Concentrations of VOCs and ozone in indoor environments: A case study in two Mediterranean cities during winter period

CONCENTRATIONS OF VOCS AND OZONE IN INDOOR ENVIRONMENTS: A CASE STUDY IN TWO MEDITERANEAN CITIES DURING WINTER PERIOD

John G. Bartzis[1*], Costas Michael[2], Stella Michaelidou[2], Dafni A. Missia[1], Dikaia E. Saraga[3], Evangelos I. Tolis[1], S. Psoma[1], Christine Petaloti[1], Dimitrios Kotzias[4] and Josefa M. Barero-Moreno[4]

[1]University of West Macedonia, Dept. of Eng.& Manag. of Energy Resources, Sialvera & Bakola Street, 50100 Kozani, Greece

[2]State General Laboratory, Section of Environmental Chemistry, Pesticides, Ecotoxicology and Radioactivity, 44 Kimonos Street, 1451 Nicosia, Cyprus

[3]Environmental Research Laboratory, Institute of Nuclear Technology - Radiation Protection, NCSR "DEMOKRITOS", 15310 Aghia Paraskevi Attikis, Athens, Greece

[4]Joint Research Centre (JRC), Institute for Health and Consumer Protection, TP. 260, 21020 Ispra (VA) Italy

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ABSTRACT

Building materials represent the largest surfaces indoors and are the major contributors of volatile organic compounds (VOCs) in the indoor environment. This study which is conducted in the frame of BUMA project (Prioritization of Building Materials Emissions), aims at assessing the human exposure to air hazards emitted by building materials. In this study, indoor and outdoor VOCs and ozone measurements from field campaigns in two Mediterranean cities (Nicosia and Athens in winter period) are presented and discussed. The field campaigns concern weekly measurements. The campaigns were conducted in four buildings in each city (1 Public building, 1 school and 2 houses) and concern weekly measurements. Passive samplers were used for collecting VOCs and ozone.

Eight (8) hydrocarbons (benzene, toluene, ethylbenzene, m,p-xylene, a-pinene, o-xylene and d-limonene), five (5) carbonyl compounds (formaldehyde, acetaldehyde, proprionaldehyde, acetone and hexanaldehyde) and ozone have been measured. Additional air exchange measurements have been conducted using tracer gas techniques. Hazardous substances such as benzene, formaldehyde and acetaldehyde present indoor concentrations that range between 1.5–10.2, 5.8-43.2 and 4.5 – 15 μg/m^3, respectively. VOC concentration data show a considerable variability due to the different indoor emission sources, ventilation rates and outdoor environment's influence. A significant contribution to indoor measured concentrations seems to come from the building materials. Ozone outdoor concentrations are reduced substantially inside, indicating relatively strong indoor ozone sinks.

KEYWORDS: Indoor air quality, VOCs, formaldehyde, passive sampling, ozone

INTRODUCTION

It is a fact that people spend on average 90% of their life indoors, and during the last decades, great concern has been focused on the adverse health effects that may be caused by significant indoor pollutant concentrations. Both indoor and outdoor sources contribute to the development of pollutants' concentration and composition profiles in an internal environment. Ventilation plays a crucial role for estimating and evaluating the levels of pollution and its contingent source. Many inorganic and organic compounds have identified in indoor air. Among these, VOCs and ozone comprise a group of pollutants that gained particularly significant attention due to their various sources and their harmful effects on humans (carcinogenicity, irritations etc).

VOCs that commonly detected in indoor air are aliphatic hydrocarbons, benzene and alkylated aromatic hydrocarbons, chlorinated hydrocarbons as well as aldehydes, ketones, and alcohols [1]. For many of these chemicals, the risk on human health and comfort is almost unknown and difficult to predict because of lack of toxicological data. In the frame of INDEX project the existing knowledge worldwide has been assessed on type and levels of chemicals in indoor air as well as the available toxicological information.

Thus, INDEX Project concluded in a priority ranking of 14 chemicals assigned to three groups [2].

Indoor ozone, which originates from both indoor (photocopiers and other machines) and outdoor (ventilation and infiltration systems) sources, is a common highly reactive oxidizing agent in indoor environment [3]. Ozone concentrations could be high enough to drive chemical reactions with monoterpenes and form ultrafine particles and irritating gaseous organic compounds [4].

This study was conducted in the framework of a European project partly funded by PHEA (Public Health Executive Agency), called "Prioritization of Building Materials Emissions (BUMA)''. The aim of the present work is the evaluation of the indoor and outdoor air quality, regarding VOCs and ozone, at Nicosia, Cyprus and Athens, Greece, focusing on organic compounds that belong to the first two priority groups of INDEX Project, such as benzene, formaldehyde, toluene, xylenes, and acetaldehyde.

MATERIALS AND METHODS

This study was carried out in 2007, from 9th to 16th of February and 8th to 15th of March for Nicosia and Athens, respectively. Measurements were conducted simultaneously in four buildings in order to evaluate the indoor VOCs and ozone levels. The study plan firstly included the selection of the buildings in which passive samplers were installed. The buildings employed in the present study were selected according to the following criteria: (1) the age of the building (2) the last reconstruction or renovation, as far as (3) the position (urban sites preferred) of the building. The main characteristics of the selected buildings summarized in Table 1. The buildings are four in every case, one public building, one school and two private houses. In addition, for indoor temperature and relative humidity (RH) measurements data loggers (HOBO H-8 onset) were used. Finally, ventilation measurements were conducted using tracer gas technique.

Moreover, questionnaires were filled in, giving valuable information regarding the sampling sites and activities taken place during sampling. At indoor locations, the passive sampling equipment was placed on sites on the wall approximately 1.5 m above the ground. Outdoor sampling locations were chosen to avoid significant point sources of pollution, such as building exhaust vents.

Indoor and outdoor measurements of BTEX, carbonyls and ozone were conducted using passive samplers named Radiello in each tested room and outside for one week. The samplers used for BTEX was Activated Charcoal Cartridges, CS_2-desorption for GC-Analysis (code 130), for Aldehydes DNPH-covered cartridges, acetonitrile desorption for HPLC-VIS (code 165) and for ozone 1, 2- di-(4-pyridyl) - ethylene covered cartridges for MBTH (3-Methyl - 2-Benzothiazolinone Hydrazone) solution desorption, UV-VIS (code 172). The analysis of BTEX was carried out by GC/FID after desorption of the analytes with CS_2 and included determination of benzene, toluene, xylenes, ethylbenzene, 1,2,4 trimethylbenzene, d-limonene, a-pinene. The determination of all analytes was confirmed by GC-MS. The analysis of carbonyls and ketones was carried out using HPLC-VIS after desorption of the analytes with acetonitrile and included determination of formaldehyde, acetaldehyde, acetone, propanal and hexanal. The analysis of ozone was conducted using spectrophotometer-VIS after desorption with (MBTH) solution. The analysis of the samples was conducted in the State General Laboratory (SGL) of Cyprus.

With tracer gas technique, air exchange rates were estimated using NORDTEST METHOD NT VVS 118. This method can be used in types of buildings, dwellings, offices, schools etc. The testing of ventilation is performed by using homogeneous emission of tracer gas at a constant rate in the ventilated system and subsequent analysis of the steady state concentration of that tracer gas in different parts of the system [5].

TABLE 1 - Main characteristics of selected buildings.

Nicosia	Public Building	School/Kindergarten	House 1	House 2
Location	City, heavy traffic	City, calm area, light traffic	Suburban, calm area, light traffic	Suburban area, No traffic
Building Status	A newly constructed building (2007) No human activity	New paint in 2005	New paint three (3) months ago. New furnishing in 2004	No major renovation. No human activity for three (3) days
Specific air flow rate (ACH)(h^{-1})	1.28	0.62	0.51	1.1
Athens	Public Building	School/Kindergarten	House 1	House 2
Location	Suburban area, light traffic	Suburban area, light traffic	Suburban area, light traffic	Suburban area, light traffic
Building status	New paint, furnishing and flooring in 2004	New paint in 2006	Constructed in 2005	New paint, flooring and furnishing in 2006. Smoking
Specific air flow rate (ACH) (h^{-1})	0.41	0.4	0.24	0.28

RESULTS AND DISCUSSION

VOCs. Summary statistics for the concentrations of all measured compounds in indoor air are given in Table 2. The most prevalent VOCs in buildings were toluene, xylenes, a-pinene, formaldehyde and hexanaldehyde. Indoor concentrations usually exceeded outdoor levels. Priority compounds constituted large proportion of sum of VOCs in Nicosia and Athens schools, respectively, (Figure 1) greater than those reported in Michigan classrooms. Moreover, VOCs concentrations tended to differ significantly between elementary (Nicosia) and middle schools (Athens) as it has been observed in similar studies at Michigan schools [6].

Reported public buildings' indoor concentrations of individual VOCs are generally below 50 μg/m^3 except for toluene and m,p- xylene in Nicosia public building. Levels of VOCs in Nicosia's office is much greater than those observed in Athens due to its age (newly constructed and not occupied until and during the sampling period). Mean concentrations of the majority of VOCs in both cities are below 10 μg/m^3, a common trend for both European and American countries [7]. However, new furnishing, renovation of some of the selected buildings or indoor human activities may result in temporarily higher concentrations e.g. Nicosia's public building and Athens' selected houses. High VOCs and O_3 concentrations in Athens houses can be

TABLE 2 - Average indoor measured concentrations of VOCs and ozone in all buildings (μg/m^3).

	Public Buildings		Schools		Houses	
	Athens	Nicosia	Athens	Nicosia	Athens	Nicosia
Benzene	1.6	ND*	2.4	4.5	6.4	2.6
Toluene	3.4	66.4	4.6	20.4	53.9	9
Ethylbenzene	0.8	25.6	0.8	1.9	13.4	1
m,p- xylene	1.8	110.3	2.3	5.3	55.6	4.5
o-xylene	0.8	27.8	0.9	2.3	14.2	1.6
a-pinene	1.2	24.3	2.1	1.7	22.2	3.1
1,2,4- TMB	1.1	7.5	1.4	4.8	5.4	2.3
d-limonene	2.6	3.5	2.3	24.1	43.5	9.4
Formaldehyde	11.1	24.2	6.3	21	28.8	16.8
Acetaldehyde	5.7	7.8	4.6	12.2	13.2	5.7
Acetone	26.7	39.9	11.9	24.5	56.5	106.7
Proprionaldehyde	2.6	5	1.9	2.5	4.7	2.7
Hexanaldehyde	17	35.9	6.8	14	41	13.7
Ozone	7.6	1.7	13.9	1.1	1.7	4.6

* ND: Non detected

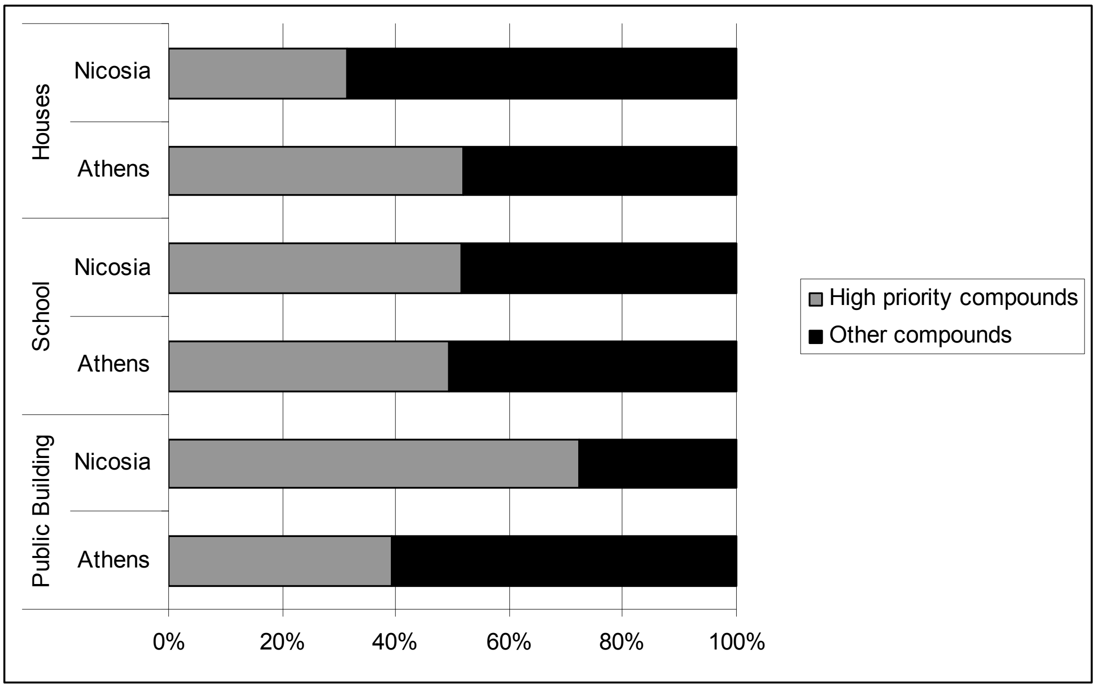

FIGURE 1 - Average percentage of sums of high priority compounds in selected buildings.

TABLE 3 - Indoor to Outdoor ratios in public buildings.

	Athens	Nicosia
Benzene	1.2	-
Toluene	1.2	4.3
Ethylbenzene	1.3	9.4
m,p-xylenes	1.2	13.5
o-xylene	1.1	8.6
1,2,4- trimethylbenzene	1.2	1.1
a-pinene	2.9	4.7
d-limonene	-	3.9
Formaldehyde	5.8	5.8
Acetaldehyde	3.2	3.5
Acetone	4.6	10.9
Proprionaldehyde	2.8	4.1
Hexanaldehyde	8.5	15.6
Ozone	0.1	0.03

attributed to the low air exchange rates (0.28 and 0.24 h^{-1}), as it is obtained from the ventilation measurements results.

Acetaldehyde and hexanaldehyde levels are lower than those found for private houses in Paris [8]. Such observations suggest probably the absence of indoor sources for acetaldehyde since acetaldehyde is mainly emitted from combustion processes. Propionaldehyde concentrations in houses were measured greater than those found in private houses [9]. The levels of formaldehyde did not exceed the WHO guideline value of 100 μg/m^3, which may cause nose and throat irritation in humans after short-term exposure [10]. Formaldehyde in Athens school exhibited the same levels observed in the same type of schools at Uppsala City [11] in contrast to Nicosia schools which presented greater concentrations due to the pupil's activities indoors (painting with markers etc.) and shown greater concentrations than schools in Shangai, China [12].

It is worth to notice that concerning priority compounds, except for benzene, indoor to outdoor ratios (I/O) in public buildings (Table 3) are substantially greater than unity (>1) suggesting important indoor sources for these VOCs. More specifically, for hexanaldehyde I/O ratio is up to 15.6, for m,p-xylene 13.5, for acetone 10.9, and for formaldehyde 5.8.

Ozone. The importance of measuring ozone in indoor environments comes from its ability to react with high molecular organic compounds and specifically with terpenes forming ultrafine particles and free radicals. As it is observed, outdoor concentrations are significantly higher in contrast with indoor levels. The indoor to outdoor ozone concentration ratio generally ranged between 0.2 and 0.7 indicating ozone – indoor chemistry relationship as mentioned by Nicolas *et al* [13]. Thus, for Nicosia's office, the I/O ratio, in combination with the occupants' absence inside the building, indicates that there are no strong indoor sources of ozone. In contrary, the indication is that there exist strong sinks of ozone indoors.

CONCLUSIONS

The concentration data show a considerable diversity due to the different indoor emission sources, ventilation rates and outdoor environments concentrations. Benzene, formaldehyde and acetaldehyde levels in public buildings are lower than those expected in indoor environments. The sum of priority compounds consist a large proportion of the sum of VOC in all selected buildings. The relatively high I/O ratios indicate strong indoor emissions sources except for benzene. Ozone outdoor concentrations seem to be reduced substantially inside; indicating relatively strong indoor ozone sinks.

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CORRESPONDING AUTHOR

John G. Bartzis
University of West Macedonia
Department of Engineering and
Management of Energy Resources
Sialvera & Bacola Str.
50100 Kozani
GREECE

Phone: +302461056620
Fax: +302461021730
E-mail: bartzis@uowm.gr

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