BTEX compounds in screen printing risk assessment on occupational health

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Abstract: In the printing facilities different chemicals (varnishes, adhesives, inks, cleaning agents) are used and they all have a negative impact on employees' health and the environment. The aim of the paper is to examine levels of benzene, toluene, ethyl-benzene and o- m-, p- xylene (BTEX) in the air of the working area where the process of screen printing takes place, as it is the most toxic technique since the inks used in screen printing contain several volatile organic compounds. Also, most of screen printing industry in Serbia have not automated the processes of printing form preparation, printing and screen cleaning after printing. Air samples were taken in the breathing zone of employees ~ 150 cm above ground level during the operations of preparing, printing and screen washing for two seasons. Identification and quantification were performed using the GC-FID technique. The paper also presents the average concentration of exposure, the individual effect and the cumulative effect of ethyl-benzene, m + p xylene and o- xylene. The maximum value for average exposure concentration (AEC) was measured for m + p xylene 16.99 ppm, individual effect (IE) was 0.16, and the additive effect of these three pollutants was 0.278. Concentrations of BTEX compounds were below the acceptable national and international exposure limits. Although the concentrations were below the permissible value, most printing shops work eight hours a day five days a week. In these conditions, the risks of exposure of employees cannot be negligible.

Key words: screen printing, pollutant, GC-FID technique, exposure limit

1. Introduction

The indoor air of an industry can be contaminated, depending on the kind of activities occurred, the emissions of the sources and the type of equipment used (Saraga *et al*., 2011). Respiratory and cardiovascular problems, even potential carcinogenicity have been reported after long-term exposure to certain indoor air contaminants. Screen printing is a printing process in which printing ink, coating or adhesive material is passed through a taut web or fabric to which a refined form of stencil has been applied. The stencil openings determine the form and dimensions of the imprint (OSHA, 2015). It is a well known fact that in the printing process hazardous substances occur in the air, threatening human health. The materials containing hazardous air pollutants HAPs used in the screen printing are the printing inks, coatings, adhesives and cleaning solvents. Other HAPs emission sources of screen printing production include the operations of washing machines, binding and finishing equipment, and some prepress equipment (Kiurski *et al*., 2013).Volatile organic compounds (VOCs) are an important class of air pollutants which can react with ozone and OH radicals to generate HOx (HOx = OH, HO_2, RO_2), organic acids, peroxides, and other products. VOCs are common in various fields with biogenic or other hazardous effects. The volatile organic compounds, include a large group of air pollutants such as benzene, toluene, xylene, acetone, isopropanol, methyl ethyl ketone. Workers can be exposed to contaminants by inhalation, ingestion, and dermal contact. Inhalation exposure to air pollutants is the most significant pathway compared to other exposure pathways. (Guo *et al*., 2004).

Most typical exposure to benzene is through inhalation and in the later stages through ingestion and skin. Benzene is carcinogenic and chronic exposure to it causes leukaemia and other cancers. Toluene is absorbed immediately after inhalation and ingestion and causes the systemic effects but it is more slowly absorbed through the skin. Xylene is a solvent liquid that is clear and sweet taste. Its vapour can be a stimulus for the eyes, nose, throat, skin, mucous membranes. Chronic occupational exposure to unspecified concentrations of its vapours causes difficulties in breathing and damage to lung function. During contact with the skin or inhalation Ethyl benzene can be rapidly absorbed.

The scientific interest is focused on different characteristics of the sources located or the activities occurred in the environments of different use without excluding the outdoor environment's contribution.

The purpose of this study was to examine the level of BTEX compounds in the breathing zone of workers using gas chromatography with flame ionization detection (GC-FID). Additionally, based on the variability of the activities that occur in indoor environment, this study aims at identifying the main sources contributing to the measured volatile organic compounds concentrations.

2. Materials and Methods

The experimental part of this work shows:

determination of benzene, toluene, ethyl-benzene and xylene (BTEX compounds) in samples of air taken in the breathing zone of workers using gas chromatography with flame ionization detection (GC-FID) and the determination of volatile organic compounds by means Voc Pro Photovac.

2.1. Sampling locations

Concentrations of VOCs were determined in indoor air at four screen printing industries, located on the territory of Novi Sad. Sampling of volatile organic compounds benzene, toluene, ethyl benzene and xylene (BTEX) was done in the screen printing also but in three enterprises.

The printing facility is located in the city of Novi Sad. It is a typical building, of 30 m^2 in size and it employs a total of 9 workers, two workers were employed in the printing room one, five workers in the printing room 2 and two workers in the printing room 3. All workers were in charge of all operations in the printing facility. All printing facilities consist of three rooms: a room for the reception of clients, a special part for printing and a separate small room in which the screens are washed. The rooms for screen printing are equipped with the screen, a table for ironing T-shirts, a table for prepress and for making patterns, a table for material disposal and a stripe for drying imprints. The printing facilities are not equipped with ventilation system. Scope of production depends on business volume and on the type of the printing material. One of screen printing facilities is represented in the Figure 1. Materials used in the work process are the porous meshes (stretched tightly over a metal frame), paper, cardboard, emulsions, inks, oil and PVC colors, solvents and adhesive.

2.2. Air sampling

Air samples were collected using the procedure described in the NIOSH 1501 (NIOSH, 2003). Apex Personal Air Sampling Pump was used for air sampling. Sampling lasted for 10 min, at the flow rate of 1 l/min on charcoal tubes as sampling media. Air samples were taken from standing breathing zone of employees, about 150 cm above the ground level. Blank samples were also collected in the same manner, but pump was turned off. After sampling, samples and blanks were separated stored and taken to the laboratory and stored in refrigerator at -200 °C until the analysis.

2.3. Sample preparation

Desorption of BTEX compounds from charcoal tubes was performed using carbon disulfide (CS2) as solvent. After removing the plastic end caps of the tube and removing glass wool, front and back absorbent of tube were transfer into separate vials of 2 ml volume. Adding 1.5 ml of solvent to each vial, vials were gently shaken in the shaker (IKA) 30 min.

2.4. Instrumental analysis

Gas chromatograph Agilent, 7890A equipped with the flame-ionisation detector (GC-FID) was used for analysis of the BTEX. Gas-chromatographic separation of BTEX was performed by using a column HP-5MS column (Agilent, 30 m, 0.25 mm id., 0.25µm film thickness) and helium as a carrier gas. The injection volume was 1µl in the splitless mode. Inlet and detector temperature were 230 and 300°C, respectively. The oven temperature program was as follows: initial temperature 40°C held for 2 min, increased to 230°C at 20°C/min, held for 2 min.

Measuring total volatile compounds in the air of the screen printing facilities was carried out by means of device Voc Pro Photovac (serial number: VPAJ006; manufactured by Casella, England). Scope of measurement of this device is from 0,1 – 20.000 ppm, measuring range from -20 to +250 (°C), operating temperature ranging from 0 to 40 (°C), inlet flow above 300 ml/min, nickel-cadmium rechargeable battery, device accuracy at 2 ppm, response time 3 seconds.

Figure 1. Appearance of screen printing

3. Results and discussion

Figure 2 shows changes in the concentration of measured total values of easily volatile organic compounds during summer period at a workplace: screen washing. Highest concentrations of easily volatile organic compounds are detected when screens are washed due to the use of solvents in the printing room 2 where it amounts to 72.9 ppm, then in the printing room 4 where it amounts to 53.9 ppm and in the printing room 3 where it amounts to 48.3 ppm.

Obtained results of BTEX compounds in tested facilities for screen printing are presented in Table 1. The results recorded represent an average concentration of three measurings. Benzene and toluene were not detected in either of the printing rooms. Ethyl-benzene was not detected in the printing room 1, while in the printing room 2 the concentration of ethyl-benzene was ranging between 1.09 and 8.41 mg/m^3 (average value at 3.92 mg/m^3) during summer and from nd to 5.21 mg/m^3 (average value at 2.49 mg/m^3) during winter. Ethyl-benzene was not detected in the printing room 3 during summer, while the concentration was ranging between 1.25 and 4.98 mg/m^3 (average value at 3.03 mg/m^3) in winter. Concentration of xylene in the printing room 2 was ranging from 6.20 to 52.9 mg/m^3 (average value at 24.5 mg/m^3) in summer, while in winter it was ranging from nd to 33.3 mg/m^3 (average value at 15.9 mg/m^3). In the printing room 3 the sums of xylene were ranging from 0.46 to 1.81 mg/m^3 in summer (average value at 1.12 mg/m^3), while in winter it is ranging from 10.07 to 49.5 (average value at 27.9 mg/m^3). Maximum concentrations of compounds were measured while washing the screen. The use of the solvent wile washing the screen is potentially the main source of these compounds in the air of the screen printing room. When results obtained from measuring are compared to a limit presented in the Rulebook on prevention measures for safe and healthy work when exposed to chemical substances, we can conclude that concentrations are under the permissible limit of exposure (PEL). The maximum value for average exposure concentration (AEC) was measured for m + p xylene 16.99 ppm, individual effect (IE) was 0.16, and the additive effect of these three pollutants was 0.278. Concentrations of BTEX compounds were below the acceptable national and international exposure limits. The maximum value for average exposure concentration (AEC) is calculated by the following formula:

$$AEC = \frac{(C_1T_1 \pm C_2T_2 .....C_nT_n)}{T_1 \pm T_2 \pm .....T_n}$$

where: Cn is the concentration measured in the workplace; Tn is the time of the sampling period (15min);1,2,…, n are indications of the sampling period and

Due to the exposure to a single organic and inorganic substance and a mixture of substances the adverse health effects can be determined by the individual effect (IEi) and the additive effect (AE), respectively, expressed by formula

Table 1 Average values of BETEX compound in

$$IE_i = \frac{AEC_i}{PEL_i}$$

$$AE = \sum IE_i = \sum_i \frac{AEC_i}{PEL_i}$$

where AECi and PELi are average exposure concentration of VOC.

Average values of benzene, toluene, ethyl benzene, o-, and m+p-xylene are presented in the following table.

Binding limit values of exposure to chemical substances at a workplace in the Republic of Serbia are regulated by the Rules on prevention measures for safe and healthy work while exposed to chemical substances (RS Official Gazette No. 106/09), and the Rules on prevention measures for safe and healthy work while exposed to carcinogenic and mutagenic substances (RS Official Gazette, No. 96/2011) . Table 2 shows limit values of BTEX compounds at a workspace

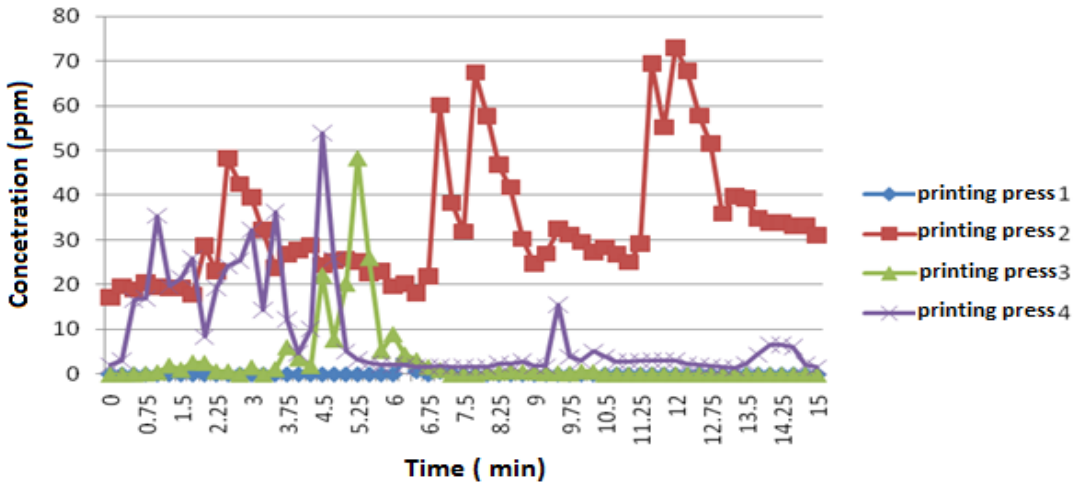

Figure 2. Change in concentration of VOC compounds in the air of printing rooms over time

Table 1. Average values of BTEX compounds in the air of printing facilities in Novi Sad (mg/m^3)

Screen printing industry		No. 1	No. 2	No. 3
benzene	Summer	nd	nd	nd
	Winter	nd	nd	nd
toluene	Summer	nd	nd	nd
	Winter	nd	nd	nd
Ethyl benzene	Summer	nd	3.92	nd
	Winter	nd	2.49	3.03
m+p-xylene	Summer	nd	17.0	nd
	Winter	nd	11.8	21.8
o- xylene	Summer	nd	7.50	1.12
	Winter	nd	4.14	6.20
m+p+o-xylene	Summer	nd	24.5	1.12
	Winter	nd	15.9	27.9

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Table 2. Limits of exposure to BTEX compounds by Rulebooks

Rulebook	EINECS No.	CAS No.	Name of substance	Limit values			
				PEL		STEL	
				mg/m3	ppm	mg/m3	ppm
(1)	200-753-7	71-43-2	Benzene	3,25	1		
	203-628-9	108-88-3	Toluene	192	50	384	100
	202-849-4	100-41-4	Ethyl-benzene	442	100	884	200
	203-876-3	108-38-3	m-xylene	221	50	442	100
	202-422-2	95-47-6	o-xylene	221	50	442	100
	203-396-5	106-42-3	p-xylene	221	50	442	100
(2)	200-753-7	71-43-2	benzene	3,25	1		

Key:

1 – Rules on prevention measures for safe and healthy work while exposed to chemical substances,

2 – Rules on prevention measures for safe and healthy work while exposed to carcinogenic and mutagenic substances,

EINECS No. – identification number from European Inventory of Existing Commercial Chemical Substances.

CAS No. – identification number from Chemical Abstracts Service.

4. Conclusion

As it is apparent from these results, ethyl-benzene and xylenes were detected only in the printing room 2 and there they are within the limits of permissible exposure stated in the Rules on prevention measures for safe and healthy work while exposed to chemical substances. Although the concentrations were below the permissible value, most of the printing shops work eight hours a day five days a week. In these conditions, the risks of exposure of employees cannot be negligible. However, it is of great importance that the employees follow the rules of protection measures, so as to avoid health and safety hazard while performing their tasks at the workplace. It is very important that the employees be informed about all risks and hazards typical of their workplace and trained to react in risky circumstances.

By following all stipulated prevention measures of protection, by using personal safety gear and by substituting harmful chemical by those which are less harmful work conditions will be improved while the likelihood of the occurrence of hazard will be reduced.

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