Monoterpenes and Isoprene in the city of Athens: Natural vs anthropogenic origin and estimation of their contribution in secondary atmospheric pollutants' levels

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Scientific interest and Strategy

* Monoterpenes & Isoprene: Highly reactive Volatile Organic Compounds (VOC) → **Precursors of O_3 and Secondary Organic Aerosols (SOA)**
* Mediterranean basin: "Hotspot" of air pollution → Increased levels of secondary pollutants
* Monoterpenes are rarely studied in urban areas, even less in Mediterranean cities

→ **What are their levels in Athens and**

→ **Which factors determine their abundance?**

→ **Are their sources mainly biogenic?**

→ **Which is their impact on urban air quality?**

* First time **(year-basis) continuous** measurements of monoterpenes' **(α-pinene, limonene)** and **isoprene's (BVOC)** ambient **levels** in **Athens (Eastern Mediterranean basin)**
* **Examination of their temporal variability**
* Investigation of their **sources (natural vs anthropogenic)**
* Estimation of their **contribution** to **secondary atmospheric pollutants**

* **High-resolved** (1-hour) **13-month (2016 – 2017)** measurements of **monoterpenes, isoprene** and other VOC at the **Thissio urban background station in Athens**
* **Short-term near source campaigns**
* Estimation of **sources contribution (natural vs anthropogenic)** using **enhancement ratios**
* Estimation of the **contribution to oxidants** and **SOA levels (use of ASCM data)**

Methodology

* Measurements at the **urban background Thissio Air Monitoring Station** (Athens, Greece):
* Monitoring of tracers and other pollutants **(CO, BC, O3 , NOx, PM)**
* Sampling campaigns with an **ACSM** in parallel to VOC measurements
* Meteorological data

* Quasi-continuous measurements of VOC including **monoterpenes (α-pinene & limonene)** and **isoprene** using two autonomous GC-FIDs (C2 – C6 and C6-C12)
* Sampling period from **February 2016 to February 2017** → **>9000 1-hour data for each species**
* Intensive sampling campaigns in February and September 2017 with off-line sampling for intercomparison of the results.

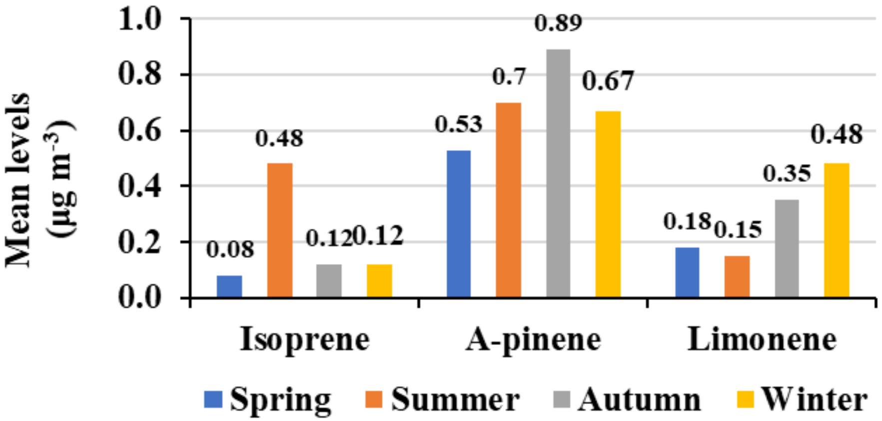
* **Calibration** with certified gas standard
* **Intercomparison** with off-line measurements

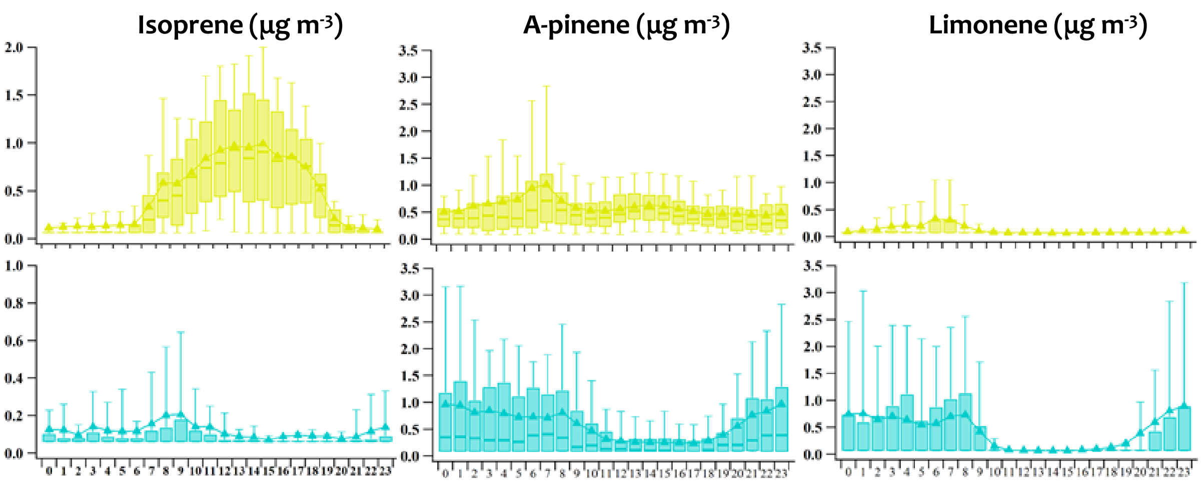
↓

Robustness of results

Variability of monoterpenes & isoprene

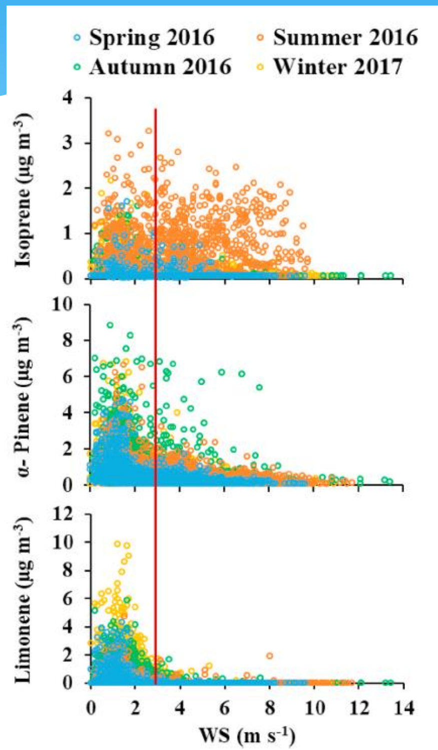
* **Annual mean levels:** 0.70 ±0.83 µg m^{-3}, 0.33 ±0.78 µg m^{-3} and 0.19 ±0.36 µg m^{-3} for α-pinene, limonene and isoprene respectively
* **Monoterpenes:** Higher mean levels in autumn and winter
* **Isoprene:** Higher mean levels in summer
* **Important day-to-day variability**





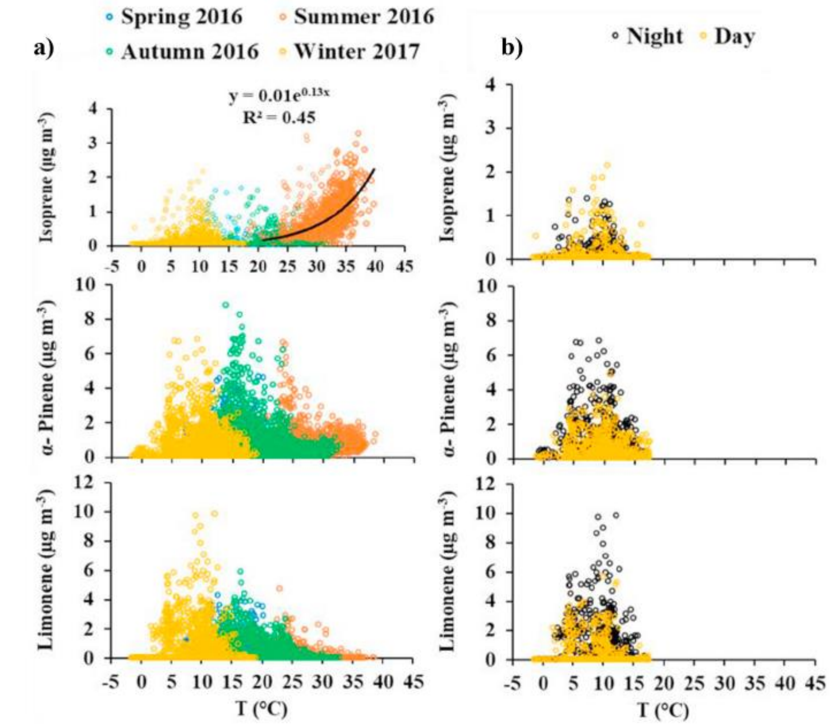
* **Monoterpenes:** Morning maximum (both summer and winter) and night-time enhancement (winter)
* **Isoprene:** day-time enhancement (summer) and morning peak in winter

Driving parameters of BVOC levels



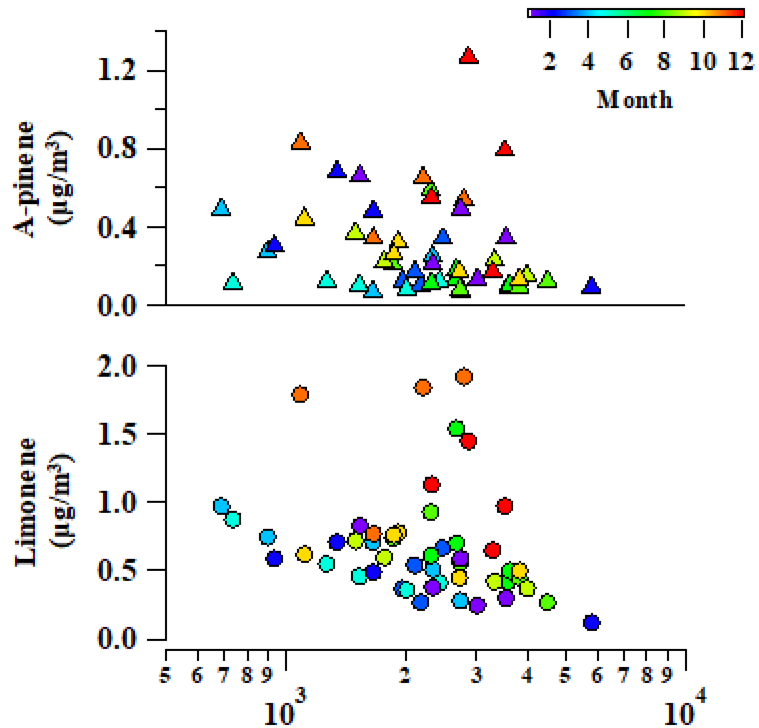
- Relationship of monoterpenes and isoprene to Wind Speed (WS): **Higher levels for low WS (< 3 m s^{-1})**
- Two exceptions: **Isoprene** in **summer (biogenic emissions)** and **α-pinene** in **autumn (possible link to rain events)**

- Relationship of monoterpenes and isoprene to ambient temperature: Only **isoprene's levels** present an **exponential increase** with increasing **temperature** in **summer**
- High levels of **monoterpenes** in **winter** during **night**



Relationship to temperature (a) on a seasonal basis and (b) during winter day (06:00–17:00 LT) and night (18:00–05:00 LT) for WS < 3 m s^{-1}.

Driving parameters of BVOC levels



Weekly variation of the Ventilation coefficient

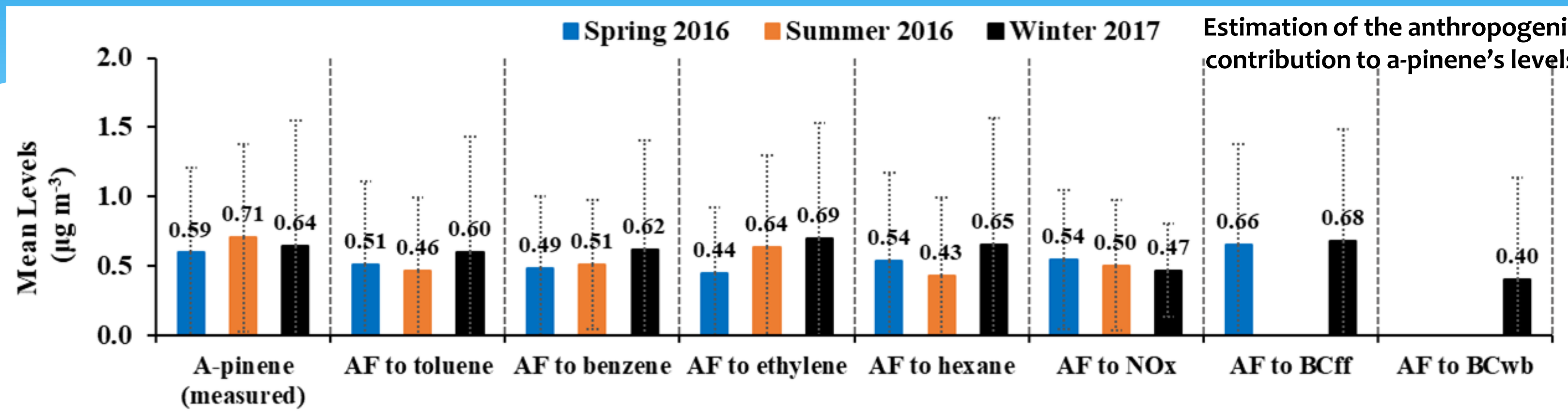
Ventilation coefficient:

VC = Mixing Layer Height x wind speed (Gani et al., 2019)

* Examination of monoterpenes' variation as a function of VC was examined on a **weekly basis → Decrease of levels with increase of VC → Higher concentrations** are associated to **low wind speed** and **low mixing layer height (MLH)**

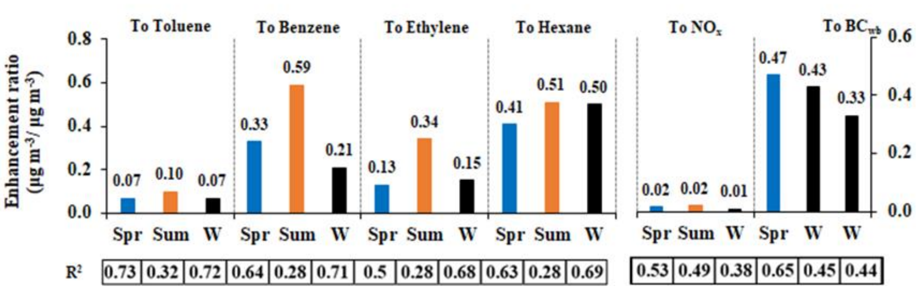
* Pearson's coefficient (**R^2**) of linear relationship **to CO** (inert gas) → Indicator of the effect of **photochemistry**
* **In summer, oxidation is responsible for the decrease of monoterpenes and isoprene in both day and night**

Enhancement ratios for the estimation of the anthropogenic and biogenic fractions: **A-pinene's case**



Anthropogenic fraction of α-pinene: estimated from the **night-time enhancement ratios** to other compounds (tracers of sources) **: AF = Enhanement ratio x [Tracer]**

Biogenic fraction of α-pinene**: BF=A-pinene measured - AF**



Night-time enhancement ratios

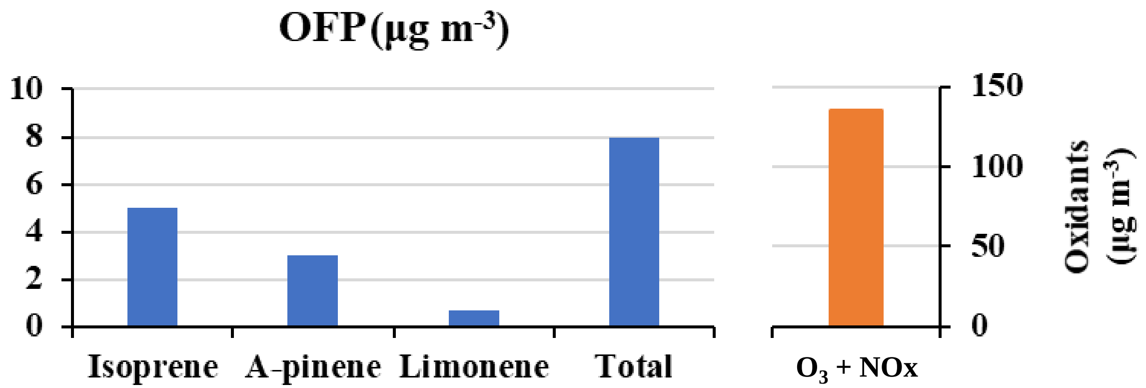
- Important **anthropogenic contribution (AF)** in **all seasons (70 to 97%)**
- **AF:** Higher in winter **(0.62 μg m^{-3})**, lower in summer **(0.50 μg m^{-3})**
- **BF:** Highest in summer **(0.26 μg m^{-3})**

The observations highlight the anthropogenic sources of α-pinene

Estimation of the contribution to secondary pollutants: Ozone Formation Potential (OFP)

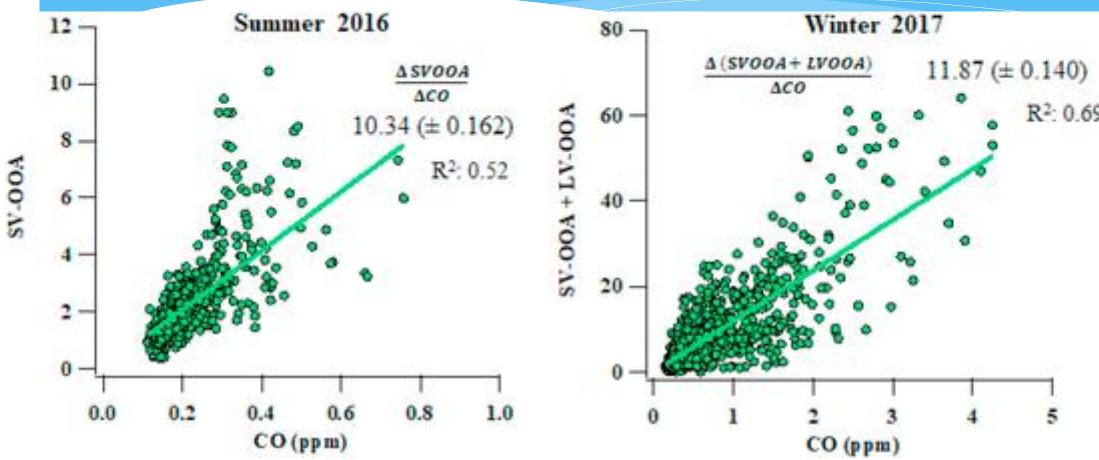
$$OFP_i = \sum_{i=1}^{n} C_i \, x \, MIR_i$$

- **OFP** is estimated **for each sample** from the **concentration** in µg m^{-3} and the maximum incremental reactivity **(MIR)** of the compound
- OFP in **summer** was **5 µg m^{-3}, 3 µg m^{-3} and 0.7 µg m^{-3}** for isoprene, α-pinene and limonene respectively
- Considering the **sum** of **O3** and **NOx (oxidants) of ~ 135 µg m^{-3}** →Monoterpenes and isoprene yielded **~8µg m^{-3} or 6%**



Estimation of the contribution to secondary pollutants: SOA Formation Potential

Δ(SOA/CO) experimental for summer and winter



SOAFP is estimated from the comparison of **Δ(SOA/CO) experimental** and **Δ(SOA/CO) theoretical**

- **Δ(SOA/CO) experimental:** Calculated from **real data (concurrent ASCM measurements).** Different approaches for **summer** and **winter** (left figure)
- **Δ(SOA/CO) theoretical:** Estimated from **night-time enhancement ratios** to **CO** and **experimentally** calculated **SOA yields**

$$\frac{\Delta SOA}{\Delta CO} = ER_i * SOAyield_i$$

Theoretical Δ(SOA/CO) ratios

A-pinene: 1.24 μg m^{-3} ppm^{-1}CO and 0.56 μg m^{-3} ppm^{-1}CO for summer and winter respectively.

Limonene: 1.08 μg m^{-3} ppm^{-1}CO and 1.02 μg m^{-3} ppm^{-1}CO for summer and winter respectively.

By the ratio Theoretical $\frac{\Delta SOA}{\Delta CO}$ $/Experimental$ $\frac{\Delta SOA}{\Delta CO}$ → **22% and 13% of measured SOA could originate from monoterpene**s!

Reported SOAFP is a lower estimate! The equation doesn't consider the monoterpenes that have already reacted to form SOA!

Conclusions

* **A-pinene** and **limonene** demonstrate **significant** levels in **winter opposite** to their **expected behavior.**
* **Isoprene's** seasonal variability **follows the biogenic activity** (**highest** values in **summer**).
* **Higher levels** of monoterpenes and isoprene for **low wind speed** + **low mixing layer height** (except of isoprene in summer). No relationship to temperature is observed for monoterpenes; only **isoprene's levels** in **summer** exhibit an **exponential increase** with increased **temperature.**
* The **anthropogenic contribution (AF)** to α-pinene's levels is **higher** than **biogenic** in **all seasons,** indicating **important anthropogenic sources** of **monoterpenes** in the **urban areas.**
* **6%** contribution to **O3+NOx** and **13%-22%** contribution to **SOA formation.**

Perspectives

* Investigation of **spatial distribution** of **VOCs** and **BVOCs.**
* Investigation of **near-source emission ratios** for detailed **characterization** of the biogenic vs anthropogenic sources.
* Consideration of $\mathbf{AF_{BVOCs}}$ **contribution** to improve emission inventories.

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A. Panopoulou et al., 2018: Non Methane Hydrocarbons variability in Athens during winter-time: The role of traffic and heating", Atmos. Chem. Phys., 18, 16139-16154, 2018 DOI: https://doi.org/10.5194/acp-18-16139-2018

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