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 and 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. Within this project, stable reference gas mixtures of priority oxygenated and halogenated VOCs were produced at low amount-of-substance fractions and uncertainties (≤ 100 nmol/mol, ≤ 5 % expanded uncertainty and at least 18 months temporal stability). For some VOCs, this was the first time that stable and traceable standards were produced. Furthermore, the project provided well-characterised sampling and analytical methods and SI-traceable spectral parameters for spectrum-based techniques. Moreover, the project provided a user-friendly on-line tool to calculate uncertainties, guidelines and training on metrological aspects to monitoring stations. In addition, this project reinforced the collaboration between two communities (i.e. metrology and atmospheric research) that are crucial to ensure the comparability and quality of atmospheric data. These outputs contributed to address some of the main needs of atmospheric stakeholders.

Need

The WMO-GCOS (Global Climate Observing System) defined 55 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 needed 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 were no references available to ensure traceability and uncertainty. Finally, remote sensing methods, which show high potential to avoid sampling issues, were 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

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DQOs had 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.

The project contributed to some extent 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 was 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 were also 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 enabled the consortium to fulfil the objectives of data quality as specified by the corresponding measuring networks.

The specific objectives of the project were:

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, in many cases monitoring networks use in-house non-SI-traceable RGMs for a large number of VOCs or, to achieve atmospheric trace levels, diluted highly-concentrated RGMs, which might have lost metrological traceability during the dilution. Furthermore, they use sampling and analytical techniques (e.g. on-line, off-line and remote methods) that are not fully characterised nor metrologically validated in an homogeneous way among monitoring stations. Consequently, the accuracy and comparability of their measurement results are not guaranteed. As a result, the identification of global atmospheric VOC trends is difficult as well as the adoption of effective mitigation measures.

Objective 1
RGMs of priority VOC identified by stakeholders were developed during this project at amount-of-substance fractions ≤100 nmol/mol (expanded uncertainty < 5 %) for oxygenated VOCs and < 1 nmol/mol (expanded uncertainty < 3 %) for halogenated VOCs. Temporal stability of at least 18 months was proved. Thus, this project went 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.

Objective 2
Moreover, a better understanding of VOC reactivity with surfaces and matrix gas was gained to optimise the methods needed for generating RGMs and working standards 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 were defined. Results from the protocol assessment, suggested that some of the protocols (e.g. SI-traceable dilution of RGMs) could be transferred to the field. In addition, this project developed a user-friendly online tool to calculate uncertainty budgets for VOC measurements and guidelines stating common instructions on how to use the working standards, techniques and software, which was disseminated to the project's stakeholders.

Objective 3
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) − were selected, optimised, validated and metrologically characterised for the first time. Within the analytical methods, PTR-MS and laser spectroscopy were selected. Sampling methods such as sorbent tubes and sampling elements like particle filters, water removal systems and/or ozone scrubbers were also assessed. Results from these exercises formed 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) contributed 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, which the new RGMs should have, were established.
The priority compounds considered were as follows:

- Oxy-VOCs: ethanol, methanol, acetone, acetaldehyde, methyl vinyl ketone (MVK), 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 included 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 of preparation was < 5 % (coverage factor (k) = 2) in agreement with the project objective. The temporal stability of the cylinders during the first 18 months after preparation was tested. Most of the compounds remained stable in all the cylinder types. The exception was methanol (loss) and acetaldehyde

(gain). The best stability results, particularly for methanol, were found for cylinders with specific treatment for VOCs and a low-dead volume cylinder valve.

Within the framework of the project, an improved cryo-filling system was used, which precisely controls the mass flow, pressure and filling time (improved version of EMRP JRP ENV52 HIGHGAS). This system was 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 (1.0-74.6 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 oxy-VOCs (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, the objective was not fulfilled for any of the terpenes. The low purity of the pure compounds used to fabricate the permeation units (< 90 %) together with their low temporal stability seemed to be the main reasons for that.

A new methodology to study adsorption and desorption kinetics of oxy-VOCs in different cylinder types based on isotopes was tested for methanol. Thanks to differences in the measured amount-of-substance fractions of methanol isotopes, methanol losses linked to surface effects could be tracked and quantified.

Except for the priority terpenes and three of the priority oxy-VOCs (methanol, acetaldehyde and MVK), for which further research is needed, Objective 1 was achieved. RGMs of priority VOCs – selected in close collaboration with stakeholders – were produced at the target amount fractions and uncertainties. For the priority oxy-VOCs, RGMs were prepared at around 100 nmol/mol with relative expanded uncertainty < 5 % (k = 2). RGMs of selected halogenated VOCs were produced at amount fractions < 1 nmol/mol and relative expanded uncertainty < 3 % (k = 2). Temporal stability of at least 18 months was ensured for the produced RGMs.

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 Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Chromatography-Mass Spectrometry (GC-MS) and Proton Transfer Reaction-Mass Spectrometry (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 PTR-MS, the strategies followed are the use of non-SI-traceable gas standards or, alternatively, the ion transmission curve. Currently, SI-traceable transmission curve reference material developed by NPL for PTR-MS is available (https://doi.org/10.5194/amt-16-1061-2023). The report highlighted the extended use of non-SI-traceable approaches to calibrate the instruments at monitoring stations measuring VOCs. The project, therefore, targeted 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 were compared with current standards used at monitoring stations to assess the best practice protocol for working standards. Several steps were done to assess the protocols. In the case of whole air samples in high-pressure cylinders and canisters, the first step was to certify the samples previously spiked with the priority oxy-VOCs and terpenes. Certification, however, was only possible in the high-pressure cylinder for methanol, ethanol, acetone and methacrolein and in the low-pressure canisters for methacrolein and acetone. After the certification, a batch of cylinders and canister was sent to the participants of the round-robin comparison. Participants used different analytical instruments and calibration protocols to measure the oxy-VOC amount-of-substance amount fractions in the air samples. Results were quite diverse. Whereas high-pressure cylinders seem to be suitable for the less polar oxy-VOCs (acetone and acetaldehyde) for up to 12 months, the low-pressure canisters should not be used for these compounds. For more polar compounds, such as methanol and ethanol, this kind of working standard is not suitable. Terpenes showed an initial loss in both types of vessels (high-pressure cylinders and low-pressure canisters). Myrcene and β-caryophyllene could not be observed neither during the certification nor during the comparison measurements although both compounds were spiked into the vessels. α-Pinene and β-pinene were observed but with an uneven behaviour. It was concluded, therefore, that whole air samples shouldn't be considered as working standards for terpene monitoring.

Concerning the other SI-working standards, several instruments (two PTR-MS, two GC-FID and an analyser based on laser spectroscopy) were used during the assessment, as well as different calibration protocols. Results suggested that the new SI-traceable working standard protocols seem to be suitable for acetone monitoring but not for MVK, MEK or methanol. Although SI-working standards based on diluted reference gas mixtures seem to be suitable for acetaldehyde, SI-working standards based on permeation were not. For methanol, clear conclusions could not be extracted, but it seems that it remains a challenging compound. Because of the broad variety of instruments and calibration standards, the conclusions should be taken with caution. SI-traceable working standards based on permeation seem to be unsuitable for terpene monitoring, particularly for α- and β-pinene. This was due, most likely, to the low long-term stability and purity of the permeation units. Alternatives to SI-WS based on permeation, such as the dilution of reference gas mixtures using SI-traceable dilution systems should be explored.

A comparison was performed between whole air samples and the newly developed halogenated VOC scale. Samples were preconcentrated and subsequently analysed by gas chromatography-mass spectrometry. According to the results, the preparation of SI-traceable reference gas mixtures and its subsequent intercomparison with real-air standards was proven to be the best method for monitoring halogenated VOCs. For compounds that are not yet present in the air or whose amount fractions are too small (sub pmol/mol level), the spiking of the real-air standards can be considered the state-of-the-art method.

Uncertainty budgets of each measurement were calculated considering all the processes involved in the measurement: sampling, calibration and analysis. For each of the analytical methods used during the working standard assessment, the main sources of uncertainty were identified, described and quantified. Based on the project outputs for GC-FID, as well as on the guidelines described by ACTRIS and WMO-GAW regarding the uncertainty of this technique for VOCs, an on-line tool for the calculation of uncertainties (TUCAVOC) was developed and made available for monitoring stations. The first version of the on-line tool is currently under a review and improvement process based on the implementation of comments provided by NMIs and monitoring station operators.

Objective 2 was achieved for all priority compounds except for terpenes and some oxy-VOCs (methanol, MVK and MEK). For that purpose, several protocols for generating SI-traceable working standards were defined and assessed for oxy-VOCs, terpenes and halogenated VOCs. The new traceable working standards, especially the ones based on RGM dilution seemed to be appropriate for all oxy-VOCs (except for methanol, MVK and MEK) and for halogenated VOCs. Moreover, the uncertainty budget of each working standard was calculated and on-line tool to calculate the uncertainty of VOC measurements was developed and distributed among the atmospheric monitoring community.

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 inlets are 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 an effect on the sampled oxy-VOCs and halogenated VOCs. For terpenes, the tested ozone scrubbers were suitable except MnO_2, which showed effects on the sampling of mono- and sesquiterpenes. Results on the selected water removal systems (cold finger, 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 were affected by the use of cold fingers 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) was Tenax TA (commercial), while for oxy-VOCs (acetaldehyde, methanol, acetone, ethanol, methacrolein and methyl vinyl ketone) they were 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 were included in the report written on the evaluation of sorbent tubes as an off-line method for measuring oxy-VOCs and terpenes.

Six different techniques to monitor formaldehyde were evaluated in a side by side intercomparison organised within the project: three instruments based on Hantzsch fluorimetry, one instrument based on microfluidics Hantzsch fluorimetry, two DNPH samplers, one analyser based on IR spectroscopy, a PTR-MS and one instrument based on CRDS. According to the comparison results, the DNPH as a reference technique performed very well compared to theoretical generation. Moreover, the CRDS-based instrument was the least noisy method to measure formaldehyde at low amount fractions followed by the 3 Hantzsch-based instruments and microfluidics. The great majority of the instruments succeeded to measure all the different levels of formaldehyde apart from the IR-spectrometry-based instrument, which was noisy. A fast response when changing the formaldehyde amount-of-substance fractions was observed for all the instruments except the microfluidics Hantzsch fluorimetry. The PTR-MS instrument overestimated the amount-of-substance fractions by about 40-80 %, which reflects clearly that the instrument was not suitable for measuring formaldehyde at such low amount fractions, most likely due to calibration and corrective actions that should be performed.

As a result of a collaboration with the instrument manufacturer GASERA, a fit-for-purpose methanol analyser was developed and characterised. Based on the characterisation, some considerations should be taken into account to ensure the quality of the measurements, such as providing humidity to the instruments, as it helps to passivate the sampling lines. At amount-of-substance fractions above 1000 nmol/mol of methanol, the measurement parameters started to have a significant impact on the values obtained due to transient effects inside the instrument associated to wall interactions. In general, the variability of readings after stabilisation was improved significantly when the number of cell flush cycles increased in order of magnitude, even with the same short default duration of flush through cell and bypass. At high levels of methanol, after fast switches, a minimum time of 5 minutes was required for the system to stabilise to a new value.

A new SI-traceable PTR-MS standard developed by NPL (https://doi.org/10.5194/amt-16-1061-2023) was tested using three different PTR-MS instruments. Based on the developed transmission curve reference material, a protocol for retrieving the transmission parameter of the instrument, assessing the slope of local transmission, assessing primary ion purity, collision energetics, humidity in the reaction chamber and water cluster ions.

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. CF_4, SF_6 and CHF_3 spectra were accurately measured under pressure and temperature conditions that were fully traceable to the SI. For these measurements, a dynamic dilution system was used, which allowed a significantly better control over the absorbed amount-of-substance fractions measured by FTIR. For room temperature, a technique to reconstruct the absorption cross sections over a large span of amplitudes was used. Two spectra for CF_4 and SF_6 each and one spectrum for CHF_3 were obtained with this technique. Generation of the composite spectra proved to be very accurate and straightforward for the non-polar molecules. Analysis of the integrated intensities yielded accurate values with uncertainties below 1.8 % ($k = 2$), with the absorption path being the major contributor.

Several sampling methods were evaluated and recommendations based on these findings were elaborated. Some of the analytical methods used for VOC monitoring were assessed and improved, given as results, guidelines, a fit-for-purpose methanol analyser and SI-traceable calibration protocols for PTR-MS. Moreover, accurate spectral measurements of halogenated VOCs were done, to ensure the traceability of temperature and pressure (two crucial parameters for spectral measurements). The obtained spectra and information were presented at the HITRAN database community, which will consider them for inclusion in the database upon publication. Furthermore, initial uncertainty budgets for selected analytical methods (PTR-MS, GC-FID, Medusa-GC-MS and laser spectrometry) were calculated. Therefore, Objective 3 was fully achieved.

Impact

In order to maximise the impact of the project and ensure a wide dissemination of the knowledge generated, the consortium presented the project and its results 32 times at international conferences focusing on a broad range of topics, such as remote sensing, chemistry, geosciences, metrology and atmospheric monitoring, kept the project website updated (https://www.metclimvoc.eu), published (every two months) blog posts on the VOC measurement topic, particularly during the first half of the project and organised open training courses and workshops. The consortium was also active in social media (ResearchGate, LinkedIn and Twitter) and its activities were advertised through the EMN COO website/newsletters. A fifteen-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 was informed every 3 months about the progress achieved.

The final stakeholder workshop (March 2023) was organised as a satellite event of the International Congress of Metrology (CIM2023), which was held together with Global Industry 2023 in Lyon (France). Sixty participants attend the half-day workshop, which was divided into two sessions. During each session, the consortium and some of the project collaborators presented the main outputs of the project. Each session finished with a round table where stakeholders discussed two topics: "Can SI-traceability be achieved at atmospheric monitoring stations? – needs and challenges" and "Metrology for atmospheric monitoring – uptake and further steps". Oral presentations and round-tables were recorded and the videos were uploaded to the project webpage. This enhanced 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 actively searched for collaborations with gas, tubing and instrument manufacturers. In addition to the Mediterranean Center for Environmental Studies CEAM (research institute), the collaborators were Fine Metrology, Swagelok Switzerland, Ionicon, Aerodyne Research and Gasera. These manufacturers were able to apply the project outputs to ensure the robustness of their analytical devices and the accuracy of their reference materials. This created 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 the metrological characterisation of 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 organised by the consortium. Several industrial and atmospheric researchers participated in this comparison with their own instruments. Participants compared 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. The development of a user-friendly on-line tool to calculate uncertainties of the VOC measurements and its distribution among the monitoring stations contributed to the project impact on these communities. Furthermore, thanks to the progress achieved during the project concerning reference gas mixtures of halogenated VOCs at low amount-of-substance fractions (few pmol/mol), one member of the consortium was designated as the Central Calibration Laboratory for ten halogenated VOCs within the WMO-GAW programme. This is a clear impact on atmospheric monitoring communities.

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 during a visit to one of the consortium members. This presentation rose awareness of the important role that metrology could play in the *Exhalomics* projects. For example, by providing SI-traceable RGMs of VOCs that may be present in the breath at very low amount fractions, which could improve the accuracy of breath analysis.

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 enhances 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.

One of the partners participated actively in EURAMET TC-IM 1449 towards the development of guidelines on data management plans and on research data management for EMP projects. The project MetClimVOC was selected for the technical committee as a case study and example to follow by coordinators to elaborate and follow data management plans.

For the scientific communities, impact was 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 parametrised and improved 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 were not possible. The consortium started creating impact through knowledge transfer by publishing three research papers in peer-reviewed journals [1, 2, 3]. Four popular press articles – in the WMO-GAW letter number 81, ACTRIS newsletter number 19 and Contrôles Essais Mesures (CEM) numbers 82 and 83 – and periodic blog posts on the project webpage will create additional 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 actively participated 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. Their findings on CCl_4 and SF_6 spectra will be considered for contribution to HITRAN database as soon as the submitted manuscripts are published in peer-review journals. Moreover, the contribution of the consortium, which covered the topic of new SI-traceable RGMs of VOCs, to the Mediterranean Geophysical Union conference was submitted to a special issue on contributions to the conference, which will be published in Earth System and Environment.

Impact on relevant standards

The consortium disseminated 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. In addition to the active presentation of project outputs at CEN-TC 264 Air quality (WG13), discussions on the use of best sampling materials and sampling conditions based on MetClimVOC inputs have taken place with this standard body. Furthermore, the priority list of VOCs selected at the beginning of the project was suggested (currently under consideration) for inclusion in the "Proposal for a revision of the Ambient Air Quality Directive (AAQD)". The consortium also 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 took place in September. During the workshop, project results (which will be included in the mentioned guidelines) were presented.

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 resulted 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
[2] Worton, D.R.; Moreno, S.; O'Daly, K.; Holzinger, R. Development of an International System of Units (SI)-traceable transmission curve reference material to improve the quantitation and comparability of PTR-MS measurements. *Atmospheric Measurement Techniques* **2023**, *16*, 1061-1072. https://doi.org/10.5194/amt-16-1061-2023
[3] Persijn, S.T. and Baldan, A. A new look at the sorption kinetics in reference gas standards. *Measurement Science and Technology* **2023***,* 34, 115018. https://doi.org/10.1088/1361-6501/ace9ee

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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Internal Funded Partners: 1. METAS, Switzerland 2. FMI, Finland 3. LNE, France 4. PTB, Germany 5. TUBITAK, Türkiye 6. VSL, Netherlands	External Funded Partners: 7. DWD, Germany 8. Empa, Switzerland 9. IMTelecom, France 10. KIT, Germany 11. POLITO, Italy 12. UoL, United Kingdom 13. UU, Netherlands	Unfunded Partners: -
RMG: -		