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Health risk assessment of the volatile organic compounds in children's toys

S.H. Sun[1], G.Z. Huang[1*], Y. Wang[2], Q. Bi[3]

[1] *Department of Safety Science and Engineering, School of Civil and Resource Engineering, University of Science and Technology Beijing, China*

[2] *AQSIQ Defective Product Administrative Center, Beijing, China*

[3] *Department of Safety Science and Engineering, School of Civil and Resource Engineering, University of Science and Technology Beijing, China*

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This study focuses on a health risk assessment of volatile organic compounds (VOCs) in Children's Toys. First, the toy samples were collected and analyzed by HS-GC-MS. The geometric mean concentrations of individual VOCs obtained in all of the sampling campaign were 3.987, 6.672, 7.262, 3.756, 3.126 and 3.727 mg/kg for benzene, toluene, ethylbenzene, xylene, dichloromethane and trichloroethylene, respectively. Then, a risk assessment methodology was employed to evaluate the potential adverse health effects of the individual VOCs according to their carcinogenicities. Referring to the EU chemicals exposure model, the exposure and risk representation model were established. Finally, the USEPA model was applied to calculate the risk. The corresponding mean non-carcinogenic risks for benzene, trichloroethylene, dichloromethane, toluene, ethylbenzene and dimethylbenzene were 3.32E-06, 3.10E-06, 1.74E-06, 2.78E-07, 2.42E-07, and 6.26E-08, respectively. With respect to mean cancer risk for trichloroethylene, benzene and dichloromethane were 6.07E-05, 3.99E-05 and 6.69E-06, respectively. In addition, the total carcinogenic risk level of VOCs in toys was 1.07E-04 exceed the maximum acceptable risk level of 10-4 and the total non-carcinogenic risk was 8.75E-06 which exceeds the EPA's acceptable risk level of 10-6.

Key words: Toys; VOCs; Exposure model; Health risk assessment.

INTRODUCTION

The world's largest toy producer is China [1]. However, more and more attention has been paid to the safety of children's toys, due to toy safety hazards and recall problems, in recent years. According to the official website statistics, the U.S.CPSC (Consumer Product Safety Commission) issued a total of unsafe products recall notification 307, including 162 cases of origin in China, children's products 34, accounting for 20.99%; the European Commission issued 1585 notifications through the RAPEX system about a serious risk to health and safety of consumer goods, which children's toys 461 items, accounting for 29.1%. Chemical damage has become one of the main reasons for the recall.

Benzene, dichloromethane, trichloroethylene and other volatile organic compounds (VOCs) with different degrees of toxicity are often used as additives in the production of toys, and this has a huge impact on health when the toys are exposed to the human body. In order to guarantee the children's health and safety, countries all over the world formulated strict laws, regulations and relevant standards for the quality of toy products, which put forward corresponding requirements regarding toxic chemical substances including organic chemical compounds in toys. [2]

There have been extensive studies on the VOCs. For example, J. Hoshi [3], H.T. Nguyen [4] et al. studied on the VOC types and concentrations in urban air. Choi E [5], Cailin Huang [6],Bin Xu[7], Liangui Bai[8], Wolkoff P. [9] et al. studied on the VOCs' health risks of indoor furniture. Some[10-15] scholars tested and evaluated the VOCs generated by the garbage disposal plant. Durmusoglua E[15]studied on the health risk assessment of BTEX emissions in the landfill environment. Xuezhang Chen [16]and Xiaohong Zeng [17]carried on the risk analysis of harmful chemicals in textiles and children's books, respectly. However, there are few studies on the health risk assessment of VOCs in children's toys.

In order to assess the risk of VOCs in toys, this paper will first analyze the scene of exposure. Afterwards, a risk assessment model of VOCs in toys will be established for quantitative calculation, which can then provide a basis for safety management of toys.

EXPERIMENTAL

Sample collection and detection

There are many methods for the determination of volatile organic compounds at home and abroad

To whom all correspondence should be sent:
E-mail: hjxhuanggz@163.com

[18-21]. After the analysis and comparison of the other areas of the determination of volatile organic matter, the method, headspace gas chromatography coupled with mass spectrometry (HS-GC-MS), was adopted to detect the residues of 8 kinds of volatile organic compounds such as benzene series in toys.

65 toy samples were collected from domestic market, 35 plastic toys and 30 plush toys. The detection results showed that 31 of the 65 samples were in the detection limit of the organic volatile matter content. The geometric mean concentration of VOCs in children's toys were 3.987, 6.672, 7.262,3.756, 3.126 and 3.727 mg/kg for benzene, toluene, ethylbenzene, xylene, dichloromethane and trichloroethylene, respectively.

EXPOSURE ASSESSMENT

Exposure scenario

The route and level of exposure to chemicals in toys is linked to both the physico-chemical properties of the chemical and how the toy is used by the child, which can be described through exposure scenarios. These scenarios usually include environmental exposure, route of exposure, the exposed population, chemical property, absorption rate and other factors. Concentrations of chemicals can be determined by sampling and analysis of samples. When resources are limited, concentrations can be estimated by using a trend model [22]. Human behavior characteristic information can be obtained through hypothesis or survey questionnaire by selecting a part of representative populations. Some of these exposure parameters are found in the "exposure factors handbook" promulgated by the USEPA.

For the volatile organic compounds in toys, respiratory exposure and oral exposure are the main exposure pathways to human. It should be noted that mouthing behavior studies demonstrated that children place a broad range of items in their mouths, including toys [23-24]. Although the dimensions of some toys may be such that they cannot be placed in the mouth, ridges can still be sucked on. Therefore, mouthing of toys is an important exposure scenario. VOCs in toys can evaporate into the air indoor and may cause local effects in the lung, so respiratory exposure scenarios should also be considered.

Children are the main group exposed to toys. As a special group of people, they are more sensitive and vulnerable to harmful substances than adults. Exposure frequency and exposure time for toys can be different for children of different ages. Most studies have shown that mouthing of toys often occurs in children under 6 years old. In consideration of the worst scenario, this paper mainly studied the children under this age.

Exposure model and exposure parameters

Based on the relevant exposure scenarios which have been analyzed above, the exposure to chemicals can be assessed by using the applicable mathematical formulas and the appropriate values of the variables, or exposure factors.

Oral exposure Uptake of VOCs in toys via the oral route can be calculated by the following steps:

To calculate the intake of the organic volatile compounds in toys via oral route:

$$I_{\mathrm{oral}} = C \times \frac{S_0}{S} \times Q \times ABS \times ED \times \mathrm{n} \qquad (1)$$

Where C is the concentration of volatile organic compounds in toys, mg/kg; S0is the contact area with the mouth, cm^2; S is the toy's area, cm^2; Q is the toy's weight, kg; ABS is the percentage of the migration; ED is the exposure duration, d; and n is the mouthing frequency, event/d.

To calculate the daily exposure dose per unit of body weight:

$$E\mathrm{x}_{\mathrm{oral}} = I_{\mathrm{oral}} \times \frac{1}{BW \times AT} \qquad (2)$$

Where BW is body weight, kg; AT is the averaging time, d.

Breathing exposure Organic volatile compounds in toys will spread in the air, which will not only affect the health of children, but also can produce toxic effects to adults to a certain extent. The dose of VOCs inhaled via the respiratory pathway can be calculated by the following steps:

To calculate the intake of the VOCs in toys via respiratory patterns:

$$I_{\mathrm{inh}} = C \times Q/V_{\mathrm{m}} \times F_v \times D \times IR \times ET \times ED \qquad (3)$$

Where V_m is the space volume around the body, m^3; F_v is the volatile coefficient, unitless; D is the dilution factor, unitless; Q is the weight of the toy, kg； IR is the respiratory rate, m^3/h; ET is the exposure time, h/d; and ED is the continuous exposure time, d.

To calculate the daily exposure dose per unit of body weight:

$$E\mathrm{x}_{\mathrm{inh}} = I_{\mathrm{inh}} \times \frac{1}{BW \times AT} \qquad (4)$$

where C, Q, ED, BW and AT are the same variables as mentioned above.

Exposure parameters

Exposure parameters are key parameters in the assessment of exposure and health risk; they are critical in determining whether the assessment itself is accurate and scientific. The United States, the European Union, Japan, South Korea and other countries have issued their own exposure factors handbooks. However, due to the differences in race, living habits and other aspects, the foreign exposure parameters cannot represent the residents' exposure characteristics and behavior in China[25]. China has not yet promulgated its own exposure manual, but according to the existing research, the exposure parameters of the children's toys in China can be estimated.

The parameter values in exposure assessment are listed in Table 1.

Table 1. Parameter values in the exposure model.

Parameters	Unit	Value
Toy's weight Q	kg	1
Toy's area S	cm2	1000
Contact area with the mouth S0	cm2	10
Migration percentage ABS	-	1
Mouthing frequency n	event/d	4
Space volume around body Vm	m3	225
Volatile coefficient Fv	-	1
Dilution factor D	-	1
Respiratory rate IR	m3/h	0.25
Exposure time ET	h/d	12
Exposure duration ED	d	365×6
Average time AT	d	2190
Lifetime LT	d	25550
Average body weight BW	kg	16

Dose-response

Dose-response parameters of the organic volatile compound in toys include reference dose of RfD and the slope factor of SF and both of them come from USEPA's integrated risk information system (IRIS) [26].

RISK CHARACTERIZATION

Carcinogenic risk

In consideration of the various exposure pathways of chemical carcinogen, the health risk model of carcinogenic pollutant [27-28] can be calculated as:

$$R^{c}{}_{ij} = 1 - \exp(-SF_{i} \times Ex_{ij}) \qquad (5)$$

where Rc_{ij} is the cancer risk of its chemical carcinogen through the exposure pathways, unitless; Ex_{ij} is the daily exposure dose per unit of body weight for its chemical carcinogen via the exposure pathways, mg/(kg·d); and SF_{ij} is the carcinogenic potency factor of its chemical carcinogen through the exposure pathways, [mg/(kg·d)]-1.

The total carcinogenic risk of a variety of carcinogens via various exposure routes can be calculated as follows:

$$R^{c} = \sum_{i} \sum_{j} R^{c}_{ij} \qquad (6)$$

Non-Carcinogenic risk

The health risk model of non-carcinogenic pollutant [29] can be calculated as:

$$\mathrm{R}^{nc} = \frac{Ex}{Rfd} \times 10^{-6} \qquad (7)$$

Where Rnc is the no-carcinogenic risk, unitless; Ex is the daily exposure dose per unit of body weight for non-carcinogenic pollutants, mg/(kg·d); and RfD is the reference dose of the specific chemical substance, mg/(kg·d).

The total no-carcinogenic risk of a variety of no-carcinogens via various exposure routes can be calculated as:

$$R^{nc} = \sum_{i} \sum_{j} R^{nc}_{ij} \qquad (8)$$

RESULTS AND DISCUSSION

Risk analysis

The non-carcinogenic risk levels of 3 non-carcinogens and 3 carcinogens were calculated using the established risk characterization model of the toys. The results are shown in Table 2.

Table 2. Non-carcinogenic risk levels of VOCs in toys for children aged 1-6.

Exposure pathways	Toluene	Ethylbenzene	Dimethylbenzene	Benzene	Dichloromethane	Trichloroethene
Oral	2.09E-07	1.82E-07	4.70E-08	2.49E-06	1.30E-06	2.33E-06
Inhalation	6.95E-08	6.05E-08	1.57E-08	8.31E-07	4.34E-07	7.77E-07
Sum	2.78E-07	2.42E-07	6.26E-08	3.32E-06	1.74E-06	3.10E-06

Table 2 illustrates that non-carcinogenic risk ranking result of VOCs in toys is benzene>trichloroethylene > dichloromethane> toluene> ethylbenzene> dimethyl benzene and the risk values are 3.32E-06, 3.10E-06, 1.74E-06, 2.78E-07, 2.42E-07, 6.26E-08, respectively. The risk of toluene, ethylbenzene and dimethylbenzene are less than EPA's negligible risk level of 10-6, so these three kinds of volatile organic compounds do not cause non-cancer health effects on the human body. The non-carcinogenic risk level of benzene, trichloroethylene and dichloromethane were within the USEPA's acceptable risk level of the scope of 10-4~10-6 [30] but there also have potential risk to human body.

The carcinogenic risk levels of 3 kinds of carcinogens were calculated using the established risk characterization model of the toys. The results are shown in Table 3.

Table 3. Carcinogenic risk levels of VOCs in toys for children aged 1-6.

Exposure pathways	Benzene	Dichloromethane	Trichloroethene
Oral	2.99E-05	5.02E-06	4.55E-05
Inhalation	9.97E-06	1.67E-06	1.52E-05
Sum	3.99E-05	6.69E-06	6.07E-05

Table 3 illustrates that the carcinogenic risk ranking result of VOCs is trichloroethylene>benzene>dichloromethane and the risk values are 6.07E-05, 3.99E-05 and 6.69E-06, respectively. The risk levels are within the scope of 10-6~10-4, which shows that there is a potential carcinogenic risk to children. In the research of Zhang Qing et al. [31], the carcinogenic risk of benzene is ranging between 1.77E-06 to 5.98E-05 range. The research conclusion of this paper, the carcinogenic risk of benzene 3.99E-05, is just in this section.

The non-carcinogenic and carcinogenic total risk values of VOCs in toys on humans are calculated and compared, and the results are 8.75E-06 and 1.07E-04, respectively. The result illustrates that Rc (carcinogenic total risk level of VOCs in toys) >Rnc (non-carcinogenic risk level of VOCs in toys) and the Rc is 12.3 times as much as Rnc, which shows that cancer risk is the main risk of VOCs in toys. In the risk management of toxic and hazardous substances in toys, the carcinogen should be the first consideration.

It should be also noticed that total carcinogenic risk level exceeds the maximum acceptable risk level of 10-4 and non-carcinogenic risk level exceeds 10-6, which may have great impact on the health of children. Relevant government departments should pay close attention to the risk of VOCs in toys.

CONCLUSION

In this paper, the individual exposure risks of 6 kinds of VOCs were evaluated. The results show that the non-carcinogenic risk ranking for VOCs in toys is benzene > trichloroethylene > dichloromethane > toluene > ethylbenzene > xylene and the risk values are 3.32E-06, 3.10E-06, 1.74E-06, 2.78E-07, 2.42E-07, 6.26E-08, respectively. On the other hand, the carcinogenic risk ranking is trichloroethylene> benzene> dichloromethane and the risk values are 6.07E-05, 3.99E-05 and 6.69E-06, respectively. The carcinogenic and non-carcinogenic risk for dichloromethane, trichloroethylene and benzene were between 10-6 and 10-4, which indicates that there is potential risk to human. The total carcinogenic risk level of VOCs in toys is larger than total non-carcinogenic risk level, and the average values are 1.07E-04 and 8.75E-06, respectively, exceed the maximum acceptable risk level of 10-4 and 10-6. This indicates that there will be great impact on the health of children. Relevant government departments should pay close attention to the risk of VOCs in toys.

It should be noted that the human health risk assessment is an iterative process having lots assumptions. Health risks may have been overestimated or underestimated due to the fact that the risks calculated based on the chemical concentrations measured in a short time were compared to specified risks developed based on the toxicological data established for exposures over a lifespan. On the other hand, the potential cumulative effects and combined effects of each volatile organic compound should be evaluated. The uncertainties in toxicological indices also contributed to overestimating or underestimating risks. We still need to make a deep study of this direction.

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