International Journal of Earth, Energy and Environmental Sciences
ISSN: 2517-942X
Vol:10, No:3, 2016

Statistically Significant Differences of Carbon Dioxide and Carbon Monoxide Emission in Photocopying Process

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Abstract**—**Experimental results confirmed the temporal variation of carbon dioxide and carbon monoxide concentration during the working shift of the photocopying process in a small photocopying shop in Novi Sad, Serbia. The statistically significant differences of target gases were examined with two-way analysis of variance without replication followed by Scheffe's *post hoc* test. The existence of statistically significant differences was obtained for carbon monoxide emission which is pointed out with *F*-values (12.37 and 31.88) greater than F_{crit} (6.94) in contrary to carbon dioxide emission (*F*-values of 1.23 and 3.12 were less than F_{crit}). Scheffe's *post hoc* test indicated that sampling point A (near the photocopier machine) and second time interval contribute the most on carbon monoxide emission.

Keywords**—**Analysis of variance, carbon dioxide, carbon monoxide, photocopying indoor, Scheffe's test

I. INTRODUCTION

INDOOR air quality is considered to be one of the main environmental issues, as most of the society still face the problem of poor air quality. The scientific interest is focused on the different characteristics of the located sources or the activities occurred in the environments of different use, without excluding the outdoor environment’s contribution [1]. The increasing uses of office equipment, including computers, printers and photocopier machines, warrant a systematic evaluation of pollutant emissions [2], [3].

Photocopier machines are essential office equipment in modern time. During the photocopying processes, the components of toner and paper will react under the influence of light and high temperatures [4]. A powdered toner, used during photocopying process, contains organic components which are pressed or heated, and they become available for emission to the indoor air. Depending on the characteristics of the toner and fuser materials, various volatile organic compounds (VOCs) can be easily emitted: benzene, toluene, styrene, ethylbenzene, xylenes, acetophenone, alkanes, aldehydes, as well as phenols, cresols, phthalates, phosphorous esters, siloxanes as semivolatile organic compound (SVOCs) [5], [6]. Pollutants like nitrogen dioxide (NO_2), carbon dioxide (CO_2), carbon monoxide (CO) and sulfur dioxide (SO_2) can be emitted directly from the stack and/or process equipment. These pollutants are known as primary pollutants. Secondary pollutants are formed during the reactions between primary pollutants in the atmosphere or between a primary pollutant and naturally occurring compounds in the atmosphere. The most well recognized category of secondary pollutants includes ozone and other photochemical oxidants generated during the UV-light initiated reactions of nitrogen oxides, volatile organic compounds and carbon monoxide [7], [8]. Carbon monoxide and carbon dioxide can be produced when toner is heated if there is inadequate air supply during photocopying process. As a trace atmospheric constituent, carbon monoxide adversely impacts human life and contributes to climate change at different spatial scales. Locally, it is poisonous to humans and its long-term exposure may result in heart diseases and damage to the nervous system. Regionally, it reacts with other pollutants and produces photochemical smog [9], [10].

Paper and electricity consumption, as well as human activity during the photocopying process can indirectly contribute to the formation of CO_2. The importance of controlled carbon dioxide emission is reflected through global warming potential, considering carbon dioxide as a principal greenhouse gas. Since 36% of CO_2 emission is attributable to manufacturing industries, controlled emission is considered as a major requirement and a principal part of environmental maintenance [10]. The increasing prevalence of photocopier machines in the working environment along with the presence of fine powders of carbon black in toner composition and the heating of toner in an inadequate air supply can contribute to the indoor emission of carbon monoxide and carbon dioxide [5], [11], [12]. Additionally, the level of both pollutants increase if not enough outdoor air is brought to dilute emissions from indoor sources [13], [14]. The introduction of enough amount of clean air into the photocopying environment will ensure the emissions’ dilution to the acceptable levels. Otherwise, a variety of health problems related to the use of a photocopier and laser printer, including headaches, dizziness, confusion, nausea, eye irritation, and dry nose and throat, can occur [15].

The objectives of the research were to determine:

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- The emission rates of carbon dioxide and carbon monoxide during the photocopying procedure;
- The statistically significant differences of gases emission considering different sampling points and time intervals, using ANOVA and Scheffé's test.

II. MATERIALS AND METHODS

A. Site Description, Sampling and Analysis

Experimental investigation was performed in a small photocopying shop located on Faculty of Technical Sciences in Novi Sad, Serbia. Selected photocopying shop occupies an area of 16 m^2. Three sampling points A, B and C (A - near photocopier Ricoh Aficio MP6500 (2); B - between photocopier Ricoh Aficio MP6000 (3) and photocopier Konica Minolta Bizhub C224e (4); C - near desktop computer (1) and window) were selected according to the locations of photocopier machines as target gas sources [9]. The technological scheme of a photocopying shop is presented in Fig. 1.

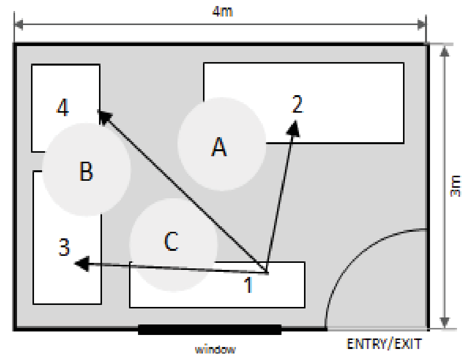

Fig. 1 Technological scheme of the photocopying shop [9]

Sampling of gases was carried out during five days in three different time intervals: at beginning of the working time (from 8 to 10 a.m.), at the maximum productivity time (from 13 to 15 p.m.) and at the end of the working time (from 16 to 18 p.m.). Each time interval included five measurements in the range of two minutes [16]. During the sampling, the process conditions were constant: three copier machines worked, the door was opened permanently and ventilation system continuously worked.

The concentration levels of carbon monoxide and carbon dioxide were measured by using an instrument Aeroqual Series 200 (Aeroqual Limited, New Zeland). Instrument primarily uses gas semiconductor sensor (GSS) technology. GSS technology presents a combination of smart measurement techniques and mixed metal oxide semiconductor sensors that exhibit an electrical resistance change in the presence of a target gas. Detection limits of instrument are: 0-100 ppm and 0-5000 ppm for carbon monoxide and carbon dioxide, respectively. The precision of instrument is 1 ppb [16], [17].

B. Analysis of Variance

Analysis of variance (ANOVA) is a collection of statistical models used to analyze the differences among group means and their associated procedures, such as "variation" among and between groups. It is used in the analysis of comparative experiments, those in which only the difference in outcomes is of interest. In its simplest form, ANOVA provides a statistical test of whether or not the means of several groups are equal, and therefore generalizes the *t* test to more than two groups. In the case of multiple two-sample, *t* tests would result in an increased chance of committing a statistical type I error. Appearance probability of statistical error type I represent the probability of the risk that the null hypothesis is rejected although it is true. The analysis of variance can be presented in terms of a linear model, which makes the following assumptions about the probability distribution of the responses:

- ✓ Independence of observations – an assumption of the model that simplifies the statistical analysis;
- ✓ Normality – the distributions of the residuals are normal;
- ✓ Equality (homogeneity) of variances - the variance of data in groups should be the same [18], [19].

The term "interaction" in a two-way ANOVA indicates whether the effect of independent variables on the dependent variable is the same for all values of other independent variable, and vice versa. Additionally, if a statistically significant interaction is found, it is possible to determine whether there are any "simple main effects", and if there are, what these effects are [20]. In two-way ANOVA it is necessary to define and test the null and alternative hypothesis. The null hypothesis assumes that there is no significant difference between groups that are tested, and therefore no significant results will be revealed. On the other hand, the alternative hypothesis states that there is a difference between groups [9], [21]. The null and alternative hypotheses are expressed by (1)-(4) [21]:

$$H_0 : \mu(A_1)=\mu(A_2) = ... = \mu(A_m)=\mu \tag{1}$$

$$H_0 : \mu(B_1)=\mu(B_2)=...= \mu(B_s)=\mu \tag{2}$$

$$H_1 : \mu(A_1)\neq\mu(A_2)=... = \mu(A_m)=\mu \tag{3}$$

$$H_1 : \mu(B_1)\neq\mu(B_2) ...= \mu(B_s)=\mu \tag{4}$$

where μ_1 and μ_2 stands for the average values for the first and second group and *m* and *s* are number of observations within the factor *A* and *B*. Acceptance or rejection of the null hypothesis is based on the comparison of the experimentally obtained values of parameter *F* for each factor, with critical value, F_{crit}, that is obtained from the table of limit values of *F* distribution for a certain degrees of freedom (Table I). If the value of parameter *F* is less than F_{crit}, the null hypothesis is accepted and it brings to the conclusion that between observed groups does not exist statistically significant differences.

Otherwise, some of the alternative hypothesis will be accepted, and the mean values of some or all studied groups differ significantly [21]. However, the calculated *F* value using the ANOVA test does not give an answer to the question whether a statistically significant difference occurs between the mean values of all groups or only between particular groups. Therefore, it is necessary to test the differences between arithmetic means of samples and to determine the correctness of certain alternative hypothesis, which is performed using various *post hoc* tests. The extremely conservative *post hoc* test is the Scheffé's test, representing a single-step multiple comparison procedure, which applies to the set of estimates of all possible contrasts among the factor level means, not just the pair wise differences. In this case it is necessary to compare the two mean values, using all possible combinations, with Scheffe's critical value. The difference between two samples is significant if the difference between two sample means (Scheffe's coefficient) is larger than Scheffe's critical value, and vice versa [22].

TABLE I
Limit Values of F Distribution for a Certain Degrees of Freedom

df_2	df_1 [a]				
	1	2	3	4	5
1	161,4	199,5	215,7	224,6	230,2
2	18,51	19,00	19,16	19,25	19,30
3	10,13	9,55	9,28	9,12	9,01
4	7,71	6,94	6,59	6,39	6,26
5	6,61	5,79	5,41	5,19	5,05
6	5,99	5,14	4,76	4,53	4,39
7	5,59	4,74	4,35	4,12	3,97

[a] Degrees of freedom

Determination of statistical significance was performed by using software Microsoft Excel 2007.

III. Results and Discussion

A. Indoor Gas Emission

The measured concentrations of carbon dioxide and carbon monoxide in three time intervals are presented in Table II. The highest and lowest concentrations of carbon dioxide (2545.20 and 828.00 ppm, respectively) were occurred during the second and first measurement day in third and second time interval. Carbon monoxide showed the highest and lowest concentrations (4.69 and 0.12 ppm, respectively) during fifth measurement day in second and first time intervals. Obtained concentration levels were lower than the Short-Term Exposure Limit (STEL - 200 and 30,000 ppm, respectively) and Recommended Exposure Limit (REL - 35 and 5,000 ppm, respectively) regulated by the National Institute for Occupational Safety and Health (NIOSH) [23] indicating still acceptable working conditions in terms of workers' and customers' health. Because of relatively short lifetime and distinct emission patterns, CO and CO_2 have large gradients in the atmosphere. Based on the prescribed PEL values, carbon monoxide and carbon dioxide burden of photocopying environment are about 13.4% and 50.9%, respectively.

Evidently, carbon monoxide and carbon dioxide concentrations showed the temporal variations during measurements. Significant increase was observed in second and third time interval. The reason is retention of gases in a photocopying environment, which could not be repressed into the outdoor environment due to the poor ventilation system. Authors [16] indicated that the retention of hot air in the photocopying workspace addition to the poor continuous operation of the ventilation system is responsible for the presence of carbon monoxide and carbon dioxide. Therefore, authors recommended the pollution prevention opportunities of photocopier through the machine redesign, as well as reformulation of used toner.

TABLE II
Concentration of Target Pollutants

Sampling point/ sampling day	**Gas concentrations in three time intervals (ppm)**					
	CO_2_1 [b]	**CO_2_2** [c]	**CO_2_3** [d]	**CO_1** [e]	**CO_2** [f]	**CO_3** [g]
A1	979.40	**828.00**	1190.60	1.09	0.66	0.34
B1	937.40	897.00	955.60	1.10	0.52	0.26
C1	999.40	1100.60	931.80	0.98	0.44	0.19
A2	1231.60	1170.20	940.00	0.56	1.07	0.83
B2	1054.00	1105.00	944.80	0.45	0.92	0.79
C2	1063.60	1089.60	**2545.20**	0.32	0.78	0.73
A3	972.20	968.60	1115.40	1.06	0.56	1.08
B3	958.40	970.80	1150.20	1.09	0.58	0.94
C3	964.60	934.00	1182.20	0.91	0.69	0.69
A4	931.60	834.00	1056.80	1.23	1.34	0.71
B4	952.00	842.20	1110.40	0.33	1.53	0.56
C4	933.00	842.40	1116.40	0.15	1.48	0.70
A5	980.00	1049.80	1086.00	1.11	**4.69**	1.89
B5	1010.40	1027.60	1047.40	0.24	3.29	1.79
C5	1027.00	989.40	1026.40	**0.12**	2.10	1.57

[b] CO_2 concentration in 1st time interval; [c] CO_2 concentration in 2nd time interval; [d] CO_2 concentration in 3rd time interval;
[e] CO concentration in 1st time interval; [f] CO concentration in 2nd time interval; [g] CO concentration in 3rd time interval

B. Statistical Significance

Owing to the complexity and a large data volume only the average concentration levels of carbon dioxide and carbon monoxide during five day measurements (Tables III and IV) were subjected to two-way ANOVA without replication. By using two-way ANOVA, it was possible to test the significant differences among experimental variables. A probability level $\alpha<0.05$ was considered as significant.

TABLE III
AVERAGE CARBON DIOXIDE CONCENTRATION IN PHOTOCOPYING INDOOR ENVIRONMENT

Sampling point	Time interval		
	first	second	third
A	1018.960	970.120	1077.760
B	982.440	968.520	1041.680
C	997.520	991.200	1360.400

TABLE IV
AVERAGE CARBON MONOXIDE CONCENTRATION IN PHOTOCOPYING INDOOR ENVIRONMENT

Sampling point	Time interval		
	first	second	third
A	1018.960	970.120	1077.760
B	982.440	968.520	1041.680
C	997.520	991.200	1360.400

Two influence factors, sampling point and time interval, are defined as independent variables, whereas carbon dioxide and carbon monoxide concentrations represent dependent variables.

The results of two-way ANOVA without replication are presented in Tables V and VI.

TABLE V
RESULTS OF TWO-WAY ANOVA WITHOUT REPLICATION FOR CARBON MONOXIDE

Source of Variation	*SS*[h]	d_f[j]	*MS*[k]	*F-value*	*P-value*[l]	F_{crit}
Sampling point	0.277	2	0.139	**12.372**	0.019	**6.944**
Time interval	0.714	2	0.357	**31.880**	0.003	**6.944**
Error	0.045	4	0.011			
Total	1.036	8				

[h] Sum of squares; [j] Degrees of freedom; [k] Mean square; [l] Statistical significance

The obtained F-values were compared to the F_{crit} value of 6.944 for significance level α = 0.05 and the degrees of freedom d_f = 2 and 4, Tables V and VI. Obtained values of factor A (12.37) and factor B (31.88) for carbon monoxide are significantly higher than F_{crit} (6.94), Table V. In that case, for both factors - sampling point and time interval, the null hypothesis is rejected and the alternative hypothesis, H_1: $\mu_1 \neq \mu_2$, is accepted with a risk of error α = 5%. Acceptance of the alternative hypothesis (H_1: $\mu_1 \neq \mu_2$) confirmed that the selection of sampling point and time interval had influence on carbon monoxide emission, i.e. there were the statistically significant differences between observed phenomena. On the other hand, value of factor A (1.23) and factor B (3.12) for carbon dioxide are lower than the F_{crit}, indicating that the null hypothesis, H_0: $\mu_1=\mu_2$, is accepted. Therefore, the selection of sampling point and time interval had no influence on carbon dioxide emission, i.e. there were no statistically significant differences between observed phenomena.

TABLE VI
RESULTS OF TWO-WAY ANOVA WITHOUT REPLICATION FOR CARBON DIOXIDE

Source of Variation	*SS*[h]	*df*[j]	*MS*[k]	*F-value*	*P-value*[l]	F_{crit}
Sampling point	$23*10^3$	2	$11*10^3$	**1.231**	0.383	**6.944**
Time interval	$59*10^3$	2	$29*10^3$	**3.122**	0.152	**6.944**
Error	$38*10^3$	4	$9*10^3$			
Total						

[h] Sum of squares; [j] Degrees of freedom; [k] Mean square; [l] Statistical significance

As the results of ANOVA indicate that the selection of sampling points and time intervals only significantly affects the carbon monoxide emission in a photocopying indoor environment, the comparison of statistical differences between mentioned factors was performed. For that purpose, a Scheffé's test is applied. The difference between two samples is calculated based on the equation (5) [24]:

$$F_s = \frac{(\overline{x_i} - \overline{x_j})^2}{V[(1/n_i) + *(1/n_j)]} \tag{5}$$

where F_s is Scheffe's coefficient, $|\overline{x_i}|$ and $|\overline{x_j}|$ are the mean values of compared samples; V is variance between group; n_i and n_j are number of samples for each factor. In addition, Scheffe's critical value is calculated based on relation (6):

$$F' = (m-1) \cdot F_{crit} \tag{6}$$

where F' is Scheffe's critical value; m is a number of observed groups; F_{crit} is a critical value obtained from ANOVA test [24].

The results of Scheffé's test are presented in Table VII, where x_1, x_2 and x_3 represent the average CO concentration at sampling points A, B and C, as well as the concentrantions measured in first, second and third time interval, respectively.

TABLE VII
RESULTS OF SCHEFFÉ'S TEST

F_s[m]	Sampling point	Time interval
$\lvert\overline{x_1} - \overline{x_2}\rvert$	**19.12**	**59.42**
$\lvert\overline{x_1} - \overline{x_3}\rvert$	**24.85**	3.32
$\lvert\overline{x_2} - \overline{x_3}\rvert$	3.94	**34.73**
F'[n]	**13.88**	

[m] Scheffe's coefficient; [n] Scheffe's critical value

In the case of the sampling point's observation, obtained results of Scheffé's test (Table VII) pointed out that highly significant difference exists between first and second, as well as first and third observed group. In addition, highly significant difference is occurred in first and second, as well as in second and third time intervals. Given that, the results pointed out that sampling point A (nearest to the photocopier machine) and second time interval (during the maximum productivity time) had the greatest influence on carbon monoxide emissions.

IV. CONCLUSION

The concentration levels of carbon dioxide and carbon monoxide were determined in one photocopying shop in Novi Sad, Serbia, during five-day measurement. The major factor affecting the presence of target hazards was the extensive heating of photocopier and the usage of dry toner in the course of photocopying process. However, obtained concentration levels were lower than the prescribed STEL and PEL values indicating still acceptable working conditions in terms of workers' and customers' health. The obtained dataset was subjected to two-way ANOVA without replication and Scheffe's *post hoc* test to statistically investigate significant differences of both gas emissions by observing different sampling points and time intervals. The results of two-way ANOVA confirmed a statistically significant difference only in the case of carbon monoxide, indicating that the sampling point A and a second time interval contributed the most to the carbon monoxide emission in the photocopying environment.

ACKNOWLEDGMENT

The authors acknowledge the financial support of the Ministry of Education, Science, and Technological Development of the Republic of Serbia within the Projects No. TR 34014.

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