Indoor Air Pollution: The Case of Ozone in Three Regions in Greece

Dionysios Koulougliotis¹, Anastasios Kalimeris¹, Sotiria Potozi¹, Roxanne-Suzette Lorilla¹, Georgios Kefalas¹ and Dimitrios Nikolopoulos*²

¹Technological Educational Institute (TEI) of Ionian Islands, Department of Environmental Technology, Neo Ktirio-Panagoula, Zakynthos, Greece
²Piraeus University of Applied Sciences, Department of Electronic Computer Systems Engineering, Petrou Ralli and Thivon 250, Aigaleo, Greece

Abstract

Ozone concentrations of indoor air were measured in dwellings in three areas of Greece, namely Athens, Salamina Island and Zakynthos Island. The measurements were conducted as a function of the following four parameters: the time during the day, the time period that the openings of a dwelling (windows, doors) remained closed, the degree of urbanization and the floor of the dwelling. The statistical analysis of the data showed that there was a strong dependence of the indoor ozone levels on the first three of the above mentioned parameters while this was not the case for the floor of the dwelling. The indoor versus outdoor ozone levels (I/O ratios) were calculated and their dependence on the same four experimental parameters was also examined.

Keywords: Indoor air pollution; Ozone; I/O ratios

Introduction

The study of indoor air quality (IAQ) is an active research field for more than 30 years. It showed quite early that the concentrations of indoor air pollutants (IAP) are often non-negligible and that they may have negative effects on human health and works of art [1-5]. Ozone (O₃) is a secondary air pollutant which results from photochemistry. According to the World Health Organization [6], the exposure to photochemical pollutants is connected with several adverse health effects such as pulmonary and respiratory malfunction. The specific study of indoor ozone levels, chemistry and exposure has been a subject of scientific investigation since many years [3,4,7-9]. Concentrating on the studies that have been conducted in Greek dwellings, the following short review can be made.

In the study of ref. [10], simultaneous indoor and outdoor ozone measurements were conducted over a period of several days in two buildings of similar size but very different in construction materials, operation and use. It was shown that the differences between the two buildings are reflected in the indoor/outdoor (I/O) ozone concentration ratios. In addition, it was deduced that the I/O ozone concentration ratios are a sensitive indicator of an indoor VOCs source and of abrupt changes in the air exchange rate.

The effect of smoking in indoor ozone concentrations in a controlled environment (a small flat in Athens, Greece) was investigated by ref. [11]. Elevated I/O ozone concentration ratios (above 2.0) were reported and correlated with the presence of high TVOCs (total volatile organic compounds) concentrations in the tobacco smoke.

Measurements of ozone levels in two buildings of tertiary education have been reported [12,13]. In the one case [12], the indoor ozone concentrations were similar to those outdoors, especially during the summer months. In the other case [13], the indoor ozone concentrations were low (ranging between 1 and 10 ppb) and consistently much lower relative to the corresponding outdoor levels.

Finally, two studies have investigated the main processes that control indoor air ozone levels in three residential flats [14] and an office microenvironment [15] all located in the Athens (Greece) metropolitan area. Both studies provided strong evidence that transport from the outdoor air and the deposition into indoor surfaces are the main mechanisms that can (largely) account for the production and consumption of indoor ozone respectively, as also originally proposed by ref. [3]. The relative contribution of other source (chemical reactions) and sink (transport, chemical reactions, filtration) mechanisms to the steady-state ozone concentration was also estimated.

In this work, a systematic set of measurements of ozone levels in indoor air of several dwellings in three areas of Greece was undertaken (59 dwellings in Athens, 20 dwellings in Salamina Island and 23 dwellings in Zakynthos Island). Ozone concentrations were measured as a function of three parameters: the time of day, the time period of air exchange and the floor of the dwelling. In addition, the indoor vs outdoor (I/O) ratio of ozone concentration was systematically explored.

Materials and Methods

Indoor and outdoor ozone levels were measured with a GSS type (Gas Sensitive Semiconductor) portable ozone monitor (Aeroqual Series 200) equipped with the OZL head which is suitable for measuring ozone levels in the 0-0.5 ppm range (minimum detection limit: 1 ppb). The ozone level is recorded every 1 min. Each ozone measurement corresponds to an average of the 10 values recorded during a sampling period of 10 min. Two different measurement protocols were employed.

Protocol 1 involved measurement of ozone levels in four different times during the day (A: morning between 10.00 h-11.00 h, B: early afternoon between 13.30 h-14.30 h, C: early night between 18:30 h-19:30 h, D: late night between 23.00 h-24.00 h). At each daytime (i.e., A, B, C or D), indoor measurements were performed as a function of the time period that the openings of the specific dwelling remained opened/closed (denoted with codes b, c, d as explained below). More specifically, the following four measurement steps were applied sequentially at each time of day for each specific dwelling:

*Corresponding author: Dimitrios Nikolopoulos, Piraeus University of Applied Sciences, Department of Electronic Computer Systems Engineering, Petrou Ralli and Thivon 250, GR-122 44, Aigaleo, Greece, Tel: 3-6977-208318; E-mail: dniko@teipir.gr

Received November 02, 2015; Accepted November 09, 2015; Published November 11, 2015


Copyright: © 2015 Koulougliotis D, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
• Step 1: Measurement of outdoor ozone level
• Step 2: Measurement of indoor ozone level with the openings of the dwelling having remained open for 30 min (Code: b)
• Step 3: Measurement of indoor ozone level with the openings of the dwelling having remained closed for 15 min (Code: c)
• Step 4: Measurement of indoor ozone level with the openings of the dwelling having remained closed for 30 min (Code: d)

Ozone measurements via Protocol 1 were performed in dwellings in two areas namely Athens (38 dwellings) and Salamina Island (20 dwellings) between mid-May and mid-June 2014.

Protocol 2 involved measurement of ozone levels in a single time during the day according to the following sequential steps:
• Step 1: Measurement of outdoor ozone level
• Step 2: Measurement of indoor ozone level with the openings of the dwelling having remained closed for 15-20 min

Ozone measurements via Protocol 2 were performed in dwellings in two areas namely Athens (21 dwellings which are different from those of Protocol 1) and Zakynthos Island (23 dwellings) between mid-April and mid-June 2013 (Zakynthos) and 2014 (Athens).

In order to detect statistically significant differences (at the 95% significance level, p<0.05) between the mean values of the measured ozone concentrations the ANOVA or t-test (independent or paired) were employed. The statistical analysis and graphical representation of the data was performed via the program OriginPro 7.5.

Results and Discussion

Dependence of indoor ozone on the floor of the dwelling

In the Figures 1-3, the measured ozone concentrations (by following Protocol 1) in 29 (non-basement) dwellings in Athens are shown as a function of the dwelling floor via the use of box whisker plots for three specific daytimes, namely time A (Figure 1), time B (Figure 2) and time C (Figure 3). The floor distribution of the dwellings was the following:
• Groundfloor: 6 dwellings (Code: 0);
• First floor: 8 dwellings (Code: 1), Second floor: 5 dwellings (Code: 2);
• Third or higher floor: 10 dwellings (Code: 3)

It is noted that the measurements taken in 9 basements have not been included in Figures 1-3 since in this type of dwellings, all measured ozone levels were equal to zero (or lower than the minimum detection level of 1 ppb) in all daytimes. This is not an unexpected result since research has shown that the main source of indoor ozone (>95%) is transport from the outdoor environment [15]. In addition, the production of ozone via chemical reactions is expected to be minimal (or non-existent) in the basement dwellings since they are not naturally lighted during the whole day. It is also noted that all outdoor and indoor ozone measurements taken during daytime D (late night) were equal to zero (or lower than the minimum detection level of 1 ppb) and, thus, they are not reported separately.

In order to detect the existence of a dependence of the ozone levels as a function of the dwelling floor, the ANOVA test was applied for comparing the mean ozone concentrations of measurements that were taken under the same conditions. Such measurements were those that correspond to boxes of the same color (for example, between all measurements conducted with openings closed for 15 min, i.e., blue boxes). No statistically significant differences (at the 95% significance level) were detected between the mean ozone concentrations for all daytimes (A, B, or C). Thus, it may be concluded that there is no evidence for any dependence of the ozone levels from the dwelling floor.

However, an observation of Figures 1-3 shows a tendency for a decrease in the ozone levels as a function of the time period that dwelling openings remain closed. The ANOVA analysis provides corroborating evidence for this dependence. In the following section, this dependence will be examined in more detail by taking into account all dwellings, i.e., irrespective of floor.

Dependence of indoor ozone on the time of day and the time period of air exchange

In Figure 4 the ozone concentrations measured in all non-basement dwellings in Athens (29) are presented in the form of box-whiskers plots of outdoor and indoor ozone measurements during daytime A (morning) taken in 29 dwellings in Athens depicted as a function of the dwelling floor (Ground floor=0, First floor=1, Second floor=2, Third floor and above=3). The following color code has been used: Black (outdoor ozone), Red (indoor ozone with openings open for 30 min – In0b, In1b, In2b, In3b), Blue (indoor ozone with openings closed for 15 min – In0c, In1c, In2c, In3c), Purple (indoor ozone with openings closed for 30 min – In0d, In1d, In2d, In3d).
plots grouped together for each daytime (A, B, C, D) and as a function of the time period of air exchange (time period that openings remained open/closed) within each daytime. The same color was employed for the same type of measurement (step of Protocol 1) namely black, red, blue and purple for steps 1, 2 (Code: b), 3 (Code: c) and 4 (Code: d) respectively.

With the exception of late night where the measured ozone concentrations were always (both indoors and outdoors) below the minimum detection limit (1 ppb), a specific motif is repeated during all the other daytimes: The indoor ozone concentration is elevated in step 1 (i.e., when the openings have remained open for 30 min) and systematically somewhat smaller (p<0.05 via paired t-test) than the corresponding outdoor concentration. Subsequently, as the openings remain closed for an increasing time period (15 min in step 3 and 30 min in step 4) the indoor ozone concentration is systematically decreasing. In fact, the mean indoor ozone concentrations of steps 2, 3 and 4 (Codes: b, c and d respectively) show pairwise statistically significant differences (p<0.05 via paired t-test), irrespective of the daytime of the measurement (Morning, Early afternoon, Early night). The decrease in the indoor ozone level as the openings remain closed for an increasing amount of time is most probably attributed to deposition into indoor surfaces and less to consumption via chemical reactions. As evaluated by ref. [15] the percentage contributions for an increasing amount of time is most probably attributed to deposition into indoor surfaces and less to consumption via chemical reactions. As evaluated by ref. [15] the percentage contributions of deposition, chemical transformation, transport to outdoors and filtration to the overall indoor ozone loss rates are ca. 57%, 20%, 20% and 3% respectively. In our case, the transport to outdoors is drastically diminished since the openings have remained purposefully closed. In addition, by making pairwise comparisons (paired t-tests) of the mean indoor ozone concentrations of a specific step (1, 2, 3, or 4) in different daytimes, the following trend is shown to take place in all steps of Protocol 1.

\[
\begin{align*}
\text{O}_3^{\text{early afternoon-B (step 1)}} & > \text{O}_3^{\text{morning-A (step 2)}} > \text{O}_3^{\text{early night-C (step 3)}} > \text{O}_3^{\text{late night-D (step 4)}} \quad \text{for } i=1, 2, 3, 4
\end{align*}
\]

Subsequently, by making pairwise comparisons (paired t-tests) of the mean ozone concentrations of a specific step (1, 2, 3, or 4) in different daytimes, the following trend is shown to take place in all steps of Protocol 1.

\[
\begin{align*}
\text{O}_3^{\text{early afternoon-B (step 2)}} & > \text{O}_3^{\text{morning-A (step 1)}} > \text{O}_3^{\text{early night-C (step 3)}} > \text{O}_3^{\text{late night-D (step 4)}} \quad \text{for } i=1, 2, 3, 4
\end{align*}
\]

In accordance to the case of Athens, the measurements in Salamina Island show that the diurnal behavior of the indoor ozone level is followed by the indoor ozone level as well. However, there exists a small difference between the diurnal behaviors of the ozone level in the two areas; more specifically the mean ozone concentrations measured in the morning and in early night in Salamina Island are statistically similar (p>0.05 via paired t-test) while they are statistically different (p<0.05 via paired t-test) in Athens.

**Indoor vs Outdoor ozone concentrations (I/O ratios)**

Tables 1-3 show the indoor/outdoor (I/O) ozone concentration ratios as a function of the conditions of air exchange (Openings open-
Step 2, Openings closed for 15 min-Step 3, Openings closed for 30 min-Step 4) for each daytime (Morning, Early afternoon, Early night) for Athens (29 non-basement dwellings), Salamina Island (20 groundfloor dwellings) and for all 49 dwellings in both areas, respectively. The paired samples t-test was employed in order to compare the mean values along one row or along one column for statistically significant differences. The use of letters (α, β, γ) as superscripts has been employed for denoting statistically significant differences along one row. The use of numbers (1, 2) as superscripts has been employed for denoting statistically significant differences along one column.

As shown in the above tables, both in Athens (Table 1) and Salamina Island (Table 2), as well as when all dwellings are examined together (Table 3) there is a systematic trend for a decrease in the I/O ozone concentration ratio as the possibility for air exchange is diminished along step 2 to step 3 to step 4 of the measurement Protocol 1. This trend is observed in all daytimes (Morning, Early afternoon, Early night) and it is denoted by the different superscripts (α, β, and γ) along one row. Interestingly, all I/O ratios (i.e., irrespective of daytime and measurement Step) in the two areas (Athens and Salamina) are statistically similar.

When comparing the I/O mean values along columns, the following results are obtained (as denoted in the numerical superscripts of Table 3): In Step 2 (openings open for 30 min) the I/O ratios are similar in all daytimes (common superscript equal to J). In both Steps 3 and 4 (i.e., as the openings remain closed for either 15 min or 30 min) the I/O ratios of morning and early afternoon are statistically similar (common superscript equal to J) while this ratio is lowered in early night (as denoted by the different superscript equal to 2). In fact, the I/O ratio is a parameter that is always examined during the study of indoor air pollution and it has received particular attention in the case of ozone [9]. In the dwellings examined in the current study (both in Athens and Salamina Island), the mean ozone I/O ratios range between 0.47 and 0.90 depending on the daytime and most importantly on the conditions of air exchange. These I/O values are in the same range with those reported by ref. [10], however lower values (close to 0.3 or lower) have been reported as well [4,15,17]. The rather elevated I/O ozone concentration ratios in our study is probably due to a low deposition velocity in the indoor surfaces in combination with a low air exchange rate [10,17].

Dependence of outdoor/indoor ozone on the degree of urbanization

By using the data of Figures 4 and 5, the mean ozone concentrations of Athens and Salamina Island were compared for each daytime. The independent samples t-test was employed in order to detect statistically significant differences at the 95% significance level. For all daytimes (Morning, Early afternoon, Early night) the following result was obtained: For each Step (1-4) of Protocol 1, the mean ozone concentrations in Athens were statistically higher than those in Salamina Island. In other words, the higher outdoor mean ozone concentrations in Athens relative to Salamina Island were accompanied by higher indoor mean ozone concentrations as well under all conditions of air exchange (Open openings, Openings closed for 15 min, Openings closed for 30 min). In fact, all mean ozone levels measured in Salamina (either indoors or outdoors) were below 56 ppb which is the target value for the protection of human health [16].

In Figure 6, indoor and outdoor ozone measurements conducted in 18 non-basement dwellings in Athens and 23 dwellings in Zakynthos Island by following Protocol 2 (Step 1: outdoor ozone, Step 2: indoor ozone with openings closed for 15-20 min) are shown as a function of the time of measurement during the day. It is noted that the 18 dwellings in Athens are different from those of Protocol 1 and that in Athens measurements were conducted in 3 basement dwellings as well in which the ozone levels were below the detection limit (1 ppb). The error bars in the data of Figure 6 correspond to the standard deviation of the mean value of the 10 instrument readings taken during the 10 min sampling period.

It is worth noting that even though each measurement of Figure 6 corresponds to a different dwelling and often in a several day, the diurnal behavior of the ozone level (both in indoor and outdoor air) in Athens displays a distinct characteristic maximum in the early afternoon hours (ca. between 14.00 h-15.00 h) as already seen in the literature [14,15] and as seen in the measurements of Protocol 1.
The outdoor experimental data taken in Zakynthos Island display also a similar characteristic peak of the ozone concentration (i.e., between 14.00 h-15.00 h). However, these data show a rather not systematic behavior during the night hours (ca. between 19.00 h-21.00 h). This could be related with the fact that these measurements were taken in different days. During all daytimes (until around 19.00 h) the outdoor ozone levels in Zakynthos Island were ca. a factor of 2 lower relative to those in Athens, a fact which is not unexpected if one takes into account the significantly lower degree of urbanization of the insular environment. With regard to the indoor ozone levels in Zakynthos Island, it is worth noting that they were almost always (with the exception of two dwellings for which the I/O ratio ranged between 0.55-0.60) below the minimum detection limit (1 ppb).

The above described comparisons of ozone levels between a fully urban and a less urban environment (Athens vs Salamina Island, Athens vs Zakynthos Island) showed that the lower outdoor mean ozone concentrations in the less urban area seem to also translate into lower indoor ozone concentrations.

Acknowledgements

This research has been co-financed by the European Union (European Social Fund-ESF) and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) Research Funding Program: THALES Investing in knowledge society through the European Social Fund-ESF) and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) Research Funding Program: THALES Investing in knowledge society through the European Social Fund.

References