The Ozone Situation in Germany

State of knowledge, research gaps and recommendations

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Documentation of a workshop on ozone pollution in Germany,
which took place on 19 and 20 November 2019 at the German Environment Agency in Dessau

Organized by the

Institute for Advanced Sustainability Studies and the German Environment Agency

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Imprint

Kurzbeschreibung: Ozonsituation in Deutschland

Die Gefährdung der menschlichen Gesundheit und der Vegetation durch Ozon ist nach wie vor ein wichtiges Thema in Deutschland. Ein vom Umweltbundesamt (UBA) und dem Potsdamer Institut für transformative Nachhaltigkeitsforschung (IASS Potsdam) organisierter Workshop widmete sich diesem Thema. Expertinnen und Experten diskutierten den derzeitigen Wissensstand zu ozonrelevanten Prozessen, den Verbesserungsbedarf bei Modellierung und Messungen, die Aussagekraft der vorliegenden Emissionsinventaren und den Beitrag der regionalen Ozonbildung an der Gesamtbelastung. Es wurden außerdem allgemeine Empfehlungen zu Emissionsminderungen der Ozonvorläuferstoffe in Deutschland erarbeitet und Wissenslücken sowie weiterer Forschungsbedarf identifiziert. Beispielhaft für die Ergebnisse der Diskussion sind folgende Empfehlungen des Workshops zu nennen:

► weitere Minderung der anthropogenen NO_x-Emissionen,

► Verbesserung des Detailgrads der NMVOC-Spezifikation in den anthropogenen Emissionskatastern,

► Aktualisierung der biogenen VOC-Emissionen für Chemie-Transport-Modelle,

► regelmäßige Überwachung von Isopren-Konzentrationen und kampagnenbasierte Messungen der Isopren-Emissionen aus der Vegetation unter deutschen Bedingungen,

► parallele Messungen von NO, NO_2 und Ozon an städtischen und verkehrsnahen Stationen sowie am Stadtrand,

► Durchführung von Modellvergleichsstudien auf verschiedenen räumlichen Ebenen

Abstract: The Ozone Situation in Germany

Ozone is still a threat to human health and vegetation and therefore an important topic in Germany. A workshop organized by the German Environment Agency (Umweltbundesamt) and the Institute for Advanced Sustainability Studies (IASS Potsdam) addressed this issue. Experts discussed the current state of knowledge on processes relevant for ozone, the need for improvement concerning models and measurements, the quality of the current emission inventories, and the contribution of regional ozone production to overall pollution. In addition, general recommendations for reducing emissions of ozone precursors in Germany were discussed and knowledge gaps and further research needs identified. The following recommendations emerged from the discussions:

► Take steps to further reduce anthropogenic NO_xemissions;

► Improve the level of detail of NMVOC-speciation in anthropogenic emission inventories;

► Update biogenic VOC-emissions for chemistry transport models;

► Add regular isoprene monitoring and further campaign-based measurements of isoprene emissions from vegetation under German conditions; and

► Establish model intercomparison studies with a focus on ozone at different scales.

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List of abbreviations

AOT40	Accumulated dose Over a Threshold of 40 ppb
BVOC	Biogenic Volatile Organic Compounds
CEIP EEA	Centre on Emission Inventories and Projections (CEIP) at the European Environmental Agency (EEA)
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
DOAS	Differential Optical Absorption Spectroscopy
EU NEC Directive	National Emission Ceilings Directive
HCHO	Formaldehyde
LRTAP	Convention on Long-Range Transboundary Air Pollution
NH_3	Ammoniac
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides – the sum of nitrogen dioxide (NO_2) and nitric oxide (NO)
NMVOC	Non-Methane Volatile Organic Compounds
OH	Hydroxyl radical
O_3	Ozone
O_x	$O_x = NO_2 + O_3$
OVOC	Oxygenated Volatile Organic Compounds
PAN	Peroxyacetyl nitrate
$PM_{2.5}$	Particulate matter (PM) with a maximum diameter of 2.5 micrometres
SO_2	Sulphur dioxide
VOC	Volatile Organic Compounds

1   Introduction

Peak values for ground-level ozone concentrations in Germany have fallen considerably since the 1990s. Even in extreme conditions, like the hot summers of the past two years, ozone concentrations above the alert threshold are very rare. Public discussions of air pollution have focussed instead on particulate matter and nitrogen dioxide. However, ozone continues to pose a threat to human health and vegetation. Although there are less acute health problems and plant damage, the long-term effects are still increasing due to the continued rise in average ozone pollution. The adverse health impacts of ozone include compromised lung function, inflammatory airway diseases, and other respiratory problems. Physical exertion, i.e. with increased respiratory volume, can exacerbate these effects. When plants absorb ozone through the leaf stomata, the leaf organs can be damaged. Long-term exposure to ozone can hinder plant growth and threaten harvests and the quality of agricultural produce.

But what are the reasons for ozone pollution? This question was the starting point for a workshop organized by the Institute for Advanced Sustainability Studies (IASS Potsdam) and the German Environment Agency (UBA). The results of that workshop are summarized in this report.

Discussions with experts focused on the following issues:

► What is the current state of knowledge on ozone-relevant processes or influences (ozone formation, transport, emissions, meteorology, background pollution)?

► In what areas can modelling and measurements be improved?

► How helpful are existing emission inventories?

► What does regional ozone formation contribute to the total pollution?

During the workshop general recommendations on reducing emissions of ozone precursors in Germany were discussed and knowledge gaps and further areas of research were identified. Key recommendations for reducing emissions and closing knowledge gaps are presented in Part 1 of the report. Part 2 summarizes the current state of knowledge on the aforementioned topics.

2 Recommendations

2.1 Reducing emissions

2.1.1 Anthropogenic nitrogen oxides (NO$_x$)

A reduction in anthropogenic NO$_x$ emissions (NO$_x$ = the sum of nitrogen dioxide (NO$_2$) and nitric oxide (NO)) leads to higher average ozone concentrations in urban areas due to the "titration" effect (see chapter 3.1). Further reductions in anthropogenic NO$_x$ emissions are nevertheless advisable, because those emissions continue to contribute to peak ozone concentrations and high NO$_2$ concentrations.

Recommendation:

► Sustained reductions in anthropogenic NO$_x$ emissions.

2.1.2 Anthropogenic Non-Methane Volatile Organic Compounds (NMVOC)

It is less clear whether reducing anthropogenic NMVOC emissions should be a priority in Germany for ozone control. Fundamental understanding of anthropogenic NMVOC emissions and their reactivity should be improved before existing control of NMVOC is made more stringent.

Recommendations:

► Improve the level of detail of NMVOC speciation in anthropogenic emission inventories using as much primary data as possible, even though reporting obligations only require total NMVOC.

► Obtain data from the solvent industry and discuss the possibility of voluntary reporting of NMVOC speciation. Each new piece of information can contribute to improving speciation.

2.1.3 Methane (CH$_4$) und carbon monoxide (CO)

Methane and CO emissions both contribute significantly to background ozone on hemispheric scales, since these species are so long-lived in the atmosphere. The contribution of German emissions is relatively small. Thus simply reducing German emissions of methane and CO would not have a significant effect on ozone concentrations in Germany. International coordination is required for control of methane and CO emissions to reduce background ozone.

Recommendations:

► Use international bodies such as the LRTAP[1]Convention to lobby for a reduction of these emissions on the hemispheric scale.

► Support future efforts to reduce methane emissions in Germany to set a good example to the rest of the world.

2.1.4 Biogenic Volatile Organic Compounds (BVOC)

Biogenic VOC emissions within Germany contribute strongly to ozone production within Germany, especially to peak values associated with higher temperatures. The most relevant

[1] Convention on Long-Range Transboundary Air Pollution

BVOC emissions for ozone are the isoprene emissions associated with some species of trees. Germany is currently in the process of changing the mix of tree species in its forests and cities to make them more resilient to climate change. Many of the new tree species being planted are high isoprene emitters.

Recommendations:

► Consider BVOC emissions, especially isoprene, in active forest adaptation and other revegetation measures. Efforts to control ozone should, however, be weighed up against the desire to establish climate-resilient mixed deciduous forests in Germany that correspond largely to natural conditions.

► Update data on BVOC emissions in chemical transport models.

2.2   Knowledge Gaps and Research Needs

Substantial knowledge gaps need to be closed in order to devise effective ozone reduction measures in Germany.

2.2.1   Biogenic Volatile Organic Compounds (BVOC)

Measurements of emissions and ambient concentration of isoprene in Germany are extremely scarce. Isoprene emission models are based on a very small set of observations in different regions of the world. Given its importance for ozone formation, improved monitoring of isoprene should be a high priority.

Recommendations:

► Carry out regular isoprene monitoring at measurement stations in rural and urban areas, including those managed by UBA and the federal states.

► Further campaign-based measurements of isoprene emissions from vegetation in Germany under German conditions are required to improve mechanistic emission models for Germany.

2.2.2   Urban Air Quality

Current monitoring in German urban areas is not detailed enough for the characterization of the ambient mix of VOCs and other aspects of atmospheric composition and dynamics that influence ozone production. Data on dynamics like the vertical mixing of emitted pollutants is also lacking.

Recommendations:

► Carry out parallel measurements of NO, NO_2 and ozone at urban and suburban stations to ensure that the full budget of NO_x and O_x ($O_x = NO_2 + O_3$) can be monitored.

► Combine this with parallel measurements of NO, NO_2, and ozone at selected roadside stations, which may provide data on primary NO_2 emissions.

► Establish a small number of "supersites" in selected cities, where comprehensive measurements of even highly speciated VOCs (biogenic and anthropogenic VOCs, including formaldehyde) and total OH (hydroxyl radical) reactivity can be carried out.

► Supplement long-term measurements with campaign-based measurement of ambient concentrations of speciated VOC, total OH reactivity, and vertical distribution of NO_x in urban areas.

2.2.3 Numerical models

For reasons not yet fully understood, there are large discrepancies in the background ozone concentrations simulated by different global models. Regional models, which often take their boundary conditions from global models, also show considerable uncertainty with regard to evaluation against hourly measurement data and ozone-relevant process description. In the case of BVOC emissions, this input data is known to be poorly represented in all current models.

Recommendations:

► Use land-use maps that provide more detailed information on tree species.

► Improve isoprene emission models.

► Apply the more thorough methods for model evaluation (e.g. dynamic evaluation) that are already available.

► Conduct model intercomparison studies with a focus on ozone at the global, European, German, and urban scales, combined with corresponding measurement campaigns. This can help to understand and reduce model uncertainties.

► Carry out more direct measurements of ozone deposition to vegetation for the purpose of evaluating models.

3 State of knowledge on ozone pollution in Germany

3.1 Background

The introduction of EU regulations on air pollution by ozone in 1992, and their subsequent tightening in 2003, led to higher densities of surface ozone measurements in Germany. Ozone concentrations are currently measured at around 260 stations in the monitoring networks of the federal states and the German Environment Agency (UBA). Since 1992, almost 100% of urban stations in Germany have exceeded the long-term target value of 120 μg/m^3 to protect human health at least once a year, and almost 100% of rural stations have exceeded the long-term target of 6000 μg/m^{3}h to protect vegetation (accumulated ozone dose over a threshold of 40 ppb (AOT40)) at least once a year. Unlike other pollutants (eg. NO_2), the concentration and exposure threshold values for ozone are not legally-binding "limit values", but rather "target values", "long-term objectives", "information threshold", or "alert threshold values".

Since about 1995, exceedances of the European alert and information threshold concentration values (240 and 180 μg/m^3) have been decreasing, which is also the case for very low hourly ozone concentrations (between 0 and 20 μg/m^3) particularly at urban stations and in all seasons. This is consistent with lower NO_x emissions in the same period, which leads to a weakening of the "titration effect" during periods of weak photochemistry (night-time and all seasons except summer) and slower local photochemical production during periods of strong photochemistry (summer daytime).

The titration effect refers to the depletion of ozone by freshly emitted NO (and the formation of NO_2 in the process). In regions with high NO emissions (e.g. city centres/urban areas), this can lead to the complete removal of all the ozone in the air. However, the ozone removed through titration is not permanently lost, as NO_2 is quickly photolysed through UV radiation to form ozone again. The sum of ozone and NO_2 is often referred to as O_x. This total concentration stays the same even during ozone titration, making it a useful indicator of local photochemical ozone production and ozone loss.

Overall, the average ozone concentration is increasing, especially in urban areas, and in all seasons (1991–2018). The strongest increase was, however, in the 1990s. This increase is driven largely by increasing trends in the middle of the concentration distribution (40 to 100 μg/m^3).

Since the measured O_x values in cities are similar to those in the surrounding rural areas, the rise in urban ozone values can be attributed to decreased titration due to a reduction in NO_x emissions rather than an increase in urban ozone production. Given the relatively small number of stations that measure both ozone and NO_2, it is difficult to come to a firm conclusion in this case.

In Germany, long-term measurements of ozone have been carried out at the Hohenpeissenberg Observatory since 1971. Depending on the origins of the transported air masses, these measurements are representative of background conditions in Central Europe ("clean" sector) or in nearby regions including urban areas ("polluted" sector). The long-term measurements show a rise in annual average ozone of approximately 20 μg/m^3 from 1971 until the mid-2000s (from about 60 μg/m^3 to about 80 μg/m^3), and a slightly decreasing trend in annual average background ozone since then.

3.2   Ozone formation, transport and modelling

3.2.1   Temporal and spatial scales of ozone production and transport

Ozone is a secondary pollutant, which is not itself emitted, but rather formed in the troposphere through photochemical reactions of emitted precursors (NO_x and VOC) in the presence of solar radiation. Due to its long lifetime (up to several weeks), it can be transported over intercontinental distances (long-range transport) and from the stratosphere to the troposphere. The timescales for the production and transport of tropospheric ozone are dictated by its chemical lifetime and the lifetimes of its NO_x and VOC precursors. These range from hours (NO_x, and the most highly reactive VOCs, such as isoprene) to decades (methane). Corresponding spatial scales range from the entire globe down to urban scales.

The highest concentrations of ozone occur in summer, when local photochemical production of ozone becomes more important than long-range transport of background ozone. This local photochemical production occurs over short time periods (days to hours) and small spatial scales. Local photochemical production of ozone is highly sensitive to biogenic VOC emissions (especially isoprene) in regions with high levels of anthropogenic NO_x. Titration effects are important at even smaller scales, for example in locations very close to strong sources of NO_x (eg. individual plumes and street canyons).

3.2.2   Numerical models

Numerical models are commonly used to understand and predict ozone-relevant processes, including precursor emissions, chemical production of ozone, and long-range transport and loss processes. In order to capture all the processes important for the formation, transport, and loss of ozone, models have to represent all the relevant temporal and spatial scales. Since no single model can represent all the relevant scales in a single simulation, hierarchies of models at different scales are used. The choice of models thus depends on the scale of interest.

Global models simulate background ozone concentrations based on: the transport of ozone from the stratosphere; the oxidation of long-lived VOC precursors such as methane and carbon monoxide in the presence of nitrogen oxides; loss through photolysis; and hemispheric transport over intercontinental distances. Global models differ considerably in terms of their simulated surface ozone concentrations, and all of them tend to overestimate the measured ozone values and underestimate peak values. Source attribution studies that work with global models show that annual average hemispheric background surface ozone is highly influenced by the relatively long-lived organic precursors methane and carbon monoxide. Several factors could be responsible for this: differing methane lifetimes, vertical mixing, and the chemical mechanisms used in the models. Due to their coarse resolution (about 100 km), global models tend to dilute NO_x emissions too quickly, especially from isolated point sources such as individual cities and international shipping. This artificial dilution of NO_x emissions, especially from international shipping, is likely to contribute to the high ozone bias of many global models.

Regional models can simulate ozone over domains the size of Europe while resolving spatial scales as small as the urban background. Each model must make trade-offs with respect to the level of detail being represented, and the degree of computational complexity required. Regional models rely either on global models or observations of background concentration for their lateral boundary conditions, and thus for their representation of long-range transport of ozone.

3.2.3   Meteorology

Ozone concentration is highly temperature dependent. While models consider the temperature dependence of many processes, they are often incapable of simulating the peak ozone concentrations that occur at extremely high temperatures. One reason for this could be deficiencies in the time-dependent quantification of BVOC emissions by the models. These emissions are highly dependent on temperature as well as other model parameters such as land use (tree species) and the choice of BVOC emission algorithm.

The vertical resolution of models in the boundary layer appears to be a further important factor in the simulation of surface ozone. This allows the model to represent both the entrainment of ozone from above the boundary layer in the morning and the vertical mixing of precursor emissions during the day.

3.2.4   Chemistry

Current models show that anthropogenic NMVOCs do not play an important role either in annual average background ozone or in peak ozone events. However, they do appear to contribute significantly to the formation of springtime hemispheric background ozone. A major caveat here is that all models currently use very simplified representations of NMVOC chemistry. There are various reasons for this: lack of detail in emission inventories; lack of available detailed measurements with which to evaluate models; and the need for computational efficiency.

Many models use chemical mechanisms dating back to the 1980s. In spite of that, they simulate comparable amounts of ozone to models with much newer chemical mechanisms. The ozone production rate simulated by models depends on the total reactivity of the simulated VOC mix, rather than the specific identities of the VOC being simulated. Systematic differences in the chemical mechanisms for the oxidation of NMVOC could account for some of the discrepancies in the global background ozone simulated by different global models. But on the regional scale, BVOCs are more important than anthropogenic NMVOC, and deficiencies in model NMVOC chemistry are only likely to be important if the models are missing some highly reactive NMVOC, for which there is no clear observational evidence in Germany.

3.2.5   Dry deposition

A major loss process for surface ozone is dry deposition to vegetation. This deposition occurs when ozone is absorbed through open stomata. It is thus closely linked with the physiology of the vegetation. High temperatures can lead to lower ozone deposition (and thus higher ozone concentrations) when plants close their stomata in order to conserve water. Extended dry periods can lead to loss of foliage, which also results in lower deposition of ozone. The photochemical production of ozone is also lower in dry conditions due to reduced emissions of BVOCs. Current models do not capture the observed relationship between aridity and increased ozone. Direct measurements of ozone flux to vegetation would be very useful for model evaluation, but these measurements are scarce.

3.2.6   Knowledge gaps and recommendations

The spread of simulated ozone concentration in model ensembles (at both global and regional scale) is often large. The reasons for this are not well understood. Methods for evaluating and comparing models against observations should therefore be developed further. Dynamic evaluation of model response to meteorological conditions (eg. temperature), improved diagnostic information from models (eg. ozone budgets), and improved statistical evaluation techniques can all help to understand the differences between models and bring them more into

line with observations. In particular, the atmospheric chemistry modelling community could look to the climate modelling community, which has far more well-developed methods for statistical evaluation of models.

3.3 Emissions of ozone precursors

3.3.1 Anthropogenic precursors

Germany reports its anthropogenic emissions of air pollutants and precursors with the primary aim of satisfying its obligations under the LRTAP Convention and the EU NEC[2] directive. The use of this reported emissions data for numerical modelling of air pollution is a secondary consideration. The reporting guidelines of the Centre on Emission Inventories and Projections (CEIP) at the European Environmental Agency (EEA) specify the pollutants and sectors for which emissions should be reported. These guidelines have recently been updated to require that emissions be reported on a grid. The guidelines also stipulate that the emissions reports be complete and of high quality. Annual average emissions are reported each year for all years beginning in 1990. Most countries in Western Europe, including Germany, have reported decreasing emissions of NO_x, NMVOC, and CO since 1990. Changes in reporting methodology, or the availability of new information, mean that emissions for earlier years are regularly revised.

In order to simulate ozone and other air pollutants, numerical modellers require additional information about emissions, such as temporal profiles (amount of mass per unit of time; seasonal, weekly, and diurnal), the NO/NO_2 split, and the speciation of NMVOCs. Modellers must either add this information themselves or use products based on the reported data and created by third parties, who also perform consistency checks to correct for discrepancies between the emissions reported for different countries. Some emission sectors benefit from a dynamic modelling approach to temporal profiles. For example, residential combustion is highly dependent on ambient temperature. Model results are improved when the temperature dependence of heating emissions is accounted for.

3.3.1.1 Anthropogenic nitrogen oxides (NO_x)

The sector with the largest reduction in NO_x emissions since 1990 is road transport. However, this sector still accounts for over 80% of total NO_x emissions in Germany. Further NO_x sources include industrial processes, manufacturing, agriculture and private households.

3.3.1.2 Anthropogenic Non-Methane Volatile Organic Compounds (NMVOC)

For anthropogenic NMVOC, industrial processes, in particular the use of solvents, are currently the most important source. Most of the reductions in reported NMVOC emissions since 1990 have been in the transport and solvent sectors, but the latter continues to be the most important sector for Germany's national NMVOC emissions. There is a high level of uncertainty regarding emissions from the solvent sector, both in terms of the total magnitude of the NMVOC emissions and their speciation. The speciation of NMVOC emissions is uncertain due to the reporting requirements. Since these only specify that total NMVOC emissions be reported, information about speciation is not collected at all. Speciation of NMVOC emissions must be done by modelling groups, or third parties who produce emission inventories. The speciation of NMVOC as actually used in model simulations also depends strongly on the number and type of NMVOCs that are included in the chemical mechanism of each model.

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[2] EU National Emission Ceilings Directive (NEC directive for short)

Given that anthropogenic NMVOCs do not appear to be major ozone precursors, it is not clear how important a detailed NMVOC speciation really is for modelling of ground-level ozone. Yet it may prove important if anthropogenic NMVOC turns out to be a lot more reactive than currently assumed in emission inventories and model speciation. It might well be the case that modern solvent emissions are more reactive than assumed in current speciations, which were developed some time ago. Model sensitivity studies would be helpful here. Improved speciation of NMVOC emissions would require changes to the reporting obligations for the solvent industry. But the solvent industry may also be willing to provide the required information on a voluntary basis. Modellers would not necessarily need a detailed speciation, but rather a general indication of the types of molecules that constitute modern emissions from the solvent sector and their reactivities.

3.3.1.3   Carbon monoxide (CO) and methane (CH$_4$)

Due to their long chemical lifetimes in the troposphere, carbon monoxide and methane are important precursors of ozone over large spatial scales. Emissions of methane and carbon monoxide in Germany do not significantly influence local ozone production in Germany, but contribute rather to the production of ozone in the hemispheric background.

3.3.1.4   Knowledge gaps and recommendations

Uncertainties are not usually stated in emission inventories; when available, uncertainty calculations are only available for the entire inventory. UBA reports uncertainties for nitrogen oxides (NO_x), sulphur dioxide (SO_2), NMVOCs, ammoniac (NH_3) and particulate matter ($PM_{2.5}$) in Germany. New findings in emission inventories take a long time (often years) to reach modellers. To improve ozone modelling with regard to emissions, cooperation between emissions experts and modellers should be continued and strengthened.

3.3.2   Biogenic precursors

A wide variety of BVOCs are emitted by vegetation, including isoprene, terpenes, and oxygenated VOCs (OVOCs). Of these different compounds, isoprene emissions are the most important for ozone production. Terpenes generally react directly with ozone at a faster rate than they produce ozone, and their oxidation products generally have a low vapor pressure, meaning that they condense readily into the aerosol phase and are thus not available for subsequent ozone production. OVOCs are generally less reactive than isoprene and are emitted in smaller quantities. Model studies show that isoprene is especially important for high ozone episodes in the summer.

BVOC emissions are dependent on the characteristics of the vegetation as well as the ambient meteorological conditions and seasonal factors. Isoprene emissions are predominantly from trees, and are highly species-dependent, as well as dependent on the individual situation of each tree. Environmental conditions that influence isoprene emissions are temperature, solar radiation, CO_2 concentration, and soil moisture, as well as stress factors such as parasites and elevated ozone concentrations.

Heatwaves lead directly and indirectly to higher emissions – except in cases of extreme drought. A comparison of the summers of 2015 and 2018 illustrates this. High temperatures were measured in both years, but unlike 2015, 2018 was characterised by extremely dry conditions, which probably led to lower BVOC emissions. Peak ozone values in 2018 were also lower than in 2015. However, a lack of robust BVOC measurements means that this correlation is difficult to prove.

3.3.2.1   Knowledge gaps and recommendations

Models of BVOC emissions are currently highly simplified. They calculate total emissions as a linear combination of a subset of the factors that are known to contribute to the emissions (e.g. vegetation type, temperature and irradiation) and neglect nonlinear interactions between these factors. These models generally also do not distinguish between different species of trees, but instead classify trees into vegetation categories with similar emission characteristics. But, depending on species composition, these categories may have very different emission patterns. Furthermore, models do not consider any effects due to the stage of development, parasites, or stress from ambient ozone. Many of these simplifications are due to a lack of measurements, for example of the emission patterns of individual specis. Others can be attributed to a lack of understanding of the impact of environmental influences. Measurements of BVOC fluxes from a variety of ecosystem types, coupled with data on different environmental factors in urban and rural areas, would help in the development and evaluation of models. Measurements of formaldehyde (HCHO) would also be useful, as this is a major oxidation product of all VOCs, including BVOCs.

Vegetation inventories are an important point of reference and should be kept up-to-date. Due to frequent changes to the vegetation mix (as a result of forest adaptation, agriculture, urban landscaping, etc.), these inventories can vary significantly over time. Forest adaptation is also leading to rapid changes in the mix of tree species in German forests, with a knock-on effect on emissions of isoprene and other BVOCs. For BVOC emission models to take advantage of detailed vegetation inventories, the algorithms need to be updated to allow for greater differentiation between different tree species.

3.4   Measurements of ozone and precursors

In addition to the aforementioned measurements required by the LRTAP convention and EU law, several other long-term or campaign-based measurements of precursors are carried out. Long-term measurements are especially useful for determining trends, while campaign-based measurements can deliver detailed process understanding. Measurements are further divided into in-situ measurements and remote sensing.

3.4.1   In-situ measurements of volatile organic compounds (VOCs) and nitrogen oxides (NO$_x$)

In addition to the long-term measurements of ozone at Hohenpeissenberg described above, long timeseries also exist for ozone precursors at that location. Measurements of NO$_x$ have been performed since 1996, but they show no clear trend in the period to date either for air masses that can be assigned to the "clean" sector and are therefore representative of the background atmosphere in Central Europe, or for air masses that are transported from the "polluted sector". The lack of a decline in NO$_x$ is inconsistent with the decline in reported NO$_x$ emissions. Anthropogenic NMVOCs do show a small decreasing trend over this period, while BVOCs show an increasing trend. This increase is most notable for isoprene.

The total OH reactivity measurement of an air mass is a more useful measure of the contribution of VOCs to the ozone production rate. OH reactivity is also a useful metric for evaluating models, since models represent VOC chemistry in a highly simplified way. Measurement campaigns in urban areas of Germany show decreasing trends for NO$_x$ concentrations, along with even stronger decreasing trends in the OH reactivity of VOCs. A measurement campaign in Berlin in 2016 revealed that the OH reactivity of VOC in the "urban background" is dominated by BVOC, while VOC measurements in the "city centre" have a similar reactivity composition to traffic

emissions. No evidence was found for highly reactive emissions from the solvent sector in this campaign.

3.4.2   Use of satellite measurements of volatile organic compounds (VOC), nitrogen oxides (NO_x) and ozone (O_3)

Instruments on board satellites can measure various chemical species relevant to tropospheric ozone. In addition to ozone itself, they can provide information on NO_2, CO, and formaldehyde (HCHO). In Germany, carbon monoxide can only be measured via satellite if the local sources are very strong (e.g. fires). Formaldehyde cannot be detected from satellite measurements over Germany in winter and in summer only with a high rate of error. However, monthly satellite maps do show elevated HCHO values over some parts of Europe such as the Po Valley, over certain forested areas, and over fires. In the absence of fires, individual measurements are below the detection limit, and as such cannot provide any information about VOCs. Ozone measurements are difficult in Germany due to the low thermal contrast between the ground and the overlying atmosphere. Only NO_2 measurements via satellite are currently viable on a regular basis over Germany.

Since 2018, the TROPOMI instrument on board the Sentinel 5P satellite measures total column NO_2 to within 30% accuracy once per day at the overpass time of 13:30 with a resolution of 3.5×5.5 km^2 under cloud-free conditions. Spatial coverage and measurement accuracy can be improved by averaging data from multiple overpasses. This spatial resolution allows a direct comparison with regional chemistry transport models. TROPOMI data is already being used for model evaluation. TROPOMI NO_2 measurements can also be used directly to locate sources of NO_2 and determine their strength. This allows for a direct evaluation of emission inventories.

A major source of uncertainty in satellite NO_2 measurements is the vertical distribution of NO_2. The retrieval algorithm must assume an a-priori vertical distribution, which is commonly taken from model simulations, but the vertical distribution of NO_2 in models is itself uncertain. Independent measurements of the vertical distribution of NO_2 from sondes are therefore needed to improve the accuracy of satellite NO_2 retrievals.

Due to the relatively recent launch of Sentinel 5P, first results are only beginning to emerge. Future generations of geostationary satellites will be able to measure the diurnal cycle of atmospheric composition, providing further opportunities for evaluating inventories and models.

3.4.3   Knowledge gaps and recommendations

In general, there are not enough measurements of ozone precursors available for the evaluation of models. Different measurements are needed in order to understand the long-range transport of ozone, background conditions, and urban photochemistry. Measurements must be easily accessible to modellers, and modellers should make better use of available data. The ACTRIS (Aerosols, Clouds and Trace gases Research Infrastructure) programme provides an accessible data portal, which includes measurements from sites in Germany and other parts of Europe.

In addition to regular ozone measurements in the free troposphere, additional measurements of PAN (peroxyacetyl nitrate) would be helpful for understanding the role of long-range transport. Additional VOC measurements would be useful in both rural background and urban background locations. Given the important role of isoprene in the production of ozone, and the high degree of uncertainty regarding isoprene emissions, regular, long-term measurements of isoprene in both urban and rural locations would contribute to a better understanding of isoprene and improved modelling of ozone production.

Given the poor understanding of the speciation of anthropogenic NMVOC emissions in current inventories, detailed, ongoing, highly speciated measurements of NMVOC in urban areas would help to constrain this speciation and its OH reactivity. Measurements of total OH reactivity in urban areas would also be very useful as a check on the completeness of speciated NMVOC measurements, as well as the ozone production potential of urban air masses. As a common oxidation product of every VOC, formaldehyde should be included in such measurements.

In order to understand NO_x – ozone chemistry, it is also important that NO, NO_2, and O_3 are measured simultaneously at selected measurement stations. NO and NO_2 should be measured together to provide information on total NO_x emissions. The combination of NO_2 and O_3 ("O_x") provides information on ozone production and destruction independent of the titration effect. Measurements of all three at roadside stations and nearby urban background stations provides information on primary NO_2 emissions from traffic. In the measuring networks of the federal states, this parallel measurement at traffic stations is often not carried out, as the measuring programs are geared to the requirements of the relevant EU directives.

Currently, routine measurements of NO_x are only conducted at the surface monitoring stations. Knowledge of the vertical profile of NO_x in the Planetary Boundary Layer is lacking. Measurements of the vertical profile of NO_x would help to constrain the simulated vertical mixing in models, as well as providing a-priori information for satellite retrievals.

A small number of "supersites" in selected major German cities would help to close many of the current knowledge gaps in our understanding of the emissions and chemistry of BVOC, anthropogenic NMVOC, NO_x, and ozone. Long-term measurements at such supersites could be supplemented with occasional measurement campaigns. The combination of long timeseries at fixed, representative locations, and highly detailed campaign data over shorter periods would be ideal for model evaluation and improving process understanding.

More information is needed on the vertical distribution of NO_x. This data is important for evaluating models in the vertical plane and improving the accuracy of satellite measurements. In this case, balloon measurements using sondes and DOAS (Differential Optical Absorption Spectroscopy) would be useful.