

Investigation of BVOC levels in a coastal urban environment: The Piraeus Port in Greece

LIAKAKOU E.^{1,*}, PANOPOULOU A.¹, GRIVAS G.¹, GERASOPOULOS E.¹, SAUVAGE S.² and MIHALOPOULOS N.¹

¹National Observatory of Athens, Institute for Environmental Research and Sustainable Development, GR-15236P. Penteli, Athens, Greece

²IMT Lille Douai, Institut Mines-Télécom, Univ. Lille, Centre for Energy and Environment, F-59000 Lille, France

*corresponding author: Liakakou Eleni

e-mail: liakakou@noa.gr

Abstract Biogenic volatile organic compounds (BVOC) constitute organic species of high reactivity, influencing thus the composition of the atmosphere through participation in various reactions leading to the formation of secondary pollutants. Despite their well established origin from vegetation, focus is given recently on the role of the anthropogenic emission sources. Monoterpenes, which are under investigation in the current work, have been measured in environments affected by traffic, shipping, biomass burning and industrial activities. Monitoring of monoterpenes (α -pinene and limonene) during 2019 was implemented at the recently established Atmospheric Pollution Monitoring Station of the Municipality of Keratsini-Drapetsona located close to the Piraeus Port in Greece. An automatic gas chromatograph with flame ionization detector on 30 minutes time resolution was used to measure a wide range of non methane hydrocarbons (NMHCs) from 6 to 12 carbon atoms. The seasonal variability of α -pinene and limonene demonstrated slightly higher values during summer and winter respectively. The correlations with other pollutants of anthropogenic origin indicated the impact of non-natural emission sources on their levels. Their potential to form ozone and aerosol was estimated and compared with already published data obtained at the urban background environment of Athens.

Keywords: BVOC, monoterpenes, urban environment, harbor, Greece

1. Introduction

Biogenic Volatile Organic Compounds (BVOC) contribute significantly to the formation of secondary organic aerosol (SOA) and tropospheric ozone (O₃) due to their high reactivity (Guenther et al. 1995, Atkinson 2000, Camredon et al. 2007), which in turn affect directly and indirectly climate, vegetation and human health (Fehsenfeld et al. 1992, Laothawornkitkul et al. 2009). The emission of BVOC from vegetation is closely linked to the synthetic processes and storage capability in plants, being thus influenced from temperature and solar radiation (Fuentes et al. 2000, Geron et al. 2000,

Laothawornkitkul et al. 2009). Isoprene and monoterpenes are the most well-known BVOC, with estimated global isoprene and monoterpenes emissions of 500 and 162 Tg year⁻¹ respectively (Guenther et al. 2012). However, studies in urban environments indicate that these compounds are also linked with anthropogenic sources like traffic, wood burning, use of cleaning products and oil-related industrial emissions (Borbon et al. 2001, Bari & Kindzierski 2018, Hellén et al. 2012, McDonald et al. 2018). In the Mediterranean, monoterpenes as a sum and isoprene have been reported in urban sites in Athens (Greece), Barcelona (Spain), Beirut (Libanon) and Istanbul (Turkey) (Seco et al. 2013, Salameh et al. 2015, Kaltsonoudis et al. 2016, Thera et al. 2019). The only year-long study in the area reporting levels of individual monoterpenes so far, was conducted in Athens and denoted the importance of anthropogenic sources of monoterpenes and their contribution to locally formed secondary pollutants (Panopoulou et al., 2020). Monitoring levels of compounds that are typically considered as BVOCs in urban areas contributes to the understanding of emission sources and of their role in the oxidation capacity of the atmosphere and SOA formation. In this context, the current work examines a 12-month dataset of monoterpenes acquired at an urban coastal site, focusing on the investigation of their temporal variability and their O₃ and SOA formation potential.

2. Experimental

2.1. Site and measurements

The current work concerns the analysis of monoterpenes among other VOCs, obtained at an urban coastal area 2km westerly of the passenger terminals of the Piraeus Port in Greece during 2019. High temporal resolution measurements were implemented at the Atmospheric Pollution Monitoring Station of the Municipality of Keratsini-Drapetsona (37°56'48"N, 23°36'58"E). The site is affected by emissions of road transport, shipping

and industrial activity, along with residential biomass burning emissions during the winter period.

An automatic gas chromatograph equipped with a flame ionization detector (GC – FID), the “airmoVOC C6–C12” (Chromatotec, Saint Antoine, France) was used for the determination of monoterpenes and non-methane hydrocarbons from six to twelve carbon atoms (C6–C12 NMHCs). The total analysis cycle was set to 30 minutes with a sampling time of 22.5 minutes, resulting in more than 13.000 samples in total. An automatic calibration sequence using benzene as reference was applied with frequency of one injection per day.

The ambient temperature and solar radiation were monitored at the same site by means of a collocated DAVIS meteorological station. In addition, two seasonal short-term campaigns were implemented at this site on January and June 2019, providing hourly data for carbon monoxide (CO), nitrogen dioxide (NO₂) and ozone (O₃) concentrations. Details about the measurements of the latter compounds are provided in Dimitriou et al, 2020 and references therein.

3. Results

3.1. Levels and sources of BVOCs

During the period of measurements, higher mean levels of α -pinene were observed compared to limonene, equal to $0.9 \pm 3.1 \mu\text{g m}^{-3}$ and $0.4 \pm 0.6 \mu\text{g m}^{-3}$ respectively. The important variability of the time-resolved measurements was reflected on the dispersion of the observations (i.e. the standard deviation) and could be an indication of non-uniform emission processes in the area. Both α -pinene and limonene levels were comparable to those previously reported at the Thissio site in central Athens, Greece ($0.7 \pm 0.8 \mu\text{g m}^{-3}$ and $0.3 \pm 0.8 \mu\text{g m}^{-3}$ respectively) by Panopoulou et al (2020), suggesting thus limited spatial variability within the Attica basin. Regarding the Mediterranean basin, α -pinene and limonene can only be compared to the reported levels from a regional background site in Cyprus (Debevec et al. 2018) for March 2015. Our mean values were higher by a factor of 2 at least compared to those observed in the CAO station (Agia Marina Xyliatou, Cyprus) at a rural background site ($0.3 \pm 0.7 \mu\text{g m}^{-3}$ and $0.2 \pm 0.2 \mu\text{g m}^{-3}$ for α -pinene and limonene respectively), although the latter is adjacent to a forested area. Nevertheless, a published work on volatile organic compounds at industrial sites that reports α -pinene concentrations close to oil sands in Alberta, Canada (Bari & Kindzierski, 2018), presented levels of α -pinene similar to 50% higher compared to ours.

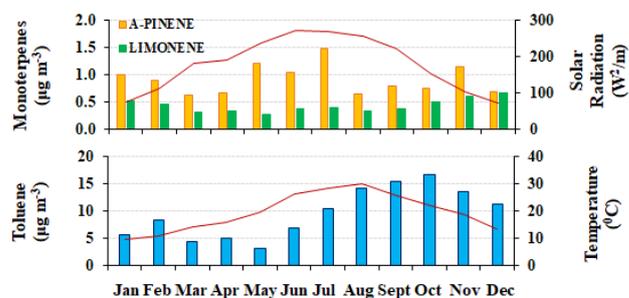


Figure 1. Mean seasonal variability of α -pinene, limonene and toluene relative to the temperature and solar radiation.

The monthly mean levels of monoterpenes are depicted in Figure 1 along with solar radiation and temperature that are the main drivers of biogenic emissions. Toluene, which is considered a tracer of anthropogenic sources, like traffic emissions and solvent usage (Baudic et al. 2016), is also included for comparison purposes. α -pinene demonstrated slightly higher levels in summer ($1.1 \pm 4.4 \mu\text{g m}^{-3}$) than in winter ($0.8 \pm 2.5 \mu\text{g m}^{-3}$), whereas limonene exhibited the opposite trend with increased mean concentration during the cold period by almost 60% ($0.3 \pm 0.2 \mu\text{g m}^{-3}$ and $0.5 \pm 0.8 \mu\text{g m}^{-3}$ respectively). In addition, toluene met its seasonal maximum in autumn ($15.1 \pm 29.1 \mu\text{g m}^{-3}$), whereas the mean annual value of $9.4 \pm 19.5 \mu\text{g m}^{-3}$ was higher to the one reported for Thissio for 2017 by almost 40% ($6.7 \pm 8.8 \mu\text{g m}^{-3}$). Under warm and high insolation conditions the biogenic emissions should be triggered. Nevertheless, only α -pinene levels respond to this expected pattern, without ignoring the significant levels also during winter that could be related to emission processes from various sources. These discrepancies indicate that both limonene and α -pinene emissions are not exclusively of natural origin in the area of interest.

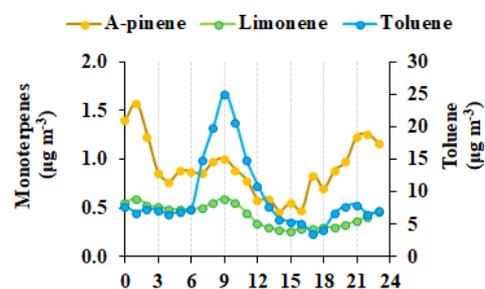


Figure 2. Mean annual diurnal variability of α -pinene, limonene and toluene.

Same conclusion was reached based on their diurnal variability. The mean annual patterns depicted in Figure 2, demonstrated a bimodal pattern for all three examined compounds. The three compounds share some common characteristics, which are probably related to their similar origin. Taking into account the typical variability of toluene as tracer of vehicular emissions, the major morning peak could be related to traffic. Despite that the early night to midnight peak of α -pinene was observed almost throughout the year, the maximum was observed mainly during winter and spring and could be related to

the combination of increased emissions (i.e. residential wood-burning; Panopoulou et al., 2020) and the lower mixing layer. The lower mean night-time levels of limonene during spring and summer relative to autumn and winter, resulted in decreased mean evening level compared to α -pinene in annual basis. This observation could indicate different emission sources relative to α -pinene or lower emission strength.

To better assess the origin of monoterpenes, the relationship of α -pinene and limonene to gaseous pollutants were examined during the short-term campaigns (January and June 2019). In January, α -pinene recorded statistically significant correlations with CO and NO₂ (R²: 0.57 and 0.74 respectively). On the contrary, limonene correlated with all pollutants apart from NO, during both periods, with R² > 0.6. Similar findings were reported also in Panopoulou et al. (2020) for the Thissio station; thus, the anthropogenic origin of monoterpenes in Attica region is further corroborated.

3.2. Contribution of BVOCs to secondary atmospheric processes

The oxidation of monoterpenes by the OH radical during day-time can result to the formation of ozone and secondary organic aerosols. For the estimation of monoterpenes' ozone formation potential (OFP), which is expressed as the amount of ozone formed (in gram) per gram of VOC added to initiate the VOC–NO_x reactions (Carter 1994, 2009), the concentration of each compound was multiplied with the maximum incremental reactivity (MIR of 4.38 and 4.4 for α -pinene and limonene respectively; Carter, 2009). The OFP of α -pinene and limonene, calculated only for summer (June, July, August), was $4.6 \pm 19.3 \mu\text{g m}^{-3}$ and $1.6 \pm 2.2 \mu\text{g m}^{-3}$ respectively, which was slightly higher than the reported ones for Thissio ($3.1 \pm 2.9 \mu\text{g m}^{-3}$ and $0.7 \pm 1.4 \mu\text{g m}^{-3}$). Given that, the O₃ mean level during June 2019 was $60.9 \pm 39.7 \mu\text{g m}^{-3}$ and the OFP of α -pinene and limonene for the same period was $6.2 \pm 14.9 \mu\text{g m}^{-3}$ and $2.0 \pm 1.5 \mu\text{g m}^{-3}$ respectively (Table 1), our results indicate that both measured monoterpenes could in total potentially contribute by ~13% to the observed O₃ in the area.

Table 1. Ozone and secondary aerosol formation potential for the BVOCs.

Compounds	OFP ($\mu\text{g m}^{-3}$)	
	January	June
α -pinene		6.2±14.9
limonene		2.0±1.5
SOAFP (SOAP ppm ⁻¹ CO)		
	January	June
α -pinene	5.7	
limonene	2.9	

Finally, the SOA formation potential (SOAFP) of monoterpenes, which reflects the simulated mass of aerosol formed per mass of reacted VOC (relative to toluene which used as anthropogenic SOA precursor). SOAFP is estimated from an adapted method of

Dominutti et al (2019) by multiplying the night-time (20:00 – 05:00 LT) enhancement ratios of VOC to CO (ppb/ppm) with a model-derived SOA-potential (SOAP). The enhancement ratios are the slope of the linear relationship of the monoterpenes to CO expressed in ppb and ppm respectively. The correlation of the terpenes to CO during summer wasn't strong, limiting thus the calculations during winter. For January 2017 total SOAFP values of 8.6 SOAP ppm⁻¹CO were calculated (Table 1, sum of the individual contributions). This value is similar to 8.8 SOAP ppm⁻¹ CO calculated for Thissio in January (3.8 ppm⁻¹ CO from α -pinene and 5.0 SOAP ppm⁻¹ CO from limonene) and indicates that during the cold period the studied monoterpenes present similar potential for both sites, probably due to the dominance of common emission sources e.g. traffic and residential heating that influence the correlation to CO.

4. Conclusions

The levels, variability and role of the monoterpenes on secondary atmospheric processes were investigated in an urban coastal site close to the Port of Piraeus during 2019 by means of high resolution measurements. Comparable mean annual levels of α -pinene and limonene were measured relative to recent observations in Attica. The seasonality of α -pinene and limonene seems to be independent of the typical biogenic emission forcers, i.e. temperature and solar radiation. Based on correlations with other combustion tracers, the role of anthropogenic sources was highlighted, especially during the cold period of the year. Furthermore, monoterpene levels were important due to their potential contribution to the local formation of ozone by up to $8 \mu\text{g m}^{-3}$ or 13% in summer and for secondary organic aerosols in winter.

Acknowledgement

EL acknowledges support by the National Observatory of Athens internal grant "VOCURBAN - Sources and Impacts of Volatile Organic Compounds (VOCs) in two Contrasted Urban Sites in the Greater Athens Area" (no 5073).

References

- Atkinson, R., (2000), Atmospheric chemistry of VOCs and NO_x, *Atmospheric Environment* **34**, 2063–2101.
- Bari, Md.A. and Kindzierski, W.B., (2018), Ambient volatile organic compounds (VOCs) in communities of the Athabasca oil sands region: Sources and screening health risk assessment, *Environmental Pollution* **235**, 602–614.
- Baudic, A., Gros, V., Sauvage, S., Locoge, N., Sanchez, O., Sarda-Estève, R., Kalogridis, C., Petit, J.-E., Bonnaire, N. and Baisnée, D., (2016), Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France), *Atmospheric Chemistry and Physics* **16**, 11961–11989.
- Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J.C. and Guillermo, R., (2001), An investigation into the traffic-related fraction of isoprene at an urban location, *Atmospheric Environment* **35**, 3749–3760.

- Camredon, M., Aumont, B., Lee-Taylor, J. and Madronich, S., (2007), The SOA/VOC/NO_x system: an explicit model of secondary organic aerosol formation, *Atmospheric Chemistry and Physics* **7**, 5599–5610.
- Carter, W.P., (1994), Calculation of reactivity scales using an updated carbon bond IV mechanism, Systems Applications International.
- Carter, W.P., (2009), Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. California Air Resources Board Contract 07–339.
- Debevec, C., Sauvage, S., Gros, V., Sellegri, K., Sciare, J., Pikridas, M., Stavroulas, I., Leonardis, T., Gaudion, V. and Depelchin, L., (2018), Driving parameters of biogenic volatile organic compounds and consequences on new particle formation observed at an eastern Mediterranean background site, *Atmospheric Chemistry and Physics* **18**, 14297–14325.
- Dimitriou, K., Liakakou, E., Lianou, M., Psiloglou, B., Kassomenos, P., Mihalopoulos, N. and Gerasopoulos, E., (2020), Implementation of an aggregate index to elucidate the influence of atmospheric synoptic conditions on air quality in Athens, Greece, *Air Quality Atmosphere & Health* **13**, 447–458.
- Dominutti, P., Keita, S., Bahino, J., Colomb, A., Liousse, C., Yoboué, V., Galy-Lacaux, C., Morris, E., Bouvier, L., Sauvage, S. and Borbon, A., (2019), Anthropogenic VOCs in Abidjan, southern West Africa: from source quantification to atmospheric impacts, *Atmospheric Chemistry and Physics* **19**, 11721–11741.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A.B., Hewitt, C.N., Lamb, B., Liu, S., Trainer, M., Westberg, H. and Zimmerman, P., (1992), Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biogeochemical Cycles* **6**, 389–430.
- Fuentes, J.D., Gu, L., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J., Ciccioli, P., Lamb, B., Geron, C. and Guenther, A., (2000), Biogenic hydrocarbons in the atmospheric boundary layer: a review, *Bulletin of the American Meteorological Society* **81**, 1537–1575.
- Geron, C., Rasmussen, R., Arnts, R. and Guenther, A., (2000), A review and synthesis of monoterpene speciation from forests in the United States, *Atmospheric Environment* **34**, 1761–1781.
- Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M. and McKay, W., (1995), A global model of natural volatile organic compound emissions, *Journal of Geophysical Research: Atmospheres* **100**, 8873–8892.
- Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K. and Wang, X., (2012), The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geoscientific Model Development* **5**, 1471–1492.
- Hellén, H., Tykkä, T. and Hakola, H., (2012), Importance of monoterpenes and isoprene in urban air in northern Europe, *Atmospheric Environment* **59**, 59–66.
- Kaltsonoudis, C., Kostenidou, E., Florou, K., Psichoudaki, M. and Pandis, S.N., (2016), Temporal variability and sources of VOCs in urban areas of the eastern Mediterranean, *Atmospheric Chemistry and Physics* **16**, 14825.
- Laothawornkitkul, J., Taylor, J.E., Paul, N.D. and Hewitt, C.N., (2009), Biogenic volatile organic compounds in the Earth system, *New Phytologist* **183**, 27–51.
- McDonald, B.C., Gouw, J.A. de, Gilman, J.B., Jathar, S.H., Akherati, A., Cappa, C.D., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.-W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B. and Trainer, M., (2018), Volatile chemical products emerging as largest petrochemical source of urban organic emissions, *Science* **359**, 760–764.
- Panopoulou, A., Liakakou, E., Sauvage, S., Gros, V., Locoge, N., Stavroulas, I., Bonsang, B., Gerasopoulos, E. and Mihalopoulos, N., (2020), Yearlong measurements of monoterpenes and isoprene in a Mediterranean city (Athens): Natural vs anthropogenic origin, *Atmospheric Environment* **243**, 117803.
- Salameh, T., Sauvage, S., Afif, C., Borbon, A., Léonardis, T., Brioude, J., Waked, A. and Locoge, N., (2015), Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: very high loadings dominated by local emissions and dynamics, *Environmental Chemistry* **12**, 316–328.
- Seco, R., Peñuelas, J., Filella, I., Llusia, J., Schallhart, S., Metzger, A., Müller, M. and Hansel, A., (2013), Volatile organic compounds in the western Mediterranean basin: urban and rural winter measurements during the DAURE campaign, *Atmospheric Chemistry and Physics* **13**, 4291–4306.
- Thera, B.T.P., Dominutti, P., Öztürk, F., Salameh, T., Sauvage, S., Afif, C., Çetin, B., Gaimoz, C., Keleş, M., Evan, S. and Borbon, A., (2019), Composition and variability of gaseous organic pollution in the port megacity of Istanbul: source attribution, emission ratios, and inventory evaluation, *Atmospheric Chemistry and Physics* **19**, 15131–15156.