18 Reactive gases, ozone depleting substances and greenhouse gases

Long-term time series supporting international treaties Trend analysis & early warning

Brigitte Buchmann, Christoph Hueglin, Stefan Reimann, Martin K. Vollmer,
Martin Steinbacher, Lukas Emmenegger

Empa, Swiss Federal Laboratories
for Materials Science and Technology,
Dübendorf

The Swiss contribution to international atmospheric measurement programmes has a long tradition. Continuous measurements of air pollutants supporting the "OECD Cooperative Technical Programme to measure the long-range transport of air pollutants" started in 1972. Thereafter, these activities continued in the frame of the Ottar Programme, which was one of the first devoted to the acid rain issue. Today, long-term time series of more than 70 gaseous atmospheric compounds are measured at the high-Alpine site Jungfraujoch, contributing to the European Monitoring and Evaluation Programme (EMEP) of the United Nations Economic Commission for Europe (UNECE) and the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO). Long-term time series provide the basic information for estimating trends and emissions in support of international treaties, such as the Kyoto and the Montreal Protocols as well as for the EMEP. The latter is a scientifically based and policy-driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international cooperation.
The following provides examples of analyses of long-term measurements for trend and emission estimates and illustrates their benefit and impact for international protocols and treaties.

18.1 Historical Background

In the 1950s, attention of governments from all over Europe turned to the traces of harmful substances present in the Earth's atmosphere. The first measurements were started mainly targeting local sources and industrial emissions. For the purpose of investigating the long-range transport of pollutants, Switzerland installed the first two continuous measurement sites at Payerne and Jungfraujoch in 1968. Sulfur dioxide (Figure 18.1), particulate sulfate and total suspended particulates (TSP) were the first three parameters to be scrutinized for air pollution and to support international treaties (Filliger et al. 1994).

In addition, triggered by scientific interests such as the investigation of the radiation budgets and ozone depletion, regular measurements started in Arosa 1926

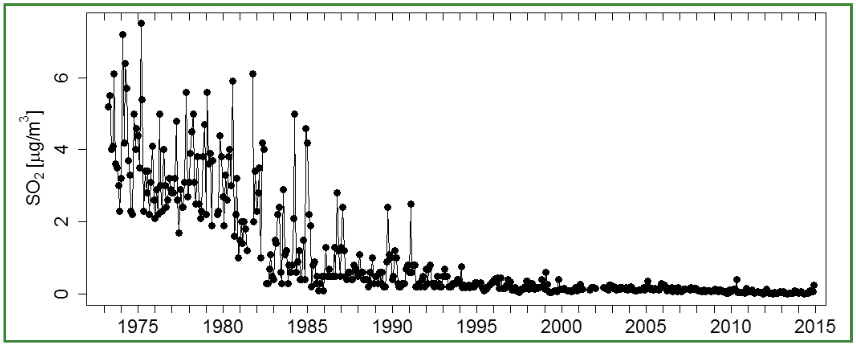

Figure 18.1: Time series of long-term sulfur dioxide (SO_2) measurements at the high-Alpine site Jungfraujoch. Data are aggregated to monthly averages.

for in-situ ozone and in 1956 for total column ozone (Staehelin et al. 2009), in Payerne 1968 for ozone profiles (Chapter 16), and at Jungfraujoch in the 1970s for total vertical column abundances of chlorofluorocarbons (Zander et al. 2008).

It rapidly became clear that continuous time-series are essential for providing answers to the emerging air pollution issues. Therefore, in 1978, the National Air Pollution Monitoring Network (NABEL) was initiated as a joint activity of Empa and the Swiss Federal Office for the Environment (FOEN). The NABEL network was initially established with eight sites emerging from activities that had started already in 1968 as the above contributions to international observation networks (WMO and OECD). In 1990/1991, the NABEL network was extended to 16 monitoring stations that are distributed throughout Switzerland. The locations of these mon-

NABEL

The National Air Pollution Monitoring Network (NABEL) measures air pollutants at 16 locations in Switzerland. The stations are distributed throughout the country and monitor pollution at typical locations (e. g., urban traffic locations, residential areas, rural locations).

The monitoring network commenced operations in stages since 1979 and is jointly operated by the Federal Office for the Environment (FOEN) and Empa. Article 39 of the Ordinance on Air Pollution Control (OAPC) requires FOEN to collect data on air pollution throughout Switzerland. The fulfilment of this legal mandate is among the principal purposes of the NABEL network. NABEL measures indicator pollutants of national significance (e. g., nitrogen dioxide, ozone, particulate matter). It is an important instrument for enforcing the OAPC, e.g., through monitoring the success of air-pollution control measures (Art. 44 of the Environmental Protection Law).

NABEL also performs measurements for international monitoring programmes and participates in the European and world-wide exchange of data. Since monitoring activities commenced, various rural stations have formed part of the European Monitoring and Evaluation Programme (EMEP), which principally investigates the long-range transport of air pollutants across Europe. In addition, NABEL places its data at the disposal of EUROAIRNET, which was established by the European Environment Agency and primarily comprises stations from urban and suburban areas of all European countries. Data from selected NABEL stations are also available at the World Data Centre for Greenhouse Gases in Japan. The Jungfraujoch station is part of the World Meteorological Organization (WMO)'s Global Atmosphere Watch (GAW) programme and serves as a background station for the free troposphere across the Central European region.


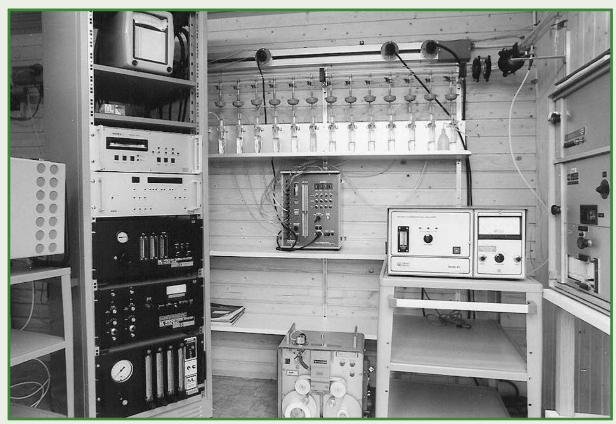

Figure 18.2:
First station of the Swiss National Air Pollution Monitoring Network (NABEL) in 1978 at Dübendorf, Switzerland.

Technischer Bericht zum Nationalen Beobachtungsnetz für Luftfremdstoffe (NABEL) (http://www.empa.ch/documents/56101/246436/Nabel-technischer-bericht-15/075614a2-8b51-44b8-9caf-0be22617d58e)

NABEL – Luftbelastung: Messresultate des Nationalen Beobachtungsnetzes für Luftfremdstoffe (http://www.bafu.admin.ch/publikationen/publikation/01822/index.html?lang=de)) itoring stations are representative for the most significant air pollution levels in Switzerland, ranging from urban kerbside in city centres to the relatively unpolluted tropospheric background station Jungfraujoch. Parallel to these long-term continuous measurements, several research programmes were initiated in Switzerland as well as in Europe. In Switzerland, one of the most comprehensive programmes was POLLUMET, with several field campaigns between 1990 and 1993 (Chapter 16).

18.2 Measurements at Jungfraujoch

In 1973, Empa started continuous measurements of reactive gases as part of an early engagement of Switzerland in a programme organised by the Organisation for Economic Co-operation and Development (OECD). This programme, designed to investigate changes in the atmospheric composition, aimed at the collection of data needed to ensure a sustainable development in the member states – and consequently in the entire world. Today, more than 70 gaseous species including reactive gases, greenhouse gases and some of their isotopes (e.g., $^{12}CO_2$ and $^{13}CO_2$), are currently being measured at Jungfraujoch, 3580 m above sea level.

Measurements at this unique site in the heart of the Swiss Alps are representative for clean tropospheric air masses and hence are well suited for the analysis of long-

Figure 18.3:
High-Alpine ambient air measurement site at the Sphinx – Observatory at Jungfraujoch (left), air inlet system under harsh conditions in winter time (right).

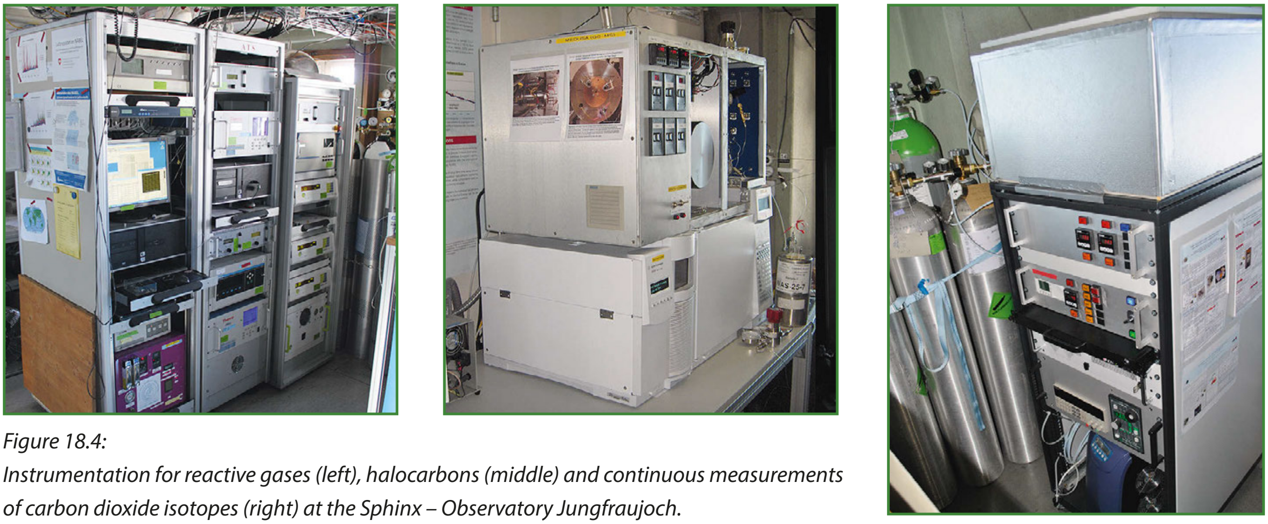

Figure 18.4:
Instrumentation for reactive gases (left), halocarbons (middle) and continuous measurements of carbon dioxide isotopes (right) at the Sphinx – Observatory Jungfraujoch.

term changes of an unpolluted atmosphere. However, occasionally air from the lowest level of the troposphere, the so-called atmospheric boundary layer, is advected to the station. Thus, emissions of anthropogenic greenhouse gases from the European continent can be quantified for verifying the compliance of international treaties, complementary to traditional emission inventories.

In 1988, the Paul Scherrer Institute (PSI) started continuous aerosol measurements on Jungfraujoch with newly developed instrumentation, showing for the first time that vertical transport results in high particulate concentrations even at Alpine altitudes (Chapter 19). In 1994, GAW-CH was launched as a national contribution to the international Global Atmosphere Watch (GAW) programme. GAW-CH is coordinated by MeteoSwiss and relies on strong collaborations between national research institutions and federal offices involved in atmospheric observations and analyses. The Swiss GAW programme includes the monitoring of various physical and chemical atmospheric variables, research activities and advanced services. In recognition of the long-term, comprehensive and high-quality measurement programme at Jungfraujoch covering all Essential Climate Variables (ECVs) for atmospheric surface sites, Jungfraujoch became a global station in the network of the GAW programme (Figure 18.5) in February 2005.

The comprehensive, high-quality data have led to a number of trend analyses that are of great relevance for identifying and understanding atmospheric composi-

Figure 18.5:
The global measurement sites of the GAW Programme.

tion change (Zellweger et al. 2009; Gilge et al. 2010; Cui et al. 2011; Logan et al. 2012; Pandey Deloal et al. 2012; Parrish et al. 2012, 2014).

From 2000 onwards, Empa successfully used long-term datasets to quantify and localize European emissions of halogenated ozone-depleting substances and greenhouse gases for the verification of the Montreal and Kyoto Protocols (Zander et al. 2008; Reimann et al. 2004, 2005, 2008; Stemmler et al. 2007; Vollmer et al. 2011, 2015; Keller et al. 2011; Brunner et al. 2012).

The current measurement programme of reactive and greenhouse gases at Jungfraujoch includes continuous in-situ analyses of ozone (O_3), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), the sum of nitrogen oxides (NO_y), sulfur dioxide (SO_2), methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O). These data are stored as 10-min averages. Furthermore, the concentrations of CH_4, N_2O and H_2 are monitored at half-hourly intervals. An extended set of halocarbons, sulfur hexafluoride (SF_6) and a selection of volatile organic compounds (VOCs) are measured with a time resolution of two hours. The concentration of particulate matter < 10 μm (PM10) is determined both continuously and in 24-hour integrated samples. Daily samples are taken to quantify particulate sulfur. More recently, continuous measurements of the stable CO_2 isotopes were started, contributing to its source attribution.

With this comprehensive suite of measurements, Empa's activities at Jungfraujoch go beyond the operational setup at other NABEL stations. On the one hand, this is driven by the wide range of scientific aims at such a remote site. On the other hand, it is also a response to the various international projects and programmes (EMEP, GAW, CLRTAP, UNECE) in which the observations at Jungfraujoch are embedded. The observations of the halogenated greenhouse gases are furthermore part of the Advanced Global Atmospheric Gases Experiment (AGAGE) with nine stations worldwide striving for a comprehensive picture of the composition of ozone-depleting substances and their replacement products. On the European scale, Jungfraujoch is one of the monitoring stations of the atmospheric network of the Integrated Carbon Observation System (ICOS) research infrastructure. ICOS aims at establishing harmonized high-precision greenhouse gas observations across Europe in order to understand the greenhouse gas budgets and perturbations. With an envisaged time frame of 20 years, ICOS provides the long-term observations necessary to understand the present state and to predicting future behaviour of the global carbon cycle and greenhouse gas emissions. Figure 18.6 shows 5-year time series of CO_2, CH_4, and CO, which are integral parts of the ICOS research infrastructure programme.

On shorter time scales, Jungfraujoch is also a prime-site in the European Commission's Seventh Framework Programmes InGOS (Integrated non-CO_2 Greenhouse gas Observing System) and ACTRIS (Aerosol, Clouds, and Trace Gases Research Infrastructure Network), both of which run for 4 years. A close liaison with many programmes is beneficial on various aspects: Round-robin comparisons as part of the GAW programme and the InGOS project (both for greenhouse gases) and the ACTRIS project (for nitrogen oxides and VOCs) allow additional quality control activities, which are crucial for time series that support international treaties and protocols.

Human-induced changes of the atmosphere's composition and its feedback on the global climate system are major challenges in the future. In order to face them, modern research increasingly relies on three pillars: targeted laboratory and field experiments to assess processes, long-term research monitoring from

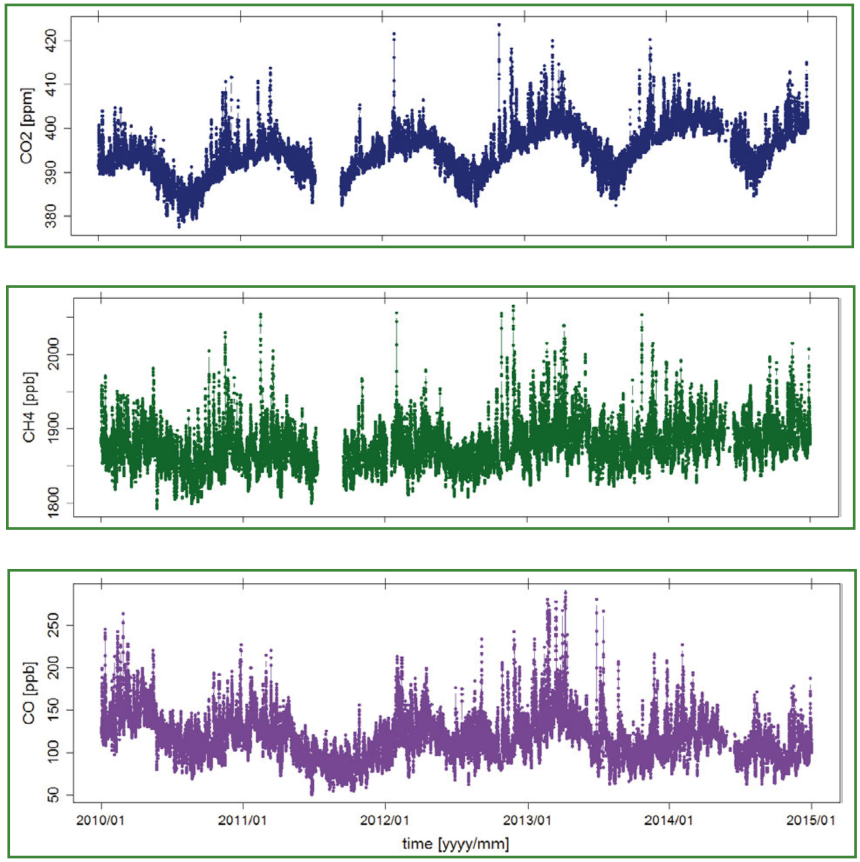

Figure 18.6:
Time series of high-precision CO_2, CH_4 and CO observations (hourly averages) from January 2010 to December 2014.

different platforms (ground based, airborne and satellites) to quantify trends, and models to integrate findings to spatial information and provide forecasts.

Therefore, high-quality, long-term continuous measurements of air pollutants and greenhouse gases are essential to understanding and quantifying changes of the atmosphere. Moreover, relevant to policymakers, these scientific findings provide independent verification of European greenhouse gas emissions, allow source allocation of specific pollutants, and act as an early-warning system. In the following, examples are given for illustration of the relevance of long-term time series.

18.3 Atmospheric composition change

Chlorofluorocarbons (CFCs), halons and long-lived chlorinated solvents (e.g., 1,1,1,-trichloroethane), which are globally banned from usage by the Montreal Protocol, have shown a steady decline of the background concentrations and pollution events (Figure 18.7). Mixing ratios of their first-generation substitutes, the hydrochlorofluorocarbons (HCFCs), are still slowly increasing because of ongoing emissions in developing countries. However, second-generation substitutes, i.e., hydrofluorocarbons (HFCs, e.g., such as HFC-134a, a cooling agent in mobile air conditioners), regulated only in the Kyoto Protocol, still show large increases (Figure 18.7).

18.4 Identification of European sources of greenhouse gases

European emissions of halogenated greenhouse gases can be derived from continuous atmospheric trace gas measurements combined with sophisticated meteorological models (Reimann et al. 2004, 2005; Keller et al. 2011; Brunner et al. 2012). Our approach has revealed large emissions from Italy of a fluorinated greenhouse gas (HFC-152a: 1,1-difluoroethane), used in insulation foams (Figure 18.7). Surprisingly, the official Italian emission inventory performed under the Kyoto Protocol does not declare these emissions. Thus, our findings provide independent support for the evaluation of the compliance to international treaties.

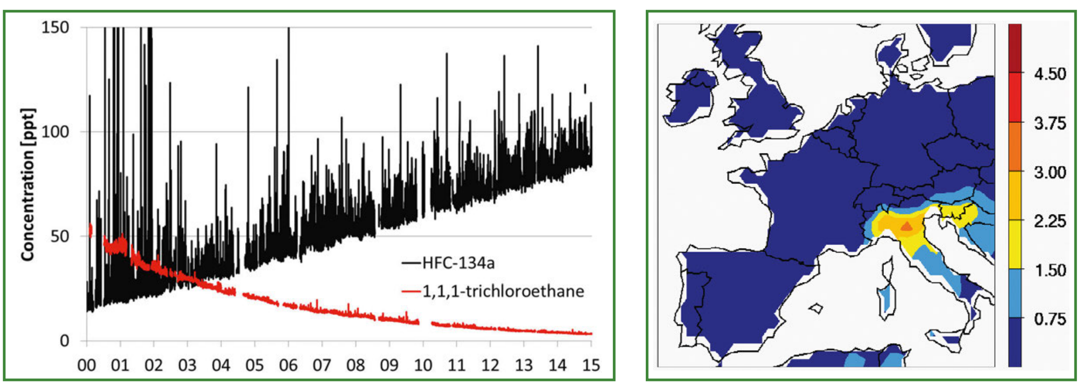

Figure 18.7:
Time series (2000–2015) of the cooling agent HFC-134a and 1,1,1-trichloroethane at Jungfraujoch (2-hourly averages) and their modelled European emission regions of HFC-152a (2011–2015)

18.5 Independent emission estimation

Current emission inventories of fluorinated greenhouse gases are derived mainly from sales statistics. They are thus limited to those countries and compounds for which adequate data are available. In contrast, emission estimates based on atmospheric measurements can provide a more complete picture of European sources (e.g., Brunner et al. 2012). These emission estimates are becoming ever more important, given that they offer independent verification of the production/consumption-based emission data and include also countries without complete inventories.

Western European emission inventories of the potent greenhouse gas trifluoromethane (HFC-23) have been validated by combining atmospheric in situ measurements at Jungfraujoch (Switzerland) and Mace Head (Ireland) with transport models (Keller et al. 2011). In 2009, we observed emissions that were 60–140 % higher than the official data in the national inventory report. Altogether, our work demonstrates the importance of independent validation of reported emissions data – and it corroborates the potential of top-down methods (derived from measurements) to assess greenhouse gas emissions with high spatial and temporal resolution and a sufficient accuracy of 30–50 %. Together with other nations – such as Australia and the UK – Switzerland is one of the first countries to include this type of independent verification in their national inventory reporting. In the future, this approach may well become binding for international treaties (Nisbet and Weiss 2010).

18.6 Early warning system

Cutting-edge instrumentation allows data to be gathered with very high precision even at extremely low concentrations. This enables us to capture the first appearance of newly produced greenhouse gases such as hydrofluorocarbons [HFCs: e.g., HFC-365mfc, HFC-245fa, HFC-227ea and HFC-236fa (Stemmler et al. 2007, Vollmer et al. 2011)] with very high global warming potential. These anthropogenic substances, predominantly used as refrigerants, foam blowing agents, fire retardants and propellants, replace the stratospheric ozone-depleting CFCs and hydrochlorofluorocarbons (HCFCs). Our results show that the mole fractions of the above-mentioned four HFCs have grown rapidly over the past years, although their abundance is still low compared to other greenhouse gases. Given the upcoming phasing-out of HCFCs in developing countries, the use of these four new substances is expected to increase significantly in the near future (Velders et al. 2012). This may be attenuated by a currently pending proposal to include HFCs under the Montreal Protocol.

18.7 Conclusions and Outlook

Scientific data collection requires continuity. Trends and new developments cannot be detected with an isolated snapshot (Reimann et al. 2005). Examples for trend analyses, source identification and emission estimation illustrate the benefit and importance of long-term, continuous measurements of air pollutants and greenhouse gases such as those at Jungfraujoch and other European background sites. These measurements will be invaluable in future legally binding international treaties for limiting greenhouse gases. This makes emission commitments of individual countries verifiable by independent emission estimations based on real-world observations. It may become even more important in the future when more demanding goals, rigorous enforcement mechanisms and penalties for non-compliance possibly become an integral part of international agreements.

The **Global Climate Observing System GCOS** was established in 1992. It supports the implementation of systematic climate observation in accordance with the requirements of the UN Framework Convention on Climate Change and the Kyoto Protocol. The necessary climate-relevant information is made available to all potential users from science, politics and business – an enormous challenge.

GCOS is coordinated at the global level by four organisations: the World Meteorological Organization (WMO), the UN Environment Programme (UNEP), the Intergovernmental Oceanographic Commission (IOC) of UNESCO, and the International Council for Science (ICSU). The GCOS Secretariat is based at WMO headquarters in Geneva. GCOS comprises measurements of some 40 so-called Essential Climate Variables in the atmosphere, the oceans and on land. The global network is supported by more detailed networks at regional and national level according to user requirements in order to effectively plan and implement the overall response to climate change.

Brochure about GCOS Switzerland: Local observations for global understanding, 2008 (Seiz and Foppa 2007).

We conclude that long-term time-series, combined with models, are essential for environmental research. This is particularly important because atmospheric composition change and independent emission estimations, supporting international treaties and protocols, rely on quality-controlled and homogeneous time series over several decades. Therefore, establishing long-term monitoring activities, as planned in the European Strategy Forum on Research Infrastructures (ESFRI), is crucial for future environmental and climate research.

References

Brunner, D., S. Henne, C.A. Keller, S. Reimann, M.K. Vollmer, S. O'Doherty, and M. Maione, 2012: An extended Kalman-filter for regional scale inverse emission estimation. *Atmos. Chem. Phys.*, **12**, 3455–3478.

Cui, J., S. Pandey Deolal, M. Sprenger, S. Henne, J. Staehelin, M. Steinbacher, and P. Nedelec, 2011: Free tropospheric ozone changes over Europe as observed at Jungfraujoch (1990–2008): An analysis based on backward trajectories. *J. Geophys. Res.*, **116**, D10304, doi: 10.1029/2010JD05154.

Filliger, P., B. Buchmann, and B. Schwarzenbach, 1994: The Proceedings of EUROTRAC Symposium, 94, SPB Academic Publishing bv, The Hague, The Netherlands, 229–262.

Gilge, S., C. Plass-Duelmer, W. Fricke, A. Kaiser, L. Ries, B. Buchmann, and M. Steinbacher, 2010: Ozone, carbon monoxide and nitrogen oxides time series at four Alpine GAW mountain stations in Central Europe. *Atmos. Chem. Phys.*, ***10***, 12295–12316.

Keller, C.A., D. Brunner, S. Henne, M.K. Vollmer, S. O'Doherty, and S. Reimann, 2011: Evidence for under-reported western European emissions of the potent greenhouse gas HFC-23. *Geophys. Res. Lett.*, **38**, L15808, doi: 10.1029/2011GL047976.

Logan, J.A., and Coauthors, 2012: Changes in ozone over Europe: analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites. *J. Geophys. Res.*, **117**, D09301, doi: 10.1029/2011JD016952.

Nisbet, E., and R. Weiss, 2010: Top-down versus bottom-up, *Science*, **328**, 1241–1243.

Pandey Deloal, S., D. Brunner, M. Steinbacher, U. Weers, and J. Staehelin, 2012: Long-term in-situ measurements of NOx and NOy at Jungfraujoch 1998–2009: time series analysis and evaluation. *Atmos. Chem. Phys.*, **12**, 2551–2566.

Parrish, D.D., and Coauthors, 2012: Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes. *Atmos. Chem. Phys.*, **12**, 11485–11504.

Parrish, D.D., and Coauthors, 2014: Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern mid-latitudes. *J. Geophys. Res.*, **119**, 5719–5736, doi: 10.1002/2013JD021435.

Reimann, S., D. Schaub, K. Stemmler, D. Folini, P. Hofer, B. Buchmann, P.G. Simmonds, B.R. Greally, and S. O'Doherty, 2004: Halogenated greenhouse gases at the Swiss high Alpine site of Jungfraujoch (3850 m asl): Continuous measurements and their use for regional European source allocation. *J. Geophys. Res.*, **109**, D5, D05307 10.1029/2003JD003923.

Reimann, S., and Coauthors, 2005: Low European methyl chloroform emissions inferred from long-term atmospheric measurements. *Nature*, **433**, 506–508.

Reimann, S., M.K. Vollmer, D. Folini., M. Steinbacher., M. Hill, B. Buchmann, R. Zander., and E. Mahieu, 2008: Observations of long-lived anthropogenic halocarbons at the high-Alpine site of Jungfraujoch (Switzerland) for assessment of trends and European sources. *Sci. Total Environ.,* **391**, 224–231.

Seiz, G., and N. Foppa., 2007: National Climate Observing System (GCOS Switzerland), Publication of MeteoSwiss and ProClim, 92 pp.

Staehelin, J., C. Vogler, and S. Brönnimann, 2009: The long history of ozone measurements: Climatological information derived from long ozone records. Twenty Years of Ozone Decline – Proceedings of the Symposium for the 20th Anniversary of the Montreal Protocol, Springer, 119–131.

Stemmler, K., D. Folini, S. Ubl, M.K. Vollmer, S. Reimann, S. O'Doherty, B.R. Greally, P.G. Simmonds, and A. Manning, 2007: European emissions of HFC-365mfc, a chlorine-free substitute for the foam blowing agents HCFC-141b and CFC-11. *Environ. Sci. Technol.,* **41**, 1145–1151.

Velders, G.J.M., A.R. Ravishankara, M.K. Miller, M.J. Molina, J. Alcamo, J.S. Daniel, D.W. Fahey, S.A. Montzka, and S. Reimann, 2012: Reducing HFC influence: Preserving Montreal Protocol climate benefits. *Science*, **335**, 922–923.

Vollmer, M.K.,and Coauthors,. 2011: Atmospheric histories and global emissions of the anthropogenic hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa. *J. Geophys. Res.,* **116**, D08304, doi: 10.1029/2010JD015309.

Vollmer, M.K., S. Reimann, M. Hill, and D. Brunner, 2015: First Observations of Fourth Generation Synthetic Halocarbons HFC-1234yf, HFC-1234ze(E), and HCFC-1233zd(E) in the Atmosphere. *Environ. Sci. Technol.*, **49**, 2703–2708.

Zander, R., E. Mahieu, P. Demoulin, P. Duchatelet, G. Roland, C. Servais, M.D. Mazière, S. Reimann, and C.P. Rinsland, 2008: Our changing atmosphere: Evidence based on long-term infrared solar observations at the Jungfraujoch since 1950. *Sci. Total Environ.*, **391**, 184–195.

Zellweger, C., C. Hueglin, J. Klausen, M. Steinbacher, M.K. Vollmer, and B. Buchmann, 2009: Inter-comparison of four different carbon monoxide measurements techniques and evaluation of the long-term carbon monoxide time series of Jungfraujoch. *Atmos. Chem. Phys.*, **9**, 3491–3503.