



Exposure profile of volatile organic compounds receptor associated with paints consumption☆



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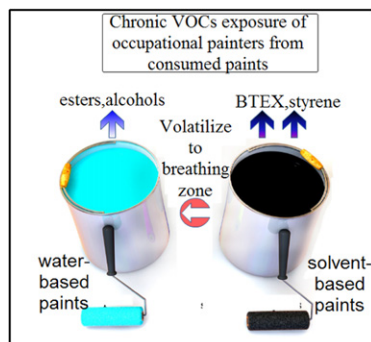
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HIGHLIGHTS

- Ambient VOCs concentration can barely represent real exposure level occupationally.
- Real-time exposure concentration fluctuates with different activity patterns.
- Actual exposure level merely depends on the paint type that was consumed.
- Higher potential inhalation does imply probability of increasing inhalation dose.

GRAPHICAL ABSTRACT

Tendency of substituting solvent-based paints by water-based paints and emission profiles which account for chronic VOCs inhalation of occupational painters.



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ABSTRACT

Epidemiologic studies regarding solvent-based paints (SBPs) containing VOCs have demonstrated a strong correlation between chronic and acute adverse health effects and the SBPs. Therefore, new environmentally friendly paints as substitutes containing less or none VOCs have been rapidly developed in research for future sustainable use. However, a few studies focusing on penetration and exposure condition of the substitute have been reported due to the complexity and inaccessibility of painting industry. Surveys specifically looking at the present status of exposure condition were conducted to ascertain the popularization of water-based paints (WBPs) which concluded that markers of SBPs were detected in all 134 samples indicating bad industrial penetration. VOCs exposure concentrations of painters ranged from 3.8 to 18.2 mg/m³ for WBPs, 3.5×10^3 to 14.8×10^3 mg/m³ for SBPs, respectively. The negative correlation between ambient concentration and breathing zone concentration suggested the former was incapable of representing the actual exposure concentration. The real-time concentration was proved to be closely associated with the activity patterns while the mean concentration level was found mostly dependent on the paint types. Authentic inhalation dose ranged from 7.68 to 15.84 mg (WBPs) and 3.84 to 15.59 g (SBPs), respectively, for occupational painters (work 8 h per day) and the total inhalation dose was estimated through a new conception. The findings suggested that WBPs could significantly reduce VOCs emission and occupational exposure.

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Abbreviations: VOCs, volatile organic compounds; WBPs, water-based paints; SBPs, solvent-based paints; TIL, total inhalation level; BMR, basal metabolic rate; MET, metabolic equivalent; H, volume of oxygen; VQ, ventilatory equivalent; BZC, breathing zone concentration; AC, ambient concentration; SD, standard deviation; U.S. EPA, U.S. environmental protection agency; WHO, world health organization.

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1. Introduction

Painting operation is an essential procedure in many industries which involve surface coating in manufacturing of automobile, light duty truck, furniture, can, large appliance, magnetic tape, metal coil, pressure sensitive, steel and ship, etc. Surface coating normally consists of prime coat (and cured), guide coat (and cured), topcoat (and cured) and final repair (and cured) to serve the purpose of applying decorative or protective materials in liquid or powder form to substrates. Consequently various kinds of paints and solvents are attached to the surface, including solvent-based paints (SBPs), varnishes, lacquers, thinner and water-based paints (WBPs) (U.S. EPA, 1981). It was estimated that painting operations had generated about 1883 kt and 2235 kt VOCs in 2005 and 2010, respectively, which accounted for 13% of anthropogenic emissions in China, and it would approach 5673 kt in 2020 assumedly absence of regulation (Wei et al., 2009; Zbigniew et al., 2002). The VOC species consist of aromatics, esters, ketones, alkenes and alkanes that are volatile and constantly emitted in all painting processes. Toluene and other aromatics are determined to be the most abundant compounds with a contribution of 76% (Chen et al., 2012; Ugur and Nurten, 2008; Yuan et al., 2010; Liu et al., 2008; Hou et al., 2012; Qu, 2010; Wang et al., 2012). Although more and more robots have been deployed instead of the human painters, many substrates, in specified requirements, cannot be painted automatically, especially in furniture and steel manufacturing. Therefore, painting occupations leads to acute and chronic exposure to high level of VOCs compared to other occupations (Qu, 2010; Dimonsthenis et al., 2011; Young et al., 2002; Noelia et al., 2012).

Painter's VOCs exposure profile which are primarily resulted from the exhaust gas derived from paints consumption, are affected by many factors such as the weight of paint coating, air flow rate in the workshop, diffusion coefficient and partition coefficient, substrate effect, coating process, coating material and source proximity effect (Li et al., 2006; Kim et al., 2001; Xiong et al., 2013; McBride et al., 1999; Furtaw et al., 1996; Acevedo-Bolton et al., 2012). Rim and Novoselac (2010) concluded that the convective heat transfer from an occupant's body would induce the buoyancy-driven flow transporting pollutants near the occupant to the breathing zone, and the concentration of pollutants in breathing zone accumulated to nine times greater than the uniform mixing airflow when the source located in the occupant's front chest. Malherbe and Mandin (2007) quantified the diffuse VOCs emissions during outdoor ship painting, and the concentration of repair site ($278 \mu\text{g}/\text{m}^3$) was found to be significantly higher than construction site ($26.5 \mu\text{g}/\text{m}^3$). Therefore, different occupational painters working in different microenvironments could uptake different VOCs species and concentrations which might result in adverse health issues.

The relationship between inhaling VOCs emitted from paints and health effects has been confirmed. According to epidemiological studies, benzene has been classified as a human carcinogen by the International Agency for Research on Cancer (IARC) (U.S. RAIS, 1998), while other VOCs which could be irritative or damage viscera, reproductive system, central nervous system, asthma and other respiratory effects are categorized of non-carcinogen (Rumchev et al., 2007; Venn et al., 2003). Due to the fact that occupational exposure to paints is associated with several adult cancers, IARC has classed it as carcinogenic (WHO, 2012). Toluene being the emission marker of painting operation has been well recognized to be neurotoxic and reproductive toxicity. Recent studies confirmed its efficacy of crossing the blood-brain barrier resulting in DNA damage in the developing brain (Gerasimov et al., 2002). By monitoring the levels of hippuric acid, creatinine and cotinine of the industrial painters, Moro et al. (2012) indicated that toluene could cause hepatic damage by creating free radicals during toluene biotransformation, which could increase the serum liver enzymes causing low levels of albumin. DNA damage in painters might be ultimately ascribed to the blood toluene levels. Furthermore, the presence of toluene at

occupationally relevant level, alters the metabolism of benzene even at low doses which would modify health risk estimates after lifelong exposure (Sarigiannis and Gotti, 2008). Clearly, traditional paints and solvents as the source of adverse health effect and atmospheric pollution are required to be replaced by new type paints, such as WBPs.

Mechanism of forming membrane on substrate is the essence of reducing VOCs for WBPs, which is a chemical process that relies on the polymerization of the polymers compared to that of SBPs which depends on evaporation of solvents. The new types of paints have greatly reduced the VOCs emission. However the disadvantages like low water and solvent resistance, low hardness, poor glossiness, and slow drying rate result in weak feasibility, and thus studies of applying WBPs to different industries specially are still in progress (Zhang et al., 2009; Linder, 2001; Lu et al., 2010; Scalarone et al., 2007). Additionally, a few studies focused on the emission of WBPs and other low-VOCs paints. Geipel and Stephan (2005) reported that the heat-up characteristics and air velocity were the dominated influential factors on drying process of automotive industry using WBPs which are based on fundamental experiments and CFD-software simulation. Zhao et al. (2016) discovered that water-based wall paints with polyvinyl acetate resin emitted more BTEX and carbonyls than paints with acrylic resin, and both of them had highest emissions in the beginning, which then decreased to a much lower level within 3 to 24 h and maintained at 96 h. Personal VOCs exposure concentrations are mostly determined by means of passive stainless steel diffusion tubes containing diverse adsorbents, canisters or active adsorbent tubes (Noelia et al., 2012; Shin et al., 2015; Khanchi et al., 2015; Wu et al., 2012; Delgadosaborit et al., 2009; Park and Jo, 2004; Bratveit et al., 2004). All of them represented the mean values during the sampling period which could be used for health assessment. Nevertheless, real-time concentrations are more important for occupational painters due to its capability of interpreting the influences factors by cooperating with time-activity pattern.

Therefore, it is necessary to investigate the VOCs exposure conditions of occupational painters when they are spraying paints, given the fact that real-time VOCs concentration fluctuates instantaneously with the movement of painters and SBPs/WBPs have different volatility. The objectives of our study are focusing on: (1) determining whether the ambient concentration in workshop can represent real breathing zone concentration; (2) measuring the distinction of exposure levels between SBPs and WBPs, and deduce the influence factors of real-time concentration; (3) establishing a new concept of "total inhalation level" (TIL) specific to occupational painters to calculate VOCs inhalation intake dose concisely. To more important, the TIL could be applied to predict actual and potential exposure level based on consumed paints rapidly and accurately.

2. Material and methods

2.1. Exposure survey

Six industries including automobile manufacturing, bus manufacturing, furniture manufacturing, steel manufacturing, can manufacturing and car repairing were selected as the representatives of painting industry in Beijing, while the numbers of enterprise were 3, 2, 3, 1, 1, 2 respectively. 10 L Tedlar bags were used for collecting air samples in ducts and indoor ambient air near emitting sources, and the flow rate of pump (Beijing Municipal Institute of Labour Protection Air sampler, Model QC-2B) was set at 500 mL/min which meant the total sampling duration of one sample was 20 min. 3.2 L Summa canisters (Entech, 3.2 L Can Silonite TOV-2) were used for collecting air samples in workshops with a flow rate of 54 mL/min adjusted by flow controller (Entech, CS1200E Passive Canister Sampler). The pre-study, namely exposure survey, were conducted during March–June 2016 with the purpose of recognizing the present exposure situation of occupational painters in painting industry.

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