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# CONTRIBUTION OF FLEXOGRAPHIC PRINTING PROCESS TO GROUND-LEVEL OZONE CONCENTRATIONS

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Abstract: *The concentration levels of ground-level ozone in the flexographic printing plant were determined in two campaigns during five working days. The first campaign was conducted in the middle, and the second at the end of the eight-hour working time. In the second campaign, the mean ozone values per day (3.81, 3.60, 4.25, 4.71, and 3.18 μg/m$^3$) were almost two times higher than in the first. Still, they were 32 to 47 times lower than the emission limit value prescribed by the Regulation of the Republic of Serbia.*

Keywords: flexographic printing process, ground-level ozone, emission limit value

## 1. INTRODUCTION

The ozone layer is a band of natural gas called ozone ($O_3$). It is found in the stratosphere 15 to 30 kilometers above the Earth and is a shield against the sun's harmful ultraviolet B (UVB) radiation. When stratospheric ozone is found in the lower layers of the atmosphere, it is considered a pollutant (Morales-Méendez & Silva-Rodríguez, 2018).
Printing materials, such as printing inks and solvent-based cleaners used in the machine cleaning process, cause the release of ozone and volatile organic compounds (VOCs) and contribute to air pollution (Aydemir & Özsoy, 2020). Experimental data suggest that the solvents typically used in printing inks will photo-degrade rapidly in the atmosphere into water and carbon dioxide and are not significant contributors to lower atmospheric ozone. The emission of solvents from the printing industry is such that their contribution is minimal compared to road transport and energy generation. Also, the amounts of solvents emitted into the atmosphere during printing are strictly controlled (EuPIA, 2013).
Solvent-based inks are widely used in the flexographic printing process because these inks dry by evaporation. Unfortunately, the flexographic solvents usually contain significant VOCs, which have notable health and safety concerns. Also, VOCs contribute to the formation of ground-level ozone, which causes substantial respiratory and other health problems (USEPA, 2002).
When printing on an absorbing substrate (paper or board), the ink is absorbed into the fibres or pigment coating as it dries and binding to the substrate surface. In contrast, on a non-absorbing substrate (polymeric materials), physical binding is far more limited, and adhesion must rely more on chemical mechanisms, thus demanding chemical compatibility between ink formulation and substrate surface (Rentzhog, 2006). Polymeric materials such as polyolefins are the most common substrates in flexographic printing.
Factors causing poor ink adhesion on untreated polyolefins are: low substrate surface energy, low polar functionality, and potential weak boundary layers. The surface modification, good ink wettability, and adhesion on these surfaces require increasing their very low surface energy. Corona discharge treatment in the air is one of the most widely used methods. In this treatment, the substrate passes through a high-energy electrical discharge zone where the surface is exposed to reactive species in the high-energy plasma (or "corona"). Free radicals created at the polymer surface by hydrogen abstraction form covalent chemical bonds with the mixture of reactive species representative of the local atmosphere. These species include free oxygen in its elemental form, ozone, and activated oxygen in air corona. In addition to oxidation, the free radicals cause crosslinking of polymer molecules at the surface, increasing their molecular weight. The oxidation occurs first in the outermost polymer layer and subsequently penetrates deeper (on the order of nanometres), which increases with treatment energy (Rentzhog, 2006). Therefore, corona discharge treatment contributes to the formation of ground-level ozone.

The quantitative concentration levels of ground-level ozone emitted due to the flexographic printing process are presented in this paper. Also, the obtained ozone concentrations were compared to the emission limit value prescribed by the Regulation of the Republic of Serbia.

## 2. METHODS

### 2.1 Flexographic printing plant

Measurements of ground-level ozone concentration were carried out in a flexographic printing plant located on the territory of Novi Sad. The flexographic printing machine, model No: JXG 6750 (manufactured by Shenzhen Fungshengtai Industry CO., LTP, China), was used to print polymer bags.

### 2.2 Analysis of ground-level ozone in the flexographic printing plant

The potassium-iodide method was used to determine ground-level ozone in the air of a flexographic printing plant (GZZZ, 2002). The air with ground-level ozone was collected with a PRO-EKOS AT-401X sampler with four Drechsel gas washing bottles with filter disks. The air from the printing house was passed through the Drechsel bottles at a speed of 0.5 $dm^3$/min. Also, the absorption solution for ground-level ozone (10 ml of 1% potassium iodide in 1 M sodium hydroxide) was found in the Drechsel glass washer. After the sampling, an acidified reagent (5 g of sulfamic acid, 84 $cm^3$ of 85% phosphoric acid, and distilled water up to 200 $cm^3$) was added to the absorption solution. The prepared solution was well stirred and allowed to cool to room temperature. A stable compound was formed, which could be stored for several days. The analysis was completed in the laboratory by adding a phosphorus-sulfamine reagent, which releases iodine. The absorptions of the yellow-coloured ground-level ozone solutions were determined by UV/VIS spectrophotometer DR 5000 at 352 nm.
The absorptions of ground-level ozone present in the collected samples were determined based on the calibration curve made with standard solutions of potassium iodate concentrations of 0.2, 0.4, 0.8, 1.0, 1.2, 1.6, and 2.0 mg/L (Figure 1).

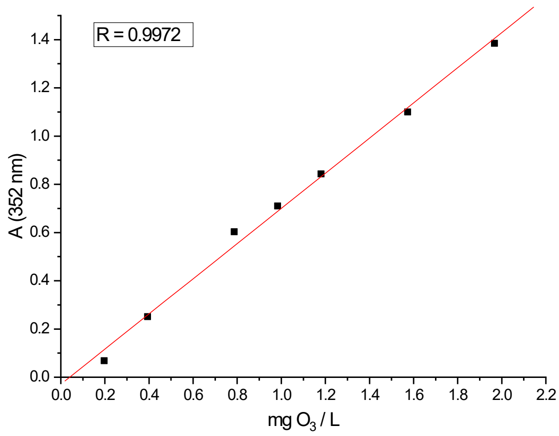


*Figure 1: Calibration curve of ozone*

Campaigns 1 and 2 were carried out after four and eight hours of working time, respectively. In each campaign, absorption samples of ground-level ozone were collected simultaneously in four Drechsel gas washing bottles.
The concentration (μg/$m^3$) of ground-level ozone in the flexographic printing plant (in campaigns 1 and 2) was determined according to the formula (1) (GZZZ, 2002):

$$C(O_3) = \frac{(\mu g / 10 cm^3 O_3) \cdot 1000}{V_{kor}} \quad (1)$$

Where, $V_{kor}$ is the volume of sampled air corrected to standard conditions (temperature of 25°C and pressure of 101325 Pa), according to formula (2):

$$V_{kor} = \frac{P \cdot V}{T} \cdot \frac{T_K}{P_K} \qquad (2)$$

Where V – a volume of sampled air ($m^3$), $P$ – air pressure, Pa, $T$ – air temperature, °C, $T$ = 25°C, and $P_k$ = 101325 Pa.

## 3. RESULTS AND DISCUSSION

Concentration levels of ground-level ozone in the flexographic printing plant in campaigns 1 and 2 for four Drechsel gas washing bottles during five days of monitoring are shown in Figure 2.
The obtained results show that in campaign 1, the concentration levels of ground ozone were in the intervals: from 2.20 to 2.75 μg/$m^3$ (on the 4$^{th}$ day), from 2.35 to 2.65 μg/$m^3$ (on the 3$^{rd}$ day), from 2.10 to 2.30 μg/$m^3$ (1$^{st}$ day), from 1.80 to 2.00 μg/$m^3$ (2$^{nd}$ day), and from 1.60 to 1.80 μg/$m^3$ (5$^{th}$ day). Therefore, the highest ground ozone concentration was detected on the 4$^{th}$ day (2.75 μg/$m^3$), and it was 3.6%, 16.4%, 27.3%, and 34.5% higher in comparison to the highest values detected on days 3, 1, 2, and 5 of the monitoring, respectively.

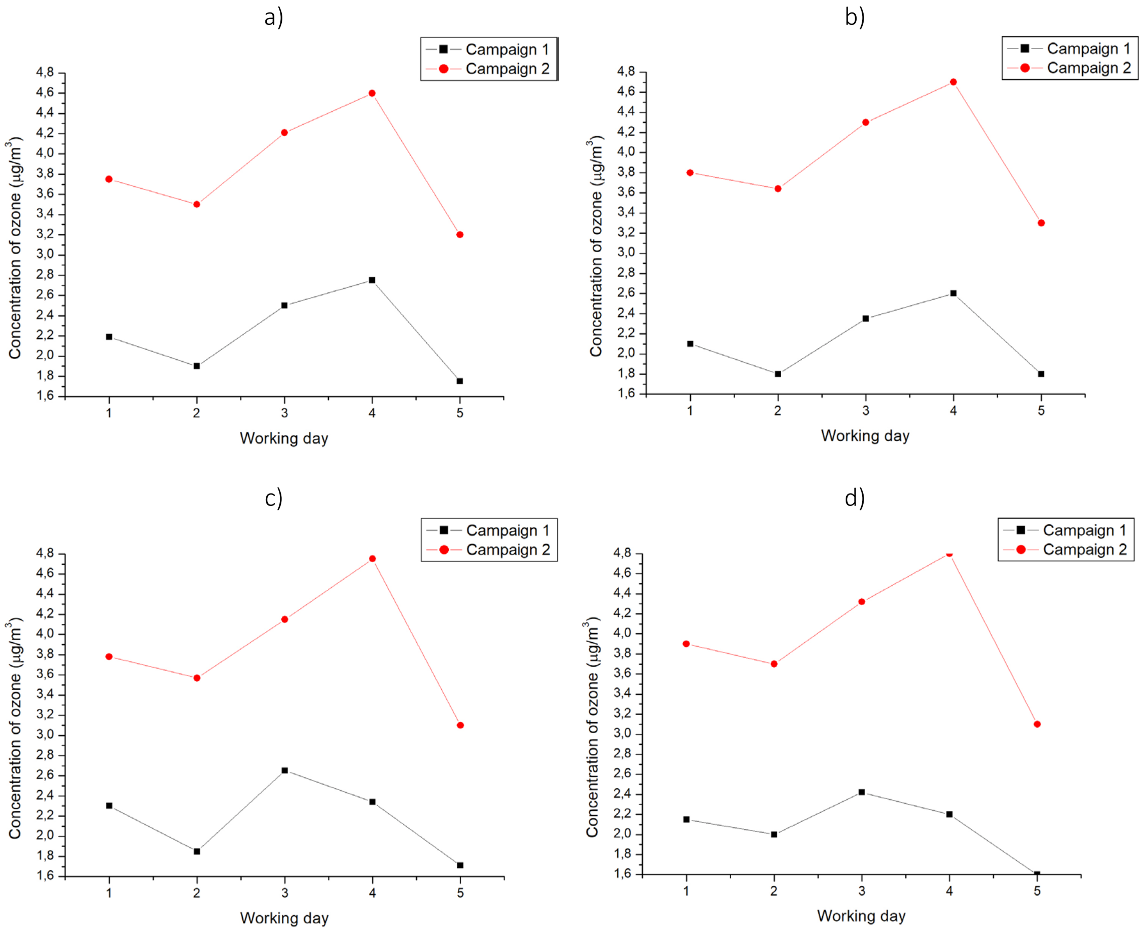


*Figure 2: Comparison of ground-level ozone concentrations in the flexographic printing plant in campaigns 1 and 2 for a) the first, b) the second, c) the third, and d) the fourth Drechsel gas washing bottles*

In campaign 2, the ground ozone concentration levels decreased from: 4.60 to 4.80, 4.15 to 4.32, 3.75 to 3.90, 3.50 to 3.70, 3.10 to 3.30 μg/$m^3$ for the 4$^{th}$, 3$^{rd}$, 1$^{st}$, 2$^{nd}$, and 5$^{th}$ days, respectively. On the other hand, the highest concentration of ground-level ozone was detected on the 4$^{th}$ day (4.80 μg/$m^3$), and it was 10%, 18.8%, 22.9%, and 31.3% higher in comparison to the highest values detected on days 3, 1, 2, and 5 of the monitoring, respectively.
The mean values of ground-level ozone concentrations from the 1$^{st}$ to the 5$^{th}$ day of monitoring were 2.19, 1.89, 2.48, 2.47, and 1.72 μg/$m^3$ (campaign 1) and 3.81, 3.60, 4.25, 4.71, and 3.18 μg/$m^3$ (campaign 2). By comparison, the stated values in campaigns 1 and 2 for the same day increased from 42 to 48%. As

expected, after 8 hours of work and with the increase in the volume of flexographic production, ground-level ozone concentrations are more than 1.7-1.9 times compared to the values after 4 hours.
In the Republic of Serbia, the Regulation on monitoring conditions and air quality requirements (Official Gazette of the RS, 2013) defines the limit value of emission as the highest allowed concentration of pollutants in the air. According to the Regulation mentioned above, the limit value for ground-level ozone is 150 μg/m$^3$ for 1 hour of monitoring. However, the analysis of ground-level ozone produced by the flexographic printing plant in the middle and at the end of the eight-hour working time during the five-day shows that the highest measured values were from 32 to 47 times lower than the limit value.

## 4. CONCLUSIONS

The results of the five-day analysis show that the flexographic plant produces ground-level ozone. Based on the measured ground-level ozone concentrations of the flexographic printing plant, the following conclusions were drawn:

• In the campaign conducted in the middle of working hours, ground-level ozone concentrations are from 1.60 to 2.75 μg/m$^3$. At the end of the eight-hour working time, ground-level ozone concentrations are from 3.10 to 4.80 μg/m$^3$. In both campaigns, concentration levels during the working week decrease in an order: 4$^{th}$ > 3$^{rd}$ > 1$^{st}$ > 2$^{nd}$ > 5$^{th}$ day of monitoring.
• As expected, ground-level ozone concentrations are increasing with the increase in the volume of flexographic production. Still, they are lower than the emission limit value defined by the Regulation of the Republic of Serbia.

## 5. ACKNOWLEDGMENTS

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