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

Overview

Climate change poses high risks to society. Long-term, accurate, worldwide measurements of volatile organic compounds (VOCs) are pivotal to understanding changes in the Earth's climate and to addressing the effects of climate change. VOCs are direct and indirect greenhouse gases, as they can influence the oxidising capacity of the atmosphere and hence the lifetime of methane. Furthermore, VOCs are precursors of ozone and aerosols, which both contribute to the radiative forcing. As the abundance of atmospheric VOCs is low (parts-per-trillion (pmol/mol) to parts-per-billion (nmol/mol)), with some compounds being very reactive, their sampling, analysis and calibration are challenging. The availability of high-quality reference materials and well-defined methods is essential to reach the necessary accuracy, as expressed in the World Meteorological Organization (WMO) data quality objectives (DQOs). This project will improve the quality of reference gas mixtures and it will ensure the correct dissemination of references to the field via adequate working standards and recommendations, along with well-characterised sampling and analytical methods. Finally, it will provide SI-traceable spectral parameters for spectrum-based measurement techniques.

Need

VOCs are chemical compounds that have a high vapour pressure at ambient temperature. VOCs include alkanes, alkenes, alkynes, aromatic compounds and terpenes as well as oxygenated compounds (e.g. alcohols) and halogenated VOCs.

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 substances need to be monitored. Stable traceable references with a low uncertainty along with well-defined measuring methods are indispensable for reliably measuring amount-of-substance fractions of these VOCs. 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, these data quality objectives are currently not met for all specified compounds. It is very challenging to measure VOCs in the atmosphere because they occur at very low amount-of-substance fractions; oxy-VOCs and terpenes in the range of pmol/mol to nmol/mol, and halogenated VOCs in the range of pmol/mol. 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 challenging. For some compounds, such as hydrofluoroolefins, which are used as substitutes for restricted (Kigali amendment) long-lived hydrofluorocarbons (HFCs), 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.

Nevertheless, significant progress has been made during the past years. For example, new traceable reference gases were established, mobile, dynamic reference gas generators were developed and coatings for tubing and fittings that minimise adsorption and desorption effects are available on the market (e.g. EMRP JRPs ENV56 KEY-VOCS and ENV52 HIGHGAS). However, some of the DQOs are currently not met for all specified compounds or they are still under estimation. This 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.

This 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 and results

In order to fulfil the DQOs that have been 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 standards of low amount-of-substance fractions (< 1 µmol/mol) and low uncertainties (e.g. < 5 %) are required. However, the monitoring networks currently use in-house VOC standards that are not SI-traceable for a large number of oxy-VOCs, terpenes and halogenated VOCs or they make improper dilutions of highly-concentrated reference gas mixtures 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 VOC trends in the atmosphere might be difficult as well as the adoption of effective mitigation measures.

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)
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, it will reduce their uncertainty, improve their stability and ensure their traceability to the SI-units. Through active communication with stakeholders, relevant VOCs will be identified to meet their needs. VOC standards will then 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. Moreover, this project will pursue a better understanding of VOC reactivity with surfaces and matrix gas to optimise the methods needed for the generation of static and dynamic standards and, in turn, to improve the stability of 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)
This project will define protocols for the preparation of accurate traceable fit-for-purpose oxy-VOC, terpene and halogenated VOC working standards. These protocols will then be transferred to the field protocols. The project will also develop user-friendly software to calculate uncertainty budgets for VOC measurements. In addition, guidelines stating common instructions on how to use the working standards, techniques and software will be disseminated to the project's stakeholders. These guidelines will guarantee the full SI-traceability of the field measurement results and the comparison of the results among monitoring networks, going, therefore, beyond the state of the art.

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)
This project will consider at least four of the sampling and analytical methods that are used in two complementary approaches to monitor VOCs: in-situ (on- and off-line analytical methods) and remote sensing observations (broadband spectroscopic methods). These methods will be characterised, optimised and validated, and their contribution to the uncertainty of the measurement results will be well-characterised. The results from these exercises will form the basis for detailed guidelines on the best methods to be applied to measure oxy-VOCs, terpenes and halogenated VOCs. The knowledge compiled during this 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.

Impact

Impact on industrial and other user communities

Fit-for-purpose outputs (new reference materials, working standards, improved and well-characterised measurement methods, best practice guides and recommendations) will be developed to address and fulfil the requirements of the WMO-GAW for climate relevant compounds (amount-of-substance fraction < 1 µmol/mol, uncertainty < 10 %) – i.e. oxygenated VOCs, terpenes and halogenated VOCs. These outputs will create impact on the atmospheric monitoring communities by supporting the harmonisation of data across Europe and beyond (as WMO-GAW is an international body) for the long-term monitoring of climate and air quality. An additional impact will be achieved by improving the quality of existing measurements carried out by well-established networks, such as WMO-GAW VOC, WMO-GAW GHG, ACTRIS, EMEP, AGAGE and AQUILA.

The focus on dissemination to the field will directly enhance the early uptake of the project outputs including fit-for-purpose working standards and well-characterised and harmonised measurement methods. This will create additional impact on the atmospheric monitoring communities by ensuring the traceability of measurement results, reducing the measurement uncertainty and improving the comparability between monitoring sites. As a result, additional impact will be created on the policymaker communities by facilitating the identification of VOC emission and climate trends and, in turn, making more effective implementation decisions (e.g. emission regulations, Kyoto protocol).

In addition, manufacturers of e.g. PTR-MS or gas handling devices, and gas cylinder and permeation device manufacturers will greatly benefit from the project results. These manufacturers will be able to select the best surface materials and to optimise the sampling protocols of their devices in order to minimise undesired reactions between VOCs and surfaces. This will ensure the robustness of their analytical devices (e.g. PTR-MS) and the accuracy and stability of their reference materials (gas cylinders, permeation devices). Both cases will create impact on these industrial communities by enhancing the trust of buyers (e.g. air monitoring networks) in the new beyond the state-of-the-art products and this will increase market demand, which will help them to be market leaders.

Impact on the metrological and scientific communities

This project fully aligns with the goals of the newly created European Metrology Network "Climate and Ocean Observation" by bringing together several NMIs/DIs with high priority stakeholders as identified in one of the first tasks of the EMPIR JNP 18NET04 ForClimateOcean. High priority stakeholders are involved as they are part of well-established monitoring networks or they are even mandated as a so-called "topical centre" or "world calibration centre" for the whole network. These synergies will enhance direct uptake by end-user communities.

In addition to the impact that the project will have at the European level, the collaboration with international measuring networks (AGAGE and WMO-GAW) will enhance the recognition of the European NMIs as well as the European Metrology Network "Climate and Ocean Observation". This will increase the chances of European NMIs being mandated by the WMO-GAW to become a Central Calibration Laboratory for compounds that currently have not been appointed.

Through the generation of accurate, stable and fit-for-purpose reference materials as well as the provision of sound input to measurement guidelines, this project will create impact on the scientific communities by enabling traceable, high quality and long-term harmonised atmospheric measurements. These long-term harmonised datasets will create impact by fulfilling the data quality objectives of WMO-GAW and, in turn, this will facilitate the assessment of long-term climate and air quality trends.

Furthermore, this project will parametrise and improve the accuracy of spectral intensity measurements, which will benefit remote sensing facilities and databases. These accurate measurements will generate impact on the scientific community by predicting spectral intensities in frequency regions where actual spectroscopic measurements of spectral intensities are not possible. This will allow the creation of theoretical models.

Finally, the consortium will create impact on the scientific community through knowledge transfer by publishing several research papers in peer-reviewed journals and by organising a workshop orientated to stakeholders (atmospheric monitoring experts, climate researchers), which will focus on novel sampling and analytical methods, working standards, SI-traceability dissemination to the field and uncertainty propagation calculations.

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). Furthermore, the work will especially support the Directive 2008/50/EC for air quality as well as regulation (EC) No 842/2006 - specifically for fluorinated gases that are banned by the Kyoto protocol - by increasing the confidence in the immission measurements and by enabling improved evaluation tools for implemented emission reduction measures.

Long-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. Moreover, infrastructure damages from extreme weather events are expected to increase together with the number of victims. The outputs of this project (traceable reference standards, fit-for-purpose working standards and optimised analytical protocols) 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 the economic and social impacts, the effective mitigation policies will also 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. This in turn, will improve our understanding of other aspects of the global chemistry of the atmosphere (e.g. ozone formation) and its response to anthropogenic emissions. This will help us to adopt effective policies to further reduce anthropogenic impacts on climate.

Furthermore, the project outputs will considerably improve the capabilities of European NMIs to disseminate traceability for global atmospheric monitoring communities, which will provide the foundation to underpin the work of monitoring networks and instrument and standards manufacturers. This will enable them to remain or become competitive.

List of publications

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<table>
<tr><td colspan="2">Project start date and duration:</td><td>1 June 2020, 36 months</td></tr>
<tr><td colspan="3">Coordinator: Celine Pascale, METAS Tel: +41 58 38 70381 E-mail: celine.pascale@metas.ch
Project website address: www.metclimvoc.eu</td></tr>
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1. METAS, Switzerland
2. IL, Finland
3. LNE, France
4. PTB, Germany
5. TUBITAK, Turkey
6. VSL, Netherlands</td><td>External Funded Partners:
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11. POLITO, Italy
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