field surveys, the equipment transportation and the sampling time require considerable effort by the investigator. Therefore, an efficient method for conducting field surveys is needed. Since the SVOCs for which guideline values were established have relatively similar physical properties, such as boiling points and vapor pressures, insecticides and phthalates can be analyzed simultaneously. Analyzing several SVOCs with a single method enhances the survey's efficiency and cost-effectiveness.

This study aimed to improve our previously reported insecticide analysis method and establish a simultaneous analysis of insecticides and phthalates by the gas chromatograph-mass spectrometer (GC-MS) method. Field surveys in residential buildings were conducted, and samples were subjected to simultaneous analysis of insecticides and phthalates.

MATERIALS AND METHODS

Chemicals and Equipment Chlorpyrifos (1000 μg/mL in hexane), diazinon (1000 μg/mL in hexane), fenobucarb (100 μg/mL in methanol), and phthalates (100 μg/mL in hexane) were purchased from AccuStandard Co. (CT, USA) and FUJIFILM Wako Pure Chemical Co., (Osaka, Japan). Chlorpy-

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rifos-d_{10} (100 µg/mL in nonane, Kanto Chemical Co., Tokyo, Japan), di-*n*-butyl phthalate-d_4 (DBP-d_4) (Fujifilm Wako Pure Chemical Co., Osaka, Japan, purity 98%), and di-2-ethylhexyl phthalate-d_4 (DEHP-d_4) (Kanto Chemical Co., Tokyo, Japan, purity 98%) were used as the internal standards. Acetone for the pesticide residue and polychlorinated biphenyl tests, were purchased from Fujifilm Wako Pure Chemical Co. (Osaka, Japan). AERO LE Cartridge SDB400HF was purchased from GL Science Inc. (Tokyo, Japan), and MP-∑300NII (Sibata Scientific Technology LTD., Tokyo, Japan) was used as the air-sampling pump.

Analytical Methods Details of the GC-MS analyses are presented in Table 1. All quantitative GC-MS analyses were performed in selected-ion monitoring mode, and the quantification and confirmation of ions are shown in Table 2. The calibration curves were plotted in the range of 1–100 ng/mL for chlorpyrifos and 4–400 ng/mL for diazinon, fenobucarb, and phthalates. The concentrations of the internal standards were 100 ng/mL for chlorpyrifos-d_{10} and 1000 ng/mL for DBP-d_4 and DEHP-d_4. The internal standard for insecticides was chlorpyrifos-d_{10}. For phthalates, DBP-d_4 was used for DBP and D*n*PP, while DEHP-d_4 was used as the internal standard for the others.

Air Sampling and Analyte Extraction from the Cartridge Indoor air was collected by connecting the AERO LE Cartridge SDB400HF (hereinafter, called cartridge) to the MP-∑300NII air pump and aspirating 1.44 m^3 of air (1 L/min for 24 h). For the extraction of the analytes, the quartz filter and styrene divinylbenzene copolymer were transferred to a 10 mL centrifuge tube, 5 mL of acetone was accurately added, and then sonicated for 20 min. Subsequently, the sample was centrifuged (1740 × *g*, 10 min), and 1 mL of the supernatant was collected in a GC vial, to which 0.1 mL of the internal standard mixture was added.

Recovery Tests and Calculation of Limits of Quantitation (LOQ) The recovery tests were conducted in a laboratory dedicated to VOCs under positive pressure conditions. All the standards were dissolved in acetone. The mixture of chlorpyrifos (0.1 µg/mL), diazinon (0.35 µg/mL), and fenobucarb (0.5 µg/mL) was prepared, and 0.1 mL was added to the cartridge. The phthalates mixture (1 µg/mL each) was prepared separately, and 0.2 mL was added to the cartridge. After adding the mixtures, the cartridge was allowed to dry at room temperature. To eliminate the influence of ubiquitous phthalates in the indoor air,[5,6] the blank cartridge (front stage) and treated cartridge (adsorbent pre-loaded with the standard mixtures of the target compound) (back stage) were connected using a connection assembly for an AERO dual cartridge holder (GL Science) to the air sampling pump. After connecting to a pump, 1.44 m^3 (1 L/min, 24 h) of indoor air was aspirated and extracted in the same manner as in the previous section. This recovery test was conducted with n = 8 replicates. The LOQ was calculated at ten σ (LOQ) of the concentrations obtained in the recovery test.

Field Survey of SVOCs in the Residential Buildings The survey of indoor air was conducted from September to October 2023 at 14 houses in Kanagawa and Tokyo. An aluminum foil-wrapped cartridge was transported to the sampling point in a metal container. Two blank cartridges were prepared as follows: One was transported to the sampling point as a travel blank to check for contamination during transport. The other was a diffusion blank, which was transported to the sampling point and placed around the pump to check for contamination. Indoor air was aspirated at 1.2–1.5 m above ground level at a rate of 1 L/min for 24 h.

RESULTS AND DISCUSSION

Simultaneous Analysis of Insecticides and Phthalates The study aimed to enhance the efficiency of indoor air field surveys by simultaneously analyzing insecticides and phthalates. By modifying the GC conditions reported in the method for insecticides,[2] we successfully separated the 11 target insecticides and phthalates (Fig. 1). This modification allowed for the analysis of phthalates, including those without established guideline values, alongside DBP and DEHP. Several phthalates with different alkyl chain lengths were detected in past surveys,[5] and simultaneous analysis was considered effective for field surveys.

Next, the recovery test was conducted to assess the performance of the analysis. The recovery rates and relative standard deviations (RSDs) for insecticides were 97.4–103% and 3.58–9.65%, respectively. The recovery rates of phthalates were 87.4–102%, with RSDs of 1.35–8.22%. Based on the recov-

Table 1. GC-MS Conditions for Simultaneous Analysis of Three Insecticides and Phthalates

GC	
Gas chromatograph	Agilent Technologies 8890
Column	VF5-MS 30 m x 0.25 mm, i.d., 0.25 µm
Oven temperature	80 °C (1 min), 20°C/min to 120°C, 6°C/min to 290°C, 30 °C/min to 320°C (3 min)
Carrier gas	Helium, 1 mL/min (constant flow)
Auto sampler	PAL3 RTC 120
Injection mode	Splitless mode
Injection volume	2 µL
Injector temperature	280°C
Transfer line temperature	280°C
MS	
Instrument	Agilent Technologies 5977B
Ionization	Electron ionization (70 eV)
Quantitative analysis	Selected-ion monitoring mode
Interface temperature	280°C
Ion source temperature	280°C

Table 2. Quantification and Confirmation Ions (*m/z*) for the Insecticides, Phthalates and Its Internal Standards

Ions monitored (*m/z*)		
Components	Quantification	Confirmation
Fenobucarb	121	150
Diazinon	179	137
Chlorpyrifos	314	197
Chlorpyrifos-d_{10}	324	200
Di-*n*-butyl phthalate (DBP)	149	205, 223
Di-2-ethylhexyl phthalate (DEHP)	149	167, 279
Diethyl phthalate (DEP)	149	177, 222
Di-*n*-propyl phthalate (D*n*PP)	149	191, 209
Di-*n*-pentyl phthalate (D*n*PeP)	149	219, 237
Di-*n*-hexyl phthalate (D*n*HP)	149	223, 251
Butyl benzyl phthalate (BBP)	149	206, 238
Di-cyclohexyl phthalate (DCHP)	149	167, 249
DBP-d_4	153	209, 227
DEHP-d_4	153	171, 283

ery and RSD, the results obtained by the simultaneous analysis method were satisfactory (Table 3). Following the study's recovery tests, three phthalates, DEP, DBP, and DEHP, were detected in the blank cartridge (front stage) and were >0.0157, 0.0160–0.0756, and 0.0181–0.0933 μg/m^3, respectively (Blank cartridge concentrations (front stage) were calculated from the concentrations identified within the calibration curves). These three phthalates have been reported to be ubiquitous in indoor air.[5, 6] The recovery rates were considered excellent because the blank cartridge placed in the front stage prevented the influence of ubiquitous phthalates in the indoor air (Fig. 2).

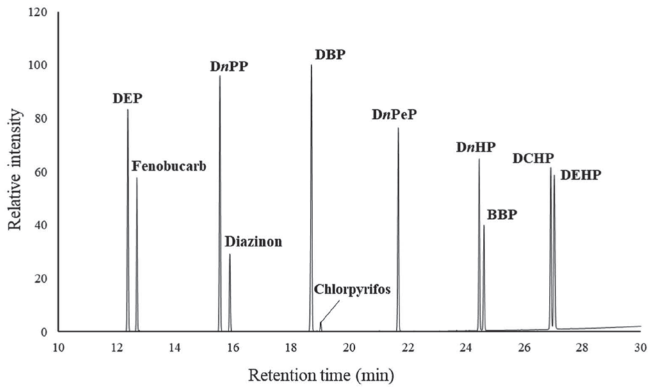

Fig. 1. Total Ion Current Chromatogram of Insecticides and Phthalates

The LOQs were calculated using the results of the recovery tests. The guideline values for insecticides are 1 (0.1 for children) μg/m^3 for chlorpyrifos, 0.29 μg/m^3 for diazinon, and 33 μg/m^3 for fenobucarb (Table 3). The LOQs of chlorpyrifos, diazinon, and fenobucarb are 0.0128, 0.0201, and 0.00667 μg/m^3, respectively, all of which are less than 1/10 of the guideline values (Table 3). The guideline values for phthalates are 17 μg/m^3 for DBP and 100 μg/m^3 for DEHP (Table 3). The LOQs of phthalates (0.0882 μg/m^3 for DBP and 0.107 μg/m^3 for DEHP) are well below the guideline values (Table 3). Other phthalates were also confirmed to be measurable at low concentrations. The above results of recovery rates, RSDs, and LOQs for both insecticides and phthalates demonstrated satisfactory performance of the method.

Field Survey of SVOCs in the Residential House We conducted a field survey in residential buildings using the method developed for simultaneous analysis. None of the three target insecticides were detected in the field survey samples. According to Saito *et al.*, in 2003, fenobucarb, diazinon, and chlorpyrifos were detected in indoor air at a frequency of 18%, 2.1%, and 10%, respectively.[7,8] However, the maximum concentrations of fenobucarb, diazinon, and chlorpyrifos were 8.10 ng/m^3, 3.30 ng/m^3, and 12.4 ng/m^3, respectively, suggesting that these insecticides were already at low concentrations in indoor air in the early 2000s.[7,8] A survey was conducted by MHLW in 2019 for the distribution of these three insecticides. According to the report, chlorpyrifos is no longer used

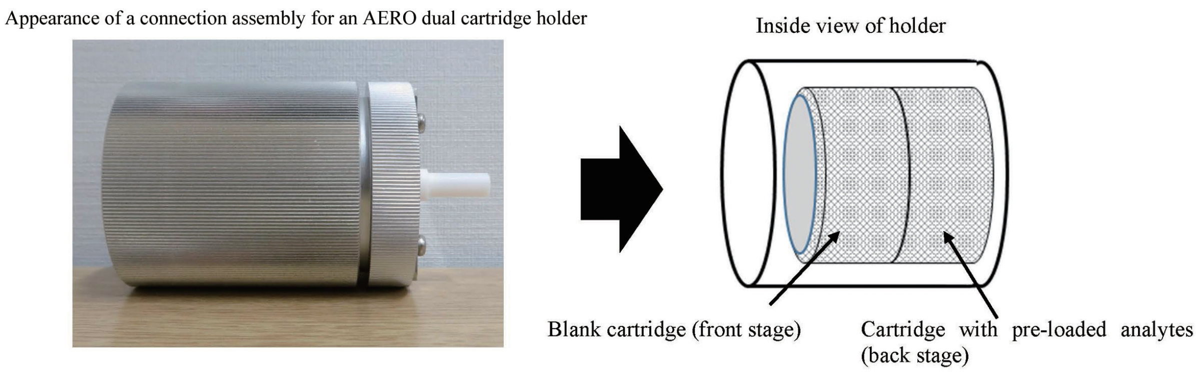

Fig. 2. Recovery Test Using a Connection Assembly for an AERO Dual Cartridge Holder

Table 3. Simultaneous Analysis of Insecticides and Phthalates (n=8)

	Recovery (%)	RSD (%)	LOQ (μg/m^3)	Additive concentration on cartridge (ng)	Guideline values# (μg/m^3)
Fenobucarb	103	3.58	0.0128	50	33
Diazinon	97.4	8.50	0.0201	35	0.29
Chlorpyrifos	99.5	9.65	0.00667	10	1 for adults, 0.1 for children
DBP	87.4	7.27	0.0882		17
DEHP	94.1	8.22	0.107		100
DEP	96.0	6.26	0.0835		-
D*n*PP	96.9	1.50	0.0202	Each 200	-
D*n*PeP	102	2.70	0.0384		-
D*n*HP	97.7	1.35	0.0184		-
BBP	99.5	2.82	0.0390		-
DCHP	96.3	1.77	0.0237		-

The guideline values for indoor air concentration in Japan

Table 4. Result of Field Survey of SVOCs in Residential Houses (µg/m^3)

Sample No.	Fenobucarb	Diazinon	Chlorpyrifos	DBP	DEHP	DEP	D*n*PP	D*n*PeP	D*n*HP	BBP	DCHP	Sampling Location
1	<LOQ	<LOQ	<LOQ	1.4	0.24	0.18	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Bedroom
2	<LOQ	<LOQ	<LOQ	0.29	0.86	0.093	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
3	<LOQ	<LOQ	<LOQ	0.31	<LOQ	0.14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
4	<LOQ	<LOQ	<LOQ	0.38	0.47	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
5	<LOQ	<LOQ	<LOQ	0.58	0.29	0.14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
6	<LOQ	<LOQ	<LOQ	0.20	0.52	0.14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
7	<LOQ	<LOQ	<LOQ	0.72	<LOQ	0.15	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
8	<LOQ	<LOQ	<LOQ	0.66	0.44	0.59	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Children's room
9	<LOQ	<LOQ	<LOQ	0.62	0.20	3.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
10	<LOQ	<LOQ	<LOQ	0.21	0.29	0.17	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
11	<LOQ	<LOQ	<LOQ	0.98	<LOQ	0.37	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
12	<LOQ	<LOQ	<LOQ	0.24	0.52	0.19	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
13	<LOQ	<LOQ	<LOQ	0.24	<LOQ	0.099	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
14	<LOQ	<LOQ	<LOQ	0.14	0.14	0.11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	Living room
LOQ	0.013	0.020	0.0067	0.088	0.11	0.083	0.020	0.038	0.018	0.039	0.024	

Table 5. Comparison Phthalates in Indoor Air: Current Levels and Previously Reported Levels from a Study Conducted in the Early 2000s.

	This study			The previous study [11]		
	DBP	DEHP	DEP	DBP	DEHP	DEP
Median (µg/m^3)	0.35	0.36	0.15	0.47	0.31	0.049
Maximum (µg/m^3)	1.4	0.86	3.8	7.2	2.4	0.86
Minimum (µg/m^3)	0.14	0.14	0.093	0.078	0.052	<0.005
Detection rate of concentration distribution0.1–0.9 µg/m^3 (%)	86	71	71	70	71	No data
Adsorbent	Quartz filter and Styrene divinylbenzene copolymer			Quartz filter and C18 filter		

[11] Saito *et al*. 2002.

as a household insecticide, and diazinon is presumed to have decreased in household use as shipments have declined.[9] Furthermore, chlorpyrifos was previously used in Japan to control termites in building materials, but it was banned in 2003. In contrast, fenobucarb was in continuous use from 2002 to 2019.[8] However, most fenobucarb is used in solid form and is intended primarily for outdoor insecticidal use.[9,10] Thus, the scarce detection of these three insecticides in the indoor air was considered reasonable.

Among the phthalates, DBP, DEHP, and DEP were predominantly detected. However, none of the phthalate concentrations exceeded the guideline values (Table 4), similar to the observations of the field survey conducted in the early 2000s.[11] A comparison of concentrations in the current survey with previous surveys showed a slightly higher trend in median DEP value, while median DBP and DEHP remained comparable (Table 5). The maximum values of DBP and DEHP showed a decreasing trend, while DEP was detected at 3.79 µg/m^3 (Table 5). Interviews with residents revealed that they regularly used aerosol air fresheners and deodorizers in this residence. Sato *et al*. surveyed phthalates in commercial aerosol air fresheners and deodorizers and found that DEP was frequently detected in the products, with the highest concentration of 104 µg/m^3.[12] According to Saito *et al*., fragrances and cosmetics were the primary sources of DEP in the 2000s.[11] Aerosol air fresheners and deodorizers should also be closely monitored as new sources in the future. Finally, the concentration distribution was compared with the surveys conducted in the 2000s. The concentration tended to be in the 0.1–0.9 µg/m^3 range in all cases (Table 5).[11] The frequency and concentration distributions of DBP and DEHP for which guideline values have been set were plotted for <0.1 µg/m^3, 0.1–0.3 µg/m^3, 0.3–0.9 µg/m^3, and >0.9 µg/m^3, which revealed a decreasing trend compared with the concentrations in the early 2000s (Fig. 3).[11] The findings indicate that current concentrations of DBP and DEHP are lower than those observed previously. However, this survey was limited in time and region. A national level survey must be conducted to verify the latest concentration trends.

In conclusion, we conducted the simultaneous analysis of 11 insecticides and phthalates, including five SVOCs, using GC-MS to determine the current trends against the established guideline values for indoor air pollutants. The target components were completely separated using the developed method, with satisfactory performance in terms of recovery rates, RSDs, and LOQs. The field survey conducted using this method revealed that none of the SVOCs exceeded the guideline values. Moreover, none of the three target insecticides were detected in the indoor air samples. In contrast, the phthalates DEP, DBP, and DEHP were detected. The concentration distribution of DBP and DEHP, for which the guideline values are known, showed a trend of decreasing compared to that found in the 2000s. However, this study was confined to a specific time and geographic area. Hence, a nationwide survey will be required in the future.

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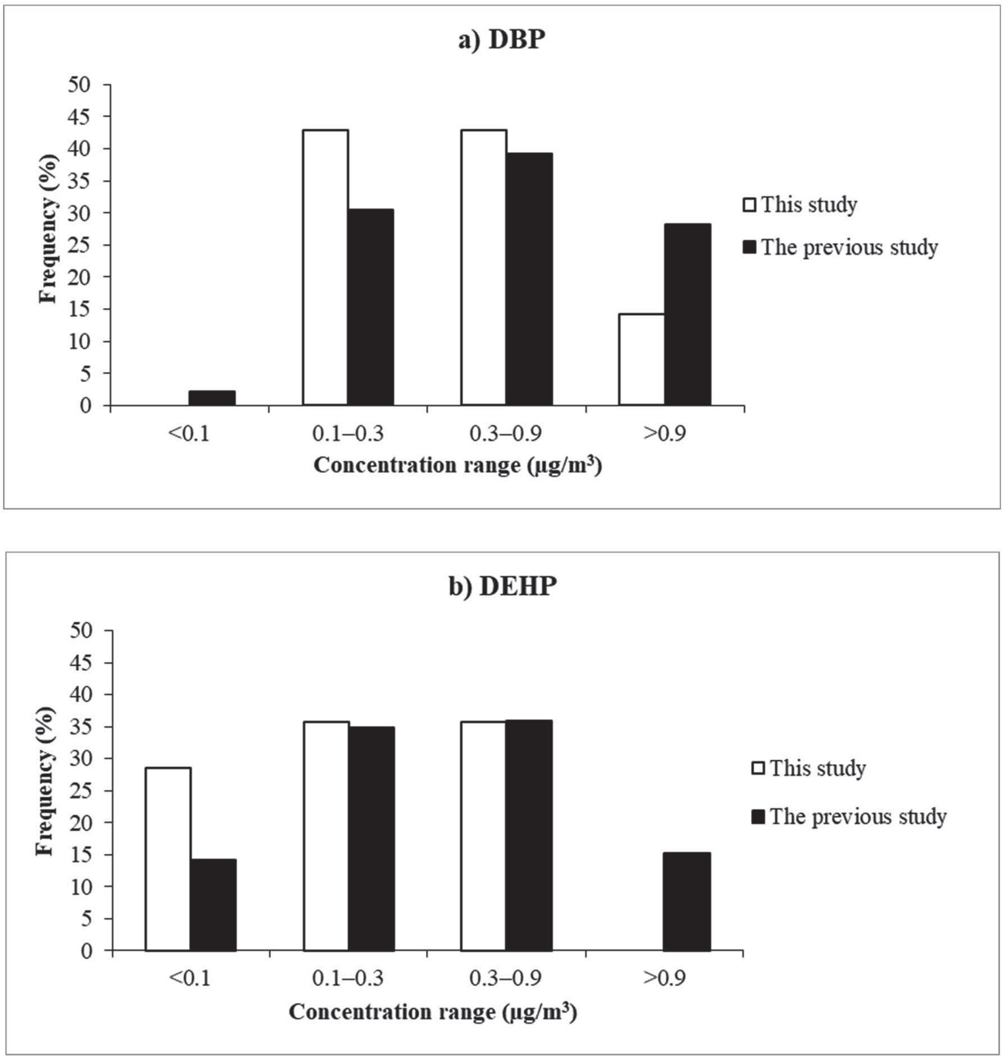

Fig. 3. Comparison of Field Surveys for a) DBP and b) DEHP Between This Study and the Previous Study.[11)]

[11)] Saito *et al*. (2002).

Conflict of interest The authors declare no conflict of interest.

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