Detection and Quantification of Ozone in Screen Printing Facilities

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***Abstract*—**Most often the contaminants are not taken seriously into consideration, and this behavior comes out directly from the lack of monitoring and professional reporting about pollution in the printing facilities in Serbia. The goal of planned and systematic ozone measurements in ambient air of the screen printing facilities in Novi Sad is to examine of its impact on the employees health, and to track trends in concentration. In this study, ozone concentrations were determined by using discontinuous and continuous method during the automatic and manual screen printing process. Obtained results indicates that the average concentrations of ozone measured during the automatic process were almost 3 to 28 times higher for discontinuous and 10 times higher for continuous method (1.028 ppm) compared to the values prescribed by OSHA. In the manual process, average concentrations of ozone were within prescribed values for discontinuous and almost 3 times higher for continuous method (0.299 ppm).

***Keywords*—**indoor pollution, ozone, screen printing

I. Introduction

OZONE has two antagonistic effects in the Earth's atmosphere. In the tropospheric layer of the atmosphere ozone is a dangerous pollutant, but in the stratospheric layer it prevents penetration of harmful ultraviolet rays to the Earth. Without stratospheric ozone life on Earth would not have been possible. Tropospheric ozone is in direct contact with living organisms, damaging the surface tissue of plants and animals, and it is harmful to human health (respiratory system). It is known that ozone has negative effect on metals, construction materials, rubber, polymeric materials, lacquered materials, etc [1]-[2]. Due to the increased traffic, as a powerful source of volatile organic compounds, the amount of ozone in the troposphere has been growing steadily. All electric motors that use brushes create a certain amount of ozone is more or less proportional to the size and engine power. Also, many electric devices can generate ozone, especially those that use high voltage, such as laser and ink-jet printers, and photocopiers. It is unknown fact in Serbia that screen printing facilities produces ozone.

Screen printing is arguably the most versatile of all printing processes. It can be used to print on a wide variety of substrates, including paper, paperboard, plastics, glass, metals fabrics, and many other materials. Because of the simplicity of the application process, a wider range of inks and dyes are available for use in screen printing than for use in any other printing process. This has been a result of the development of the automated and rotary screen printing press, improved driers, and UV curable ink. UV drying inks are cured by polymerization with UV lamps. The rate of screen printing production was once dictated by the drying rate of the screen printing inks. Nevertheless, there are still existing potential hazardous resulting from the UV light, the possible appearance of ozone, cleaning agents and the UV ink itself [3]-[4]. Ultraviolet lamps have been used for decades to generate ozone. This lamp emits UV light at 185 nm. Ambient air is passed over an ultraviolet lamp, which splits oxygen (O_2) molecules in the gas. The resulting oxygen atom (O), seeking stability, attach to other oxygen molecules (O_2), and forming ozone (O_3).

UV lamps are not the only generator of ozone in the screen printing facilities. Liquid printing materials such as inks, solvents, varnishes, and cleaning products are producing volatile organic compounds and have a large impact on ozone production. Environmental emission of high-VOC solvents may cause ground level ozone formation and same may contribute to ozone depletion [5]. Ozone formation in a polluted printing environment is mainly caused by photochemical reactions between volatile organic compounds (VOCs) and nitrogen oxides NO_x according to the following equation [6]:

$$NO_x + VOC + h\nu \rightarrow O_3 + B \qquad (1)$$

where are B - other compounds and hν - lights quantum.

It is generally known that for some conditions the process of ozone formation is controlled almost entirely by NO_x and is largely independent of VOCs concentration. Whereas, in other conditions, ozone production increases with increasing of VOCs concentration and does not increase (or sometimes even decreases) with increasing NO_x concentration. However, it has been difficult to determine whether ozone production during specific events is associated with NO_x-sensitive chemistry or VOC-sensitive chemistry. Particulates and other secondary air

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pollutants also show a complex dependence on NO_x and VOCs concentrations [7].

Concentration of ozone inside depends on concentration of ozone outside. Proportion of these concentrations depends on many factors which are the following: air infiltration or air exchange between environment levels, circulation of air indoor, structure of room surfaces, ozone reaction with other chemical compounds, daytime, season etc. [8]-[10]. Many published studies reported that indoor air pollutant concentrations are higher than those observed outdoor [11]. Currently, investigations are being conducted on indoor air pollution as increasingly number of people which spend more and more time living in confined areas [12]. Photochemical pollutants, such as ozone, affects human health, irritating to the eyes, nose and throat, causing coughing being above the exposure limits. The workers exposure to ozone depends on the concentration levels of ozone, exposure time, and ventilation systems installed in the printing facility [13]-[14].

In this study, the concentrations of ozone were discontinuous and continuous measured during working time (8-24 hours), in order to investigate the level of exposure of the employed workers in screen printing facilities in Novi Sad.

II. Materials and Methods

A. Reagents

All the chemicals used were of analytical reagent grade (Merck, Germany). Throughout the experiments deionized water was used.

B. Ozone Discontinuous and Continuous Measurements

The detection and quantification of ozone using discontinuous method was performed *in situ* during working time (8 hours) by ozonometer, Aeroqual Series 200, Aeroqual Ltd. In the continuous method ozone was collected during 24 hours, by air sampler PRO-EKOS AT. 401X. The ambiental air was infiltrate through the gas washing bottles (acc. to Drechsel) with filterdisks containing absorption solution for ozone (1% potassium iodide in 0.1 M sodium hydroxide). Ratio of air flow was from 0.2 to 0.4 dm^3/min. By adding a phosphorus-sulfamine reagent the iodine was dispose, and the intensity of the yellow colored absorption solution was determined by spectrophotometric measurement of absorbance at 352 nm. The concentrations of ozone were directly determined from the calibration curve using the standard solution of potassium iodate (8.85 M), such as 1 cm^3 of this solution is equivalent to 0.1 cm^3 of ozone [15]. Based on the determined concentrations of ozone and the amount of air transmitted through the absorbing solution, unknown ozone concentrations in ambient air of the screen printing facilities in Novi Sad were calculated.

Microclimate during discontinuous and continuous methods of ozone was measured by an instrument Mannix DLAF-8000.

III. Results and Discussion

Concentration levels of ozone were determined in two small screen printing facilities (4-12 employers) in Novi Sad, Serbia. The screen printing process in printing facility 1 is automatic with a significantly higher production compared to printing facility 2 with manual process. The production process in screen printing facility 1 is shown schematically in Fig. 1. Also, Fig. 1 shows the locations of sampling points for discontinuous measurement (locations 1-5) and location of air sampler for continuous measurement (location X).

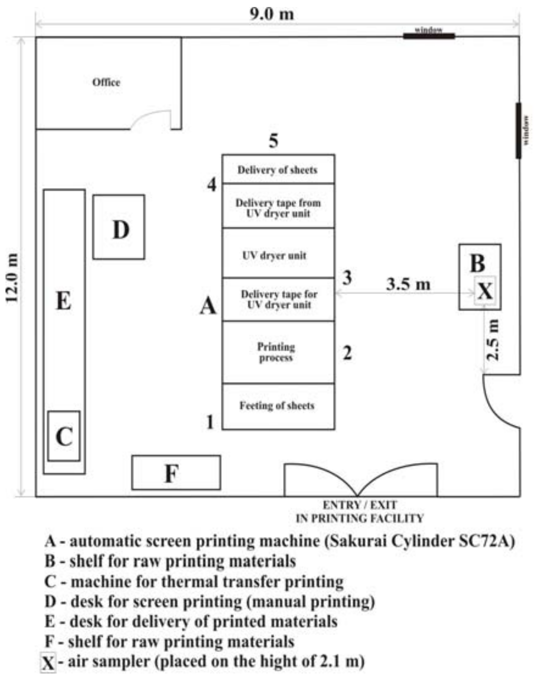

Fig. 1 Scheme of screen printing facility 1

Whereas, the locations of sampling points for discontinuous measurement (location 6) and location of air sampler for continuous measurement (location Y) in screen printing facility 2 are shown in Fig. 2.

The positions of sampling points during discontinuous method were determined by the technical characteristics of screen printing machine. Number of sampling points during discontinuous method was different, due to the type of production process (automatic and manual). Description of sampling points in two screen printing facilities is given in Table I. During continuous method, air was sampled from one sampling point. There is no official standard layout of machines in the screen printing facility. The positions of air sampler during continuous method was determined by positions screen printing machine and UV lamps as well as characteristics of the printing area in which is housed the production process.

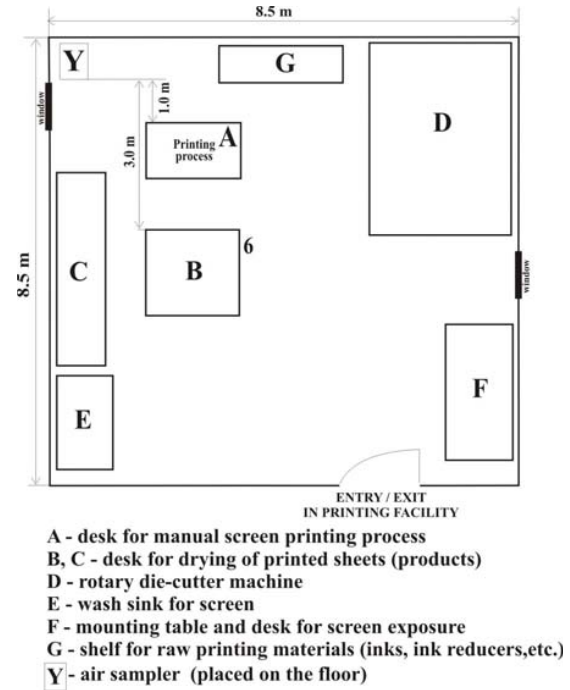

Fig. 2 Scheme of screen printing facility 2

In screen printing facility 1 air sampler was placed on distance 3.5 m (location X) from screen printing machine, and 1 m from entrance at a height of 2.1 m. In screen printing facility 2 air sampler was placed on the floor for distance 1.0 m and 3.0 m from desk for manual screen printing process and desk for drying products, respectively (location Y).

TABLE I
DESCRIPTION OF SAMPLING POINTS FOR DISCONTINUOUS MEASUREMENT

Sampling point	Description
1	Fitting of sheets
2	Printing process
3	Entrance to the UV drying unit
4	Exit from UV drying unit
5	Delivery of sheets
6	Desk for manual screen printing process

Values of ambiental parameters, temperature, light intensity and relative humidity varied from 22.3 to 23.8°C, from 58 to 402 lx and from 44.5 to 49.4%, respectively, in automatic screen printing facility. Whereas, in manual screen printing facility temperature, light intensity and relative humidity were 22°C, 388 lx and 50.5%, respectively.

The results of discontinuous measurements of ozone concentrations during working time (8 hours) in printing facilities 1 and 2 are presented in Table II.

Ozone concentrations at the sampling points 1 and 2 (Table II) were in range from 0.436 to 0.738 ppm and 0.436 to 0.794 ppm, respectively. Concentrations of ozone at sampling points 3 and 5 (Table II) were in range from 0.695 to 0.812 ppm and 0.794 to 0.812 ppm, respectively. The detected concentrations at the sampling points 1 and 2 are in similar intervals of values, as well as concentrations detected at the sampling points 3 and 5.

TABLE II
OZONE CONCENTRATIONS DURING 8 H DISCONTINUOUS IN PRINTING FACILITIES 1 AND 2

Sampling time (h)	Ozone concentrations (ppm)						
	Sampling facility	Automatic*					Manual**
	Sampling point	1	2	3	4	5	6
1		0.436	0.647	0.812	0.213	0.812	0.118
2		0.647	0.541	0.754	0.775	0.803	0.085
3		0.738	0.712	0.695	1.041	0.794	0.080
4		0.712	0.695	0.712	1.332	0.000	0.090
5		0.689	0.738	0.775	2.228	0.000	0.058
6		0.647	0.436	0.812	8.132	0.000	0.000
7		0.689	0.647	0.803	8.503	0.000	0.018
8		0.712	0.794	0.794	0.000	0.000	0.000

* Automatic screen printing process, printing facility 1
** Manual screen printing process, printing facility 2

Higher concentration levels of ozone were detected at the sampling points 3 and 5 as a result of a short distance from the UV drying unit. The highest concentration levels of ozone in the automatic printing process for discontinuous method were detected at the sampling point 4. Ozone concentrations on sampling point 4 were in range from 0.213 to 8.503 ppm. High concentrations of ozone were generated by UV lamps during the drying of final products. After completing of the printing process and termination of automatic screen printing machine and UV lamps ozone concentrations were reduced to 0 ppm. The ozone concentrations dependence on the sampling time during discontinuous measurements in automatic screen printing process (printing facility 1) is shown in Fig. 3.

Significantly lower concentrations of ozone were detected in a manual screen printing facility, primarily as a result of remarkably lower production volume compared to the automatic screen printing process. The manual process of screen printing does not use UV lamps. In the absence of powerful sources of ozone, such as UV lamps, we assume that the detected amounts of ozone originate from VOCs emitted by liquid printing materials. Concentrations of ozone during the manual process were in range from 0.018 to 0.118 ppm.

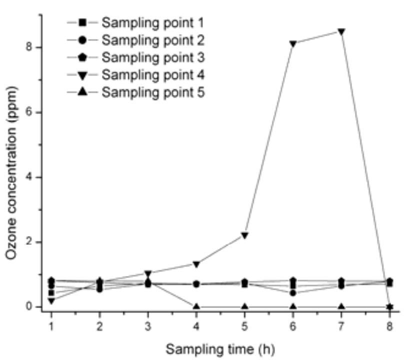

Fig. 3 Ozone concentrations during 8 h discontinuous measurements in printing facility 1

Fig. 4 represents the ozone concentrations dependence on the sampling time during discontinuous measurements in manual screen printing process (printing facility 2).

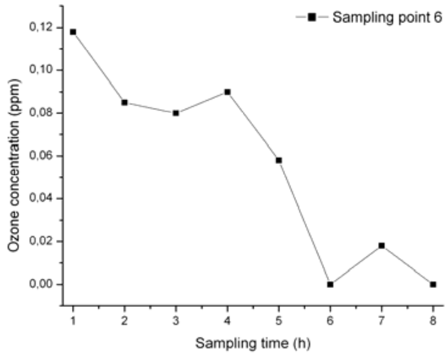

Fig. 4 Ozone concentrations during 8 h discontinuous measurements in printing facility 2

The average ozone concentrations measured during the automatic process at six sampling points (locations 1-6) for discontinuous method were 0.659, 0.651, 0.770, 0.778 and 0.301 ppm, respectively. Whereas, the average ozone concentrations in the manual process was 0.056 ppm (Table III). Table III also shows the concentration values of ozone obtained by continuous method.

TABLE III
AVERAGE OZONE CONCENTRATIONS DURING 8 H DISCONTINUOUS AND 24 H CONTINUOUS MEASUREMENTS IN PRINTING FACILITIES 1 AND 2

Sampling time (h)	Average ozone concentrations (ppm)						
	Sampling facility	Automatic*					Manual**
	Sampling point	1	2	3	4	5	6
8		0.659	0.651	0.770	2.778	0.301	0.056
24				1.028			0.299

* Automatic screen printing process, printing facility 1
** Manual screen printing process, printing facility 2

Average ozone concentrations in automatic and manual process were 1.028 and 0.299 ppm, respectively. Comparison of the results obtained by the discontinuous and continuous method is shown at Fig. 5.

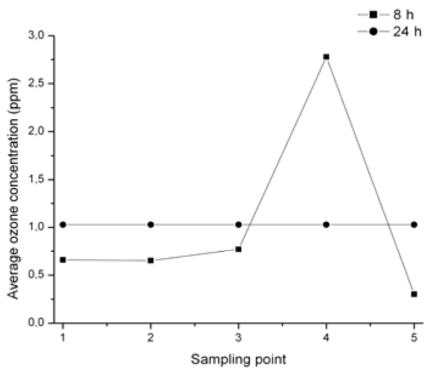

Fig. 5 Average ozone concentrations during 8 h discontinuous and 24 h continuous measurements in printing facility 1

As can be seen from Table III and Fig. 5, the average ozone concentrations quantified by continuous method during the automatic process are almost 3 times higher than in the manual process. The average values of ozone concentration quantified by the discontinuous method, in automatic screen printing process, are almost 5 to 50 times higher than in the manual process. High ozone concentrations in automatic process are in a relation with the presence of UV lamps and the high-volume production.

According to the Occupational Safety and Health Administration (OSHA), time weighted average (TWA) of ozone in workplace air is 0.1 ppm [16], and we can conclude that ozone concentration levels in screen printing facilities are much higher. The average ozone concentrations during 24 hours continuous measurements were almost 10 times higher in automatic and almost 3 times higher in manual printing process. Whereas, the average ozone concentrations during 8 hours discontinuous measurements were almost 3 to 28 times higher in the automatic process. In the manual process, average concentrations of ozone were within prescribed values for discontinuous measurements. Since ozone concentrations in automatic process during discontinuous method exceed 5 ppm prescribed by the National Institute for Occupational Safety and Health (NIOSH) [17], it is dangerous and does affect the workers health. The Serbian Regulation of ozone concentration in workplace air propose the maximum allowed concentration (MAC) of 0.05 ppm [18]. Maximum allowed concentration of ozone according to Serbian law is twice lower than the values prescribed by OSHA, therefore exceeding the allowable limits is twice higher.

Most people can detect about 0.01 ppm of ozone in air where it has a very specific sharp odor somewhat resembling chlorine bleach [19]. Obtained concentration of ozone were hundred times larger then 0.01 ppm, but qualitative detection of ozone by odor is impossible in screen printing facility due to the usage of organic solvents, varnishes and other similar substances.

Because of the short half-life of ozone (15 minutes) and its known interaction with other pollutants (VOC, NO, NO_2, PAN) present in ambient air of screen printing facilities, detected concentrations are probably lower than real generated concentrations.

Environmental regulations and new EU directives are increasingly pushing printing industry to reduce emission of VOC or find alternatives low-VOC liquid materials. The use of alternative liquid printing materials is environmentally responsible choice that will reduce the concentrations of ozone generated in the presence of large amounts of VOCs.

To ensure that exposure of ozone is properly controlled, ventilation system needs to be placed above the housing of UV lamps to vent ozone outside of the screen printing facility. Polluted ambient air with ozone should pass through an activated charcoal filter.

IV. Conclusions

In our research, continuous as well as discontinuous measurement methods are to be taken in screen printing facilities due to the assumption about the generation of significant ozone concentrations. Continuous measurement method fully registers low, temporal concentrations of ozone and has the advantage of providing uninterrupted air monitoring over a certain period of time (in our case 24 hours) in ambient air of working environment. Whereas, discontinuous measurement method is most useful for current, random sampling of ozone on certain sampling points in an examination area.

Existing studies clearly show that concentration of ozone depends on the type of printing process (automatic and manual) and increases with the volume of production. Also, the ozone concentration decreases with increase of distance from UV lamps in automatic screen printing process. In manual screen printing process detected concentrations of ozone are the result of production of ozone by volatile organic compounds and ozone infiltration from the outside. Our suggestion to future improve air quality in printing environment could include substitution of toxic products for safety alternatives and ensuring that solvent contains were kept closed when not needed.

This study provides interesting data concerning the indoor pollution in screen printing facilities in Novi Sad. The detected concentration levels of ozone in both screen printing processes (automatic and manual) much exceed 0.05 ppm and 0.1 ppm prescribed by the Serbian Regulation and the OSHA, respectively.

We can conclude that high levels of ozone concentration do affect the employee's health in screen printing facilities. Considering the observed high ozone concentration, it is strongly recommended to carry out further investigation and long-term monitoring in order to better quantify the level of workers exposure.

This research has been conducted for the first time in the screen printing facilities of Novi Sad. Therefore, this paper could be a starting point in a discontinuous and continuous detection and quantification of ozone in other types of press process in Novi Sad. Also, the detected concentration levels of ozone can be easily integrated in the model development of risk assessment in screen printing facilities of Serbia. The modeling enables to predict the environmental impacts of the printing contaminants, as well as the impacts on the reduction of hazardous substances in printing environment.

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