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Emissions of amides (N,N-dimethylformamide and formamide) and other obnoxious volatile organic compounds from different mattress textile products

Ki-Hyun Kim [a], Sudhir K. Pandey [b,*], Yong-Hyun Kim [a], Jong Ryeul Sohn [c], J-M Oh [d]

[a] Department of Civil & Environmental Engineering, Hanyang University, Seoul 133-791, South Korea
[b] Department of Botany, Guru Ghasidas central University, Bilaspur 495009, Chhattisgarh, India
[c] Department of Environmental Health, Korea University, Seoul 136-075, South Korea
[d] Department of Environmental Science & Environmental Engineering, Kyunghee University, Suwon 446-701, South Korea

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ABSTRACT

The emission rates of N,N-dimethylformamide (DMF), formamide (FAd), and certain hazardous volatile organic compounds (VOCs) were measured from seventeen mattress textile samples with four different raw material types: polyurethane (PU: $n=3$), polyester/polyethylene (PE: $n=7$), ethylene vinyl acetate (EV: $n=3$), and polyvinyl chloride (PC: $n=4$). To simulate the emissions in a heated room during winter season, measurements were made under temperature-controlled conditions, i.e., 50 °C by using a mini-chamber system made of a midget impinger. Comparison of the data indicates that the patterns were greatly distinguished between DMF and FAd. PU products yielded the highest mean emission rates of DMF (2940 $\mu g\ m^{-2}\ h^{-1}$: $n=3$) followed by PE (325 $\mu g\ m^{-2}\ h^{-1}$: $n=7$), although its emission was not seen from other materials (EV and PC). In contrast, the pattern of FAd emission was moderately reversed from that of DMF: EV > PC > PE > PU. The results of our analysis confirm that most materials used for mattress production have the strong potential to emit either DMF or FAd in relatively large quantities while in use in children's care facilities, especially in winter months. Moreover, it was also observed that an increase in temperature (25 °C to 50 °C) had a significant impact on the emission rate of FAd and other hazardous VOCs. In addition to the aforementioned amides, the study revealed significant emissions of a number of hazardous VOCs, such as aromatic and carbonyl compounds.

1. Introduction

Various rodent reproductive toxicants have been identified by coordinated efforts made at many levels, e.g., the National Toxicology Program (NTP) Reproductive Assessment by Continuous Breeding (RACB) protocol (Moorman et al., 2000). However, if one attempts to evaluate the harmful impact of those toxins on the human reproductive system, it becomes a highly complicated task due to the combined effects of different hard and soft factors (e.g., time, expense, resources, logics, etc). To resolve such complicated issues, the prioritiazation technique is a preferred option through which their potential is sorted out or ranked to decide the target chemicals for field study. According to an evaluation based on potency of toxic effect and population at risk, the four top priority targets – dibutyl phthalate, boric acid, tricresyl phosphate, and N,N-dimethylformamide (DMF) – were recommended for the human reproductive field study (Moorman et al., 2000).

The environmental cycle of DMF, although known as an unconventional air pollutant, has drawn a great deal of attention due to its large-scale consumption worldwide (US EPA, 2006). In fact, its presence in outdoor ambient air has been reported from areas close to strong source environments (e.g., a synthetic leather industrial zone (Wei et al., 2011a,2011b)). Likewise, the environmental significance of DMF as indoor pollutant is also recognized greatly due to its abundance in and around recreational and/or living facilities (e.g., components of arts and crafts materials or leather products). Frequent usage of certain furniture products in routine conditions may also increase the rate of exposure to hazardous substances like DMF (Ho et al., 2011). As such, much effort has been directed to elucidation of relationship between its exposure levels and its human health impact (e.g., Lucier and Schecter, 1998).

In Korea, several negative effects (e.g., allergy, asthma, malodor, etc.) have been reported from various mattress products used in children's nursing facilities. In compliance with such public

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[*] Corresponding author. Fax: +91 7752 260148.
E-mail address: skpbhu@gmail.com (S.K. Pandey).

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concern, a special evaluation plan was organized by a national broadcasting company to investigate the emissions of DMF from a number of mattress products sold in local Korean markets. As part of this effort, we conducted a series of lab experiments to measure emission flux of DMF and some relevant VOCs (e.g., aldehydes and aromatic hydrocarbons (e.g., benzene, toluene, ethyl benzene, and xylene – widely known as BTEX)) by mini-chamber. To learn more about the emission characteristics of DMF from household sources, a total of seventeen mattress textile samples were chosen to explore the basic aspects of the toxicant emissions. Its emission rates were hence measured by employing a small-scale chamber system made of an impinge sampler. The results of our study can provide basic insight into the emission of DMF from mattress products and into the factors governing its emissions in indoor environment.

2. Materials and methods

2.1. Sample collection & analysis

In order to obtain the emission data of DMF and other VOCs from mattress textile samples, we collected a total of seventeen mattress textile samples produced by thirteen manufacturers; information regarding the manufacturer is treated anonymously by the capital letters of A through M as the last digits of the sample code (Table 1). To this end, a simple experimental system was devised to allow the collection of DMF exiting an impinger (as micro-chamber) placed inside a temperature controlled heater line (Fig. 1). Information concerning the sample size (weight, surface area, and dimension) of each mattress product used for the flux measurements is also provided in Table 1.

The application of this micro-chamber system has been reported elsewhere for the flux measurements of mercury (Kim et al., 2012). To measure the emission of DMF from mattresses used in child care facilities, we conducted lab experiments to simulate their emissions under the following conditions. During cold period, commercial mattress products used in most childcare facilities are placed above a temperature regulating floor (on-dol system in Korea) or a temperature-controlled electronic heating device constructed in the form of mattress pad. Hence, the most significant emissions are expected to occur during the cold season (especially between late fall and early spring). In our preliminary survey, we observed that in some facilities using electronic mattress pad, the temperatures measured between common mattress (without and electric heating) and electronic heating device occasionally go up to significantly high level (e.g., 50 °C: a maximum temperature range set for commercial electric heating mattress system). As we attempted to measure the maximum emission under most severe conditions, we arbitrarily set 50 °C as the main temperature criterion in this study. For comparative purposes, emission rates were also measured at 25 °C using some of the mattress samples.

A total of thirteen compounds containing DMF were selected as the target analytes in this study: (1) amide: N,N-dymethylformamide (DMF) and formamide (FAd), (2) aromatic: benzene (B), toluene (T), p-xylene (p-X), m-xylene (m-X), o-xylene (o-X), and styrene (S), and (3) carbonyl: formaldehyde (FA), acetaldehyde (AA), propionaldehyde (PA), butyraldehyde (BA), and acetone (AT). The target compounds were prepared in a liquid phase standard (L-WS) through gravimetric dilution of the primary-grade chemicals with methanol (e.g., Kim et al., 2013). The calibration of L-WS was carried out to quantify target compounds in samples. Basic tests for quality assurance/quality control (QA/QC) were also assessed using the same L-WS. For the reader's reference, most of our target compounds other than DMF and FAd belong to a list of offensive odorants with low odor thresholds (Kim et al., 2013).

To initiate each experiment, the inlet and outlet of each impinger are connected to the purging system (cylinder filled with ultrapure air) and the sample collection system (either sorbent tube for amides and aromatics or cartridge sampler for carbonyl), respectively (Fig. 1). To collect the gaseous samples, we initially ran the impinger system to pass 1 L of air (10 min at 0.1 L min^{-1}). Then, 0.1 L of samples were collected for the analysis of VOC (containing amides). Subsequently, 8 L of samples (8 min at 1 L min^{-1}) were collected for the analysis of carbonyls.

For the analysis of amides and aromatics, a GC system (Agilent GC 7890A, USA) equipped with time-of-flight mass spectrometry (TOF-MS) (Bench TOF-dx, Almsco, UK) was interfaced with a thermal desorption system equipped with an electrically cooled focusing trap (UNITY, Markes International, Ltd, UK). The sorbent tube for amide (and aromatic) sampling was prepared as a three-bed type (100 mg of Tenax TA, Carbopack B, and Carbopack X) to induce optimal adsorption of target compounds. The thermal desorber focusing trap was packed with an equi-volume ratio of Tenax TA and Carbopack B (Table 2A). The analysis of carbonyl compounds (CCs) was carried out by high performance liquid chromatography (HPLC) equipped with a UV detector. The analytical conditions of the HPLC system are mentioned in Table 2B. The cartridges loaded with CCs were eluted slowly with 5 mL acetonitrile and filtered through 0.45 μm, 13 mm, GHP Acrodisc filters (PALL, NY, USA) into a 25 mL capacity borosilicate glass volumetric flask. The eluate was manually injected into the HPLC system equipped with a 20 μL sample loop. The basic QA parameters (e.g., calibration results (in terms of response factor (RF)), precision, detectability, etc.) for the quantitation of each target compound are provided in Table 3.

2.2. Derivation of DMF flux

The emission rate of DMF was quantified by inputting the concentration determined from each mattress sample into the following formula:

$$F = C(L + Q/A) \quad (1)$$

Table 1
Information regarding selected mattress samples to measure emission rates of DMF and VOCs.

Order	Group	Sample code	Raw material[a]	Sample weight	Sample dimension	Sample quantity	Surface area	
				(g)	(cm × cm × (cm))	(ea)	(cm^2)	(m^2)
A. Measurements at 50 °C								
1	PU	PU1A	Polyurethane (E)	11.1	30 × 15	1	450	0.045
2		PU2B	Polyurethane (E)	9.93	30 × 15	1	450	0.045
3		PU3C	Polyurethane (E)	11.2	30 × 15	1	450	0.045
4	PE	PE1A (I)	Polyester/Polyethylene (I)	2.91	15 × 3 × (1.5)	2	288	0.0288
5		PE2B (I)	Polyester/Polyethylene (I)	3.51	15 × 3 × (1.5)	2	288	0.0288
6		PE3C (I)	Polyester/Polyethylene (I)	4.28	15 × 3 × (1.5)	2	288	0.0288
7		PE4D	TR+Polyester/Polyethylene (E)	10.8	5 × 15	6	450	0.045
8		PE4D (I)	Polyester/Polyethylene (I)	8.16	15 × 3 × (1.5)	2	288	0.0288
9		PE5E	Polyester/Polyethylene	3.46	15 × 3 × (1.5)	2	288	0.0288
10		PE6F	Polyester/Polyethylene	5.30	15 × 3 × (1.5)	2	288	0.0288
11	EV	EV1G	Ethylene vinyl acetate	9.56	15 × 3 × (1.5)	2	288	0.0288
12		EV2H	Ethylene vinyl acetate	8.50	15 × 3 × (1.5)	2	288	0.0288
13		EV3I	Ethylene vinyl acetate	14.7	15 × 3 × 1.5	2	288	0.0288
14	PV	PV1J	Polyvinyl chloride	22.7	15 × 3 × 1.5	2	288	0.0288
15		PV2K	Polyvinyl chloride	19.7	15 × 3 × 1.5	2	288	0.0288
16		PV3L	Polyvinyl chloride	20.6	15 × 3 × 1.5	2	288	0.0288
17		PV4M	Polyvinyl chloride	39.0	30 × 15	1	450	0.045
B. Measurements at 25 °C								
18	PV	PV2K(25)	Polyvinyl chloride	19.7	15 × 3 × (1.5)	2	288	0.0288
19		PV4M(25)	Polyvinyl chloride	39.0	30 × 15	1	450	0.045

[a] Capital letters of E and I in parentheses denote exterior and interior material, respectively.