

**GUIDANCE DOCUMENTS ON MEASUREMENTS & MODELLING
OF NOVEL AIR QUALITY POLLUTANTS:
VOLATILE ORGANIC COMPOUNDS**



**Research Infrastructures Services Reinforcing Air
Quality Monitoring Capacities in European Urban &
Industrial Areas (GA n. 101036245)**

By

with collaboration



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Table of Contents

ABBREVIATIONS.....	I
CHEMICAL SYMBOLS.....	II
1. ABOUT THIS DOCUMENT	1
2. DEFINITION OF VOC.....	1
3. VOC MEASUREMENT METHODS AND QUALITY CONTROL	3
3.1 REFERENCE METHODS.....	6
3.2 OTHER EXISTING RELEVANT GUIDANCE	7
3.2.1 NMHC online measurements.....	7
3.2.1.1 Sampling.....	8
3.2.1.2 Analysis	8
3.2.1.3 Calibration.....	8
3.2.1.4 Uncertainty calculation	9
3.2.2 VOC online measurements using PTR-MS	9
3.2.2.1 Sampling.....	10
3.2.2.2 Analysis	10
3.2.3 NMHC offline measurements	10
3.2.3.1 Sampling.....	10
3.2.4 OVOC offline measurements	11
3.2.4.1 Sampling.....	11
3.2.5 Instrument performance evaluation	11
4. PAN-EUROPEAN OVERVIEW	11
4.1 CONCENTRATIONS	11
4.2 EMISSIONS.....	16
4.3 IMPACTS	18
5. RECOMMENDATIONS	19
6. REFERENCES	21

ABBREVIATIONS

AAQD	Ambient Air Quality Directive (2024/2881/EC)
ACTRIS	Aerosols, Clouds and Trace gases Research InfraStructure
ACTRIS – CiGas	ACTRIS Center for Reactive Trace Gases In Situ Measurements
CCL	Central Calibration Laboratory
CEN	European Committee for Standardization
CIMS	Chemical ionization mass spectrometry
DC	Direct current
EMEP	European Monitoring and Evaluation Programme
EN	European Standard
FID	Flame ionisation detector
GAW	Global Atmospheric Watch programme by WMO
GC	Gas chromatography
HPLC	High-performance liquid chromatography
IN	Industry
ITEX	In-tube extraction
MIR	Maximum incremental reactivity
MOFP	Maximum O ₃ formation potential
MS	Mass spectrometry
MSD	Mass spectrometry detector
NMHC	Non-methane hydrocarbons
NPL	The National Physical Laboratory
NTME	Needle trap microextraction
PID	Photoionisation detector
PTR	Proton transfer reaction
QA/QC	Quality assurance and quality control
QMS	Quadrupole mass spectrometer
RI-URBANS	Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial AreaS EU-project
SBSE	Stir bar sorptive extraction
SI	International System of Units
SIFT	Selected ion flow tube
SOA	Secondary organic aerosols
SOAP	SOA formation potential
SOP	Standard operating procedures
SPDE	Solid-phase dynamic extraction

SPME	Solid-phase microextraction
ss	Statistically significant
TD	Thermal desorption
ToF-MS	Time of flight mass spectrometry
TR	Traffic
UB	Urban background
UV	Ultraviolet radiation
WMO	World Meteorological Organization

CHEMICAL SYMBOLS

AVOC	Anthropogenic volatile organic compounds
Br	Bromine
BVOC	Biogenic volatile organic compounds
CH₄	Methane
Cl⁻	Chlorine
CF₃O⁻	Trifluoromethoxide
CH₃COO⁻	Acetate
DNPH	Dinitrophenylhydrazine
H₃O⁺	Hydronium ion
HCHO	Formaldehyde
I⁻	Iodine
KI	Potassium iodide
NH₄⁺	Ammonium
NO	Nitrogen monoxide
NO₂	Nitrogen dioxide
NO₃	Nitrate
NO_x	Nitrogen oxides (NO+NO ₂)
O₂	Molecular oxygen/dioxygen
O₃	Ozone
OH	Hydroxyl radical
OVOC/oxy-VOC	Oxygenated volatile organic compounds
SF₆⁻	Sulfur hexafluoride
VOC	Volatile organic compounds

1. ABOUT THIS DOCUMENT

This document is connected to the Ambient Air Quality Directive 2024/2881/EC (AAQD) of the European Parliament and of the Council on ambient air quality and cleaner air for Europe (published on 20th November 2024). This document was prepared as part of the "Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial AreaS" (RI-URBANS) EU-project that aims at integrating the atmospheric observation expertise from the Aerosols, Clouds and Trace gases Research InfraStructure (ACTRIS) and the urban air quality observation capacities of the regulatory air quality monitoring networks.

The directive underlines the importance of emerging pollutants to air quality and well-being of the citizens. The main objectives of the measurements of ozone precursor substances are to analyse any trend in ozone precursors, to check the efficiency of emission reduction strategies, to check the consistency of emission inventories, to support the understanding of ozone formation and precursor dispersion processes, as well as the application of photochemical models, and to help attribute emission sources to observed pollution concentrations (Annex VII, Section 3, A.). It was also mentioned that Member States may use the method they consider suitable for the objective sought and methods that are being standardised by the European Committee for Standardization (CEN) once available.

In order to ensure that the information collected on air pollution is sufficiently representative and comparable across the Union, it is important that standardised measurement techniques and common criteria for the number and location of measuring stations are used for the assessment of ambient air quality. The aim of this document is to facilitate upscaling of measurement techniques for volatile organic compounds (VOCs) within air quality monitoring networks. We provide an up-to-date summary of the methodologies related to VOC sampling and analysis, summarize recent scientific synthesis of Pan-European observations and provide recommendations on the measurements of VOCs. However, this document does not describe methane measurement techniques.

This is a RI-URBANS/ACTRIS guidance for this specific service tool that is part of the RI-URBANS deliverable D46 (D6.1, containing guidance for all service tools provided in the project) with the support for publication from AXA Research Fund to build up the final dissemination D55 (D7.6). Any dissemination of results must indicate that it reflects only the author's view and that the European Commission is not responsible for any use that may be made of the information it contains.

In addition, source apportionment of VOCs is described in another guidance document [ST11](#) by RI-URBANS, see <https://riurbans.eu/project/#service-tools>.

2. DEFINITION OF VOC

Volatile organic compound (VOC) means any organic compound having an initial boiling point¹ less than or equal to 250°C measured at a standard pressure of 101,3 kPa, based on the EU Directive 1999/13/EC of 11 March 1999. Since the volatility² of a compound is generally higher when the boiling point is lower, the volatility of organic compounds is usually classified using their boiling points.

¹ Initial boiling point is the lowest temperature at which the liquid begins to boil.

² Volatility is indicated by a substance vapor pressure. Substances with higher vapor pressure will vaporize more readily at a given temperature than substances with lower vapor pressure.

Complexity of the pool of ambient VOCs

The compounds classified as VOCs exhibit a variety of functional groups and can be categorized by certain structural and reactive features, according to the way carbon bonds to itself or another element, e.g. carbon double bonded to oxygen. These different ways of bonding will lead to different reactivities with ambient oxidants (OH, NO₃, O₃). Table 1 presents the different families of VOCs based on their functional groups.

Table 1. Chemical families of VOCs.

Family	Molecular formula	Functional group (R=Alkyl group)
Alkanes	C _n H _{2n+2}	-C-C-
Alkenes	C _n H _{2n}	-C=C-
Alkynes	C _n H _{2n-2}	-C≡C-
Halocarbons	C _n H _{2n+1} X	-X: F, Cl, Br, I
Alcohols	C _n H _{2n+2} O	-OH
Ethers	C _n H _{2n+2} O	R-O-R
Aldehydes	C _n H _{2n} O	R-CH(O)
Ketones	C _n H _{2n} O	R-C(O)-R
Carboxylic acids	C _n H _{2n} O ₂	R-C(O)OH
Esters	C _n H _{2n} O ₂	R-C(O)-OR
Amines	C _n H _{2n+1} NH ₂	-NH ₂
Nitriles	C _n H _{2n-1} N	≡N

Typically abundant compounds observed in ambient air and commonly reported in the literature include hydrocarbons such as alkanes (ethane, propane, and higher compounds), alkenes (ethylene, propene, etc.), aromatics (benzene, ethylbenzene, toluene, C₈- and C₉-aromatics, styrene), biogenic compounds (isoprene, monoterpenes, sesquiterpenes), and oxygenated VOCs (oxy-VOCs) such as alcohols (methanol, ethanol, etc.), ketones (acetone, methyl ethyl ketone, etc.), aldehydes (formaldehyde, acetaldehyde, etc.), carboxylic acids (formic, acetic, etc.) and other families reported in Table 1. Terpenes are in general highly reactive and their oxidation leads, among others, to the formation of oxy-VOCs of various volatilities and chemical structures with different properties (reactivity, stickiness, etc.). Oxygenated VOCs also play an active role in the chemical reactions chain of the atmosphere and are precursors of photochemical ozone and Secondary Organic Aerosol (SOA), as all the VOC chemical families. These compounds (oxy-VOCs including formaldehyde, and terpenes) are among the recommended World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) measurement variables (GAW-WMO, 2017). The measurement of these compounds is challenging due to their reactivity, as these compounds interact with surfaces, leading to possible artefacts during the sampling stage due to adsorption and desorption effects or to the ozonolysis of unsaturated VOCs in the sampling lines.

The VOCs listed in Annex VII of the Ambient Air Quality Directive 2024/2881/EC cover different chemical families including non-methane hydrocarbons (NMHCs), oxygenated VOCs and terpenes.

The AAQD mentions that measurement of ozone precursors shall include at least nitrogen oxides (nitrogen monoxide NO and nitrogen dioxide NO₂), and as appropriate, methane (CH₄) and VOCs. The selection of the specific compounds to be measured will depend on the objective sought and may be completed by other compounds of interest.

3. VOC MEASUREMENT METHODS AND QUALITY CONTROL

Figure 1 reports on different techniques that have been recently used for VOC measurements, including chemical ionization mass spectrometry (CIMS), proton transfer mass spectrometry (PTR-MS), selected ion flow tube mass spectrometry (SIFT-MS), and atmospheric pressure interface CIMS (API-CIMS), together with chromatography associated with various detection methods. On the one hand, a technique using mass spectrometry can offer a very good temporal resolution (few seconds to few minutes) compared to gas chromatography (GC) and high-performance liquid chromatography (HPLC) techniques (one hour in general), but on the other hand these techniques are limited in the number of compounds that can be speciated. In contrast, GC techniques provide a better speciation for a large number of compounds at the expense of time resolution.

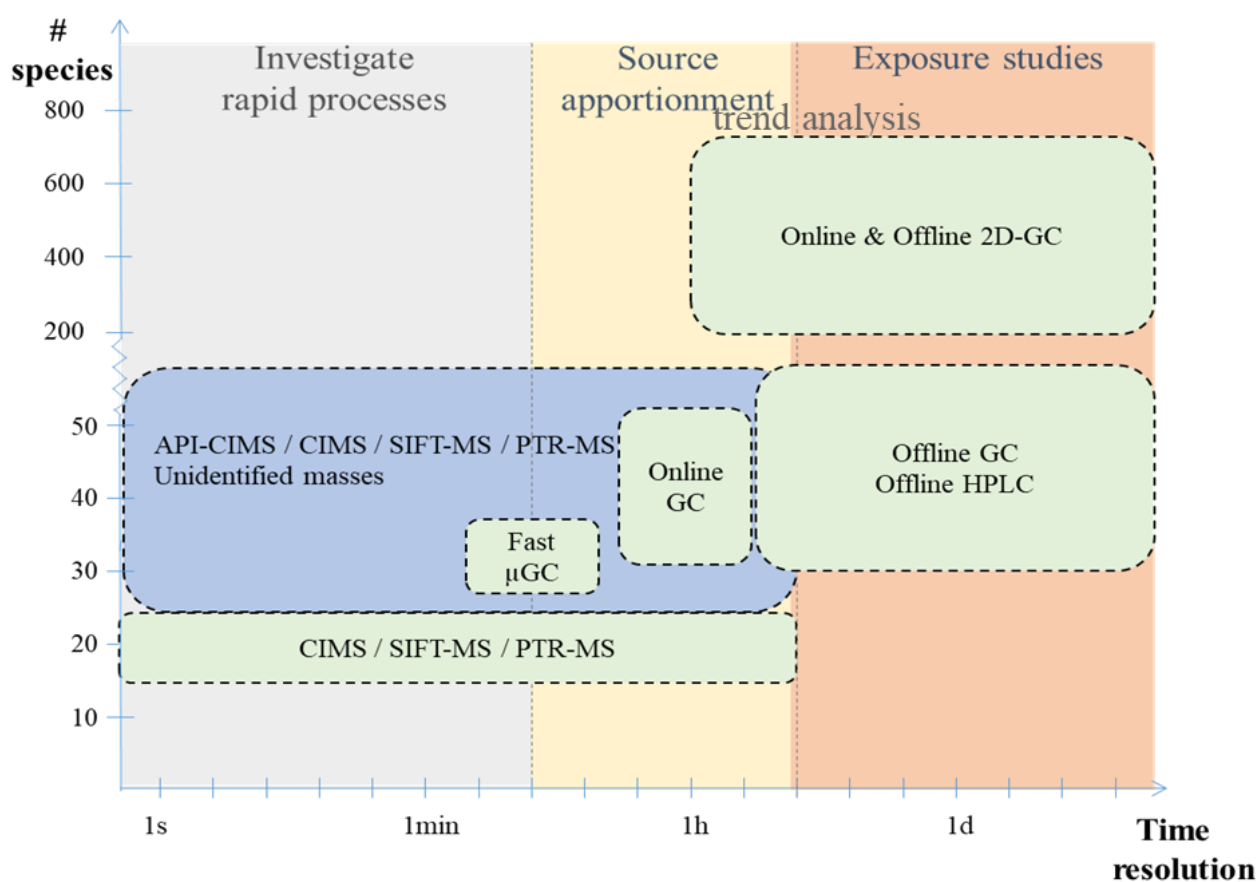


Figure 1. Schematic diagram of different techniques commonly used for ambient VOCs measurements. Technique performances are shown based on the number of speciated species and the measurement time resolution. Green boxes correspond to molecular and isomer identification and blue boxes to molecular identification only.

These techniques have to be chosen depending on the application. The use of online instrument with a high temporal resolution is particularly useful in studies where probing fast processes is the main point of interest, such as emissions of pollutants and possible chemical reactions and/or transformations. Online GC and offline methodologies (i.e., HPLC, canister or tube sampling/offline analysis by GC) permit the measurement of a large pool of compounds with a time resolution ranging from 1 hour to several days, which is of particular interest for source apportionment, trend analysis or exposure studies. A summary of the general features, the advantages and some drawbacks of the abovementioned techniques is given in the table below (Table 2).

The AAQD indicates that Member States may use the method which is considered to be suitable for the monitoring objective sought, however, once available, standardised reference methods shall be applied.

Table 2. Overview of VOC measurement techniques (including formaldehyde), advantages and drawbacks, general features and considerations (Salameh et al., 2022). Continues on next pages.

Sampling and analysis techniques		Advantages	Drawbacks	General features and considerations
Off-line sampling	Pumped sampling with sorbent tubes	Extended range of different VOC families (captured simultaneously) with multi-layered adsorbent-packed tubes or traps with up to four different adsorbents, good adsorption properties, sorbent tubes can be re-used, analysed by GC-FID/MS	Possible instability of the particles of the adsorbent, possible degradation during preparation or over time, possible losses due to stickiness or through aerosol formation and/or back-diffusion of target compounds	When selecting a suitable adsorbent or adsorbent combination consider: adsorbent strength, artefacts, hydrophobicity, inertness, thermal stability and fragility, sampling times: few hours, sampling flows: 50-200 mL min ⁻¹
	Passive sampling with sorbent material	Extended range of different VOC families (captured simultaneously) by axial or radial diffusion into a sampler containing typically one sorbent material (e.g. Carbopack X, Carbograph 5TD, Tenax TA), low sampling Costs, analysed by GC-FID/MS	Relative low sampling rates and large uncertainties; sampling of VOCs is sorbent specific (no universal solution); possible influence of humidity and temperature; need of protection shields; limitation in desorption efficiency (solvent desorption)	When selecting a suitable sorbent consider: sorbent sampling rate for the specific VOC, artefacts, hydrophobicity, inertness, thermal stability and fragility; sampling periods of 1 day – 4 weeks
	Miniaturized adsorbent-based air sampling techniques	Easy operation, short sampling times, small sampling volumes, small/no organic solvent consumption, automation of analytical operations, and on-line coupling with analytical instruments (GC-MS, PTR-MS)	Storage instability, possibly not quantitative	Techniques: needle trap microextraction (NTME), in-tube extraction (ITEX), sorption trap, solid-phase microextraction (SPME fiber, SPME Arrow, retracted SPME fiber), thin-film microextraction (TFME), solid-phase dynamic extraction (SPDE), and stir bar sorptive extraction (SBSE)
	Pumped sampling with 2,4-Dinitrophenylhydrazine (DNPH) cartridge	Robust method: Specific for carbonyl compounds (aldehydes and ketones)	Possible contamination during preparation, storage at dark and at <4 °C, biases due to RH impact on ketones and ozone interferences; the cartridge cannot be re-used	Sampling times: 1–24 h, sampling flow 1–1.5 L/min Liquid extraction and analysis by HPLC/UV
	Canisters	Whole air sampling, filled canisters are either analysed on-site or transported back to a laboratory and analysed (GC-MS, GC-FID)	Possible contamination (memory effects), adsorptive losses of larger or more functionalized compounds (>C ₇) during storage or transport, potential interactions with co-collected water vapor and oxidants	Sampling times: grab samples or time averaged samples from minutes to hours

Sampling and analysis techniques		Advantages	Drawbacks	General features and considerations
Online techniques	Gas Chromatography	Medium cost, high sensitivity, excellent reproducibility, large resolving power (MS)	Slower time resolution (if more than a few species are measured), difficult to identify more polar, surface sticky compounds, sensitivity might decrease with time	Sampling times: 20–90 min, limits of detection: low pmol/mol range
	Proton Transfer Reaction Mass Spectrometer	Trace gases analysed shortly after sampling, continuous meas., soft ionization & limited fragmentation, large resolving power, high sensitivity, high time resolution, powerful to detect oxy-VOCs	High cost, blind to alkanes, no selective measurements of most alkenes and alcohols, no isomeric separation	Ionization based on proton affinity (reagent ions: H_3O^+ , NH_4^+), sampling times: down to hundreds of milliseconds, limits of detection: low pmol/mol range
	Selected ion flow tube mass spectrometry	Soft ionization technique (softer than PTR-MS), fast analysis of specific trace gases in polluted atmosphere and exhaled breath	High cost, unit mass resolution, lower sensitivity than PTR-MS, larger losses of reagent ions than PTR-MS	Dilution with helium, reagent ions: H_3O^+ , NO^+ , and O_2^+ , sampling times: seconds, limits of detection: nmol/mol range
Online techniques (continuation)	Chemical ionization mass spectrometer	Trace gases analysed shortly after sampling, continuous meas., soft ionization & limited fragmentation, large resolving power, high sensitivity, high time resolution, powerful to detect oxy-VOCs	High cost, no isomeric separation, no isobaric separation	Ionization based on charge transfer or hydride abstraction (reagent ions: Br^- , I^- , Cl^- , CF_3O^- , CH_3COO^- , SF_6^-)
	Micro Sensors	Low-cost technology	Poor specificity, poor accuracy, poor sensitivity, long-term instability, possible interferences by atmospheric oxygen or humidity, only for certain VOCs	Different types: metal oxides, PID, electrochemical

Sampling and analysis techniques		Advantages	Drawbacks	General features and considerations
Formaldehyde	Diffusion with DNPH cartridge	Low sampling costs	Possible contamination during preparation, storage at dark and at $<4^\circ\text{C}$, biases due to humidity impact on ketones and ozone interferences	Sampling times: 24–72 hours, detection limits: 40 pmol/mol Liquid extraction and analysis by HPLC/UV
	Pumped with DNPH cartridge	Low sampling costs	Possible contamination during preparation, storage at dark and at $<4^\circ\text{C}$, biases due to humidity impact on ketones and ozone interferences	Sampling times: 1–24 h, sampling flow 1–1.5 L/min, detection limits: 40 pmol/mol Liquid extraction and analysis by HPLC/UV
	Fiber laser-induced fluorescence	Continuous meas., based on absorption laser beam tunable in the 353–355 nm range	Single absorption feature, one detector	Sampling times: Hz–sec, detection limits: <50 pmol/mol

Sampling and analysis techniques		Advantages	Drawbacks	General features and considerations
Formaldehyde (continuation)	Non-resonant laser-induced fluorescence	Time-resolved meas., multiple absorption features simultaneously, two detectors, increased selectivity	Decreased sensitivity	Sampling times: 1 sec, detection limits: <130 pmol/mol at 1 sec, 60 pmol/mol at 10 sec
	Hantzsch fluorimetry	Well established online method, liquid and gaseous measurement modes available	Data provided represent a running average due to a low response time of the instrument (~1.5 min depending on liquid flow rates); Interference from Methanediol possible	Sampling times: continuously (Data acquisition time ≥ 1 sec), detection limits: 50–80 pmol/mol
	Incoherent Broadband Cavity Enhanced Absorption Spectroscopy	Based on the absorption properties of HCHO near UV, broad spectral fitting	Possible poor precision in UV range due to attenuation and scattering of the UV light by ambient air, limitations on powerful materials availability (LED, charge coupled device, cavity mirrors) for the UV range	Sampling times: 30 sec, detection limits: 65 pmol/mol at 450 sec, 210 pmol/mol at 30 sec
	Cavity ring-down spectroscopy	Based on time rate of adsorption, continuous fast photodetection, amount fractions independent of laser intensity fluctuations	Single-frequency continuous-wave laser, not sensitive to trace gases	Sampling times: few sec, detection limits: 300 pmol/mol at 300 sec
	Microfluidic Hantzsch fluorimetry (microF)	Near real-time continuous measurement. Based on Hantzsch reaction and fluorimetry detection. Portable analyser	Requires reagent refill or consumable change every 3–4 days, 10–15 min response time. Ongoing upgrade of the system by the manufacturer	Sampling time: continuous (acquisition frequency 10 sec), Detection limits: 1000 pmol/mol
	Tunable infrared laser direct absorption spectroscopy	Direct absorption measurements in the mid-infrared region, increased sensitivity	High cost, tuning of the instrument depending on the application	Sampling times: 1 sec, detection limits: <100 pmol/mol, high Flow rate (12 L/min)

3.1 Reference methods

Currently, reference methods are available only for the measurement of benzene. The five European standards related to benzene measurements published by the European Standardization Body (CEN/TC 264/WG12) are:

- EN 14662-1:2024: «Ambient air quality - Standard method for measurement of benzene concentrations - Part 1: Pumped sampling followed by thermal desorption and gas chromatography »
- EN 14662-2:2005: « Ambient air quality - Standard method for measurement of benzene concentrations - Part 2: Pumped sampling followed by solvent desorption and gas chromatography »
- EN 14662-3:2015: « Ambient air — Standard method for the measurement of benzene concentrations — Part 3: Automated pumped sampling with in situ gas chromatography »
- EN 14662-4:2005: « Ambient air quality Standard method for measurement of benzene concentrations - Part 4: Diffusive sampling followed by thermal desorption and gas chromatography »
- EN 14662-5:2005: « Ambient air quality Standard method for measurement of benzene concentrations - Part 5: Diffusive sampling followed by solvent desorption and gas chromatography »

The three first European standards are European reference methods, while the two latter may be used for, e.g., indicative measurements. More specifically, the “EN 14662-3:2015 - Ambient Air Quality - Standard method for the measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography”

specifies a semi-continuous measurement method for the determination of the concentration of benzene present in ambient air based on automated sampling and analysis by gas chromatography. This standard describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate automated gas chromatograph (GC) by means of type approval tests. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the data quality requirements as specified in Annex I of Directive 2008/50/EC and requirements during sampling, calibration and quality assurance for use.

In 2019, a new working group (CEN/TC 264/WG13) was established, where ACTRIS – CiGas (<https://www.actris.eu/topical-centre/cigas>) contributes, with the objectives of developing validated standard measurement methods for the measurement and monitoring of VOC ozone precursors in ambient air in order to ensure a harmonized implementation of the Air Quality Directive (2008/50/EC). The Commission mandated CEN TC264/WG13 to develop European Standards for the measurement of ozone precursors listed in Annex X of the 2008/50/EC directive (with exclusion of total non-methane hydrocarbons) using the following techniques:

- Automatic pumped sampling, preconcentration and online analysis by thermal desorption gas chromatography (TD/GC) with flame ionisation detector (FID) and/or mass spectrometry detector (MSD) for non-methane hydrocarbons (alkynes, alkanes, alkenes, aromatic hydrocarbons) with exclusion of formaldehyde;
- Manual or automatic pumped sampling, followed by offline TD/GC with FID and/or MSD for non-methane hydrocarbons (alkynes, alkanes, alkenes, aromatic hydrocarbons) with exclusion of formaldehyde;
- Manual or automatic canister sampling, followed by offline TD/GC with FID and/or MSD for non-methane hydrocarbons (alkynes, alkanes, alkenes, aromatic hydrocarbons) with exclusion of formaldehyde;
- Diffusive sampling, followed by offline TD/GC with FID and/or MSD for non-methane hydrocarbons (alkynes, alkanes, alkenes, aromatic hydrocarbons) with exclusion of formaldehyde;
- Manual or automatic pumped sampling of formaldehyde on dinitrophenylhydrazine (DNPH) followed by off-line high-performance liquid chromatography (HPLC) / ultraviolet (UV) detection;
- Diffusive sampling of formaldehyde on DNPH followed by off-line HPLC/UV detection.

While these six techniques expected to be later published as technical specifications (TS), are particularly applicable to the measurement of the 30 VOCs (29 NMHCs plus formaldehyde) listed in Annex X of the 2008/50/EC directive, some of them also enable the measurement of additional VOCs listed in the AAQD 2024/2881/EC. For instance, aldehydes (acetaldehyde, methacrolein) and ketones (acetone, methyl ethyl ketone, methyl vinyl ketone) can be directly measured applying DNPH sampling plus HPLC analysis, while other oxygenated VOCs (alcohols: methanol, ethanol) or terpenes (p-cymene, limonene, β -myrcene, α -pinene, β -pinene) can be measured by gas chromatography technique with suitable methods and analytical set-ups.

In addition, ISO 16000-3 and ISO 16000-4 describe the collection of ambient air samples for the measurement of formaldehyde and carbonyls, such as ketones or aldehydes, by respectively pumped sampling and diffusive sampling of indoor air.

3.2 Other existing relevant guidance

In addition to these existing or under-development standards, the World Meteorological Organization - Global Atmosphere Watch (WMO GAW), the co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP), and the European Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) - Central Facility for reactive trace gases in-situ measurement (CiGas) have developed guidelines and Standard Operating Procedures (SOP) for the main online and offline measurement techniques, which are described briefly below:

3.2.1 NMHC online measurements

The ACTRIS topical centre for reactive trace gases in-situ measurement has developed a measurement guideline for the measurement of NMHC (ACTRIS, 2018) with the objectives of harmonizing methodologies, Quality Assurance/Quality Control (QA/QC) procedures, and uncertainty calculation considering the specificities of the various types of instruments used. This guideline focuses on NMHC measurements by GC-FID/PID/MS techniques. In respect to the quality assurance, the guideline forms the basis of the WMO guideline (GAW-WMO, 2023). As for monoterpenes and oxygenated VOCs (OVOCs) as well as other VOC analysis techniques (e.g. PTR-MS) separate measurement guidelines will be published within ACTRIS.

According to the ACTRIS guideline, recommendations for NMHC measurements are:

3.2.1.1 Sampling

- If online sampling is possible then it should be prioritized to offline sampling. In case of offline sampling, sorbent tubes, stainless-steel canister or passivated stainless-steel canister (SilcoNert 2000[®] treated) should be prioritized following the SOP described in the GAW-WMO Report 204 (GAW-WMO, 2012), and in the future CEN technical specification.
- The inlet line connecting the instrument to the manifold should be optimized for minimum surface area and residence time, and it should be flushed prior to sampling for a sufficient time to equilibrate surfaces. The residence time between the manifold and the instrument should not exceed a few seconds. It is recommended to use a high flow inlet manifold to transfer samples with short residence time from the inlet to the laboratory (<1 min). From there, small diameter and short sampling lines go to the sampling devices or directly to the instruments. For NMHCs, the manifold and sampling line should preferentially consist of surface passivated steel (e.g. silcosteel[®] or sulfinert[®]) or glass.
- An ozone (O₃) scrubber should be used to remove O₃ from the sampling line and avoid the reaction of unsaturated, reactive NMHCs with O₃, and it should be changed regularly every few months.
- A particle filter should be installed to avoid contamination of the system with particles, and changed regularly every few months.
- A water removal system is necessary for GC instruments. Water management can be achieved by different methods such as a Nafion[®] dryer or a cold trap. The use of cold traps is recommended because these systems are less prone to artefacts. For NMHCs measurements, a Nafion[®] dryer is usually used despite artefacts for some alkenes (1-butene and isobutene). The Nafion[®] dryer is not adapted to the measurement of OVOCs (neither terpenes).

3.2.1.2 Analysis

A blank or zero air/gas supply, such as dry air or nitrogen, is required for determining analytical blanks during the measurements. The presence of interfering compounds in the zero gas shall be lower than 10 % of the lowest mass of any reported compound introduced in the lowest-level calibration standard. During the assessment of the zero air/gas purity, the same volume shall be introduced as the volume of ambient air sampled during routine monitoring. Blanks should be analysed at least once per month and ideally once per week.

3.2.1.3 Calibration

- Central Calibration Laboratories (CCL, <https://community.wmo.int/en/activity-areas/gaw/research-infrastructure/qaqc/central-facilities>) maintain the primary standards that define the calibration scale for GAW sites. The calibration scale is transferred to the stations and laboratories through laboratory standards that are prepared by the CCL and that are directly traceable to the primary standard. In case a laboratory does not use a laboratory standard from the CCL, it has to demonstrate that the laboratory standard used is linked to the CCL primary standard by direct comparisons in time intervals that correspond to the stability of the standard mixture. This standard will have a higher uncertainty than the laboratory standard produced from the CCL as uncertainties increase the further you move down the traceability chain away from the primary standard.

The calibration of NMHC measurements may require:

- A (secondary) laboratory standard which has to be a multi-component standard (synthetic mixture), traceable to the primary standard, for ensuring traceability of the measurements. The recommended frequency of use is 2/year or at least 1/year for periods without irregularities of the GC system.
- One or more (tertiary) working standards that cover most (ideally all) components measured and are used for regular calibration of the measurements, regular or high consumption applications like standard addition or dilution series, etc. These working standards can be either other certified or custom-made synthetic mixtures and are calibrated versus the laboratory standard. The recommended frequency of use is 2/month or at least 1/month for periods without irregularities of the GC system.
- A target gas which is preferably compressed whole air but could also be a synthetic mixture calibrated at least by the station against the laboratory standard: it is used to check the assigned values of the calibration mixtures and the calibration process itself and is treated as an air sample with unknown mole fraction. Monitoring of the target gas results yields information about the performance of the instrument, drifts of the laboratory standard and potential instrumental problems. The recommended frequency of use is 1/month.

For oxygenated VOC and terpenes, calibration standards are under development by the National Metrology Institutes or becoming available with limited stability.

3.2.1.4 *Uncertainty calculation*

A specific method for uncertainty calculation of VOC data obtained from online measurements with GC systems is proposed in the ACTRIS Guideline (ACTRIS, 2018) and should be prioritized when calculating uncertainties.

3.2.2 *VOC online measurements using PTR-MS*

The ACTRIS Guideline for VOC online measurements using PTR-MS is to be published by the end of 2024 and will replace the current draft which can be obtained from the EU Document Download Module (Dusanter et al. , 2019). While VOC analysis by online gas chromatography remains the standard technique for many purposes, PTR-MS is complementary for the following reasons:

- It minimizes potential losses or the spurious formation of VOCs during the sampling stage since ambient air is directly analyzed (within seconds after sampling) without any pre-concentration step;
- It reduces artifacts due to sample conditioning since PTR-MS does not require sample pretreatment to remove O₃ or water before analysis;
- It provides fast time resolution (as high as 10 Hz) together with high sensitivity and low limits of detection;
- It makes untargeted quantitative analysis possible.

The aim of this guideline is to provide information that enables proper operation of many types of PTR-MS for trace gas measurements in ambient air, and appropriate QA/QC procedures. The report also provides the information needed to produce high-quality data sets that meet the ACTRIS guidelines. It covers:

- Commercial instruments equipped with conventional drift tubes (DC electrical field and operating pressure of a few mbar) and time of flight mass spectrometers (ToF-MS). For PTR-MS equipped with quadrupole mass spectrometers (QMS) that are not commercialized anymore, only remarks are provided;
- Proton transfer reactions using hydronium ions (H₃O⁺). Other ionization methods using NO⁺, O₂⁺, NH₄⁺ and other reagent ions are not covered;
- Proper operations: sampling, zeroing, calibrating, extracting and reporting data.

According to this guideline draft version, recommendations for sampling and analysis are listed below in 3.2.2.1 and 3.2.2.2. Further details on sampling and analysis can be found in the referred document.

3.2.2.1 Sampling

- Depending on the measurement objectives, the sampling time response should be quantified, especially if high-time resolution measurements are needed (e.g. 10 Hz for flux measurements).
- Ambient monitoring at a time resolution of a minute or more is less stringent on time response but potential memory effects for 'sticky' compounds such as methanol and other OVOCs should be checked.
- In order to assess the sampling time response and how VOCs are transmitted in the instrument, a short pulse (less than 1s) of different volatile organic compounds (e.g. isoprene) should be provided at the entrance of the sampling line and monitored by the PTR-MS.
- Sampling lines should be made of inert material (e.g. silcosteel[®] or sulfinert[®]) and can be slightly heated to reduce sorption of VOCs on surfaces.
- The sampling line can be slightly heated to reduce VOC sorption effects. Measurements of compounds exhibiting a good thermal stability can be performed with a sampling line heated to 40-50°C.
- Typical inner diameters of the sampling lines are in the range 2–12 mm and the length will depend on the measurement height and place. Generally, the sampling line should be as short as possible, and the flow rate should be high enough (a few L/min to a few tens of L/min) to reduce the residence time below a few seconds.

3.2.2.2 Analysis

- The sorption rates of VOCs inside the sampling line and the drift tube are strongly dependent on ambient humidity and the frequency for blank measurements should therefore depend on how fast humidity changes at the measurement site. Automated hourly determinations are usually enough, with at least one blank every six hours to ensure that diurnal variations in instrumental blanks are well captured during operation in the field.
- VOCs free air can be produced from ambient air using preferably a catalyst (Platinum Pt, Palladium Pd) held at high temperature (350–400°C).
- The addition of a calibration standard should be performed once a week, to track potential drifts in sensitivity.

Recently, NPL has developed an International System of Units (SI)-traceable transmission curve reference material to improve the quantitation and comparability of proton-transfer-reaction mass-spectrometry measurements (Worton et al., 2023). With this novel traceable reference material, the use of a reference material for all observable compounds could be replaced with a single mix of certain compounds with high accuracy and improved stability.

3.2.3 NMHC offline measurements

If online measurements are not possible, recommendations of the GAW-WMO Report # 204 (2012) for offline sampling with canisters of C₂–C₆ NMHC (and the CEN TS regarding canister sampling, once published) should be followed:

3.2.3.1 Sampling

- Air samples are to be collected in commercially available or custom-built electro-polished two-valve stainless steel canisters. A metal bellows or membrane pump with an in-line membrane filter is used to prevent contamination of samples. Filled canisters are either analyzed on-site or shipped to a laboratory.
- Canisters must be checked for leaks and blank values before air sampling. The entire sampling system and the main inlet tubing have to be clean and tight.
- For the GAW NMHC target compounds, the effect of ozone on sample integrity is assumed to be negligible and an ozone scrubber during air sampling is not required.

- The sampling equipment must be stored after sampling with capped inlets and outlets in normal conditions (extreme temperatures and humidity have to be avoided) away from organic solvents. The canisters are recommended to be analyzed as soon as possible and within a time for which their stability is guaranteed. Storage time must not exceed 2 weeks.

3.2.4 *OVOC offline measurements*

At the time of writing this report, solely the guideline for measuring OVOC by EMEP (EMEP, 2001) is available. This guideline is focusing on aldehydes and ketones sampling by DNPH cartridges and subsequent analysing by HPLC with UV-detection. Recommendations for sampling and analysis in this guideline are given below in 3.2.4.1 and 3.2.4.2.

3.2.4.1 *Sampling*

- Before use, the equipment should be leakproof-tested and tested for appropriate air flow rate (typically 1–2 L/min).
- A potassium iodide (KI) coated ozone scrubber must be used.
- In order to avoid the KI film being dissolved by water, a weather-protection "device" has to be mounted on the scrubber (Teflon funnel or the upper half of a Teflon bottle).
- "Stock-cartridges" should be stored in sealed pouches at 4°C.
- After completion of the sampling, the exposed cartridges should be disconnected from the sampling line and sealed with the Luer plug and cap as soon as possible.
- The cartridges are stored into glass containers with Teflon lined screw caps.
- If the exposed cartridges have to be stored for some days, it should be done in dark at a cool place (4°C), i.e., a refrigerator. Do not store the cartridges at places where carbonyls are stored (acetone etc.).

3.2.5 *Instrument performance evaluation*

Interlaboratory comparisons for VOCs (and NO_x) measurements as well as round-robin tests are organized regularly (every 5 years and 2 years, respectively) by ACTRIS CiGas for ACTRIS National Facilities and open to external users, targeting NMHC (in 2013; see Hoerger et al., 2015), oxygenated VOCs (in 2015–2018) including formaldehyde (in 2022), and terpenes (in 2018). Additionally, European national reference laboratories participate in regular interlaboratory comparisons for aromatics (BTEX) and other VOCs (Pérez Ballesta et al., 2018; Pérez Ballesta et al., 2023). CiGas also performs station audits and two of its units are GAW WCC for VOC and NO_x. For individual networks using online methods, parallel online and offline sampling of the same VOCs is encouraged to be conducted regularly (e.g., once or twice a year) to support the measurement sites to obtain high quality data.

4. PAN-EUROPEAN OVERVIEW

4.1 Concentrations

In the framework of RI-URBANS, Liu et al. (2024a) compiled 21 VOC datasets across mostly urban Europe, including Belgium (7 sites), Finland (2), France (7), Switzerland (1), Spain (1), and the UK (3). The dataset comprised 3 industrial (IND), 2 traffic (TR), 15 urban background (UB), and 1 suburban background (SUB) sites (Figure 2). Furthermore, Liu et al. (2024b) included an additional UB site in Greece in a study focusing on BTEX in urban Europe (Figure 2).

Measurements of VOCs were carried out using different methodologies and instrumentation. These included thermal desorption gas chromatography with flame ionization detectors (TD-GC-FID/2FID), thermal desorption gas chromatography-mass spectrometry (TD-GC-MS), proton transfer reaction-time of flight-mass spectrometry (PTR-TOF-MS), PTR-Quad-MS, and passive samplers followed by GC-MS and LC-MS determinations. Specifically, among

the monitoring stations: At 10 out of 21 stations (C₂–C₉) species were measured. At 7 out of 21 stations (C₄–C₉), chloroethane and chloroethene species were identified. Other stations measured distinct combinations of VOCs, including C₆–C₉ aromatics and C₅–C₁₅ biogenic VOCs (BVOCs), C₅–C₁₀ and C₁–C₄ oxygenated VOCs (OVOC) and acetonitrile, C₇–C₁₀ and C₅–C₁₀ BVOC, and OVOC, along with some C₅–C₉. There is a limitation to data comparison due to the different protocols used for VOCs measurements without harmonisation in each case, and also because the disparity of VOCs species measured at each site. Furthermore, some of the techniques used are not able to trap specific VOCs for subsequent desorption and analysis, and other tools are not specific for a number of VOCs but for ions from a group of VOCs (such as in some cases for PTR-MS and specific groups). In this study, all monitoring stations monitored benzene since it is regulated, as well as toluene, ethylbenzene, and xylene species.

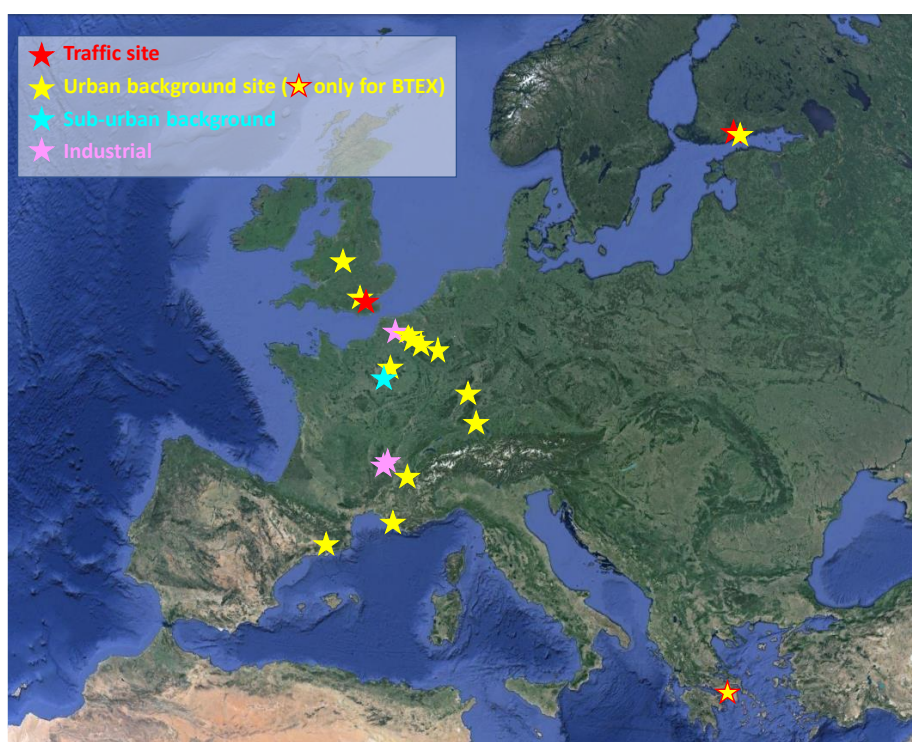


Figure 2. Location of the 21 sites providing data for VOCs and an additional one only for BTEX.

None of the supersites yielding the 21 datasets cover all 45 VOCs of the EU Air Quality Directive 2024/2881/EC. Eight out of the 21 sites cover between 25 and 29 VOCs from the list, while 17 sites cover between 21 and 29 VOCs. This is reflecting the difficulty in measuring the 45 VOCs species.

It was observed that the 20 most commonly analysed VOCs at the monitoring sites were n-butane, n-pentane, i-pentane, n-hexane, n-heptane, n-octane, i-octane, 1,3-butadiene, 1-butene, trans-2-butene, cis-2-butene, 1-pentene, benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and isoprene.

For facilitating the comparison of these VOCs' datasets, the Maximum O₃ Formation Potential (MOFP) was calculated for each site by multiplying the Maximum Incremental Reactivity (MIR, see Section 4.3) of each species by its concentration at that site (Carter, 2010; Venecek et al., 2018). The SOA Formation Potential (SOAP) was calculated in a similar manner, by multiplying VOC concentrations by the SOA yield (YSOA) of each species obtained from Gu et al. (2021). Average values for all sites and species included are ranked in Figure 3.

The results evidenced that toluene, m,p-xylene, 1-butene, n-butane, and isopentane collectively contributed on average over 50% to the total MOFP (calculated as the sum of the individual 20 MOFPs) for the sites studied, with individual contributions of $15\% \pm 9\%$, $13\% \pm 7\%$, $9\% \pm 8\%$, $9\% \pm 6\%$, and $7\% \pm 5\%$, respectively. This is primarily attributed to their relatively high concentrations and high MIR values.

In parallel, aromatic hydrocarbons accounted for most of the SOAP ($>85\%$), with toluene ($55\% \pm 16\%$), benzene ($20\% \pm 10\%$), m,p-xylene ($7\% \pm 3\%$), and o-xylene ($4\% \pm 2\%$) being the major contributors.

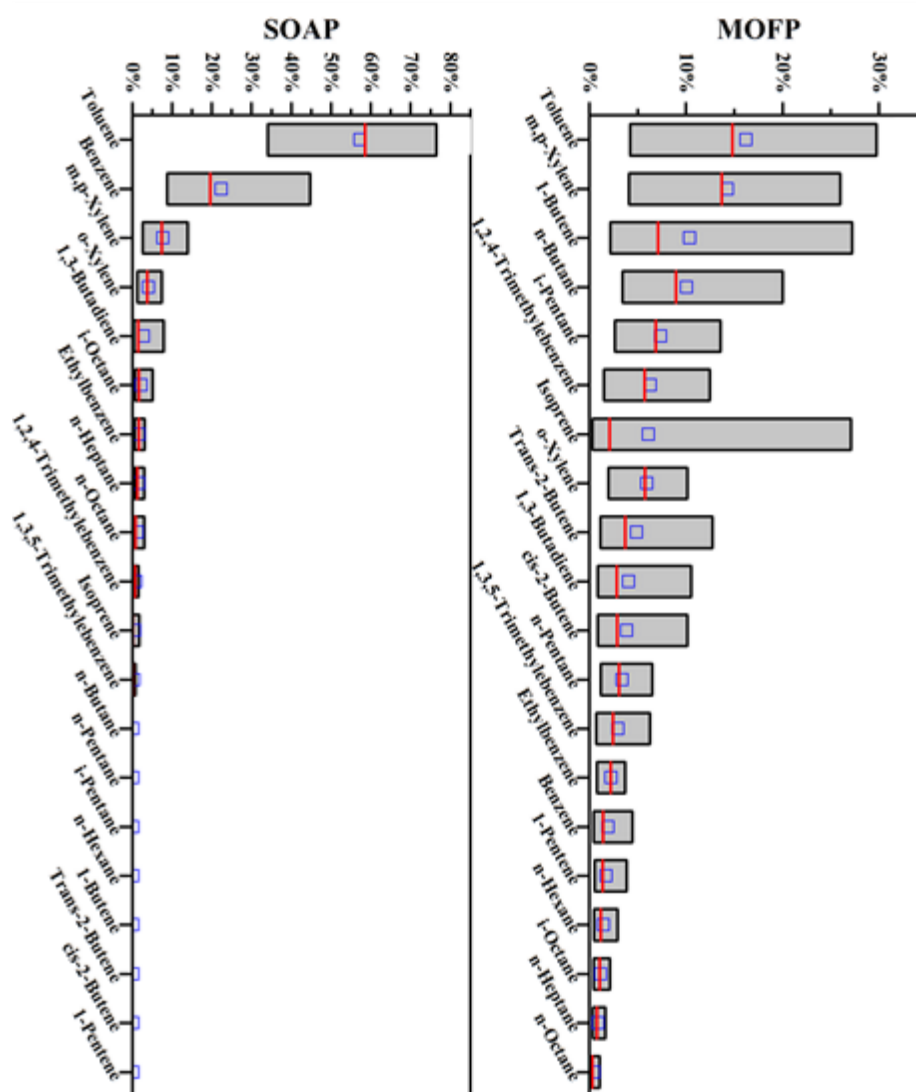


Figure 3. Individual contributions of 20 VOCs to (left) the total (sum of the 20) SOA formation potential (SOAP), in $\mu\text{g SOA}/\text{m}^3$ and (right) the maximum O_3 formation potential (MOFP), in $\mu\text{g O}_3/\text{m}^3$, as averages for the collected datasets. The box represented the 5th–95th percentiles of ratios. The middle line and middle square represented the median values and mean values of ratios, respectively (Liu et al., 2024).

Liu et al. (2024a) also carried out a meta-analysis for the individual trend analysis for 18 VOCs at 10 monitoring sites over the period 2008–2023. Figure 4 shows a statistically significant (ss) decrease of $-2.2\%/yr$ at UB sites for the sum of the concentrations of each of the 18 VOC species. A ss decreasing trend was found at UB sites for most alkanes, excluding n-butane and n-pentane, ranging from -2.6 to $-3.7\%/yr$. Alkenes, excluding 1-butene and 1-

pentene, exhibited ss decreasing trends ranging from -1.7 to -2.4%/yr. Aromatic hydrocarbons, excluding o-xylene and 1,2,4-trimethylbenzene, followed a ss decreasing trends ranging from -2.2 to -3.4%/yr. Conversely, isoprene (BVOC and AVOC) increased with a ss trend of +2.8%/yr at UB sites but decreased at TR and IND sites. It is important to note that ss decreases ranging from -2.2 to -7.4%/yr were observed at TR sites for all 18 VOCs, except n-octane.

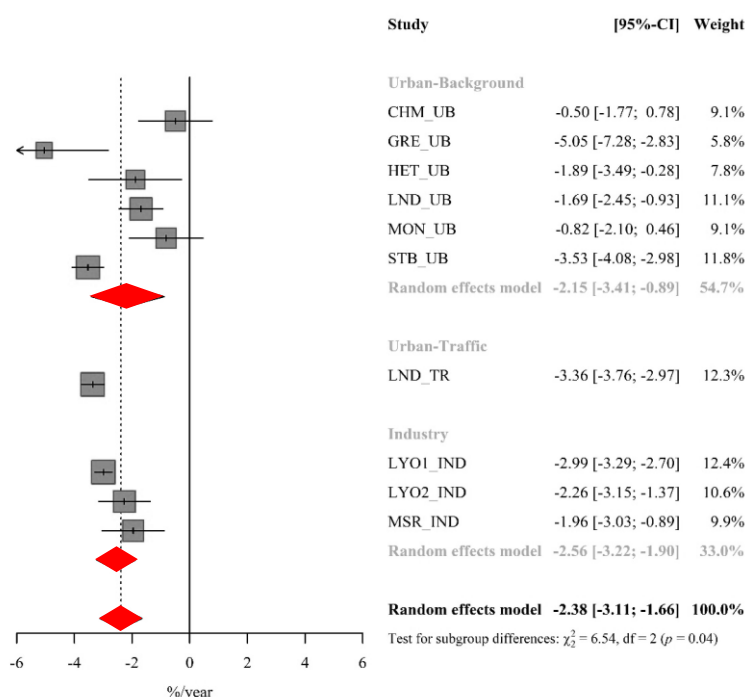


Figure 4. Results from the meta-analysis of the trends obtained at 10 sites for the selected 18 VOC species. Data are given and represented for slope [95% CI] in %/yr. The abbreviations stand for the following European cities: CHM for Charleroi, GRE for Grenoble, HET for Herstal, LND for London, LYO1 for Lyon (Feuzin stade), LYO2 for Lyon (Vernaison), MON for Mons, MSR for Mouscron, and STB for Strasbourg. Adopted from Liu et al. (2024a).

Based on 22 datasets from urban areas in Europe, Liu et al. (2024b) reported that BTEX can be ranked according to their 2017–2022 average concentrations as toluene > benzene > m,p-xylene > o-xylene > ethylbenzene, with mean concentrations of 1.5 ± 1.7 , 0.8 ± 1.0 , 1.0 ± 1.3 , 0.4 ± 0.5 , and $0.3 \pm 0.5 \mu\text{g}/\text{m}^3$, respectively. Figure 5 shows the average concentrations observed at each site.

According to emission inventories, VOCs emissions from traffic have decreased dramatically in the last decades (Figure 6, CEIP, 2024).

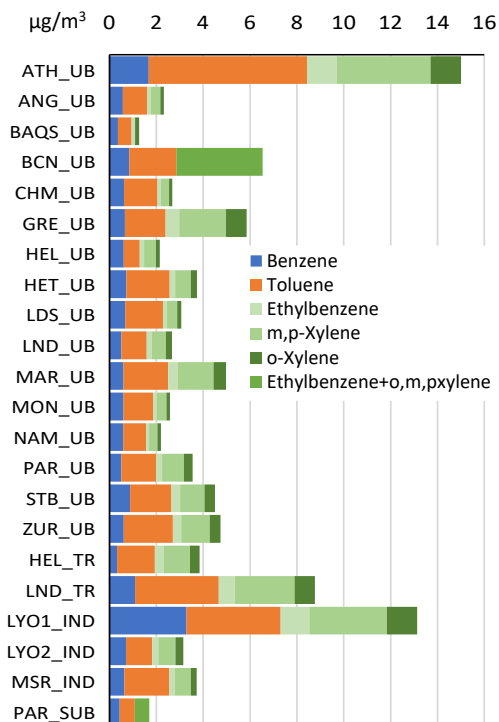


Figure 5. Average 2017–2022 concentrations for specific BTEX in the 22 study sites. The abbreviations stand for the following European cities: ATH for Athens, ANG for Angleur, BAQS for Birmingham, BCN for Barcelona, CHM for Charleroi, GRE for Grenoble, HEL for Helsinki, HET for Herstal, LDS for Lodelinsart, LND for London, LYO1 for Lyon (Feuzin stade), LYO2 for Lyon (Vernaison), MAR for Marseille, MON for Mons, MSR for Mouscron, NAM for Namur, PAR for Paris, STB for Strasbourg, and ZUR for Zürich. Modified from Liu et al. (2024b).

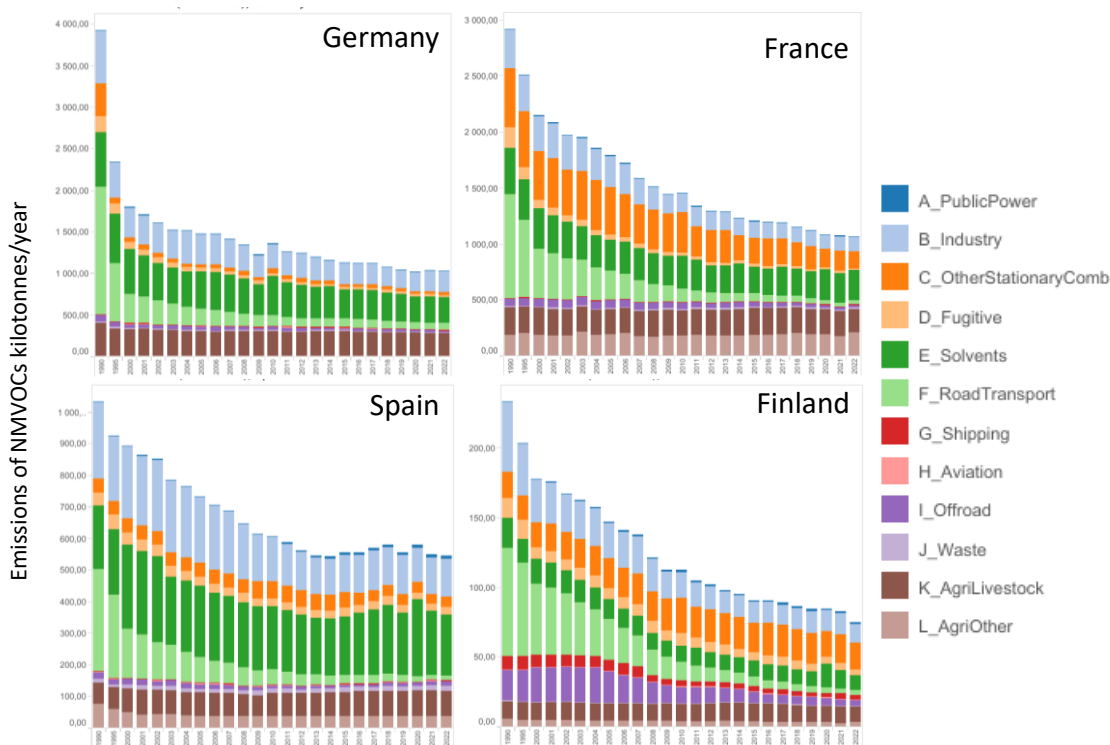


Figure 6. Annual 1990–2022 emissions in kilotonnes of NM-VOCs, showing a marked decrease of VOCs from road transport. Four countries have been selected as examples. Data from CEIP (2024).

4.2 Emissions

Table 3 shows the origin of the VOC species included in Annex VII of the AAQD 2024/2881/EC. Here below we summarise the current knowledge on VOC origins (see also Figure 7), as reviewed by the UK Air Quality Expert Group (AQEG-UK, 2020).

VOCs from natural gas production, distribution and use include methane, ethane, propane, butane. Many of them have a limited O₃ formation potential but should still be considered as significant O₃ precursors due to their high concentrations.

VOCs from fuels such as gasoline (production, distribution, engine emissions and evaporation) include i/n-butane and i/n-pentane, hexane, mono-aromatics (such as benzene, toluene, and m/p xylene) and a fraction of unsaturated hydrocarbons (alkenes and alkynes). In recent decades, the amount of ethanol added to gasoline (up to 5–10%) has increased, while its content in PAHs (<30%), benzene (<1%) and di-enes (<1%) has been reduced to comply with the European standards EN 228 (2012 and A1:2017). In addition to these measures, the reduction of emissions by refineries, VOC traps at petrol stations, 3-way catalysts, together with the reduction in the use of direct petrol injection (AQEG-UK, 2020), have contributed to a very marked reduction in emissions from road transport and associated products. In particular, 3-way catalysts have greatly reduced the emissions of VOCs due to poor combustion, primarily traced by alkenes, alkynes and benzene. Thus, concentrations of 1,3-butadiene, which was classically attributed to road traffic, has been reduced by one third at traffic air quality monitoring stations (AQEG-UK, 2020). In addition to road traffic, benzene emissions can be partly attributed to off-road machinery, aviation, gas and biomass boilers, as well as forest fires and agricultural waste burning (Lewis et al., 2013).

Solvent VOCs include those emitted from industrial processes (manufacturing and application of paints and varnishes) to domestic use of products (personal hygiene, cleaning, adhesives, inks, paints, sealants, air fresheners and varnishes, among others). Species emitted by solvents include toluene, m,p,o-xylene, ethylbenzene, trimethylbenzenes, acetone, methanol, ethanol, isopropyl alcohol, formaldehyde, and halogenated alkanes (dichloromethane, among others). Many of these are not routinely analysed. The introduction of the EC Paints Directive 2004/42/EC may have had a major effect on reducing VOC emissions.

Biogenic VOCs (BVOCs) are isoprenoids that are emitted by wild and cultivated plants (e.g. isoprene in deciduous forests, and monoterpenes in evergreen forests). In addition to being emitted in large volumes during the summer in regions with high levels of sunlight, their potential for the formation of O₃ and secondary organic PM is very high. Although BVOC emissions are much lower than anthropogenic VOC (AVOCs) emissions on an annual basis, their relative importance is much greater during the critical O₃ pollution season. In addition, the spatial distribution of BVOCs and AVOCs (as well as NO_x) emissions is different, and the former may determine the O₃ formation regime (controlled by the VOC/NO_x ratio) across large areas.

Furthermore, **a large proportion of VOCs in ambient air is of secondary origin**, and they are generated from reactions such as ozonolysis and oxidation of hydrocarbons to oxygenated VOCs or OVOCs (aldehydes, ketones, among others). There are species such as formaldehyde that can have both primary and secondary origins, and some species that can have both anthropogenic and biogenic origins. Thus, in regions with high solar radiation and O₃ concentrations, OVOC concentrations can be very high, due to their fast generation from primary NMHCs. In urban environments, OVOCs reach higher concentrations than the NMHCs normally measured by air quality monitoring networks.

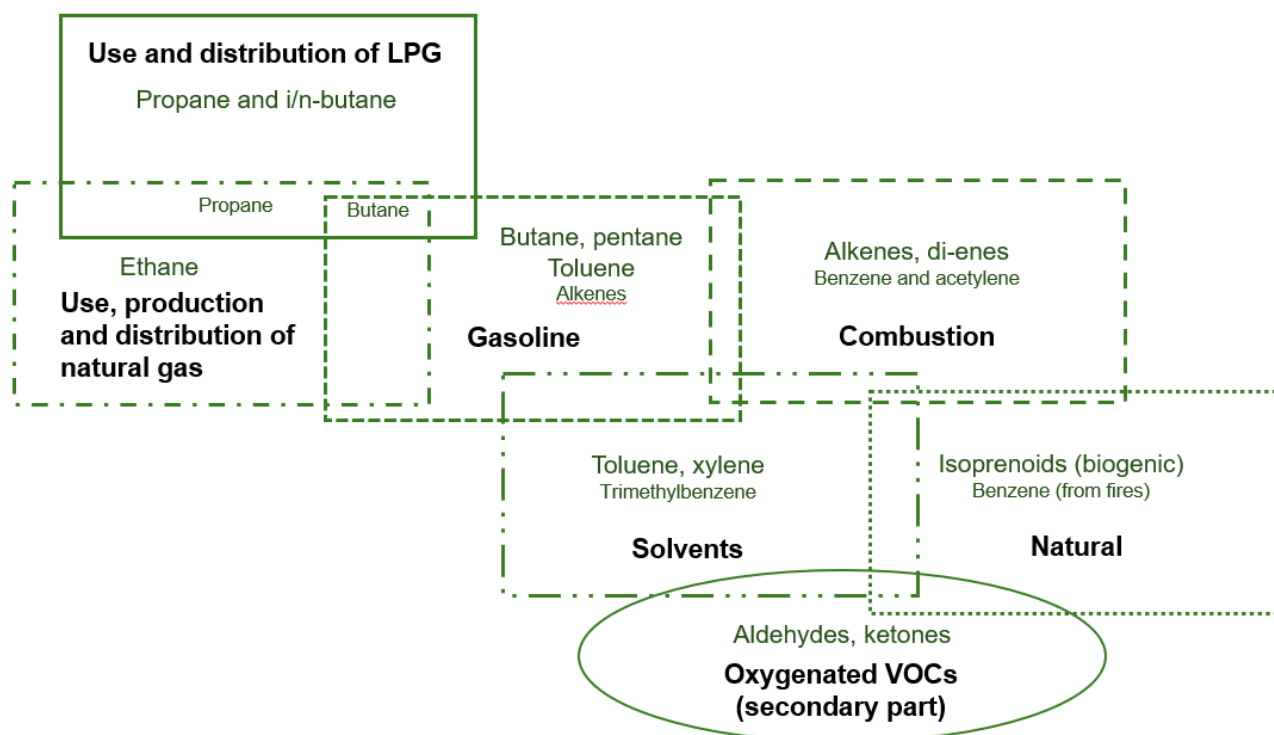


Figure 7. Summary of VOC tracers of different sources based on AQEG-UK (2020).

Table 3. Summary of origin of VOCs with high capacity to generate O_3 and SOA for species listed in Annex VII of the AAQD.

Methanol	Biogenic, solvent use, combustion	Butane	Natural gas, fuel evaporation	Trans-2-butene	Combustion, fuel evaporation	1,3,5-trimethylbenzene	Combustion, fuel evaporation, solvent use
Ethanol	Biofuels, solvent use	i-pentane	fuel evaporation	Cis-2-butene	Combustion, fuel evaporation	Isoprene	Biogenic mainly, combustion
Formaldehyde	Photochemistry of isoprene, anthropogenic	Pentane	fuel evaporation	1-pentene	Combustion, fuel evaporation	P-cymene	Biogenic mainly
Acetaldehyde	Photochemistry, solvent use	i-hexane	fuel evaporation, exhaust emissions	Trans-2-pentene	Combustion, fuel evaporation	Limonene	Biogenic mainly
Methacrolein	Photochemistry of isoprene	Hexane	fuel evaporation, exhaust emissions	Cis-2-pentene	Combustion, fuel evaporation	β -Myrcene	Biogenic mainly
propanone	Biogenic, solvent use,	Heptane	fuel evaporation, exhaust emissions	<u>Benzene</u>	Combustion	α -pinene	Biogenic mainly
MVK	Photochemistry of isoprene	i-octane	fuel evaporation, exhaust emissions	Toluene	Combustion, fuel evaporation, solvent use	β -pinene	Biogenic mainly
MEK	Biogenic	Octane	fuel evaporation, exhaust emissions	Ethylbenzene	Combustion, fuel evaporation, solvent use	Camphene	Biogenic mainly
Ethyne	Combustion	Ethene	Combustion	M,p-xylenes	Combustion, fuel evaporation, solvent use	Δ -Carene	Biogenic mainly
Ethane	Long-lived species, natural gas	Propene	Combustion	O-xylene	Combustion, fuel evaporation, solvent use	1,8-cineole	Biogenic mainly
Propane	Long-lived species, natural gas	1,3-butadiene	Combustion, industrial sources	1,2,4-trimethylbenzene	Combustion, fuel evaporation, solvent use		
i-butane	Natural gas, fuel evaporation	1-butene	Combustion, fuel evaporation	1,2,3-trimethylbenzene	Combustion, fuel evaporation, solvent use		

Table 4. Selection of SOAP (% with respect to the toluene SOAP) and MIR ($\mu\text{g O}_3 \text{g}^{-1} \text{VOC}$) values of selected VOC species ordered by decreasing SOAP (Data from Derwent et al., 2010 and Venecek et al., 2018). Species with high SOAP or MIR are shadowed in clear grey, and the ones with high MIR and SOAP with dark grey.

VOC species	SOAP	MIR	VOC species	SOAP	MIR
Benzaldehyde	216	-0,3	trans Pent-2-ene	3,1	9,7
Styrene	212	1,7	Nonane	1,9	1,0
Ethylbenzene	112	6,1	2-Methylbut-2-ene	1,9	10,0
Propylbenzene	110	5,6	Isoprene	1,9	9,7
m-Ethyltoluene	101	6,7	1,3-Butadiene	1,8	12,0
Toluene	100	4,0	Propylene	1,6	2,0
i-Propylbenzene	96	5,6	Ethylene	1,3	2,0
o-Xylene	96	7,2	cis Hex-2-ene	1,3	7,8
o-Ethyltoluene	95	5,3	trans Hex-2-ene	1,3	8,0
Benzene	93	0,8	But-1-ene	1,2	9,3
m-Xylene	85	8,5	2-Methylbut-1-ene	0,9	5,7
p-Ethyltoluene	70	4,3	Propylene glycol	0,9	2,5
p-Xylene	67	5,5	Octane	0,8	1,2
1,2,3-Trimethylbenzene	44	9,9	Ethylene glycol	0,8	3,4
Dodecane	35	0,8	Formaldehyde	0,7	7,2
1,2,4-Trimethylbenzene	21	7,9	Ethanol	0,6	1,8
β -Pinene	18	3,5	3-Pentanol	0,6	1,8
α -Pinene	17	4,0	sec-Butanol	0,6	1,5
Undecane	16	0,9	Butylene	0,6	9,3
1,3,5-Trimethylbenzene	14	9,4	3-Methylbut-1-ene	0,6	6,8
3,5-Dimethylethylbenzene	12	6,4	Acetaldehyde	0,6	6,1
3,5-Diethyltoluene	7,5	7,1	Methylethylketone	0,6	1,5
Decane	7,0	0,9	Methylpropylketone	0,6	2,0
trans But-2-ene	4,0	13	Methyl-i-butylketone	0,6	3,5
cis But-2-ene	3,6	13	Diacetone alcohol	0,6	0,1
cis Pent-2-ene	3,1	9,6	Propionaldehyde	0,5	6,8
High SOAP or MIR					
High SOAP and MIR					

5. RECOMMENDATIONS

The RI-URBANS compilation of long-term VOC datasets shows that, at maximum, 33 VOCs are currently being analysed at European urban sites, whereas 45 VOCs are listed in the EU Air Quality Directive 2024/2881/EC.

Table 4 summarises the analytical techniques that are recommended for the analysis of these volatile organic compounds. It is worth mentioning that to cover the 45 VOC species of the Directive, several instruments should be working together. There is not a single one available covering all the species.

Not only the purchase and maintenance costs of the instruments should be considered, but also the availability of specific calibration standards for the VOCs to be analysed and the required expertise of the staff running the instruments. It is for this reason that in many cities research groups are contracted by the air quality monitoring networks to be responsible for these measurements.

Table 4. Summary of measurement techniques suitable for the measurement of the VOCs listed in Annex VII of the AAQD.

Chemical family	Substance				Measurement technique(s)	
	Trivial name	IUPAC name	Formula	CAS number		
Alcohols	Methanol	Methanol	CH ₄ O	67-56-1	GC (FID and/or MS detection); PTR-MS	
	Ethanol	Ethanol	C ₂ H ₆ O	64-17-5		
Aldehyde	Formaldehyde	Methanal	CH ₂ O	50-00-0	DNPH cartridges/HPLC analysis; other online analysers see Table 2	
	Acetaldehyde	Ethanal	C ₂ H ₄ O	75-07-0	DNPH cartridges/HPLC analysis; GC (FID and/or MS detection); PTR-MS	
	Methacrolein	2-Methylprop-2-enal	C ₄ H ₆ O	78-85-3		
Alkynes	Acetylene	Ethyne	C ₂ H ₂	74-86-2	online GC (FID and/or MS detection); canister sampling/analysis by GC	
Alkanes	Ethane	Ethane	C ₂ H ₆	74-84-0	GC-FID and/or MS; offline sampling can be done by canisters or sorbent tubes for > C5	
	Propane	Propane	C ₃ H ₈	74-98-6		
	n-Butane	Butane	C ₄ H ₁₀	106-97-8		
	i-Butane	2-Methylpropane	C ₄ H ₁₀	75-28-5		
	n-Pentane	Pentane	C ₅ H ₁₂	109-66-0		
	i-Pentane	2-Methylbutane	C ₅ H ₁₂	78-78-4		
	n-Hexane	Hexane	C ₆ H ₁₄	110-54-3		
	i-Hexane	2-Methylpentane	C ₆ H ₁₄	107-83-5		
	n-Heptane	Heptane	C ₇ H ₁₆	142-82-5		
	n-Octane	Octane	C ₈ H ₁₈	111-65-9		
Alkenes	Ethylene	Ethene	C ₂ H ₄	75-21-8	GC (FID and/or MS detection); offline sampling with canisters with some caveats, possible for some species with adequate sorbent tubes	
	Propene / Propylene	Propene	C ₃ H ₆	115-07-1		
	1,3-Butadiene	Buta-1,3-diene	C ₄ H ₆	106-99-0		
	1-Butene	But-1-ene	C ₄ H ₈	106-98-9		
	Trans-2-Butene	(E)-but-2-ene	C ₄ H ₈	624-64-6		
	cis-2-Butene	(Z)-but-2-ene	C ₄ H ₈	590-18-1		
	1-Pentene	Pent-1-ene	C ₅ H ₁₀	109-67-1		
	2-Pentene		(Z)-Pent-2-ene	C ₅ H ₁₀		627-20-3 (cis-2 pentene)
			(E)-Pent-2-ene			646-04-8 (trans-2 pentene)
	Aromatic hydrocarbons	Benzene	Benzene	C ₆ H ₆		71-43-2
Toluene / Methylbenzene		Toluene	C ₇ H ₈	108-88-3		
Ethylbenzene		Ethylbenzene	C ₈ H ₁₀	100-41-4		

Chemical family	Substance				Measurement technique(s)
	Trivial name	IUPAC name	Formula	CAS number	
	<i>m + p-Xylene</i>	1,3-Dimethylbenzene (<i>m-Xylene</i>)	C_8H_{10}	108-38-3 (<i>m-Xylene</i>)	
		1,4-Dimethylbenzene (<i>p-Xylene</i>)		106-42-3 (<i>p-Xylene</i>)	
	<i>o-Xylene</i>	1,2-Dimethylbenzene (<i>o-Xylene</i>)	C_8H_{10}	95-47-6	
	1,2,4-Trimethylebenzene	1,2,4-Trimethylbenzene	C_9H_{12}	95-63-6	
	1,2,3-Trimethylebenzene	1,2,3-Trimethylbenzene	C_9H_{12}	526-73-8	
	1,3,5-Trimethylebenzene	1,3,5-Trimethylbenzene	C_9H_{12}	108-67-8	
Ketones	Acetone	Propan-2-one	C_3H_6O	67-64-1	GC (FID and/or MS detection); PTR-MS; DNPH cartridges/HPLC analysis; (offline sampling with canisters might be possible)
	Methyl ethyl ketone	Butan-2-one	C_4H_8O	78-93-3	
	Methyl vinyl ketone	3-Buten-2-one	C_4H_6O	78-94-4	
Terpenes	Isoprene	2-Methylbut-1,3-diene	C_5H_8	78-79-5	GC (FID and/or MS detection); offline measurements with Tenax sorbent tubes/analysis with GC; PTR-MS can measure isoprene and gives the sum of monoterpenes
	<i>p-Cymene</i>	1-Methyl-4-(1-methylethyl)benzene	$C_{10}H_{14}$	99-87-6	
	Limonene	1-methyl-4-(1-methylethenyl)-cyclohexene	$C_{10}H_{16}$	138-86-3	
	β -Myrcene	7-Methyl-3-methylene-1,6-octadiene	$C_{10}H_{16}$	123-35-3	
	α -Pinene	2,6,6-Trimethyl-bicyclo[3.1.1]hept-2-ene	$C_{10}H_{16}$	80-56-8	
	β -Pinene	6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane	$C_{10}H_{16}$	127-91-3	
	Camphene	2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane	$C_{10}H_{16}$	79-92-5	
	Δ^3 -Carene	3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene	$C_{10}H_{16}$	13466-78-9	
	1,8-Cineol	1,3,3 trimethyl 2 oxabicyclo[2,2,2]octane	$C_{10}H_{18}O$	470-82-6	

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Useful resources:

- ACTRIS SOP and measurement guidelines, reports on intercomparisons and round robin exercises for NO_x and VOC available at: <https://actris.nilu.no/Content/?pageid=68159644c2c04d648ce41536297f5b93>.
- WMO/GAW reports: https://library.wmo.int/doc_num.php?explnum_id=11565.
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- Project reports: MetNO₂ (<http://empir.npl.co.uk/metno2/>) and MetClimVOC reports, online trainings and blogs (<http://www.metclimvoc.eu/>).
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