Publishable Summary for 19ENV06 MetClimVOC
Metrology for climate relevant volatile organic compounds

Overview

Volatile organic compounds (VOCs), as ozone and aerosol precursors, play an important role in the oxidative capacity of the lower atmosphere. Moreover, VOCs contribute to radiative forcing. Thus, long-term, accurate and traceable VOC measurements are pivotal to understanding changes in climate and their effects on environment and society. However, VOC low atmospheric amount-of-substance fractions, their reactiveness and the lack of stable and traceable standards for some VOCs make their sampling, analysis and calibration challenging. This project will improve the quality of reference gas mixtures, ensuring their correct dissemination to the field via working standards and recommendations. Furthermore, the project will provide well-characterised sampling and analytical methods and SI-traceable spectral parameters for spectrum-based techniques.

Need

The WMO-GCOS (Global Climate Observing System) defined 54 essential climate variables (ECV) that contribute critically to the characterisation of the Earth's climate. VOCs are designated as ECV in the categories "aerosol and ozone precursors" (oxygenated VOCs and terpenes in this project) and "carbon dioxide, methane and other greenhouse gases" (halogenated compounds in this project). VOCs are regulated by the European Air Quality Directive 2008/50/EC and emission ceilings for air pollutants defined in the directive (NEC) 2001/81/EC, which includes VOCs as ozone precursors. For the halogenated gases, which are direct greenhouse gases, fluorinated halocarbons are regulated in the regulation (EU) No 517/2014 (F-gas regulation). Furthermore, the Kyoto Protocol, developed under the United Nations Framework Convention on Climate Change (UNFCCC), obligates member states to report emissions of these greenhouse gases. Recently, these fluorinated halocarbons have been included into the Kigali Amendment of the Montreal Protocol, which already restricts the use of chlorinated and brominated halocarbons, as they destroy the ozone layer.

To control the effectiveness of these treaties and to assess climate and air quality trends, the amount-of-substance fractions of these compounds need to be monitored. Stable traceable references with a low uncertainty along with well-defined measuring methods are indispensable for reliable VOC measurements. The WMO-GAW, the European Monitoring and Evaluation Programme (EMEP), research infrastructures (e.g. ACTRIS, AGAGE) and national air pollution networks included VOCs in their long-term monitoring programs. WMO-GAW or ACTRIS for instance, defined data quality objectives on the final measurement (ACTRIS: < 10 %). However, measuring atmospheric VOCs is challenging because they occur at very low amount-of-substance fractions (pmol/mol to nmol/mol level). In addition, some of these compounds are highly reactive and are prone to adsorption effects on surfaces, which makes the calibration of analysers, sampling and field measurements difficult. For some VOCs, there are no references available to ensure traceability and uncertainty. Finally, remote sensing methods, which show high potential to avoid sampling issues, are currently missing SI-traceable spectral parameters.

Significant progress has been made to improve the accuracy of VOC measurements during the past years, e.g. new traceable reference gas mixtures were established and mobile dynamic reference gas generators were developed (EMRP JRPS ENV56 KEY-VOCS and ENV52 HIGHGAS); new coatings for tubing and fittings that minimise adsorption and desorption effects are available on the market. Despite this progress, some DQOs have not been met yet for all specified VOCs. This fact is underpinned by the WMO-GAW implementation plan 2016–2023, which states, as a key activity, that "uncertainty calculation" and "full

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traceability to the primary standard" for all measurements reported is needed. Currently, no WMO-GAW guidelines exist for the classes of VOCs addressed in this project.

The project will contribute to meeting the DQOs by developing novel, stable and traceable references for VOCs (objective 1), improving sampling and analytical methods (objective 3), establishing guidelines and procedures for the correct sampling, calibration and analysis of VOCs (objectives 2, 3), along with the dissemination of metrological concepts (e.g. traceability of working standards, calibration and measurement uncertainty) to the field monitoring stations (objectives 2, 3, 4).

Objectives

The overall objective of the project is to provide and improve reference gas standards for oxygenated VOCs, terpenes and halogenated VOCs with a high focus on the dissemination of these standards to ensure the metrological traceability to the working standards and their use in the field. The measurement techniques will also be validated to ensure SI-traceable measurements with a realistic and complete uncertainty budget. Assessing the major influencing factors of the measurement results and incorporating them in the uncertainty budget will enable the consortium to fulfil the objectives of data quality as specified by the corresponding measuring networks.

The specific objectives of the project are:

1. To select relevant gas compounds (oxy-VOCs, terpenes, halogenated VOCs) and to clarify the overall measurement uncertainty needed in close collaboration with stakeholders (ACTRIS and WMO-GAW monitoring networks). In addition, to develop new primary Reference Gas Mixtures (RGMs) at amount of substance fractions between 1 nmol/mol and 1 µmol/mol (expanded uncertainty < 5 %) for oxy-VOCs and terpenes and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs.
2. To define and select fit-for-purpose protocols for the preparation of working standards that ensure an unbroken SI-traceable calibration chain for oxy-VOCs, terpenes and halogenated VOCs. In addition to validate these protocols (proof of concept) and to compare them with field calibration protocols as well as calculating the uncertainty budget for each protocol following the principles of GUM (ISO 1995) and taking into account other uncertainty sources on-site (e.g. water removal). To provide a homogenous tool for uncertainty calculation for end-users.
3. To evaluate the sampling methods for the on-line/off-line in-situ analytical measurement of the selected gas compounds and to assess relevant influence parameters. In addition, to evaluate and improve the on-line/off-line in-situ analytical methods. To determine spectral molecular parameters for spectroscopic techniques, used in remote sensing methods to assess VOCs, with SI-traceability and contribute these to the HITRAN database. To establish an uncertainty budget for the selected measurement methods.
4. To facilitate the take up of the technology and measurement infrastructure developed in the project by: the measurement supply chain (accredited laboratories, instrument manufacturers), standards developing organisations (CEN, Air Quality directive NEC 2001/81/EC) and end users (e.g. WMO-GAW, EMEP, ACTRIS, AGAGE and AQUILA).

Progress beyond the state of the art

In order to fulfil DQOs set for VOCs (e.g. uncertainty < 10 % for VOCs measurement within ACTRIS), as well as the objectives set by the WMO-GAW for its implementation plan 2016-2023, highly accurate, stable and traceable reference gas mixtures (RGMs) of low amount-of-substance fractions (< 1 µmol/mol) and low uncertainties (e.g. < 5 %) are required. However, monitoring networks currently use in-house non-SI-traceable VOC RGMs for a large number of VOCs or they make improper dilutions of highly-concentrated RGMs to achieve atmospheric trace levels. Furthermore, they use sampling and analytical techniques (e.g. on-line, off-line and remote methods) that are not fully characterised nor metrologically validated. Consequently, the accuracy and comparability of their measurement results are not guaranteed. As a result, the identification of global atmospheric VOC trends are difficult as well as the adoption of effective mitigation measures.

Objective 1
This project will go beyond the state of the art by producing standards of amount-of-substance fractions that are closer to measured atmospheric levels, reducing their uncertainty, improving their stability and ensuring their traceability to the SI-units. RGMs of priority VOC identified by stakeholders will be developed during this project at amount-of-substance fractions between 1 nmol/mol and 1 µmol/mol (expanded uncertainty < 5 %) for oxygenated VOCs and terpenes and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs.

Objective 2
Moreover, a better understanding of VOC reactivity with surfaces and matrix gas will be pursued to optimise the methods needed for generating RGMs and improving their stability. To ensure SI-traceability of the field measurements and data comparability among networks, protocols on the preparation of accurate traceable fit-for-purpose VOC working standards will be defined and transferred to the field. Moreover, this project will develop user-friendly software to calculate uncertainty budgets for VOC measurements and guidelines stating common instructions on how to use the working standards, techniques and software, which will be disseminated to the project's stakeholders.

Objective 3
Furthermore, by characterising, optimising and validating sampling and analytical methods, and characterising their contribution to the uncertainty of VOC measurements, the project will go beyond the state of the art. At least four sampling and analytical methods used in two complementary approaches to monitor VOCs − in-situ (on- and off-line analytical methods) and remote sensing observations (broadband spectroscopic methods) − will be selected. Results from these exercises will form the basis for detailed guidelines on the best methods to measure VOCs. The knowledge compiled during the project (i.e. on the reactivity of VOCs with surfaces during sampling, analytical methods, water and ozone artefacts, sample filtering and novel measurement techniques) will contribute to improving the reliability of VOC measurements.

Results

To select relevant gas compounds (oxy-VOCs, terpenes, halogenated VOCs) and to clarify the overall measurement uncertainty needed in close collaboration with stakeholders (ACTRIS and WMO-GAW monitoring networks). In addition, to develop new primary RGMs at amount of substance fractions between 1 nmol/mol and 1 µmol/mol (expanded uncertainty < 5 %) for oxy-VOCs and terpenes and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs. (Objective 1)

In close collaboration with the stakeholder committee, a list of priority VOCs was elaborated. The selection was based on their importance on climate research and the lack of stable and SI-traceable reference gas mixtures (RGMs).
The priority compounds considered are as follows:

- Oxy-VOCs: ethanol, methanol, acetone, acetaldehyde, methyl vinyl ketone, methacrolein
- Terpenes: α-pinene, β-pinene, myrcene, terpinolene, β-caryophyllene
- Halogenated VOCs: 1,2-dichloroethane, HFO-1336mzz-Z, HFC-134, HFC-124, desflurane

In addition, the amount-of-substance fraction and the metrological requirements that the new RGMs should have were established. For oxy-VOCs and terpenes, the established amount-of-substance fraction range was from 1 nmol/mol to 1000 nmol/mol and for halogenated VOCs from 0.1 nmol/mol to 1 nmol/mol. The stability requirement for static reference standards should be greater than 24 months for the three VOC categories. The target relative expanded uncertainty for oxy-VOC and terpene RGMs should be ≤ 5 % and ≤ 3 % for halogenated VOCs.

For the spectral activities, other compounds relevant in VOC monitoring using remote sensing were selected from a more extended preliminary list of compounds in collaboration with the remote sensing contact group (i.e. stakeholders with expertise on satellite remote sensing (MIPAS, ACE-FTS, GOSAT), spectroscopic database (HITRAN) and experimental cross-section (PTB, UoL-NCEO)). The selected compounds were CFC-14, CFC-12 and HFC-23.

Within the framework of the project, a new automated cryo-filling system was developed, which precisely controls the mass flow, pressure and filling time. The system is an improved version of the cryo filling system developed in EMRP JRP ENV52 HIGHGAS. This system will be used to fill cylinders with the dynamically generated RGMs of halogenated VOCs (Objective 1) for storage and transportation. During the filling procedure, the cylinder is submerged in liquid nitrogen, which makes the gas condense in the cylinder (no pump required). Among other features, the system is coated with SilcoNert® 2000 and is Teflon-free. Thereby, the system is suitable for reactive and halogenated gases.

To define and select fit-for-purpose protocols for the preparation of working standards that ensure an unbroken SI-traceable calibration chain for oxy-VOCs, terpenes and halogenated VOCs. In addition to validate these protocols (proof of concept) and to compare them with field calibration protocols as well as calculating the uncertainty budget for each protocol following the principles of GUM (ISO 1995) and taking into account other uncertainty sources on-site (e.g. water removal). To provide a homogenous tool for uncertainty calculation for end-users. (Objective 2)

In order to fulfil Objective 2, the first step done by the project was to elaborate a report summarising the existing VOC calibration strategies that are currently applied to the GC-FID, GC-MS and PTR-MS instruments that are used at European measurement sites for VOC monitoring. The most common calibration strategies for GC-FID and GC-MS are the direct use of SI-traceable RGMs in cylinders, the effective carbon number, the dilution of higher amount fraction RGMs and permeation tubes. In the case of terpenes, the dilution of pure compounds (liquid form) in methanol and its preconcentration on adsorption tubes is also a common strategy. For calibrating PRT-MS, the strategies followed are the use of non-SI-traceable gas standards or, alternatively, the ion transmission curve. The report highlighted the extended use of non-SI-traceable approaches to calibrate the instruments at monitoring stations measuring VOCs. The project, therefore, targets the gaps in SI-traceability in order to develop fit-for-purpose SI-traceable working standards.

To evaluate the sampling methods for the on-line/off-line in-situ analytical measurement of the selected gas compounds and to assess relevant influence parameters. In addition, to evaluate and improve the on-line/off-line in-situ analytical methods. To determine spectral molecular parameters for spectroscopic techniques, used in remote sensing methods to assess VOCs, with SI-traceability and contribute these to the HITRAN database. To establish an uncertainty budget for the selected measurement methods. (Objective 3)

Several tests were planned to evaluate the sampling methods used for the analytical measurement of the priority VOCs (oxy-VOCs, terpenes and halogenated VOCs). Protocols were defined for testing sampling lines, particle filters, water removal systems and ozone scrubbers, which are commonly part of the VOC sampling strategy. Preliminary results on some of the selected water removal systems (coldfinger) and ozone scrubbers (MnO_2) suggest that none of these elements might have effects on the amount fraction measured for halogenated VOCs. However, this potential lack of effects should be taken with caution until definitive results are available.

In order to improve the off-line methods used for measuring oxy-VOCs and terpenes, different tests were set to evaluate sorbent tubes. Different sorbent materials (Tenax TA and Carbopack B among others), tube type (coated vs. non-coated), loading flows (e.g. 100 mL/min) and relative humidity (30 %, 70 %) were tested in terms of breakthrough volume, sampling efficiency and storage stability. Once definitive results are available, they will be included in a recommendation report on the most suitable sorbents and sampling protocols for priority oxy-VOC and/or terpene measurements.

In consultation with a remote sensing group established during the project, which includes experts on satellite remote sensing, spectroscopic database and experimental cross-section, a list of relevant halogenated VOCs for remote sensing applications was elaborated. The halogenated VOCs selected were CF_4 (CFC-14), CF_2Cl_2 (CFC-12), CHF_3 (HFC-23), CH_2F_2 (HFC-32) and SF_6. In addition, to evaluate the current state of the art in terms of quality of spectral parameters a report was elaborated. This report allowed the project to identify quality shortcomings and, in that way, to identify potential improvements to work on, particularly the SI-characterisation of spectral parameters.

Impact

During the first months of the project, to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium gave presentations at two conferences and created a website (https://www.metclimvoc.eu). The consortium is also active in social media (e.g. ResearchGate, LinkedIn). A fourteen-member stakeholder committee was set up (WMO, WMO-GAW, ACE, TOAR-II, HITRAN, ACTRIS, WMO-GAW SAG-AERO, AGAGE, CREAF-CEAB-CSIC-UAB Global Ecology Unit, ICOS-ATC, NILU, WMO

SAG-RG, ASF KIT-IMK, ETHZ Zenobi Group), which is informed about the progress achieved (every 3 months).

Impact on industrial and other user communities

To facilitate the uptake of the new primary reference gas mixtures, working standards and other project outputs by the industry, the consortium has been actively searching collaborations with gas, tubing and instrument manufacturers. Up to now, the collaborators are Fine Metrology, Swagelok Switzerland, Ionicon, Aerodyne Research and Gasera. These manufacturers will be able to apply the project outputs to ensure the robustness of their analytical devices and the accuracy of their reference materials. This will create impact by enhancing the trust of buyers on the new products, which may translate into an increased market demand.

The active involvement of several partners from the consortium with atmospheric monitoring networks (e.g. AGAGE, ACTRIS, WMO-GAW), together with the implication of these networks in the project stakeholder committee, will facilitate the uptake of fit-for-purpose outputs (e.g. working standards, best practice guides and recommendations). The uptake will create impact on the atmospheric monitoring communities by supporting the harmonisation of data across Europe for the long-term monitoring of climate and air quality and by ensuring the traceability and accuracy of measurement results.

Impact on the metrology and scientific communities

This project fully aligns with the goals of the European Metrology Network "Climate and Ocean Observation" by bringing together several NMIs/DIs with high priority stakeholders (identified in EMPIR JNP 18NET04 ForClimateOcean), which will enhance direct uptake by end-user communities. Furthermore, the project outputs will considerably improve the capabilities of European NMIs to disseminate traceability for global atmospheric monitoring communities.

For the scientific communities, impact will be created by enabling traceable, high quality and long-term harmonised atmospheric measurements, which will facilitate the assessment of long-term climate and air quality trends. Moreover, the project will parametrise and improve the accuracy of spectral intensity measurements, which will benefit remote sensing facilities and databases and generate impact by predicting spectral intensities in frequency regions where actual spectroscopic measurements of spectral intensities are not possible. The consortium started creating impact through knowledge transfer by publishing a research paper in a peer-reviewed journal [1] and a blog on the project webpage, which will create impact not only on the metrology and scientific communities, but also on the non-specialised public. Furthermore, the consortium started its contribution to other research projects and programs (e.g. TOAR-II) to enhance its impact.

Impact on relevant standards

The consortium will disseminate its findings through new or revised guidelines and recommendations with their active participation in several working groups (e.g. CEN/TC264/WG12, ISO/TC158, new WMO-GAW measurement guidelines). The project started creating impact on standards by presenting the project activities at the last EURAMET TC-MC (Metrology in Chemistry) and CEN TC 264 Air quality (WG13) meetings. Moreover, the consortium provided input to the new WMO-GAW Measurement guidelines that is being elaborated by the WMO-GAW VOC Expert Team.

Longer-term economic, social and environmental impacts

Many economic activities will be affected by climate change leading to economic loses. Human health impacts associated with current air quality and climate change trends are also expected to place additional economic stress on health and social support systems. The outputs of this project will result in more accurate and harmonised data that will improve the identification of climate and air quality trends. This will lead to the adoption of more effective mitigation strategies, which will generate long-term economic impact by decreasing the costs related to air pollution and climate change. Besides, effective mitigation policies will create environmental impact by limiting the use and emissions of VOCs through more strict legislation and treaties. The future harmonised datasets will additionally lead to a better understanding of long-term global VOC emissions and of the chemistry involved by the scientific community.

List of publications

[1] Sassi, G.; Khan, B.A.; Lecuna, M. Reproducibility of the quantification of reversible wall interactions in VOC sampling lines. *Atmosphere* **2021**, *12*, 280. https://doi.org/10.3390/atmos12020280

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	1 June 2020, 36 months	
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