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Assay of volatile organic compounds in urban air using passive sampling and gas chromatography coupled to mass spectrometry

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Abstract

Volatile organic compounds (VOCs) include a wide range of air pollutants emitted from diverse anthropogenic and biogenic sources. VOCs in air have great importance as they have direct and indirect effects on climate change, ecosystems and human health. The goal of this study was optimization of sampling, sample preparation and quantification of volatile organic compounds in air and implementation of the method for air monitoring in Skopje, Macedonia.

Radiello® passive samplers with special radial design, that provides higher capacity and faster sampling rates than traditional passive samplers were used for VOCs sampling. Different sampling times were tested and dichloromethane was selected as an efficient solvent for desorption and further analysis. GC-MS method for separation was optimized and anisole as an internal standard was used for semi-quantification.

The optimized method was then applied for analysis of extracts of real samples of air taken on Radiello® passive samplers placed on several locations in Skopje in two consecutive months. More than 30 compounds were identified and semi-quantitatively determined using anisole as an internal standard. Most of them can be attributed to transport fuels and derivatives such as BTEX (benzene, toluene, ethyl benzene and xylenes) and alkanes, such as undecane, dodecane, tridecane and tetradecane. In addition, naturally occurring terpenes were found (α-pinene and limonene) in many samples that can originate from both natural sources or domestic cleaning products. The concentrations of the detected compounds have been below the established reference concentrations by EPA that cause critical effects but they should be continuously monitored.

The long-term goal is to set up efficient, accurate and sensitive methods for monitoring VOCs concentrations throughout the year to reveal the sources of outdoor pollution in urban areas and plan control measures for their reduction.

Keywords: Volatile organic compounds, air, passive sampling, GC-MS, internal standard, anisole

Introduction

Ambient air quality is one of the main concerns in developing countries because the rapid and uncontrolled urbanization leads to high concentrations of air pollutants that can adversely affect human health. Air pollution is particularly concerning during winter months when all individuals, especially younger population and the ones with chronic diseases, feel the negative health effects (Roemer et al. 1993; Wichmann et al. 2009).

Volatile organic compounds (VOCs) present one of the most important groups of air pollutants because of the growing awareness of the impact they have on both human health and ecosystems. VOCs and their degradation products can cause different diseases such as respiratory disorders and cancer (Montero-Montoya et al. 2018). Moreover, these compounds play an

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important role in the chemistry of the atmosphere since they can lead to formation of tropospheric ozone and particles smaller than 2.5 μm in large cities, as well as to depletion of the stratospheric ozone (Ait-Helal et al. 2014). Tropospheric ozone is a secondary photochemical pollutant formed primarily from the reaction of VOCs with NO_x (NO and NO_2) in the presence of sunlight. It is a major component of smog and has negative effects on human health, vegetation and materials (Sillman 1999; Jenkin & Clemitshaw 2000). Stratospheric ozone, which protects earth from UV radiation, reacts with VOCs (e.g., tetrachloromethane, 1,1,1-trichloroethane, the chlorofluorocarbons CFC-11, CFC-12 and CFC-113) which leads to its depletion (Derwent et al. 1998).

There are several definitions for VOCs in literature. The World Health Organization defines VOCs as organic compounds having a lower boiling point limit of 50–100 °C and an upper boiling point limit of 240–260 °C (U.S. Environmental Protection Agency, 2021). According to US Environmental Protection Agency (EPA), this class of substances includes C2–C10 substituted and unsubstituted hydrocarbons with a vapor pressure greater than 0.01 kPa at 25 °C (USEPA 2019). They can be further classified into polar and nonpolar VOCs. VOCs include a wide range of compounds with different functional groups: alkanes, alkenes, saturated and unsaturated alkyl halides, carbonyls (such as aldehydes and ketones), alcohols, aromatic and halogenated aromatic hydrocarbons.

In the atmosphere, these compounds can be of primary (directly emitted from biogenic and anthropogenic activities) or secondary origin (products formed by oxidation and transformation of other directly emitted VOCs). Many VOCs come from natural sources, like vegetation, volcanic eruptions, forest fires, oceans etc. Yet anthropogenic activities are also important sources of toxic VOCs in the atmosphere, so that they account for 25% of VOCs present in the global atmosphere (Montero-Montoya et al. 2018). Major anthropogenic sources of VOCs are vehicle emissions, manufacture and use of petroleum products, paints, lubricants, adhesives, solvent and fuel evaporation, biomass burning, landfills and sewage treatment plants, consumer products (Wang & Austin 2006; Montero-Montoya et al. 2018). Air pollution with VOCs is a complex problem that requires an interdisciplinary approach and the first step is developing suitable methods for their analysis.

Chromatographic methods are most commonly used for qualitative and quantitative analysis of these compounds, especially gas chromatography coupled to mass spectrometry (GC-MS) (Wang & Austin 2006; Król et al. 2010). The main challenges and critical steps of the analytical procedure are the air sampling and sample preparation. High volume of air sample and a preconcentration step in the procedure are necessary to obtain sufficient concentrations in order to determine the compounds of interest with the required accuracy and precision. Sample preconcentration can be done either simultaneously with sampling or in the laboratory following grab air sampling in the field using canisters or plastic bags (Wang & Austin 2006; Kumar & Viden 2007; Król et al. 2010). Sampling and simultaneous preconcentration on adsorbents enables collection of larger volume of gas and sorbent tubes are easier to handle than canisters. Enrichment of VOCs onto solid sorbents can be performed either by active or passive sampling. Active sampling occurs by pumping air through a bed of sorbent(s) in a tube at a rate in the 10–100 mL/min range for a period of minutes to hours. In passive (diffusive) sampling, the sorbent material is exposed to air for a period in the order of days. Passive samplers are convenient due to their simpler construction, lower cost and they do not require pumps that should be checked and calibrated regularly. These samplers allow for integrative (time-averaged concentration) sampling that is very convenient for continuous monitoring and can be used in remote and multiple locations where active samplers are not applicable due to the need for electrical supply (Demeestere et al. 2007; Kumar & Viden 2007; Yusà et al. 2009; Król et al. 2010). Passive sampling techniques rely on unassisted molecular diffusion of gaseous analytes through a diffusive surface onto an adsorbent as a result of a difference in chemical potentials (in accordance with Fick's first law of diffusion) (Kumar & Viden 2007; Król et al. 2010). Most passive samplers consist of an adsorbent with high retention capacity for the target analytes that is fixed in a protective housing that regulates the airflow through the sampler and protects the adsorbent from rain and direct sunlight.

After sampling, the analytes retained on the sorbent are desorbed by thermal desorption or solvent extraction (Wang & Austin 2006; Król et al. 2010). Solvent extraction is a preferred desorption method since the obtained extract is then analyzed using a standard GC-MS instrument. The concentration of each analyte in the extract is then calculated using different calibration approaches (e.g. external calibration, internal standard). Finally the concentration of the target analytes in air can be calculated by using the their concentrations in the extract, the known exposure time and a previously determined calibration constant, that is characteristic for a given sampler and analyte (Partyka et al. 2007).

The goal of this study was to optimize a sampling method on Radiello passive sampler and the solvent desorption procedure as well as to develop a GC-MS method for identification of VOCs in the extracts and their quantification. The optimized method for passive air sampling of VOCs, their solvent desorption and analysis by GC-MS was then used for a short-term monitoring on seven locations in an urban area and the results are discussed.

Materials and methods

Chemicals and standard solutions

Dichloromethane was used as a solvent (99,8 % stabilized with amylene, Fisher Chemical).

A standard mixture stock solution was prepared by transferring 100 µL of each substance into a 10 mL volumetric flask filled to volume with dichloromethane: *n*-tetradecane (≥ 99.0%), toluene (≥99.9%), *p*-xylene (≥99%), *R*-(+)-limonene (≥98.0%), α-pinene (≥97.0%), *p*-cymene (≥99.5%), butyl acetate (≥99.7%), dibutyl phthalate (> 99.0 %), and anisole (≥ 99.9%) (all from Sigma-Aldrich). A working standard solution was prepared by dilution of 10 µL of the stock solution to 50 mL with dichloromethane and it was used for optimization of the separation using GC-MS. The concentrations of all substances in the working standard were in the range from 7.54 to 18.8 µmol/L.

Anisole was used as an internal standard (IS). Standard solution with a concentration of 995 mg/L was prepared by transferring 100 µL of anisole in a 100 mL volumetric flask in dichloromethane. 10 µL of this solution were added in 2 mL dichloromethane for desorption of each sample and transferred into a vial for analysis with GC-MS.

Sampling method, sites and time

Radiello diffusive passive samplers designed and developed by the Fondazione Salvatore Maugieri (Padova, Italy) were used for trapping and enrichment of the analytes from ambient air (Cocheo et al. 1996). The sampler is a stainless steel cylindrical cartridge (60´ 5.8 mm) packed with activated charcoal (530 ± 30 mg with particle size of 35-50 mesh suitable for solvent desorption) stored in a sealed glass tube suitable for short-term storage and transport. When sampling, the cartridge is placed coaxially inside a cylindrical diffusive body of polycarbonate and microporous polyethylene (Cocheo et al. 1996; Król et al. 2010). Radiello samplers were placed 1.5-2 m above ground level in a polypropylene mountable shelter to protect them from the atmospheric conditions (precipitation and direct sunlight). After sampling, the cartridge with the adsorbent was put in a tightly sealed glass tube and brought to the laboratory and stored in a fridge at 4 °C until analysis (within a week after sampling).

In the first phase, for optimizing sampling time, 6 cartridges divided into 3 pairs were placed at one location (Novo Lisiče) and exposed to atmospheric air for three different time periods in August-September 2020. This location was chosen because the data from the national Ministry of Environment and Physical Planning suggested high air pollution at this location in Skopje (MOEPP 2020). The exposure time was 1, 2 and 4 weeks for the three pairs of samplers.

After finding the optimal sampling time, the VOC monitoring experiment was conducted in two different months – in October and November at seven locations in the area of Skopje (a map is given in Figure 1) that included locations close to emission sources and busy roads. The sampling period was one month (four weeks). Average air temperature was followed during sampling.

Sample preparation and GC-MS analysis

Solvent desorption was performed at room temperature by adding 2 mL of dichloromethane in the glass tube with the adsorbent for 45 minutes contact time at ambient temperature with occasional shaking (the cartridge itself acting as an inner stirrer). Ten microliters of anisole (995 mg/L) was added as an internal standard before the extraction. The extraction

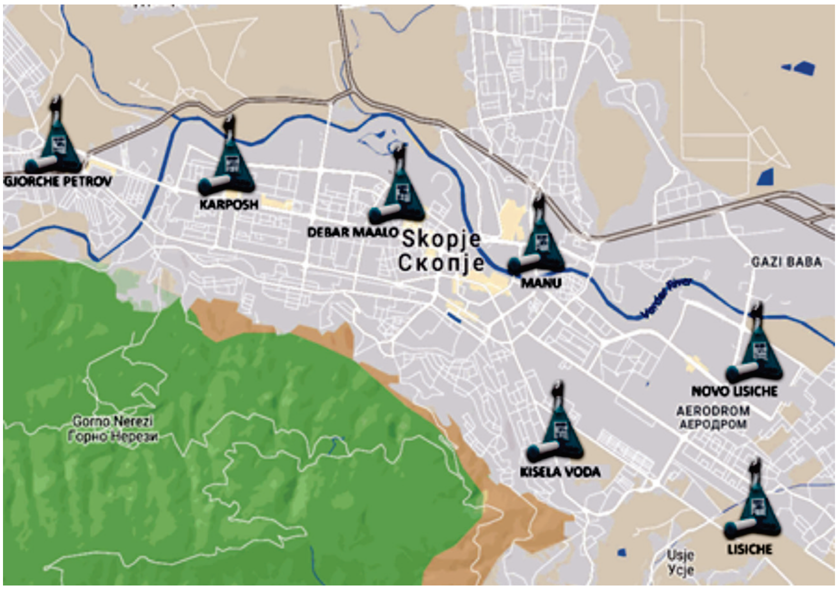

Figure 1. Sampling locations in Skopje

was repeated three times in the same manner and the combined extract was analyzed.

The analyses were performed by gas chromatography coupled to mass spectrometry, split injection and internal standard method. GC–MS analysis was carried out using an Agilent 6890N gas chromatograph coupled to a single quadrupole 5975B mass selective detector. HP-5 capillary column (30 m×0.25 mm ID, film thickness 0.25 µm) with (5%-phenyl)-methylpolysiloxane nonpolar stationary phase was used with helium as a carrier gas with a constant flow of 1 mL/min. The injected volume was 2 µL and the split ratio was 1:2. The temperature of the injector was 240 °C and the separations were carried out in a temperature programmed mode: initial temperature 35 °C (hold 5 min), ramp to 90 °C at 5 °C/min; ramp to 220 °C at 10 °C/min; ramp to 300 °C at 5 °C/min. Electron impact ionization was used with ion source voltage of 1505,9 eV, and the ion source and detector temperatures were 270 °C and 150 °C, respectively. Compounds were identified based on their retention times compared to available standards, and also by using target and qualifier ions and the NIST Library of mass spectra (NIST MS Search 2.0). The compounds for which standards were not available were identified using the NIST Mass Spectral Database with probability values greater than 85 %.

Results and discussion

Optimization of sample preparation and analysis parameters

The analysis of volatile organic compounds in air in large cities is a serious problem and different approaches are used to address it but the first step is characterization of the type and content of these compounds. In this study, passive air sampling was used on activated charcoal inside a cylindrical diffusive body of microporous polyethylene that enables passive diffusion of the compounds from ambient air and their trapping on the adsorbent. The exposure time and method of desorption play a key role during sampling and sample preparation and these parameters were optimized in this study.

Activated charcoal has a large surface area and a complex surface structure containing a wide range of functional groups, so it can be used for adsorption of a wide range of compounds (Ramírez et al. 2010). As volatile organic compounds are mainly hydrophobic, hydrophobic solvents are required for efficient desorption by extraction. Our goal was to replace the recommended carbon disulfide with an alternative solvent that will be as efficient and more convenient to work with. From this point of view, dichloromethane (DCM) was considered as a suitable extraction solvent due to its low to moderate polarity (dipole moment: 1.14 D). It is a very good solvent for hydrophobic molecules (log K_{ow} = 1.25) and is sufficiently volatile (T_b 39.6 °C) to be early eluted in the subsequent analysis with gas chromatography. In a previous study, the extraction efficiency of carbon disulfide and dichloromethane for BTEX (benzene, toluene, ethylbenzene, xylenes) has been compared. It was found that dichloromethane gave best results although on most stationary phases it has co-eluted with benzene whereas carbon disulfide gave extensive tailing especially on polar columns (Joos et al. 2003). Therefore, dichloromethane was used and demonstrated as a suitable extraction solvent for VOCs in our study.

Three consecutive extractions of each sample with 2 mL DCM were performed at room temperature. Comparative chromatograms obtained with GC-MS after the three consecutive extractions of the same adsorbent are shown in Figure 2. From the chromatograms it is

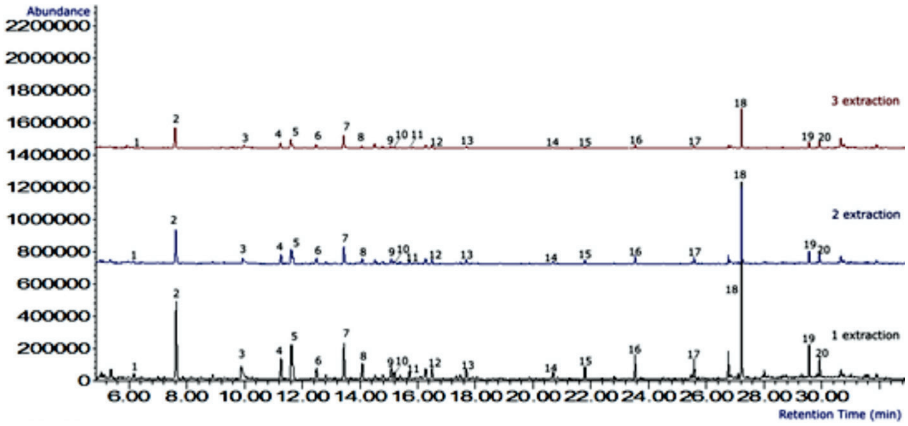

Figure 2. Chromatograms obtained after the first, second, and third extraction for desorption of volatile organic compounds from the carbon adsorbent in DCM. (Identified compounds: 1) methylcyclohexane; 2) toluene; 3) butyl acetate; 4) ethylbenzene; 5) *p*-xylene; 6) *o*-xylene; 7) anisole (IS); 8) α-pinene; 9) *n*-propylbenzene; 10) C6-C3 substituted benzene; 11) C6-C3 substituted benzene; 12) *n*-decane; 13) limonene; 14) C6-C4 substituted benzene; 15) *n*-undecane; 16) *n*-dodecane; 17) *n*-tridecane; 18) *n*-tetradecane; 19,20) alkane with *n* > 14)

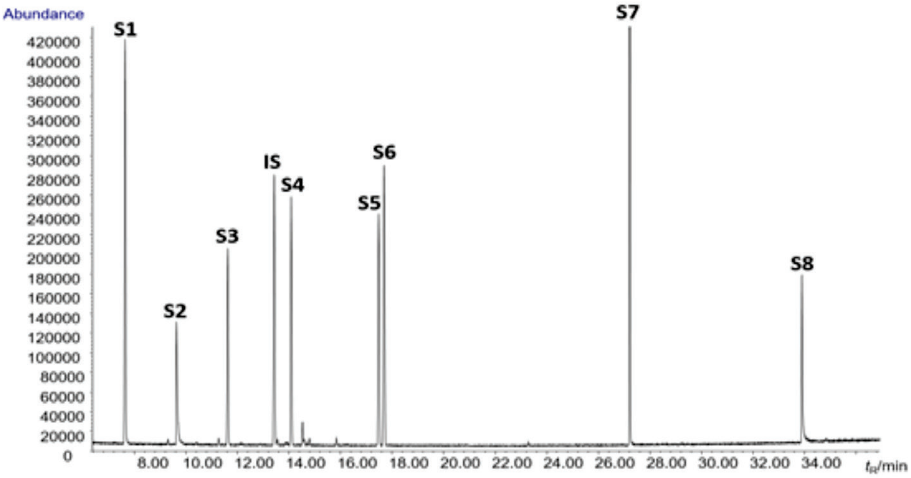

Figure 3. Chromatogram of the working standard mixture of: S1) toluene; S2) butyl acetate; S3) *p*-xylene; IS) anisole; S4) α-pinene; S5) *p*-cymene (C6-C4); S6) limonene; S7) *n*-tetradecane; S8) dibutyl phthalate with concentration in the range from 7.54 to 18.8 μmol/L

evident that for a quantitative desorption of all adsorbed compounds, a second extraction is necessary and even a third one. Therefore, for a quantitative analysis three extractions were performed and combined into one total extract that was analyzed with GC-MS.

A standard mixture was prepared containing different classes of compounds in order to optimize the chromatographic separation conditions, determine the retention times of the compounds expected to be found in real samples and choose a suitable internal standard for quantification. It contained *n*-tetradecane, toluene, *p*-xylene, *R*-(+)-limonene, α-pinene, *p*-cymene, dibutyl phthalate and anisole that were all baseline separated. The peak of anisole was well separated from the peaks of the other compounds (Figure 3) and this compound meets the requirements for an internal standard: it is not expected in the samples, it is eluted as a well separated peak, and it has a similar structure as some of the substances in the samples and therefore similar behavior is expected during sample preparation and analysis.

Adsorbent exposure time was another important parameter that was optimized in the method development. In order to determine the ideal exposure time, six cartridges were exposed at the same location in an urban area for one, two and four weeks in duplicate and were then analyzed using the previously developed method. Evaluation of the exposure time was based on the estimated quantities of each detected compound since peak areas in a chromatogram are proportional to the concentration of each substance in the sample. The concentrations of volatile organic compounds present in air samples were estimated using this and the internal standard method. Since the concentration (*c*) of the added internal standard in a sample is known as well as the areas under the peaks of the internal standard and each of the identified components (C), the concentration and mass of each compound in the extract retained on the filter can be calculated as follows (G. Guiochon, C.L. Guillemin, 1988):

$$c(\mathrm{C}) = c(\mathrm{IS})\frac{A(\mathrm{C})}{A(\mathrm{IS})}$$

$$m(\mathrm{C}) = c(\mathrm{C}) \cdot V \cdot M(\mathrm{C})$$

where: V – volume of extract; A – area; M(C) – molar mass of the compound.

The experimentally obtained mass of each compound was then used for calculation of its concentration in the air. It depends on the parameters that influence the uptake rate of analytes. The sampling rate (*Q*) for passive samplers has to be known in order to determine the time-weighted average concentrations of an analyte trapped for a specific exposure time. For Radiello passive samplers, the VOCs sampling rates have been determined under standard conditions (25 °C and 1013 hPa) and should be recalculated for the actual mean sampling temperature (Istituti Clinici Scientifici Maugeri 2019). So, the time-weighted average VOCs concentrations (*c*) were calculated based on the knowledge of the exposure time (*t*) of the passive samplers, the mass (*m*) of the analyte trapped by the sorption medium, and sampling rates (*Q*):

$$c = \frac{m}{t \cdot Q} \cdot 10^6$$

where: c - concentration of analyte in ambient air (μg/m^3); m - mass of analyte (μg); Q - sampling rate (mL·min^{-1}); t - exposure time (min).

The Q values from the manufacturer (Q_{298}) were adjusted or the mean sampling temperature (T) to obtain the sampling rate at the actual temperature (Q_K):

$$Q_K = Q_{298}\left(\frac{T}{298}\right)^{1.5}$$

Table 1. Estimated concentrations of the identified compounds in the air samples with retention and mass spectral data for three different exposure times (1, 2 and 4 weeks)

Group	Compound	t_R/min	M_r	Detected peaks in MS	c/(μg/m^3)		
					1 week	2 weeks	4 weeks
Aliphatic hydrocarbons	2-Methylbutane	2.44	72.15	72; 57; **43**	3.32	2.83	2.97
	n-Heptane	5.37	100.21	100; 71; 57; **43**	nd	0.33	0.64
	n-Octane	8.90	114.23	114; 85; **43**; 29	0.60	0.18	0.51
	n-Nonane	12.82	128.2	128; 99; 85; 71; 57; **43**	nd	0.38	0.69
	n-Decane	16.50	142.29	142; 113; 99; 85; 71; **57**; 43	1.15	1.15	2.22
	n-Undecane	20.69	156.31	156; 85; 71; **57**; 43	2.44	2.07	2.51
	n-Dodecane	23.53	170.33	170; 85; 71; **57**; 43	57.57	27.77	15.34
	n-Tridecane	25.58	184.37	184; 85; 71; **57**; 43	21.88	13.26	8.10
	n-Tetradecane	27.21	198.39	198; 85; 71; **57**; 43	236.3	124.5	77.93
	Methylcyclohexane	6.18	98.19	98; **83**; 55	nd	0.18	0.29
Aromatic hydrocarbons	Benzene	4.44	78.11	**78**	nd	nd	0.81
	Toluene	7.65	92.14	92; **91**	4.82	4.08	5.88
	Ethyl benzene	11.26	106.17	106; **91**	0.77	1.39	1.74
	p-Xylene	11.62	106.16	106; **91**	1.22	2.06	3.37
	m-Xylene	11.67	106.16		1.94	0	3.23
	o-Xylene	12.49	106.16		0.70	0.56	1.23
	n-Propylbenzene	14.80	120.2	120; **91**	nd	0.33	0.81
	Ethyl methyl benzene	15.07	120.19	120; **105**	nd	0.77	1.28
	C6-C3 (substituted benzene)	15.20	120.19		nd	0.27	nd
	Trimethylbenzene	16.27	120.19	120; **105**	1.35	0.81	1.72
	p-Cymene	17.47	134.21	134; **119**; 91	0.78	0.19	0.83
Terpenes	*α*-Pinene	14.08	136.23	136; 121; 105; **93**; 77; 39	1.61	1.05	1.77
	Limonene	17.68	136.24	136; 121; 107; 93; 79; **68**	4.50	1.79	2.36
Hydrocarbon derivatives	Butyl acetate	9.64	116.16	73; 57; **43**	0.17	1.13	2.09
	Chloromethyl acetate	5.95	108.52	73; 49; **43**	nd	nd	0.29

*nd – not detected

The results for the identified compounds (name, retention time, relative molecular weight and main fragments in the mass spectrum and estimated concentrations in ambient air) in these samples are given in Table 1. Overall, 25 different volatile organic compounds were identified in the extracts, out of which ten are aliphatic hydrocarbons, eleven are aromatic hydrocarbons, two are terpenes and two are esters. From the estimated concentrations of the compounds, it can be seen that unbranched long-chain alkanes, especially *n*-tetradecane, *n*-dodecane and *n*-tridecane are most abundant and aromatic compounds (toluene, xylene) and limonene are next in prevalence.

As for the exposure time effect, from the semi-quantitative data given in Table 1 it can be observed that by increasing the passive sampler exposure time, the number of compounds of interest and their mass retained on the filter increases for most compounds. Nevertheless, care must be taken to ensure that the exposure time is not too long as it may lead to cartridge saturation as well as desorption of some of the retained compounds.

Implementation of the method for VOCs monitoring

After optimizing the method for volatile organic compounds sampling, sample preparation and analysis, the next step was its implementation for VOCs monitoring in an urban area. Therefore, seven Radiello passive samplers were installed at seven different locations for two consecutive months in order to semi-quantitatively determine the type and content of various VOCs in air in the urban area of Skopje (Figure 1). The first goal was to identify the VOCs present at the

Table 2. Results from the analysis of VOCs at seven urban locations during two months using passive sampling and GC-MS analysis

Location in Skopje		1-Gjorče Petrov		2-Karpoš		3-Debar Maalo		4-MANU		5-Kisela Voda		6-Lisiče		7-Novo Lisiče	
Exposure period: O: 12.10-10.11; N: 10.11-10.12		O	N	O	N	O	N	O	N	O	N	O	N	O	N
Group	Compound	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3	µg/m^3
Alkanes	2-Methylbutane	nd	2.14	nd	2.49	nd	3.13	nd	4.70	nd	4.58	nd	2.84	nd	3.25
	n-Heptane	nd	1.29	nd	1.69	nd	1.85	nd	2.35	nd	1.97	1.20	2.53	nd	1.97
	n-Octane	nd	1.11	nd	1.14	nd	1.17	0.37	1.27	0.07	1.50	nd	1.08	nd	1.03
	n-Nonane	nd	1.09	0.71	1.43	0.80	1.33	0.85	2.15	nd	1.57	1.81	2.17	nd	3.42
	n-Decane	0.40	2.46	1.97	2.75	1.87	2.81	0.41	4.66	0.52	3.34	3.99	5.18	0.53	9.73
	n-Undecane	18.45	2.65	37.62	3.75	82.77	3.80	89.74	4.13	17.13	4.16	114.87	7.59	22.69	16.93
	n-Dodecane	3.51	4.50	10.92	3.46	13.46	6.26	9.10	11.69	3.19	4.80	11.09	4.22	3.69	10.44
	n-Tridecane	1.34	4.53	3.69	1.34	3.66	2.51	nd	2.48	0.91	0.56	nd	2.35	2.12	2.57
	n-Tetradecane	8.23	9.09	10.01	8.43	22.84	13.00	28.17	15.12	2.89	8.45	12.28	15.63	6.16	16.62
	Methylcyclohexane	nd	0.48	nd	0.62	nd	0.74	nd	1.13	nd	0.93	nd	1.11	nd	0.98
Aromatic hydrocarbons	Benzene	0.83	11.28	1.17	7.32	3.23	9.55	2.87	14.42	0.95	11.18	9.43	15.62	0.35	15.95
	Toluene	0.20	12.02	3.63	13.02	7.29	14.16	10.15	21.28	2.20	16.76	22.30	16.53	1.93	18.05
	Ethylbenzene	0.08	2.36	nd	4.93	2.84	4.92	0.12	7.56	0.86	5.52	7.14	5.11	nd	6.09
	p-Xylene	0.01	4.54	0.11	7.49	2.31	7.49	6.90	11.90	1.86	8.97	14.80	8.00	0.53	9.30
	m-Xylene	nd	0.07	nd	0.09	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	o-Xylene	nd	1.78	nd	2.44	nd	2.48	nd	4.07	nd	3.39	nd	3.14	nd	4.25
	n-Propylbenzene	nd	0.83	nd	1.45	nd	1.62	nd	5.70	nd	1.85	nd	2.20	nd	2.48
	Ethyl methyl benzene, isomer-1	nd	2.34	0.93	3.21	nd	nd	0.06	0.14	1.05	5.05	7.20	4.77	0.35	4.98
	Ethyl methyl benzene, isomer-2	nd	1.17	nd	1.75	nd	2.05	nd	1.39	nd	2.73	nd	2.36	nd	2.77
	Ethyl methyl benzene, isomer-3	nd	nd	nd	1.28	nd	1.30	nd	nd	nd	1.58	nd	1.59	nd	1.63
	Trimethylbenzene, isomer-1	nd	nd	nd	0.83	nd	Nd	nd	nd	nd	1.66	nd	1.76	nd	nd
	Trimethylbenzene, isomer-2	nd	0.48	0.66	2.08	nd	2.13	nd	nd	nd	1.86	2.68	nd	0.40	4.15
	2- Furfural	nd	1.079	nd	0.843	nd	0.238	nd	0.716	nd	0.459	0.556	2.427	nd	2.154
	C6-C4 substituted benzene-1	nd	0.180	nd	0.475	nd	0.493	nd	0.387	nd	0.975	nd	0.472	nd	1.754
	C6-C4 substituted benzene-2	nd	nd	nd	nd	nd	nd	nd	0.734	nd	nd	nd	nd	nd	1.486
	p-Cymene	nd	0.125	0.130	0.292	nd	0.198	nd	0.432	nd	1.195	1.355	0.638	0.071	1.625
Terpenes	α-Pinene	nd	2.888	nd	2.825	nd	2.633	nd	2.034	nd	3.089	2.994	3.524	nd	4.726
	Limonene	nd	2.624	0.102	2.464	0.075	3.027	0.119	2.887	nd	3.553	3.675	3.977	0.574	7.806
Hydrocarbon derivatives	Butyl acetate	nd	1.774	8.265	4.559	nd	3.718	nd	4.617	nd	3.277	10.901	0.115	nd	4.838
	Chloromethyl acetate	nd	0.733	nd	0.196	nd	nd	nd	0.056	nd	nd	nd	0.890	nd	0.687
	Tetrachloroethylene	nd	0.0275	nd	0.864	nd	0.740	nd	0.436	nd	0.388	nd	nd	nd	nd

*nd – not detected

different locations in order to determine compounds that could serve as markers so their concentrations could be determined and monitored. The other important aspect was to establish a monitoring system that could be used for evaluation of the various measures that have been planned to reduce the air pollution with respect to the volatile organic compounds.

The content of volatile organic compounds, expressed in μg/m^3, was semi-quantitatively determined by using anisole as an internal standard. The average monthly temperature was also taken into account in the calculations, because it affects the sampling rate and adsorption efficiency of these compounds on the cartridge, as explained above. All the results obtained for the concentrations of VOCs at the seven locations during the exposure time of one month (O: 12.10-10.11; N: 10.11-10.12.2020) are given in Table 2. Graphical presentation of the total concentrations of the different classes of compounds is given in Figure 4.

The obtained results show significant qualitative and quantitative differences in the nature and content of the compounds determined at different locations, which indicates the dominant type of air pollutants in a given area. In addition, there is a higher presence of volatile organic compounds both in terms of number of detected compounds and higher concentrations in the October-November period compared to the November-December one. Some deviation from this trend is observed in Debar Maalo, Lisiče and MANU due to the higher concentrations of alkanes, especially *n*-undecane, *n*-dodecane and *n*-tetradecane, in October compared to November. The most common, in both periods, are the acyclic alkanes (especially undecane, dodecane, tridecane and tetradecane) together with the aromatic compounds (benzene and its derivatives).

Discussion on the possible origin of the identified substances

Volatile organic compounds are emitted in the atmosphere from natural and anthropogenic sources. They can travel in the atmosphere and transform in the environment (water surfaces, soil, vegetation) or be directly or indirectly subjected to photochemical degradation. Vegetation is considered as the main natural source of these compounds that very often include ethylene, isoprene and monoterpenes.

Anthropogenic sources and activities include production, processing, storage and distribution of fossil fuels, combustion processes, application of volatile organic substances as solvents and solvent-containing products for various consumers, industrial and biotechnological processes. The main products of complete combustion of fossil fuels are carbon dioxide and water. In practice, combustion also produces carbon monoxide and hydrocarbons as by-products, mainly due to lack of oxygen, inadequate air/fuel ratio and combustion temperatures. The hydrocarbons (alkanes and aromatic compounds) can be emitted as non-oxidized or partially oxidized to carbonyl compounds. Production, storage and distribution of liquid fossil fuels comprise a variety of activities that result in hydrocarbon emissions into the atmosphere.

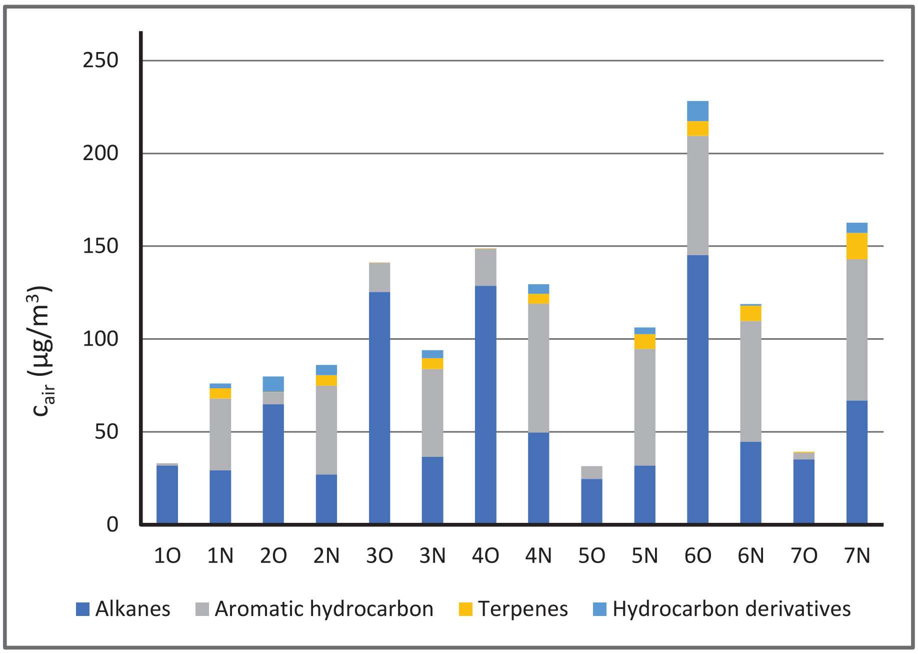

Figure 4. Concentrations of the four groups of compounds expressed in μg/m^3 at seven locations in two consecutive months (O: 12.10-10.11.2020; N: 10.11-10.12.2020)

Volatile organic compounds that can very often be found as air pollutants from vehicle emissions include methane; toluene; ethylene; *m*-, *p*- and *o*-xylene; *n*-butane and benzene. Besides these, air pollutants can originate from households as well because they often use heating systems that involve crude oil (benzene, xylenes, toluene, 2-butanone), wood, timber and pellets (formaldehyde) as well as cleaning products which may include dichlorobenzene, trichloroethene, crude oil distillates etc. Some building materials can be considered as another source of these compounds such as: paints, glues and floor coverings (benzene, xylenes, styrene, diisocyanate, ethylbenzene, benzyl chloride, 2-butanone) (Yu & Crump 1998; Salthammer 2004; Harčárová et al. 2020).

From all this, we can conclude that the aliphatic hydrocarbons identified in our samples most likely originate from fuels. For example, 2-methylbutane (isopentane) can be found in gasoline vapors and is also present in tobacco smoke. This compound is commercially available and used as a solvent for preparation of polystyrene and other substances and for cooling. Isopentane is an integral part of many household products such as car maintenance products, shaving creams, etc. (National Center for Biotechnology Information 2022).

Benzene, toluene, ethylbenzene and xylenes (*o*-, *m*- and *p*-) are found in crude oil, diesel and gasoline, so they are released into air even when these fuels are not combusted. Also, BTEX have wide application in industry: benzene as an additive and precursor for synthesis of different synthetic materials and consumer products (such as plastics, nylon, paints, insecticides etc.); toluene as a solvent for paints, coatings, rubbers, oils and resins; ethylbenzene in paints, plastics and pesticides; xylenes as solvents in the printing, leather and rubber industries (Huang et al. 2011; Bolden et al. 2015; Miri et al. 2016; Montero-Montoya et al. 2018). These compounds may be found as pollutants not only in air but also in water and soil because their physical and chemical properties allow great dispersion capacity and ability to evaporate, dissolve in water or adhere to soil particles once they are emitted into the environment (Bolden et al. 2015; Montero-Montoya et al. 2018). High BTEX concentrations have been found in areas with intensive industrial activity and large cities (mostly due to vehicular traffic emissions) (Batterman et al. 2014; Montero-Montoya et al. 2018)

EPA has used information from the IRIS database to establish reference concentrations (RfCs) that cause critical effects for different pollutants in the environment (Montero-Montoya et al. 2018). The maximum environmental exposure concentration of benzene in air for an individual is 0.03 mg/m^3 based on the hematological effect of benzene in humans (USEPA, 2012). For toluene, a maximum concentration of 5.0 mg/m^3 has been estimated, based on neurological effects in humans and increase in liver size (USEPA 2012). For ethylbenzene, it is 1.0 mg/m^3 based on respiratory effects, hepatotoxicity and nephrotoxicity (USEPA 2000). For a xylene mixture, a maximum exposure concentration in air of 0.1 mg/m^3 was estimated based on respiratory and neurological effects and low birth weight (USEPA 2000). The above values refer to non-carcinogenic effects. For benzene, an individual's chronic exposure to a reference value of 0.03 mg/m^3 accounts for an increase in the potential risk for developing leukemia to 1 out of 10 000, compared to a baseline of 1 in 1 million for a population with 2 orders of magnitude lower exposure (Montero-Montoya et al. 2018). The estimated concentrations of these compounds in our samples from all seven locations in Skopje were below these limit values with a maximal detected value of approx. 0.016 mg/m^3 for benzene, 0.022 mg/m^3 for toluene, 0.008 µg/m^3 for ethylbenzene and 0.016 mg/m^3 for xylenes that implies the need for continuous monitoring and alarm if values near the RfCs are reached.

Trimethylbenzene (TMB) isomers (including 1,3,5-, 1,2,4-, and 1,2,3-TMB) are another group of components of fuels and mixed hydrocarbon solvents that together with other compounds of the same empirical formula are referred to as the C_9 aromatics. There is evidence that inhalation exposure to TMBs induces neurotoxic effects in in humans and animals (USEPA 2016). The abundance of C_6-C_3 benzene derivatives together with the C_6-C_4 group of benzene derivatives has been found to be in the low range of maximum approximately 6 µg/m^3 for and even not detected for most of these compounds.

Monoterpenes (e.g. limonene and *α*-pinene) are compounds with the formula $C_{10}H_{16}$ that are emitted by many plant species and are best known as the group of compounds responsible for the pleasant and distinctive odor of pine forests. Plants also synthesize compounds with 15, 20, 30, and 40 carbon atoms, known collectively as the classes of sesquiterpenes, diterpenes, triterpenes, and tetraterpenes, respectively, but their vapor pressures are much lower than those of C_{10} compounds (monoterpenes), and they seem unlikely to be present in the atmosphere in the gas phase. Limonene is the monoterpene compound representative of the emissions from fresh or green plant waste or the intermediate products of aerobic reactions. Air fresheners and fragrant household detergents are other sources of direct terpene emissions (Wang et al. 2019). Limonene and α-pinene have been detected in almost all samples in concentrations of up to 8 and 5 µg/m^3, respectively. Moreover, there are other non-terpene plant-derived substances, such as *p*-cymene (isopropyl methyl derivative of benzene) with formula $C_{10}H_{14}$ (as opposed to monoterpenes with formula $C_{10}H_{16}$). Its presence in air that has been found in this study in the range of maximum 2 µg/m^3 can probably be attributed to natural emissions from plants.

Many fragrance materials are produced by steam distillation of plant material under controlled conditions. Similar processes occur during production of wood pulp, plywood veneer, etc. by the wood industry. During these operations, some of the volatile compounds in the raw material escape to the atmosphere. These are anthropogenic sources of terpenes and terpenoids (Graedel 1979).

Conclusion

A convenient method for monitoring volatile organic compounds in an urban air has been developed using passive sampling and GC-MS analysis after solvent desorption with dichloromethane. The conditions for measuring average month concentrations have been optimized and semi-quantification performed using anisole as an internal standard. It has been employed for a two months assay at seven locations in Skopje in October-November period in 2020 and the results have shown the presence of 31 compound from which: 10 hydrocarbons from the group of alkanes (from C_5 to C_{14}), 16 aromatic hydrocarbons (including BTEX, C_6-C_3, C_6-C_4 derivatives and *p*-cymene), 2 terpenes (limonene and α-pinene), 3 other hydrocarbon derivatives (esters and chlorinated hydrocarbons).

The estimated concentrations of all detected compounds were found to be below the established reference concentrations by EPA that cause critical effects but they should be continuously monitored in order to raise alarm if they are reached.

The long-term goal is to set up efficient, accurate and sensitive methods for monitoring VOCs concentrations throughout the year to reveal the sources of outdoor pollution in urban areas and plan control measures for their mitigation.

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