

## ASSESSMENT OF AIR QUALITY FROM PRIMARY SCHOOL CLASSROOMS AND THE PRESENCE OF VOLATILE ORGANIC COMPOUNDS (VOCs)

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**Abstract:** The concentrations of volatile organic compounds (VOCs) in the indoor and outdoor environment of five primary schools from Alba County were monitored during September 2011 and January 2012. Air samples from both indoor and outdoor environments were collected using Radiello passive air samplers. The VOCs were analyzed using a gas chromatograph with a DSQ II quadrupole mass spectrometer detector (GC-MS), following a desorption process. Generally, the VOCs levels were higher in the indoor environment than in the outdoor. Compounds as octane, nonane, decane, undecane, dodecane and tridecane were detected in 90% of the samples and the measured concentrations ranged between 7.59 – 44.2  $\mu\text{g}\cdot\text{m}^{-3}$  in indoor and 4.26 – 20.24  $\mu\text{g}\cdot\text{m}^{-3}$  in outdoor. Other compounds as toluene, ethylbenzene, xylene or styrene were detected in 35 – 60% of the collected samples and their levels ranged between 0.24 – 31.00  $\mu\text{g}\cdot\text{m}^{-3}$  in indoor and 10.25 – 66.24  $\mu\text{g}\cdot\text{m}^{-3}$  in outdoor. Elevated indoor VOCs concentrations were associated with the presence of building materials like polystyrene isolation, presence of plastic laminated or composite furniture, and the PVC panel; with an increase number of occupants, with low ventilation rates, and outdoor pollution, while the outdoor VOCs, especially the aromatics, reflect the level of urbanization/industrialization, the traffic proximity and intensity.

**Keywords:** volatile organic compounds, indoor air pollution, gas chromatography, mass spectrometer detector, Alba County, Romania.

### 1. INTRODUCTION

VOCs are considered to be any organic compounds resulted from human activities, other than methane, capable to produce photochemical oxidants through reaction with nitrogen oxides, in the presence of sunlight. Concerns regarding the presence of VOCs are raised by their potential adverse health effects on humans (Roba et al., 2013) and also, by their unwanted impact on the global environment. Most of the VOCs that are regulated through national and international laws seem to be able to produce carcinogenic, teratogenic and/or mutagenic effects on living organisms, based on the scientific evidences available, and these compounds are considered to be directly implicated in

phenomena such as global warming (Grasso & Singh, 2008), stratospheric ozone depletion (Ma & Weele, 2000; Amanatidis & Ott, 1995; Rozema et al., 2005), photochemical ozone formation (Jenkin & Clemitshaw, 2000; Ling et al., 2011; Derwent, 1990; Derwent et al., 2007) and odor nuisance (Demeestere et al., 2007; Gallego et al., 2008; Peng et al., 2009).

Considering the hazard posed by the volatile organic compounds both in the outdoor and/or in the indoor environment, their study became a major issue at worldwide level.

The aims of this paper were: (1) to quantify the presence of VOCs in the indoor and outdoor environments from five primary schools in Alba County, Transylvania; (2) to characterize the distribution and the variability of VOCs in the

investigated environments; and (3) to evaluate the potential health risks caused by the exposure to VOCs.

The novelty of this study is that it provides a comprehensive set of data regarding the presence and distribution of 18 VOCs in the indoor and outdoor environments of five schools from Alba County. No such study has been conducted in the area by focusing on these compounds. Only few international studies have monitored the presence of some of these pollutants in the indoor air from schools, generally their presence is studied in the outdoor urban areas, in residential areas, or workplace. This study has a major importance, considering the severe health effects associated with the presence of VOCs in the indoor air from schools. The individuals directly affected by the exposure to such pollutants are the children, a major risk group, vulnerable to air pollution, which spend inside the school buildings approximately 30% of their time, which is more than in any other building type other than their homes. Moreover in Romania, comparing to other European countries, there are no regulations regarding the age, the furniture, or the building materials allowed to be used for redecoration in a school building, in order to limit the indoor emission of VOCs and other pollutants. The present study provides important information in this regard.

## 2. MATERIALS AND METHODS

### 2.1. Sampling

Five primary schools were selected from five locations (rural and urban area) from Alba County: Unirea, Aiud, Alba Iulia, Sebeş and Vinţu de Jos (Table 1).

The VOCs sampling was performed during November (2011) and January (2012). The air samples were collected by passive method using Radiello cartridges, which were placed in three classrooms in each of the five primary schools. The Radiello cartridge absorbents were exposed for 5 days, the equivalent of 120 hours, starting from Monday until Friday. In case of all five locations, it was also selected a sampling location from outdoors, in order to evaluate if there are any correlation between indoor and outdoor VOCs level. Samples were collected in duplicate, each time. The air samples were transported in the laboratory, where they were kept in refrigerator (4°C at dark) and analyzed within 48 hours from sampling.

### 2.2. Chemicals and materials

VOCs mix standard containing 50 components (49149-U) at 1000 µg·mL<sup>-1</sup> in

methanol:water (97:3) was purchased from Supelco (Bellefonte, PA, USA). Carbon disulfide (CS<sub>2</sub>) (Chromasolv for HPLC, ≥ 99.9 %) was purchased from Sigma-Aldrich (St. Louis MO, USA).

The VOCs were sampled using Radiello cartridges, activated with charcoal (RAD130), from Supelco (Bellefonte, PA, USA).

### 2.3. Chemical analysis of VOCs

The VOCs absorbed on the active charcoal were eluted with 2 mL CS<sub>2</sub> through dynamic condition, over 30 minutes. 1 µL of supernatant was injected in the GC-MS system. Volatile organic compounds were measured using a Focus gas chromatograph (GC) with DSQ II quadrupole mass spectrometer detector (GC-MS, Thermo Electron Corporation, USA) provided with a split/splitless injection port.

TR-5 MS non polar capillary column (5% diphenyl – 95% dimethyl polysiloxane, Thermo Electron Corporation, USA) with 30 m length x 0.25 mm. I.D., x 1 µm film thickness was used for chromatographic separation of volatile organic compounds.

Oven temperature was set as follows: 40°C (hold constant for 7 min) followed by a heating at 100°C with a rate of 7°C·min<sup>-1</sup>, after which the temperature was raised continuously till 280°C with a rate of 10°C·min<sup>-1</sup>. This final temperature (280°C) was maintained for 3 minutes. Full scan mode was used during GC-MS analysis. Chromatographic and mass spectrometric data were recorded and processed using the XCalibur software (Thermo Electron Corporation, USA).

### 2.4. Quality assurance / Quality control

Methods performance was evaluated for all volatile organic contaminants that were measured. Blank samples were analyzed as a routine, at every six air samples, for those samples where no chromatographic peaks of the target VOCs were recorded.

The limits of detection (LOD) for the investigated VOCs were established by calculating the concentration of the target analytes that correspond to three times the background of noise level. The LOD values for the analyzed VOCs ranged between 0.002 – 0.052 µg·m<sup>-3</sup>. Extraction methods recovery was performed on spiked blank samples (n = 10) with the following amounts of volatile organic compounds: 1 µg·m<sup>-3</sup>, 5 µg·m<sup>-3</sup> and 10 µg·m<sup>-3</sup>. The spiked samples were left for equilibration for 12 hours before performing the extraction and analysis,

respectively. The recovery tests were performed in triplicate for each sample. The recovery levels ranged between 73 – 122% for all the analyzed VOCs. No additional corrections for recoveries were added to the final results.

### 3. RESULTS AND DISCUSSIONS

Several statistic data regarding the level of the investigated VOCs in both indoor and outdoor environments are summarized in table 2.

#### 3.1. The presence and distribution of VOCs in the indoor environment

The analysis of indoor air samples proved the presence of 12 VOCs as follows: 6 alkanes (octane,

nonane, decane, undecane, dodecane and tridecane), 4 aromatic compounds (toluene, ethylbenzene, total xylene and styrene) and 2 chlorinated compounds (trichloroethylene and tetrachloroethylene).

Except for styrene, tetrachloroethylene and trichloroethylene, which were not detected in the classrooms from Sebeş and Vințu de Jos, the other VOCs were present in all the investigated schools. The total VOCs was considerably higher in the classrooms from Alba Iulia ( $235.30 \mu\text{g}\cdot\text{m}^{-3}$ ) than in Aiud ( $186.38 \mu\text{g}\cdot\text{m}^{-3}$ ), Vințu de Jos ( $165.90 \mu\text{g}\cdot\text{m}^{-3}$ ), Unirea ( $156.08 \mu\text{g}\cdot\text{m}^{-3}$ ) and Sebeş ( $119.15 \mu\text{g}\cdot\text{m}^{-3}$ ).

The difference of total VOCs concentration in the five schools shows the influence of local sources on VOCs level.

Table 1. Characterization of the investigated indoor and outdoor environments.

Characteristics	Alba-Iulia	Aiud	Unirea	Vințu de Jos	Sebeş
Surface (m <sup>2</sup> )	27 - 42	37.6 - 55	32 - 68	40 - 48.6	49.5 - 64
High (m)	3.8	3.2	3.5	3.2 - 3.8	1.5 – 3.80
Window surface (m <sup>2</sup> )	3 - 6	5.7 - 17	6.5 - 13	5.1 - 9.3	6.6 – 7.2
Children	20 - 24	26 - 28	20 - 24	15 - 32	27 - 32
Year of construction	1890	1973	1904	1974 / 2007	1875
Renovation	2007	1989 / 2009	2006/2007	2009	2008/2010
Hours of class / week	25 – 40	20 - 21	20 – 21	20 – 21	25 – 40
Ventilation	natural	natural	natural	natural	natural
Heating system	hot water radiators / convectors	hot water radiators / convectors	hot water radiators / convectors	hot water radiators / convectors	terracotta (natural gas); hot water radiators / convectors
Furniture	plastic laminate / composite; wood; <sup>1</sup> PVC panel (h=1.30 m)	plastic laminate / composite	plastic laminate / composite	plastic laminate / composite	plastic laminate / composite
Floor covering material	laminated over wood parquet	beech parquet, recently painted (February 2011)	laminated parquet	beech and fir parquet	old painted beech parquet covered by carpet; laminated
Ceiling	polystyrene	concrete	wallpaper	plasterboard	polystyrene; plasterboard; wood
Paint	solvent and water based paint	oil paint (h = 1.25 m)	solvent and water based paint	oil paint (h = 0.8 m)	solvent and oil based paint
Walls (thickness)	double and simple (80 cm)	simple (33 cm)	double (60 cm)	double (45 cm)	double and simple (75 cm)
Isolation	polystyrene (15 cm)	no	no	no	no
Foundation	concrete	concrete	concrete	concrete	concrete
Location	commercial/residential	commercial/residential	rural	rural	commercial/residential
Heavy traffic road	road at 15 m; train station at 500 m	-	road at 10 m	road at 1.5 km; railway at 2 km	road at 25 m
Gasoline stations	3 gasoline stations on 0.5 km area	-	-	-	8 gasoline stations on 8 km area
Industry in the area	-	metallurgical <sup>2</sup>	-	wood-based panels <sup>3</sup> ; textiles and leather <sup>4</sup>	wood-based panels <sup>5</sup> ; furniture <sup>6,7</sup> ; leather <sup>8</sup>

<sup>1</sup>PVC- Polyvinyl chloride; <sup>2</sup>Metallurgical industry (400 workers) - 1 km distance; <sup>3</sup>Wood-based panels factory (550 workers) – 5-6 km distance; <sup>4</sup>Textiles and leather factory (150 workers) - 0.5 km distance; <sup>5</sup>Wood-based panels factory (550 workers) - 2 km distance; <sup>6</sup>Furniture factory (1,230 workers) - 2 km distance; <sup>7</sup>Furniture factory (233 workers) - 2 km distance; <sup>8</sup>Leather factory (700 workers) - 2 km distance

Table 2. Summarized statistics for the VOCs level in the indoor and outdoor air.

VOC compounds	No. of samples		Range of conc. ( $\mu\text{g}\cdot\text{m}^{-3}$ )		Average ( $\mu\text{g}\cdot\text{m}^{-3}$ ) $\pm$ SD*	
	indoor	outdoor	indoor	outdoor	indoor	outdoor
Alkanes						
4-methyl-2-pentane	30	10	ND**	4.12 – 10.27	ND	6.68 $\pm$ 2.72
Octane	30	10	7.59 – 17.9	5.15 – 12.51	13.00 $\pm$ 4.22	9.85 $\pm$ 2.69
Nonane	30	10	18.22 – 31.00	8.15 – 17.11	24.06 $\pm$ 5.40	13.13 $\pm$ 3.81
Decane	30	10	16.80 – 44.20	10.22 – 20.24	29.82 $\pm$ 10.23	15.23 $\pm$ 4.05
Undecane	30	10	9.25 – 23.60	4.59 – 17.05	15.43 $\pm$ 5.77	7.41 $\pm$ 4.85
Dodecane	30	10	8.16 – 19.20	5.21 – 16.32	13.33 $\pm$ 4.36	9.26 $\pm$ 4.44
Tridecane	30	10	11.90 – 20.20	4.26 – 15.33	15.54 $\pm$ 3.29	6.47 $\pm$ 4.14
<i>Total alkanes</i>	<i>30</i>	<i>10</i>	<i>79.71 – 149.00</i>	<i>57.41 – 102.61</i>	<i>111.19 <math>\pm</math> 25.55</i>	<i>72.95 <math>\pm</math> 17.46</i>
Aromatic compounds						
Toluene	30	10	18.90 – 31.00	35.26 – 66.24	23.63 $\pm$ 4.95	39.54 $\pm$ 12.30
Ethylbenzene	30	10	12.30 – 20.20	10.25 – 40.02	16.72 $\pm$ 3.21	20.28 $\pm$ 11.30
Total xylene	30	10	8.24 – 11.90	11.25 – 22.01	9.94 $\pm$ 1.37	12.72 $\pm$ 4.35
Styrene	30	10	0.24 – 17.11	ND	8.66 $\pm$ 8.44	ND
<i>Total aromatic</i>	<i>30</i>	<i>10</i>	<i>39.44 – 80.21</i>	<i>70.61 – 128.27</i>	<i>55.48 <math>\pm</math> 15.29</i>	<i>89.50 <math>\pm</math> 25.09</i>
Alcohols						
Ethanol	30	10	ND	3.18 – 6.37	ND	4.77 $\pm$ 2.25
1-propanol	30	10	ND	3.91 – 27.99	ND	13.19 $\pm$ 9.46
1-butanol	30	10	ND	2.15 – 6.18	ND	3.84 $\pm$ 2.09
<i>Total alcohols</i>	<i>30</i>	<i>10</i>	<i>ND</i>	<i>7.09 – 34.36</i>	<i>ND</i>	<i>17.40 <math>\pm</math> 11.98</i>
Chlorinated compounds						
Dichloromethane	30	10	ND	5.12 – 6.11	ND	5.61 $\pm$ 0.70
Trichloroethylene	30	10	0.18 – 9.05	ND	5.46 $\pm$ 4.67	ND
Tetrachloroethylene	30	10	0.06 – 7.11	ND	4.36 $\pm$ 3.77	ND
1,4-dichlorobenzene	30	10	ND	5.11 – 12.05	ND	8.58 $\pm$ 4.91
<i>Total Chlorinated</i>	<i>30</i>	<i>10</i>	<i>6.09 – 16.16</i>	<i>5.11 – 18.16</i>	<i>9.82 <math>\pm</math> 5.52</i>	<i>9.46 <math>\pm</math> 7.53</i>
<b>VOCs<sub>total</sub></b>	<b>30</b>	<b>10</b>	<b>119.15 – 235.30</b>	<b>129.59 – 261.08</b>	<b>192.59 <math>\pm</math> 39.97</b>	<b>176.77 <math>\pm</math> 48.96</b>

\*SD –standard deviation; \*\*ND – not detected

The distribution of the 12 VOCs detected in the investigated classrooms is presented in figure 1. The results indicate the predominance of nonane, decane, toluene and ethylbenzene among the investigated VOCs.

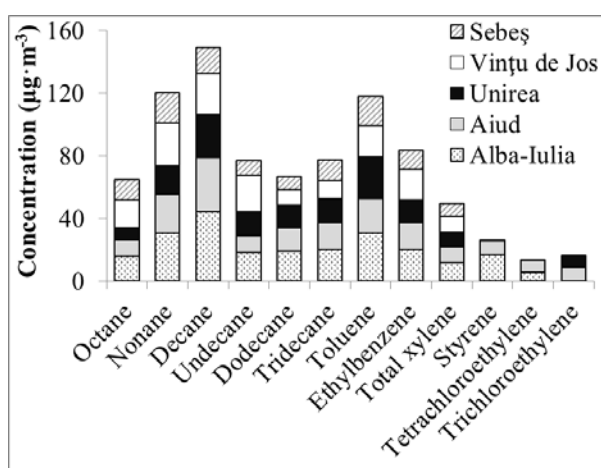


Figure 1. VOCs distribution in indoor environment.

The highest levels of VOCs were registered in the classrooms from Alba-Iulia school. One of the causes is the building material used in these indoors

such as: the polystyrene isolation (the other schools have no isolation), the polystyrene ceiling, the presence of plastic laminated or composite furniture, the presence of the PVC panel (h=1.30 m) in the classrooms (the other schools do not have PVC panels) (Table 1). The presence of high levels of aromatic VOCs (toluene, ethylbenzene and xylene) in the classrooms from Alba-Iulia reflects the influence of outdoor pollution; these are common urban pollutants related to traffic emissions (Clobes et al., 1992). In the close vicinity (500 m) of the school from Alba-Iulia, 3 gasoline stations are located, as well as a heavy traffic road (25 m distance) and a train station (500 m) (Table 1). All these are important sources of aromatic VOCs.

The chlorinated VOCs, namely tetrachloroethylene (0.06 - 7.11  $\mu\text{g}\cdot\text{m}^{-3}$ ) and trichloroethylene (0.18 - 9.05  $\mu\text{g}\cdot\text{m}^{-3}$ ), were detected only in the indoor air, having high levels in the classrooms from Alba-Iulia. Their presence is the consequence of the polyvinyl chloride panels used only in the classrooms from this school and the frequently use of cleaning products. Another VOC detected only in the indoor air was styrene. The high

level of styrene registered in the Alba-Iulia school reflects the presence of polystyrene wall isolation and polystyrene ceiling from these classrooms.

A particular problem raised in the classrooms from Alba-Iulia as a result of the low air-change rate. These classrooms have the lowest window surface (3-6 m<sup>2</sup>) (Table 1). The low ventilation rate causes the accumulation of pollutants originated from indoor air. Furthermore, the classrooms from Alba-Iulia were very crowded, having relatively small areas and a large number of children. For example in the classrooms from Alba-Iulia the assign area for a children was approximately 1.57 m<sup>2</sup>, comparing to the classrooms from Aiud (1.71 m<sup>2</sup>), Vințu de Jos (1.88 m<sup>2</sup>), Sebeș (1.92 m<sup>2</sup>) and Unirea (2.27 m<sup>2</sup>). Such high indoor densities are limiting the volume of fresh air available for children.

### 3.2. The presence and distribution of VOCs in the outdoor environment

15 individual VOCs were detected in the outdoor air samples as follows: 7 alkanes (4-methyl-2-pentane, octane, nonane, decane, undecane, dodecane and tridecane), 3 aromatic compounds (toluene, ethylbenzene and total xylene), 3 alcohols (ethanol, 1-propanol, and 1-butanol) and 2 chlorinated compounds (dichloromethane and 1,4-dichlorobenzene). Except for 4-methyl-2-pentane, ethanol, 1-butanol and the chlorinated compounds, the other VOCs were present in all the investigated outdoor environments. The total VOCs was considerably higher in the outdoor environment around Alba-Iulia school (261.08 μg·m<sup>-3</sup>) than in Aiud (172.63 μg·m<sup>-3</sup>), Vințu de Jos (164.20 μg·m<sup>-3</sup>), Unirea (146.34 μg·m<sup>-3</sup>) and Sebeș (139.59 μg·m<sup>-3</sup>). The distribution of the 15 VOCs detected in the outdoor environments is presented in figure 2.

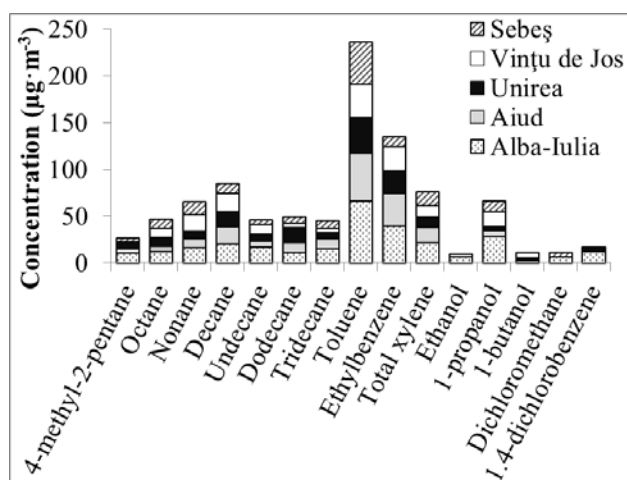


Figure 2. VOCs distribution in outdoor environment.

In all the five locations, the distribution of VOCs in the outdoors is dominated by the presence of aromatics compounds such as toluene, ethylbenzene and xylenes. In some cases, their levels were higher even with 10 – 30% than the values measured in the correspondent indoor environment.

High levels of toluene, ethylbenzene and xylenes were registered in Alba-Iulia, Aiud and Sebeș, which are located in urban area, with heavy traffic street, gasoline stations located nearby and industrial activities (metallurgical, wood-based panels, furniture, leather).

There were several VOCs (1-butanol, 1,4-dichlorobenzene, ethanol, 4-methyl-2-pentane, 1-propanol and dichloromethane) which were not detected in the indoor air. Their level ranged between 2.15 and 27.99 μg·m<sup>-3</sup>. These compounds are emitted especially by the gasoline stations located nearby and by the industrial activities in the area (metallurgical, wood-based panels, furniture and leather). As such the VOCs concentrations, especially for aromatic compounds, reflect the general level of urbanization /industrialization from the area and the traffic proximity and intensity.

Generally, the VOCs level was higher in the indoor environment as compared to the outdoor environment. In the case of aromatic compounds such as toluene, ethylbenzene and xylenes, the outdoor values were higher even with 50 % than the indoor levels.

### 3.3. Possible health effects caused by the exposure to VOCs

As it is shown in table 3, the levels of VOCs registered in the investigated indoor environments fell far below the reference concentration (R<sub>f</sub>C) which is an inhalation exposure concentration at/or below which adverse health effects are not likely to occur. As a consequence a short time exposure to such concentrations cannot produce chronic and subchronic effects on children and teachers.

The presence of xylene (mutagenic and toxic), toluene (toxic for reproduction), tetrachloroethylene (likely to be carcinogenic to humans), styrene (possible human carcinogen), ethylbenzene (possible human carcinogen), trichloroethylene (probable human carcinogen) and dichloromethane (probable human carcinogen) in the investigated classrooms, represents a potential health risk, because a long time exposure to such mixtures of pollutants can generate a cumulative impact which can lead to a severe health outcomes. The long time exposure (4 hours of class and four hours of afterschool each day) to indoor VOCs, for the children from some of

the classrooms from Alba-Iulia and Sebeş represent a significant risk factor for their health.

Table 3. Chronic and subchronic reference concentrations, critical effects for VOCs in quantitative risk assessment (McKenzie et al., 2012).

VOC compounds	Chronic R <sub>f</sub> C* (µg·m <sup>-3</sup> )	Subchronic R <sub>f</sub> C (µg·m <sup>-3</sup> )	Critical effect/target organ
Alkanes C <sub>5</sub> –C <sub>8</sub>	600	27000	Neurological
Alkanes C <sub>9</sub> –C <sub>18</sub>	100	100	respiratory
n-Nonane	200	2000	neurological; respiratory
Toluene	5000	5000	neurological; developmental; respiratory
Ethylbenzene	1000	9000	auditory neurological, respiratory, renal
Total xylene	100	400	neurological developmental, respiratory
Dichloro methane	600	-	neurological
1,4-dichlorobenzene	800	-	neurological liver, skin
Styrene	1000	3000	neurological
Tetrachloro ethylene	40		respiratory; kidney; neurological
Trichloro ethylene	100	-	kidney; liver; lymphatic system; fetal developmental

\* R<sub>f</sub>C - reference concentration

An important issue in the investigated indoors was the increased air-tightness of the classroom, for energy conservation and comfort reasons, providing less dilution air and thus increasing the levels of VOCs due to inside sources. Moreover, some of the classrooms (especially those from Alba-Iulia) have high densities, decreasing the volume of fresh air. In order to decrease the exposure of children/teachers to high indoor VOCs level, the ventilation improvement is highly recommended by a frequent opening of the windows and entry door of the classrooms. It is also recommended for children to leave the classrooms during each break (10 minutes) and to get in the school yard at fresh air.

#### 4. CONCLUSIONS

Volatile organic compounds in indoor and outdoor environment from five primary schools were evaluated during September 2011 and January 2012.

The dominant VOCs from indoor environment were nonane, decane, toluene and ethylbenzene, while in the outdoor environment predominated the aromatics VOCs such as toluene, ethylbenzene and xylenes.

Elevated indoor VOCs concentrations were associated with the following sources or activities: building materials (polystyrene isolation, presence of plastic laminated or composite furniture, or the PVC panel), number of occupants, lower ventilation rates and outdoor pollution.

Generally the VOCs levels were higher in the indoor environment as compared to the outdoor environment, excepting for the aromatic compounds such as toluene, ethylbenzene and xylenes. The VOCs concentrations from outdoor, especially for aromatic compounds, reflect the general level of urbanization/industrialization from the area, the traffic proximity and intensity.

The VOCs levels registered in the investigated indoor environments are far below the reference concentration (R<sub>f</sub>C) leading to no chronic and subchronic effects on children and teachers for a short time exposure. The presence of some possible /probable human carcinogen VOCs in the investigated indoors represents a potential health risk, because a long time exposure to such mixtures of pollutants can generate a cumulative impact which can lead to severe health outcomes.

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