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Potential hazard of volatile organic compounds contained in household spray products

Md Mahmudur Rahman [1], Ki-Hyun Kim *

Department of Environment and Energy, Sejong University, 98 Gun-Ja Dong, Gwang-Jin Gu, Seoul 143-747, Republic of Korea

HIGHLIGHTS

- The emission of hazardous pollutants was investigated from spray products.
- Common indoor pollutants have been detected frequently in the majority of spray products.
- Analysis of carcinogenic risk level indicates potential health effects of spray products.

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ABSTRACT

To assess the exposure levels of hazardous volatile pollutants released from common household spray products, a total of 10 spray products consisting of six body spray and four air spray products have been investigated. The body spray products included insect repellents (two different products), medicated patch, deodorant, hair spray, and humectant, whereas the air spray products included two different insecticides (mosquito and/or cockroach), antibacterial spray, and air freshener. The main objective of this study was to measure concentrations of 15 model volatile organic compounds (VOCs) using GC/MS coupled with a thermal desorber. In addition, up to 34 'compounds lacking authentic standards or surrogates (CLASS)' were also quantified based on the effective carbon number (ECN) theory. According to our analysis, the most common indoor pollutants like benzene, toluene, styrene, methyl ethyl ketone, and butyl acetate have been detected frequently in the majority of spray products with the concentration range of 5.3–125 mg L^{-1}. If one assumes that the amount of spray products released into air reaches the 0.3 mL level for a given space size of 5 m^3, the risk factor is expected to exceed the carcinogenic risk level set for benzene (10^{-5}) by the U.S. EPA.

1. Introduction

Historically, a whole host of personal care products have provided substantial benefits to human life (Nilsen et al., 2002; Rusin et al., 1998). Due to the increasing demand of body spray products, the inherent hazards of the ingredients and their exposure limits should be evaluated to warrant their safe usage (ECETOC, 1993; U.S.EPA, 1997). In many investigations, a list of volatile organic compounds (VOCs) (in particular, benzene, toluene, xylenes, and styrene) and carbonyls (formaldehyde and acetaldehyde) have been designated as the most sensitive indicator of indoor pollution (Hodgson et al., 2000; Katsoyiannis et al., 2008; Wilke et al., 2004).

The status of VOC pollution has been commonly assessed with respect to the abundance and magnitude of target pollutants to help diagnose the potential health risks (cancer or other related diseases) (Sarigiannis et al., 2011). In fact, in many residential indoor environments, a list of hazardous VOCs have been found at significantly high concentration levels (Son et al., 2003). The use of certain household cleaning products such as air fresheners can maximize exposure risk of volatile (gas phase) or non-volatile (liquid or solid particulate matter) components upon inhalation or through dermal contact (Nazaroff and Weschler, 2004). Moreover, some active ingredients or fragrances (terpenoids and related compounds) released from the cleaning products (or air fresheners) are found to react with atmospheric ozone to form formaldehyde and fine particles as secondary pollutants (Singer et al., 2006).

Apart from household cleaning products, body spray products (i.e., deodorants and hair spray) contain various types of

* Corresponding author. Tel.: +82 2 499 9151; fax: +82 2 3408 4320.
E-mail addresses: khkim@sejong.ac.kr, kkim61@nate.com (K.-H. Kim).
[1] Now at: International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane, QLD 4001, Australia.

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Table 1
Sample information for spray products investigated in this study.

Order	Sample code[a]	Type	Use	Spray gas	Extra info.
1	S-L-1	Skin	Insect repellent (A)	LPG (for human body)	
2	S-L-2	Skin	Insect repellent (B)	LPG (for human body)	
3	S-L-3	Skin	Medicated patch	LPG (for human body)	
4	S-L-4	Skin	Deodorant	LPG (for human body)	
5	S-L-5	Skin	Hair spay	LPG (for human body)	Jasmine fragrance
6	S-N-1	Skin	Humectants	N_2 (for human body)	
7	A-L-1	Air	Insecticide (A)	LPG	No smell
8	A-L-2	Air	Insecticide (B)	LPG	Herb fragrance
9	A-L-3	Air	Antibacterial spray	LPG	
10	A-L-4	Air	Air freshener	LPG	Herb fragrance

[a] In sample code naming, 'S','A', 'N', and 'L' were used to represent body spray products for skin, air, nitrogen propellant, and liquefied petroleum gas (LPG) propellant, respectively.

ingredients which can generate toxic effects in the respiratory tract (Rothe et al., 2011). The prime components of hair sprays are resins with inert (or low) biological reactivity (Carthew et al., 2002). However, if they are present in the form of poorly soluble particles in excessive quantity, they can impair human body (e.g., lungs) (Greim et al., 2001; Muhle and Mangelsdorf, 2003). In a recent report by the U.S. EPA (2012), fragrance used in cosmetics and cleaning products has been classified into nine different categories in terms of human toxicity, especially carcinogenicity, genetic toxicity, respiratory and skin sensitization, etc. Considering the health effects of fragrances, more restrictive regulations were made in Japan by banning nitro-musk compounds in the 1980s, which in turn helped reduce allergies from the use of common fragrances (Bridges, 2002).

In this investigation, the risk of VOC exposure due to the use of spray products were investigated using ten types of spray products that can be classified as follows: (1) six body spray products (insecticides (two different brands), deodorant, hair spray, medicated patch and facial humectant) and (2) four air spray products (insecticides of two different brands, antibacterial spray, and air freshener). The overall goal of this study is to acquire information concerning a list of volatile (or hazardous) chemicals that are contained in and released from various spray products. Based on this comparative analysis of chemical ingredients between diverse spray products, we attempted to elucidate the potential health risks stemming from the use of these spray products.

2. Experimental

2.1. Spray products

In this investigation, six types of body spray products and four household air sprays were investigated (Table 1). The target body spray products can be classified into insecticides, medicated patch, deodorant, hair spray, and facial humectants. All body spray products did not reveal any information regarding the specific fragrance except the hair spray product, which identified a jasmine fragrance. In this study, body spray products were purchased from local (Korean) markets with consideration of high market share and necessity to every daily life. To analyze diverse chemicals contained in household spray products, a total of four aforementioned air spray products were also purchased to expand the target investigation.

2.2. Sample collection

In this study, 15 target pollutants were initially selected as the criteria standard for the quantification of VOCs (Table 2). These selected compounds have been used as model compounds for odor analysis in many of our recent studies (Kim et al., 2009; Rahman and Kim, 2012a,b). Well known as offensive odorants, most of these compounds are regulated by the malodor prevention law in Korea (KMOE, 2008). For the analysis of chemicals contained in each spray product, each sample was initially collected into 20 mL vials in liquid form by spraying each product into the mouth of the vial. Each sample was then diluted 100 times using methanol as solvent. Then 1 μL of the diluted liquid samples was loaded into a three bed sorbent tube (Tenax TA + Carbopack B + Carboxen 1000) by injection via a 5 μL capacity syringe (Kim and Kim, 2012). Injection was made directly into the sampling end of sorbent tubes with a supply of pure nitrogen (99.9%) contained in a polyester aluminium bag (PEA), with the aid of a mini-pump (Sibata pump-∑30, Japan) at a flow rate of 50 mL min^{-1} for 10 min.

2.3. Instrumental system

For the analysis of target VOCs from the ST sample, a GC system (Shimadzu GC-2010, Japan) equipped with a mass spectrometry (Shimadzu GCMS-QP2010, Japan) was used along with the thermal desorption (TD) system (Unity, Markes, UK) (Fig. 1). The operational conditions of the analytical system (GC MS and TD) are described in Table 3. In the TD system, the cold trap (CT) unit packed with an equivolume ratio of Carbopack C and Carbopack B is employed to

Table 2
Basic information of 15 target VOCs investigated in this study.[a]

Order	Full name	Abbreviation	MW (g mol^{-1})	Density (g cm^{-3})	Formula	CAS number	Purity (%)
1	Acetaldehyde	AA[a]	44.1	0.79	C_2H_4O	75-07-0	99
2	Propionaldehyde	PA[a]	58.1	0.8	C_2H_5CHO	123-38-6	97
3	Butyraldehyde	BA[a]	72.1	0.81	C_3H_5CHO	123-72-8	99
4	Isovaleraldehyde	IA[a]	86.1	0.8	C_4H_9CHO	590-86-3	97
5	Valeraldehyde	VA[a]	86.1	0.81	C_4H_9CHO	110-62-3	97
6	Benzene	B	78.1	0.87	C_6H_6	71-43-2	99.5
7	Toluene	T[a]	92.1	0.87	$C_6H_5CH_\#$	108-88-3	99.5
8	Styrene	S[a]	104	0.91	C_8H_8	100-42-5	99
9	p-Xylene	p-X[a]	106	0.86	$C_6H_4(CH_3)_2$	106-42-3	99
10	m-Xylene	m-X[a]	106	0.86	$C_6H_4(CH_3)_2$	108-38-3	99
11	o-Xylene	o-X[a]	106	0.86	$C_6H_4(CH_3)_2$	95-47-6	97
12	Methyl ethyl ketone	MEK[a]	72.1	0.81	$C_2H_5COCH_3$	78-93-3	99
13	Methyl isobutyl ketone	MIBK[a]	100	0.8	$(CH_3)_2CHCH_2COCH_3$	108-10-1	99.5
14	Isobutyl alcohol	i-BuAl[a]	74.1	0.8	$C_4H_{10}O$	78-83-1	99
15	Butyl acetate	BuAc[a]	116	0.88	$CH_3COOC_4H_9$	123-86-4	99.5

[a] Compounds designated as the key offensive odorants according to the malodor prevention law of KMOE (2008).