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Spatial variability of VOCs, ozone, and carbonaceous aerosols during the 2022 European summer heatwave

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Abstract This study presents results from an Intensive Measurement Period conducted during the European heatwave of July 2022, focusing on ozone, volatile organic compounds (VOCs), and carbonaceous aerosols at 31 sites across Europe. The episode featured persistent high-pressure systems, record-breaking temperatures, widespread ozone exceedances and concurrent atmospheric new particle formation and growth events. Although the roles of biogenic and anthropogenic precursors in ozone, secondary organic aerosol (SOA) formation and nanoparticle growth are recognized, their relative importance during extreme events remains poorly constrained. This work therefore aimed to quantify these interactions using coordinated measurements and model simulations. Measurements showed that oxygenated VOCs formed the largest fraction of total VOCs, followed by non-methane hydrocarbons (NMHCs) and aromatics, with substantial contributions from both anthropogenic and biogenic sources. Elevated ozone and SOA levels were driven by the combined influence of biogenic VOCs and NO_x emissions under predominantly NO_x-limited conditions. Isoprene, NMHCs, and O-VOCs dominated the ozone formation potential, while aromatics and monoterpenes were the most important SOA precursors. Model simulations indicated that higher NO_x concentrations can reduce SOA formation by about 10 %. The campaign also highlighted observational gaps underscoring the need for broader and higher-resolution VOC monitoring across Europe. Overall, further reductions in NO_x emissions, alongside targeted control of key anthropogenic VOCs, would benefit air quality, during extreme pollution episodes. These findings illustrate the complex interplay between meteorology, emissions, and atmospheric chemistry during heatwaves and emphasize the need for comprehensive precursor monitoring and improved modelling for effective air-quality management under future climate conditions.

1 Introduction

Air pollution continues to pose major risks to human health and ecosystems despite decades of emission reductions. A significant proportion of the European population is still exposed to harmful levels of air pollutants (EEA, 2024). This problem becomes particularly critical during extreme heat events, when pollution levels often escalate. Elevated concentrations of ozone and particulate matter (PM) intensify stress on human health, and when combined with the direct harmful effects of high temperatures, contributes significantly to increased mortality rates (Anenberg et al., 2020).

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry, serving as key precursors for the formation of both tropospheric ozone and secondary organic aerosol (SOA). In the presence of sunlight and nitrogen oxides (NO_x), VOCs undergo photochemical reactions that produce ozone. Simultaneously, VOC oxidation can form SOA, a major component of fine particulate matter ($PM_{2.5}$) (Monks et al., 2009; Seinfeld and Pandis, 1998). The atmosphere contains a diverse variety of VOC species from both anthropogenic and biogenic sources. In Europe, biogenic VOC (BVOC) emissions are dominated by oxygenated VOCs (O-VOCs), monoterpenes, and isoprene, with O-VOCs constituting the largest share (Oderbolz et al., 2013). The relative contributions vary regionally, reflecting differences in vegetation composition. Furthermore, large uncertainties remain regarding the factors controlling emissions from different vegetation types (Bourtsoukidis et al., 2024, 2025; Guion et al., 2023; Seco et al., 2007). High temperatures increase the BVOC emissions from vegetation and can significantly increase the production of biogenic SOA (BSOA) and ozone (Guion et al., 2023; Hallquist et al., 2009; Hamer et al., 2025; Li et al., 2025; Vazquez Santiago et al., 2024). The hot and stagnant atmospheric conditions during heatwaves promote the formation and accumulation of reactive chemical species such as ozone. In addition, lower stomatal uptake under heat and drought stress decreases dry deposition and thus limits ozone removal (Emberson et al., 2001; Lin et al., 2020). Additionally, the lack of precipitation reduces the wet deposition of precursors, thus enhancing concentrations even further.

The reactivity of VOCs in the atmosphere varies widely, influencing their potential to contribute to ozone and SOA formation (Seinfeld and Pandis, 1998), and their impact on the hydroxyl radical (OH) concentrations and methane lifetime (Boy et al., 2022). This variability stems from differences in their molecular structure and the environmental conditions. The capacity of a VOC species to form ozone depends largely on the OH concentration and reaction rate, and the availability of NO_x. Under high-NO_x conditions, unsaturated hydrocarbons such as isoprene and aromatics like trimethylbenzenes are significant contributors to ozone production as they undergo rapid photochemical reactions (Derwent et al., 1998; Holland et al., 2023; Jenkin et al., 2017). The ability of a VOC specie to contribute to SOA formation is influenced by the volatility of its oxidation products. Extremely low and low-volatility organic compounds (ELVOC and LVOC, respectively) are more efficient in growing ultrafine particles, especially newly formed sub-10 nm particles, compared to semi-volatile organic compounds (SVOC) (Tröstl et al., 2016; Yan et al., 2020).

BVOCs, including isoprene, monoterpenes, and sesquiterpenes emitted primarily by vegetation, are major precursors to BSOA (Gu et al., 2021; Hallquist et al., 2009). More recently also diterpenes have received attention as an important BVOC (Yáñez-Serrano et al., 2025). BVOCs have been shown to play a key role in the early growth of newly formed nanoparticles (Mohr et al., 2019; Tröstl et al., 2016). Among anthropogenic VOCs, aromatics like toluene and xylenes are particularly important SOA precursors (Hallquist et al., 2009; Henze et al., 2008). Environmental factors, such as temperature and the presence of other pollutants, influence VOC reactivity. For example, NO_x concentration strongly affects the pathways and efficiency of ozone and SOA formation. The influence of NO_x on the VOC pathways is not straightforward, as it depends on VOC structure and environmental conditions such as temperature, humidity and solar radiation. If the VOC concentration is sufficient, high NO_x levels favor ozone production, while low NO_x conditions favor SOA formation (Seinfeld and Pandis, 1998; Wang et al., 2024). However, NO_x-dependent SOA formation can be highly non-linear. At low-NO_x conditions, increasing the NO_x concentration can increase SOA formation. The opposite occurs at high-NO_x conditions, where increased NO_x suppresses SOA yield (Nie et al., 2023; Sarrafzadeh et al., 2016; Yan et al., 2020).

Efforts to improve air quality in Europe have been guided by legally-binding emission reduction commitments under the Gothenburg Protocol of the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) and the EU National Emission reduction Commitments (NEC) Directive (EU, 2016; UNECE, 2012). These measures have resulted in substantial declines in the emissions of ozone and SOA precursors. From 2000 to 2022, anthropogenic emissions of NO_x and non-methane volatile organic compounds (NMVOC) decreased by 24 and 16 %, respectively, across the European Monitoring and Evaluation Programme (EMEP) area (EMEP, 2023). Within the EU27+UK+EFTA (European Free Trade Association regrouping Iceland, Liechtenstein, Norway, and Switzerland) region, reductions were even more pronounced, with 45 % for NO_x and 55 % for NMVOC (EMEP, 2023). Observations of ambient NO_2 concentrations reduced by 32 ± 7 % from 2000 to 2019, suggesting a smaller decline compared to the reported emissions (Aas et al., 2024). Although there are few consistent long-term VOC measurements, observations at Hohenpeissenberg (DE0043G) in southern Germany showed a 10-30 % decline in the least reactive species and 45-55 % in the most reactive ones from 2003 to 2022 (Solberg et al., 2024). The reductions in NO_x have contributed to decreased summer peak ozone concentrations (Aas et al., 2024), yet exceedances of limit values are still commonly observed in Europe. Despite the reduction in peak levels of European background ozone concentrations, some urban areas experience increased ozone concentrations, due to climate-warming-driven BVOC emissions or the weakening of the NO titration effect (Querol et al., 2016; Vazquez Santiago et al., 2024; Wang et al., 2024). Further temperature increases may also enhance the temperature-dependent emissions of anthropogenic non-combustion VOCs, such as from volatile chemical products (VCP), as well as increase the reaction rates towards OH radical (Cao et al., 2023; Qin et al., 2025). The heatwave in Europe in summer 2003 showed that various factors such as increased biogenic emissions, reduced dry deposition, and increased residence time in the boundary layer as well as the occurrence of wildfires contributed to elevated surface ozone concentrations (Solberg et al., 2008). With climate change expected to increase the frequency and severity of extreme weather events, including heatwaves(Ban et al., 2022; IPCC, 2023), the risk of exceeding health limits for ozone and PM may rise. This will necessitate more stringent pollution control strategies (Sadiq, 2020; Sokhi et al., 2021). In 2024, the EU revised its Ambient Air Quality Directive (EU, 2024) with stricter pollution limits, aligning more closely with the air quality guidelines of the World Health Organization (WHO, 2021).

To assess the relative importance of the different precursors when setting emission targets and forecasting episodes, it is crucial to accurately measure their concentrations. The EMEP monitoring programme includes a range of VOCs to assess levels and trends in ozone and SOA precursors (UNECE, 2019), however, the programme does not specifically target ozone episodes, which poses challenges in assessing these events. VOC measurements are also part of the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) (Laj et al., 2024) and the World Meteorological Organisation's (WMO) Global Atmosphere Watch (GAW) programmes. Most EMEP, ACTRIS and European GAW VOC sites are collocated and follow harmonised measurement and reporting guidelines.

There are two primary limitations in the current monitoring of VOCs: (1) Only a few sites measure a comprehensive suite of VOCs, with especially sparse spatial coverage for O-VOCs and terpenes, and there is a lack of NMHC measurement sites in the Mediterranean and Eastern Europe (Solberg et al., 2024); (2) the conventional manual sampling approach for O-VOCs collects only one or two samples per week (EMEP, 2014), offering insufficient temporal resolution for the study of ozone episodes. Finally, SOA tracers are not part of the regular EMEP monitoring programme, although they provide valuable insights into SOA sources by identifying compounds linked to biogenic or anthropogenic origins.

To address these gaps, the EMEP Task Force on Measurement and Modelling (TFMM) conducted an Intensive Measurement Period (IMP) in the summer of 2022. The goal was to improve understanding of ozone and SOA formation under heatwave conditions. The IMP focused on intensified VOC measurements at selected sites, supported by analyses of carbonaceous aerosol and organic tracers in PM. Particle number size distribution (PNSD) measurements were included to investigate atmospheric new particle formation (NPF) and growth during the measurement period. The IMP was timed (12–19 July 2022) to coincide with a forecasted heatwave, which subsequently developed into a severe European event with record-breaking temperatures and widespread wildfires that contributed to the observed air pollution episode.

2 Materials and methods

2.1 Setup of the campaign and methods used

The IMP 2022 summer campaign focused on one week of intensive VOC observations at selected sites from July 12 to 19, 2022. The campaign began when forecasts indicated the onset of a heatwave over Central Europe. Participating sites

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supplemented their regular EMEP/ACTRIS observations (if applicable) by expanding the range of measured VOCs and/or increasing their sampling frequency to daily or hourly intervals.

Manual devices for VOC sampling were distributed at sites lacking regular monitoring or certain component groups, and subsequent analyses were conducted at centralized laboratories. Additionally, aliquots of filters for regular elemental- and organic carbon (EC-OC) measurement were collected to analyse specific BSOA tracers. The various devices and centralized analyses are summarized below:

- NMHCs were sampled with Silcosteel canisters (SilcoCan). The canisters were equipped with a suitable flow reducer and an ozone scrubber ($Na_2S_2O_3$). Each sample collected air for one hour between 12:00 and 16:00 UTC. Analysis was performed at Forschungszentrum Jülich (FZJV) GmbH using gas chromatography coupled to a mass spectrometer and flame ionization detector (GC-MS/FID, Agilent 6890N) (Hoerger et al., 2015; Klemp, 2021).
- O-VOCs were collected using solid adsorbent cartridges (Waters Sep-Pak XPOsure Plus Short Cartridge) coated with 2,4-dinitrophenylhydrazine (DNPH) (EMEP, 2014). Two DNPH cartridges, connected back-to-back behind a KI/Cu ozone scrubber, were used for each sample. Sampling occurred at a flow rate of ~1.5 L min^{-1} between 12:00 and 16:00 UTC. The DNPH cartridges were eluted with 3 mL of acetonitrile to extract hydrazones. The derivatives were analyzed by high-performance liquid chromatography (HPLC, Thermo Fisher Ultimate 3000) with UV detection at 360 nm at the ACTRIS Centre of Reactive Trace Gases in-situ measurements (CiGas) at Institut Mines Télécom (IMT) Nord Europe, France.
- Monoterpenes, sesquiterpenes, and larger hydrocarbons were collected using Tenax TA – Carbopack B tubes and analyzed by thermal desorption–gas chromatography–mass spectrometers (TD-GC-MS) at the Finnish Meteorological Institute (FMI), Finland (Hellén et al., 2024). An ozone trap ($Na_2S_2O_3$ impregnated filter) was connected in front of the sampling tube. Samples were collected at a flow rate of ~80 mL min^{-1} over a two-hour sampling period between 12:00 and 16:00 UTC.
- SOA tracer analysis from quartz fibre filters was carried out for sites with regular EC-OC measurements from either PM_{10} or $PM_{2.5}$ samplers. Most of the EC-OC analyses were performed by operators using the EUSAAR-2 protocol (Cavalli et al., 2016), while filter aliquots were cut from the filters and analysed for selected tracers at the Institut des Géosciences de l'Environnement (IGE), France. Filters were exposed for 24 hours, except at Birkenes (one week). Sampling typically occurred from midnight to midnight, though some samples were collected from 09:00 UTC. Pure water extracts were analysed for light organic acids using ion chromatography - mass spectrometry (IC-MS, Thermo-Fisher Integrion + ISQ EC MS) with separation on an AS11HC column. Sugars, polyols, and monosaccharide anhydrides were quantified high-performance liquid chromatographic (HPLC) with hydrophilic interaction (HILIC) columns and tandem mass spectrometry detection (Exion LC30 AD +AB Sciex 5500 QTRAP) (Bros et al., 2025).

Three sites (CZ0003R, DE0008R, DE0007R) used manual sampling of NMHCs with stainless steel canisters. However, their setup differed from the centralized analysis and fewer compounds were detected. In addition to manual sampling, several sites were equipped with automated monitors. Various GC-FID/MS instruments, commonly used for regular NMHC monitoring, were incorporated into the campaign. O-VOCs were measured using two GC–GC/FID systems in Switzerland, and some O-VOC compounds were detected using Proton Transfer Reaction–Mass Spectrometry (PTR-MS) instruments. PTR-MS was also used to measure the sum of monoterpenes.

VOC identification by PTR-MS relies on the molecular mass of the compounds, making this technique unable to distinguish between species with the same nominal mass when operated in the H_3O^+ mode (Dusanter et al., 2025; Yuan et al., 2017). This limitation is particularly relevant for PTR-Quadrupole-Mass Spectrometry (PTR-QMS) instruments, which have unit mass resolution. The more recent PTR-Time-of-Flight-Mass Spectrometry (PTR-ToF-MS) instruments offer higher mass resolution and allow separation of isobaric compounds. For instance, isoprene and furan are both detected at integer m/z 69 in PTR-QMS, but can be separated by PTR-ToF-MS. VOC quantification by PTR-MS can also be complicated by interferences from fragments of protonated VOCs at higher masses. For example, fragments of protonated nonanal and 2-methyl-3-buten-2-ol can appear at the same m/z as protonated isoprene. The contribution from such interferences depends on the measurement environment and the energetic conditions in the drift tube reactor of the PTR-MS instrument. Moreover, isomeric compounds cannot be separated by PTR-MS using H_3O^+ reactant ions; therefore, the sum of isomers is often quantified, as is the case for monoterpenes. Assignment of compounds to m/z values in the PTR-MS instruments followed the GLOVOCs database (Yáñez-Serrano et al., 2021). Several of these VOC measurements are part of the EMEP monitoring programme described in the annual data report (Solberg et al., 2024).

All sites that measured VOCs also monitored ozone using standard UV instruments. Most sites were also equipped with a NO_x chemiluminescence instrument, though different converters were used (Table 1). A molybdenum converter is biased compared to a photolytic converter due to interference from other nitrogen oxides (e.g. peroxyacetyl nitrate, HNO_3). Most ozone and NO_2 measurements at regional sites are reported to EMEP (Hjellbrekke, 2024; Hjellbrekke and Solberg, 2024). The PNSD measurements follow the ACTRIS guidelines as outlined by Wiedensohler et al. (2012)

A total of 31 sites participated in the campaign. Of these, 14 sites measured the main VOC species across all compound classes (NMHCs including isoprene, O-VOCs, aromatics, and monoterpenes), and 23 analysed organic tracers. Table 1 provides an overview of the participating sites and the analyses performed, while Table S1 lists site coordinates and land-use characteristics. In total, more than 120 VOC species, as well as 47 tracers and other compounds in PM, were measured during the campaign. Some sites that did not include organic tracer analyses still performed EC/OC and PM measurements, although these were not included in the present analysis.

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Table 1. Overview of the sites participating in the measurement campaign, variables measured, and methods used.

Code 1)	Name	O_3	NO_2 2)	O-VOCs	NMHCs	Terpenes	Tracer	EC/ OC	PM	PNSD3)
AT0002R	Illmitz	x	Mo.	DNPH	Canister (Jülich)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
BE0007R	TMNT09 Vielsalm	x	Mo.	DNPH PTR-ToF-MS	Canister (Jülich) PTR-ToF-MS	Tenax PTR-ToF-MS	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	SMPS
CH0010U	Zürich-Kaserne	x	Mo.	GC-GC/FID	GC-GC/FID					
CH0053R	Beromünster	x	CAPS	GC-GC/FID	GC-GC/FID					
CY0002R	Agia Marina, CAO	x	Photo.	PTR-ToF-MS	PTR-ToF-MS	PTR-ToF-MS				
CZ0003R	Kosetice, NAOK	x	Photo.	DNPH	Canister (CHMI)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	SMPS
DE0007R	Neuglobsow	x	Photo.	DNPH	Canister (UBA)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	SMPS
DE0008R	Schmücke	x	Photo.	DNPH	Canister (UBA)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
DE0043G	Hohenpeißenberg	x	Photo.		GC/FID					V-SMPS
DE0044R	Melpitz				Canister (Jülich)	Tenax	PM_{10}	PM_{10},	PM_{10}	V-SMPS
ES0019U	Barcelona	x	Mo.	PTR-ToF-MS	PTR-ToF-MS	PTR-ToF-MS	PM_{10}	PM_{10}	PM_{10}	
ES0021U	Madrid (CIEMAT)		Mo.	DNPH	Canister (Jülich)	Tenax	PM_{10}	PM_{10}		SMPS
ES0025U	Bilbao	x	Mo.		GC/FID					
ES1778R	Montseny	x	Mo.	PTR-QMS	PTR-QMS	PTR-QMS	PM_{10}	PM_{10}	PM_{10}	SMPS
FI0050R	Hyytiälä	x	Photo.	PTR-QMS	PTR-QMS	PTR-QMS				DMPS
FR0008R	Donon	x	Photo.	DNPH	Canister (Jülich)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
FR0013R	Peyrusse Vieille	x	Photo.	GC/FID	GC/FID	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
FR0018R	La Coulonche	x	Mo.	DNPH	Canister (Jülich)	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
FR0020R	SIRTA	x	Photo.	PTR-QMS	GC/FID	PTR-QMS	PM_{10}	PM_{10}		
FR0022R	Obs. Perenne Env.						PM_{10}	PM_{10}		
FR0027U	ATOLL (Villeneuve d'Ascq)	x	Photo.	DNPH	Canister (Jülich)	Tenax				SMPS
FR0030R	Puy de Dôme	x		DNPH			$PM_{2.5}$	$PM_{2.5}$		
FR0035U	Marseille						PM_{10}	PM_{10}	PM_{10}	
FR0038U	Grenoble Frenes						PM_{10}	PM_{10}	PM_{10}	
FR0041U	Paris Chatelet						$PM_{2.5}$	$PM_{2.5}$		
GB0048R	Auchencorth Moss	x		DNPH	GC/FID	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
GB1055R	Chilbolton	x	Mo.	DNPH	GC/FID	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	
IE0031R	Mace Head	x		DNPH	Canister (Jülich)	Tenax				
IT0004R	Ispra	x	Mo.	DNPH	GC/FID	Tenax	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$	SMPS
IT0009R	Monte Cimone	x	Photo.	DNPH	GC/MS	Tenax	PM_1			
NO0002R	Birkenes	x	abs.	DNPH	Canister (Jülich)	Tenax	PM_{10}	PM_{10}	PM_{10}	DMPS

1)Sites marked in bold are compared to ADCHEM model calculations.
2) "Mo." indicates a molybdenum converter while "Photo." means photolytic and "abs." corresponds to a manual method with NO_2 absorbed on KI-impregnated glass sinters. CAPS is a Cavity Attenuated Phase Shift Spectroscopy instrument
3) DMPS: Differential Mobility Particle Sizer; SMPS: Scanning Mobility Particle Sizer; V-SMPS: Volatility-SMPS

2.2 Screening and preparation of measurement data

To ensure comparability with manual measurements, all data were averaged to daytime means, between 12:00 and 16:00 UTC, during which manual samples were collected over varying durations (1 - 4 hours) within this timeframe, except for ozone, where the 1-hour daily maximum concentration was used. Manual measurements, originally recorded in mass units, were converted to mixing ratios (pptv), using standard temperature (273.15 K) and pressure (1013.25 hPa) to ensure consistency across all VOC data. VOCs are thus reported as mixing ratios; for simplicity, these are hereafter referred to as concentrations.

The total dataset was screened and a prioritization of methods for different VOC component groups was done.

- NMHCs: (1) C_2–C_6 data from canisters and GC/FID monitors were used, and monitor data were prioritized when both sources were available; (2) for C_7–C_{12} compounds, data from Tenax tubes and GC/FID monitors were used, and monitor data were prioritized when both sources were available; (3) Isoprene data (similar to C_2–C_6 range above) were selected, with the addition of PTR-MS data (m/z 69 for PTR-QMS and 69.070 for PTR-ToF-MS). FR0020R has both a PTR-QMS and GC/FID. Data from the GC/FID was used.

- Aromatic hydrocarbon data were collected from canisters, Tenax tubes and monitors. Prioritization was as follows: (1) Monitor data were prioritized over manual measurements when available; (2) Benzene and toluene data from canisters were prioritized before data from Tenax tubes, while data from Tenax tubes were prioritized for the other aromatic compounds; (3) for PTR-MS, xylenes+ethylbenzene were assigned to m/z 107 for PTR-QMS and 107.086 for PTR-ToF-MS, while trimethylbenzenes were assigned to m/z 121.101 and 121 respectively for the PTR-ToF-MS and PTR-MS instruments.

- Terpenes: Monoterpenes were collected from Tenax tubes and measured online by PTR-MS (at m/z 137 for PTR-QMS and 137.132 for PTR-ToF-MS). Tenax tube data were prioritized when both measurements were available. Sesquiterpene data were exclusively taken from Tenax tubes.

- Oxygenated VOC data were collected from DNPH cartridges, GC/FID and PTR-MS. DNPH data were prioritized. For PTR-MS, acetone was assigned to m/z 59 and 59.049 for PTR-QMS and PTR-ToF-MS, respectively. Propanal was also assigned to this mass, but not considered since acetone is the dominant component. 3-buten-2-one (MVK) + 2-methylpropenal (MACR) were assigned to m/z 71 and m/z 71.049 while butanal + 2-methylpropanal + butanone were assigned to m/z 73 and m/z 73.065, referred to as butanals + butanone. Methanol was collected with the canister sampler and PTR-MS, and PTR-MS data were prioritized.

- Chemical speciation of aerosols and tracer analysis. Chemical analyses were performed by a single laboratory per compound family across all sampling sites. The PM mass and EC-OC were measured at several sites as part of the regular EMEP monitoring. These data were prioritized when both were available.

2.3 Setup for the EMEP and ADCHEM models

To map the ozone concentration field during this summertime campaign, we used the EMEP Meteorological Synthesizing Centre-West (MSC-W) chemical transport model (Simpson et al., 2012, 2025 and references therein).

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We used the 1D-vertical column Lagrangian chemistry transport model ADCHEM (Roldin et al., 2011, 2019) to investigate the sources and sinks of tropospheric ozone, OA particles, and atmospheric NPF in air masses transported to 15 of the 31 sites listed in bold in Table 1. ADCHEM was run along air mass trajectories generated using the Lagrangian particle dispersion model FLEXPART v10.4 (Pisso et al., 2019). Air mass trajectories were computed 10 days back in time, with arrival at each modelled site every third hour. FLEXPART is driven by meteorology from the ERA5 reanalysis product (Hersbach et al., 2023). The meteorology relevant for the ADCHEM simulations was also stored alongside the air mass trajectories. ADCHEM's vertical domain, 0 to 2100 m, was divided into 20 logarithmically spaced layers, ranging from 10 m at the surface to 200 m aloft. Emissions of trace gases and primary aerosol particles were taken from the CAMS (Copernicus Atmosphere Monitoring Service) global ocean, biogenic and anthropogenic emission inventories (Granier et al., 2019; Lana et al., 2011; Simpson et al., 2023; Sindelarova et al., 2014; Ziska et al., 2013) while ocean surface parameters such as ammonium, salinity, and pH from Copernicus Marine Service products were used to calculate the ocean-atmosphere ammonia exchange (Wollesen De Jonge et al., 2024; Xavier et al., 2024).

NPF was modelled using the ClusterIn module (Olenius and Roldin, 2022), which simulates molecular cluster formation, coagulation, and evaporation that can grow into aerosol particles with an initial diameter of ~1 nm. In the present work, we employed ion-mediated NPF involving ammonia and sulfuric acid, sulfuric acid and dimethylamine (DMA), and iodic acid (HIO_3) and iodous acid (HIO_2), as described by Xavier et al., (2024). Particle growth occurred via condensation of a suite of semi- and low-volatility organic compounds, inorganic and organic acids (H_2SO_4, HNO_3, HIO_3, MSA, MSIA), and bases (NH_3, DMA). Production and chemical degradation of ozone and condensable organic and inorganic vapours are represented by detailed multiphase chemical mechanisms (6,425 species and 17,970 reactions) which combine the Master Chemical Mechanism (MCM) v3.3.1 (Bloss et al., 2005; Jenkin et al., 1997, 2003, 2012, 2015; Saunders et al., 2003), the Peroxy Radical Autoxidation Mechanism (PRAM, (Roldin et al., 2019), the CAPRAM halogen module v3 (Hoffmann et al., 2019), an updated dimethylsulfide (DMS) oxidation chemistry scheme (Wollesen De Jonge et al., 2021), and a 3-carene mechanism (Luo et al., 2024). SOA formation was represented by the gas-particle partitioning of 1,223 semi- and low-volatility oxidized organic compounds, including highly oxygenated organic compounds (HOM) formed from monoterpenes, *α*-pinene, *β*-pinene, limonene, and 3-carene (Luo et al., 2024; Nie et al., 2023; Roldin et al., 2019), and aromatic compounds, benzene, toluene, *p*-xylene, *o*-xylene, and *m*-xylene (Iyer et al., 2023; Pichelstorfer et al., 2024). To explore the influence of terrestrial BVOC and anthropogenic NOx emissions on ozone, OH, SOA, and particle number levels during the campaign, and to assess whether ozone formation was VOC- or NOx-limited, we performed simulations using five model setups:

1. **Base case**: Includes all known anthropogenic and biogenic emissions of trace gases and aerosol particles.
2. **Without isoprene**: Terrestrial biogenic isoprene emissions were removed.
3. **Without BVOC**: All terrestrial BVOC emissions were removed.
4. **2 × NO_x**: Anthropogenic NO_x emissions were doubled.

5. **0.5 × NO_x**: Anthropogenic NO_x emissions were halved.

3 Results and discussions

3.1 Characterizing the heatwave and ozone episode

The summer of 2022 was the warmest on record in Europe at the time. Combined with a lack of rain, this led to severe drought conditions, particularly in southern and central Europe (Copernicus, 2023; Martins et al., 2024). At the beginning of the measurement period (July 12-13), some parts of southwestern Europe were under the influence of a persistent high-pressure system, with daily 1-hour maximum ozone concentrations exceeding 100 ppb in Spain. In the following days, several sites in Italy also recorded high ozone levels, while the BeNeLux region, the UK, and Scandinavia benefited from clean marine air masses. The Mediterranean was affected by a high-pressure system the whole week, while another high-pressure system was initially located west of Ireland and moved slowly eastward. At the start of the period, the central and northern parts of Europe experienced westerly winds on the northern side of the approaching high, bringing marine air masses to the region. From July 14 to 16, the high pressures gradually entered northwestern parts of the continent, dominating the weather situation over large parts of central Europe by July 17, with its center over Germany. The high-pressure system continued to move slowly eastward over the following days, and then gradually broke up. On July 18-19, the high set up southerly winds over central Europe and the UK, bringing continental air masses to the region (Tsyro et al., 2022).

On July 19, monitoring sites in France, the UK, the Netherlands, Switzerland, and Germany observed hourly mean ozone concentrations exceeding 100 ppb (Fig. 1). The highest value (116 ppb) was observed at the Sibton regional background site in East England. This coincided with record-breaking temperatures in the UK, which exceeded 40 °C for the first time (MET Office, 2022). Norway was also affected by the heatwave, particularly in the south, where an ozone peak of 89 ppb was measured, the highest annual maximum since 2006. Fig. S1 shows the temperature changes during the study period, and the observed peak ozone concentrations clearly correlated with the site temperatures.

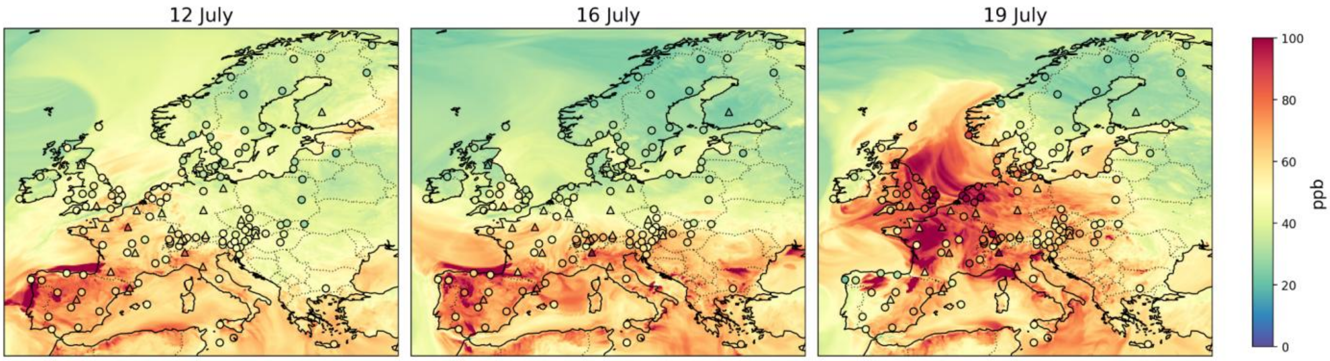

Fig. 1. 1-hour maximum ozone concentrations (ppb) based on the EMEP model and observations superimposed for the 12, 16 and 19 July 2022. The sites participating in the campaign are marked as triangles and regular EMEP sites as circles.

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The modelled ozone concentrations were comparable to observations, with an average positive bias of 8 % for ozone daily maxima during the IMP week. The model slightly overestimated (by 11 %) at sites with low concentrations (below 50 ppb) and slightly underestimated (-3 %) at high-concentration sites (above 80 ppb).

Fig. S2 provides an overview of the development of ozone concentrations at the sites studied in this work, along with measurements of NO_2, and sulfate, OC and EC in PM. For NO_2, no clear spatial pattern was observed, although some sites exhibited high levels. In contrast, sulfate concentrations displayed a distinct south-to-north gradient, with the highest values in southern Europe and minimal variation throughout the week. However, OC concentrations increased in central and northern Europe by the end of the week.

3.2 Volatile organic compounds (VOCs)

3.2.1 Chemical speciation of the VOC component groups

The relative contributions of different VOC component groups, such as C_2-C_6 and C_7-C_{12} NMHCs, O-VOCs, aromatics, isoprene, and monoterpenes, were analysed at fourteen sites that measured all major VOCs (Fig. 2). O-VOCs and C_2-C_6 NMHCs dominated the total VOC concentrations at most locations. On average O-VOCs contributed 56 ± 7 % to total VOCs, NMHCs (not including isoprene) 32 ± 8 %, and isoprene 7 ± 7 %. Given their known impact on atmospheric chemistry, the significant contribution of O-VOCs across all sites highlights the need to expand monitoring networks to more effectively capture their spatial and temporal variability.

Methanol, one of the most abundant VOCs, is not included in Fig. 2. Seven of the sites in Fig. 2 also measure methanol, and pie plots that include methanol can be found in Fig. S3. When included, methanol contributed 27 ± 9 % to the total, while the remaining O-VOCs contributed 40 ± 8 %, and NMHCs (not including isoprene) 23 ± 7 %.

The chemical speciation of VOCs including sites lacking measurements for some component groups are shown in Fig. 3. Note that methanol is not included. The sites are sorted from north to south, with urban sites in a separate panel on the right. The data in Fig. 3 differ from those in Fig. 2 in that they omit C_7-C_{12} NMHCs, while including sesquiterpenes. The relative contributions of the different VOCs are detailed in the Supplement, however only sites with data for all major species within each component group are included (Fig. S4). Fig. 4 illustrates the spatial variation of the different VOC groups.

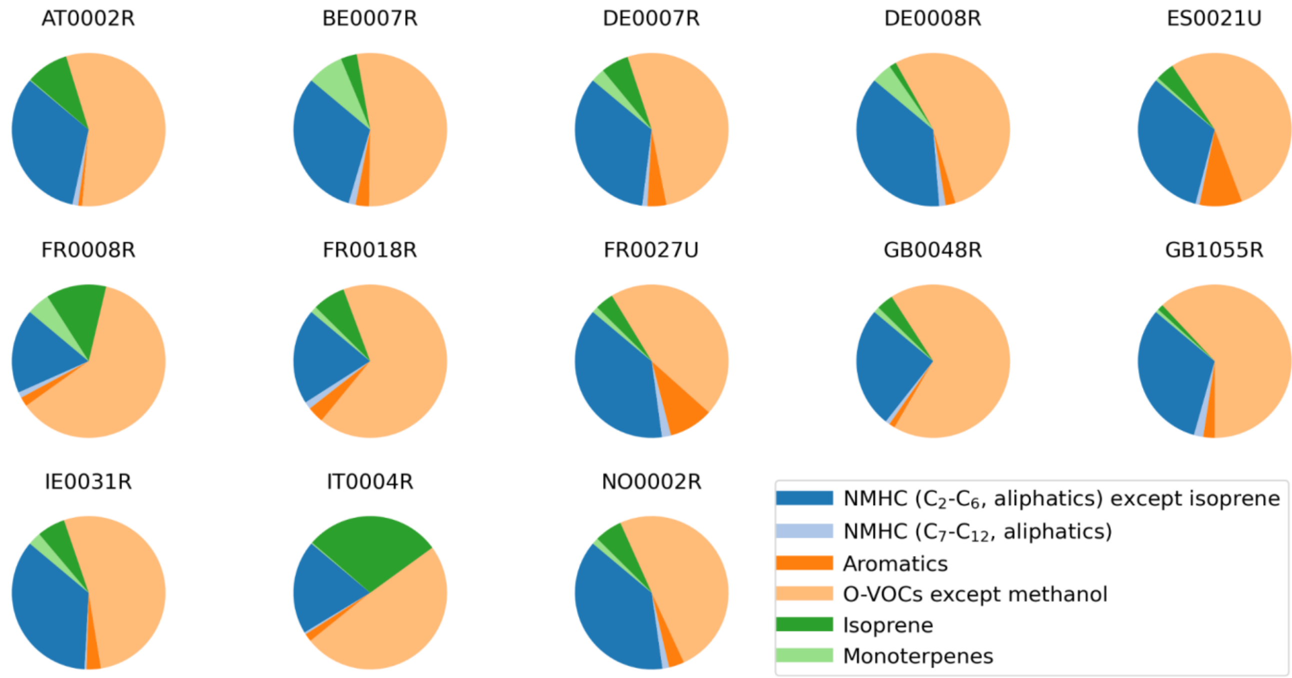

Fig. 2. Distribution of different VOC groups at sites where the most relevant component groups were measured. The Fig. is based on the relative contribution of the sum of the average concentrations (pptv), 12-19 July.

The concentrations of NMHC (C_2-C_6 excluding isoprene) and aromatic compounds were generally highest at urban sites (Fig. 3) as expected as these are mainly from anthropogenic sources. However, some regional sites exhibited relatively high levels of these compounds, likely due to their proximity to major cities or densely populated regions in Europe (Fig. 4), as indicated by elevated NO_2 values at Ispra (IT0004R) and Chilbolton (GB1055R). Ispra (IT0004R) is influenced by emissions from the Po Valley, and Chilbolton (GB1055R) is influenced by populated areas throughout southern England as seen in regular measurements from these sites (Solberg et al., 2024). In contrast some sites show relatively high NMHC and/or aromatics concentrations (e.g. AT0002R, FR0008R, FR0018R) without correspondingly high NO_2 levels, while others such as Kosetice (CZ0003R) exhibit elevated NO_2 levels but only modest NMHC and aromatic concentrations. Urban sites showed significantly higher concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX), a subset of aromatic compounds, than regional sites, consistent with European observations by Liu et al., (2025). The relative contributions of aromatic hydrocarbons were highest for toluene (38 ± 15 %), benzene (25 ± 10 %), and the sum of xylenes (16 ± 8 %).

Ethane was the most dominant C_2-C_6 NMHC on average, comprising 32 ± 12 % of the total NMHC concentration, followed by isoprene at 20 ± 19 %. Considering their respective lifetimes (2 months vs. 1 hour), this suggests large isoprene emission fluxes during the IMP. There were significant variations between sites, with isoprene contributing up to 75 % of NMHCs at

Peyrusse Vieille (FR0013R) and 59 % at Ispra (IT0004R). These are likely from biogenic emissions, Peyrusse Vieille being located far from large anthropogenic sources, while a clear diel cycle with low nighttime concentrations of isoprene at Ispra also suggests a dominant biogenic source.

Isoprene contributed only with 2-3 % at Beromünster (CH0053R), Schmücke (DE0008R), and Chilbolton (GB1055R). The latter two sites (GB1055R and CH0053R) are located in agricultural areas and were likely not strongly influenced by biogenic emissions. In contrast, DE0008R is located in the Thuringian forest, where a stronger biogenic influence would be expected. Nevertheless, monoterpene concentrations remained relatively high, as expected for a forested site dominated by coniferous trees. Both monoterpenes and sesquiterpenes showed spatial patterns distinct from the other VOC groups (Fig. 3). Spatial variations of the different terpenes are mapped in Fig. S5. The mean concentrations of these compounds varied widely across sites, reflecting the surrounding biogenic environment. Forested sites such as Vielsalm (BE0007R) and Donon (FR0008R) showed the highest concentrations of monoterpenes. While sesquiterpenes were generally lower, elevated levels were observed at Mace Head (IE0031R). α-Pinene was the dominant monoterpene, contributing 24 ± 15 %, followed by sabinene (15 ± 17 %) and β-pinene (10 ± 10 %). The relative importance of individual monoterpenes varied by site, reflecting differences in vegetation. For example, limonene dominated at Auchencorth Moss (GB0048R), whereas it was 3-carene at Birkenes (NO0002R) and Mace Head. β-Farnesene dominated sesquiterpenes at all sites, with an average contribution of 75 ± 15 %. The high concentration of sesquiterpenes at Mace Head was surprising, given the relatively low levels of monoterpenes and isoprene at the site. Considering its proximity to the Atlantic Ocean, phytoplankton activity, which can emit sesquiterpenes (Park et al., 2023), might be a potential source. These emissions may also originate from flowering plants and diverse plant types, such as shrubs, grasses, and herbaceous species, which are known to produce sesquiterpenes (Duhl et al., 2008). Some broadleaf trees, such as downy birches, may emit more sesquiterpenes than monoterpenes (Hellén et al., 2021).

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Fig. 3. Chemical composition of different VOC groups at all sites, averaged over the measurement period (12-19 July 2022). The sites are sorted from north to south, with the urban sites separated to the right. The NMHC and aromatic measurements at ES0025U were divided by five. MVK is 3-buten-2-one, MACR is 2-methylpropenal, and MEK is butanone. The different trimethylbenzenes and xylenes were summed. The xylenes for the PTR-MS sites also include ethylbenzene. Note that not all sites include all components, most notably isoprene was missing at some sites, while PTR-MS sites include isoprene only; besides, some O-VOCs sites missed formaldehyde data.

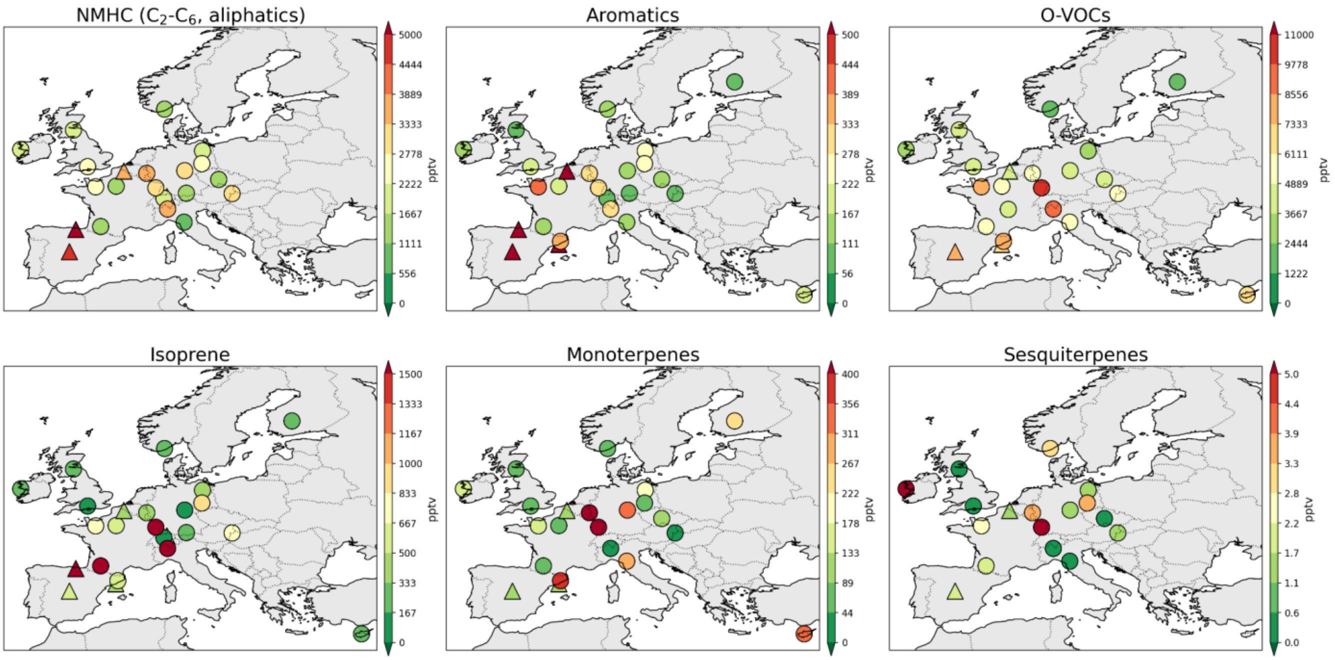

Fig. 4. Spatial variation of the average concentrations of the different VOCs from 12-19 July. The groups sum the average concentration for all the relevant components. The urban sites are marked as triangles.

There is no distinct difference between urban and regional sites regarding O-VOC concentrations, although a clear gradient is observed, with the highest concentrations in central and southwestern Europe (Fig. 3 and 4). The relative distribution of the various O-VOC species was, however, remarkably similar across sites (Fig. S4). Given the geographical and environmental diversity of the stations, this suggests high background levels of O-VOC, which also contribute to a significant fraction of urban O-VOCs, as shown by Borbon et al. (2024). Formaldehyde and acetone were the dominant O-VOC components, contributing 42 ± 6 % and 32 ± 6 %, respectively, followed by acetaldehyde 13 ± 4 %. The widespread occurrence of these compounds across Europe likely reflects both their diverse sources and their secondary formation in the atmosphere. They are emitted directly from anthropogenic activities, such as traffic (Gentner et al., 2013), VCP use (Seltzer et al., 2021) and industrial combustion (Wang et al., 2023), and episodically from wildfires (Akagi et al., 2011; Gilman et al., 2015). In addition, substantial secondary production occurs through oxidation of hydrocarbons from both anthropogenic and biogenic precursors, including ethane, isoprene, and terpenes (Khan et al., 2015; Millet et al., 2010; Seinfeld and Pandis, 1998).

Within ACTRIS, an important part of the QA/QC procedure is to compare VOCs with similar sources or atmospheric lifetimes, to identify specific local influences (e.g., meteorological effects, nearby emissions) or potential technical issues (Laj et al., 2024; Reiman et al., 2018). Fig. 5 presents a selection of relevant ratio plots, whereas Fig. S6 includes all ACTRIS-recommended ratios. Such ratios are useful for assessing source characteristics and atmospheric processing.

A correlation between ethane and propane was observed at most sites, consistent with both species being influenced by leakage from the production and use of oil and natural gas. However, because propane's atmospheric lifetime is approximately one-fourth that of ethane (Ge et al., 2024), higher propane/ethane ratios are indicative of proximity to local sources. This is clearly seen at urban sites such as Zürich (CH0010U), Madrid (ES0021U), and Bilbao (ES0025U), as well as at the regional background site Auchencorth Moss (GB0048R), as also documented in earlier studies (Derwent et al., 2007) .

The i/n-pentane ratio further distinguishes between source types (Baker et al., 2008). Most regional and rural sites showed values between 1 and 2, consistent with mixed anthropogenic influences, while Zürich (CH0010U) exhibited a higher ratio (~3.6) typical of urban or traffic emissions. In contrast, Bilbao (ES0025U) displayed an unusually high ratio (~7.6), suggesting additional local influences such as liquefied petroleum gas (LPG) handling, petrochemical activity, or harbour emissions.

The benzene-to-acetylene ratio is often used within ACTRIS as a QA/QC indicator, since both compounds originate from incomplete combustion and have comparable atmospheric lifetimes. A ratio around 0.3 is typically expected for well-mixed combustion sources (Reiman et al., 2018), while significant deviations may reflect either measurement issues (e.g., acetylene breakthrough) or differences in emission source profiles. In our dataset, ratios varied widely (0.1-3.2) across Europe. Low ratios at Zürich (CH0010U) suggest strong local acetylene sources, plausibly linked to nearby human activities such as restaurants and outdoor smoking, while elevated ratios at Bilbao (ES0025U), ATOLL Villeneuve d'Ascq (FR0027U), and Melpitz (DE0044R) indicate benzene-rich emissions, likely related to industrial or solvent use rather than measurement artefacts.

Some of the first-generation photooxidation products of isoprene, methacrolein (MACR) and methyl vinyl ketone (MVK), are further oxidized to formaldehyde and other products (Wennberg et al., 2018; Wolfe et al., 2016). When isoprene is the dominant source, their ratio is typically around two (Ling et al., 2019). A linear regression between MVK and MACR for all sites shown in Fig. 5 (bottom left), yielded a slope of 2.32 ± 0.07, consistent with this expected relationship and confirming isoprene as their main precursor.

Examining the relationship between MVK+MACR and their oxidation product formaldehyde (HCHO) shows a fairly strong correlation across sites, with a slope of 4.7 ± 0.3 (Fig. 5, bottom middle). Formaldehyde is produced secondarily from the oxidation of isoprene (both directly and through MVK and MACR), methanol, methane, and other hydrocarbons, but it can also have primary contributions from combustion and volatile chemical products (VCPs). Some sites, such as Madrid (ES0021U) and ATOLL Villeneuve d'Ascq (FR0027U), show somewhat elevated HCHO concentrations, likely due to influence from anthropogenic sources. At several locations, the correlation between MVK+MACR and HCHO weakens at high MVK+MACR levels. This may reflect nearby isoprene sources where photochemical processing has not yet produced large amounts of HCHO, and/or enhanced HCHO loss under hot, sunny conditions through photolysis and OH oxidation. Ispra (IT0004R) and Donon (FR0008R) stand out from the other sites when comparing the sum of MVK, MACR, and HCHO 480 relative to isoprene (Fig. 5, bottom right), likely reflecting higher isoprene emissions and differences in photochemical age. While anthropogenic isoprene sources are generally minor, episodic petrochemical or solvent emissions could sporadically contribute at some sites.

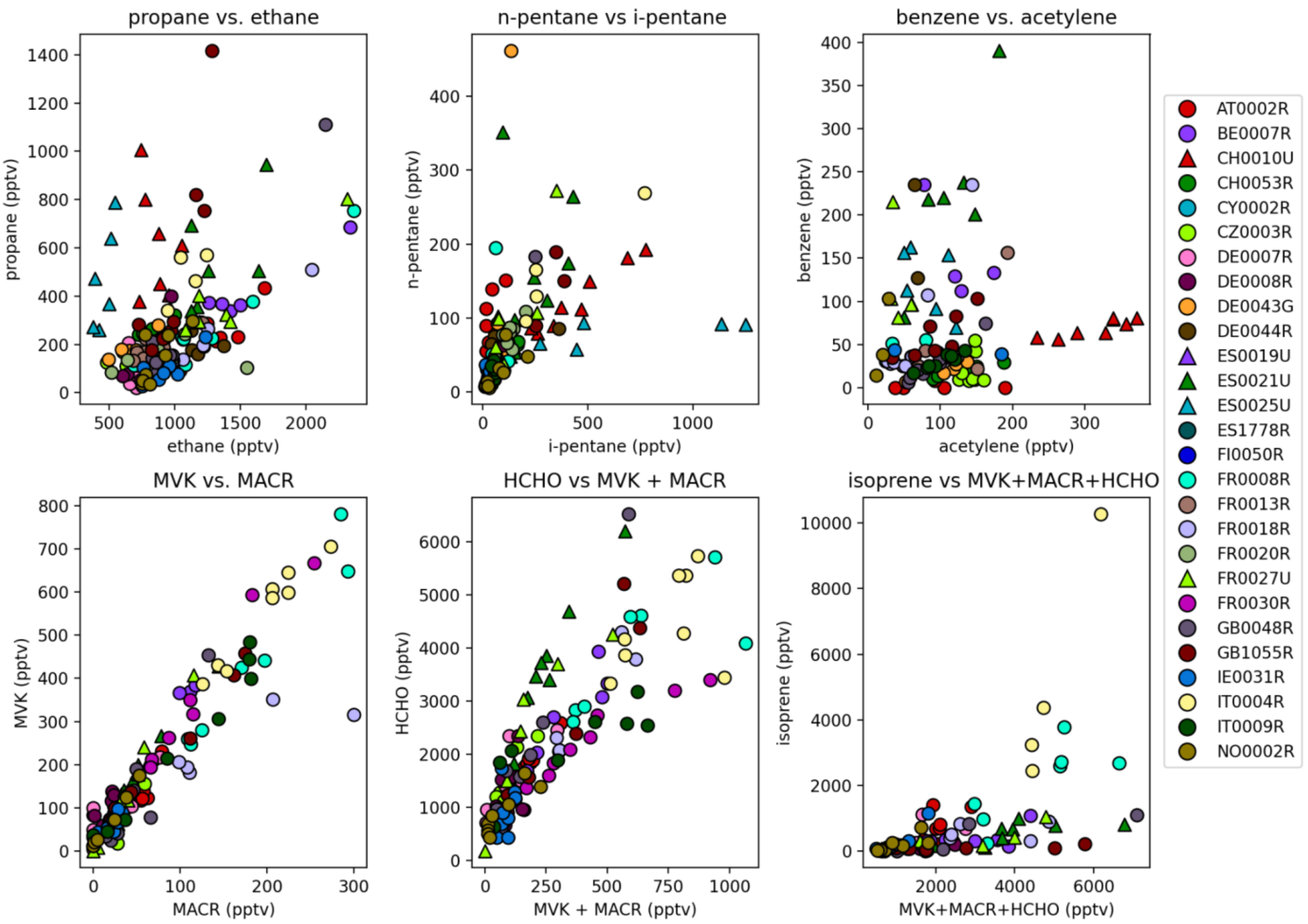

Fig. 5. Ratio of selected VOCs for daily-averaged concentrations. Urban sites are marked as triangles. Note that VOC concentrations 485 at ES0025U are divided by five.

3.2.2 Temporal variations of the VOCs

Long-term VOC observations are available at only a subset of the IMP sites, limiting the ability to contextualise 2022 levels against typical July conditions. Between one and seven of the IMP sites have reported VOC data to EMEP and/or ACTRIS for at least four years during the period 2015–2021 (Solberg et al., 2024), depending on the compound. At these sites, the midday

(12–16 UTC) July averages indicate that NMHCs and aromatics during the IMP week were broadly comparable to long-term July levels. For O-VOCs, only Peyrusse Vieille (FR0013R) has a sufficiently long time series. At this site, acetone and acetaldehyde concentrations in 2022 were three and five times higher, respectively, than during July 2015–2021. For isoprene, long-term measurements are available at four sites. At Hohenpeissenberg (DE0043G) and Peyrusse Vieille (FR0013R), isoprene levels were approximately twofold and fourfold higher, respectively, during the IMP week compared with long-term July averages. In contrast, the Swiss site (CH0053R) and the Finnish site (FI0050R) showed concentrations consistent with typical July conditions.

The temporal evolution of the VOC groups across Europe during the heatwave is illustrated in Fig. S7. As the high-pressure system moved northward, elevated VOC levels developed in central and northwestern Europe (e.g., France, Germany, the UK) during 16–19 July (Fig. S7). This progression broadly followed the large-scale warming pattern, although the northward signal was less pronounced than for ozone (Fig. 1). Most VOC groups show somewhat elevated concentrations across northwestern Europe during the final days of the period, as exemplified in Fig. 6 by the sites in Norway (NO0002R), the UK (GB1055R), Belgium (BE0007R), and northern Germany (DE0007R), likely reflecting the transport of air masses influenced by southerly winds. Donon (FR0008R), which is also located in the northwest, does not show clear temporal variations, although levels are somewhat elevated at the end of the week. Interpretation of these changes is complicated by the differing atmospheric lifetimes of VOCs, making it difficult to distinguish between local and long-range influences.

The isoprene emissions recently published by Hamer et al. (2025) show a similar spatial development as temperature during the IMP week (12–19 July; Fig. S1), with the highest emissions over Portugal, northern Spain, and southern France at the start of the week, increasing across central Europe as the heatwave progressed northward (Fig. S8). Around half of the sites show a significant correlation between the in-situ observed isoprene concentrations and the modelled emissions (Fig. S9). The sites furthest from the continent (NO0002R, GB0048R, FI0050R) show the best correlations, suggesting that these were mainly influenced by the regional increase in biogenic isoprene emissions associated with rising temperatures. Bilbao (ES0025U) also shows a strong correlation, although most Spanish sites exhibit weaker relationships. It is difficult to establish a direct correspondence between emissions and observed concentrations within the same model grid cell, despite the relatively short atmospheric lifetime of isoprene. A forthcoming model intercomparison study within the EMEP TFMM framework will address these aspects in more detail.

The strongest temporal gradients are seen for O-VOCs, with distinctly higher concentrations in central and northwestern Europe toward the end of the week (Fig. S7). Monoterpenes exhibited a more scattered spatial pattern and weaker temporal variability. High monoterpenes levels at the start of the heatwave were found not only in southern Europe but also in central Europe and in Finland on 12–13 July.

While ozone concentrations during the heatwave were strongly linked to the movement of the high-pressure system and associated air-mass transport, VOCs displayed more diverse temporal patterns. This reflects the variety of VOC sources, formation mechanisms, and sinks, including anthropogenic emissions, biogenic processes, and secondary formation under different photochemical conditions.

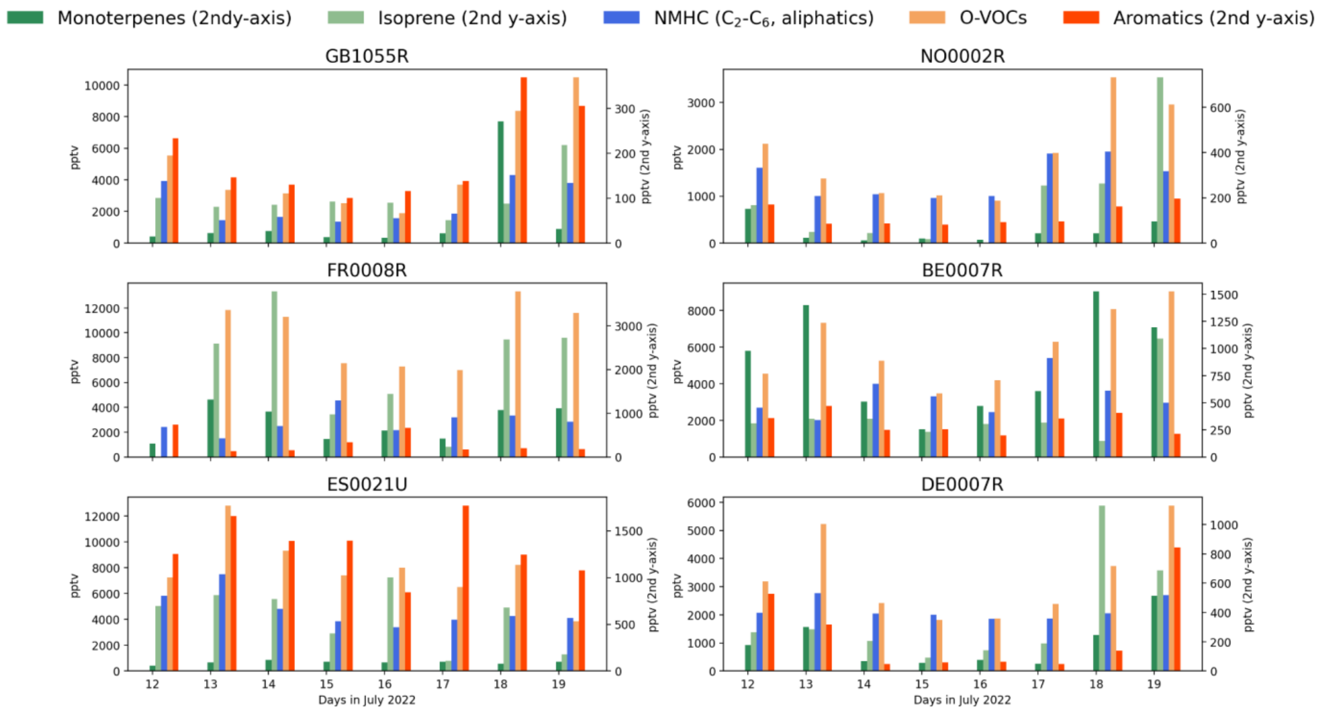

Fig. 6. Temporal variations of selected VOCs and VOC groups at 6 sites across Europe on 12-19 July.

3.3 Ozone production and losses

To explore effects of changes in VOC and NO_x concentrations on the ozone production rate, we simulated the local ozone production at different VOC and NO_2 reactivity levels using the MCM v3.3.1 boxmodel and compared it to the VOC and NO_2 reactivities observed at the participating sites similar as outlined by Ehlers et al. (2016). Ozone production rates calculated for 21 sites are shown in Fig. S10. The highest ozone concentrations were typically located in regions with the highest ozone production rates. However, there were large variations between sites. For example, Monte Cimone (IT0009R) showed high ozone levels, but little ozone formation, probably due to ozone being transported to the site. In contrast, lower O_3 daily maxima were observed at e.g. Illmitz (AT0002R) and La Coulonche (FR0018R) while higher O_3 production rates were calculated at these sites.

Most sites in this study are background locations where reactive ozone-forming VOCs, particularly those of anthropogenic urban origin, may already have undergone atmospheric oxidation. This limits our ability to assess the role of specific emission sources in ozone formation. However, the measurements still provide useful information on the relative importance of the remaining VOCs present at the sites. We estimated the commonly used ozone formation potential (OFP) of the measured VOCs using literature-based Photochemical Ozone Creation Potential (POCP) values (Holland et al., 2023; Jenkin et al., 2017). Representing POCP as fixed values is a substantial simplification, as the actual ozone formation depends strongly on atmospheric conditions such as NO_x concentrations, VOC/NO_x ratios, and relative humidity. Nevertheless, these estimates offer an approximation of the relative contribution of different VOC groups and components to ozone formation under typical conditions. Fig. S11 shows that isoprene, NMHCs, and O-VOCs contribute most to the calculated OFP at the participating sites, with aromatics mainly important in the urban areas. Among individual compounds, isoprene was on average twice as influential as ethene and formaldehyde, followed by acetaldehyde, propene, and ethane. When categorising the NMHCs according to their dominant sources, combustion emerges as the most important. Overall, biogenic, combustion, and mixed sources (mainly O-VOCs) contribute roughly equally to the total OFP (Fig. S11).

To better understand the processes that control observed ozone levels, we used the ADCHEM model to quantify ozone production and loss over the past three days upwind of the 15 measurement stations indicated in Table 1. The ozone budget is governed by the odd oxygen family (O_x), which includes O_3, NO_2, and other rapidly interchanging species (Jacob, 2000; Wang et al., 1998). O_x is removed through dry and wet deposition and reactions with radicals such as OH, HO_2, VOCs, and halogens. The rate-limiting steps in O_x production are the reactions of NO with HO_2, CH_3O_2, and other organic peroxy radicals (RO_2) radicals (Jacob, 1999). Ozone is primarily produced during daytime when peroxy radicals react with NO to form NO_2 which photolyzes back into NO and atomic oxygen, which subsequently forms ozone.

Model performance compared to observations is summarized in Tables S3–S4. The model underestimates ozone near oceanic sites (e.g., Birkenes, Mace Head) due to air masses from the open sea, and overestimates ozone at Ispra in the Po Valley, mainly because of misrepresented nighttime conditions. At the mountain site of Hohenpeissenberg (DE0043G), the model likely underestimates nighttime ozone due to inadequate representation of the free troposphere influence. Modelled and measured VOC concentrations (data not shown) agree well in northern and central Europe, but NMHCs and aromatics are generally overestimated in southern regions, particularly at urban and suburban sites, likely due to overestimated emissions and limited vertical mixing. Aromatic VOCs tend to be underestimated in northwestern Europe, while monoterpenes show large site-to-site differences, reflecting the influence of local sources and the coarse resolution of the emission inventory.

Fig. 7 shows the modelled campaign-averaged ozone production expressed in Dobson Units (DU). Net ozone production (production minus losses) is shown for the basecase as well as for sensitivity simulations without isoprene, without BVOCs, and with half and twice the NO_x emissions. At all stations except Hyytiälä (FI0050R) in the Finnish boreal forest, ozone production exceeds sinks, resulting in positive net ozone production. Across all sites, BVOC emissions generally enhanced ozone production and concentrations, as demonstrated by comparing the basecase to simulations without terrestrial BVOC emissions. This effect was particularly pronounced at the southern European stations Ispra (IT0004R), Montseny (ES1778R), and Madrid (ES0021U) (see Fig.S12 for details on the temporal variations at each site).

At Hyytiälä (FI0050R), ozone production was relatively insensitive to BVOC emissions but highly sensitive to NO_x. Doubling NO_x emissions resulted in an average 20 % increase in ozone concentrations, while halving them led to a 15 % reduction (Fig. 8). This behaviour aligns with the study of Zhang et al. (2024), who showed that ozone production in air masses arriving at Hyytiälä during summer 2018 was generally NO_x-limited. In most regions, doubling NO_x emissions increased ozone production and surface ozone concentrations, while halving NO_x emissions consistently lowered ozone production and concentrations at all stations. This indicates that ozone formation was generally NO_x-limited during the campaign. The only exceptions were Vielsalm (BE0007R) and ATOLL Villeneuve d'Ascq (FR0027U), where average surface ozone concentrations decreased slightly in the 2×NO_x scenario; at some stations including Chilbolton (GB1055R), such reductions were occasionally observed. However, during the episodes with the highest ozone concentrations, the 2xNO_x simulations always resulted in substantially higher ozone concentrations (additional 10 to 36 ppb), while simulations without BVOCs led to significantly lower ozone (reduction of 2 to 40 ppb) compared to the basecase. This suggests that the exceptionally high ozone peaks, particularly toward the end of the campaign, were driven by a combination of high (B)VOC emissions and anthropogenic NO_x under NO_x-limited conditions. These findings indicate that further reductions in NO_x emissions would be beneficial for lowering ozone levels at a large range of sites across Europe, especially during extreme pollution events. Accurate quantification of NO_2 is therefore essential for identifying ozone production regimes and guiding effective mitigation strategies. Stations that use a molybdenum converter for their measurements (Table 1) overestimate NO_2, due other reactive nitrogen oxide compounds (Reiman et al., 2018).

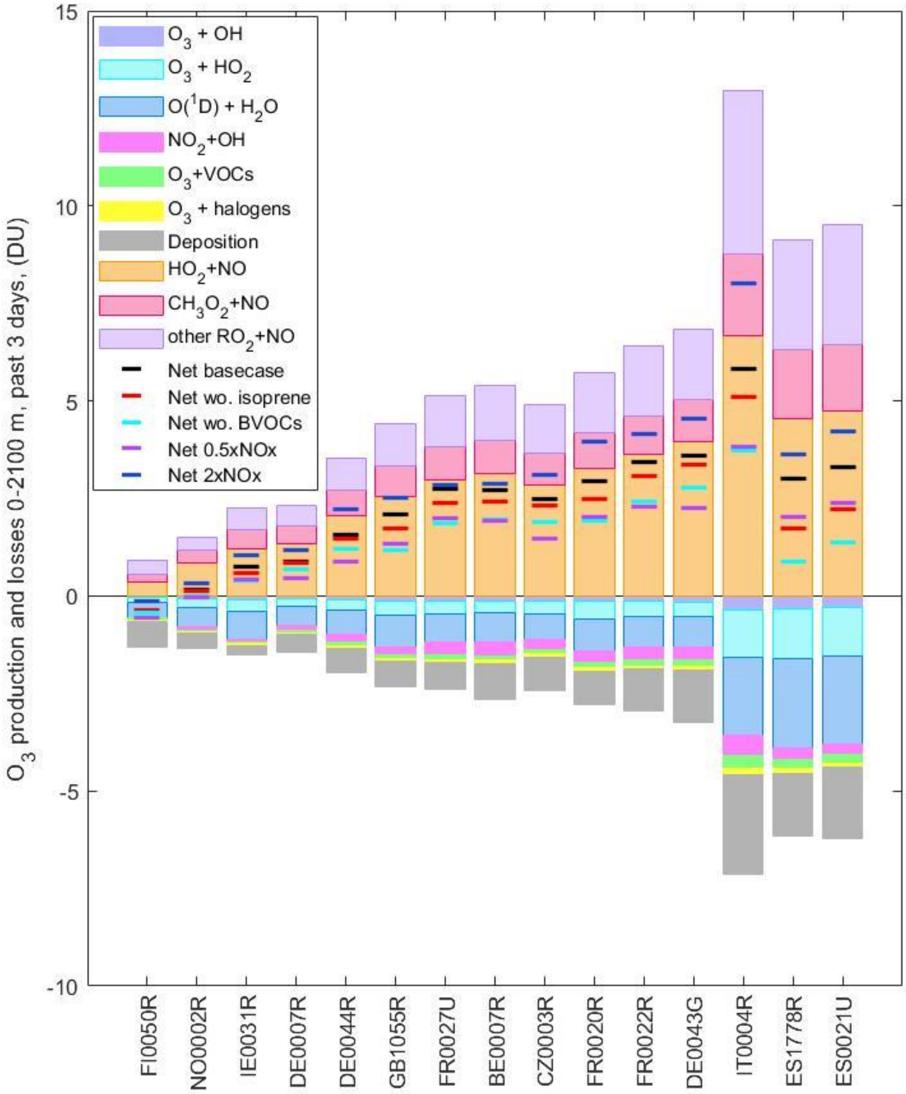

Fig. 7. Modelled (ADCHEM) 8-day averaged cumulative O_3 production and losses in the lowest 2,100 m of the atmosphere for the past 3 days upwind of 15 targeted measurement stations. Ozone is lost by reactions with OH, HO_2, unsaturated VOCs and various halogen (Br, I, Cl) radicals, when $O(^1D)$ reacts with H_2O and when NO_2 reacts with OH. Ozone is produced when HO_2, CH_3O_2 and other RO_2 radicals react with NO. Also shown by horizontal lines are the net ozone formation (production minus losses) from the basecase simulations (Net basecase), for simulations without terrestrial biogenic emissions of isoprene (Net wo. isoprene), without any terrestrial BVOC emissions (Net wo. BVOC) and with anthropogenic NO_x emissions scaled with a factor of 0.5 or 2.0 (Net 0.5xNO_x and Net 2xNO_x, respectively).

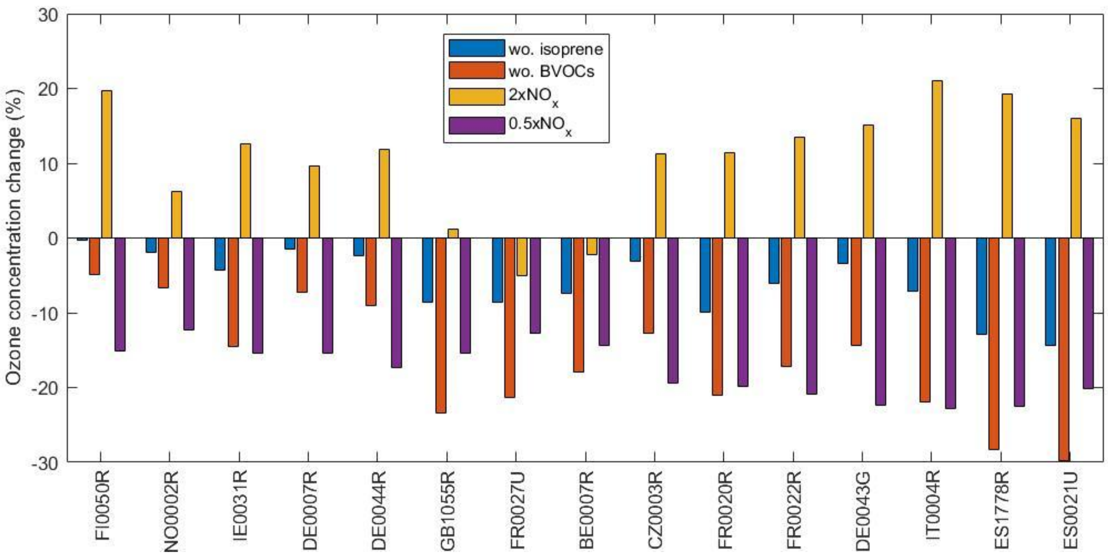

Fig. 8. Modelled 8-day averaged surface ozone concentration changes relative to the basecase simulations for 4 different model sensitivity tests: without biogenic terrestrial isoprene emissions (wo. isoprene), without terrestrial BVOC emissions (wo. BVOCs), with 2 times higher anthropogenic NO$_x$ emissions (2xNO$_x$) and with 50 % lower anthropogenic NO$_x$ emissions (0.5xNO$_x$).

3.4 Carbonaceous aerosols

Consistent with previous findings (Yttri et al., 2007), OC and EC concentrations decreased along the south-to-north transect, with levels at the three southernmost sites being 5 to 6 times higher than the northernmost sites. However, OC and EC concentrations increased at central and northern European sites during the IMP week, as was observed for ozone and some VOCs, in alignment with the heatwave plume (Fig. S2). The EC/TC ratio remained relatively stable throughout the heatwave (Fig. S2), averaging 3-5 % at most French and German regional sites, and 10-15 % at urban sites and the Ispra (IT0004R) regional site. The generally low ratios suggest a minor influence of primary organic aerosol (POA) from combustion, a dominant contribution from SOA, and some influence from primary biological aerosol particles (PBAP).

During the summer of 2022, EC and OC levels were consistent with long-term July averages at sites with multi-year data (Table 2). However, Montseny (ES1778R) and Ispra (IT0004R) recorded particularly high OC levels, corresponding to the 95th and 83rd percentiles of their long-term means, respectively.

Table 2. Mean concentrations of OC and EC (in µgC m^{-3}) during IMP Summer 2022 and corresponding percentile of the long-term mean for July 2010-2020.

Site	OC (IMP) Mean (percentile)	OC July (2010 – 2020) Mean (min – max)	EC (IMP) Mean (percentile)	EC July (2010 – 2020) Mean (min – max)
ES1778R (Montseny)	3.7 (95)	2.6 (1.5 – 4.7)	0.26 (77)	0.22 (0.07 – 0.49)
FR0038U (Grenoble)	4.2 (60)	3.8 (0.8 – 9.9)	0.39 (18)	0.65 (0.14 – 1.7)
IT0004R (Ispra)	3.9 (83)	2.7 (0.28 – 7.9)	0.39 (47)	0.18 (0.03 – 1.1)
DE0008R (Schmücke)	2.0 (59)	1.9 (0.36 – 5.8)	0.13 (53)	0.13 (0.04 – 0.40)
DE0044R (Melpitz)[1]	3.0 (32)	4.2 (1.2 – 12.8)	0.16 (26)	0.22 (0.05 – 0.710)
DE0007R (Neuglobsow)	1.7 (43)	2.2 (0.65 – 6.4)	0.11 (28)	0.15 (0.04 – 0.39)
NO0002R (Birkenes)	0.8 (33)	1.1 (0.48 – 2.8)	0.06 (50)	0.06 (0.01 – 0.14)

[1] Measurements from 2013 – 2020.

Carbonaceous aerosols constitute the major fraction of PM during the IMP, contributing approximately 34 ± 6 % in PM$_{10}$ and 72 ± 27 % in PM$_{2.5}$, based on a conversion factor of 1.8 from OC to OM (Fig. S13). The undetermined mass in PM$_{10}$ size was relatively high, averaging around 50 %, whereas in PM$_{2.5}$ it was only about 3 %. It should be noted, however, that at some sites, the measured PM$_{2.5}$ mass exceeded the sum of the component masses, indicating bias in some of the measurements. The substantial part of undetermined mass in PM$_{10}$ can partly be attributed to mineral dust (MD). Only a few sites measured aluminium and/or iron, which are commonly used to estimate MD. In total, twelve EMEP sites reported iron in PM$_{10}$ in July 2022, of which two were IMP sites with PM$_{10}$ measurements. The average MD contribution across these twelve sites during the IMP period was 13 ± 6 % (data not shown), with the highest concentrations observed in southern Europe. The urban sites exhibited the largest fraction of unknown mass, likely reflecting a stronger influence from dust compared to the regional EMEP sites.

3.4.1 Organic tracers

Approximately 50 organic species were analysed to assess the contributions of various OA sources during the heatwave. These included source-specific tracers such as levoglucosan, indicative of biomass burning emissions (Simoneit et al., 1999); sugars and sugar alcohols, linked to PBAP (Primary Biological Aerosol Particles) (Elbert et al., 2007; Graham et al., 2003; Sánchez-Ochoa et al., 2007); and 2-methyltetrols (2-MT) and 3-methyl-1,2,3-butane-tricarboxylic acid (3-MBTCA), formed from the oxidation of isoprene and α-pinene, respectively (Paulot et al., 2009; Szmigielski et al., 2007). The spatial distribution of mean concentrations for selected tracers during the IMP is shown in Fig. 9. The upper panels display 3-MBTCA and 2-MT levels, and these BSOA tracers decreased along the south-to-north transect, reflecting the expected reduction in BVOC emissions poleward. At most sites (16 out of 23), the mean concentration of 2-MT was equal to or exceeded that of 3-MBTCA. Notably, the 3-MBTCA/2-MT ratio shown in Fig. 9 exhibits a clear spatial relationship, with lower values in western Europe indicating a shift in the relative importance of biogenic sources.

The middle panels in Fig. 9 show arabitol, glucose, and the sum of 13 sugars and sugar alcohols indicating the distribution of PBAP, while the bottom panels present oxalic acid, pinic acid, and levoglucosan. The temporal development of a selection of organic tracers are found in Fig. S14-S15. 650

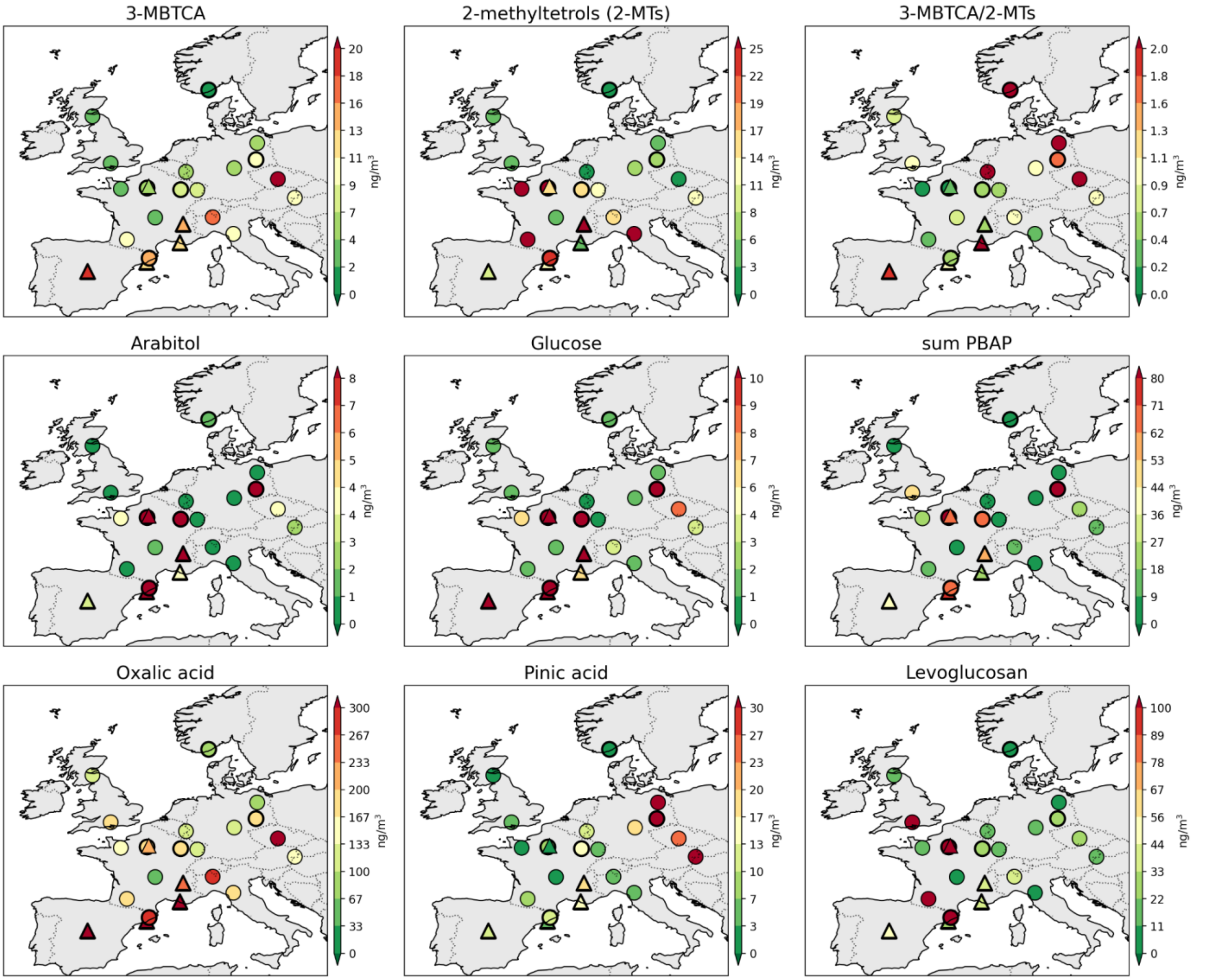

Fig. 9. Spatial distribution of the mean concentration of selected organic tracers, their respective ratio, and the sum of PBAPs. Urban sites are denoted with a triangle, and sites with a PM_{10} cut-off size are marked with a thicker border than $PM_{2.5}$.

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Although oxalic acid can originate from primary sources, its atmospheric presence is primarily driven by secondary formation. Like 3-MBTCA it shows a clear north-south gradient. In contrast, for pinic acid, a first-generation oxidation product of α-pinene (Vestenius et al., 2014 and references therein), concentrations were highest in central and eastern Europe. This spatial distribution aligns with the 3-MBTCA/2-MT ratio, which highlights the relative importance of BSOA from α-pinene in these regions. Interestingly, α-pinene does not show a spatial pattern similar to that of pinic acid or 3-MBTCA (Fig. S5). Furthermore, the relationships between the daily ratios of concentrations between pinic acid and α-pinene, and between 3-MBTCA and α-pinene, vary significantly across sites (Fig. S16). Similar variability is observed for β-pinene versus cis-pinonic acid and for isoprene versus 2-MT (Fig. S16). This discrepancy arises from multiple factors, including BVOC emissions, photosynthetically active radiation, ambient temperature, mixing layer height, yields, formation pathways, gas-to-particle partitioning, and atmospheric lifetimes (El Haddad et al., 2011; Hellén et al., 2024). In particular, oxidation during atmospheric transport leads to reduced concentrations of the precursor and increased concentrations of oxidation products downwind of the emission source.

Mean levoglucosan concentrations exceeded 100 ng m^{-3} at five sites spanning northern Spain, France, and southern England, with 24-hour levels surpassing 700 ng m^{-3}. These elevated concentrations were likely driven by several wildfires in Europe in July 2022, particularly in Portugal, Spain, and southwestern France (San-Miguel-Ayanz et al., 2023). The evolution of the wildfire plume is supported by EMEP model simulations, which show good agreement with the observed levoglucosan enhancements in France and the UK toward the end of the IMP week (Fig. S17). In contrast, other sites recorded much lower mean levoglucosan levels (4 to 50 ng m^{-3}), consistent with typical levels during summer periods in rural areas (Golly et al., 2019).

PBAP tracers such as arabitol and glucose show similar variability, with elevated levels at individual sites (DE0044R and FR0020R), but no clear spatial gradient despite the highest concentrations seen in central and southern Europe (Fig. 9). Summed PBAP concentrations (arabitol, mannitol, glucose, trehalose, fructose, mannose, sucrose, maltose, rhamnose, lactose, sorbitol, adonitol, inositol, and melezitose) support patterns observed for individual markers, highlighting the importance of local sources such as vegetation, soil, and microbial activity (Samaké et al., 2020).

Methane-sulfonic acid (MSA) primarily originates from the oxidation of dimethyl sulfide (DMS) emitted by marine phytoplankton. The spatial distribution shows the highest concentrations in coastal areas (Fig. S15); however, some continental sites also exhibit elevated levels, suggesting additional terrestrial biogenic sources, such as DMS emissions during warm periods from soil, leaf litter, or anoxic lakes, as indicated by Golly et al., (2019).

3.4.2 Source apportionment of organic aerosols

The sum of all the measured organic tracers for each sample correlates quite well with OC concentrations ($r^2 = 0.67$) during the IMP (Fig. S18), indicating that these compounds explained a large OA fraction. However, due to mixed origins, chemical degradation, and uncertainties in their spatial and temporal representativeness, relatively few of the measured tracers can be used directly to quantify contributions from different sources. Nevertheless, we used several of the most well-established organic tracers to apportion some of the OA mass.

We apportioned carbonaceous aerosol into biomass burning (BB) and fossil fuel combustion (FF) contributions using levoglucosan as the biomass burning tracer and factors derived from European studies (Zotter et al., 2014 and references therein), as shown in Eq. (3) and (4). Elemental carbon from fossil fuel (EC_{FF}) was calculated as total EC minus $[EC_{BB}]$ (Eq. 5), and $[OC_{FF}]$ was derived from $[EC_{FF}]$ using a factor of 0.6 (Eq. 6) from Gilardoni et al. (2011) and Yttri et al. (2011):

$$[OC_{BB}] = [\text{Levoglucosan}] \times 7.65 \tag{3}$$

$$[EC_{BB}] = [\text{Levoglucosan}] \times 0.985 \tag{4}$$

$$[EC_{FF}] = [EC] - [EC_{BB}] \tag{5}$$

$$[OC_{FF}] = [EC_{FF}] \times 0.6 \tag{6}$$

OC associated with primary biological aerosol particles (OC_{PBAP}) was estimated from the five PBAP tracers (arabitol, mannitol, fructose, glucose, and trehalose) using an OC-to-$PBAP_{Tracer}$ ratio of 6.4 (Eq. 7). Since trehalose concentrations were not measured during this IMP, they were estimated from arabitol concentrations using an arabitol-to-trehalose ratio of 2, based on European data (Yttri, 2025a, b, c). It is important to note that there is not necessarily a linear relationship between these compounds, and the ratio is different in other parts of the world. For example, a study at three sites on the Qinghai–Tibetan Plateau found no correlation between arabitol and trehalose (Zhu et al., 2022).

$$[OC_{PBAP}] = [\text{sum of } PBAP_{Tracers}] \times 6.4 \tag{7}$$

SOA (OC_{SOA}) was then derived by subtracting the sum of the primary OC fractions (BB, FF and PBAP) from the total OC, as shown in Eq. (8):

$$[OC_{SOA}] = [OC] - [OC_{FF}] - [OC_{BB}] - [OC_{PBAP}] \tag{8}$$

SOA includes both the biogenic (BSOA) and the anthropogenic (ASOA) fractions. BSOA from α-pinene oxidation ($OC_{BSOA\,(\alpha\text{-pinene})}$) was estimated using 3-MBTCA concentrations and an OC-to-3-MBTCA conversion factor of 57 (Eq. 9), based on PMF-derived source apportionment (Borlaza et al., 2021). The remaining SOA ($OC_{SOA\ rest}$) is primarily attributed to oxidation of isoprene, other terpenes beyond α-pinene, and anthropogenic precursors.

$$[OC_{\ BSOA\ \alpha\text{-pinene}}] = [\text{3-MBTCA}] \times 57 \tag{9}$$

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Figure 10 illustrates the average apportioned OA categories for all sites with both tracer and OC measurements (in PM_{10} or $PM_{2.5}$). The sum of SOA is indicated with a red border. OC_{SOA} constituted the major fraction of OC, with averages of 84 ± 11 % in $PM_{2.5}$ and 75 ± 11 % PM_{10}. Biomass burning contributed similarly to both size fractions (ca. 10 % on average), but with large site-to-site differences. For example, [OC_{BB}] contributed nearly 25 % or more of OC at sites in Spain (ES1778R), France (FR0013R and FR0041U), and the UK (GB1055R) during the IMP week, consistent with occurrences of wildfires in western Europe during this period (San-Miguel-Ayanz et al., 2023 and Fig S17).

OC from fossil fuels differed little between $PM_{2.5}$ and PM_{10} (averaging 4-5 %), with the largest contributions in urban areas, e.g., around 10 % in Marseille (FR0035U) and Barcelona (ES0019U). On the other hand, PBAP contributions differed significantly between size fractions: 2 ± 2 % in $PM_{2.5}$ versus 10 ± 11 % in PM_{10}. At Melpitz (DE0044R), as much as 37 % of OC in PM_{10} was from PBAP with 1.1 $\mu gC\ m^{-3}$, whereas at SIRTA (FR0020R), PBAP contributed 1.4 $\mu gC\ m^{-3}$, but the relative PBAP contribution was lower (18 %) due to a larger SOA fraction. Approximately one-third of OC_{SOA} was attributed to α-pinene oxidation: 19 ± 13 % of total OC in $PM_{2.5}$ and 16 ± 6 % in PM_{10}.

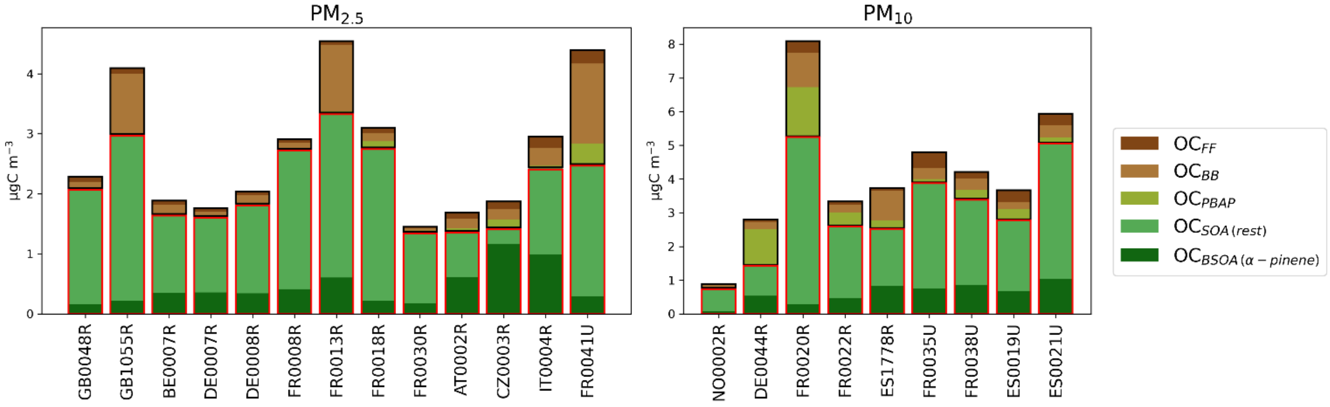


Fig. 10. OC apportioned into categories with $PM_{2.5}$ (left) and PM_{10} (right) size fractions. Secondary OCs are indicated with a red border and primary OCs with a black border.

At Ispra, SOA contributed 76 % of the total OC during the IMP week, which is in line with the radiocarbon-based source apportionment by Gilardoni et al. (2011), who found that SOA accounted for about 81 % of OC in summer 2007, with 53 % attributed to BSOA, as estimated from their data. At Peyrusse Vieille (FR0013R), SOA represented on average nearly 90 % of the organics in $PM_{2.5}$ in July during 2012–2021, with biomass burning (BB) contributing 6 %, based on a similar tracer approach (Font et al., 2024). During the IMP period, SOA accounted for 78 % and BB for 24 %, the latter increase linked to the wildfires. At Birkenes (NO0002R), the long-term summer average shows that primary biological aerosol particles (PBAP) account for as much as 31 % of OC in PM_{10} (Yttri et al., 2021), substantially different from the IMP week, when SOA dominated with 87 % and PBAP contributed only 3 %.

3.4.3 OA formation and losses

ADCHEM was used to quantify OA production and losses at the sites (Fig. 11). OA production includes primary emissions and condensation (SOA formation), while losses occur through dry and wet deposition, as well as evaporation. Net OA production (production minus sinks) was assessed for the basecase and for some sensitivity runs: i.e., without isoprene, without BVOCs, and with anthropogenic NO_x scaled by factors of 0.5 and 2. Changes in OC concentrations relative to the basecase are shown in Fig. 12. With the exception of the three northernmost stations (Hyytiälä (FI0050R), Birkenes (NO0002R), and Mace Head (IE0031R)), net OA productions were positive over the past three days of upwind transport at each site (Fig. 11). The northern and western sites were influenced by marine air masses with significant MSA (CH_3SO_3H) production, whereas the OA concentrations at more southern sites were dominated by ASOA, BSOA and primary OA from traffic. Simulations without terrestrial BVOC emissions showed reduced OA production and lower OC concentrations, with the strongest reduction observed at Hyytiälä (-55 %) (Fig. 11). The 0.5xNO_x scenario resulted in higher (3 ± 1 %) OA production and OC levels, while the 2xNO_x scenario led to substantially reduced (5 ± 3 %) OC levels, despite lower OH and ozone levels (Fig. 12). This reflects higher SOA yields under low-NO_x conditions, which more than compensate for slower VOC oxidation at lower NO_x levels.

Aromatic compounds, such as benzene, toluene, xylenes, and phenols, are key ASOA precursors. Their oxidation is initiated by OH radicals and followed by autoxidation, leading to the formation of HOM (Iyer et al., 2023; Pichelstorfer et al., 2024). In the model, the aromatics SOA mass yields (i.e. the ratio of formed SOA mass to the mass of reacted SOA precursors (VOC)) are significantly higher than those of monoterpenes and isoprene (Fig. S19). Consequently, aromatics account for over 50 % of the modelled SOA mass at several sites, despite the substantially higher emissions of monoterpenes and isoprene (Fig. 13).

However, the model underestimates the total measured OC by about 50 % on average across the stations, while Ispra (IT0004R) showed a slight overestimation (Table S5), likely due to missing SOA precursors (e.g., large alkanes), missing oxidation pathways for the formation of low-volatility compounds (underestimated SOA yields), and underestimated POA emissions (Roldin et al., 2024; Simpson et al., 2020). Although ADCHEM incorporates state-of-the-art VOC oxidation mechanisms (Iyer et al., 2023; Luo et al., 2024; Pichelstorfer et al., 2024; Roldin et al., 2019), it only considers HOM formation from a limited range of VOCs (i.e. α-pinene, β-pinene, limonene, 3-carene, benzene, toluene, xylenes). Even for these, oxidation pathways and volatility distributions remain highly uncertain, especially under high-NO_x conditions and at temperatures below 20 °C.

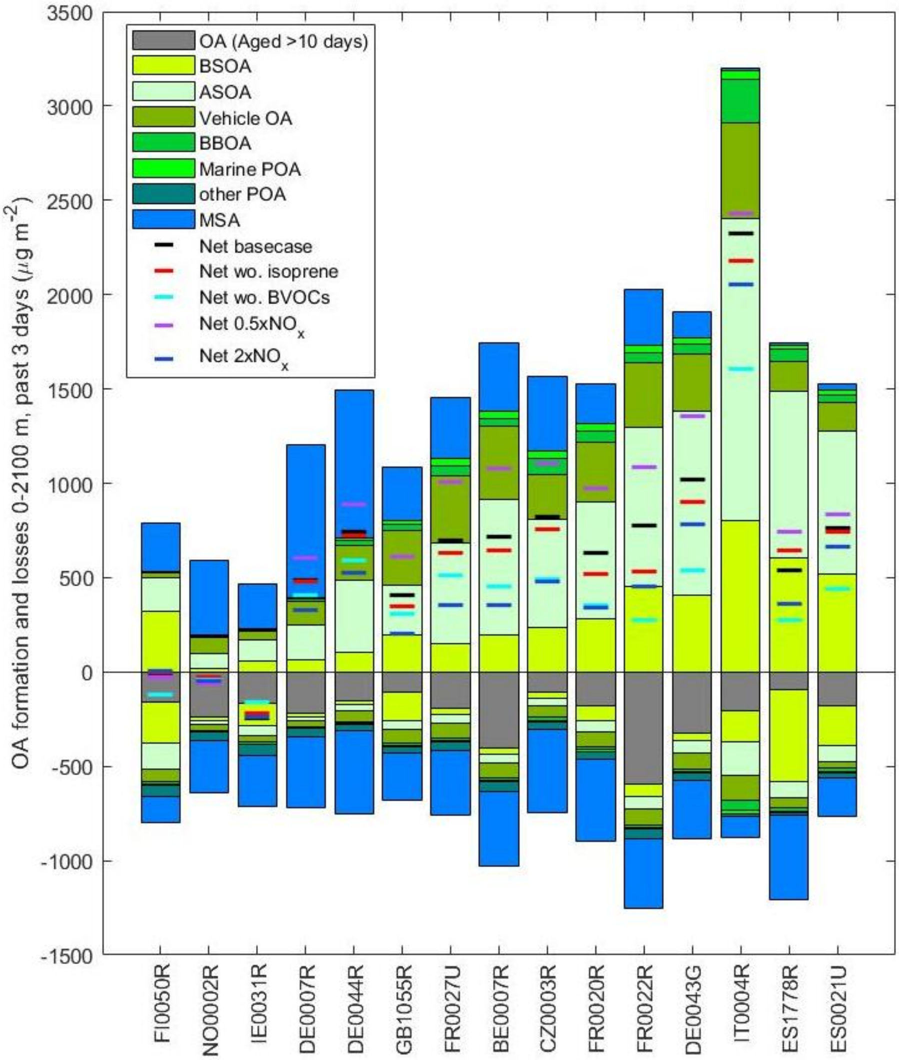
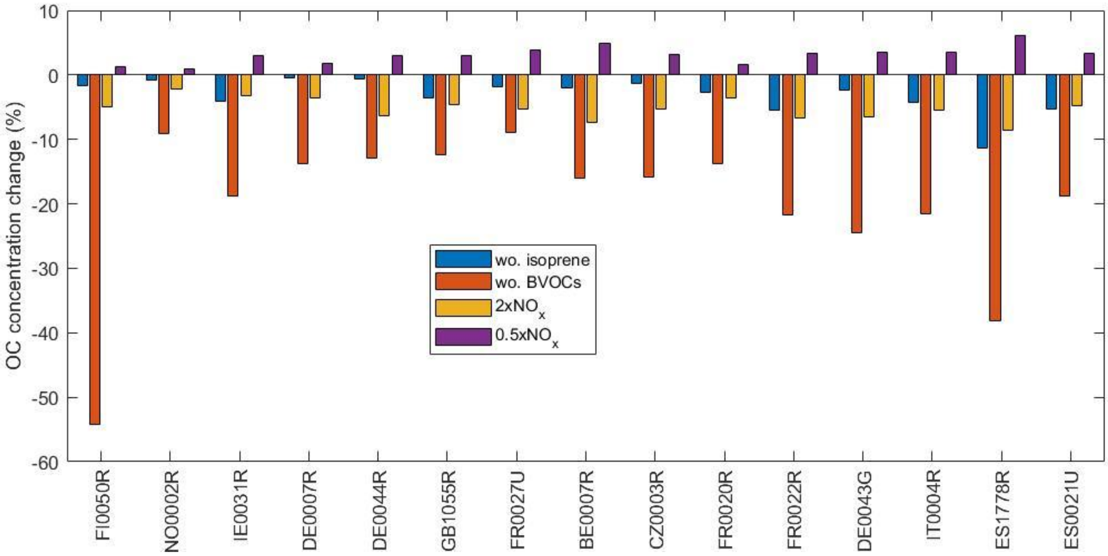


Fig. 11. Modelled (ADCHEM) 8-day averaged cumulative OA formation and losses during the past 3 days upwind of the measurement stations. OA formation includes primary emissions (POA) and secondary formation (SOA), while losses comprise dry/wet deposition and evaporation. OA is divided into source categories: aged background OA (>10 days), BSOA, ASOA, vehicle OA, biomass burning OA (BBOA), marine POA, other POA, and methyl sulfonic acid (MSA). Net OA formation (production minus losses) is shown for the base case and sensitivity simulations without isoprene, without all BVOCs, and with anthropogenic NO$_x$ scaled by 0.5× and 2×. 780



785 **Fig. 12. Modelled 8-day averaged surface OC concentration changes relative to the basecase simulations for 4 different model sensitivity tests: without biogenic terrestrial isoprene emissions (wo. isoprene), without terrestrial BVOC emissions (wo. BVOCs), with twice the anthropogenic NO$_x$ emissions (2xNO$_x$) and half the anthropogenic NO$_x$ emissions (0.5xNO$_x$).**

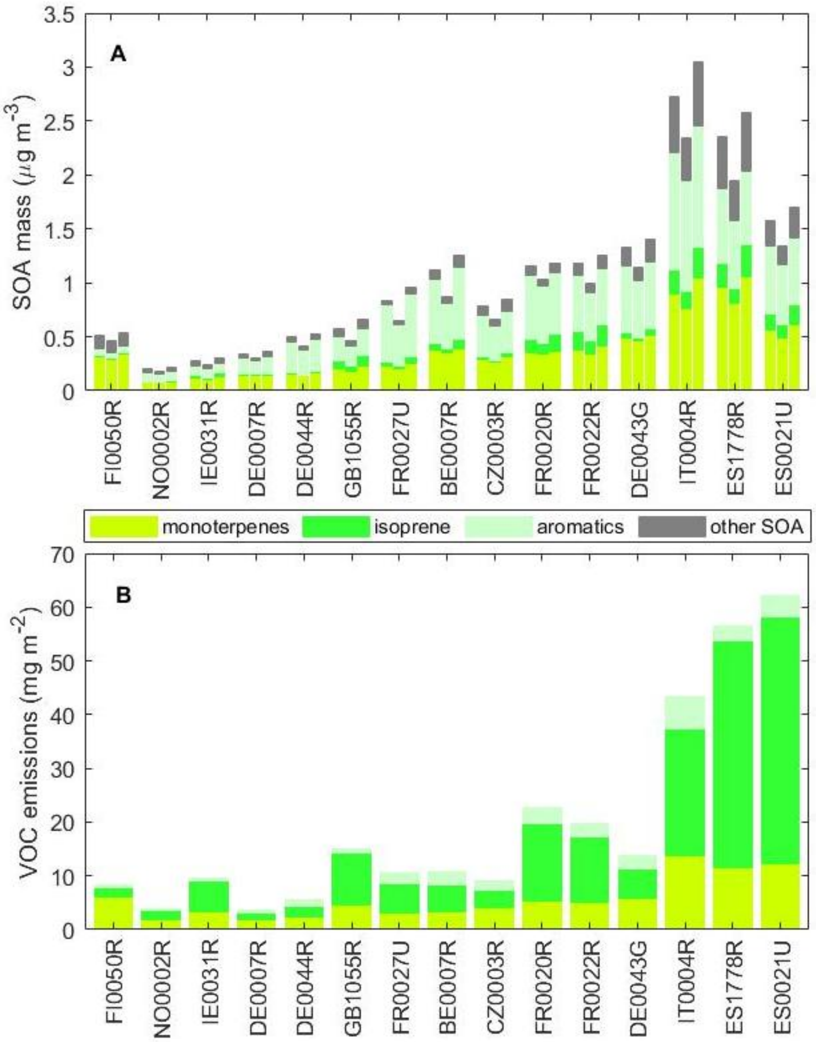


Fig. 13. Modelled averaged surface SOA mass concentrations (A) and 10-day cumulative SOA precursor emissions along the simulated air mass trajectories (B). In panel A, the three bars for each site represent the modelled average SOA mass for the basecase (left), 2xNO$_x$ (middle) and 0.5xNO$_x$ (right) simulations.

Another approach to evaluate the potential of VOCs to form aerosols is the SOA Potential (SOAP) concept as outlined by Derwent et al. (2010), which is commonly used to quantify the contribution of observed VOCs to SOA formation (Dufresne et al., 2025; Gu et al., 2021; In ’T Veld et al., 2024; Wu and Xie, 2018). In this study, we used literature-derived SOA yields to estimate SOAP at the participating sites (Fig. S11). Unlike ozone formation, where isoprene, ethene, and formaldehyde dominated, SOA formation was primarily driven by aromatics (46 ± 4 %), followed by monoterpenes (27 ± 4 %) and long-chain (C_7-C_{12}) NMHCs (16 ± 1 %). When categorising the NMHCs according to their dominant sources, fuel evaporation emerges as the most important (Fig. S11). Toluene was the most important SOA precursor, followed by benzene, sabinene, and α-pinene. It should be noted that using fixed SOA yields is a simplification, as actual yields depend strongly on atmospheric conditions such as NO_x concentrations, as shown above, and humidity. Moreover, the VOCs measured at these sites may not represent the SOA precursors from long-range transport.

The estimated SOAP results are broadly consistent with the ADCHEM model, which also identifies terpenes and aromatics as the dominant SOA precursors during the IMP campaign. However, the model substantially underestimates SOA concentrations relative to the tracer-based estimates shown in Fig 10, with deficits of up to a factor of ten at stations such as DE0007R, GB1055R, and FR0020R, and around a factor of two at Ispra (IT0004R) (Fig. S20). In contrast, the model tends to overestimate POA compared with the source-apportioned (OC_{FF}+OC_{BB}) components (Fig S20). These discrepancies point to either missing SOA sources or underestimated SOA yields. Only BSOA formed from α-pinene was available for model comparison, and the model underestimated this component by a factor of two to nine, despite considering monoterpenes beyond α-pinene. Notably, these discrepancies did not correspond directly to the differences between observed and modelled monoterpene concentrations (Fig. S21), indicating that local BVOC levels alone cannot explain BSOA levels at the site. This likely reflects short atmospheric lifetimes of BVOCs, which decouple local emissions from downwind oxidation, and subsequent BSOA formation. Overall, these results highlight the need for improved characterization of SOA sources and formation mechanisms across Europe.

3.5 Submicron particle number size distributions and atmospheric new particle formation events

Similar to tropospheric ozone formation, atmospheric NPF and growth is favoured by conditions with high photochemical activity which increases the production of strong inorganic acids such as H_2SO_4. H2SO4 form molecular clusters together with strong bases like ammonia and dimethyl amine which during favourable conditions can grow into new aerosol particles with an initial diameter of ~1 nm (Olenius and Roldin, 2022; Wollesen De Jonge et al., 2024). High ozone, OH concentrations and high ambient temperatures will also increase the production of low volatility HOM that contribute to the growth of the newly formed aerosol particles (Roldin et al., 2019; Wollesen De Jonge et al., 2024). However, simultaneously high ambient temperatures result in increasing evaporation rates of both molecular clusters and newly formed aerosol particles which tend to suppress the NPF and growth. To investigate further the aerosol formation and growth during the heatwave, both modelled and observed PNSD were assessed at 11 of the 15 stations included in the ADCHEM trajectory simulations (Table 1). The campaign median submicron particle number concentrations (PNC) of particles larger than 10 nm in diameter were underestimated at all stations (Fig. S22), which indicate missing particle sources. This can likely be a result of underestimated nanoparticle growth rates (GR) as a result of the underestimated SOA formation.

ADCHEM simulates PNSD from 1 nm (dry diameter) to 10 µm, while DMPS or SMPS observations typically cover diameters from about 10 nm to 800–900 nm. Apparent NPF and subsequent growth were observed at all 11 stations on several days during the campaign. At several central European sites, Neuglobsow (DE0007R), Melpitz (DE0044R), ATOLL Villeneuve d'Ascq (FR0027U), and Vielsalm (BE0007R), NPF and growth occurred almost daily. Fig. 14 compares modelled and measured submicron PNC at Vielsalm; additional comparisons for Melpitz and Kosetice (CZ0003R) are provided in the Supplement (Fig. S23-S24) to illustrate typical NPF and growth patterns at representative continental sites as all three stations are influenced by relatively clean marine NW air masses but represent cases with different distance (time over the continent) before the air mass arrives at the stations.

According to ADCHEM, the strong NPF and growth events observed at sites in central and northern European sites (Germany, Belgium, northern France, and the Czech Republic) were primarily associated with relatively clean northwesterly air masses crossing the North Sea 1–2 days prior to arrival. The most pronounced event occurred on 17 July, with particle growth continuing into 18 July, followed by a second, weaker formation event. The onset of this major regional NPF and particle growth event was qualitatively well captured by the model at all stations. During transport, newly formed particles grew by condensation of inorganic species, primarily H_2SO_4 (from marine DMS and anthropogenic SO_2), as well as organic vapours (Fig S25-S27). At Melpitz, weaker NPF events were first initiated several days upwind via ion-mediated NH_3–H_2SO_4 nucleation near the Faroe and Shetland Islands, then intensified near the North German coast. At Vielsalm, NPF began near the northern coast of Scotland and the Orkney Islands and intensified as air masses passed near Amsterdam and approached the site. For Kosetice, air masses crossed the North Sea near Hamburg on 16 July, triggering strong NH_3–H_2SO_4 nucleation over northern Germany (also observed at Neuglobsow and Melpitz), with continued growth over eastern Germany and the Czech Republic on 17 July. For Vielsalm the modelled nanoparticle growth during the NPF event on 17 July is well captured, while for Melpitz and Kosetice the nanoparticle growth is significantly underestimated (Fig. S28-S30). The ultrafine particles (UFP, <100nm), that were likely formed by NPF in the morning and measured at all three sites in the midnight between 17 and 18t of July had a geometric mean diameter (GMD) of approximately 60 nm, while the modelled GMD are around 25 nm at Melpitz, 35 nm at Kosetice and 70 nm at Vielsalm. This corresponds to average particle GR from 10 am to midnight of around 1.7, 2.5 and 5.0 nm h^{-1}, respectively.

The significantly higher modelled GR along the air mass trajectories arriving at Vielsalm compared with the other two stations is primarily a result of significantly more condensation of anthropogenic organic vapours (ASOA). This demonstrates that the SOA formation and observed NPF and growth events during the campaign are strongly interlinked, and the underestimated SOA formation in the model is likely one of the main reasons why the model underestimates the PNC at the stations. However, higher BVOC emissions do not necessarily result in increased PNC, since increasing VOC emissions also tends to reduce OH concentrations and thus lower sulfuric acid production, which can suppress NPF. Therefore, the ADCHEM model setup without BVOC emissions results in similar or lower PNC than the base case at all stations except at FI0050R (Fig S22). The model simulations with modified anthropogenic NOx emissions (2xNOx or 0.5xNOx) demonstrate that NOx has a complex impact on NPF and growth. Increasing NOx tends to increase the atmospheric oxidation capacity (OH and O_3 concentrations) enhancing the oxidation of VOCs and SO_2 and the production of O-VOCs and H_2SO_4, which may lead to more numerous particles and increased H_2SO_4 and O-VOCs driven condensation particle growth. At the same time the formed O-VOCs tend to be more volatile under high-NOx conditions, which can in contrast reduce nanoparticle GR. The net effect of increasing or decreasing NOx can therefore lead to either higher or lower PNCs (Fig. S22, S25-S30).

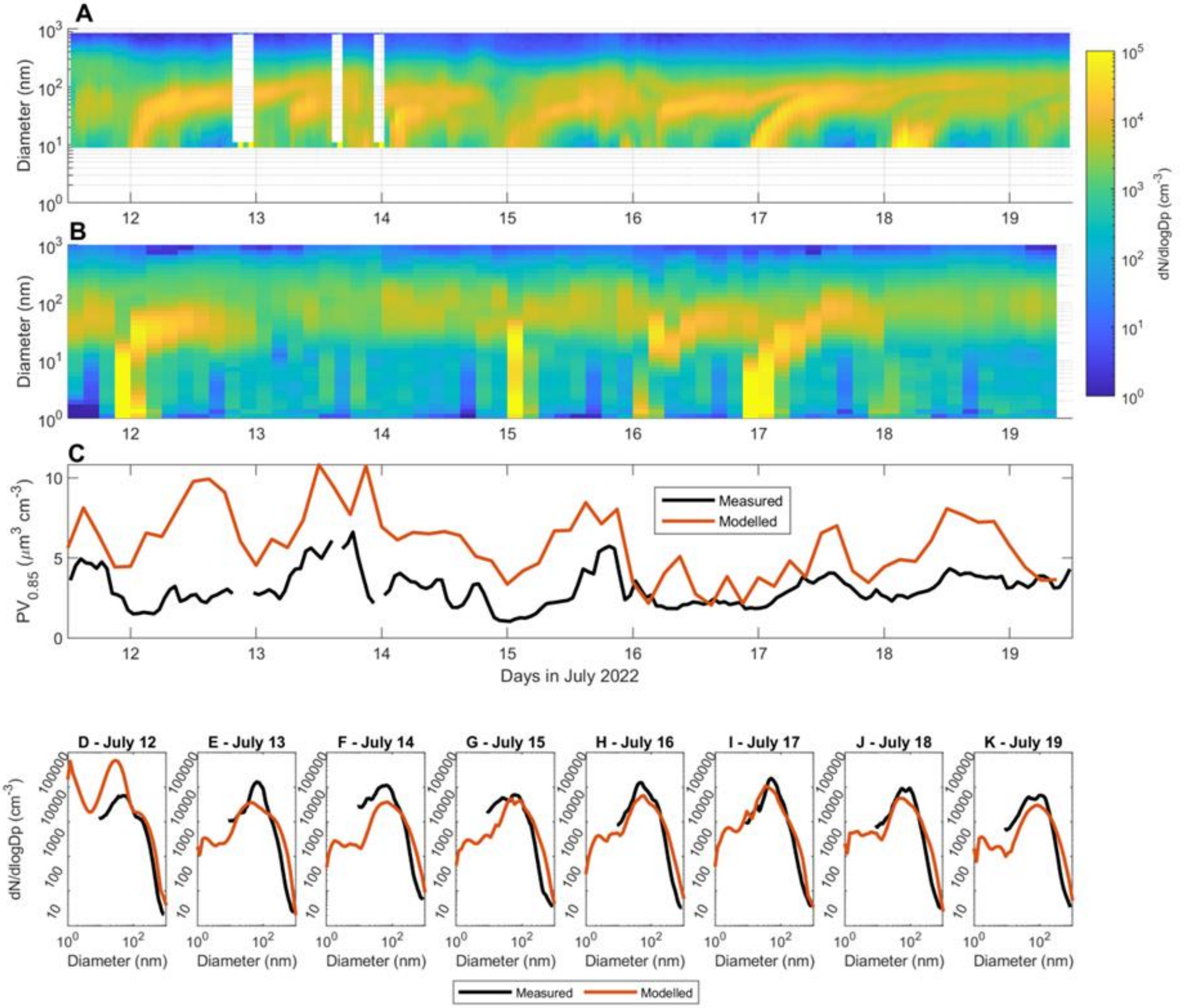


Fig. 14. Modelled and measured submicron particle concentrations at Vielsalm (BE0007R). Panels A and B show the measured and modelled PNSD at the station from July 12 to July 19, respectively. Panel C compares the measured and modelled particle volume

concentrations for particles smaller than ~0.85 µm in diameter. Panels D to K compare the measured and modelled median particle number size distributions for each campaign day.

Conclusion

The 2022 summer heatwave in Europe provided a unique opportunity to investigate the interactions between meteorology, emissions, and atmospheric chemistry during extreme climate events. The comprehensive observations and modelling in this study show that elevated ozone, OA, and ultrafine particle (UFP) levels were driven by a combination of persistent high-pressure systems, enhanced biogenic emissions due to high temperatures, and anthropogenic precursor emissions.

During the campaign, the highest ozone peaks were driven by a combination of elevated BVOC and NOx emissions, and ozone formation was similarly sensitive to both NOx and BVOC at most sites. Further reductions in NOx emissions would therefore effectively lower ozone levels during extreme pollution events. Isoprene (mainly biogenic), NMHCs (mostly from combustion sources), and O-VOCs (from mixed sources) dominated the ozone formation potential, with aromatics playing a larger role in urban areas. O-VOCs represented the largest fraction of total VOCs, yet are currently measured at only a few sites in Europe; their importance for ozone production underlines the need for broader and more long-term monitoring of these compounds. Terpenes, which are important precursors for SOA formation, are also not regularly monitored.

The majority of OA was secondary in origin (about 80 %, depending on site and size fraction), with substantial contributions from both biogenic and anthropogenic precursors. Aromatic VOCs were the dominant SOA precursors, followed by monoterpenes. Model results substantially underestimate SOA and UFP concentrations, highlighting the need for further research to fully characterize the sources and formation mechanisms of secondary aerosols in Europe.

The IMP2022 campaign was relatively short and included few online VOC measurements, limiting the assessment of temporal variability, and the dataset was too limited to perform a detailed source apportionment analysis. To address these gaps, a follow-up campaign, led by EMEP/TFMM in collaboration with ACTRIS and RI-URBANS, was conducted in September 2024, focusing on high-resolution VOC measurements near key emission sources and coordinated observations at regional sites.

Overall, these findings underline the intertwined roles of anthropogenic and biogenic emissions in shaping air quality during heatwaves. A complete understanding of air quality therefore requires monitoring both biogenic and anthropogenic precursors, as well as tracers of the various classes of OA components, both primary and secondary. As climate change is expected to increase the frequency and intensity of such extreme events, air quality management must account for the additional risks these conditions pose.

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Data availability

All data used in the present paper are open access and are available at http://ebas.nilu.no/. An Excel file with the data in harmonised units and selected aggregations are available, including a link to their respective DOIs.

Author contributions

WAa, TS, RW, HH, KEY, JLJ, SS, ST were responsible for conceptualizing the study. WAa wrote the original draft of the paper with contributions from TS, RW, HH, JLJ, PR, AT, KEY, SS, ST, JPP, BB. TS, MDf performed the centralised O-VOC analysis, HH, TT conducted the terpene analysis, RW, RD, LK, DKl did the centralised NMHC analysis while JLJ, VNT, SD, MDu performed the centralised tracer analysis. PR, AT, ÅW provided the ADCHEM model results and DS, ST, YG contributed with EMEP model results. PH provided isoprene emission data. Site measurements were provided and quality-assured by the following contributors: IB (AT0002R); BB, MDy, MG, CA, BV, NS (BE0007R); SR (CH sites); TJ, EB (Cyprus); AH, JP (CZ0003R); JR, BH (DE0007R, DE0008R); LP, UK, HaH (DE0044R); DKu, ACl, RH (DE0043G); AMYS, MPE, RS, AA (ES0019U, ES1778R); BART, FJGM, EDR, EAB (ES0021U); MCG, GG, BART (ES0025U); IY, TP (FI0050R); AF, ET, TS (FR0008R, FR0013R, FR0018R); VR (FR0027U); AB, EF, ACo (FR0030R); VG, LS (FR0020R); TS (FR0022R); DB, IS, JD, KW, CR, MT, StR, MJ (UK sites); DC, KF, JG (IE0031R); JPP, NJ (IT0004R); JA, AM, MM, LR (IT0009R); WAa, KEY (NO0002R).

Competing interests

Tuukka Petäjä is member of the editorial board of ACP

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