

Phthalates in indoor air of Canadian residences

Jiping Zhu*, Yong-Lai Feng, Stephen MacDonald, Ron Newhook and Leonora Marro

Safe Environments Program, Health Canada, AL: 0800C, Building 8, Tunney's Pasture, Ottawa, Canada K1A 0L2

*: Corresponding Author: email: jiping_zhu@hc-sc.gc.ca

ABSTRACT

Phthalates (1,2-benzenedicarboxylic acid alkyl esters) are used as plasticizers in vinyl products such as vinyl floor coverings and many other consumer products. Many of these chemicals are on the priority chemicals list under the Canadian Environmental Protection Act. Because of the low vapour pressure of phthalates, the concentrations of these compounds are relatively low in the air. In order to have the sufficient sensitivity, 0.1 m³ of air were drawn through a XAD-2 tube. Collected phthalates in XAD-2 tubes were eluted with 5-mL high-purity methylene chloride. The solution was then concentrated to 200 µL and analyzed using a GC/MS method in Selected Ion Monitoring (SIM) mode. Six commonly used phthalates, dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP) were measured in residential indoor and outdoor air in 73 randomly selected homes in the city of Ottawa, Canada. When corrected for field blank levels, the mean concentrations of phthalates in indoor air were 0.42 µg/m³ for DEP, 0.21 µg/m³ for DBP and 0.13 µg/m³ for DEHP, while the indoor concentrations for the remaining three phthalates were similar to those of field blanks and therefore considered not detected. The phthalate concentrations in outdoor air were very close to those of field blanks.

INDEX TERMS

Indoor air, Phthalate, Determination, GC/MS, sampling

INTRODUCTION

The widespread use of plastics in modern human society has raised concerns over the human exposure to phthalates. Phthalates, having a chemical structure of 1,2-benzenedicarboxylic acid diester, are the single largest group of plasticizers used in plastics. In addition, phthalates also are used in many other products and are known to have endocrine disruptive activity in animals. Several phthalates and their monoester metabolites have shown teratogenic, reproductive and developmental effects in animal tests.

An interesting finding in the monitoring of human exposure to phthalate metabolites is that the levels of mono-ethyl phthalate is the highest in urine samples, followed by mono-butyl and mono-benzyl phthalates, which are originated from exposure to diethyl, dibutyl and butylbenzyl phthalates (Blount et al., 2000). Despite the fact that Di-(2-ethylhexyl) phthalate is the most widely used phthalates in plastic products, the levels of mono ester of this phthalate in urine samples is 50 to 100 times lower than that of mono-ethyl phthalate. Identifying new exposure sources of phthalates will be the next logical step in order to understand the monitoring data of phthalate metabolites in human urine samples.

Inhalation is one of the major routes of exposure to phthalates. Due to their low vapour pressure, phthalates tend to bind to particulates in suspended indoor dust (Butte and Heinzow, 2002). Particulate-bound phthalates in residential air were first reported by Weschler (1984). Since then several measurements methods have been used to determine the particulate-bound

phthalates concentrations in air, mainly using filters as the collection media (Imanaka et al., 2002; Adibi et al., 2002, Matsumura et al., 2002).

In this paper, we present an analytical method using XAD resin as the collection media for the total air borne phthalates. The method is based on relatively small sampling volumes (100 L) that can be easily applied to survey the levels of airborne phthalates in residential air and other non-industrial settings.

METHODS

A standard solution containing six phthalates at a level of 2000 ng/ μ L per compound was purchased from Supelco (Bellefonte, PA, USA). It contained dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP). DBP-d₄, (100 ng/ μ L) used as internal standard for this study, was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Dichloromethane (DCM), was purchased from Fisher Scientific (New Jersey, USA). The working solution of the standards was prepared by diluting the commercially obtained standard solution in DCM in the following manner: the stock solution (100 ng/ μ L) was prepared by transferring 0.50 mL of the commercial standard solution to a 10-mL volumetric flask and diluted to the mark with DCM. Serial dilutions were made afterwards from the stock solution in the same manner. The DBP-d₄ solution was prepared separately in DCM to a concentration of 20 ng/ μ L. ORBO™-43 tubes (20/40) were purchased from Supelco. The tube is 8 mm in outside-diameter and 100 mm long and is packed with 100 mg/50 mg XAD resin.

A Hewlett Packard gas chromatograph (GC, HP 5890 series) equipped with an automated sample injector (HP 7673) and a mass selective detector (MS, HP 5972 series) (Agilent Technologies, Palo Alto, CA, USA) was used for the analysis. Analytes were separated on a 30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness DB-5 gas chromatographic column (J&W Scientific, Folsom, CA, USA) with the following oven temperature program: initial temperature was set at 55 °C for 2 min, then increased to 200 °C at 15 °C/min and kept at 200 °C for 15 min. 2 μ L of the final prepared solution were injected for instrument analyses.

Selected Ion Monitoring (SIM) mode was used for MS operation. Three ions (one target ion (T) and two qualifying ions (Q1 and Q2)) were selected for each target compound. Both retention times and ratios of the three ions were used for identifying the target compounds. A peak was considered positive if its retention time was within 1 % of that of associated standard *AND* at least one of its two ion ratios (Q1/T or Q2/T) were within \pm 30% of those of the standards.

Airborne phthalates were collected in ORBO-43 tubes by drawing 100 L of air over 100 minutes at a flow rate of 1 L/min. The samples were then eluted with 5 mL of DCM. The eluate was concentrated to 200 μ L under a gentle nitrogen stream and spiked with 10 μ L of 20 ng/ μ L DBP-d₄ (200 ng/sample) prior to being transferred to a GC vial for analyses.

RESULTS AND DISCUSSION

Instrument Performance

A commercially available standard mixture of six common phthalates, namely dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), Di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DOP) was used for the methods development. All six phthalates were well separated on a DB-5 column with the retention times between 10 min and 21 min. To achieve a higher sensitivity for the analyses,

the mass spectrometer was operated in Selected Ion Monitoring (SIM) mode. The base peak of m/z 149 for all phthalates, except for DMP whose base peak is at m/z 135, was used to quantify the phthalate peaks on the GC chromatogram, and the other two characteristic ions were used as qualifying ions for the identification of the peaks.

Instrument and method performance are summarized in Table 1. Instrument detection limits (IDLs) were estimated by analyzing seven low concentration standards of 0.1 ng/uL, which is equivalent to 20 ng/sample for a final solution of 200 μ L. The IDLs ranges for the six phthalates were between 1.3 ng/sample for DEHP to 4.3 ng/sample for BBP. The laboratory blanks showed a mean blank level of 17 ng/sample for DEHP, followed by DBP (11 ng/sample), DEP (3 ng/sample), and BBP (2 ng/sample). There was no trace level of DMP and DOP detected. The method detection limit (MDL) was calculated using the mean value of the seven laboratory blanks plus 3.143 times the standard deviation (s.d.) of seven replicates of samples spiked with same amount (20 ng/sample) as those for IDL study. DEHP and DBP had the highest MDLs of 0.24 μ g/ m^3 and 0.21 μ g/ m^3 , respectively, largely due to the levels in laboratory blanks.

Table 1: Instrument and method performance (IDL = instrument detection limit; LB = lab blank; RSD = relative standard deviation)

Unit	IDL (n=7)	Mean LB (n=7)	MDL (n=7)	Mean Recovery (RSD) (n=5)		
	ng/sample	ng/sample	μ g/ m^3	% (%)	% (%)	% (%)
DMP	2.7	0.0	0.04	84 (5)	96 (1)	100 (3)
DEP	2.4	3.4	0.05	91 (4)	100 (2)	101 (2)
DBP	1.3	11	0.21	101 (14)	99 (1)	104 (10)
BBP	4.3	1.9	0.08	90 (5)	99 (3)	102 (2)
DEHP	3.3	17	0.24	135 (27)	109 (4)	106 (2)
DOP	3.9	0.1	0.05	92 (4)	100 (4)	103 (3)

The recoveries of the analytes from the XAD tubes were evaluated at three spiking levels (150 ng/sample, 350 ng/sample and 700 ng/sample), each in five replicates. The reproducibility of the replicates was used to evaluate the precision of the method expressed in relative standard deviation (%RSD). When corrected for laboratory blank levels, the recoveries at all three levels were between 90 % and 110%, except for the relatively low recovery of DMP (84 %) and excessive recovery of DEHP (135 %) at low spiking level (150 ng/sample). The precisions at all three spiking levels were excellent with %RSD values below 10 %, with the exception of DBP (14 %) and DEHP (27 %) at low spiking level (Table 1).

In a stability test, tubes that had been spiked with 200 ng each of the phthalates and flushed with 1 L of clean air were stored in darkness at room temperature for up to 15 days. The recoveries of all analytes in all samples (storage time: 0, 1, 3, 7, and 15 days) were above 85 percent indicating no losses of target analytes during the storage time. Safe sampling volume was confirmed by the observation that there was no breakthrough at both 0.1 and 0.2 m^3 volume.

Concentration of phthalates in residential air in 73 homes

73 homes were randomly selected in the city of Ottawa, Canada for this study to determine the levels of airborne phthalates in residential air. The main reason for selecting the small sampling volume (0.1 m^3) was to incorporate this sample collection with a number of collections for other types of samples such as volatile organic compounds and carbonyls at the same time for this study.

Table 2 lists the summary results of target phthalates in residential homes, in both outdoor air and indoor air, along with the levels in field blanks. Values that were below the IDLs were substituted with IDL value when calculating mean and standard deviation (s.d.) values. Because of the ubiquitous presence of phthalates, especially DEHP, in the sampling and laboratory environment, a total of 31 field blanks were collected and analyzed during the study period to serve as the background level. The mean levels of field blanks and their standard deviations are summarized in Table 1. Among all the target phthalates, DEHP had the highest mean level ($0.24 \mu\text{g}/\text{m}^3$) in field blanks, followed by DBP ($0.08 \mu\text{g}/\text{m}^3$). The levels in the field blanks for other target phthalates were relatively low.

Table 2: Summary results of phthalates concentration ($\mu\text{g}/\text{m}^3$) in residential (*: One indoor air value of DEP ($8.95 \mu\text{g}/\text{m}^3$) was not included in the calculation)

	Field Blank (n=31)		Outdoor Air (n=70)		Indoor Air (n=73)		Indoor Air (field blank corrected)
	mean	s.d.	mean	s.d.	mean	s.d.	mean
DMP	0.03	0.00	0.03	0.00	0.03	0.01	ND
DEP	0.06	0.04	0.07	0.07	0.48*	0.27	0.42
DBP	0.08	0.02	0.08	0.05	0.29	0.15	0.21
BBP	0.04	0.00	0.04	0.00	0.05	0.02	ND
DEHP	0.24	0.08	0.27	0.10	0.37	0.25	0.13
DOP	0.04	0.00	0.04	0.00	0.04	0.00	ND

The outdoor air and indoor air concentrations of three phthalates, namely DMP, BHP and DOP were very close to each other and very similar to the levels in field blanks, indicating the absence of these three phthalates in monitored indoor and outdoor air. The concentrations of DEP, DBP and DEHP in outdoor air were also very similar to the levels in field blanks, however, their concentrations in indoor air were higher at $0.42 \mu\text{g}/\text{m}^3$ and $0.21 \mu\text{g}/\text{m}^3$ and $0.13 \mu\text{g}/\text{m}^3$ respectively after field blank corrections, implies the presence of indoor sources of these phthalates. The high background of DEHP in both lab blanks and field blanks attributes to the higher high detection limit for this compound. Since the concentration of DEHP in residential air has been found in sub $\mu\text{g}/\text{m}^3$ level, in order to adequately measure this compound in residential air, it would be desirable to have a larger sample volume than the one used in this study.

The data of all three detected phthalates however, are not normal-distributed. Figure 1 plotted the distribution of three dominant phthalates, DEP, DBP and DEHP, in indoor air. The concentrations of DEP, DBP and DEHP in indoor air at 95th percentile were $1.0 \mu\text{g}/\text{m}^3$, $0.5 \mu\text{g}/\text{m}^3$, and $0.3 \mu\text{g}/\text{m}^3$ respectively.

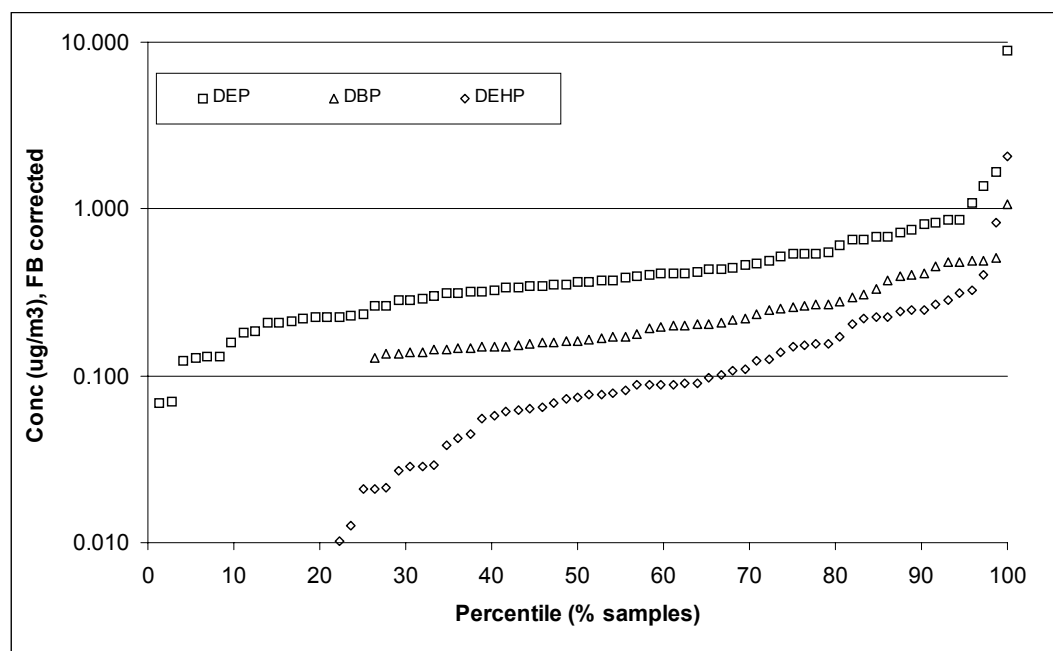


Figure 1: Percentile distribution of indoor air concentrations of three phthalates. Note that the y-axis is in log scale.

CONCLUSION AND IMPLICATIONS

The data reported in this paper represent a regional population based survey result. The data are based on randomly selected representative homes in the city of Ottawa. This is so far the largest regional data set reported for air borne phthalates in residential air in Canada, with both indoor air and outdoor air being measured concurrently. The data indicate that population has the highest inhalation exposure to DEP among the phthalates monitored, which is consistent with the highest levels of mono-ethyl phthalate in human urine samples. On the other hand, literature data have shown that DEHP has the highest concentration among the phthalates in house dust (Butte and Heinzow, 2002). Further studies of phthalates in different exposure media could improve our understanding on the exposure to phthalates.

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