ANNALS OF FACULTY ENGINEERING HUNEDOARA
– INTERNATIONAL JOURNAL OF ENGINEERING
Tome IX (Year 2011). Extra Fascicule. (ISSN 1584 – 2673)

[1.] Maja DJOGO, [2.] Jelena KIURSKI, [3.] Dragan ADAMOVIĆ,
[4.] Mirjana VOJINOVIĆ MILORADOV, [5.] Jelena RADONIĆ, [6.] Maja TURK-SEKULIĆ

# HAZARDOUS AIR POLLUTANTS (HAPs) IN PRINTING FACILITY IN NOVI SAD

[1-6.] FACULTY OF TECHNICAL SCIENCES, UNIVERSITY OF NOVI SAD, NOVI SAD, SERBIA

ABSTRACT: Solid and liquid waste from printing industry could generate hazardous materials, such as photographic and residual chemicals, metal hydroxide sludge, dyestuff and solvent residues, wiping material containing dyes and solvents and oil spills. Vapours of organic solvents and organic compounds are emitted into the air as the hazardous air pollutants (HAPs). Studies have shown that printing processes lead to emissions of HAPs such as Volatile Organic Compounds (VOCs) and ozone. The presence of VOCs (benzene, toluene and xylene, abbreviated BTEX) in ambient and indoor air is widely recognized as precursors of serious risk to human health. In addition, VOCs contribute to the production of secondary photochemical pollutants such as ozone. The monitoring of the HAPs was conducted during working time (8 hr) and samples were taken in following printing units: prepress, offset and post press. For the purpose of monitoring of the emission of VOCs in printing facility in Novi Sad, mobile gas chromatograph (MGC) Voyager, by USA company Photovac, has been used and ozonometer by company Aeroqual limited, Series 200 has been used for monitoring of ozone. Samples were analyzed during process of printing and standby mode of the machine. The measured concentrations of toluene, ethylbenzene and xylene showed levels below the recommended maximum level set by Serbian standard as a result of usage of vegetable oil based inks and solvents in printing process. Concentrations of benzene and ethylbenzene were below limit of detection, while concentrations of toluene and xylene were in range 0 - 0.151 ppm and 0 - 1.136 ppm, respectively. Ozone concentration remained below 0.04 ppm, over two months of measurement campaign, and therefore it is not much lower than the Serbian standard (0.07 ppm).
KEYWORDS: HAPs, VOCs, ozone, printing facility

## INTRODUCTION

A number of industrial activities make use of chemical products containing volatile organic compounds (VOCs), which are widely used mainly due to their high volatility. Among the activities that can result in the emission of such compounds in its working environments are the offset printing processes. The main indoor sources for VOCs are solvents and inks in the printing industry due to their low vapor pressure, significant amounts of toluene, xylenes, and other volatile compounds are emitted during the printing process, polluting the workplace environment. In addition, the cleaning procedures can result in exposures that are ten times higher than during other tasks because these cleaning products are petrol-based. The inks used in the offset process are made basically of a mixture of resins, vegetal or mineral oils, pigments, and solvents. The main ingredients of the conventional inks are pigments, binders, carriers and additives [3]. Compared with solvent-based ink, water-based ink uses water as carrier to substitute a majority of organic solvent, thus its development and application have led to the reduction of VOC emissions, as one of the main driving forces of product innovation [4]. Water-based ink is nonflammable, produces less objectionable vapors in the workplace, and does not contaminate packaged products [3]. Therefore, it has been widely used in printing, the packaging of food, drug, toy, wine product and so on. However, wastewater obtained after cleaning/washing of the laboratory and industrial equipment is highly colored by the pigments and is highly contaminated with organic materials.

The oil solubilizes the resin, controls the viscosity, stabilizes the ink at the printing roll, and induces the initial drying of the ink. Mineral oil-based inks (containing petrol-derived hydrocarbons) are generally used in the offset printing process, and of late also the “ecological” alternative, soy oil-based inks. The soy oil-based inks use a renewable resource and emit about 30% less VOCs than the mineral oil-based ones during the printing process. Apart from being more economical and cheaper, the ecological inks offer the benefit of minimizing worker’s exposure to harmful substances. Exposure to solvents can lead to a variety of adverse health effects. Many of them have been considered hazardous materials since the early 1970s, when the first environmental laws were enacted and they may produce health effects if humans are exposed to high enough concentrations. These results are the basis for determining human health effects, and serve as the basis for setting drinking water and air quality standards. In general, long-term exposure to low concentrations of VOCs in water or air, at or above regulatory standards may result in liver or kidney effects. Breathing some of these contaminants may cause irritation of the respiratory tract. These chemicals might produce cancer, especially benzene which has been placed in the first group of carcinogens by International Agency for Research on Cancer (IARC) Environmental emissions of printing solvents may cause ground level ozone formation and some may contribute to stratospheric ozone depletion. Environmental regulations and new EU directives are increasingly pushing industry to reduce emission of VOC or find alternatives to VOC containing paints and solvents.

Ozone is very reactive gas, and even at low concentrations, ozone is irritating and toxic. Ozone can oxidize many organic compounds and is used commercially as bleach for waxes, oils, and textiles, and as a deodorizing agent. Because of physico-chemical properties, ozone exerts serious adverse effects on environmental air quality. Damaging effect of ozone on human health sometimes is hard to notice, and the first disorders of health can soon disappear, though the damaging effect on health is ongoing [2]. People who live and work in areas and places where ozone levels are frequently high may find that their initial symptoms go away over time, particularly when exposure to high ozone levels continues for several days. Ozone continues to cause lung damage even when the symptoms have disappeared. Due to physico-chemical properties of ozone, ozone is a primary irritant, affecting especially the eyes and respiratory systems and can be hazardous at even low concentrations. Breathing ozone can trigger a variety of health problems including chest pain, coughing, throat irritation, and congestion. The most sensitive to ozone are children and elderly people. When concentration levels of ozone in the air increase by 40 $\mu g/m^3$, the number of children with respiratory disorders increases by 83 per cent [2]. Some sources point out that the limiting allowable concentration of ozone in a workplace is 100 $\mu g/m^3$. According to the Directive 2002/3EC EU, the State Members will inform society when the ozone concentration average in an hour reaches 180 $\mu g/m^3$ and give a warning when it reaches 240 μg/m3. In order to preserve human health, ozone concentration in environment 25 days a year, given the average of three years, may not exceed 120 $\mu g/m^3$ [1].

Ozone is a pollutant of concern because it can affect both plants and human health. High ozone levels in urban and sub-urban areas during pollution episodes are able to affect human health. Ozone ([O3]) formation is a complex non-linear photochemical reaction driven by two major classes of precursors: nitrogen oxides (NOx) and volatile organic compounds (VOCs).

## ❖ PRINTING PROCESS

Offset printing technique is based on the principal that oil and water do not mix (hydrophilic and hydrophobic process). Lithographic plates undergo chemical treatment that render the image area of the plate oleophilic (oil-loving) and therefore ink-receptive and the non-image area hydrophilic (water-loving). During printing, fountain (dampening) solution, which consists primarily of water with small quantities of isopropyl alcohol and other additives to lower surface tension and control pH, is first applied in a thin layer to the printing plate and migrates to the hydrophilic non-image areas of the printing plate. Ink is then applied to the plate and migrates to the oleophilic image areas. Since the ink and water essentially do not mix, the fountain solution prevents ink from migrating to the non-image areas of the plate.

Traditionally, isopropyl alcohol was used to control surface tension in the fountain solution, but in recent years its use has been reduced, and in many cases eliminated by using alcohol substitutes. The reason for this shift is due to the VOC emissions attributed to the evaporation of isopropyl alcohol and the level of environmental regulation this lead to. Alcohol substitutes may use glycol ethers such as butyl cello solve (2-butoxy ethanol) or other lo glycols to control surface tension.

## ❖ MATERIALS AND METHODS

Measurements of HAPs (BTEX, isopropyl alcohol, and acetone) in this study were conducted by PerkinElmer Photovac Voyager-mobile GC. The Voyager uses the principles of gas chromatography (GC) to separate and identify volatile organic compounds. The sample components become separated from one another as they are carried through the column due to differences in their rates of interaction with the sorptive material. For the separation of sample components Supelcowax10-Polyethylene glycol (PEG) column was used. The target HAPs were identified by GC retention times, comparison with authentic standards. As the compounds elute from the column, they are detected by the photo ionization detector. The detection limit of the applied method is 0.001 ppm [9]. Ozonometer by company Aeroqual limited, Series 200 has been used for monitoring of ozone. Samples were analyzed during process of printing and standby mode of the machine. Sampling of gaseous BTEX, isopropyl alcohol, acetone and ozone was performed in printing plant in Novi Sad.

## ❖ ENVIRONMENTAL CONDITIONS

Microclimate during experimental study in printing plant was measured by an instrument Mannix DLAF-8000. Temperature and relative humidity measurements in three printing plants were taken simultaneously with the ozone and HAPs measurements. The values of temperature and relative humidity in printing plant were varied from from 23 to 27°C and from 50 to 54%, respectively.

## ❖ VOC MEASUREMENT

The building of sheet-fed offset printing plant comprises approximately 2.500 $m^2$ surface area and about 70 workers are employed. Twenty samples were collected at seven sampling points, during 8 hours work shift per day. The outside sampling point was selected at the main entrance in order to compare the VOC concentrations with those measured inside of the printing plant A. The offset printing room had an area of 250 $m^2$, a height of 8 m, housed 45 workers, and had windows in every wall. Moreover, there are two doors which were permanently opened. The cleaning procedure, using an organic solvent, was performed twice a day when the printing matrix was changed. Description of the sampling points in printing plant A is given in Table 1.

Table 1. Description of sampling points in offset printing plant

| Measuring place | Sampling point | Description |
|---|---|---|
| Press department | 1 | Folding machine |
| | 2 | Printing machine Heildelberg Speedmaster 4 printing units B1 |
| | 3 | Printing machine Heildelberg Speedmaster 4 printing units B2 |
| | 4 | Printing machine Heildelberg GTO |
| Prepress department | 5 | Computer to plate |
| Postpress department | 6 | Gluing and finishing |
| Outside | 7 | Main gate |

## ❖ OZONE MEASUREMENT

Ozone emissions were detected in printing company XY in Novi Sad by Ozonometer Series 200, company Aeroqual limited. Series 200 is portable tool, and can be used fixed or handheld. The sensor measures the ozone content of ambient air and utilizes the proprietary Aeroqual "Gas Sensitive Semiconductor" (GSS) technology. GSS technology combines the principles of both HMOS technology and UV photometry to improve accuracy, T90 response (time taken to reach 90% accuracy), cross sensitivities, and sensor drift. By Series 200, ozone can be detected in following units: mg/$m^3$, ppm or ppb, under operating temperature from -5°C - 40°C, and relative humidity from 5 to 95%.

Air samples were taken in following printing company's departments: prepress, offset and post press department. Samples were analyzed *in situ* by Ozonometer Series 200 with online procedures, during process of printing and standby mode of the machine. Results were obtained promptly, registering current situation and status of the working environment, which enables swift and adequate reaction in case of accidents and abnormal activities.

## ❖ RESULTS AND DISCUSSION

Obtained results of VOC measurements, conducted in printing plant in Novi Sad, indicate on low concentration levels. The results of measurements in printing plant are shown in Table 2.

Table 2. Average concentrations VOCs and standard deviation of measurements in printing plant

| Sampling point | Statistical data | Average concentration of VOCs [ppm] | | | |
|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethylbenzene | Xylenes |
| 1 | Average STDV | <0.001 | <0.001 | <0.001 | <0.001 |
| 2 | Average STDV | <0.001 | <0.001 | <0.001 | <0.001 |
| 3 | Average STDV | <0.001 | <0.001 | 0.838 0.059 | <0.001 |
| 4 | Average STDV | <0.001 | <0.001 | 0.552 0.087 | <0.001 |
| 5 | Average STDV | <0.001 | <0.001 | <0.001 | <0.001 |
| 6 | Average STDV | <0.001 | 0.152 0.111 | 0.441 0.045 | <0.001 |
| 7 | Average STDV | <0.001 | <0.001 | <0.001 | <0.001 |

Concentration levels of benzene and xylenes were below limit of detection (0.001 ppm) at all sampling points. Presence of toluene was detected on sample point 6, with average concentration of 0.152 ppm as a result of gluing and finishing operations in post press department. Presence of ethylbenzene was detected in press department on sample points 3, 4 and 6 with average concentrations 0.838 ppm, 0.552 ppm and 0.441 ppm, respectively. Regarding ozone, two printing machines were included in the research: PressVu $UV_{200/600}$ FC - color UV printing machine (based on UV lamps), and Teleios - direct textile printing machine. Concentration levels of ozone on the machine PressVU $UV_{200/600}$ FC are presented in Figure 2. while Figure 3. (shown in Appendix) presents concentration levels of ozone on printing machine - Teleios.

Printing machine based on UV lamps (PressVu $UV_{200/600}$ FC) produced higher amounts of ambient ozone during working hours, and comparing to Serbian threshold average value per one hour (150 $\mu g/m^3$), obtained results were above standards. The reason for such amount of ozone is constant activity of UV lamp during printing process, which is one of the producing sources of this compound.

Direct textile printing machine (Teleios), due to the nature of evaporating substances which are used for color fixation, produces relatively low concentration levels of ambient ozone, but still above Serbian standards. During printing process, ozone has not been detected, since this printing machine uses colors based on water.

## ❖ CONCLUSIONS

Clean air is considered to be a basic requirement of human health and well-being. However, current global environment issues are the big concern for the printing industry. Various problems continuously arise, such as global warming issues, waste and recycling affairs, and chemicals controls. Just like business activities have no goal, there is no end for the environment activities.

Ethylbenzene can be find as a chemical in a solutions for cleaning of printing machines. That can be the reason of it's presence in press department and in postpress department. Series of measurements carried out at the sample points 7 indicate to the fact that the existing volume of production does not affect the environment in the vicinity of the printing plant.

Though scientists' understanding of ozone's effects has increased substantially in recent years, many important questions still remain to be investigated. For example, does repeated short-term exposure to high levels of ozone cause permanent lung damage? Does repeated exposure during childhood to high levels of ozone cause reduced lung function in adults? Scientists are continuing to study these and other questions to gain a better understanding of ozone's effects and make necessary revisions of safety guidelines to better protect public health and the environment.

Considering the high concentration observed for ozone, it is strongly recommended to carry out further investigation and long-term monitoring in printing facility, in order to better quantify the level of exposure and influence of ozone on printing industry worker's health.

## ❖ ACKNOWLEDGMENT

The authors acknowledge the financial support of the Ministry of Science and Technological Development of the Republic of Serbia, in frame of project applied under No. 34014.

## ❖ REFERENCES

[1.] Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air. Official Journal L 067, 09/03/2002.
[2.] Gilliland, F. D.; Berhane, K., Rappaport, E. B., Thomas, D. C., Avol, E., Gauderman, W. J., London, S. J., Margolis, H. G., Mcconnell, R., Islam, K. T., Peters, J. M.: "The effects of ambient air pollution on school absenteeism due to respiratory illnesses", *Epidemiology*, 12, 43–54, 2001.
[3.] H. Gecol, J.F. Scamehorn, S.D. Christian, B.P. Grady, F. Riddell, Use of surfactantsto remove water based inks from plastic films, Colloids Surf.A: Physicochem.Eng. Aspects 189 (2001) 55–64.
[4.] Simpson, B., Tazik, P., Moleiro, G., Randall, P. (1994). Waste reduction evaluation of soy-based ink at sheet-fed offset printer. U.S. Environmental Protection Agency, Cincinnati, OH, USA.