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 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 VOC measurements by monitoring programs, such as WMO-GAW and ACTRIS (e.g. uncertainty < 10 %), 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 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 RGMs 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. In addition, this project will develop a piece of 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
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, optimised, validated and metrologically characterised for the first time. Results from these exercises will form the basis for detailed guidelines on the best methods to measure VOCs, including their uncertainty budgets. 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). In addition, the amount-of-substance fraction and the metrological requirements that the new RGMs should have were established.
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 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.

16 RGM of the priority oxy-VOCs in nitrogen were prepared at nominal amount fraction of 100 nmol/mol. Three of the RGMs contained ethanol, methanol and acetone. The other 13 RGMs contained ethanol, methanol, acetone, acetaldehyde, MVK and methacrolein. In both cases, n-hexane was added as an internal standard. The RGMs were validated using dynamic methods (dilution, permeation and diffusion). The overall relative uncertainty was < 5 % (k = 2) in agreement with the project objective. Currently, the temporal stability of the cylinders is being tested.

Within the framework of the project, an improved cryo-filling system was developed, which precisely controls the mass flow, pressure and filling time (improved version of EMRP JRP ENV52 HIGHGAS). This system is 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. A set of 8 cylinders (METAS 2021 scale) containing 3 halogenated VOCs from the priority list (1,2-dichloroethane, HFC-134, HFO-1366mzzZ) and 4 other halogenated VOCs (HFC-32, HFC-365mfc, CH_2Cl_2, CCl_4) at near-ambient amount fraction (0-10 pmol/mol) was prepared using the cryo-filling system. The relative expanded uncertainty of the multicompound RGMs was < 3% (k = 2) in agreement with the project objective.

In addition to the methods described above, oxy-VOC dynamic RGMs were generated during the project for oxyVOCs (methanol, ethanol, acetone, acetaldehyde and MVK) and terpenes (α-pinene, β-pinene, myrcene and β-caryophyllene) at amount fractions < 100 nmol/mol. The relative expanded uncertainty of the oxy-VOC RGMs was < 5 % (k = 2) for all the compounds except for ethanol. For this compound, particular attention should be paid to the purity of the permeation unit used for the RGM generation. To achieve the targeted expanded uncertainties, periodic calibrations of the permeation units are required to assess their stability and avoid aging issues. Regarding the terpene RGM, the relative expanded uncertainty was > 5 % (k = 2; 10-13 %). Therefore, for none of the terpenes the objective was fulfil. The low purity of the pure compounds used to fabricate the permeation units (< 90 %) together with their low temporal stability seem to be the main reasons for that.

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. For that purpose, three protocols for the propagation of RGMs to working standards with an unbroken SI-based traceability chain were elaborated for oxy-VOCs, terpenes and halogenated VOCs. In these protocols, new working standards developed during the project such as the gravimetric RGMs mentioned above (100 nmol/mol, U < 5%) diluted to atmospheric levels using a SI-traceable dilution system or certified whole air working standards, were described. The novel SI-traceable working standards are being compared with current standards used at monitoring stations to assess the best practice protocol for 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 performed 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. Results showed that at relative humidity between 30-70 % the tested sampling line materials (Silcosteel, Sulfinert, stainless steel, PFA and PEEK) did not have important effects on the sampled oxy-VOCs. Under dry conditions, however, there were effects, which were minimised by using passivated sampling lines. FEP, Silcosteel-CR and Sulfinert inlet lines (internal diameter 1/8", length 10 m) are suitable for measurements of the priority compounds of the project using a sampling air flow of 1 L/min. PEEK inlet is not recommended for terpenes as losses of the priority terpenes and terpinolene were observed. Concerning ozone scrubbers, the tested scrubbers (KI/Cu, MnO_2, $Na_2S_2O_3$ and heated stainless steel tubes) had a removal efficiency of ozone > 95 %. According to the results, the use of KI/Cu, MnO_2 and $Na_2S_2O_3$ does not have effect on the sampled oxy-VOCs and halogenated VOCs. For terpenes, the tested ozone scrubbers are suitable except MnO_2, which showed effects on the sampling of mono- and sesquiterpenes. Results on the selected water removal systems (coldfinger, Nafion Dryers) suggest that none of these elements might have effects on the amount fraction measured for halogenated VOCs (CFCs, HCFCs, HFCs, PFCs, HFOs). However, amount fractions of oxy-VOCs are affected by the use of coldfingers as water removal, being MVK the compound more affected by the water trap. This effect seems to be less important when the temperature of the water trap increases to -10 °C from -40 °C. Complete loss of the more polar oxy-VOCs occurred when Nafion Dryers were used.

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. Results showed that the best sorbent material for sampling terpenes (α-pinene, β-pinene, myrcene, terpinolene and β-caryophyllene) is Tenax TA (commercial), while for oxy-VOCs (acetaldehyde, methanol, acetone, ethanol, methacrolein and methyl vinyl ketone) are Carbopack C – Carbopack B – Carbosieve SIII and Carbosieve SIII (commercial). The differences between stainless steel and coated Silco steel tubes were not significant. These and other recommendations are included in the report written on the evaluation of sorbent tubes as an off-line method for measuring oxy-VOCs and terpenes.

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. Furthermore, another report was written on recommendations on the matrix and thermodynamic conditions (gas pressure, temperature) to be used to measure the selected long-lived halogenated VOCs.

Impact

In order to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium is presenting the project and its results at international conferences (16 up to now), keeps the project website updated (https://www.metclimvoc.eu), publishes every two months blog post on the VOC measurement topic and organises open training courses and workshops. The consortium is also active in social media (ResearchGate, LinkedIn and Twitter) and its activities are advertised through the EMN COO website/newsletters. 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 every 3 months about the progress achieved.

The possibility of organizing the final stakeholder workshop (spring 2023) next to an international conference is in discussion (e.g. EGU, CIM). This will enhance the dissemination of the project results to internal and external industrial stakeholders.

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, in addition to the Mediterranean Center for Environmental Studies CEAM (research institute), 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. One example of this was the collaboration between Gasera and a member of the consortium to develop a new methanol analyser, taking into account the project findings regarding objective 3. This collaboration also allowed to metrologically characterising the new analyser, which will enhance buyers' trust once the analyser is commercialised. Another impact of the project on industrial communities (not only project collaborators) was the insight into quality and problematic of formaldehyde analysers provided by the results of the formaldehyde comparison organized by the consortium. Several industrial and atmospheric researchers participated in this comparison with their own instruments. Participants could compare the performance of the different analysers.

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.

Accurate VOCs reference gas mixtures are also of high interest for breath analysis used for medical diagnostic (biomarkers). The production of such gas mixtures were presented to the *Exhalomics* community as well.

Impact on the metrology and scientific communities

This project fully aligns with the goals of the European Metrology Network (EMN) "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. The outputs of the MetClimVOC project were used as input for the EMN strategic research agenda and further sustainable collaboration with key-stakeholder are foreseen in this framework.

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], an article in the WMO-GAW letter number 81 and periodic blog posts on the project webpage, which will create impact not only on the metrology and scientific communities, but also on the non-specialised public. Under knowledge transfer, the consortium also uploaded several training videos in the project webpage. Furthermore, the consortium started its contribution to other research projects and programs (e.g. TOAR-II) to enhance its impact. To increase the impact on scientific communities, the project is actively participating in conferences and research groups out of Europe. For example, the project experts on remote sensing contribute to the discussion on spectral quality and metrology in HITRAN database. Moreover, the consortium will present the project outputs on the Mediterranean Geophysical Union in an oral presentation and as extended abstract in the conference proceedings that will be published.

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 created impact on standards by presenting the project activities at the EURAMET TC-MC (Metrology in Chemistry), CEN TC 264 Air quality (WG13) and AQUILA (WG7) meetings. Moreover, the consortium provided input to the revised and new WMO-GAW Measurement guidelines that are being elaborated by the WMO-GAW VOC Expert Team. Finally a GAW-TECH QA/QC training workshop is planned in September for presenting the project results (which will be included in the mentioned guidelines).

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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RMG: -		