

Article

Investigation of Non-Methane Hydrocarbons at a Central Adriatic Marine Site Mali Lošinj, Croatia

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Abstract: For the first time, volatile hydrocarbons were measured in Croatia, at Mali Lošinj in the period from autumn 2004 to autumn 2005. Mali Lošinj site is conveniently located as a gateway to Croatia for any potential pollution from either Po valley in Italy, or other locations in southern Europe or even Africa. The sampling was performed on multisorbent tubes and then analyzed by thermal desorption gas chromatography with a flame ionization detector. The aim was to determine and estimate the non-methane hydrocarbons in Mali Lošinj, a location with Mediterranean vegetation and species which emit large quantities of volatile organic compounds. Ozone volume fraction and meteorological parameters were also continuously measured, from April to October 2005. Ethane, ethene, ethyne, propane, propene, *n*-pentane, *n*-hexane, benzene and toluene were identified in all air samples. Benzene and toluene have been found in ambient air and significant positive correlations between ethyne and ethane, propane and propene indicate emissions from transport.

Keywords: non-methane hydrocarbons; multisorbent tubes sampling; thermal desorption; gas chromatography flame ionization detector; ozone

1. Introduction

Volatile organic compounds (VOCs) present in the atmosphere could either have biogenic or anthropogenic origins, and together with nitrogen oxides NO_x and sunlight, participate in reactions that lead to the formation of air pollution, tropospheric ozone and other secondary pollutants, especially secondary organic aerosols (SOA) and haze [1,2]. Some of these VOCs also play important roles in stratospheric ozone depletion and the greenhouse effect [3,4]. Climate change already affects the natural seasonal cycles of vegetation and emissions of VOCs and will presumably continue to do so [5–7]. Mediterranean regions, due to the projected increases in temperature [8–10] and changes in precipitation [11,12], are threatened by such changes. There is increasing evidence to suggest that biogenic VOCs play an important role in the adaptation of plants to the changing climate; having multiple roles in communication and protection of plants against several abiotic and biotic stresses [13–16]. Characterization of VOC mixing ratios and identification of the emission sources is essential for better evaluation of photochemical oxidants generation. In the case of non-methane volatile organic compounds (NMVOCs), anthropogenic sources account for only about 10% of total emissions [17] therefore biogenic volatile organic compounds (BVOCs) play an important role in the chemistry of the troposphere. Non-methane hydrocarbons (NMHCs), a class of volatile organic compounds, are an important component of air pollution because of their

role as precursors of tropospheric ozone and SOA. Although most of the NMHC emissions into the atmosphere are biogenic, in urban areas hydrocarbons are predominantly of anthropogenic origin [18]. The dominant anthropogenic sources of hydrocarbons in urban areas are vehicular and industrial emissions, and organic solvent usage [19,20]. Additionally, the main components of air pollution, ozone, nitrogen oxides, particulate matter and many species of organic volatile pollutants in a combination have cumulative impacts (joint toxicity) and as such pose a threat to the environment and human health [21–24].

The concentration of VOCs in ambient air is influenced by various factors so the temporal changes in concentration are controlled by a combination of emission, deposition, chemical and photochemical reactions and meteorological conditions [3]. The two most common sampling techniques of VOCs in ambient air are pre-concentration on sorbent tubes and whole air collection in canisters or bags [25,26]. Reliable sampling of these compounds is not always easy. The most common problem is water vapor present in the atmosphere [27]. In solid sorbent sampling, if the amount of water uptake by the sorbent is significant it can greatly affect VOCs adsorption efficiency. Additionally, the humidity dragged in during air sampling or sample storage can cause a variety of problems during analysis leading to unreliable results. Several major problems also involve atmospheric oxidants present in the atmosphere (primarily ozone and nitrogen dioxide NO_2) that can cause analyte losses of reactive volatile organic compounds [27] and degradation of the sorbent with the formation of artifacts [25]. Solid sorbent materials, used in most for sorbent-based sampling of VOCs in ambient air are Tenax TA, Carboxpack, Carbotrape, Carbosieve S-III and their combination [26,28,29]. The right choice of sorbent material primarily depends on the selectivity of the sorbent and the amount and type of compounds to be analyzed.

Although there are a lot of emission measurements of VOCs from Mediterranean plants and trees, there is a lot of missing information about the mixing ratios of VOCs in semiurban and rural locations in the Mediterranean [30]. Therefore, the analysis of VOCs in ambient air becomes even more important. This paper describes the results from a hydrocarbon sampling campaign at a semiurban location of Mali Lošinj, Croatia. For the first time, these kinds of measurements took place in Croatia. Our purpose was to investigate temporal variations and mass concentration of major non-methane hydrocarbons and their source in this coastal region.

Since the atmosphere is composed of various components—predominantly gasses—it behaves like a fluid. Therefore, it is highly possible that air masses can be transferred from one point to another in a relatively short time. To be sure whether such occurrences really happen or not, air trajectories for the specific periods can be calculated [31–34]. Such analysis can help in the explaining of various atmospheric conditions that otherwise cannot be explained or that explanation would be rather difficult.

2. Experiments

2.1. Sampling Site Description

Mali Lošinj, situated on the south side of the Lošinj bay (Figure 1), is a significant maritime, commercial, tourist and health center on the island of Mali Lošinj and the largest island city in the Adriatic with a population of 6300 inhabitants. The sampling site at Mali Lošinj was located away from the major sources of pollution. The major business activities are tourism and fishery with a single shipyard (for the reconstruction of ships) representing industrial activity in the city. The main source of pollution is increased traffic during the tourist season when the number of tourists, in the summer, can almost quadruple the normal population. The climate is typically Mediterranean with vegetation consisting primarily of evergreen trees (Aleppo pine, Stone pine, Black pine, Maritime pine, White pine), deciduous trees (mostly of all oak), macchia and a variety of medical and aromatic herbs (rosemary, laurel, lavender).

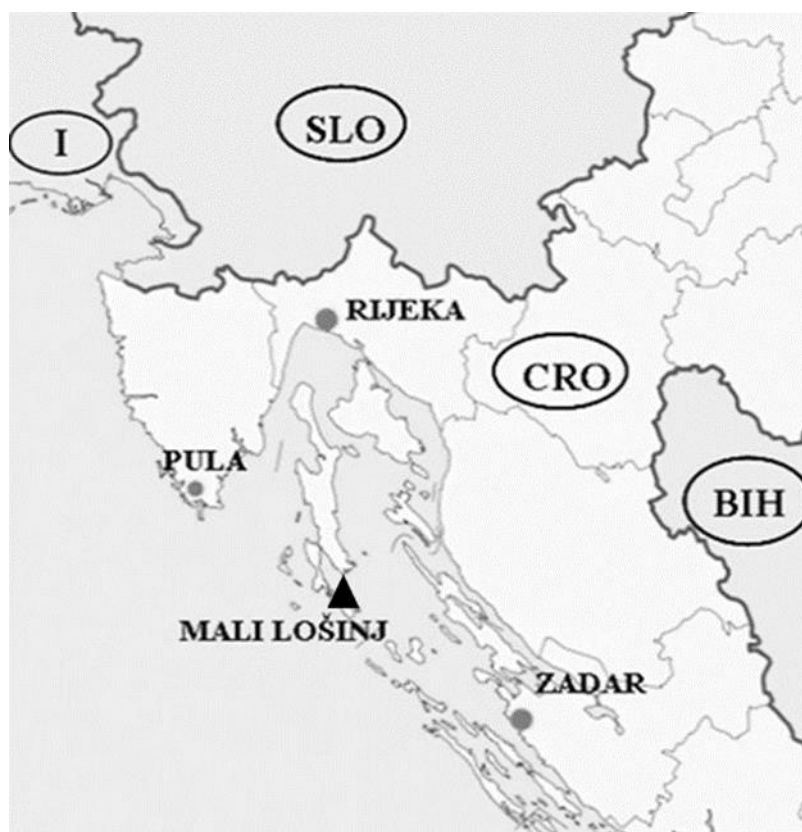


Figure 1. Location of the monitoring station Mali Lošinj, Croatia (marked with a triangle) with the surrounding area.

With over 260 sunshine days a year, Mali Lošinj is among the sunniest areas in Croatia. On the island of Mali Lošinj, a generation of sea/land breezes (SLB) during the bora wind playing an important role in local weather and climate dynamics, is observed [35,36]. Since the island is relatively narrow (maximum width is about 5 km), sea thermal effect is pronounced and prevents strong cooling. Additionally, it is located about 30 km from the mainland, so the influence of a strong bora wind and cold European anticyclone is weakened. Due to its geographical position, the influence of Mediterranean cyclones is weakened too.

Instruments for sampling hydrocarbons and ozone monitors were placed in the building of the Meteorological and Hydrological Service of Croatia, which is located on a hill in the town of Mali Lošinj (44.53° N and 14.46° E, 43 m above sea level). Samples of hydrocarbons were taken between 9 a.m. and 15 p.m. on 23 September and 22 October 2004 and 27 April, 25 May, 10 June, 15 July, 25 July, 19 August, 15 September and 25 October 2005 for preliminary measurements. The measurements were carried out during various seasons (all except winter) in Croatia, making them representative. Meteorological parameters and ozone volume fraction were continuously measured from April to October 2005.

2.2. Sampling and Analytical Method

2.2.1. Sampling

In this study, non-methane hydrocarbons were collected by pre-concentration on solid adsorbents. The system for the sampling of air used in this study consisted of a multisorbent sampling tube (14 cm length), membrane pump and flow controller. As the sampling rate depends on the concentration of the investigated compounds in the air, in the case of lower concentrations it is 100 mL min^{−1} with a sampling time of 20 min, so the sampled volume of air per tube was 2 L. In order to avoid contamination, the air first passed through the metal tubes and then through flow controller. The tubes

were made of stainless steel and filled with: Carbosieve S-III (150 mg), Carbotrap (150 mg), Tenax (150 mg) (all Merck, Darmstadt, Germany). The direction of air was Tenax TA→Carbotrap→Carbosieve S-III. Higher molecular weight hydrocarbons adsorb on Tenax TA leaking lower molecular weight hydrocarbons. If the direction is inverted, sampled hydrocarbons with higher molecular weight could be irreversibly bound to Carbotrap [28,37,38]. When analyzing, the direction of the flow during thermal desorption was reversed from the direction of adsorption. Tubes filled with sorbents can be used multiple times, but before each sampling, it is necessary to condition them (for a minimum of 8 h at 280 °C). For achieving optimal results, the tubes were placed into the thermoblock which is separated from the main chromatographic instrument.

2.2.2. Desorption

After sampling, the tubes were analyzed in the laboratory of the Chair for Analytical Chemistry of the Department of Chemistry and Biochemistry at the Faculty of Chemistry and Chemical Technology of the University of Ljubljana, Slovenia using thermal desorption cold trap injection gas chromatography with flame ionization detector (TD GC/FID) model Varian Star 3400 Cx (Agilent, Santa Clara, California). Flame ionization detector is widely used in the determination of volatile hydrocarbons due to its high sensitivity ($\sim 0.1 \mu\text{g m}^{-3}$ for all NHMC), large range of linear response, low noise, and a simple performance and handling. The instrument was equipped with a 10 port VICI valve, heated thermal block and cold trap (cryotrap). Thermal desorption of samples was carried out at a temperature of about 260 °C for 20 min with a flow rate of 100 mL/min. Desorbed volatile hydrocarbons were, using high purity helium (He 6.0) as the carrier gas, concentrated in the cryotrap where they were liquefied at the temperature of liquid nitrogen (−196 °C). After switching the valve and rapid immersion of the cryotrap in warm water, organic hydrocarbons, now in the gas phase, were injected into the capillary separation column.

2.2.3. Conditions of Analysis

For the separation of hydrocarbons, a capillary column of fused quartz covered with a stationary phase of alumina deactivated with potassium chloride (Chrompack $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT column) was used. Column length was 50 m with a diameter of 320 μm . The temperature program of the column was: $T_{\text{initial}} = 50 \text{ }^\circ\text{C}$ (5 min), $\text{gradient}_1 = 3 \text{ }^\circ\text{C/min}$ to 100 °C, $\text{gradient}_2 = 5 \text{ }^\circ\text{C/min}$ to 200 °C, $T_{\text{finally}} = 200 \text{ }^\circ\text{C}$ (25 min). Gas mixtures for the calibration of the detector were Scotty, CAN MIX 220, Scotty, CAN MIX 222, and the mixture of ozone precursors with 57 components (Restek Ozone precursor mixtures).

2.2.4. Meteorological Parameters and Ozone Data

Meteorological data were obtained from the Meteorological and Hydrological Service of Croatia and monitored parameters were: solar radiation time (*Sun*, expressed in h), temperature (*t* expressed in °C), relative humidity (*Rh*, expressed in %), cloudiness (*Clo*, expressed in %), visibility (*Vis*, expressed in km), wind speed (*WS*, expressed in km/h), precipitation (*Pr*, expressed in mm) and pressure (*p*, expressed in hPa). Ozone has been monitored with a commercial UV photometer Ansyco O341M (Environnement S.A.). The equipment was regularly maintained and calibrated.

2.3. Data Analysis and Statistics

Hydrocarbon mass concentration data (GC-FID data from Varian software) were quantified using relative response factor approach [39–42]. For the calculation of the correlation coefficients between hydrocarbon mass concentrations, meteorological parameters and ozone, appropriate modules from Statistica software (StatSoft Inc., Tulsa, USA) were used. Air trajectories are calculated using METEX software (Center for Global Environmental Research, Tsukuba, Japan) [43–45].

3. Results and Discussion

3.1. Volatile Hydrocarbon Mass Concentration in Ambient Air

During the measuring campaign in 2004 and 2005 at Mali Lošinj, ethane, ethene, ethyne, propane, propene, *n*-pentane, *n*-hexane, benzene and toluene were always identified, and their average daily concentrations are shown in Figure 2. It can be seen from Figure 2 that toluene concentrations are somewhat higher on 25 May 2005 and the same is true for the *n*-hexane and benzene on 25 October 2005. These variations may seem significant but those concentrations are still very low and common for the unpolluted sights [46].

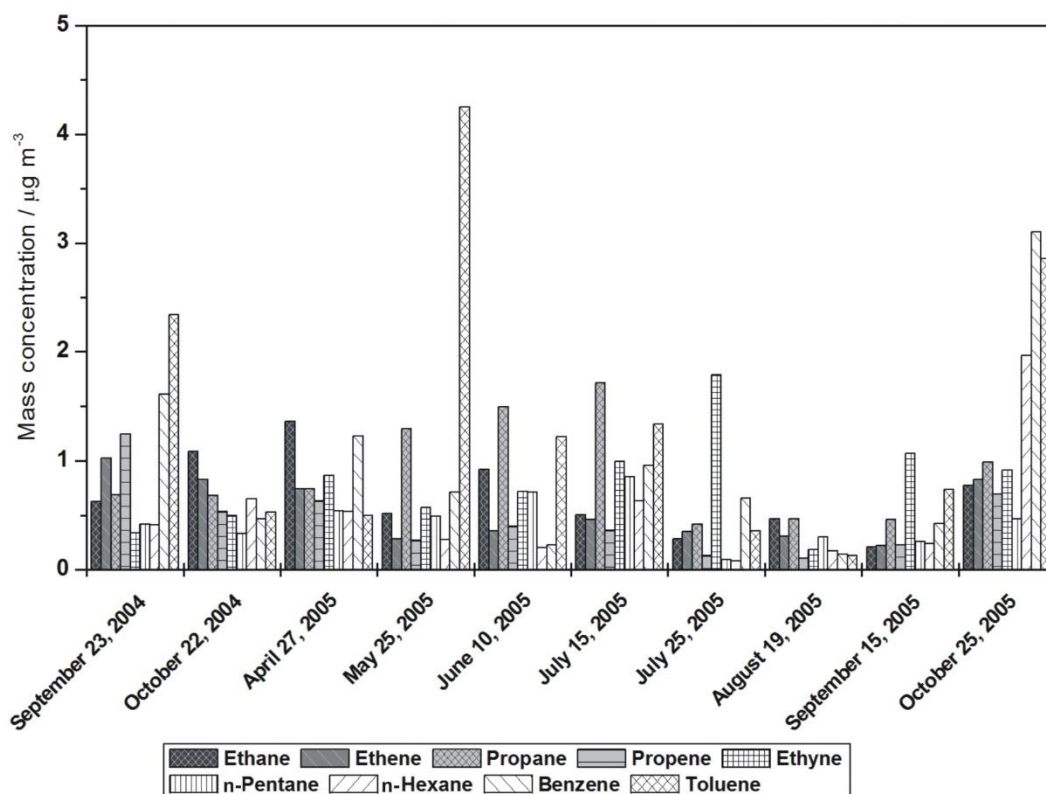


Figure 2. Average daily value of the mass concentration of some hydrocarbons measured at Mali Lošinj in 2004 and 2005.

Table 1 shows all detected compounds and their daily average mass concentration. Most of the average daily concentrations were below $1 \mu\text{g m}^{-3}$, while hourly concentrations only sometimes exceeded the value of $1.5 \mu\text{g m}^{-3}$, mostly for toluene and benzene. There were no significant increases in the concentrations around noon. The most significant changes in daily concentrations measured during the 2005 season are for ethyne ($0.19\text{--}1.8 \mu\text{g m}^{-3}$), *n*-hexane ($0.08\text{--}2 \mu\text{g m}^{-3}$), benzene ($0.1\text{--}3.1 \mu\text{g m}^{-3}$) and toluene ($0.1\text{--}4 \mu\text{g m}^{-3}$). Overall, the concentrations of volatile hydrocarbons were lower at the end of July and during August and September (except for ethyne in July and September). Reduced concentrations of volatile hydrocarbons during the late summer are associated primarily with reduced emissions of biogenic volatile hydrocarbons and favorable conditions for their decomposition (higher insolation and increased concentrations of atmospheric oxidants). Increasing concentrations of volatile hydrocarbons in October were caused by low concentrations of hydroxyl radicals and reduced UV radiation. In this case, the concentrations of *n*-hexane ($2 \mu\text{g m}^{-3}$), toluene ($2.9 \mu\text{g m}^{-3}$) and benzene ($3.1 \mu\text{g m}^{-3}$) are significantly higher than for the summer period. The most abundant volatile hydrocarbons were benzene, toluene, propane and ethyne.

Table 1. Detected compounds in ambient air samples and their daily average mass concentration ($\mu\text{g m}^{-3}$).

	23 September 2004	22 October 2004	27 April 2005	25 May 2005	10 June 2005	15 July 2005	25 July 2005	19 August 2005	15 September 2005	25 October 2005
Ethane	0.6 ± 0.4	1.1 ± 0.8	1.4 ± 0.3	0.5 ± 0.2	0.9 ± 0.1	0.5 ± 0.3	0.3 ± 0.1	0.47 ± 0.08	0.21 ± 0.03	0.8 ± 0.4
Ethene	1.0 ± 0.2	0.8 ± 0.1	0.8 ± 0.4	0.3 ± 0.1	0.4 ± 0.1	0.5 ± 0.4	0.4 ± 0.2	0.31 ± 0.06	0.22 ± 0.08	0.8 ± 0.6
Propane	0.7 ± 0.3	0.7 ± 0.2	0.8 ± 0.2	1 ± 1	1.5 ± 0.8	1.7 ± 0.8	0.4 ± 0.2	0.5 ± 0.2	0.5 ± 0.1	1.0 ± 0.2
Propene	1.3 ± 0.3	0.6 ± 0.1	0.6 ± 0.2	0.27 ± 0.09	0.4 ± 0.2	0.4 ± 0.6	0.13 ± 0.02	0.11 ± 0.03	0.23 ± 0.04	0.7 ± 0.2
Ethyne	0.34 ± 0.05	0.5 ± 0.1	0.9 ± 0.1	0.6 ± 0.3	0.7 ± 0.2	1.0 ± 0.2	1.8 ± 0.1	0.19 ± 0.06	1.1 ± 0.1	0.9 ± 0.4
<i>n</i> -Butane	0.3 ± 0.1	0.7 ± 0.3	0.6 ± 0.4	1.1 ± 0.9	1.3 ± 0.5	1.1 ± 0.7	0.5 ± 0.3	0.4 ± 0.1		0.62 ± 0.09
But-1-ene	0.49 ± 0.08	0.9 ± 0.1	0.5 ± 0.4	0.2 ± 0.1		0.1 ± 0.1	0.22 ± 0.06	0.2 ± 0.2		0.3 ± 0.1
Propyne	0.76 ± 0.07	0.60 ± 0.07	0.39 ± 0.06	0.3 ± 0.1	0.20 ± 0.04		0.5 ± 0.3		0.13 ± 0.04	1.5 ± 0.2
But-1-yne		0.27 ± 0.05							0.29 ± 0.05	
Cis-2-pentene						0.4 ± 0.1	0.15 ± 0.05			
<i>n</i> -Pentane	0.4 ± 0.3	0.3 ± 0.5	0.5 ± 0.3	0.5 ± 0.3	0.7 ± 0.3	1 ± 1	0.09 ± 0.03	0.3 ± 0.2	0.3 ± 0.1	0.5 ± 0.1
Pent-1-ene		0.3 ± 0.1	0.4 ± 0.2			0.3 ± 0.2	0.4 ± 0.2	0.11 ± 0.08		
<i>n</i> -Hexane	0.4 ± 0.1	0.7 ± 0.9	0.5 ± 0.1	0.3 ± 0.2	0.20 ± 0.09	0.6 ± 0.2	0.08 ± 0.02	0.2 ± 0.1	0.24 ± 0.08	2 ± 1
Hex-1-ene		0.4 ± 0.8		0.16		0.2 ± 0.1	0.07 ± 0.01	0.13 ± 0.08		
Methylcyclopentane		0.26 ± 0.01	0.31 ± 0.02							
Benzene	1.6 ± 0.1	0.5 ± 0.1	1.2 ± 0.3	0.7 ± 0.1	0.2 ± 0.2	1.0 ± 0.1	0.6 ± 0.2	0.1 ± 0.1	0.4 ± 0.2	3.1 ± 0.5
2,4-Dimethylpentane		0.6 ± 0.1	1.4 ± 0.1							
Cyclohexane		0.3 ± 0.1	1.2 ± 0.1							
2,3-Dimethylpentane			1.45 ± 0.06							
2-Methylhexane			0.34 ± 0.03							
3-Methylhexane		1.9 ± 0.1	1.7 ± 0.2							
<i>n</i> -Heptane		0.9 ± 0.3	1 ± 1	0.3 ± 0.1						
2,2,4-Trimethylpentane		0.4 ± 0.3	0.7 ± 0.3							
Methylcyclohexane		0.5 ± 0.2								
Toluene	2.3 ± 0.3	0.5 ± 0.3	0.5 ± 0.4	4 ± 1	1.2 ± 0.7	1.3 ± 0.3	0.3 ± 0.3	0.1 ± 0.2	0.7 ± 0.1	2.9 ± 0.8

The presence of benzene and toluene in the air suggest local sources of emissions from traffic [31–33,47–49]. Figure 3 shows the mass concentration daily ratio of benzene and toluene for the measurement period. It can be observed that in May and June the concentration ratio of toluene and benzene is much higher than in other months, suggesting that toluene and benzene do not have the same emission sources and that toluene has a different seasonal cycle from benzene which is caused by local biogenic emissions from pine trees [50–53]. Heiden et al. [50] and White et al. [53] provided evidence for a biogenic contribution to the summer toluene enhancements due to the conditions of stress like nitrogen deficiency, leaf wounding or pathogen attack.

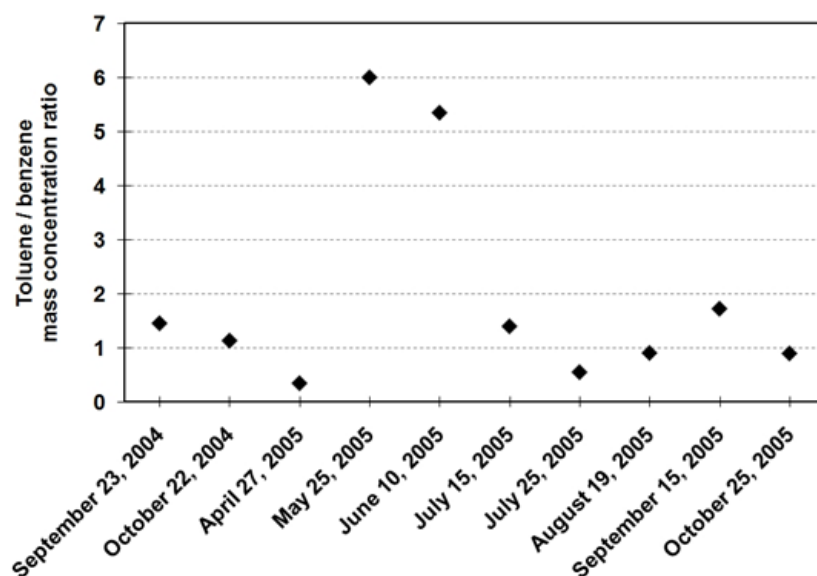


Figure 3. Average daily ratio of mass concentrations of toluene and benzene for the measuring period at Mali Lošinj.

Figure 4 shows the diurnal variation of mass concentrations of benzene and toluene in the growing season 2005 and their ratio. The hourly ratio of the mass concentration of toluene and benzene was between 0.94 and 3.53 and a downward trend in this ratio during the afternoon can be observed. The only significant reaction in the atmosphere in which toluene and benzene “lose” is the photochemical reaction with OH· radicals whose reaction rate constant is $1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for benzene and $5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for toluene [54].

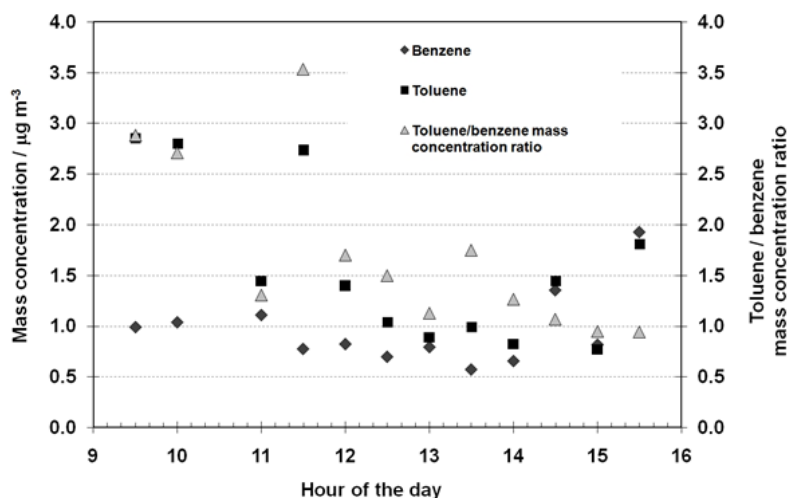


Figure 4. Average hourly variations of mass concentrations of toluene and benzene during the growing season 2005 and their ratio at Mali Lošinj.

3.2. Spearman's Nonparametric Test

Results of Spearman's nonparametric test ($p < 0.05$) performed for the measured concentrations of predominant volatile hydrocarbons, ozone and meteorological parameters at Mali Lošinj from spring to autumn 2005 are shown in Table 2.

Table 2. Spearman's rank correlation coefficients of hourly average concentrations of hydrocarbons, ozone and meteorological parameters measured at Mali Lošinj (bold marked correlations are significant at $p < 0.05$).

	Ethane	Ethene	Propane	Propene	Ethyne	n-Butane	n-Pentane	n-Hexane	Benzene	Toluene	Temperature	Solar radiation	Ozone
Ethane	1	0.52	0.67	0.34	0.62	0.24	0.46	0.32	0.41	0.40	−0.57	−0.61	−0.02
Ethene		1	0.29	0.10	0.34	−0.08	0.16	0.25	0.51	0.14	−0.12	−0.38	−0.02
Propane			1	0.38	0.75	0.64	0.70	0.46	0.33	0.65	−0.39	−0.36	0.03
Propene				1	0.37	0.31	0.20	0.29	−0.09	0.38	−0.69	−0.50	−0.64
Ethyne					1	0.38	0.43	0.22	0.23	0.50	−0.46	−0.45	0.05
n-Butane						1	0.65	0.31	−0.10	0.47	−0.23	−0.04	−0.16
n-Pentane							1	0.58	0.32	0.65	−0.26	−0.26	0.04
n-Hexane								1	0.58	0.81	−0.30	−0.44	−0.29
Benzene									1	0.52	−0.14	−0.58	0.00
Toluene										1	−0.51	−0.60	−0.27
Temperature											1	0.70	0.52
Solar Radiation												1	0.50
Ozone													1

Among the results shown, the highest number of significant correlations are for ethane, propane and toluene concentrations against the concentrations of other hydrocarbons measured. Ethane concentrations significantly positively correlate with all other concentrations of measured hydrocarbons excluding *n*-butane. With air temperature and insolation, ethane concentrations were significantly negatively correlated which is to be expected because higher temperatures and sunshine will result in faster reactions and thereby reduce the concentration of hydrocarbons. All volatile hydrocarbons have these two correlations negative (some of which are significant). The concentration of hydrocarbons with five or more carbon atoms in the molecule, *n*-pentane, *n*-hexane, benzene, and toluene, significantly positively correlate with each other, and indicate that the emission sources of these compounds are mainly similar. Significant positive correlations between ethyne and ethane, ethane, propane, propene, propane, butane, pentane and toluene suggest that their main source is vehicular emission.

Ozone concentrations significantly positively correlate with the air temperature and insolation, which is to be expected given that the insolation is an important parameter in the reactions of ozone formation. As for the volatile hydrocarbons, there is a significant negative correlation only with propene. For more detailed results for ozone please refer to [55].

3.3. Air Trajectories

Graphical depictions of the air trajectory calculation are shown in Figure 5.

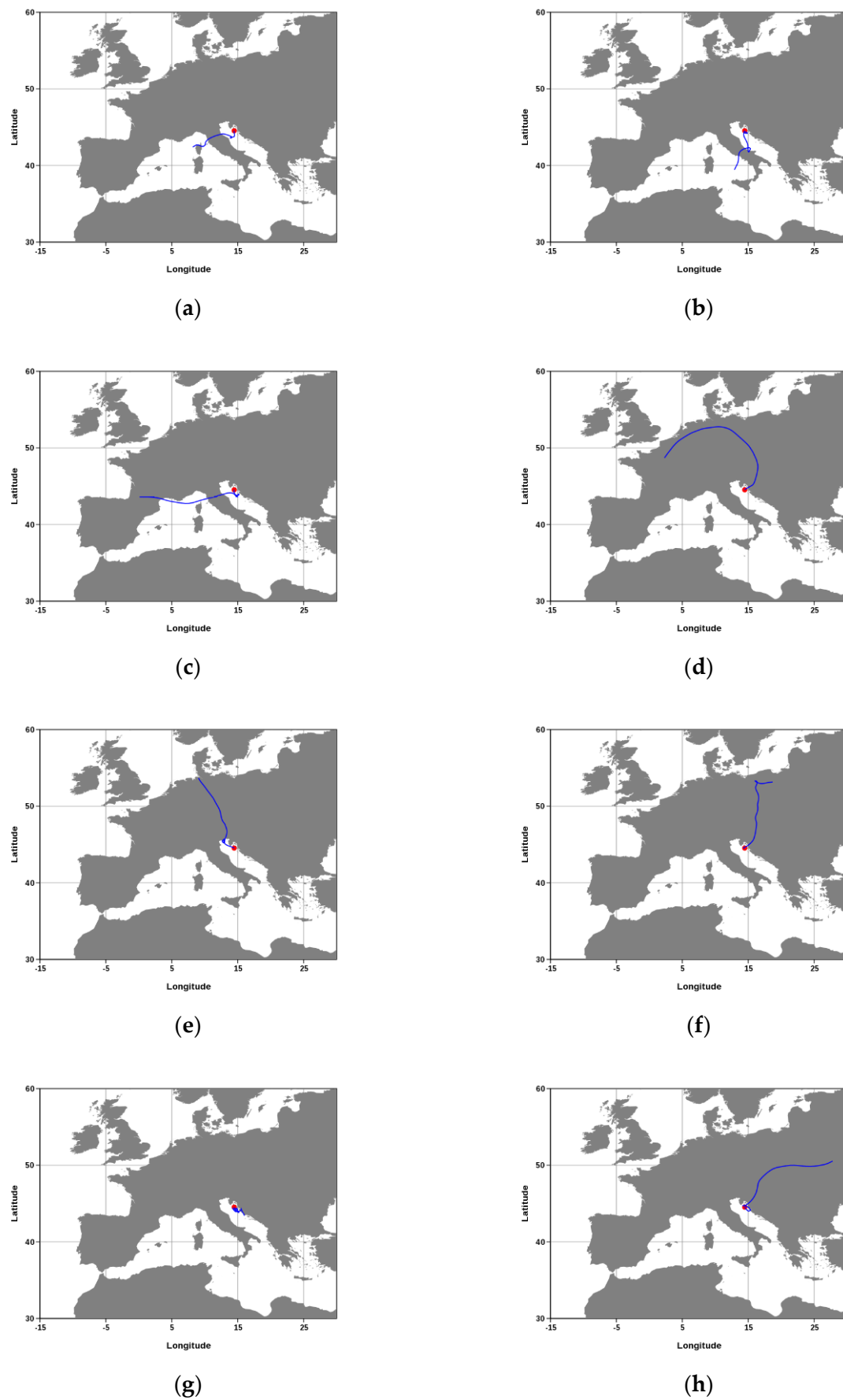


Figure 5. Cont.

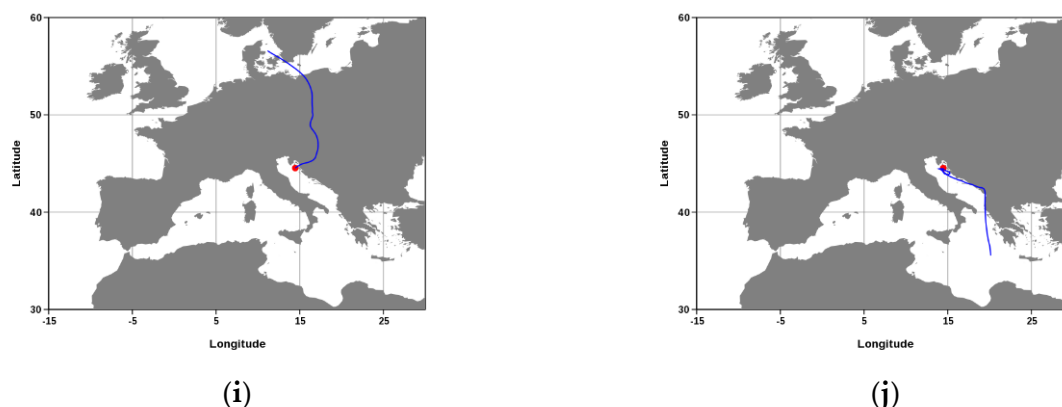


Figure 5. Air trajectories calculated for the Mali Lošinj observation site using METEX software and kinematic model. Calculations are carried on for the following days marked with letters: (a) 23 September 2004, (b) 22 October 2004, (c) 27 April 2005, (d) 25 May 2005, (e) 10 June 2005, (f) 15 July 2005, (g) 25 July 2005, (h) 19 August 2005, (i) 15 September 2005 and (j) 25 October 2005. Trajectories are calculated for 3 days backwards from the date mentioned above.

As can be seen from Figure 5, in most cases, trajectories show air mass movement from either west or north or both. Only during October measurements, some movement from the south occurred. Such southern mass transfer (Figure 5j) is known to occur sporadically in the area [56]. The analogous results are observed for the nearby Slovenian stations [57] using another FLEXTRA model, which eventually concluded that air mass in Slovenia is in fact influenced by the pollution in the Po valley, Italy. Despite the possibility of a similar influence of the pollution from the Po valley on our data too, more comprehensive measurements and data sets are needed to confirm such a situation at the Mali Lošinj site. It is, however, indicative from the calculated air trajectories that the same situation may occur here (Figure 5a,c) especially since Mali Lošinj directly faces Po valley situated less than 200 km to the west. On the other hand, massive northern influences (Figure 5d–f,h,i) could be prevented by Dinarides and Alps mountains. Still, our preliminary results can be well explained by local influences.

4. Conclusions

In 2004 and 2005 at Mali Lošinj, for the first time, a sampling campaign of volatile hydrocarbons was conducted. The purpose was to quantify and determine their temporal variations. Ethane, ethene, ethyne, propane, propene, *n*-pentane, *n*-hexane, benzene and toluene were identified in all air samples. Lower concentrations during the summer months (July, August and September) were due to the higher photochemical activity resulting in faster removal from the atmosphere. Increasing concentrations of volatile hydrocarbons in October were caused by low concentrations of hydroxyl radicals and reduced UV radiation. Benzene and toluene found in the air samples and significant positive correlations between ethyne and ethane, propane, propene indicate emissions from road transport. In May and June, the mass concentration ratio of toluene and benzene is much higher than in other months, suggesting toluene local biogenic emissions from pine trees. A downward trend of hourly mass concentration ratio of toluene and benzene during the afternoon is observed.

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