



VOC Measurements at *Kopački rit* Nature Reserve

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Key words: *Kopački rit*, VOCs, background atmosphere

Abstract

Preliminary results of volatile organic compounds (VOCs) measurements during the growing season in *Kopački rit* in May 2004 are reported. Due to the present very little anthropogenic activities in the Nature Reserve, these data were expected to represent background or «clean air» values for this region. Surprisingly high concentrations of ethene and other unsaturated hydrocarbons were found indicating that more measurements and an analysis of atmospheric trace constituents at *Kopački rit* is needed.

INTRODUCTION

The Nature Reserve *Kopački rit*, located in Baranya, the far north-east of Croatia between the rivers of Drava and Danube to the south of the Hungarian border river is one of the largest natural marshlands in Europe with an area of 330 km². Different types of forests exist in the *Kopački rit* region such as white willow, black poplar, oak and yoke elm forests. Before the war in Croatia during 1991-95 it was a frequently visited natural resource, but little activities took place there during the past decade. Thus a background clean air is expected to be present there with negligible influence by human activities. On the other hand this are as marshland could be a natural source of hydrocarbons in the atmosphere. The aim of this preliminary study was to investigate this background condition because more anthropogenic activities can be expected to take place in the future.

Volatile organic compounds (VOCs) present in the atmosphere, sometimes called as non-methane hydrocarbons (NMHC), are of biogenic and anthropogenic origin. VOCs play an important role in different photochemical processes in the troposphere (1-3). These compounds are, along with sunlight and nitrogen oxides, the main precursors for tropospheric ozone formation which has a significant role in forest injuries (4). Beside that, their oxidation products are involved in the formation of secondary organic aerosols. In order to evaluate all these processes a detailed knowledge about the presence of the individual VOCs in the atmosphere is needed.

Within one of the goals of EUROTRAC/TOR project the distribution of NMHC in Europe was investigated since 1988 and data allocated to a common European background were published (5). However, few data are available for SE Europe.

EXPERIMENTAL

Air samples for HC determination were collected in metal tubes using a membrane pump with a flow controller (Sierra Instruments

Table 1.

The temperature program for column used in GC

Temperature program	50 °C, 5 min
	3 °C/min up to 100°C
	5 °C/min up to 200°C
	200 °C, 25 min



Figure 1. Map of Kopački rit with indicated sampling sites at Lake Sakadaš and Tikveš (marked with x).

Inc. model 901CT). The tubes were filled with various types of absorbers (150 mg Tenax TA, 150 mg Carbotrap i 150 mg Carbosieve). To avoid air contamination it first passed through the metal tubes and afterwards through the flow controller. The flow was maintained at 50 mL/min for 20 minutes, so that the volume of the sampled air was 1 L.

After sampling the tubes were analysed in the laboratory on the gas chromatograph with FID detector (Varian Star 3400CX). The instrument was equipped with a specific system for the analysis of the VOC that included a thermal desorption unit, a ten-port valve and a cryo-trap.

The thermal desorption was carried out at 260 °C. The desorbed volatile organic hydrocarbons were flushed with helium to the cryo-trap cooled by liquid nitrogen (-196 °C). All the connecting tubes were made of stainless steel. They were heated to 100 up to 120 °C to prevent condensation of volatile organic compounds at possible cold spots.

After opening the valve and fast immersion of the spiral trap into hot water the organic components in the

Table 2.

Average concentrations of VOCs as measured at Sakadaš (14 May 2004) and Tikveš (19 May 2004) in micrograms per cubic metre ordered according to gc retention time.

Location Compound	Sakadaš	Tikveš
ethane	6.22	2.31
ethene	22.21	3.81
propane	20.15	0.93
propene	52.92	3.99
ethyne	0.47	
<i>n</i> -butane	31.95	0.63
1-butene	33.64	
propyne		0.69
<i>cis</i> -2-butene	87.67	
1-pentene		1.57
<i>n</i> -pentane	54.78	
1-butyne	38.23	
<i>n</i> -hexane	5.02	0.51
methylcyclopentane	2.14	
benzene	4.01	2.57
2-methylhexane	3.57	2.52
3-methylhexane		0.32
<i>n</i> -heptane	0.53	1.78

gas phase were injected into the capillary separation column. The column used was Crompack Al₂O₃ / KCl PLOT column (l = 50 m, 2r = 320 μm). The temperature program used is given in Table 1.

For the quantitative analyses of VOC a gas chromatograph with flame ionization detector was used. The gas mixture used for the calibration consisted of ethane, propane, butane, pentane and hexane (Scotty, CAN MIX 220), and ethene, propene, butene, pentene and hexene (Scotty, CAN MIX 222). All organic compounds were quantified using effective carbon number theory for the evaluation of the individual respons factors.

The air sampling locations were at Lake Sakadaš on 14 May 2004 and at Tikveš on 19 May 2004 as indicated in Figure 1.

RESULTS AND DISCUSSION

The average concentration of VOCs in air as measured at Sakadaš and Tikveš are given in Table 2. Higher concentrations for nearly all VOCs were found at Sakadaš; however, the *n*-heptane concentration was low and propyne, 1-pentene and 3-methylhexene were not found at all. On the other hand ethyne, 1-butene, *n*-pentane, 1-butyne and methylcyclopentene were not found at Tikveš. The surprising fact in the present results is the high concentration of ethene and other unsaturated hydrocarbons as compared to saturated ones at both locations, but particularly at Sakadaš. Sakadaš is the main entrance site

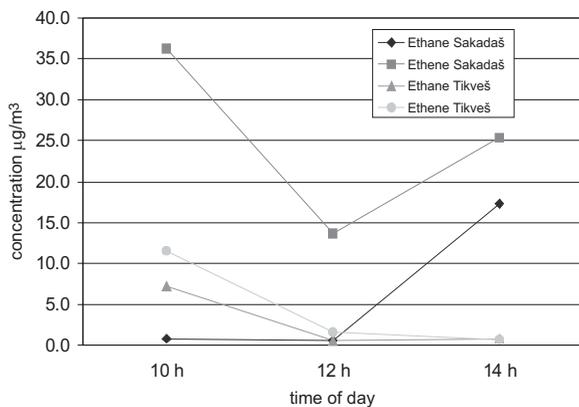


Figure 2. Observed concentrations of ethane and ethene at Sakadaš and Tikveš between 10:00 and 10:20, 12:00 and 12:20 and 14:00 and 14:20.

of the National Reserve not far away from the small village, Kopačevo. Neither of them could, however, be attributed as the source of measured VOC concentrations, which overall are higher than those we measured at the Ruđer Bošković Institute in the city of Zagreb (*to be published*) and especially than those recorded on the Adriatic island of Mali Lošinj (*to be published*). On the other hand, ethene is known as a plant growth hormone naturally produced mostly in autumn, so its high values in May are quite uncommon. Results from Finland (6), south-east USA National parks (7) and the EUROTRAC/TOR observations (5) also show much lower ethene concentrations. The observed diurnal variation (Figure 2) is also rather intriguing: the concentrations are highest in the morning disappearing at mid-day at Tikveš, but rising again during afternoon at Sakadaš.

CONCLUSION

The levels of VOC concentrations in ambient air in the area of *Kopački rit* as well as their diurnal behaviour

were found to be highly unusual and require a more detailed and systematic investigation over a longer period. Additional meteorological information will be needed in order to evaluate if present VOCs concentrations are due to local sources or due to regional transport.

Acknowledgement: This work was performed within a bilateral Slovenian-Croatian research project. The authors acknowledge their Ministries of Science (Slovenian Ministry of Science and Croatian Ministry of Science, Education and Sports) for financial support and the Croatian Ministry of Environmental Protection, Physical Planning and Construction and the administration of the Nature Reserve *Kopački rit* for the permission to take air samples.

REFERENCES

1. KESSELMEIER J, STAUDT M 1999 Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J Atmos Chem* 33: 23–88
2. GUO H, SO K L, SIMPSON I J, BARLETTA B, MEINARDI S, BLAKE D R 2006 C1–C8 volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment. *Atmos Environ: (in Press)*, Corrected Proof, Available online 14 December, 2006.
3. WANG D K V, AUSTIN C C 2006 Determination of complex mixtures of volatile organic compounds in ambient air: an overview. *Anal Bioanal Chem* 386: 1089–1098
4. CVITAŠ T, KEZELE N, KLASINC L, ŠORGO G 2006 AOT40 as preliminary indicator for ozone induced forest injury on Mountain Medvednica near Zagreb. *Period Biol* (this issue)
5. LINDSKOG A, SOLBERG S, ROEMER M, KLEMP D, SLADKOVIC R, BOUDRIES H, DUTOT A, HAKOLA H, SCHMITT R, ARESKOUG H 1995 The distribution of NMHC in Europe – results from the EUROTRACK TOR project. *Water Air Soil Poll* 85(4): 2027–2032
6. HAKOLA H, HELLÉN H, LAURILA T 2006 Ten years of light hydrocarbons (C2–C6) concentration measurements in background air in Finland. *Atmos Environ* 40: 3621–3630
7. KANG D, ANEJA V P, MATHUR R, RAY J D 2004 Observed and modeled VOC chemistry under high VOC/NOx conditions in the Southeast United States national parks. *Atmos Environ* 38: 4969–4974