

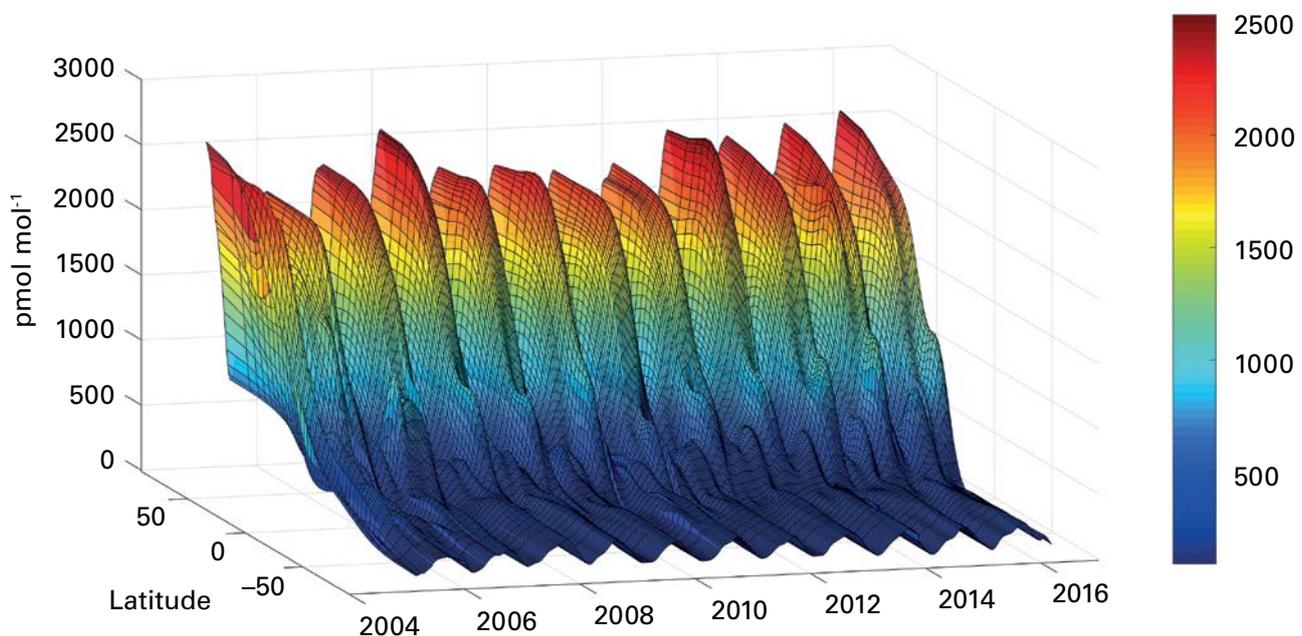


WMO REACTIVE GASES BULLETIN

Highlights from the
Global Atmosphere Watch Programme

No. 1 | May 2017

Ethane



The figure represents the ethane mixing ratio in the background atmosphere as obtained from the global monitoring of volatile organic compounds (VOCs) at more than 40 sites. Through coordination and quality assurance in the Global Atmosphere Watch Programme (GAW), it has recently become possible to assess the global distribution, the seasonal cycle, and longer-term changes of VOCs in the atmosphere. The figure includes data from the NOAA/INSTAAR global VOC monitoring program.

As demonstrated by this figure, ethane concentrations are generally much higher in the northern hemisphere, and the seasonal cycle is also much more pronounced there. Ethane maxima occur in winter in both hemispheres so that the seasonal cycles in the two hemispheres are six months out of phase. Since the class of VOCs comprises many individual compounds with different emission

sources and chemical properties, the long-term measurement of VOCs in a global network can help understand regional emissions changes. This is demonstrated in the text below where ethane and propane measurements were used to identify an increase of emissions from oil and gas extraction in North America as the dominant driver of recent hemispheric-scale rises in ethane concentrations.

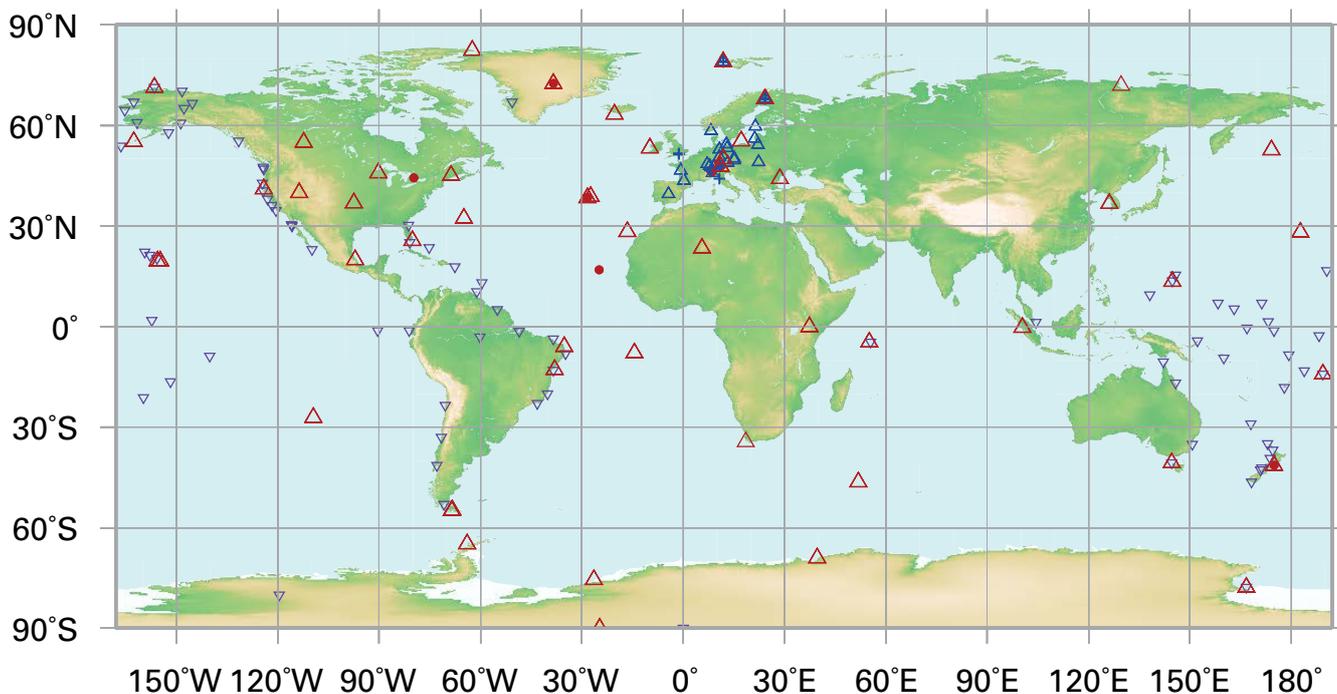


Figure 1: Locations with historic and currently ongoing global VOC observations coordinated within GAW. Red triangles show sites of the National Oceanic and Atmospheric Administration (NOAA) Global Greenhouse Gas Reference Network (GGGRN), blue triangles are the sites of the European Monitoring and Evaluation Programme (EMEP), blue inverted triangles are the sites of the University of California (UCI), and circles are sites where data from continuous in-situ measurements have been reported.

Introduction

The reactive gases are a highly diverse group of chemicals. They include surface ozone, nitrogen oxides, carbon monoxide, sulfur dioxide, and volatile organic compounds (VOCs). This first issue of the GAW Reactive Gases Bulletin describes the role of VOCs in the atmosphere, the GAW approach to making long-term background atmosphere observations of VOCs, and how GAW measurements provide evidence that global-scale increases in VOC levels are caused by the recent expansion in oil and gas extraction in North America.

Trace amounts of reactive gases in the atmosphere are crucial for regulating oxidation chemistry. By reacting with oxidants in the atmosphere these gases and their reaction products influence air pollution and climate change. To better understand the spatial and temporal scales of reactive gases, the GAW Programme of the World Meteorological Organization coordinates observations through its global network (Fig. 1).

GAW promotes the integration of reactive gas observations into information products for policymakers and for the natural, social and economic sciences [1]. Its comprehensive quality management framework ensures that observations adhere to the highest measurement standards and that data from different sources are compatible. This gives confidence in the network's ability to detect regional differences in concentrations and long-term changes in atmospheric composition, and to identify the underlying processes that are causing those changes.

The role of volatile organic compounds (VOCs)

Volatile organic compounds are carbon-containing molecules that are often present as gases in the atmosphere. This class of atmospheric constituents encompasses many individual species with a wide range of volatilities and reactivities [2]. VOCs are emitted into the atmosphere both by natural and human-caused processes. Isoprene, for example, is emitted primarily by broadleaf trees. Benzene and 1,3-butadiene are two VOCs that result primarily from combustion. These emissions are directly harmful to human health and therefore subject to air-quality regulations in many countries.

VOCs play crucial roles in modulating atmospheric oxidation processes and the production of secondary aerosols. The best-established global impact of VOCs is their role in the formation of ozone near the Earth surface, which can harm the health of humans, plants, and other lifeforms. Ozone is formed through a series of reactions involving nitrogen oxides (NO_x) and VOCs. Reductions in peak surface ozone in Europe and the United States of America over the last two decades have been attributed in part to successful cuts in VOC emissions from vehicles, industry, solvents, paints and other sources [3]. Oxidation of VOCs can also lead to the formation and growth of secondary organic compounds that can take the form of harmful particulate matter, such as the fine particles known as PM_{2.5}, which are found in urban air pollution.

The lifetimes of VOCs can range from a few minutes to several months. Consequently, the impact of VOCs on ozone and aerosols can potentially be experienced far from the

original emission point. This is why controlling VOCs is a key part of international environmental conventions (for example within the Gothenburg Protocol to the Convention on Long-Range Transboundary Air Pollution), and why they are included within GAW.

The majority of VOC emissions are from natural sources, notably trees and plants [4]. These emissions are sensitive to sunlight, temperature, rainfall, CO₂ levels, and plant infestation by insects or fungi. Human-made sources include fossil fuel extraction, distribution, combustion processes, power generation, industrial activities, and domestic uses. Emission estimates for VOCs are subject to substantial uncertainties, reflecting the complex mix of natural and human-made VOC sources and the sheer number of different compounds that need to be accounted for.

Out of the hundreds of VOCs in the atmosphere, GAW identified a core set of molecules to monitor at high priority (Table 1). This choice considers (i) the chemical's importance in atmospheric chemistry, notably their ability to provide key information on anthropogenic vs natural sources and atmospheric chemical processes, and (ii) the feasibility of developing global observations of these gases using available technologies. The GAW list of target VOCs includes natural and human-made hydrocarbons, as well as oxygenated, sulfur, and nitrogen containing compounds. Table 1 lists the VOCs' approximate lifetimes and explains why they are considered important.

Atmospheric lifetimes of VOC are determined by their reaction with atmospheric oxidants, which can vary by several orders of magnitude between species and depending on the oxidant. Further, concentrations of atmospheric oxidants, such as OH and ozone, vary by location, time of year, and with dependence on many other conditions. While most anthropogenic VOC emissions from particular source categories do not vary much by time of year, VOC emissions from the biosphere are influenced by the growing season, weather, and seasonal changes in environmental conditions. This is shown in Figure 2 by contrasting ambient concentrations of ethane, a 2-carbon VOC with predominantly anthropogenic sources associated to petroleum industries, with concentrations of the biogenic VOC emission isoprene. These data from the Hohenpeissenberg (HPB) GAW station in Southern Germany also show the high data quality and comparability that is obtained between participating network partners.

Notably, the seasonal cycles of these two VOC are reversed. For ethane, mixing ratios maximize during the winter, when oxidation rates slow due to diminishing concentrations of the OH radical, the primary removal route for this VOC. In contrast, isoprene is highest during the summer months, and winter concentrations at times drop below low pmol mol⁻¹ detection limits. Here, the determining factors are the seasonally changing emission rates, which are highest during the summer months when isoprene-emitting vegetation is at its peak.

Table 1: Target VOCs included in the GAW Reactive Gases Programme in order of their approximate atmospheric lifetime. (This priority list was identified by the Expert Group for Volatile Organic Compounds within the WMO GAW Scientific Advisory Group for Reactive Gases. This list and more program information is detailed in GAW Report No. 171 [5].)

| Molecule | Approximate Lifetime | Importance in Atmospheric Research and for GAW |
|-----------------------|----------------------|---|
| Terpenes | 1-5 hours | Plant emissions, sensitive to temperature, land use, and climate change, precursors of organic aerosol |
| Isoprene | 3 hours | Plant emissions, sensitive to temperature, land use, and climate change, ozone precursor, precursor of formaldehyde |
| Formaldehyde | 1 day | Atmospheric oxidation product and emissions from biomass burning, indicator of isoprene oxidation, source of free radicals in remote areas |
| Dimethylsulfide (DMS) | 2 days | Major natural sulfur source emitted from oceans, sulfate aerosol precursor, tracer of marine bioproductivity |
| Toluene | 2 days | Petrochemical and industrial emissions, precursor of organic aerosol, ratio with benzene used to determine age of plume air |
| <i>Iso/n</i> -pentane | 3 days | Petrochemical exploration and processing, isomeric ratio indicates impact of NO ₃ and halogen chemistry |
| Ethanol | 4 days | Plant emissions, tracer for biofuel production and use |
| <i>Iso/n</i> -butane | 5 days | Petrochemical exploration and processing, tracer for natural gas extraction and use, precursor of ozone, isomeric ratio indicates impact of halogen chemistry |
| Benzene | 10 days | Petrochemical and industrial emissions, tracer of fossil and biofuel combustion, biomass burning |
| Propane | 11 days | Natural gas exploration and extraction, biomass burning, tracer for methane sources, regional fossil fuel emission trends |
| Methanol | 12 days | Plant emissions, oxidation product from methane and other VOC, exchange with ocean |
| Acetylene | 15 days | Motor vehicle emissions, biomass burning, ratio to other hydrocarbons (age of plume air), regional trends |
| Ethane | 1.5 months | Natural gas exploration and extraction, biomass burning, tracer for methane sources, hemispheric fossil fuel emission trends |
| Acetone | 1.7 months | Oxidation product from other VOCs, source of free radicals in the upper troposphere |
| Acetonitrile | 0.5-1 year | Biomass burning and biofuel burning indicator |

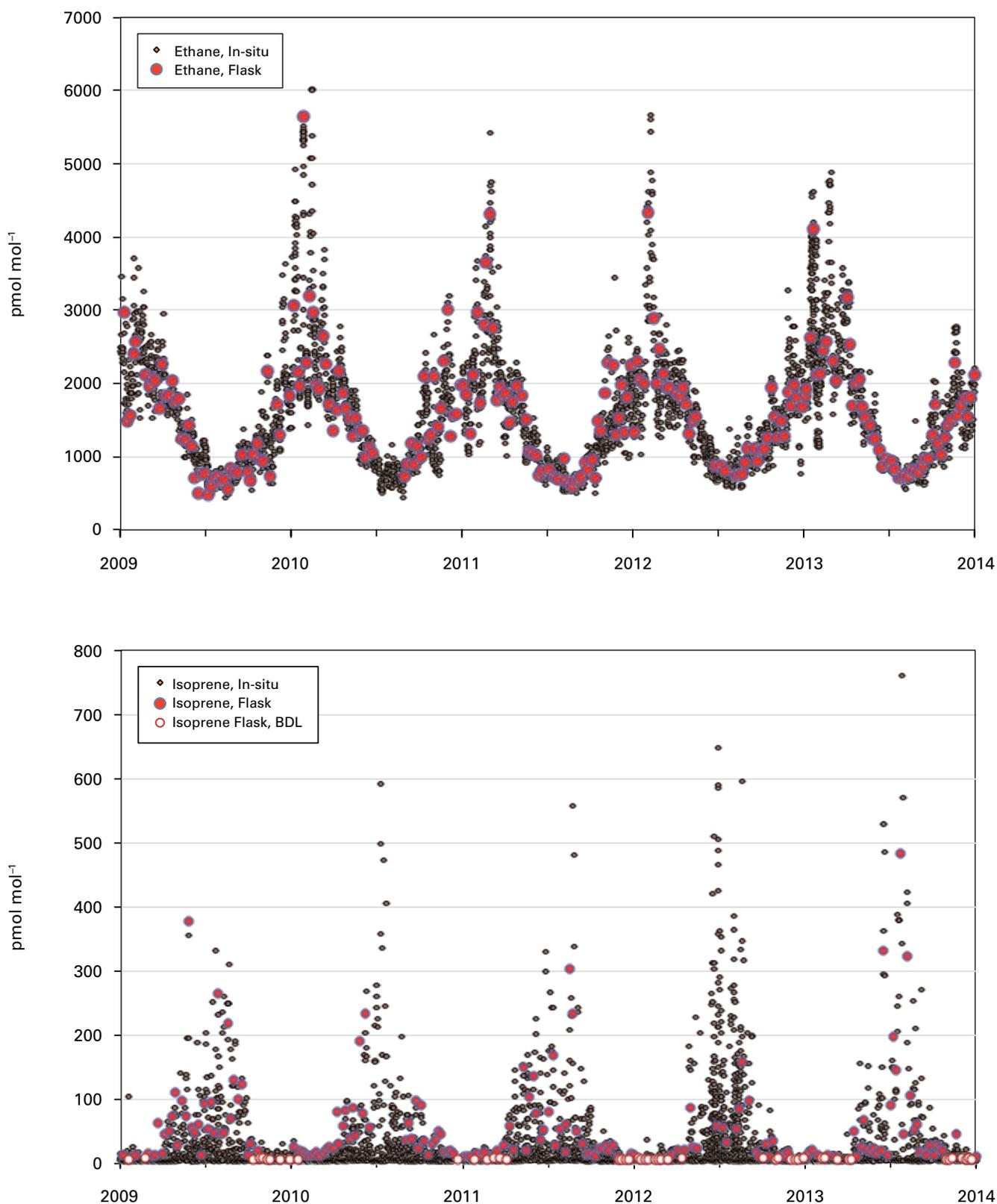


Figure 2: Two examples of ongoing VOC monitoring at Hohenpeissenberg, Germany. These graphs show comparisons between two measurement programs: (1) in-situ monitoring by a gas chromatography instrument operated at the site, and (2) by collection of whole air samples in glass flasks within NOAA's Global Greenhouse Gas Reference Network, which are then analysed at the Institute of Arctic and Alpine Research (INSTAAR) at the University of Boulder, Colorado. The upper graph shows monitoring results for ethane, and the lower graph for isoprene. Open circles in the lower graph indicate measurements with isoprene results below the detection limit (BDL). Note the opposite seasonal cycles, which are driven by the respective emission sources and atmospheric loss processes.

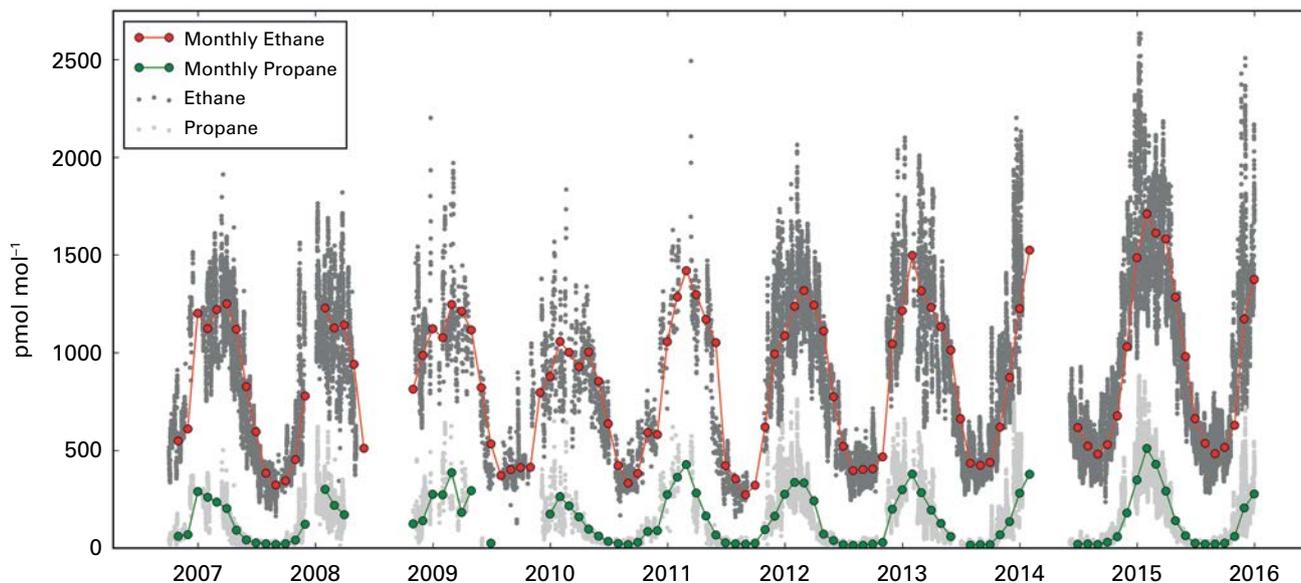


Figure 3: Ethane and propane data from hourly monitoring at Cape Verde Observatory, Cape Verde, as well as monthly averages of the data.

Light alkane hydrocarbons show similar behavior in seasonal cycles and spatial gradients, as illustrated in the comparison of ethane and propane, the next higher chain alkane VOC, at Cape Verde Observatory, a GAW station located off the West Coast of Central Africa (Figure 3). Absolute atmospheric mixing ratios of higher alkanes become smaller with increasing

molecule size, due to the higher reactivity and shorter lifetime of the higher carbon number alkanes. This also causes seasonal maxima and minima to progressively occur earlier in the year. At the most remote GAW network sites, mid-summer mixing ratios for heavier alkane VOCs drop below currently achieved instrument detection limits at times.

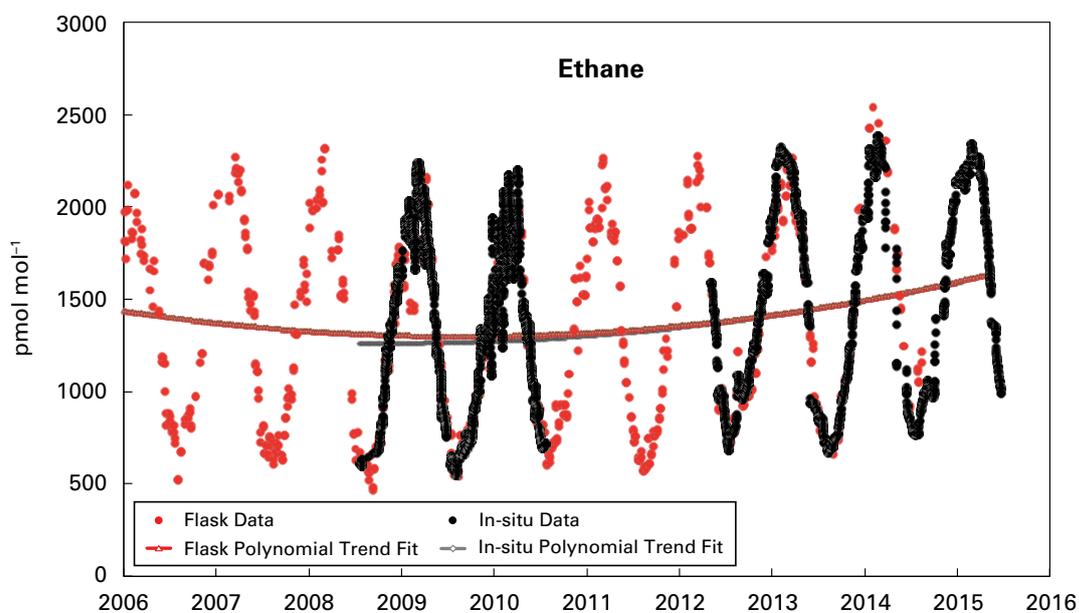


Figure 4: Monitoring results for ethane at Summit, Greenland, from two different programs. Black symbols represent measurements conducted every six hours with an in-situ gas chromatograph at the site. The red data points are results from weekly whole air sample collection by NOAA with analysis done at INSTAAR/University of Colorado. The graph also shows best fit polynomial trend curves to both data sets, indicating the increase in ethane and good agreement between both data sets and their trend results.

VOC trends and the link to hydraulic fracturing

A series of recent publications provides convincing evidence that light alkane hydrocarbons grew steadily during the 19th and 20th centuries, primarily due to increases in emissions from the energy and transport sectors [6, 7]. These reports analyzed records of ice cores and deep-firn air (firn is granular snow, especially in the upper part of a glacier). Small amounts of ethane and propane always accompany methane when it is emitted by human-made petroleum sources.

During the 1970s and 1980s, a reversal began, and by around the year 2010 concentrations of light alkane hydrocarbons had dropped by approximately 25% compared to the peak levels seen some 30 years earlier. These declining concentrations reflect a fall in emissions that can be attributed to reduced leakage from the oil and gas industries and to improved controls of fugitive and exhaust emissions from automobiles and industries.

It was a surprise, therefore, when a review of the most recent data from the GAW VOC network showed yet another reversal, but this time with concentrations of light alkane hydrocarbons trending back upwards [8]. This trend reversal can be seen at several GAW stations. Figure 4 features ethane data from the GAW site Summit, located on the top of the Greenland ice sheet. Summit is an ideal site for monitoring atmospheric background concentrations of mid- to long-lived gases as it is far removed from local emissions sources and, with its elevation of 3210 m above sea level, mostly samples well-mixed lower to mid-tropospheric air. Two independent data series show the same features – that is, declining ethane until around 2009, and increasing ethane thereafter. Trend analyses on both data sets result in very good agreement, yielding an average annual increase of 4.7% and 5.4%, respectively, for the flask and in-situ data during the July 2009 to June 2014 period.

Taken together, data from the NOAA GGGRN flask sites and five other sites that perform in situ continuous measurement (all contributing to the GAW Programme) showed a consistent pattern: ethane increases were found at the overwhelming majority of sites in the Northern Hemisphere, but not at those in the Southern Hemisphere.

These findings from the GAW surface network are backed up by another independent suite of observations: the ethane total-column Fourier transform infrared (FTIR) measurements taken by the Network for Detection of Atmospheric Composition (NDACC, www.ndacc.org) [9]. Depending on site selection and averaging method, the GAW and FTIR sets of observations produce average ethane increases of 3-5% per year in the Northern Hemisphere. This constitutes a total increase of around 20% in Northern Hemisphere atmospheric ethane during this 5-year time period. Furthermore, the geographical distribution of the rates of increase seen for the short-lived VOC propane – which cannot travel far from its source over its 11-day approximate lifetime – and the tight correlation between ethane and propane emissions, suggests that most of the new ethane emissions originate from North America [8].

These network observations are consistent with the large enhancements in light alkane hydrocarbons that have recently been seen in air samples from U.S. oil and

natural gas basins [10]. Oil and gas drilling has undergone a remarkable growth in the United States and Canada during the past ten years, largely driven by new hydraulic fracturing technologies ('fracking') that allow drillers to reach and extract petroleum from reservoirs that have hitherto been out of reach. Atmospheric observations from the GAW Programme provide compelling evidence of the hemispheric impact of increases in light alkane hydrocarbons – and, by implication, the greenhouse gas methane – from the growth of the North American petroleum industry. These emissions have also been linked to ozone production, resulting in elevated surface ozone during the photochemical summer season [11]. Surprisingly, in oil and gas basins, ozone production can also be substantial during the winter when snow covers the ground [12]. If the growth rate seen from May 2009 to May 2014 continues, it will just take a few more years until the historic maxima of atmospheric ethane will be reached again.

The GAW Programme and VOCs

Over the past 10 years, the WMO Global Atmosphere Watch Programme has made great strides towards establishing a coordinated, high-quality global network of VOC observations. While the historical rationale for observations of VOCs has been their central role in regional air quality, the long-term climate impacts resulting from the VOCs-mediated production of tropospheric ozone and secondary aerosols provide another important reason to make background GAW observations. Observations of VOCs also help to understand changes in greenhouse gas emissions, because they can be used as markers for individual emission processes or industries. For example, as described in the previous section, ethane and propane are closely associated with methane when emitted by natural gas sources [13].

GAW synthesizes long-term global trends in concentrations of the various VOCs in the background atmosphere in order to provide insights into the changing environment, including evaluation of global estimates of VOC emissions. This in turn makes it possible to assess how emissions from key industry, transport, and domestic sectors are changing at both the regional and global levels. These syntheses are the main VOC data products that GAW delivers to stakeholders. Key target users of VOC data syntheses include national environmental agencies interested in comparing actual changes in emissions to those anticipated by their policies. For global agencies and international treaties, GAW VOC products provide the only global measure currently available for assessing the impact of economic change, new control technologies, and policy interventions, on atmospheric VOC. A better understanding of atmospheric VOCs, their variability and reactions, is needed to reduce current uncertainties in the Intergovernmental Panel on Climate Change (IPCC) assessment of aerosol impacts on climate. In addition to syntheses published in the academic literature, GAW provides policy-oriented summaries through media such as the WMO Bulletin. GAW experts also engage with government agencies, through advisory structures and expert groups.

One task of the GAW VOC Expert Group has been identifying historical VOC measurements. These data, as well as newer observations from the GAW network up to the year 2015, have been assembled and are publicly available in the World Data Centre on Greenhouse Gases at <http://ds.data>

jma.go.jp/gmd/wdcgg/. In 2016, responsibility for archiving GAW VOC data was transferred to the newly established World Data Centre for Reactive Gases maintained by the Norwegian Institute for Air Research (NILU) at <http://www.gaw-wdcrg.org/>.

Acknowledgements and links

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This bulletin was produced by the GAW Scientific Advisory Group on Reactive Gases (http://www.wmo.int/pages/prog/www/CBS/Lists_WorkGroups/CAS/opag-epac/gaw%20sag%20rg).

Contacts

World Meteorological Organization

Atmospheric Environment Research Division,
Research Department, Geneva, Switzerland
E-mail: gaw@wmo.int
Website: <http://www.wmo.int/gaw>

World Data Centre for Reactive Gases

NILU, Kjeller, Norway
E-mail: kt@nilu.no
Website: <http://www.gaw-wdcrg.org/>

World Data Centre for Greenhouse Gases

Japan Meteorological Agency, Tokyo, Japan
E-mail: wdcgg@met.kishou.go.jp
Website: <http://ds.data.jma.go.jp/gmd/wdcgg/>

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Selected GAW stations with reactive gases observations



The Hohenpeissenberg Meteorological Observatory (HPB) (47.80°N, 11.01°E, 980 m asl) is located in rural southern Germany on top of a small mountain, about 40 km north of the Alps. HPB has become a testbed for GAW observations of reactive gases and aerosols. Ongoing reactive gas measurements include ozone, CO, NO, NO₂, PAN, NO_y, vertical profiles of NO₂ and HONO, SO₂, VOC (Fig. 2), H₂SO₄, the radicals OH, and RO_x, and total OH-reactivity. Besides the VOC in-situ observations whole air samples are collected weekly and shipped to Boulder for VOC analyses at the University of Colorado (Fig. 2).

Year-round VOC monitoring at Summit (SUM), near the apex of the Greenland ice Shield (72.6° N, 38.5° W; 3210 m asl) is performed in the Temporary Atmospheric Watch Observatory (TAWO), seen in the background of the photograph. Summit is also a site from which VOCs are analysed in weekly collected flask samples (Fig. 4). Currently ongoing measurements of reactive gases include ozone, CO, and VOC. PAN, OH, HO₂, NO, NO₂, NO_y, HONO, and formaldehyde have been measured during summer campaigns. Summit has also been a site of firn air and ice-core retrievals, such as from the GISP II ice core, which remains accessible through the pipe seen in the front left of the photo.



The Cape Verde Atmospheric Observatory (CVAO) Humberto Duarte Fonseca (16.8°N, 24.9°W, 10 m asl) is located upwind of Calhau on the northeastern side of São Vicente, Cape Verdes, off the west coast of Africa in the Central Atlantic Ocean. Hourly VOC measurements with an in situ gas chromatograph have been made since 2007 (Fig. 3). Other reactive gases that are being monitored are ozone, halocarbons, CO, SO₂, NO, and NO₂.