Atmospheric Environment 43 (2009) 5268–5350

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric composition change – global and regional air quality

P.S. Monks [a,*], C. Granier [b,c,d], S. Fuzzi [e], A. Stohl [f], M.L. Williams [g], H. Akimoto [h], M. Amann [i], A. Baklanov [j], U. Baltensperger [k], I. Bey [l], N. Blake [m], R.S. Blake [a], K. Carslaw [n], O.R. Cooper [c,d], F. Dentener [o], D. Fowler [p], E. Fragkou [q], G.J. Frost [c,d], S. Generoso [r], P. Ginoux [s], V. Grewe [t], A. Guenther [u], H.C. Hansson [v], S. Henne [w], J. Hjorth [o], A. Hofzumahaus [x], H. Huntrieser [t], I.S.A. Isaksen [y,z], M.E. Jenkin [aa], J. Kaiser [bb], M. Kanakidou [cc], Z. Klimont [i], M. Kulmala [dd], P. Laj [ee,ff], M.G. Lawrence [gg], J.D. Lee [hh], C. Liousse [ii], M. Maione [jj], G. McFiggans [kk], A. Metzger [ll], A. Mieville [b], N. Moussiopoulos [q], J.J. Orlando [u], C.D. O'Dowd [mm], P.I. Palmer [nn], D.D. Parrish [c], A. Petzold [t], U. Platt [oo], U. Pöschl [gg], A.S.H. Prévôt [k], C.E. Reeves [bb], S. Reimann [w], Y. Rudich [pp], K. Sellegri [ee], R. Steinbrecher [qq], D. Simpson [rr,ss], H. ten Brink [tt], J. Theloke [uu], G.R. van der Werf [vv], R. Vautard [ww], V. Vestreng [xx], Ch. Vlachokostas [q], R. von Glasow [bb]

[a] Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK
[b] UPMC Univ. Paris 6; CNRS-INSU, LATMOS-IPSL, 75005 Paris, France
[c] NOAA Earth System Research Laboratory, 80305-3337 Boulder, USA
[d] Cooperative Institute for Research in Environmental Sciences, University of Colorado, 80309-0216 Boulder, USA
[e] Istituto di Scienze dell'Atmosfera e del Clima – CNR, 40129 Bologna, Italy
[f] Norwegian Institute for Air Research, 2027 Kjeller, Norway
[g] Air Quality and Industrial Pollution Programme, DEFRA, SW1P 2AL London, UK
[h] Frontier Research System for Global Change, JAMSTEC, 236-0001 Yokohama, Japan
[i] International Institute for Applied Systems Analysis (IIASA), 2361 Laxenburg, Austria
[j] Danish Meteorological Institute, 2100 Copenhagen, Denmark
[k] Paul Scherrer Institut, Laboratory of Atmospheric Chemistry, 5232 Villigen, Switzerland
[l] ETH Zurich, 8092 Zürich, Switzerland
[m] University of California Irvine, 92697 Irvine, USA
[n] School of Earth and Environmental Science, University of Leeds, Leeds LS2 9JT, UK
[o] European Commission, Joint Research Centre, Institute for Environment and Sustainability, 21020 Ispra, Italy
[p] Centre for Ecology and Hydrology, EH26 0QB Penicuik Midlothian, UK
[q] Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[r] Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratoire de Modélisation de la Chimie Atmosphérique (LMCA), 1015 Lausanne, Switzerland
[s] Geophysical Fluid Dynamics Laboratory, Princeton University Forrestal Campus, 08540-6649 Princeton, USA
[t] DLR Institut für Physik der Atmosphäre, 82230 Wessling, Germany
[u] National Center for Atmospheric Research, 80307-3000 Boulder, USA
[v] Department of Applied Environmental Science, Atmospher Science Unit, Stockholm University, 10691 Stockholm, Sweden
[w] Empa, Swiss Federal Laboratories for Materials Testing and Research, 8600 Dübendorf, Switzerland
[x] Institut für Chemie und Dynamik der Geosphäre, ICG-2: Troposphere, Forschungszentrum Jülich, 52425 Jülich, Germany
[y] Department of Geosciences, University of Oslo, 0316 Oslo, Norway
[z] Center for International Climate and Environmental Research – Oslo (CICERO), 0318 Oslo, Norway
[aa] Atmospheric Chemistry Services, EX20 1FB Okehampton, UK
[bb] School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK
[cc] Department of Chemistry, University of Crete, 71003 Voutes – Heraklion, Greece
[dd] Department of Physics, University of Helsinki, 00014 Helsinki, Finland
[ee] Laboratoire de Météorologie Physique, Observatoire de Physique du Globe de Clermont-Ferrand, Université Blaise Pascal – CNRS, 63177 Aubière, France
[ff] Université Joseph Fourier — Grenoble 1 / CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement, 38400 St Martin d'Heres, France
[gg] Max-Planck-Institut für Chemie, 55128 Mainz, Germany
[hh] School of Chemistry, University of York, YO10 5DD Heslington, UK
[ii] Laboratoire d'Aérologie, Université de Toulouse III, UMR 5560, 31400 Toulouse, France
[jj] Universita' di Urbino, Istituto di Scienze Chimiche "F. Bruner", 61029 Urbino, Italy
[kk] School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, M13 9PL Manchester, UK
[ll] Ionicon Analytik Ges.m.b.H., 6020 Innsbruck, Austria

---

[*] Corresponding author. Tel.: +44 (0) 116 252 2141/3403; fax: +44 0 116 252 3789.

doi:10.1016/j.atmosenv.2009.08.021

[mm] *School of Physics and Centre for Climate & Air Pollution Studies, Environmental Change Institute, National University of Ireland, Galway, University Road, Galway, Ireland*
[nn] *School of GeoSciences, University of Edinburgh, EH9 3JN Edinburgh, UK*
[oo] *University of Heidelberg, 69120 Heidelberg, Germany*
[pp] *Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, 76100 Rehovot, Israel*
[qq] *Institute for Meteorology and Climate Research, Atmospheric Environmental Research (IMK-IFU), Forschungszentrum Karlsruhe GmbH, 82467 Garmisch-Partenkirchen, Germany*
[rr] *EMEP MSC-W, Norwegian Meteorological Institute, 0313 Oslo, Norway*
[ss] *Department of Radio and Space Science, Chalmers University of Technology, 41296 Gothenburg, Sweden*
[tt] *Energy Research Centre of The Netherlands (ECN), 1755 LE Petten, The Netherlands*
[uu] *University of Stuttgart, 70049 Stuttgart, Germany*
[vv] *VU University, Amsterdam, 1081 HV Amsterdam, The Netherlands*
[ww] *Laboratoire des Sciences du Climat et de l'Environnement, IPSL/CEA/CNRS/UVSQ, 91190 Gif sur Yvette, France*
[xx] *Norwegian Pollution Control Authority, 0032 Oslo, Norway*

ARTICLE INFO

Article history:
Received 29 January 2009
Received in revised form
17 July 2009
Accepted 12 August 2009

Keywords:
Atmosphere
Troposphere
Air quality
Emissions
Climate
Co-benefit
Oxidation chemistry
Aerosols
Transport of pollutants
Ozone

ABSTRACT

Air quality transcends all scales with in the atmosphere from the local to the global with handovers and feedbacks at each scale interaction. Air quality has manifold effects on health, ecosystems, heritage and climate. In this review the state of scientific understanding in relation to global and regional air quality is outlined. The review discusses air quality, in terms of emissions, processing and transport of trace gases and aerosols. New insights into the characterization of both natural and anthropogenic emissions are reviewed looking at both natural (e.g. dust and lightning) as well as plant emissions. Trends in anthropogenic emissions both by region and globally are discussed as well as biomass burning emissions. In terms of chemical processing the major air quality elements of ozone, non-methane hydrocarbons, nitrogen oxides and aerosols are covered. A number of topics are presented as a way of integrating the process view into the atmospheric context; these include the atmospheric oxidation efficiency, halogen and HO_x chemistry, nighttime chemistry, tropical chemistry, heat waves, megacities, biomass burning and the regional hot spot of the Mediterranean. New findings with respect to the transport of pollutants across the scales are discussed, in particular the move to quantify the impact of long-range transport on regional air quality. Gaps and research questions that remain intractable are identified. The review concludes with a focus of research and policy questions for the coming decade. In particular, the policy challenges for concerted air quality and climate change policy (co-benefit) are discussed.

Contents

1. Introduction

> "*Clean air is considered to be a basic requirement of human health and well-being. However, air pollution continues to pose a significant threat to health worldwide*" (WHO, 2005b).

Air pollution can be defined as "when gases or aerosol particles emitted anthropogenically, build up in concentrations sufficiently high to cause direct or indirect damage to plants, animals, other life forms, ecosystems, structures, or works of art" (Jacobson, 2002). The state of air pollution is often expressed as Air Quality (AQ). Air quality is a measure of the concentrations of gaseous pollutants and size or number of particulate matter. As previously stated air pollution has implications for a number of contemporary issues including:

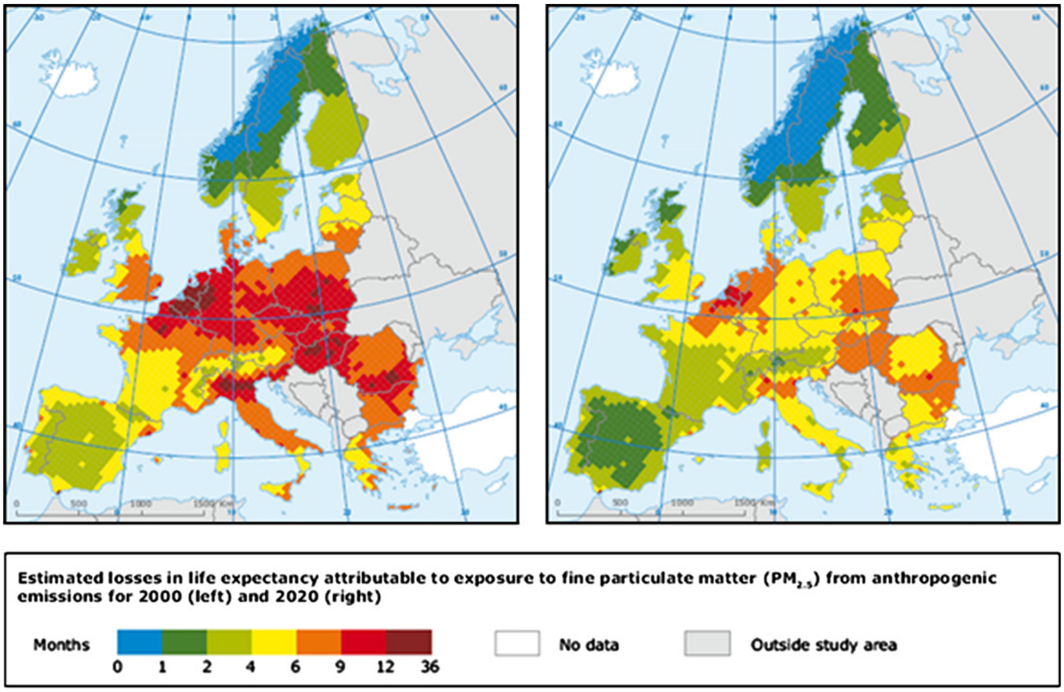
- Human health, (e.g. respiratory, cancer, allergies…),
- Ecosystems (e.g. crop yields, loss of biodiversity),
- National heritage (e.g. buildings),
- Regional climate (aerosol and ozone exhibit a strong regionality in climate forcing).

Though air quality is a measure of the anthropogenic perturbation of the "natural" atmospheric state it has to be considered in the wider context of the interactions with biogenic and other natural emissions that may have feedbacks with atmospheric composition and climate.

The World Health Organization estimates that 2.4 million people die each year from causes directly attributable to air pollution, with 1.5 million of these deaths attributable to indoor air pollution (WHO, 2002). For example in the European Union, 21,400 premature deaths each year are associated with O_3 while for particulate matter (PM) the average loss of life expectancy owing to exposure is estimated to be nine months (EEA, 2007) (see Fig. 1). Exposure to air pollutants is largely beyond the control of individuals and requires action by public authorities at the national, regional and even international levels.

Air pollution is not a modern issue and examples are available from antiquity and the middle ages (Jacobson, 2002; Stern, 1968). In modern times, interest in air quality issues rekindled when cities like Los Angeles began to experience noxious haze-like conditions (Haagen-Smit, 1952). The LA smog is often termed photochemical smog and is quite different in origin to the London smogs of the 19th and 20th centuries, which have their origins in abnormally high concentrations of smoke particles and sulphur dioxide. Though at the time photochemical smog was thought to be a relatively local phenomenon, with the understanding of its chemistry came the development of a photochemical oxidant theory for the whole of the troposphere (Chameides and Walker, 1973; Crutzen, 1973). The fundamentally shared chemical origin of air pollution across various spatio-temporal scales makes air quality both a local and global problem.

Over the last decade there has been a great deal of research on Air Quality and the control of atmospheric composition. The aim



Source: IIASA.

Fig. 1. Health impact of PM mass concentrations (μg m^{-3}). Loss in statistical life expectancy (months) that can be attributed to anthropogenic contributions to PM$_{2.5}$ for the year 2000 (left) and 2020 (right) (EEA, 2007).

of this review is to summarize, overview and integrate the main research findings over the last five years in the area of air quality and health with an emphasis on the European context. This review builds on the extensive work covered in the International Global Atmospheric Chemistry Project (IGAC) synthesis (Brasseur et al., 2003). The review does not set out to provide comprehensive coverage to the topic area, which in itself is too large, but aims to summarize what in the authors, opinions are the key research findings and their implications. The authors have been drawn from the EU ACCENT network of excellence (http://www.accent-network.org). The review deals with the science that both contributes to our understanding and quantification at a processes level as well as integrating that understanding together in a model framework.

Tropospheric chemistry has the key steps of emission, chemical transformation, transport and deposition. This is shown, as an example, for VOCs in Fig. 2. Deposition at a process level is dealt with in the sister review (Fowler et al., 2009), measurement techniques in Laj et al (Laj et al., 2009) and chemistry–climate in Isaksen et al. (2009). The review first examines emissions of trace gases and particles into the atmosphere before moving on to gas phase and aerosol processing. There is a section on cross-cutting integrative themes that places the process view in the atmospheric context. An overview of major findings in the role of atmospheric transport on atmospheric composition is also given. The review concludes with a view of the policy and science implications of the last decade's work and a consideration of future perspectives.

2. Trace gases and aerosol emissions

Trace gases are produced by physical, biological and chemical processes on land and in the oceans. The natural cycles include emissions of a large variety of chemical species, which have been perturbed over the past decades by human activities, such as agriculture and deforestation. Fossil fuel extraction and burning, energy production and consumption, industrial activities, transportation and landfills have also led to the emissions of large quantities of pollutants into the atmosphere. This section summarizes recent advances and highlights the main uncertainties remaining in the characterization of surface emissions.

2.1. Natural emissions

This section considers the major advances in biogenic emissions of non-methane volatile organic compounds (BVOCs) as well as the emission of dust and the formation of nitrogen oxides by lightning. A detailed review of the surface-atmosphere exchanges of nitrogen compounds is given in the companion paper "Ecosystems and Atmosphere Exchange" (Fowler et al., 2009).

2.1.1. Biogenic volatile organic compounds (BVOCs)

Organic molecules are signature compounds of the biosphere and include a wide range of volatile organic compounds (VOC) that are emitted into the atmosphere. There has been considerable interest in the past decades focused on quantifying the impact of these compounds on atmospheric chemistry. One major tool has been three-dimensional chemistry and transport models that require time dependent gridded emission estimates as an input.

The importance of biogenic VOC in the atmosphere was first suggested about 50 years ago (Went, 1960) but remained controversial throughout the 1970s and 80s. The evidence for the importance of biogenic VOC in the atmosphere was strengthened in the late 1980s (e.g. Chameides et al., 1988; Trainer et al., 1987) and with it the demand for time and space resolved biogenic VOC emission estimates increased dramatically. In response to the need for global emission inventories that reflected the state of the art, the International Global Atmospheric Chemistry (IGAC) Global Emissions Inventory Activity (GEIA) initiated working groups in the early 1990s to develop, review and distribute emission inventories

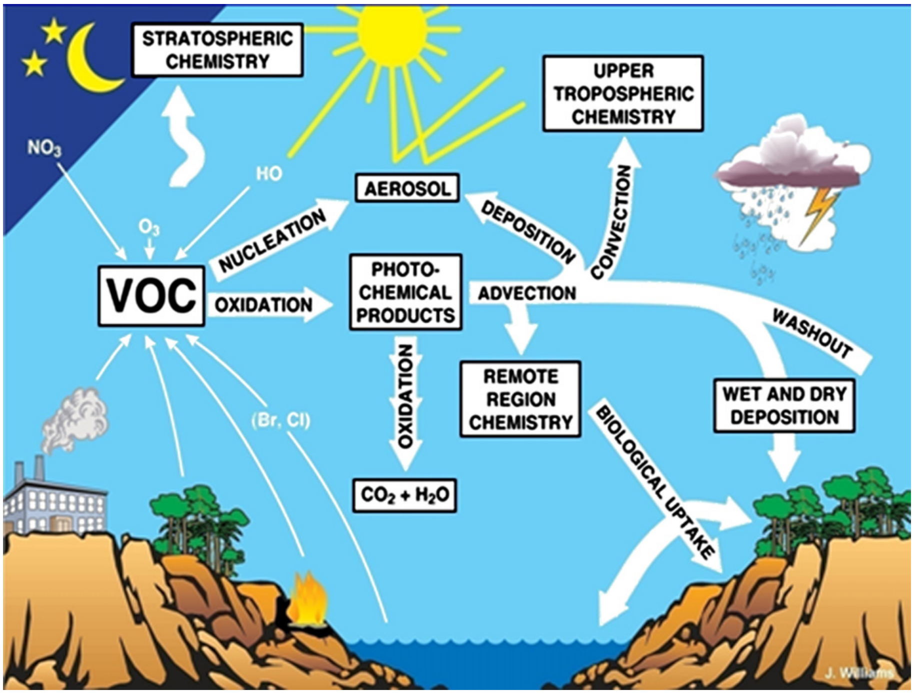


Fig. 2. A schematic overview of tropospheric chemistry (Courtesy of J. Williams, MPI Mainz).

on a 1° × 1° grid for use in global chemistry and transport models (Graedel et al., 1993). The IGAC-GEIA natural VOC working group developed an emission inventory for isoprene, total monoterpenes, other reactive VOC and other less reactive VOC (Guenther et al., 1995). The process basis for these inventories is dealt with in Fowler et al. (2009).

The inclusion of biogenic VOC emission estimates in regional air quality models began in 1986 when the US Environmental Protection Agency introduced the Biogenic Emissions Software System (BESS) followed by the Biogenic Emissions Inventory System (BEIS, (Pierce and Waldruff, 1991)) with the Regional Oxidant Model (ROM). BESS and BEIS were based on the biogenic emission modelling procedures and driving variables described by Zimmerman (1979) and Lamb et al. (1987). BVOC emissions were introduced into European regional air quality research models in the late 1980s (e.g. MacKenzie et al., 1991) and later into regulatory simulations (Simpson, 1995).

The biogenic emission estimation approaches used in past decades relied on considerably different climate and land cover databases for regional and global modelling. The result is that global and regional estimates were considerably different, even when the models were developed by the same group. The MEGAN modelling effort (Guenther et al., 2006) has combined a global scale model with high spatial resolution (1 km) suitable for regional modelling. The intent of the MEGAN effort is to incorporate all available regional information into a global model that is widely available. MEGAN currently includes the most recent information from North America and the tropics. Fig. 3 shows examples of isoprene surface emissions for different months in 2003. The total isoprene emission is estimated to be 500 Tg C yr^{-1}, with a range of 440–600 Tg C yr^{-1}.

Recent advances in emission modelling and land cover distributions in Europe has resulted in a new chemical compound specific BVOC emission inventory (NatAir-BVOC: (Steinbrecher et al., 2009)) which has been used to assess the impact of natural VOCs on air quality in Europe (Curci et al., 2009). Developments in the modelling of biogenic emissions have led to the integration of biogenic emission modules into chemistry and transport models, examples of which are the MCCM (Grell et al., 2000) or CHIMERE (Derognat et al., 2003) models. Such direct coupling is required to investigate interactions and feedbacks between the different components of the Earth system. Coupled models can also be used to evaluate the consistency in land cover and meteorological variables used to simulate the behaviour of biogenic emissions and other model components including biomass burning emissions and latent and sensible heat fluxes. Considerable effort has gone into the development of emission estimation routines that provide a more detailed representation of the processes controlling biogenic VOC emissions (Arneth et al., 2008; Zimmer et al., 2003). The ability to represent the underlying controlling processes is especially useful for predicting future responses to climate change. For example, a study by Müller et al. (2008) using a detailed multilayer canopy environment model showed the importance of taking into account the soil moisture stress factor. However, process-based models generally require parameterizations that are largely not yet suitable for application on regional and global scales.

Isoprene and monoterpenes have always been associated with a major fraction of total biogenic VOC emissions. It has long been recognized that compounds other than isoprene are emitted by vegetation. Other terpenoid compounds, such as sesquiterpenes and homoterpenes have been proven to be important owing to their strong Secondary Organic Aerosol (SOA) forming potential. Steinbrecher et al. (2009) have reported the strength of the sources for these species over Europe. Other BVOCs are mostly comprised of non-terpenoid compounds. Recent measurements suggest that alkenes make a substantial contribution to the total biogenic VOC flux, while emissions of alkanes and aromatics (e.g. ethane and toluene) make only a very small contribution. Oxygenated VOCs (alcohols, ketones, aldehydes, esters) are by far the most dominant non-terpenoid compounds emitted into the atmosphere (Seco et al., 2007) (see also Section 3.1.1.2).

The uncertainties associated with natural emissions are substantial and are highly dependent on the compound and the spatial and temporal scales used. For example, the annual global

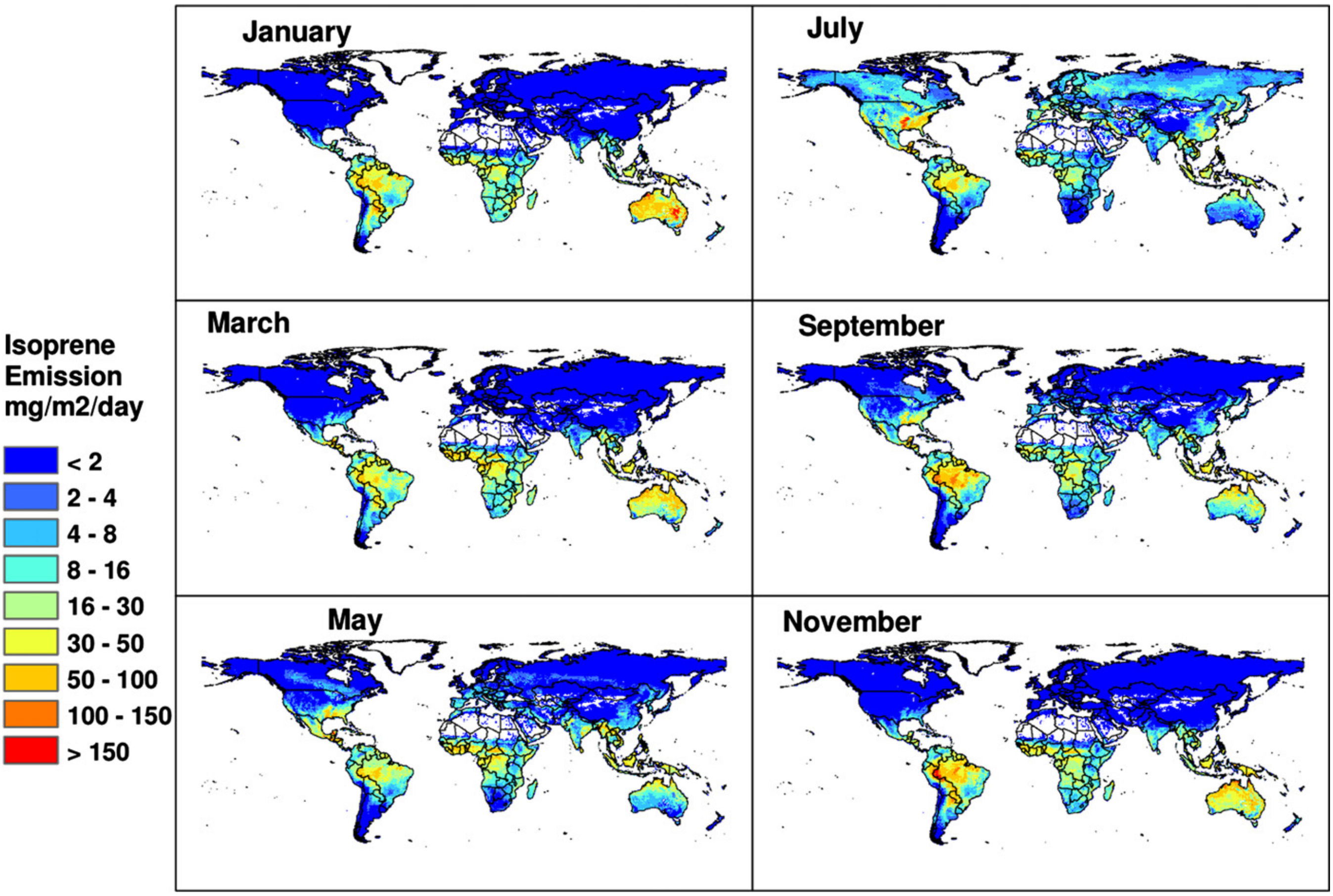


Fig. 3. Monthly average isoprene emission rates (mg m^{-2} day^{-1}) for different months in 2003 (Guenther et al., 2006).

isoprene emission is believed to be known to within about a factor of 2 but the uncertainty associated with the isoprene emissions at a particular hour and location can exceed a factor of five (Guenther et al., 2006). In addition, uncertainties vary greatly for the various biogenic compounds. For example, the uncertainties associated with the emissions of monoterpenes, sesquiterpenes and oxygenated VOCs are much higher than those associated with isoprene.

Uncertainty assessments of natural emission sources have been based on comparisons of available input databases. For example, among the driving variables required for estimating foliar VOC emissions include temperature, solar radiation, leaf area index, and vegetation type. Uncertainties in these inputs result in isoprene emission uncertainties of ~25% and 50% in global annual monoterpene emissions and in more than a factor of three for specific locations and seasons. The uncertainties associated with emission factors and emission algorithms are more difficult to quantify. Comparisons of different emission estimates for any of these species tend to agree within about a factor of two on annual global scales. However, the models are generally based on at least some of the same emissions data and so are not independent estimates. Global satellite observations are beginning to provide a valuable tool for assessing natural emissions of isoprene (Palmer et al., 2003; Shim et al., 2005).

As estimates of present day BVOC emissions have improved, research efforts have focused more on how these emissions will respond to climate and land cover change. Natural emissions of VOC are very sensitive to changes in land cover (e.g. vegetation type and density), soil moisture, temperature and solar radiation. Emission could vary by a factor of two or more on time scales of years to decades. An improved understanding of the processes controlling these variations is required for accurate prediction of future emissions.

2.1.2. *Dust emissions*

Mineral dust interacts with climate and ecosystems in several important ways. First, dust particles affect the radiative balance of the atmosphere by both absorbing and scattering incoming solar radiation and outgoing planetary radiation e.g. (Miller and Tegen, 1998; Penner et al., 2001; Tegen, 2003). Second, mineral aerosols may also influence cloud properties, since they may act as cloud condensation nuclei or ice nuclei e.g. (DeMott et al., 2003; Mahowald and Kiehl, 2003; Rosenfeld et al., 2001). Third, dust particles can decrease the photolysis rates of trace gases, which will modify the oxidizing power of the atmosphere and therefore the lifetime of some greenhouse gases (Dentener et al., 1996; Martin et al., 2003). Finally, dust provides essential nutrients for ocean ecosystems therefore contributing to biological element of the ocean uptake of carbon dioxide e.g. (Martin, 1990).

Almost 2×10^9 tons of dust are emitted every year from arid or semi-arid areas. As the lifetime of dust particles is only a few days and dust outbreaks are stochastic, their spatial distribution is highly variable. Therefore, the source locations determine the transport patterns and distribution. A large effort has been undertaken to establish inventories of dust sources since the advent of satellite aerosol products in the late 90s.

Satellite data have been used to evaluate global distributions and optical properties of aerosols. Retrieving aerosol properties from satellite remote sensing over bright surfaces, like deserts, is a challenging problem. Herman et al. (1997) defined an Aerosol

Index (AI) based on the strong signature of dust in backscattered radiances measured by the Total Ozone Mapping Spectrometer (TOMS). This index is the difference of the observed and measured ratio of radiances in the near-ultraviolet. Looking at the frequency of occurrence of elevated TOMS AI, Prospero et al., (2002) showed that their maxima are located preferentially in topographic depressions where deep layers of alluvium have been formed during the wet period of the Pleistocene. This innovative work was used by modellers to generate global dust source inventories based on topography (Ginoux et al., 2001), ephemeral lakes (Tegen et al., 2002) and geomorphology (Zender et al., 2002). However, the validity of using TOMS AI, which is biased towards elevated absorbing aerosols (owing to interactions between molecular scattering and aerosol absorption of photons) has been questioned (Mahowald and Kiehl, 2003).

The launch in 2006 of the Ozone Monitoring Instrument (OMI) which followed the first TOMS instrument launched in 1978, allowed the identification of major changes in the characteristics of dust source over the past 30 years. Fig. 4a shows a comparison of the occurrence frequency of AI values greater than 0.5 from TOMS and OMI data. Over desert areas, the isocontours relative to both instruments overlap everywhere except in East Asia, indicating that dust sources have not changed in three decades, except in East China (perhaps because of land use changes).

The method originally developed by Prospero et al. (2002) uses the absorbing property of mineral dust in the near UV, but carbonaceous aerosols also absorb in this spectral region. To avoid the identification of biomass burning as dust sources, the sub-tropical regions have been excluded from dust inventories. Since there is a significant change of land use in the subtropics, and potentially disturbed soils that are easily eroded, the importance of the anthropogenic contribution to global dust emission is an open question. Some values have been indirectly inferred from model studies: from less than 10% by Tegen (2003) up to 60% by Mahowald and Luo (2003). The uncertainties of these methods are so large that there is not a definitive value.

Aerosol products from the MODerate resolution Imaging Spectroradiometer (MODIS), Ozone Monitoring Instrument (OMI) and Multiangle Imaging Spectroradiometer (MISR) include spectral properties over land. As dust has some unique spectral signatures (Dubovik et al., 2002), it is possible to separate pixels with freshly emitted dust from other aerosols. As an example, Fig. 4b shows the frequency of occurrence of aerosol optical depth greater than 0.5, as measured by MODIS. By overlaying the distribution of frequency of occurrence with land use changes, the amount of anthropogenic dust emissions can be evaluated.

The decadal variability of dust sources has just started to be studied. Prospero and Lamb (2003) have shown that the observed increase by a factor 4 of dust concentration at Barbados (the first island West of Africa) may be due to the Sahel drought. The change of vegetation with precipitation strongly affects the area of dust emission, as the threshold of wind erosion depends first on the aerodynamic roughness length of the surface. Any sparse vegetation will reduce dust emission as a small increase of roughness length will decrease the friction velocity, the engine of wind erosion. Dust models generally assume static vegetation and have tuned their global emissions to obtain satisfactory agreement of model results with observations. Such models will not be able to reproduce the sharp increase of dust emission in the 70's from Africa, if they do not include dynamic vegetation. Since the last generation of general circulation models includes dynamic vegetation models, it is expected that a new line of studies will focus on the interactions between dust and the biosphere.

2.1.3. Lightning emissions

Lightning discharge produces nitrogen oxides (LNO_x; $NO_x = NO + NO_2$) that contribute to the global nitrogen budget. Schumann and Huntrieser (2007) have derived an estimate of the global and annual mean LNO_x emissions of 5 ± 3 TgN per year. This estimate is based on an extensive review of available data and literature; mean values of 15 (2–40) $\times 10^{25}$ NO molecules per flash and a mean flash rate of 44 ± 5 flashes per second based on LIS (Lightning Imaging Sensor)/OTD (Optical Transient Detector) satellite data are derived.

Lightning emissions depend on the strength of convective systems. Current climate-chemistry models (CCM) have parameterizations of lightning frequencies that are coupled to the convection scheme. As a consequence of this larger scale models do not resolve the driving parameters as the relevant processes are occurring on the sub-grid scale. All parameterizations of lightning NO_x production consist of (1) an estimate of total lightning frequency, (2) a separation between intra-cloud and cloud-to-ground lightning and (3) a vertical effective emission profile. The main difference among the various approaches occurs in the estimate of the lightning frequency. Most models apply a correlation between convective cloud top heights and lightning frequencies (Price and Rind, 1992). Other approaches include latent heat release (Flatøy and Hov, 1997), convective precipitation rate (Allen and Pickering, 2002; Meijer et al., 2001), convective available potential energy (Choi et al., 2005) or convective vertical mass fluxes as an indicator for updraft velocities (Allen et al., 2000; Grewe et al., 2001). None of those approaches has proven to be superior (Choi et al., 2005).

Fig. 5 shows an example of simulated production of LNO_x (Grewe, 2008). Maximum lightning emissions occur in the upper troposphere, approximately 3–4 km below the tropopause, reflecting the main convective outflow. In the Northern Hemisphere summer a clear maximum is simulated in mid-latitudes, which is not apparent in the Southern Hemisphere in DJF. It is worth noting that the only other non surface source of NO_x is aircraft emissions, which is clearly separated from the lightning source.

Currently, no trends in global lightning have been detected based on observational data. However, (Price and Asfur, 2006) detected a decrease in inferred African lightning from 1960 to 2000, based on 300 hPa water vapour re-analysis data, which they showed to be correlated to lightning activity at least for a shorter time period in which water vapour and lightning data were both available. In a transient ensemble climate-chemistry simulation from 1960 to 2020, Grewe (2008) found a decrease in lightning activity on the order of ~0.3% per decade, which results from a decrease in the number of convective events, though the individual events became stronger. Although results on the trends in convective parameters generally agree with earlier climate studies (Brinkop, 2002; Del Genio et al., 2007) their implication for trends in flash frequencies largely depend on the way the lightning process is parameterised. The trend can be reversed if lightning frequencies are not coupled to convective mass fluxes, but instead to convective cloud top heights. For an overview see Schumann and Huntrieser (2007).

2.2. Anthropogenic emissions and trends

2.2.1. Inventories of global anthropogenic emissions

Currently a variety of emission inventories exist that cover past, present and future anthropogenic emissions of greenhouse gases and air pollutants (see Table 1). Anthropogenic emissions include emissions related to fuel production, industrial and domestic combustion (fossil fuel and biofuel), transportation (road, rail, air and ships), waste disposal, industrial processes, solvent production

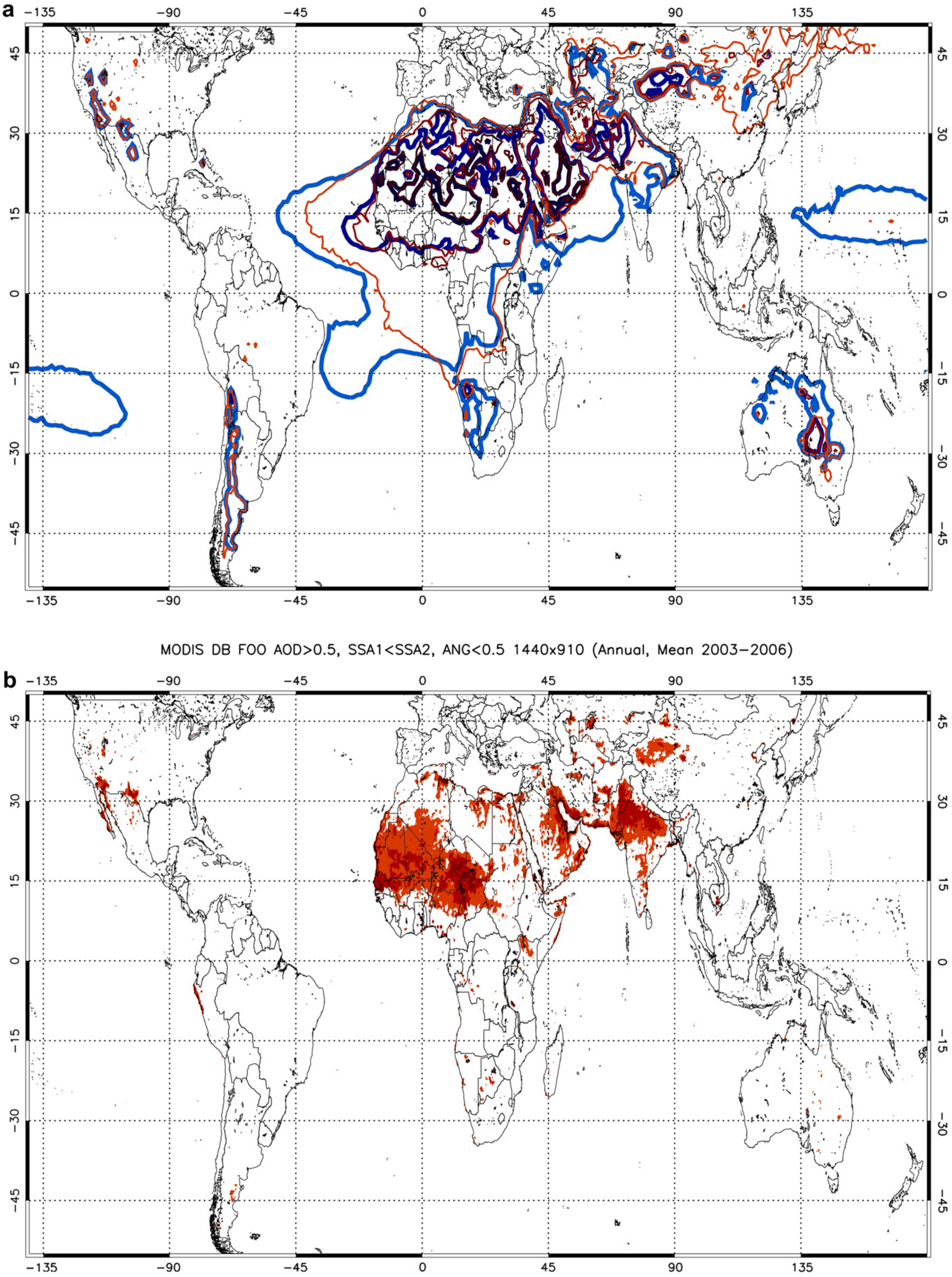


Fig. 4. a: Frequency of occurrence of having an aerosol index higher than 0.5, as calculated by TOMS (red lines) and OMI (blue lines). Lines show occurrence of 50, 75 and 95% of days per year. The maxima indicate regions with continuous atmospheric dust, which are associated with permanent sources. b: Distribution of occurrence of AOD from MODIS greater than 0.5: isocolor lines represent occurrences of 10, 25, 50 and 75% per year.

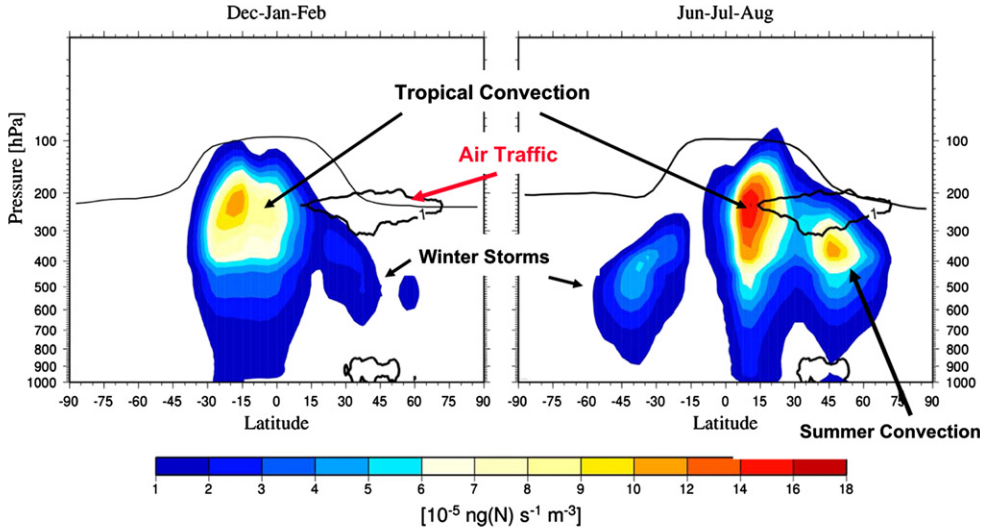


Fig. 5. Example of simulated production of nitrogen oxides by lightning (Grewe, 2008).

and use, and agriculture. Some inventories provide global coverage, while others deal with particular regions, specific compounds, or represent an official governmental submission under international agreements. At the present time, no emission inventory covers all species, sectors and years of interest for environmental impact studies. Therefore, a collection of inventories of different origins and quality are used in atmospheric models. Most inventory activities have been established in developed countries, while reliable information is still lacking for the developing world, particularly for very fast changing economies, e.g. China and India.

The list of species considered in many emission inventories includes ozone and aerosol precursors: nitrogen oxides (NO_x), carbon monoxide (CO), methane (CH_4), non-methane volatile organic compounds (NMVOCs), sulphur dioxide (SO_2), ammonia (NH_3) and particulate matter (PM). More recently, a number of inventories have estimated the emissions of particulate black and

Table 1
Characteristics of some global and regional emission inventories.

Acronym	Period covered	Spatial resolution	Temporal resolution	Chemical species	Emissions categories and reference
Global inventories					
EDGAR	2000	1° × 1°	Annual	Greenhouse gases Ozone precursors SO_2	www.mnp.nl/edgar Anthropogenic and biomass burning
HYDE	1890–2000	1° × 1°	Annual	Greenhouse gases Ozone precursors SO_2 and NH_3	www.mnp.nl/edgar/model/100_year_emissions Anthropogenic and biomass burning
RETRO	1960–2000	0.5° × 0.5°	Monthly	Ozone precursors SO_2, NH_3, BC, OC	retro.enes.org Anthropogenic and biomass burning
POET	1990–2000	1° × 1°	Annual	Ozone precursors	geiacenter.org Anthropogenic, biomass burning and natural
GAINS	1990–2030	1° × 1°	Annual	Greenhouse gases Ozone precursors SO_2, NH_3, BC, OC	gains.iiasa.ac.at Anthropogenic
J&L	1860–2000	1° × 1°	Annual	BC and OC	(Junker and Liousse, 2008) Anthropogenic
Bond	1850–2000	1° × 1°	Annual	BC and OC	(Bond et al., 2004) Anthropogenic
Regional inventories					
EMEP	1980–2020	50 × 50 km	Annual	NO_x, CO, NMVOCs, SO_2, NH_3, PM	http://www.emep-emissions.at/emission-data-webdab Anthropogenic
REAS	1980–2020	1° × 1°	Annual	Greenhouse gases Ozone precursors SO_2, NH_3, BC, OC	http://www.jamstec.go.jp/frcgc/research/p3/reas_c.html Anthropogenic
EPA NEI	1999, 2002, 2005	4 km × 4 km	Annual, average hourly	Ozone precursors SO_2, NH_3, PM	http://www.epa.gov/ttn/chief/eiinformation.html Anthropogenic– gridded air quality inventory
EPA AQ and Emission Trend Reports	1970–2006	National	Annual	Ozone precursors SO_2, NH_3, PM	http://www.epa.gov/ttn/chief/trends Anthropogenic – national air quality emissions and trends by sector
EPA GHGs	1990–2006	National	Annual	Greenhouse gases	http://epa.gov/climatechange/emissions/index.html Anthropogenic – national greenhouse gas emissions and trends by sector

organic carbon (BC and OC) at the regional and global scales (see Table 1).

Most inventories have been developed using a formula similar to equation (1):

$$\text{Emission} = A \times \text{EF} \times P_{i,i=1,\ldots} \qquad (1)$$

where A is the activity rate of a source (for example kg of coal burned in a power plant), EF is the uncontrolled emission factor (amount of emission per unit activity) by fuel, sector, technology and compound, and the P_i factors represent parameters that apply to specific abatement options, source types and species. Inventories have been developed for different purposes; they cover different areas, have different spatial resolution and consider different species over different time periods. The main characteristics of a few global and regional inventories widely used in scientific work are summarized in Table 1. Other emissions inventories are available at higher horizontal resolution (typically 1–10 km) for different parts of the world. For the European area, several of these inventories are discussed in (Cuvelier et al., 2007) as part of the City Delta project.

2.2.2. Primary emissions of anthropogenic particulate matter

While total particulate matter (PM) emissions have been reported for years, speciated PM emissions estimates have only been published recently, for some regions and/or sectors. These inventories have either considered particulate matter of different size, PM_{10} or $PM_{2.5}$ (particles with a diameter smaller than 10 µm and 2.5 µm, respectively), or black (BC) and organic (OC) carbon. Policies aiming at the reduction of health impacts target fine PM; new policies now consider the climatic impact of carbonaceous aerosols (BC and OC). Natural emissions of particulate matter, for example, sea-spray are dealt with in Fowler et al. (2009). A number of inventories now include these species, as indicated in Table 1.

Size speciated PM inventories have been compiled in the US ($PM_{2.5}$) and more recently a requirement of reporting PM_{10} and $PM_{2.5}$ emissions in Europe has been introduced following policies targeting a reduction of health impacts owing to PM. Beyond that a number of regional inventories are available and were tested against measurements and modelling efforts, e.g. (Cuvelier et al., 2007). However, the issue of verification of speciated inventories remains open as only a limited number of ambient measurements of $PM_{2.5}$, BC, and OC exist (Simpson et al., 2007a; Tsyro et al., 2007).

Large uncertainties remain in past and current global inventories of anthropogenic emissions of BC and OC. For the year 2000, available inventories of BC give rather similar values, with a total emission of 4.4 Tg C yr^{-1}, 4.7 Tg C yr^{-1} and 4.8 Tg C yr^{-1} in the (Bond et al., 2004), (Ito and Penner, 2004) and (Junker and Liousse, 2008) inventories, respectively. However, as shown in Fig. 6, and discussed in the context of ice-core measurements in Fagerli et al. (2007), the evolution of the species over the past decades differ significantly between the different inventories, which is because of the use of different sectoral resolution, activity data and emission factors.

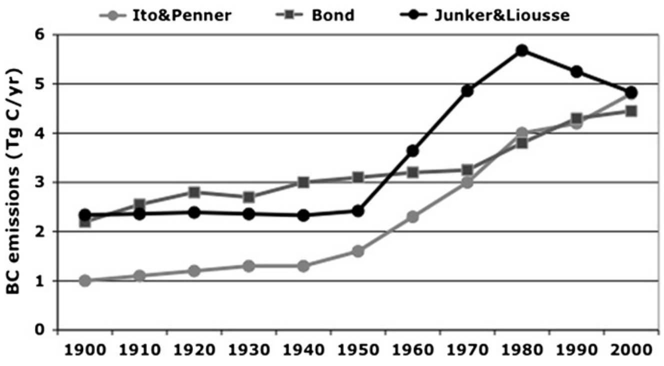


Fig. 6. Evolution of the global emission of black carbon from three different inventories.

2.2.3. Uncertainties in fossil fuel emissions

Statistical approaches to estimate uncertainties in emissions distributions and trends have been considered, for example in Frey and Zheng (2002). Two approaches are typically used: simple error propagation and Monte Carlo-type simulations. However, the main challenges in the estimation of uncertainties in emissions are related to the uncertainties in input data and in the development of methods for quantifying systematic errors. For most inventories, the random component of an uncertainty estimate will be small relative to the systematic component and uncertainties in inventories vary by region, source, pollutant and year (Klimont and Streets, 2007).

Within the recent development of emission inventories, several problems leading to difficulties in accurately quantifying anthropogenic surface emissions have been identified. Since most pollutants are produced from fossil fuel combustion, it is crucial to quantify the uncertainty in emissions from this activity. The main uncertainties of emissions from large-scale stationary combustion include the assessment of penetration and actual efficiency of abatement measures and availability of data on technological sectors. For small-scale stationary combustion, the largest uncertainties include biofuel emission factors (high variability in the emission characteristics of combustion devices, e.g. regional differences in stoves) and accounting for non-commercial biofuel use and non-registered fossil fuel use. For land transport, some countries require special attention, i.e. India and Brazil and Africa, where special vehicle types and fuel mixing lead to large uncertainties. In many developing countries, an assessment of the fraction of 'super-emitters' and their emission factors might prove critical. Furthermore, data on the numbers of unregistered vehicles (missing fuel statistics/mileage data) as well as the mixture of vehicle types and car maintenance levels are not readily available. Specific attention should be given to countries with fast-growing economies, where emissions are changing very rapidly.

The gridding of the emissions is still a challenge. Anthropogenic emissions are generally estimated at the country level, and are allocated to the grid cells within each country based on spatial surrogates, i.e. population, economic activity, location of power plants, road network and maritime traffic.

A survey of available data in most areas of the world concluded that, while for most sectors and regions fairly robust activity data are available, most non-OECD regions suffer from lack of, or poor local emission factors, especially for off-road transport, industrial processes and small-scale combustion. Only limited data exist on the technologies used and the penetration of abatement measures, with the exception of large combustion installations and road transport. The latter is also true for the OECD world, while in some regions (e.g. Latin America, Africa and India) even data for road transport are problematic.

In recent years, some new tools have become available to address the uncertainties in emission inventories, including direct (forward) and inverse modelling of air quality observations (from ground-based monitors, aircraft or satellites) and laboratory tests of combustion and similar processes. These new techniques may not only improve the accuracy of emission inventories; they also offer the possibility of providing the basis for more rapid updates of emissions than can presently be obtained using statistics-based methods. Examples of the quantification of global and regional budgets of chemical species are given in the companion paper (Isaksen et al., 2009) and for example, in Müller and Stavrakou (2005) and Konovalov et al. (2006).

2.2.4. *Trends in European emissions*

Large reductions have been observed in European emissions of air pollutants over the past 25 years (Konovalov et al., 2008; van Aardenne et al., 2001; Vestreng et al., 2007). Owing to early awareness of the effects of acidification and eutrophication, sulphur and nitrogen oxides were the first pollutants to be subject to European wide regulations by UN Protocols around 1990 (UNECE, 2004). These first two Protocols were later succeeded by other Protocols and several EU directives e.g. (Grennfelt and Hov, 2005). The 1999 Gothenburg Protocol set fixed emission ceilings for national emissions in 2010 of SO_x, NO_x, NMVOC and NH_3 to reduce the effects of air pollution.

During the period from 1990 to 2005, emissions of SO_x, NO_x, NH_3, NMVOC and CO have been substantially reduced over Europe. Changes in emissions have been evaluated from the European EMEP emissions, which are based on official national reports under the Convention on Long-range Air Pollution (CLRTAP). The emission data are available from http://www.emep-emissions.at/emission-data-webdab. These emissions are extensively reviewed and validated e.g. (Jonson et al., 2006; Konovalov et al., 2008; Vestreng et al., 2007). The uncertainty in the EMEP inventory has been shown to decrease with time and is below 25% for sulphur and NO_x after 1990 (Vestreng et al., 2007, 2009). For other pollutants like particulate matter, the uncertainty in individual national inventories has been estimated to be several hundred percent (Nielsen et al., 2008). Substantial differences in data quality exist between different regions and sectors.

Fig. 7 shows changes in the emissions over the EMEP area (continental Europe and neighbouring countries) during the 1990–2005 period based on the EMEP data. The largest relative reductions have been reported for SO_2 (66%), followed by CO (39%), NMVOC (38%), NO_x (32%) and NH_3 (23%).

Annual emissions of all pollutants have decreased continuously between 1990 and 2005, with some interannual variations. The 1990s were characterized by decreases on the order of 4–5% per year, and in the case of sulphur, 9–10%. After the year 2000, the trends have stabilized, with annual decreases of the order of 1–2%. The economic decline after the break-up of the Soviet Union is responsible for the reductions in the first half of the 1990s in Eastern Europe. The stabilization of the sulphur trends after the year 2000 is the result of abatement policies in many Western European countries, which reduced their emissions by more than 60–80% by 2005, through efficient measures like flue gas desulphurization and switching to different fuels. There is also a tendency for an increasing number of countries to report higher emissions of sulphur. Reductions owing to economic recession in Eastern Europe are a factor 1.5 higher than those in Western Europe because of the implementation of abatement measures (Vestreng et al., 2007). The European NO_x emission trend is also stabilising. Western European emissions continue to decrease, mainly owing to requirements for catalytic converters which were introduced in the 1990s by the European Commission Directive 70/220/EC. At the same time, NO_x emissions are increasing in the recovering Eastern European economies after the year 2000 owing to increased emissions from road transportation.

Reductions in emissions between 1990 and 2005 have been identified for all regions and emission sectors, with a few exceptions. The highest overall 1990 emissions and absolute reductions towards 2005 are obtained in the EU-18 (EU-15 plus Iceland, Norway and Switzerland), followed by RU-NIS (Russia and Newly Independent States) and the SEE (South-Eastern Europe), for all pollutants but ammonia, for which reductions have been largest in the RU-NIS region. There are large sectoral and some important regional differences in emission reduction patterns. Reductions are lowest in the SEE for all pollutants: for example, emissions of sulphur from power plants have been reduced in the SEE region by only 25% from 1990 to 2005, compared with 65–75% in other areas. It is interesting to note that NO_x emissions have been reduced substantially less than sulphur emissions in all regions. This change can be attributed to the source distribution of emissions, to the measures available for abatement in the largest sectors and to the actual reduction efficiency.

EMEP emissions of particulate matter ($PM_{2.5}$ and PM_{10}) are only available from the year 2000 onwards, and show a reduction of only 3% between 2000 and 2005 (Tarrasón, 2007). However, European emissions of PM declined sharply in the early 1990s, according to the GAINS model calculations (http://gains.iiasa.ac.at). $PM_{2.5}$ emissions declined by 52% between 1990 and 2005. This reduction is mainly due to a drop in Eastern German, Russian Federation and NIS emissions between 1990 and 1995. During the same period, European emissions of black and organic carbon increased owing to a fast-growing diesel car and truck population (Kupiainen and Klimont, 2007).

2.2.5. *Trends in US emissions*

This section describes temporal trends in emissions from U.S. electrical power-plant point sources and on-road vehicles as estimated in the U.S. Environmental Protection Agency (EPA) National Emission Inventories (NEIs). It also provides some evaluations of those trends through consideration of direct emission measurements or top-down tests based upon ambient concentration measurements. According to the U.S. EPA, on-road vehicles and

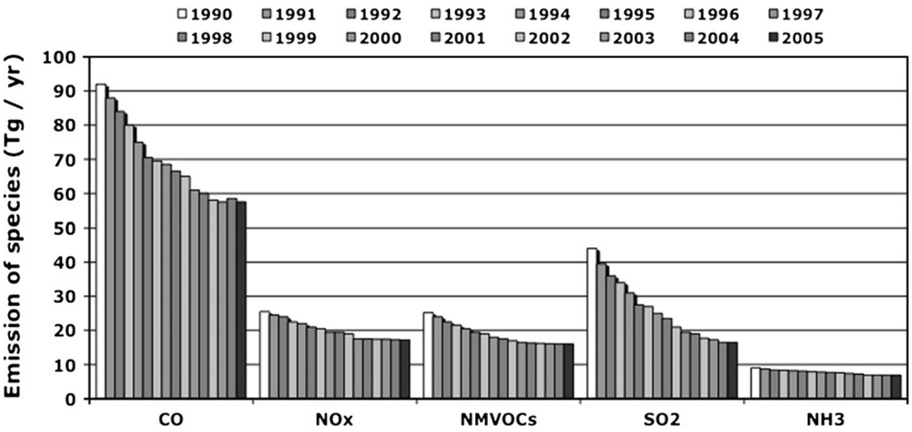


Fig. 7. Air pollutants emissions trends in the EMEP area for the 1990–2005 period, excluding international shipping (Units are Tg species $year^{-1}$).

power plants together were responsible for the majority of anthropogenic CO, NO_x, and SO_2 emitted in the U.S. over the past 25 years.

Power-plant emission inventories for the U.S. are believed to be accurate, and many detailed hourly emission data are available, because generally these emissions are measured by Continuous Emission Monitoring Systems (CEMS), which are required by the U.S. EPA Acid Rain Program. The U.S. EPA regularly reports estimated emissions and their trends over the previous decades, generally in annual National Air Quality and Emissions Trends Reports (http://www.epa.gov/ttn/chief/trends/index.html). Comparisons of a recent historical sample of these Trends Reports (EPA, 1995, 2000, 2003) with an earlier inventory developed for the National Acid Precipitation Assessment Program (Saeger et al., 1989) and the most recent emission Trends Tables ("1970–2006 Average Annual Emissions, All Criteria Pollutants", posted July 2007) are shown in Fig. 8a, for NO_x and SO_2 from fuel combustion in electrical utilities. It is clear here that there has been little variation in the emission estimates for any given year, with only the NO_x emissions in the 1995 Trends Report significantly different (as much as 19 percent higher) than the other estimates.

According to the inventories in Fig. 8a, over the last 26 years U.S. NO_x and SO_2 emissions from electrical power plants have decreased by factors of 2.0 and 1.8, respectively. The substantial reductions of power-plant SO_2 emissions during the 1990's and of power-plant NO_x emissions in the past decade are a direct result of pollutant-specific cap-and-trade control strategies mandated by the EPA's Acid Rain Program and NO_x Budget Trading Program. The power-plant emissions measured by CEMS have been checked against aircraft flux determinations based on ambient measurements in the downwind emission plumes, and the two sets of observations generally agree with one another to within the combined measurement uncertainties (Parrish, 2006a; Frost et al., 2006). A larger scale confirmation of the recent power-plant NO_x emission reductions is demonstrated by satellite observations over the Ohio River Valley, a region in the central U.S. with a high density of coal-fired power plants that dominate the NO_x emissions (Kim et al., 2006). Satellite NO_2 vertical columns over the Ohio River Valley declined by 40% between 1999 and 2005, a trend consistent with CEMS-reported declines in power plant NO_x emissions. The consistency of the CEMS-based inventory over the years and the correspondence of the CEMS data with aircraft flux and satellite determinations indicate that these inventories of U.S. power-plant emissions are accurate.

Making accurate estimates of on-road vehicle emissions is much more difficult than the analogous task for power plants. Bottom-up on-road emission models integrate the product of distance-based emission factors (e.g. grams of pollutant per km driven) for a diverse, constantly evolving vehicle fleet and highly variable activity factors. The different emission models that have been used over the years have yielded results that differ widely in some important respects.

Fig. 8b shows estimated on-road emissions of NO_x and CO from the five references discussed in the previous section plus one additional Trends Report (EPA, 1990) and compares those estimates to emissions inferred from ambient measurements (Parrish, 2006a,b).

For NO_x the inventories differ significantly in the temporal trends of the emissions. The most recent evaluation suggests decreasing NO_x emissions throughout the 26 year period, while the earlier calculations suggest increasing NO_x emissions through the decade of the 1990's. The emissions inferred from ambient data support the earlier trend estimates. All the emission models and the inferred emissions agree that the CO emissions have decreased continually by 3–5% yr^{-1}. However, there is significant disagreement regarding the magnitude of the CO emissions. The most

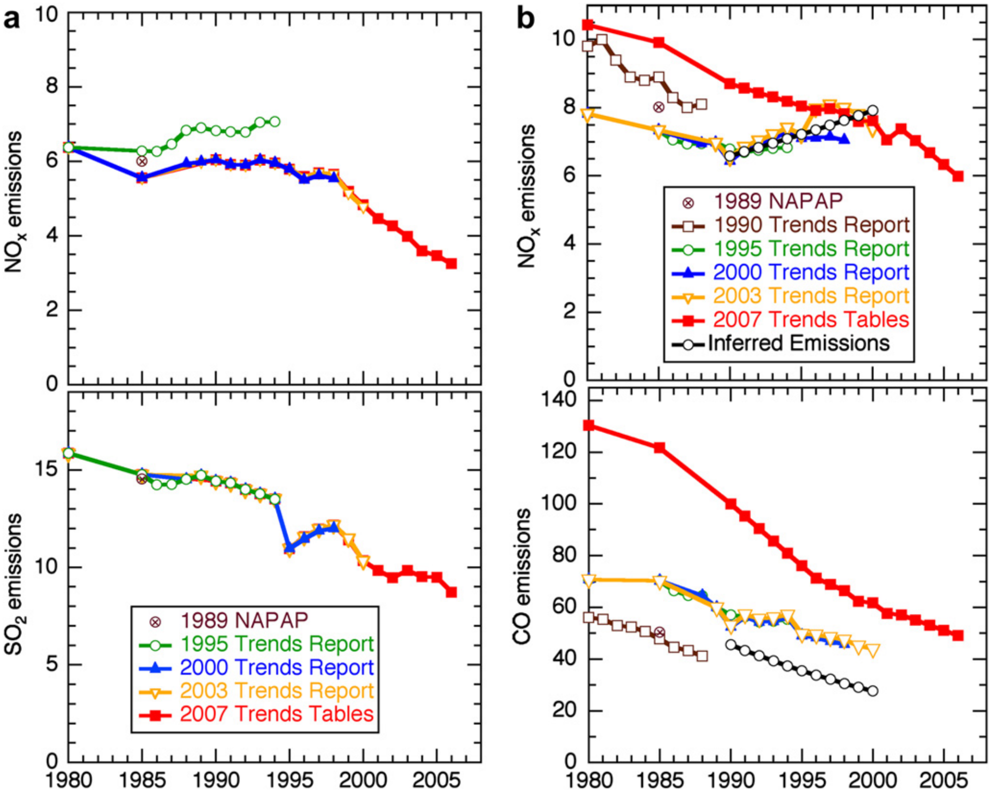


Fig. 8. Annual emissions from a) U.S. power plants and b) on-road vehicles from six U.S. inventories and inferred from ambient observations. Units are million metric tons/year. The dates indicate the year of publication of the inventory report.

recent inventory is approximately a factor of two larger than emissions inferred from ambient measurements.

Other investigators have inferred fuel-based emission factors (grams of pollutant per kg of gasoline or diesel burned) from roadside observations, which can be compared to the emission factors used in emission models. For example, multi-year monitoring programs in several U.S. cities suggest that the average CO and NO_x fuel-based emission factors for gasoline vehicles declined by an average of 7–9% yr^{-1} since the mid-1990's (Bishop and Stedman, 2008). These declines are thought to be the result of continual improvements to the emission control systems on U.S. gasoline-powered vehicles. In contrast, NO_x emission factors inferred from roadside observations of diesel-powered vehicles, which produce relatively little CO, appear to have decreased only slightly over the past decade (Bishop and Stedman, 2008).

Kim et al (2006) also examined the northeastern U.S. urban corridor stretching from Washington, DC, in the south to Boston in the north. This region, dominated by mobile source NO_x emissions, saw only a slight decrease in satellite-retrieved NO_2 vertical columns between 1997 and 2005. This finding suggests that overall mobile source NO_x emissions have not changed much over this time period. In addition to year-to-year variability of on-road emissions, clear differences between weekday and weekend U.S. urban NO_x emissions resulting primarily from motor vehicle use patterns have been documented by *in-situ* (Harley et al., 2005) and satellite methods (Beirle et al., 2003).

The emerging lesson from these evaluations is that without the support of direct measurements (as CEMS provides for the power plant sources), it is not possible to develop bottom-up inventories that are "accurate" enough for some of the scientific uses to which they are applied. However, bottom-up inventories are indispensable components of photochemical models, and the foundation upon which our knowledge of pollutants in the atmosphere is based. A continuing process of inventory development is clearly required: testing of emission inventories through top-down evaluations; inventory improvement; evaluation of the top-down tests; and then repeating this process until the top-down tests of the inventories indicate sufficient accuracy for the intended use of the inventory.

2.2.6. Trends in Asian emissions

Anthropogenic emissions in Asia are larger than those in Europe and North America today, and they will continue to increase (Akimoto, 2003). As shown by the analysis of satellite observations, NO_2 concentrations in China have dramatically increased over the past few years (Richter et al., 2005). A few emission inventories providing anthropogenic emissions for Asia have been developed in the previous years, by (Streets et al., 2003, 2006) for the year 2000, (Cofala et al., 2007; Ohara et al., 2007) (REAS inventory).

When constructing the REAS inventory, Akimoto et al. (Akimoto et al., 2006) used data reflecting coal consumption in China during the 1996–2000 period. A detailed study of these data showed a systematic underestimation of the coal consumption during these specific years; it should be noted that these statistics were recently updated (China Energy Statistical Yearbook, 2006). The emissions provided by the REAS inventory use the updated statistics. Emissions for Asia are provided by this inventory since 1980 and future emissions until year 2020 have been evaluated.

Fig. 9 shows the evolution of CO, NO_x and SO_2 from 1980 to 2003. The total emissions in Asia were 306 Tg CO, 27.3 Tg NO_x and 42.8 Tg SO_2 in 2000. An update of the emissions of CO for China has been proposed by Streets et al. (Streets et al., 2006): a total of 141.3 Tg CO yr^{-1} was estimated for the anthropogenic emissions, which is comparable to the value of 137 Tg CO yr^{-1} in the REAS inventory. In the REAS inventory, the main contributor to the emissions of NO_x is transportation (34%), followed by power plants (22%) and industrial activities (14%). For CO, the main contributions are domestic fuel use (48%), followed by industrial activities and transportation. Most SO_2 emissions are due to coal combustion (70%); in China only, 84% of the SO_2 emissions are due to coal combustion.

Between 1990 and 2003, Asian emissions of BC and OC increased by a factor of 1.3, CO by a factor 1.6, NMVOCs by a factor 2.1, SO_2 by a factor 2.2, and NO_x by a factor 2.8. The larger values for SO_2 and NO_x result from the fact that the major sources of these species are the combustion of fossil fuel. For carbonaceous particles (BC and OC), the major sources are biofuel combustion, which showed smaller increases. As indicated in Fig. 9, the increase in NO_x emissions has been large since 1980, while total Asian emissions increased by a factor 2.8, NO_x emissions in Asia increased by a factor 3.8, with the highest growth after 2000. Such large increases are compatible with the satellite observations reported in (Richter et al., 2005).

2.2.7. Comparison of European, North American and global emission trends

The European emissions of sulphur and NO_x have considerably reduced between 1980 to 1990 by 73% and 32%. These reductions are because of a decline in the energy use related to the socio-economic situation in different parts of Europe owing to fuel switches and to the implementation of technological measures (Richter et al., 2005; Vestreng et al., 2007, 2009). North American emissions also declined from 1980 (sulphur) and 1990 (NO_x), but the reductions obtained are smaller (46% and 26% for sulphur and NO_x respectively). In other regions of the world, control measures and environmental policies are not state of the art, and the global emission trends were only reduced by about 20% and 1% for sulphur and NO_x by year 2000 (Cofala et al., 2007; Stern, 2005). Global emissions as given by (Cofala et al., 2007) for the 1990–2000 decade are either slightly increasing, as for CO (from 523 to 542 Tg CO yr^{-1}), or declining as for NO_2 (from 84 to 83 Tg NO_2 yr^{-1}) and SO_2 (from 120 to 96 Tg SO_2 yr^{-1}).

Fig. 10 shows the changes in the emissions of CO, NO_x and SO_2 for the 1990–2000 period for Europe (EU-27), the USA and East Asia (including China, Japan, Korea, Mongolia and Taiwan). For all species, emissions are decreasing in Europe and in the USA, but the rate of change is smaller in the USA, particularly for nitrogen oxides emissions. The European and North American reductions are compensated at the global scale by increased emissions in Asia, particularly over East Asia (Cofala et al., 2007; Ohara et al., 2007). The changes in the emissions are consistent with the observations of NO_2 reported in Richter et al., (2005). Fig. 11 shows large increases in the observed tropospheric column of NO_2 over China, while decreases or constant values are observed in Europe and in the USA.

2.2.8. VOC speciation

Numerous organic carbon compounds are volatile enough to be present in the atmosphere. Each has its own intrinsic chemical behaviour and exhibits a different atmospheric reactivity (Carter and Atkinson, 1989). Add to this the myriad of individual sources emitting their own particular range of VOCs and you have a potentially complex and variable atmospheric cocktail that requires sophisticated sampling and analytical techniques for speciation and quantification of each component. All this must be taken into account to understand the relation of the emissions to the oxidative capacity of the atmosphere and air quality.

Speciated measurements of ambient anthropogenic VOCs, typically employing gas chromatography, were initiated several decades ago (Laj et al., 2009). These have successfully been employed to inform public policy initiatives resulting in VOC emission control strategies, such as the addition of catalytic converters to vehicle exhaust systems and the replacement of

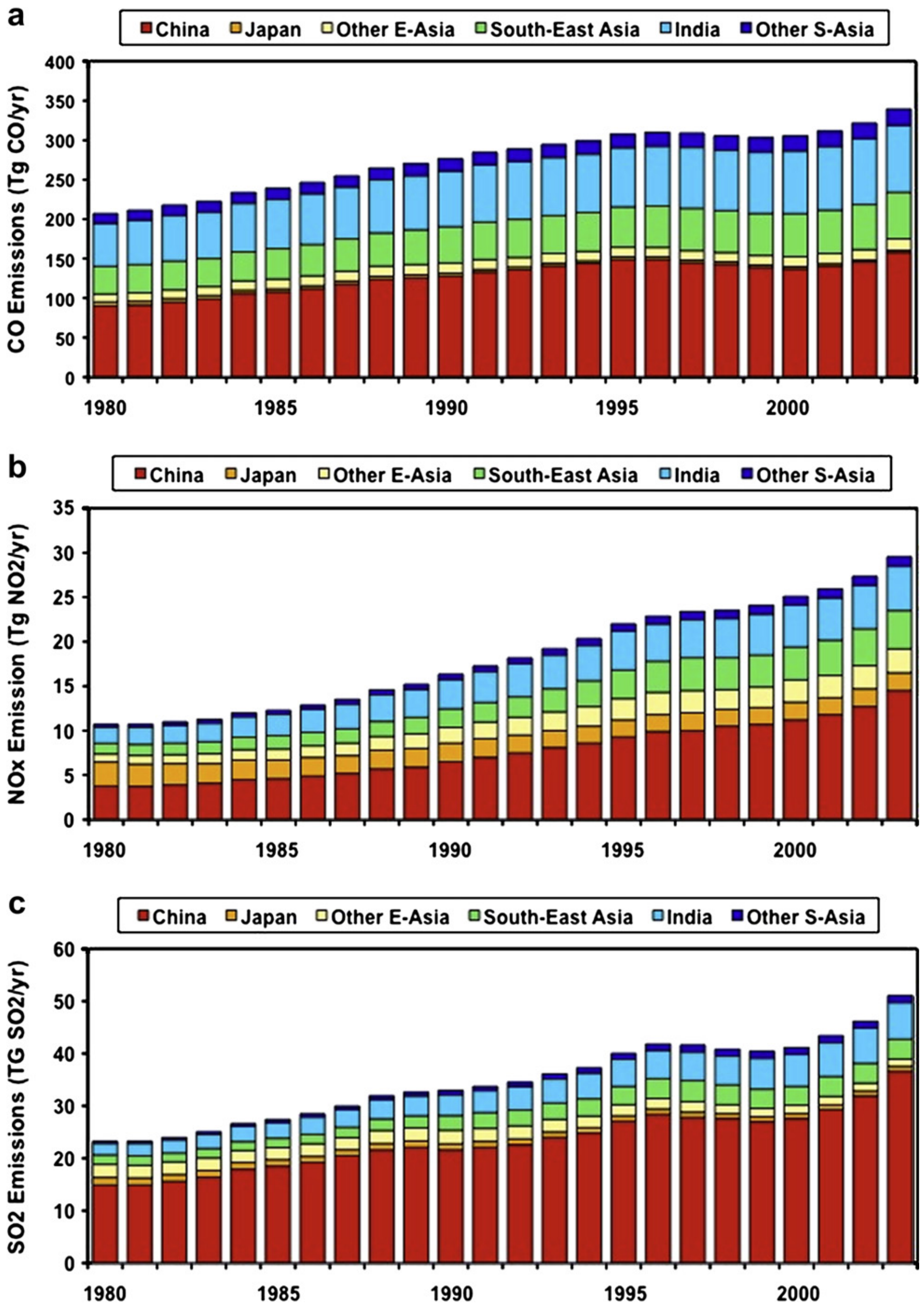


Fig. 9. Temporal evolution of emissions of CO, NO_x and SO_2 from different regions in Asia between 1980 and 2003.

organic solvents in industrial and household applications, which have caused major reductions in these large emissions. However, such reductions in turn mean that accurate speciated inventories of previously relatively minor sources assume much more important roles in the understanding and incremental improvement of local air quality. In addition, changes in manufacturing processes, newly evolving industries, vehicle technologies, and metropolitan infrastructure are occurring at an increasingly rapid pace, emphasizing the importance of inventories that reflect current conditions (Derwent et al., 2007; Miller et al., 2006).

Correct attribution of VOCs between the various emission types is crucial in terms of making regulation. However, emissions inventories for anthropogenic VOCs are associated with major uncertainties. Such inventories are time-consuming to prepare, and emissions speciation is constantly changing. Sector distributions also vary greatly, for example industrial versus mobile sources, as well as the seasonal variations of emissions.

Urban measurements of an ever-wider range of speciated VOCs are being published, for example (Baker et al., 2008) (28 US cities) and (Hoshi et al., 2008) (Tokyo) (Fig. 12). However, cities in poorly-studied regions such as Africa, are likely to have very different emission “ecotypes”, based on typical fuel use and type will produce very different emission signatures compared to the highly developed US and Japanese cities of these recent studies.

Ambient VOC measurements are crucial for the assessment of VOC speciation. For example, Parrish (2006b) found that

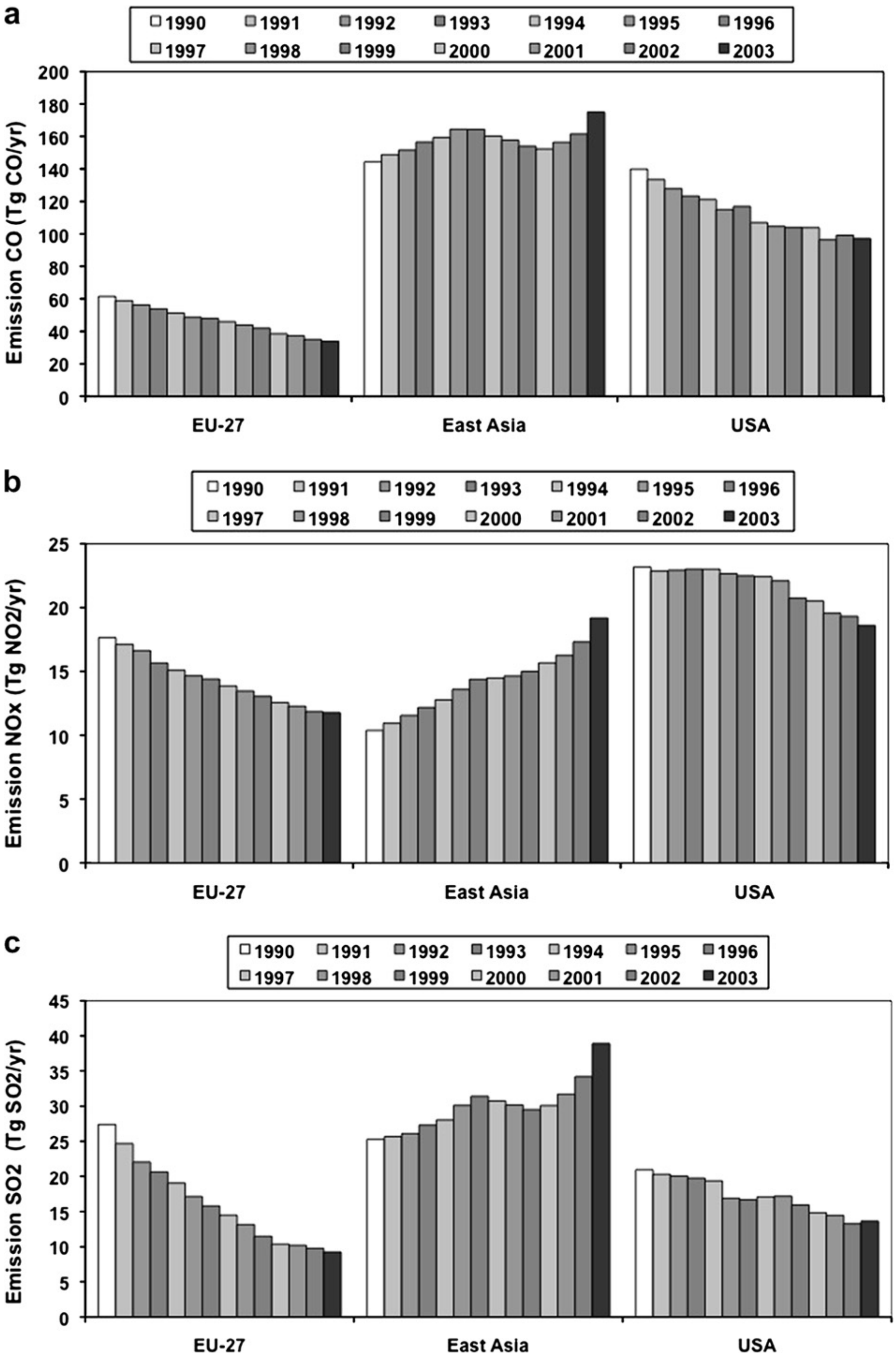


Fig. 10. Evolution of the emissions of CO (top), NO_x (mid) and SO_2 (bottom), for the EU-27 countries, the USA and East Asia for the 1990–2000 period.

a comparison between US national emission inventory and measured ambient ratios of benzene to acetylene gave quite poor results, with inventory ratios for total emissions a factor of 3–4 higher than the ambient values.

Source apportionment techniques are also being applied to better understand the contribution of the principal VOC emission sources to ambient concentrations. Chemical mass balance receptor models e.g. (Schauer et al., 2002; Watson et al., 2001), fit ambient data to specific source profiles. However, this type of model requires that up-to-date speciated profiles of all potentially contributing sources be assumed before the model can be applied to the measurement database. To address this draw-back, tools such as positive matrix factorization (PMF) have been developed that require only speciated ambient data for source identification and apportioning e.g. (Brown et al., 2007a; Xie and Berkowitz, 2006). Notwithstanding these developments, there remains a substantial gap in global and regional observed VOC speciation and emission inventories for air quality applications.

2.3. Biomass burning

2.3.1. Fire products: active fires, burned areas, fire radiative energy

Open burning of anthropogenic and biogenic organic material is a source of reactive and toxic compounds (VOCs, PAHs, soot)

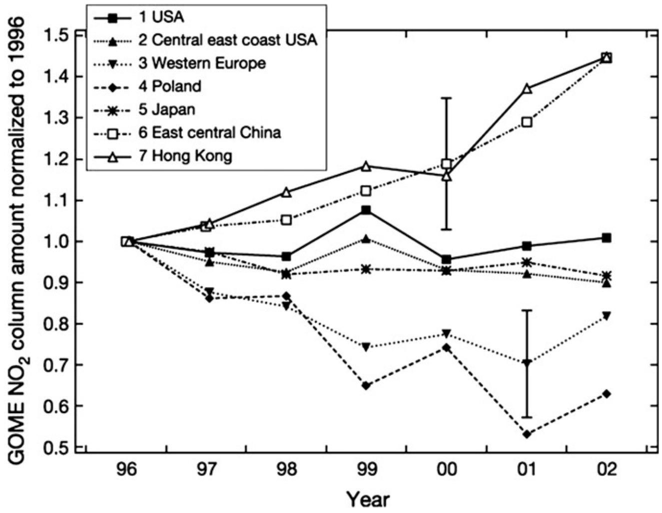


Fig. 11. The temporal evolution of tropospheric NO_2 columns from GOME for selected areas. The mean annual NO_2 column amount normalized to that in 1996 for the geographical regions USA, Central East Coast USA, Western Europe, Poland, Japan, East Central China, and Hong Kong (see (Richter et al., 2005) for details). The error bars represent the estimated uncertainty (s.d.) for an individual year, the values over China being larger as a result of the poorer knowledge and therefore larger uncertainty of the aerosol loading and its change (Richter et al., 2005).

(Lemieux et al., 2004). In particular biomass burning is a significant contributor to the emission load of the atmosphere, resulting from both natural and anthropogenic fires. Calculating emissions from savannah, forest and agricultural fires requires knowledge of the appropriate emission factors as well as the spatial and temporal distribution of burnt biomass.

The first attempts to quantify burnt biomass on a regional or global scale were based on land use statistics of the FAO and general assumptions about the percentage of the surface burnt per year (Hao and Liu, 1994; Liousse et al., 1996). The European Joint Research Center (JRC) in Ispra, Italy, published the first results with higher spatial and temporal resolution using satellite observations (Cooke and Wilson, 1996). In this work information about active fires was derived from thermal infrared data from the Advanced Very High Resolution Radiometers (AVHRR) instrument onboard the US National Oceanic and Atmospheric Administration (NOAA) satellites. The International Geosphere-Biosphere Programme's Data and Information System (IGBP-DIS) and later the Global Observation of Forest and Land Cover Dynamics (GOFC-GOLD) project took part in the coordination of efforts for better quantification of biomass burning emissions. This led to a second publication making use of AVHRR data by Stroppiana et al., (2000).

Quantitative information on the magnitude and distribution of global biomass burning can be derived from Earth-orbiting satellites. The primary sources of global data derived from satellite imagery are the active fire distributions and the detection of burnt areas. Active fire detection enables documentation of global fire events with their location, extent and seasonality. These data form

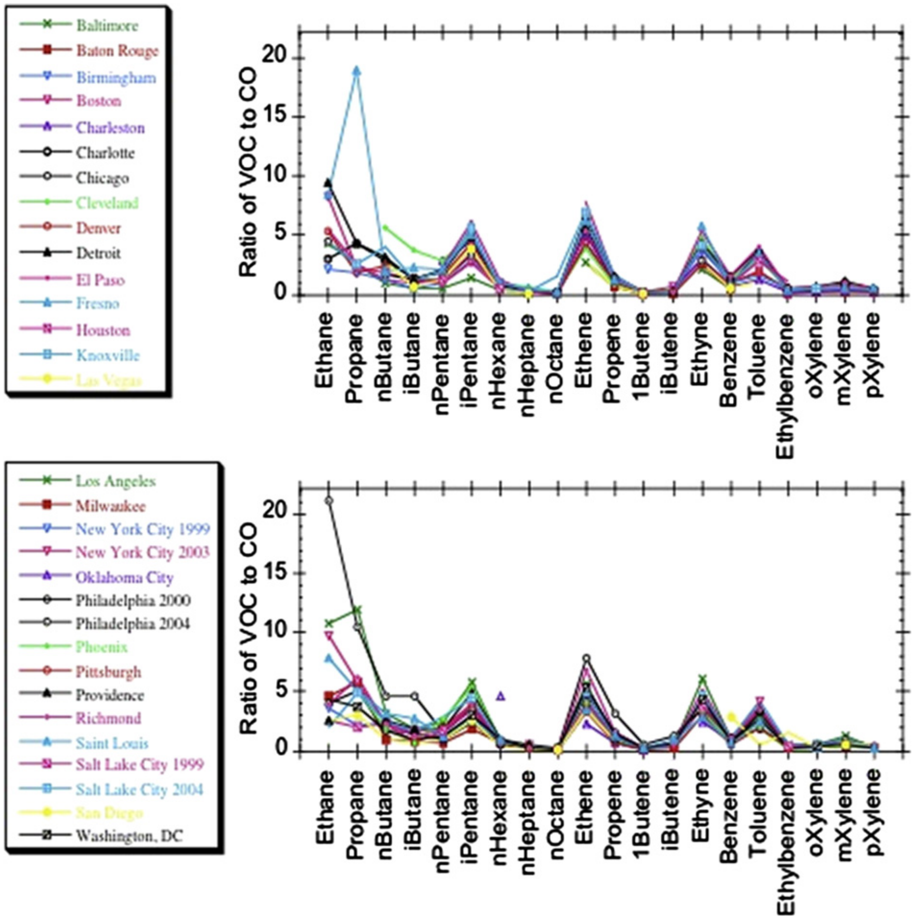


Fig. 12. Ratio of VOCs vs CO in 28 US Cities Relationships where $R^2 > 0.30$ (most have $R^2 > 0.60$). Modified from (Baker et al., 2008).

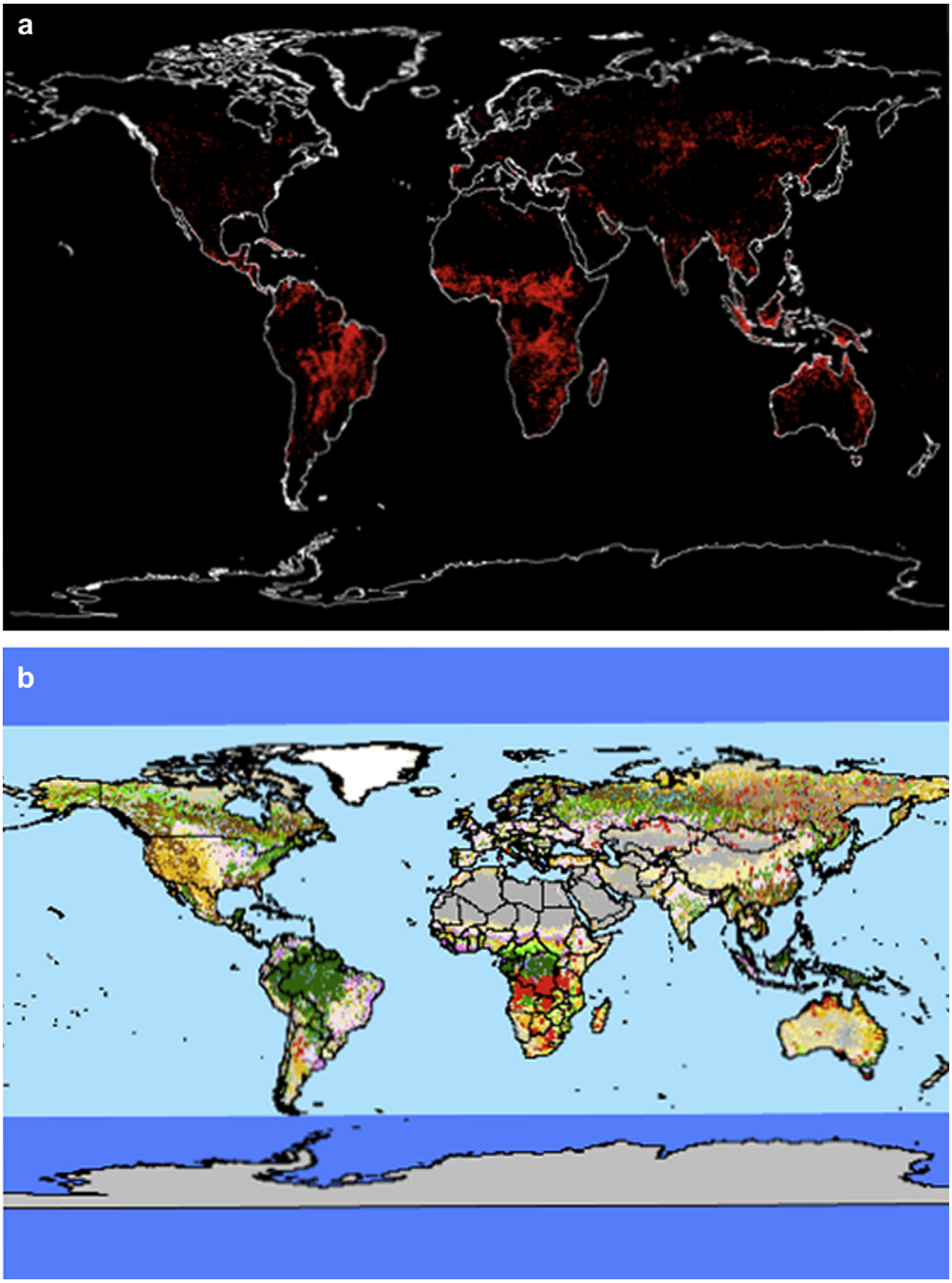


Fig. 13. a) Example of the spatial distribution of nighttime active fires given by the ATSR satellite sensor; b) example of burned area provided by the GBA-2000 product (Tansey et al., 2008).

a crucial input to identify fire regimes and to develop techniques to support fire management programmes. Technically, there are currently dozens of algorithms (Giglio et al., 2003) that use different satellite sensors to detect and monitor fire activity around the world. Fire detection may be performed using single-channel threshold or multichannel threshold algorithms and spatial contextual algorithms. The basis of these approaches is the strong emission of mid-infrared and thermal radiation from fires (Dozier, 1981; Matson and Dozier, 1981). The algorithms examine each pixel of the satellite swath, and ultimately assign the pixel to each one of the following classes: missing data, cloud, water, non-fire, fire, or unknown. Fig. 13a shows an example of the nighttime spatial distribution of active fires given by the European Space Agency's (ESA) Along-Track Scanning Radiometer (ATSR) satellite sensor.

The area and type of vegetation burned on a monthly or annual basis is one of the parameters needed in the calculation of burned biomass, gas and aerosol emissions. A series of inventories of burned area have been produced using satellite data such as AVHRR, SPOT-VGT and MODIS. The algorithms are typically composed of a set of thresholds applied to each pixel value of the satellite spectral channels, two spectral indices and their temporal difference. The threshold values are derived using a supervised classification methodology. For example, burned area can be assessed from reflectance differences between the visible and the near-infrared channels (Fraser et al., 2000) or from indices derived from the near-infrared and mid-infrared spectral domain (Barbosa et al., 1999). The SWIR band, centred on 1.65 μm, has also been proven to be useful for mapping burnt areas. Finally, different algorithms are used depending on whether the land cover is forested or not. Fig. 13b shows an example of burnt area distribution from the GBA2000 product (Global Burned Area 2000, (Tansey et al., 2008)).

Liousse et al. (2004) and Michel et al. (2005) have suggested that a combination of both burnt area and active fire information derived from satellites would improve the determination of biomass burning emissions. This approach has been adopted by Hoelzemann et al (Hoelzemann et al., 2004), who used ATSR nighttime fire counts to complement data in areas where burnt area information was lacking. van der Werf et al. (2006) have combined MODIS and ATSR products and Mieville et al. (submitted for publication) have combined burned areas from the GBA product with ATSR active fires. While progress has been achieved by individual groups in using the new satellite-based techniques for estimating biomass burning emissions, there are substantial differences in the results obtained and the methods used to derive burnt biomass maps.

Determination of the emitted radiant energy released during biomass combustion episodes (the so-called fire radiative energy, FRE) has been suggested as a new tool for determining variations in biomass combustion rates and the rate of production of atmospheric pollutants. An example is given in Ichoku and Kaufman (2005) using the MODIS sensor.

2.3.2. *Use of fire products to calculate biomass burning emissions*

Over the last three decades, fire emissions estimates have developed from early inventories based on average fire return times and biomass estimates to detailed studies based on satellite data and sophisticated modelling predicting emissions with high spatial and temporal resolution. The increased complexity has been fostered by the availability of new satellite data, as noted above, as well as by the demand from the atmospheric community to get a better handle on fire emissions, which are a major source of atmospheric trace gases and aerosols. Fire emissions, however, are still a highly uncertain component of the global carbon cycle, and estimates for the globe vary by over a factor of 2. The main reason behind this is that all of the parameters necessary for estimating fire emissions show large variability in time and space including burned area, fuel load, the fraction of fuel that is actually combusted, and the partitioning of combusted fuel into different trace gases and aerosols based on emission factors.

The first attempts to estimate how much biomass is combusted neglected the spatial and temporal variability and constructed distributions of biomes that were thought to have a similar fire regime. For each of these biomes, average fire return times, fuel loads and emission factors were estimated to calculate emissions (e.g. Seiler and Crutzen, 1980). Hao and Liu (1994) added seasonality to mean annual estimates based on climate data.

Nowadays, virtually all biomass burning estimates are based on satellite data, which are used to retrieve burned area as well as biomass loads (Hoelzemann et al., 2004; Ito and Penner, 2004; Schultz et al., 2008; van der Werf et al., 2003; van der Werf et al., 2006). Multi-year burned area products, however, have only recently emerged, so emissions estimates were either based on the year 2000 or used fire hot spots. These fire hot spots are available for multiple years but do not provide direct information on the fraction of the grid cell burned. New studies are emerging based on new multi-year burned area assessments (Roy et al., 2008; Tansey et al., 2008). Large differences in the global emissions of chemical compounds exist when using different satellite products. An example is shown in Fig. 14, built using the first results of the ongoing ACCENT BBSO intercomparison exercise (Liousse et al., 2008) demonstrating the monthly average emissions of CO for 2003 using a burned area product (JRC), an active fire product (MODIS), and a mixed active fire (ATSR)/burned area product (GBA2000: (Grégoire et al., 2003)).

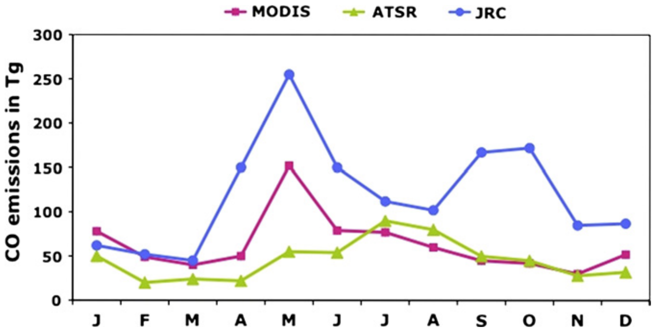


Fig. 14. Total CO emitted as a result of biomass burning in 2003 using 3 different satellite products (from Liousse et al., 2008).

Conversion of burned area to emissions nowadays mostly relies on biogeochemical models to estimate fuel loads and the fraction combusted (combustion completeness). van der Werf et al (2003) implemented a fire module in the CASA model, Hoelzemann et al. (2004) based their biomass loads on the LPJ model, while Ito and Penner (2004) developed a new fuel load model based on satellite data. The latter method was also used in a number of regional assessments based on much higher spatial resolution than the typical 1° global approach (e.g. Hély et al., 2003; Michel et al., 2005). Regional assessments have the obvious advantage of higher spatial resolution, which may be especially important especially in the savannah-forest interface, where fuel loads vary by over 2 orders of magnitude.

Initial global estimates of biomass carbon combusted from the above studies were 2–4 Pg C year^{-1}, mostly as CO_2 but also as CO, CH_4, numerous other trace gases, and aerosols. To put this number in perspective, global fossil fuel emissions in 2006 were about 8 Pg C year^{-1}. The comparison of CO_2 emissions from fires and from fossil fuels is not that meaningful, however, since a large fraction of the CO_2 emitted by fires will be taken up when the vegetation regrows. Only deforestation fires add to the build-up of CO_2 in the atmosphere. All fires, however, are a net source of CH_4, although the contribution of fires to the total burden is relatively minor. The most recent biomass burning total carbon emissions estimates are near the lower end of the initial estimate. Hoelzemann et al. (2004) estimated 1.7 Pg C year^{-1} for the year 2000 while Ito and Penner (2004) estimated 1.4 Pg C year^{-1} for the same year. Using over a decade worth of data van der Werf et al., (2006) estimates emissions ranging from 3.2 Pg C year^{-1} for 1998 to 2.0 Pg C year^{-1} for 2000, highlighting the strong interannual variability in fire emissions, mostly in tropical forest areas and the boreal region. The variability in carbon emission estimates between different studies is also reflected in trace gas and aerosol emissions, because most studies have used average emission factors based on the literature review by Andreae and Merlet (2001).

In the future, there may be a trade-off between increasing the spatial resolution and the level of complexity in the modelling of fuel loads and other parameters. New burned area datasets estimate burned area at the global scale at a 500 m resolution, while global biogeochemical models typically run at a much coarser resolution. In regions with high spatial variability in fuel loads, such as deforested regions, relatively simple approaches to estimating fuel loads in combination with high-resolution burned area data may give more realistic emissions estimates than sophisticated modelling at coarser resolution that make use of aggregated burned area. On the other hand, the inclusion of fire modules in existing or newly developed models allows for a more realistic representation of the moisture conditions of fuels, which may add seasonality to combustion completeness and emission factors. The inclusion of age classes or various vegetation types within the coarse model grid cells in combination with parameterizations based on higher resolution burned area and land cover information may be the most feasible way to move forward.

Fire emissions estimates will remain uncertain during the next few years owing to uncertainties in input parameters, even though burned area assessments are improving. One approach that estimates emissions directly from satellite data based on the fire radiative power measured by sensors which have been shown to be directly related to biomass burned (Wooster, 2002). This has a major advantage over the previous method using burned area and fuel load approach, as only one parameter is necessary to estimate emissions. Another emerging approach to lowering uncertainties is to compare emissions estimates with atmospheric measurements of, for example, aerosols or carbon monoxide (CO), using inverse modelling techniques (e.g. Arellano et al., 2004).

2.4. *Vertical profiles of emissions*

Determining the correct distribution of vertical profiles of emissions is important as the transport, chemical reactions and deposition (and thus the lifetime) of trace gases and aerosols are altitude dependent. Radiative impacts are also very sensitive to the vertical distribution of atmospheric species. Modelling regional and hemispheric air quality requires emission data sets with high spatial and temporal resolution. Uncertainties in emissions related to horizontal gridding have been briefly discussed in Section 2.2.3.

For anthropogenic emissions, the effective height levels of emissions from larger point sources depend on the stack heights, the type of fuel burned, the emitted heat flux, the wind speed at the top of the stack, and atmospheric stability. The emissions for other types of sources are generally assumed to be at ground level, including those from mobile sources, small point sources (small production plants, gasoline stations, and waste treatment sites), and area sources, like solvent use and agricultural activities. Large power plants are considered to have an effective emission height level generally higher than 250 m, and non-industrial combustion plants and combustion plants in the manufacturing industry have an effective height level between the ground level and 150 m. For example, the emission heights used in the EMEP model are given in Table 2.

In biomass burning, the heating of the surface and the initial buoyancy of the resulting plume generate strong updrafts above the fires e.g. (Freitas et al., 2006; Trentmann et al., 2006). Because of turbulence and mixing, the fire products are not entirely injected at this maximum height, but rather are distributed unevenly between the surface and the top height. The updraft induced by a fire can potentially lead to a rapid transport of tracers in the free troposphere and can have significant implications for the long-range transport of trace gases and aerosols (see also Section 3.3.9).

Recent spaceborne monitoring of aerosol vertical profiles from the Cloud Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) mission tends to show that the fire products remain within the planetary boundary layer (PBL) above some of the main tropical fire regions (Labonne et al., 2007). In the case of boreal forest fires, several studies suggest that fire products can be injected at high altitudes above the PBL. Lavoué et al. (2000) suggested injection heights of 2300 m for Russian fires and up to 7600 m for Canadian fires. Kahn et al. (2008) estimates the occurrence of plumes reaching the free troposphere in the range 5–18% during the 2004 fire season in the Alaska-Yukon region. In addition, recent observations of intense Canadian forest fires indicated that smoke can penetrate the stratosphere when ambient meteorological conditions are favourable (Damoah et al., 2006; Fromm et al., 2005). However, there are currently few observations of the frequency of such extreme events.

In most chemistry-transport models (CTMs), the fire emissions are distributed homogeneously within the PBL. In the case of boreal vegetation fires, restricting the emissions to within the PBL can lead the CTMs to significantly underestimate the top height reached by the fire products and therefore the resulting long-range transport of smoke plumes. Modelling studies have investigated this issue (Generoso et al., 2007; Leung et al., 2007; Turquety et al., 2007) and agree that fire products should be injected above the PBL in the case of boreal vegetation fires. In an analysis of the 2004 North American fires, Turquety et al., (2007) distributed part of the emissions in the upper troposphere (30% between 400 and 200 hPa), and for the 2003 Russian fires, Generoso et al., (2007) showed a good agreement between simulations and satellite observations when fire products were injected between the surface and about 4.5 km, In the case of the 1998 forest fires in Russia and North America, Leung et al., (2007) concluded that the model best matches both surface and elevated observations when at least 50% of the emissions were injected above the PBL. Kasischke et al., (2005) demonstrated that there is a larger occurrence of crown fires in the late fire season owing to differences in temperature, relative humidity, precipitation and fuel moisture content conditions relative to earlier in the season.

Table 2
Vertical distribution of anthropogenic emissions: percentage of each sector allocated to the vertical layers of the EMEP model (http://www.emep.int/OpenSource).

Source sector	Height of emission layer (m)					
	0–92	92–184	184–324	324–522	522–781	781–1106
1.Combustion in energy and transformation industries	0	0	8	46	29	17
2. Non-industrial combustion plants	50	50	0	0	0	0
3. Combustion in manufacturing industry	0	4	19	41	30	6
4. Production processes	90	10	0	0	0	0
5. Extraction of fossil fuel	90	10	0	0	0	0
6. Solvents	100	0	0	0	0	0
7. Road transport	100	0	0	0	0	0
8. Other mobile sources and machinery	100	0	0	0	0	0
9. Waste treatment and disposal	10	15	40	30	0	0
10. Agriculture	100	0	0	0	0	0

The distribution of the injection altitudes is still not well known for biomass fires. One of the main difficulties lies in the representation of the sporadic character of the vertical distribution of plumes induced by fires. A new challenge is therefore to account for this extremely high variability in models. Recently Freitas et al., (2006) and Hodzic et al., (2007) provided new parameterizations to account for a plume rise depending on the plume buoyancy and the thermodynamics of the surrounding environment. Trentmann et al. (2006) described the smoke plume from a large boreal forest fire rising to the stratosphere using a model that was initially designed for the study of explosive volcanic plumes. Improvements in terms of modelling are expected from new satellite-derived products such as fire radiative energy e.g. (Ichoku and Kaufman, 2005), fire measurements (Mazzoni et al., 2007), the continuous monitoring of aerosol vertical profiles by the CALIPSO mission (Labonne et al., 2007), or a combination of several of these products e.g. (Kahn et al., 2008).

2.5. Availability of emission datasets

An emission data portal has been developed within the ACCENT European project and the GEIA (Global Emissions Inventory Activity) project. The goal of the GEIA/ACCENT emissions data portal is to facilitate the access, use and comparison of emission data. It provides surface emissions data (total and gridded data) for anthropogenic, biomass burning, biogenic, and oceanic emissions. The compounds considered in the data portal are ozone precursors, greenhouse gases, organo-halogens, aerosols and their precursors, several heavy metals and Persistent Organic Pollutants (POPs). The GEIA/ACCENT emission data portal is accessible through http://www.aero.jussieu.fr/projet/ACCENT/Database.html.

The data portal provides emission data from several of the emission inventories mentioned in this section. For each inventory, the data portal provides: (1) gridded emission files which can be downloaded in a common Ascii or NetCDF format, (2) total annual emission data, (3) emission maps for all the species, and all the years/months considered, (4) metadata and documentation on the inventory, and (5) a visualisation tool for comparison of data sets.

3. Atmospheric processing

3.1. Ozone and its precursors

The following section reviews new discoveries in the area of gas phase atmospheric processing in the context of air quality. It deals with key oxidant precursors in terms of hydrocarbons and NO_x as well as ozone itself. A further section looks at new discoveries in radical chemistry, key intermediates in atmospheric photochemistry.

3.1.1. Hydrocarbons

3.1.1.1. Chemical mechanisms for VOC degradation. In the following sections, an overview of the current understanding of VOC chemistry in the troposphere is provided. Initially, a general description of VOC oxidation chemistry is given, followed by a summary of some recent advances during the timescale of the ACCENT project. In practice, only a very small fraction of the reactions occurring in the atmospheric degradation of VOCs have been studied experimentally. Only for the simplest hydrocarbons and oxygenates (e.g. methane, ethane, ethene, methanol, acetaldehyde, acetone and dimethyl ether) have the kinetics and products of the majority of the elementary reactions involved in their degradation to CO_2 and H_2O been investigated (Atkinson et al., 2006). Even for these compounds, however, there have been recent unexpected advances in understanding, and some uncertainties still remain (see below). For a number of larger and more complex VOCs (including isoprene and selected terpenes and aromatic hydrocarbons), some important aspects of their degradation chemistry have been studied experimentally. This information provides a partial basis for defining their degradation chemistry, which can be supplemented by the inclusion of reactions and associated parameters which are inferred from the more detailed understanding of the chemistry of the smaller compounds. For many other VOCs, little or no experimental information exists, and their degradation chemistry needs to be defined almost exclusively by inference. As a result, chemical mechanisms which treat the atmospheric degradation of a large number of significant emitted VOCs (e.g. Aumont et al., 2005; Carter, 2000; Jenkin et al., 2003) necessarily need to make the fundamental assumption that the kinetics and products of a large number of unstudied chemical reactions can be defined on the basis of the known reactions of a comparatively small number of similar chemical species. This is usually done by analogy and with the use of structure–reactivity relationships to provide relatively simple rules to guide mechanism construction e.g. Aumont et al., 2005; Jenkin et al., 2003; Saunders et al., 2003). To varying extents, such mechanisms also incorporate strategic simplifications to limit their overall size, which would otherwise include 10^5–10^6 reactions. The performance of these gas phase mechanisms can then be tested (and, if necessary, refined) using chamber data e.g. (Carter, 2000; Pinho et al., 2006, 2005, 2007). Such procedures have traditionally been focused on providing validated descriptions of ozone formation from the photooxidation of VOC/NO_x mixtures, although the development of highly-instrumented chambers has provided data to allow other aspects of the degradation mechanisms to be examined and improved e.g. (Bloss et al., 2005a,b; Wyche et al., 2008). Mechanisms constructed in this way therefore reflect a number of generic features, which are reasonably well-established for smaller VOC, and used to infer the chemistry for larger VOC and for their sequential degradation products. The most studied aspect of VOC degradation is the OH-initiated chemistry, for which a simplified schematic is shown in Fig. 15. The chemistry initiated by reaction with ozone (Johnson and Marston, 2008) and NO_3 radicals

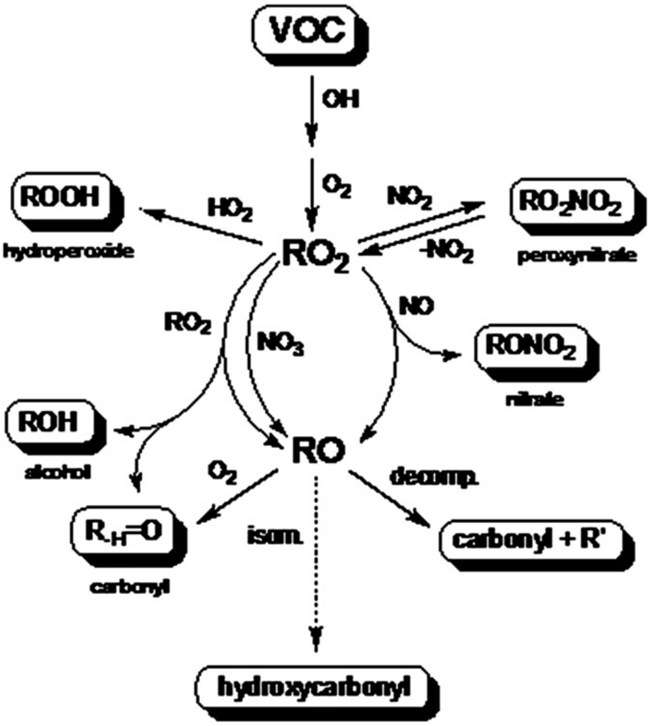


Fig. 15. Simplified schematic of generic OH initiated degradation chemistry to first generation products.

(Wayne et al., 1991), and via direct photolysis (Monks, 2005), tends to feed into similar reaction mechanisms by virtue of the formation of OH, RO_2 and RO radicals (see also Section 3.3.2).

There have been a number of recent developments (within the timescale of ACCENT) on various aspects of the general degradation chemistry (see Fig. 15) Progressive improvements in the kinetic and mechanistic database for reactions of RO_2 and RO radicals (e.g. Aschmann et al., 2006; Atkinson, 2007; Cassanelli et al., 2005; Reisen et al., 2005) and product studies for new VOC (e.g. Aschmann et al., 2004; Hurley et al., 2007) help existing descriptions of VOC degradation to be updated and refined within the established framework of understanding. However, some developments have challenged long-accepted understanding of the chemistry for comparatively small and well-studied species. As indicated above, the reactions of RO_2 with HO_2 have long been recognised as chain terminating reactions which make a major contribution to controlling atmospheric free radical concentrations under NO_x-limited conditions e.g. (Jenkin and Clemitshaw, 2000). Whereas radical termination via the near-exclusive formation of organic hydroperoxide products (ROOH) and O_2 is well-established for simple alkyl peroxy radicals such as CH_3O_2 and $C_2H_5O_2$ e.g. (Elrod et al., 2001; Hasson et al., 2004; Spittler et al., 2000; Wallington, 1991). A number of recent studies have demonstrated that selected oxygenated RO_2 radicals (in particular $CH_3C(O)O_2$) possess significant radical-forming channels for their reactions with HO_2 (Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2007)

$$RO_2 + HO_2 \rightarrow RO + OH + O_2 \qquad (2)$$

Furthermore, highly efficient regeneration of HO_x by unimolecular reactions in the atmospheric oxidation of isoprene has been predicted by theoretical chemistry (Peeters et al., 2009). This may alter our assessment of processes controlling ambient radical concentrations under NO_x-limited conditions, and may be a contributory factor in the observation of unexpectedly high radical concentrations (and therefore oxidizing capacity) in campaigns at remote locations (Lelieveld et al., 2008). It is, however, important to establish whether the reactions of HO_2 with oxygenated peroxy radicals in general are significantly propagating, and to investigate other RO_2 radical classes, in particular the β- and δ-hydroxyperoxy radicals generated from reactions of OH with alkenes and dienes, most notably isoprene and monoterpenes. In this respect, however, Dillon and Crowley (2008) found no evidence for a significant radical product channel for the reactions of HO_2 with simple β−hydroxyperoxy radicals, suggesting that additional mechanistic features may contribute to the level of radical recycling inferred from field observations in VOC rich environments (Butler et al., 2008; Hofzumahaus et al., 2009; Lelieveld et al., 2008) (see also Section 3.1.3)

The reactions of RO_2 radicals with NO_2 have long been recognised as termination reactions generating peroxynitrates, which are comparatively thermally stable in the specific case of PANs. The results of recent studies have demonstrated that selected RO_2 radicals ($HC(O)C(O)O_2$, $CH_3C(O)C(O)O_2$ and $C_6H_5O_2$) possess significant propagating channels (Jagiella and Zabel, 2007; Orlando and Tyndall, 2001)

$$RO_2 + NO_2 \rightarrow RO + NO_3 \qquad (3)$$

It is important, therefore, to establish whether this applies significantly to other RO_2 radical classes, as this could be a potentially important suite of oxidant-forming propagating reactions which are currently not represented in atmospheric mechanisms.

In general terms, the most studied aspect of VOC degradation is the OH-initiated, NO-catalyzed chemistry, which forms the essential "backbone" of the degradation mechanisms. This generally forms carbonyl products, which are themselves one of the better studied classes of oxygenate. The further degradation of "side-products" formed from radical termination processes, specifically organic nitrates and hydroperoxides, is particularly poorly characterized, even though these are comparatively significant product classes which potentially play a role in SOA formation. Various aspects of the atmospheric chemistry of organic nitrates are incompletely understood. For example, there are no reported product studies of the OH-initiated degradation of any organic nitrate, even though this is likely to be the major removal reaction in many cases. It is of particular importance to establish whether reaction with OH leads to release of NO_x, formation of more oxidized products which retain the nitrate group, or additional NO_x sequestration through formation of dinitrate products. In the latter two cases, it is possible that the sequential substitution of polar substituent groups can generate multifunctional products which more readily partition into the condensed phase, and therefore contribute to SOA and the nitrogen content of aerosols.

The formation of hydroperoxides from the global oxidation of biogenic hydrocarbons is likely to be considerable, and several recent appraisals of SOA formation mechanisms have proposed that they may play an important role by virtue of their propensity to undergo condensed phase association reactions with carbonyls to form involatile peroxyhemiacetals (Bonn et al., 2004; Jenkin, 2004; Johnson et al., 2005; Tobias and Ziemann, 2000). Despite this potential importance, hydroperoxides have not been well-studied in the laboratory (partially owing to their explosive character, no doubt). There is only limited information on their photolysis and the kinetics of the OH reaction have only been studied for CH_3OOH. Clearly, additional data for other hydroperoxides is required to allow structure–reactivity relationships to be developed, and products studies are needed to identify the extent to which the hydroperoxy group is retained in degradation products. In addition to the specific cases highlighted above, more information is generally required on the degradation reactions of multifunctional oxygenates containing combinations of the key functional groups (i.e., $-C(=O)H$, $-C(=O)-$, $-OH$, $-ONO_2$, $-C(=O)OONO_2$, $-C(=O)OH$, $-OOH$, $-C(=O)OOH$ and $-C(=O)-O-C(=O)-$) to assist the validation and refinement of existing structure–reactivity relationships.

The degradation chemistry of selected aromatic hydrocarbons and terpenes has received considerable attention e.g. (Atkinson and Arey, 2003; Calvert et al., 2002), owing in part to their established importance as precursors to SOA formation. This attention has continued in recent years e.g. (Alvarez et al., 2007; Bejan et al., 2007; Ma et al., 2007a,b ; Olariu et al., 2002; Volkamer et al., 2002, 2001; Wyche et al., 2009), leading to a progressive improvement in the understanding of some aspects of their degradation. Owing to their considerable complexity, however, substantial gaps and uncertainties remain in the detailed understanding of their gas phase degradation mechanisms.

The degradation of aromatic hydrocarbons, although usually only initiated significantly by reaction with OH, can proceed via a number of different routes to generate a large variety of structurally complex ring-retained and ring-opened products e.g. (Calvert et al., 2002; Wyche et al., 2009). Even for well-established products (e.g. α-dicarbonyls such as glyoxal and methylglyoxal, and their co-products, formed from the major ring-opening channels) there is considerable variation in the reported yields, and for many of the studied systems, only ca. 50% or less of the aromatic loss has been accounted for by observed first generation products. Particular areas where understanding is lacking include uncertainties in the mechanisms of the initial oxidation sequences to first generation products, and limitations in the available information on the subsequent chemistry of many of the classes of product known to be generated. The further degradation chemistry of first and subsequent generation products is believed to be particularly important in accounting for secondary radical generation and removal of NO_x in chamber photooxidation experiments of aromatic/NO_x systems (Wagner et al., 2003). In this respect, mechanisms constructed for aromatic hydrocarbons on the basis of established understanding tend to display evidence for a missing radical source in the system, but a simultaneous tendency towards over-production of ozone (Bloss et al., 2005a,b ; Wyche et al., 2009). This feature points to a clear gap in understanding, since these features cannot be readily reconciled within traditional understanding of VOC oxidation chemistry. Bloss et al. (2005a,b) outlined a number of speculative solutions, including the existence of novel isomerisation reactions of complex RO radical intermediates to regenerate OH directly, and the possibility that NO_2 might react with the SOA formed in the system to generate HONO. Although there was insufficient evidence to support either suggestion, the latter has subsequently received some indirect support from the recognition that photosensitized NO_2-to-HONO conversion can occur on organic surfaces e.g. (George et al., 2005; Metzger et al., 2008; Stemmler et al., 2006). They have shown that this process occurs on organic deposits on chamber walls during 1,3,5-trimethylbenzene photooxidation.

Whereas the uncertainties in aromatic degradation are, to some extent, generic (i.e., an advance in mechanistic understanding is likely to be applicable to aromatics in general), understanding of the degradation of terpenes (and related biogenics) is further hampered by the enormous variety in their structure and reactivity (atmospheric lifetimes range from minutes to days). In addition to this, their degradation in each case is likely to be initiated by reaction with OH, O_3 and NO_3, and it is often also necessary to consider reaction with $O(^3P)$ atoms in chamber hydrocarbon/NO_x photooxidation experiments. Although kinetic data are available for a wide variety of terpenes (Atkinson and Arey, 2003), experimental information on their degradation pathways is much more limited. Selected product yields (usually for first generation carbonyls) are available for a number of species, but the most detailed information has been reported for the monoterpenes $\alpha-$ and $\beta-$pinene. Even for these species, however, it is clear that the distribution of first generation products, and the elementary processes leading to their formation, remain far from fully characterized, and that experimental information on the further degradation of first generation products is very sparse indeed e.g. (Pinho et al., 2007). Detailed chemical mechanisms developed for such species therefore necessarily contain a substantial proportion of inferred reactions and estimated parameters. In recent years, theoretical methods have been applied with some success to elucidate aspects of the degradation of some complex VOC, in particular α-pinene e.g. (Fantechi et al., 2002; Peeters et al., 2001; Vereecken et al., 2007; Vereecken and Peeters, 2004). Such methods invariably identify exotic reactions pathways which are not predicted by the extrapolation methods, based on relatively simple structure–reactivity relationships as outlined above. Although such alternative pathways have been shown to have a reasonably subtle influence on simulations of oxidant formation (Pinho et al., 2007), they have a notable influence on the precise structures of the products formed, and therefore potentially have a much greater effect on the perceived propensity of product distribution to contribute to SOA formation (Vereecken et al., 2007).

From the above discussion, it is clear that, despite considerable investigation, the elementary processes involved in the degradation of complex VOC such as aromatic hydrocarbons and terpenes, remain very sparsely characterized. The majority of information relates to the initial oxidation sequences to form first generation products, with the further degradation of established first generation products often not characterized at all. It is also becoming clear that chamber datasets for the oxidation of the product compounds (and possibly their degradation products) would be valuable in assessing the performance of detailed degradation mechanisms, and for gaining insights into chemical processes occurring on timescales longer than those addressed by conventional chamber experiments. This is particularly important for large complex emitted VOC, which are typically degraded via a large number of sequential (and parallel) steps.

3.1.1.2. Oxygenated volatile organic compounds (OVOCs). The denomination oxygenated organic compounds includes a wide range of organic molecules such as alcohols (R–OH), ketones (R_1–CO–R_2), aldehydes (R–CHO), ethers (R_1–O–R_2), esters (R_1–COO–R_2) and acids (R–COOH). These compounds are either emitted directly by anthropogenic and biogenic sources or are produced in the atmosphere in the course of the oxidation of hydrocarbons. Until relatively recently, atmospheric OVOCs received little attention (Singh et al., 1995), as analytical methods were far from straightforward and their secondary formation was difficult to represent in models. Although it was well known that OVOCs are normally more abundant than hydrocarbons in rural and background air masses (Solberg et al., 1996) knowledge of sources and sinks, which has been assessed by campaign studies (e.g. Jacob et al., 2005a; Singh et al., 2004), has remained rather patchy. This has changed in the last years with the development of new analytical technologies (see (Laj et al., 2009)).

Early European OVOC data is available from Southern Germany (Schauinsland) from the 1990s, where during the European TOR-project a short-term campaign showed average concentrations of 1.0, 0.7 and 2.5 ppbV for formaldehyde, acetaldehyde and acetone, respectively (Slemr et al., 1996). Furthermore, long-term measurements of aldehydes and ketones have been performed within the framework of EMEP (Solberg, 2006). Concentrations measured from the Arctic to the Mediterranean were 0.2–2.5 ppbV for formaldehyde, 0.2–1.2 ppbV for acetaldehyde and 0.4–1.3 ppbV for acetone, with lowest values in the Arctic and highest concentrations in Southern Europe. In summer, these compounds are the dominant organic species in the European rural atmosphere (Solberg et al., 1996).

The most abundant OVOCs in the atmosphere are formaldehyde, acetaldehyde, acetone and methanol. Formaldehyde (HCHO) plays a key role in atmospheric chemistry as it readily photolyses, being a source of the hydroperoxyl radical (HO_2) and of ozone (in the presence of NO_x). It is formed either as an intermediate during the oxidation of many VOC or is emitted directly by fossil fuel combustion or biomass burning. The European background level of less than 1 ppbV (Fig. 16) increases slightly in rural regions and over the Mediterranean. Higher values are measured in urban environments, as the primary emissions get more important. In Europe highest values are measured at urban agglomerations in Southern Europe (e.g. 30 ppbV in Athens (Bakeas et al., 2003)), which are comparable to mixing ratios in developing countries (e.g. Mexico city (Grutter et al., 2005)). HCHO has also been the focus of a dedicated study in Northern Italy (FORMAT), where concentrations of more than 10 ppbV during pollution events (Hak et al., 2005) have been assigned to secondary photochemical production (Liu et al., 2007).

Acetaldehyde (CH_3CHO), as the next higher aldehyde homologue, has primary sources from vegetation, fossil fuel combustion and biomass burning and secondary sources from the oxidation of $\geq C_2$–VOCs. European acetaldehyde concentrations range from 0.3 ppbV at a high-Alpine site (Legreid et al., 2008) to 27 ppbV in Athens (Bakeas et al., 2003). Background values have been questioned because reported concentrations are too high to be easily reproduced by

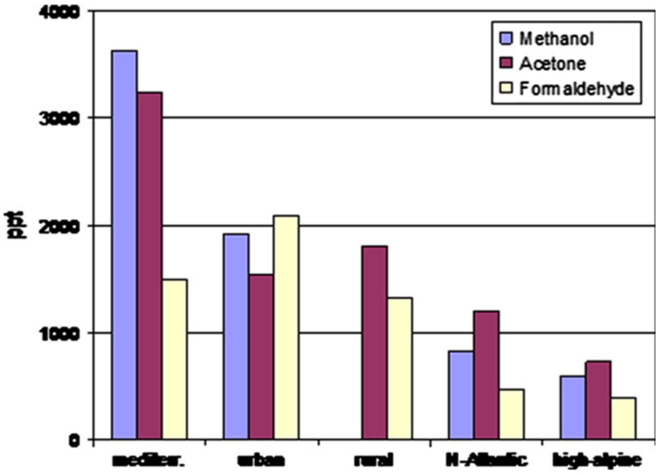


Fig. 16. Concentrations of the most abundant OVOCs within typical European environments. Medit: Mediterranean average concentrations during background conditions (MINOS campaign) (Kormann et al., 2003; Salisbury et al., 2003); urban: Zurich (Switzerland) (Legreid et al., 2007); rural: Waldhof (Germany), average 1999–2004 (Solberg, 2006); N-Atlantic: Mace Head (Ireland) (Lewis et al., 2005); high-alpine: Jungfraujoch (Switzerland) (Legreid et al., 2008).

models (Singh et al., 2004). A potential reason for this finding is unaccounted sources (Singh et al., 2001) or artificial production during analysis via ozone–alkene reactions (Northway et al., 2004).

Acetone (CH_3COCH_3) as the smallest ketone is primarily emitted by fossil fuel combustion, biomass burning and industrial processes and is a secondary product in the atmosphere from the oxidation of anthropogenic isoalkanes (Jacob et al., 2002). An oceanic source has been proposed (Jacob et al., 2002), but within a recent re-analysis of existing data no indications for such emissions could be found (Shim et al., 2007). European concentrations of acetone range from 0.7 ppbV at a high-Alpine site to several ppbV in the Mediterranean (Fig. 16). In the lower troposphere acetone is primarily destroyed by the OH-initiated reaction whereas in the upper troposphere its photolysis becomes more important. It has been suggested that in the dry conditions of the higher troposphere acetone can act as an important source for OH and peroxy radicals (HO_x) (Jaegle et al., 2001). However, recent studies concluded that this effect is less important (Arnold et al., 2005), as the quantum yield of the photo dissociation of acetone is smaller at the low temperatures in the higher troposphere (Blitz et al., 2004).

Methanol (CH_3OH) is the most abundant non-methane VOC in the atmosphere, with concentrations in the European background ranging from 0.6 ppbV at a high-Alpine site to nearly 4 ppbV in the Mediterranean (Fig. 16). In general, concentrations are more equally distributed than those of other abundant OVOCs. This is caused by a fairly long lifetime and relatively dispersed emissions from plant growth/decay and from the self-reaction of methylperoxy (CH_3OO) radicals owing to the oxidation of CH_4 and VOCs (Jacob et al., 2005a; Schade and Goldstein, 2006; Shim et al., 2007). Destruction is dominated by gas phase oxidation by OH, with smaller contributions from dry deposition. The influence of oceanic fluxes is still unclear, as Heikes et al. (2002) argued for an oceanic source of methanol, whereas Jacob et al. (2005b) found the ocean to be a net sink (see also (Fowler et al., 2009)).

Within alcohol OVOCs ethanol has a certain importance, especially in regions with anthropogenic influence. It is emitted by abiotic degradation, industry and motor vehicles. Interestingly, very high concentrations in a highway tunnel could be related to the use of window-wiper fluids (Legreid et al., 2007). The atmospheric importance of alcohols will increase in the future as there is a rise in biofuel usage.

Atmospheric OVOCs have gained increasing attention over the last few years owing to a considerable progress in analytical methods and the realisation of their extensive involvement in atmospheric processes (Laj et al., 2009). There are still considerable gaps of knowledge, especially in the field of fitting global budgets of OVOCs (sources and sinks) and their influence on secondary organic aerosols (SOA) (see Section 3.2). The importance of OVOCs in SOA has been underlined by the detection of a multitude of oxygenated organic groups within SOAs (Hamilton et al., 2004).

A future scientific challenge will be the assessment of the impact of biofuels on air pollution under European conditions. First experiments at tail-pipe show that when using biofuels, emissions for primary pollutants while dependent on driving conditions are mostly enhanced (Durbin et al., 2007). In a recent review, Niven (2005) came to the conclusion that for the reduction of air pollution a fuel containing 85% ethanol is more favourable than one with only 10%. Studies in Brazil show higher aldehyde concentrations (Correa et al., 2003; Martins and Arbilla, 2003) in biofuels which could have a potential impact on secondary organic aerosol.

A new view of OVOC distributions is becoming available from satellites which open a number of opportunities for source and sink assessment (Wittrock et al., 2006). In summary, oxygenates are ubiquitous throughout the atmosphere, their sources are becoming better understood but their chemistry and sinks are poorly represented.

3.1.1.3. Biogenic VOC oxidation. Biogenic volatile organic compounds (BVOCs) are emitted into the atmosphere in copious quantities, are in general extremely reactive, and hence can exert a controlling influence over the oxidative chemistry near their emission source. For example, as the major reaction partner for OH, these species can control OH levels, $[OH]/[HO_2]$ ratios, and ozone production rates. Furthermore, their oxidative by-products (e.g. CO) can be longer-lived than are the parent species and thus their influence can extend to the regional and even global scale. Lastly, as discussed in more detail later in this review, biogenics (isoprene, terpenes and sesquiterpenes) represent an important source of secondary organic aerosol (SOA), thus providing an additional major impact of these species on both climate-related and air quality issues.

Assessing the impact of a particular BVOC on the atmospheric chemistry requires a knowledge of 1) its atmospheric lifetime, which is controlled by its rate of reaction with the common atmospheric oxidants, O_3, OH and NO_3; and 2) the mechanism of its oxidation (i.e. the radical chemistry that occurs following initial attack by the oxidant, and the nature and fate of the stable products formed). Rate coefficients for reaction of OH, NO_3 and O_3 are well-established for most BVOC, including isoprene, all major monoterpenes, and a number of sesquiterpenes (see, for example, the comprehensive review of (Atkinson and Arey, 2003)). The mechanisms involved in the oxidation of these BVOCs and the nature of the products formed, however, are not nearly so well-established (Atkinson and Arey, 2003).

The atmospheric oxidation of isoprene is dominated by its reaction with OH during the day and its reaction with NO_3 during the night, while ozone plays a minor role day and night. The OH-initiated oxidation in the presence of NO_x is quite well understood. Methyl vinyl ketone (MVK) and methacrolein (MACR) have long been known to account for about 60% of the isoprene reacted e.g. (Tuazon and Atkinson, 1990), with formaldehyde as a co-product in each case. More recently, two isomeric hydroxycarbonyl compounds [$HOCH_2C(CH_3){=}CHCHO$ and $HOCH_2CH{=}C(CH_3)CHO$] have been detected and quantified and appear to make up much of the remainder of the mass balance (Kwok et al., 1995; Yu et al., 1995; Zhao et al., 2004). An important, but highly uncertain, aspect of the

OH-initiated isoprene chemistry in the presence of NO_x is the formation of hydroxynitrate species from reactions of the various hydroxyperoxy radicals with NO, e.g.

$$CH_2{=}CH{-}C(CH_3)(OO^{\bullet}){-}CH_2OH + NO \rightarrow CH_2{=}CH{-}C(CH_3) \times (O^{\bullet}){-}CH_2OH + NO_2 \quad (4)$$

$$\rightarrow CH_2{=}CH{-}C(CH_3)(ONO_2){-}CH_2OH \quad (5)$$

Laboratory-determined yields for these hydroxynitrates span a rather large range from 4 to 15%, (Chen et al., 1998; Chuong and Stevens, 2002; Patchen et al., 2007; Sprengnether et al., 2002; Tuazon and Atkinson, 1990) and essentially nothing is known about their subsequent chemistry. The key point is whether these compounds react further to regenerate NO_x, or whether instead they act as NO_x sinks; this represents a major uncertainty in determining the overall impact of isoprene on ozone production, particularly in the eastern USA e.g. (Fiore et al., 2005; Horowitz et al., 2007, 1998; Ito et al., 2007; Liang et al., 1998; von Kuhlmann et al., 2004; Wu et al., 2007). Some comparisons of field measurements of the isoprene-derived nitrates with models are now available (Giacopelli et al., 2005; Horowitz et al., 2007) The study of Horowitz et al. (2007), for example, tends to support hydroxynitrate yields in the lower end of the range, with partial regeneration of NO_x and a rapid rate of their dry deposition. Note that hydroxynitrate species are likely also the dominant products of the reaction of NO_3 with isoprene, thus increasing their potential impact.

There are relatively few studies of the OH-initiated oxidation of isoprene in absence of NO_x, but reduced yields of the products noted above are evident (Miyoshi et al., 1994), balanced by increases in the yield of unsaturated hydroperoxide species, e.g. $CH_2{=}CH{-}C(CH_3)(OOH){-}CH_2OH$. The fate of these species is not known, but likely involves competition between further gas phase oxidation and depositional processes, with potential for impact on, for example, the overall CO production per isoprene oxidized e.g. (Miyoshi et al., 1994; Pfister et al., 2008).

Quantification of the contribution of isoprene oxidation to the formation of SOA has been a major research thrust. Clear laboratory evidence now exists for the formation of small, but non-negligible yields of SOA from the OH– and NO_3-initiated oxidation of isoprene (e.g. Claeys et al., 2004; Dommen et al., 2006; Edney et al., 2005; Healy et al., 2008; Kroll et al., 2005; Ng et al., 2008; Surratt et al., 2006) SOA yields of about 3% (on a mass basis) appear to be appropriate for typical atmospheric conditions (Henze and Seinfeld, 2006).

It has long been established that the atmospheric oxidation of the monoterpenes and sesquiterpenes leads to the formation of substantial yields of SOA, and remarkable progress has been made in recent years in quantifying these yields and in elucidating the mechanisms involved (for a few recent examples, see Lee et al., 2006a,b ; Ma et al., 2008; Pathak et al., 2008, 2007). However, our knowledge of even the initial processes involved in the gas phase oxidation of these species remains incomplete. For example, the major product of the OH-initiated oxidation of α-pinene is thought to be pinonaldehyde, but measured yields of this species range from $\approx$20 to 80% (Atkinson and Arey, 2003; Lee et al., 2006a,b) Given that the lower yields were determined using the more species-specific analytical tools, it appears that a major gap exists in our ability to quantify the first-generation products from the OH-initiated oxidation of even this most common terpene. Lastly, given the complexity of the chemistry involved, it is not at all surprising that studies of the gas phase sesquiterpene chemistry are limited in number (e.g. the reviews of Atkinson and Arey, 2003; Jaoui and Kamens, 2003; Jaoui et al., 2003, 2004) and that mechanistic information for these species remains incomplete. Progress towards quantifying these mechanistic details will require continued input from theoretical and analytical chemists, as well as from organic synthetic chemists who can provide authentic standards of reaction products for identification and quantification.

As noted above, BVOCs (particularly isoprene) exert a controlling influence over oxidant levels in regions of high emissions; however, there are numerous indications from field studies that these impacts are not quantitatively understood. First, there is evidence to suggest that additional, reactive BVOCs are present in various forested regions that are not currently accounted for. For example, Di Carlo et al. (2004), in a study in a deciduous forest in Michigan, showed that measurements of total OH reactivity exceeded that calculated from measurements of individual [VOC] and knowledge of their OH rate coefficients (see Fig. 17). The positive correlation of this "missing reactivity" with temperature provided strong evidence for the presence of unaccounted-for biogenic emissions. From similar measurements of OH reactivity in Tokyo, (Yoshino et al., 2006) noted missing reactivity in the summer months, possibly due to a contribution from BVOCs. In a similar vein, studies at a California forested site (Goldstein et al., 2004; Holzinger et al., 2005a; Kurpius and Goldstein, 2003) show larger downward ozone deposition velocities than can be accounted for, likely the result of reaction of O_3 with very reactive, but unmeasured, BVOCs. Sesquiterpenes are certainly candidates to make up some of these imbalances e.g. (Holzinger et al., 2005a) and the ability to quantify these species is improving e.g. (Ortega and Helmig, 2008; Ortega et al., 2008, 2007), but full accounting for any missing reactivity has yet to be achieved.

Finally, there are numerous indications that levels of OH in and near forested areas are much higher than those expected from known chemistry. For example, Tan et al. (2001) noted [OH] model/measurement disagreements of about a factor of 2–3 in a deciduous forest in Michigan. At the same site, Faloona et al. (2001) measured significant levels of nighttime [OH] whose source is unknown. Thornton et al. (2002) noted in a study conducted in isoprene-impacted, suburban Nashville, USA, discrepancies in modelled versus measured ozone production rates as a function of NO_x, and postulated an overestimate of HO_x sinks in current models. In studies at the same California forested site referred to above,

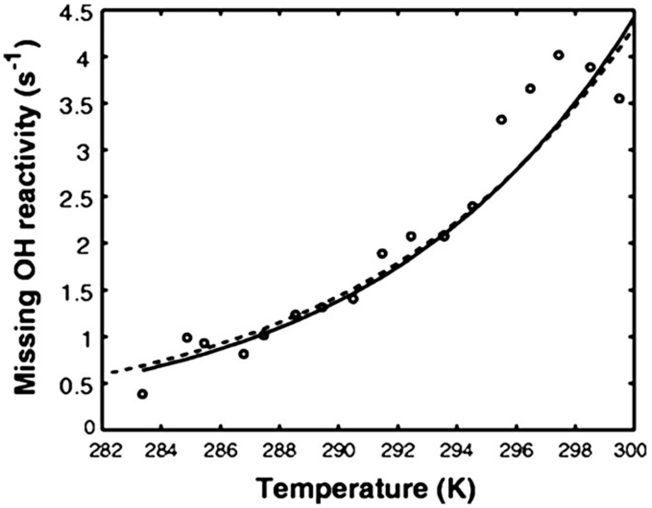


Fig. 17. The difference between measured and calculated OH reactivity versus temperature (circles). The missing OH reactivity, when fitted with the expression $E(T) = E(293)\exp(\beta(T - 293))$, yields $\beta = 0.11\ K^{-1}$ with $R^2 = 0.92$ (solid line). This temperature dependence of the missing OH reactivity is almost identical to that of a derived temperature dependence of terpene emissions (Di Carlo et al., 2004) Reprinted with permission from AAAS.

Farmer and Cohen (2008) noted significant upward fluxes for nitric acid and PANs during summertime, implying very high [OH] in the forest canopy. In heavily isoprene-impacted but low NO_x environments in South America, discrepancies between modelled and either observed or inferred levels of [OH] have been demonstrated (Karl et al., 2007; Lelieveld et al., 2008). Unexplained high OH concentrations were observed in the presence of isoprene and anthropogenic VOCs in a rural environment in Southern China, when NO_x was below 1 ppbV (Hofzumahaus et al., 2009). These imbalances in measured/modelled OH distributions can obviously result from either an underestimate of sources or an overestimate of sink terms. In case of the Southern China study, measured and modelled OH reactivities were in agreement, demonstrating that an unknown OH source was responsible for the unexplained high OH concentrations (Hofzumahaus et al., 2009). Reactions of terpenes and sesquiterpenes are known sources of OH (Atkinson and Arey, 2003) and these reactions may contribute, particularly given that not all of these species are being accounted for, as noted above e.g. (Kurpius and Goldstein, 2003). On the sink side, common to many of these studies are suppositions, first put forward by Thornton et al. (2002), that reactions of HO_2 with peroxy radicals (particularly those derived from isoprene) may not be as efficient HO_x sinks as previously believed, and may instead act to 'recycle' OH. Laboratory studies showed that at least in some specific cases, for example in the reaction of peroxyacetyl radicals with HO_2 (Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2007) regeneration of OH does indeed occur:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \tag{6}$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OH + O_3 \tag{7}$$

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3 + CO_2 + OH + O_2 \tag{8}$$

However, as discussed in Section 3.1.1.1, Dillon and Crowley (2008) have demonstrated that very little recycling occurs for reactions of HO_2 with hydroxyperoxy radicals, similar to those generated by OH reaction with isoprene. As an alternative mechanism, Peeters et al. (2009) have predicted in a theoretical study the highly efficient recycling of HO_2 by unimolecular reactions of OH-peroxy-isoprene radicals and additional OH formation by photolysis of the hydroperoxy-aldehyde co-products. Final conclusions on this issue await experiments involving the isoprene-derived peroxy radicals themselves or those derived from major isoprene oxidation products (e.g. MVK and MACR).

3.1.2. *New insights into nitrogen chemistry*

Nitrogen oxides have a key role in the atmospheric radical chemistry that leads to the oxidation of reactive trace gases and to the (photochemical) formation of ozone. Deposition of gas phase nitrogen compounds is of importance as an input of nutrients to vegetation (Fowler et al., 2009). Different species of nitrogen compounds have widely varying chemical and physical properties, thus the processes that chemically convert species of oxidized as well as reduced nitrogen compounds, are important for their transport, their influence on atmospheric chemistry and their deposition to the surface (see Fig. 18). Some important progress has been made recently in the understanding of these processes caused by field observations with new, highly sensitive measurement techniques (e.g. for measurement of HONO, N_2O_5 and NO_3 radicals see Laj et al. (2009)) and from new information about chemical reactivity obtained by laboratory studies.

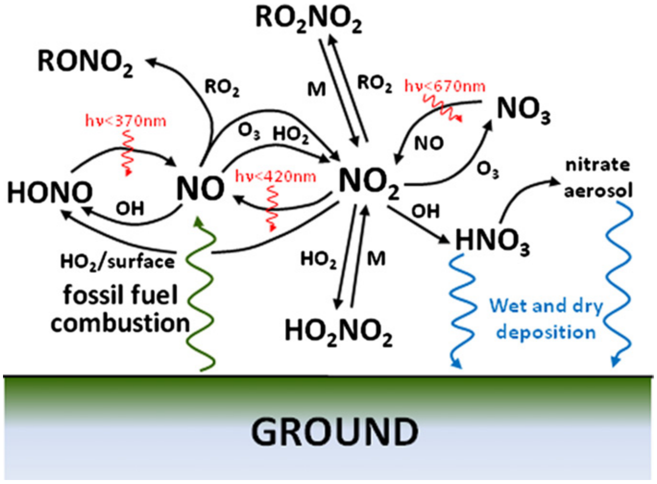


Fig. 18. Schematic representation of the nitrogen cycle (DoE, 1997).

3.1.2.1. Chemical sinks for oxidized nitrogen. Uptake of N_2O_5 on aerosol surfaces has been found to be a major mechanism for production of HNO_3 and for removal of nitrogen oxides from the atmosphere (see also Section 3.3.2). A modelling study by Liao and Seinfeld (2005) suggests that it accounts for approximately 30% of all HNO_3 formation in the atmosphere. The development of measurements of N_2O_5 (see also (Laj et al., 2009)) has allowed more direct evidence of the importance of these reactions to be obtained, as illustrated by recent field studies (Brown et al., 2006b; Wood et al., 2005). However, model simulations require detailed knowledge of the kinetics of the uptake of N_2O_5 on a variety of surfaces. Recent laboratory studies have addressed the uptake of N_2O_5 at different surfaces: dust, sea salt (which can cause Cl-activation by release of $ClNO_2$) and sulphate, thus providing an improved basis for model simulations of this chemistry. Of particular interest is the finding by Antilla et al. (2006) that organic coatings may significantly slow down the uptake of N_2O_5 on wet aerosols.

The reaction

$$HO_2 + NO \rightarrow OH + NO_2 \tag{9}$$

is a step in the atmospheric chain reactions that lead to generation of ozone. However, a laboratory study (Butkovskaya et al., 2007) has shown that a minor channel (approximately 0.5% near the Earth's surface and 0.8% in the tropopause region) forms HNO_3. This latter channel thus terminates the chain reaction and favours removal of oxidized nitrogen from the atmosphere because HNO_3 is much faster removed by deposition than NO and NO_2. A recent modelling study by Cariolle et al. (2008) estimates that tropospheric ozone concentrations decrease by 5–12% when the aforementioned reaction channel is accounted for.

3.1.2.2. HONO formation. The UV photolysis of nitrous acid, HONO (in the wavelength range from 300 to 405 nm), is an important source for OH radicals in the polluted urban atmosphere e.g. (Alicke et al., 2003, 2002; Kleffmann, 2007; Kleffmann et al., 2005; Lammel and Cape, 1996; Stutz et al., 2002; Zhou et al., 2002) and the polar boundary layer (Zhou et al., 2001). HONO is toxic and its chemistry leads to the formation of carcinogenic nitrosamines. In addition, HONO formation at chamber walls is a candidate for intrinsic 'chamber dependent' radical formation, which is observed in most smog chamber experiments e.g. (Rohrer et al., 2005).

$$HONO + h\nu \rightarrow OH + NO (300\ \text{nm} < \lambda < 405\ \text{nm}) \tag{10}$$

Recent developments of more sensitive measurement techniques for HONO, e.g. the Long Path Absorption Photometer

(LOPAP) and CRDS, (see also Laj et al. (2009)) have led to an improved knowledge of the diurnal variations of ambient concentration levels, and it has been found that daytime sources are stronger than previously believed, at urban as well as rural sites (Kleffmann, 2007; Kleffmann et al., 2005; Zhou et al., 2002). An example of the latter is the study carried out at the rural mountain site of Hohenpeissenberg (980 m a.s.l.) where HONO photolysis during a summer campaign was found to account for 42% of the integrated photolytic HO_x formation (Acker et al., 2006). Up to 1% of the emitted NO_x was found as nitrous acid in heavily polluted areas with high amounts of traffic. Kirchstetter et al. (1996) reported a $HONO/NO_x$ emission ratio of 0.35% for a North American car fleet, while Kurtenbach et al. (2001) found 0.65% of NO_x emitted as HONO in a traffic tunnel in Germany. Overall, the contribution of HONO to the oxidizing capacity of the lower atmosphere now seems to be 2–3 times higher than previously believed (Kleffmann, 2007).

It is generally accepted that reactions of NO_2 on humid surfaces can cause the observed build-up of HONO during night, but the recent observations have encouraged laboratory studies of potential photochemically enhanced formation mechanisms. Photochemically induced HONO formation has been observed from surfaces treated with nitric acid, most likely not due to direct photolysis of HNO_3 but rather due to the formation of photolabile substances such as organic nitrates or reduction of HNO_3 by photosensitized organic substances. Other studies have shown that sun-irradiation of some organic substances, particularly humic acids (George et al., 2005; Stemmler et al., 2006) can strongly enhance HONO formation by reaction with NO_2.

Titanium dioxide, which is a common component of atmospheric mineral aerosol, has also been found in laboratory experiments to act as an efficient catalyst for the reduction of NO_2-to-HONO, when activated by illumination with near UV light (Gustafsson et al., 2006). Subsequently, in a laboratory study carried out by Ndour et al. (2008), it was shown that real mineral dust samples, as well as mixtures that mimic these, caused photoenhanced uptake of NO_2 and formation of HONO. A reaction mechanism involving H_2O and O_2 was proposed. Three-dimensional modelling showed that during a dust event a strong reduction of NO_2 (37%) in the free troposphere could be expected owing to photoenhanced uptake on dust. The average global reduction of NO_2 would be 3%.

A recent laboratory study by Li et al. (2008) suggests that the reaction of electronically excited NO_2 with water vapour may be a significant source of OH and HONO in the lower troposphere, where NO_2 and H_2O are abundant gases.

$$NO_2 + h\nu(>420\ \text{nm}) \rightarrow NO_2* \quad (11)$$

$$NO_2* + H_2O \rightarrow HONO + OH \quad (12)$$

Li et al. have estimated that excited NO_2 may contribute in the order of 10–50% of the OH production from ozone photolysis at solar zenith angles of 70°–85° in the lowest 2 km. Their results differ largely from a previous study by Crowley and Carl (1997), who measured an order of magnitude smaller rate constant. Model calculations by Wennberg and Dabdub (2008) demonstrate that the new OH source could be relevant for the photochemical formation of ozone and fine particles in urban environments and recommend further investigations of the kinetics of the $NO_2^* + H_2O$ reaction. Recently, however, the results by Li et al. (2008, 2009) have been questioned by Carr et al. (2009) who failed to observe OH formation in the reaction of $NO_2^* + H_2O$ and suggest that the reaction has little impact on atmospheric chemistry.

Laboratory studies have shown that photolysis of ortho-nitrophenols leads to formation of HONO (Bejan et al., 2007) and another study suggests that photolysis is the main gas phase atmospheric loss process for methyl-ortho-nitrophenols. It seems that these reactions provide a non-negligible source of HONO at daytime that may help to explain the observed concentrations. Nitrophenols are emitted directly to the atmosphere and also formed by photooxidation and (at nighttime) by reactions initiated by the NO_3 radical.

3.1.3. *Radical chemistry*

Free radicals (OH, HO_2, RO_2 with R = organic group, NO_3) play a central role in the chemical processes that transform trace gases and pollutants in the atmosphere (Monks, 2005). OH and HO_2, collectively referred to as HO_x, and RO_2 are of major importance at daytime when they are efficiently photochemically formed. In contrast NO_3 is important at night, but has a negligible role at daytime owing to its fast photolysis. In the following, recent results related to the chemistry of HO_x ($=OH + HO_2$) in the atmospheric boundary layer will be summarized. Nighttime chemistry is discussed in Section 3.3.2.

It is generally accepted that OH represents the major atmospheric oxidant, which is responsible for self-cleaning of the atmosphere (see overview by Ehhalt (1999)). The current knowledge of atmospheric gas phase chemistry is represented by chemical mechanisms of large complexity (Jenkin et al., 2003; Saunders et al., 2003) (see also Section 3.1.1.1). Following the successful development of instruments for measurement of OH and other radicals in the 1990's, an increasing number of field studies have tested the validity of chemical mechanisms for different environments (Heard and Pilling, 2003). Over the last five years, comprehensive field campaigns of increasing complexity and instrumentation, as well as new laboratory and simulation chamber studies, and novel measurement techniques have yielded exciting new research findings. The results demonstrate significant progress in the understanding of the major production and loss processes of radicals and of atmospheric chemical mechanisms, but also reveal major uncertainties that still have to be solved in the future.

The principal source of atmospheric OH radicals through photolysis of ozone has been known for a long time, but only recently a major revision of the wavelength dependence of the $O(^1D)$ quantum yield data has been concluded (Matsumi et al., 2002) and confirmed by field measurements of ozone photolysis frequencies (Hofzumahaus et al., 2004). The revision states that the energetic threshold for $O(^1D)$ formation occurs at a longer wavelength (~340 nm) than originally thought (310 nm) and results in significantly higher OH production rates to be calculated in models. The temperature dependent effect accounts for 25–40% of the OH production from $O(^1D)$ at solar zenith angles from 40° to 80° at 298 K (Matsumi et al., 2002).

Progress in the quantification of the total amount of reactive pollutants has been achieved by the development of instruments that measure the total atmospheric OH loss rate (Lou et al., 2009; Kovacs and Brune, 2001; Sadanaga et al., 2004; Sinha et al., 2008). These techniques have been used successfully to assess the budget of measured OH in field campaigns and to quantify missing OH reactivities in forested and urban regions (e.g. (Di Carlo et al., 2004) (see Fig. 17); (Lou et al., 2009; Yoshino et al., 2006) as well as in the free troposphere (Mao et al., 2008). In most cases, the measured total OH reactivity was found to be larger than the reactivity, calculated from individually measured trace components, by as much as a factor 2, suggesting that a substantial amount of atmospheric VOCs are insufficiently captured by available measurement techniques.

Major loss reactions of tropospheric HO_2 have been reinvestigated in view of their potential to influence the OH concentration in the atmosphere. It is generally assumed that the loss of

HO_x in very clean air occurs predominantly through self reactions of HO_2 and RO_2, yielding H_2O_2 and ROOH as products. Recently it was discovered in laboratory studies that the reaction of specific RO_2 radicals with HO_2 can produce OH at significant yields (Dillon and Crowley, 2008, and references therein) (see also Section 3.1.1.1).

Recent field studies e.g. (Sommariva et al., 2004) have indicated that HO_2 can be lost heterogeneously on aerosols. Although this possibility had been pointed out long ago e.g. (Mozurkewich et al., 1987; Saylor, 1997), surprisingly few data exist for the uptake coefficient of HO_2 on atmospheric aerosols. In a recent laboratory study, Taketani et al. (2008) have measured the uptake of HO_2 at ambient concentration levels on ammonium sulphate and sodium chloride aerosols.

Polar photochemistry has received increasing attention over the last few years. In general, different radical concentration levels have been observed at different places in the polar boundary layer. OH was measured at different marine sites in Antarctica and showed small concentrations ($<1 \times 10^6$ cm^{-3}) in January/February as is expected for conditions of low insolation at polar latitudes (Bloss et al., 2007; Jefferson et al., 1998). However, surprisingly high concentrations were observed in the 10^6–10^7 cm^{-3} range at South Pole (Mauldin et al., 2004) and Summit, Greenland (Sjostedt et al., 2007) at hemispheric summer. Corresponding $HO_2 + RO_2$ concentrations reached peak values of several 10^8 cm^{-3}. The unexpected high radical concentrations could be explained by the photolysis of snow-emitted HO_x precursors (HCHO, H_2O_2) plus efficient radical recycling by NO from snow (Chen and Penner, 2005; Chen et al., 2007). In contrast, radical recycling at the marine site Halley, Antarctica was dominated by small amounts of halogen oxides ($<$5 pptV of IO and BrO, each), which were identified by absorption spectroscopy (Saiz-Lopez et al., 2007b) and contribute to ozone destruction. HONO was observed to be emitted from snow packs e.g. (Zhou et al., 2001) but its relevance as an OH source in polar boundary layer air remains uncertain (Bloss et al., 2007; Chen et al., 2007).

The chemistry of HO_x in the marine boundary layer in clean oceanic air was investigated on a ship cruise in the Atlantic Ocean along 30°W (Brauers et al., 2001) and at baseline observatories in the Pacific Ocean at Mauna Loa, Hawaii (Hauglustaine et al., 1999) and Cape Grim, Tasmania (Monks et al., 1998; Creasey et al., 2003; Sommariva et al., 2004). Reported OH values had noontime maxima in the range of $(2–10) \times 10^6$ cm^{-3} and were in general good agreement with model predictions for clean baseline conditions. At Mauna Loa during summer, however, OH observations were significantly overestimated by models by a factor 1.5–2, possibly the result of unnoticed local emissions of biogenic VOCs which were not included in the model (Hauglustaine et al., 1999). Recent field studies were performed at coastal stations, where the HO_x chemistry is influenced by emissions from the landside and the shore line e.g. (Berresheim et al., 2002; Fleming et al., 2006b; Kanaya et al., 2007a,b; Sommariva et al., 2006). Observed HO_2 concentrations were found to be generally much lower, by as much as a factor of 3.6, than predicted by atmospheric models (Carslaw et al., 2002; Kanaya et al., 2007a,b ; Sommariva et al., 2006; 2004). Heterogeneous loss reactions of HO_2 at aerosols and reactions of HO_2 with halogen oxides (XO, $X =$ Br, I) were identified as possible processes, which might explain the low levels of measured HO_2 (Bloss et al., 2005a,b ; Kanaya et al., 2007a,b; Sommariva et al., 2006). Read et al. (2008) have demonstrated by long-term measurement ubiquitous presence of daytime IO and BrO at Cape Verde in the Atlantic Ocean. They show that the coupling of halogen and HO_x chemistry contributes about 50% to the observed ozone loss in the marine boundary layer and estimate a 5–12% enhancement of OH by halogen reactions in that region (see also Section 3.3.1). Further, interesting results on radical activity in winter (Fleming et al., 2006a) in the coastal marine environment have been observed.

Recent studies of atmospheric HO_x in rural and forested areas have revealed surprising results. A long-term record of OH was measured from 1999 to 2003 at Hohenpeissenberg Observatory in Southern Germany, which is influenced by anthropogenic and biogenic emissions (Rohrer and Berresheim, 2006). Data analysis has shown that the variability of the five-year record can be statistically explained mostly by one parameter, the photolysis frequency $j(O^1D)$ of the ozone to $O(^1D)$ formation. A similar high correlation between OH and $j(O^1D)$ had been observed before at different field sites on shorter time scales (days and weeks), with different slopes in different environments e.g.(Ehhalt and Rohrer, 2000; Eisele et al., 1997; Holland et al., 2003; Poppe et al., 1994; Rohrer and Berresheim, 2006). The analysis at Hohenpeissenberg demonstrates that the controlling factors of OH abundance may exhibit correlations, which can compensate substantially their influences on OH. Thus, neither a pronounced seasonal variation, nor a long-term trend in OH was observed at Hohenpeissenberg, besides the influence of solar UV (Rohrer and Berresheim, 2006). Surprisingly, the observed correlation of OH with $j(O^1D)$ was significantly better than with OH calculated by a full chemical model, pointing to an insufficiently understood self-stabilising behaviour of the atmospheric oxidation efficiency.

An unknown stabilising effect on atmospheric OH has been proposed for unpolluted air above the Amazonian rain forest in Surinam, where measured OH (up to 10×10^6 cm^{-3}) in the lower troposphere decreased much less than expected in the presence of high isoprene concentrations (Lelieveld et al., 2008) (Fig. 19). Measured-to-modelled OH ratios were found to increase from about unity at low isoprene ($<$200 pptV) to values greater than 10 at high isoprene mixing ratios of several ppbV (Kubistin et al., 2008). A similar trend of similar magnitude was reported by Ren et al. (2008), who measured much higher than predicted OH concentrations in the lower troposphere over forested regions in the US, consistent with previous tower-based field observations in a deciduous forest in northern Michigan (Tan et al., 2001). High OH concentrations were also measured in the Pearl-River Delta in Southern China, with average noontime values of 15×10^6 cm^{-3} in the presence of high VOC loads with significant isoprene contributions and low NO (Hofzumahaus et al., 2009). These OH observations are a factor 3–5 higher than expected from atmospheric box models. Reasonably good agreement was observed for measured and modelled OH at a forested site in Whiteface Mountain N.Y., USA, where isoprene made up a small fraction of the OH reactivity (Ren et al., 2006a). Overall, major uncertainties remain in the current understanding of OH and its dependence on VOCs in low NO_x environments.

Urban air pollution impairs human health, and plumes of large (mega)cities may influence air quality and climate on regional to global scales (e.g. (Molina et al., 2007), and references therein). For these reasons radical chemistry in urban environments has received growing attention in the last years (Elshorbany et al., 2008; Emmerson et al., 2007, 2005; George et al., 2005; Holland et al., 2003; Kanaya et al., 2007a,b; Martinez et al., 2003; Ren et al., 2006a,b; 2003; Shirley et al., 2006; Volz-Thomas et al., 2003). The atmospheric chemistry in large cities is significantly different from rural and remote environments due to large emissions of NO_x, CO, VOCs and oxygenated VOCs. As a result high levels of precursors and reactants of radicals are present with correspondingly large chemical turnover rates. For example, total OH reactivities were observed to reach values of 100 s^{-1} in Mexico City (Shirley et al., 2006) and Tokyo (Yoshino et al., 2006), which is two orders of magnitude larger than the reactivity in the remote atmosphere. Despite the large complexity of trace gas composition and the large

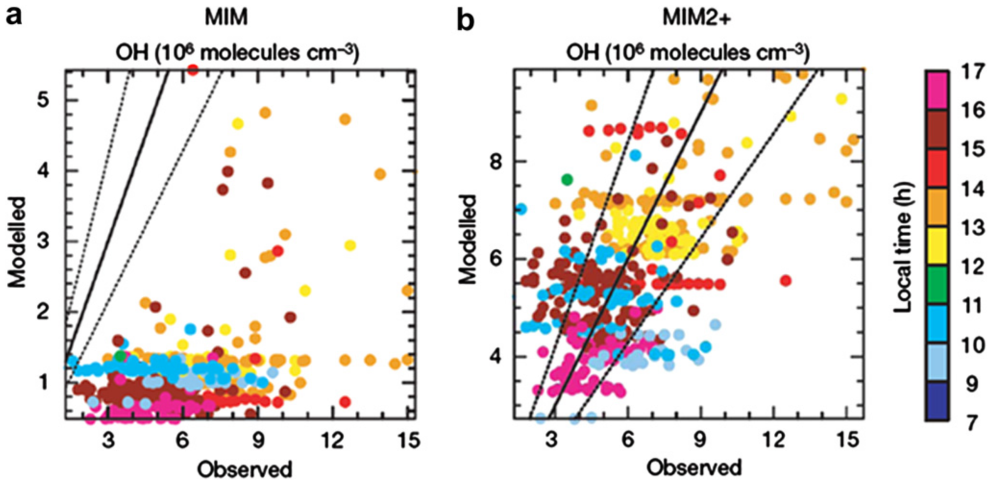


Fig. 19. Difference in OH in the boundary layer, calculated by including enhanced OH recycling in a model (Lelieveld et al., 2008) from data over Surinam.

variability of trace gas loads, summertime urban OH concentrations of (3–10) × 10^6 cm^{-3} were observed to be quite similar to values measured in the remote atmosphere (see (Kanaya et al., 2007a,b) and references therein). OH values were generally smaller in winter, but not as much as would be expected from the reduction of $j(O^1D)$ (Heard et al., 2004; Kanaya et al., 2007a; Ren et al., 2006b). The major primary sources of HO_x were identified to be the photolysis of HONO and aldehydes, ozonolysis of alkenes, and to less than 50% by photolysis of ozone e.g. (Alicke et al., 2003; Emmerson et al., 2005; Kanaya et al., 2007a,b; Ren et al., 2006a,b; Volkamer et al., 2007a,b). In general, the urban concentrations of OH and HO_2 are reasonably reproduced within a factor 2 by current atmospheric chemistry models. In some field studies, however, modelled HO_2 was significantly smaller than measured, in particular at high levels of NO, leaving uncertainty in the predictability of photochemical ozone production in city plumes (Martinez et al., 2003; Ren et al., 2006b).

3.1.4. Tropospheric ozone

Tropospheric ozone has a threefold importance. Ozone is a powerful greenhouse gas, producing an extra radiative forcing of 0.35 Wm^{-2}, about 20–25% of the human activity induced radiative forcing due to greenhouse gas changes. Ozone is also at the centre of atmospheric tropospheric gas phase photochemistry. It is the main source of hydroxyl radical, which drives the oxidizing capacity of the atmosphere, a key factor controlling, among other species, methane concentration. Finally, surface ozone is an oxidant that induces respiratory problems and is associated with premature human mortality (Bell et al., 2006; Gryparis et al., 2004), produces tree damage (Krupa and Manning, 1988), reduces photosynthesis and growth (Reich and Amundson, 1985) and therefore crop yields (Fiscus et al., 2005) (see also (Ashmore, 2005; Felzer et al., 2007) for recent reviews).

In remote regions, the overall tropospheric ozone concentrations result from a balance between chemistry and transport of precursors from polluted regions and from natural sources (biogenic VOC emissions, biomass burning, lightning) and deposition. In recent years, there has been significant evidence of large-scale, inter-hemispheric transport of ozone and precursors, over the Pacific ocean (Jacob et al., 1999; Jaffe et al., 1999), the Atlantic ocean (Lewis et al., 2007) and over the Eurasian continent (Wild et al., 2004) (see also Section 4.5). However, the largest ozone concentrations are found over continental (polluted) regions: eastern U.S., Europe and China.

The changing balance between ozone production and loss has changed during the 20th century, owing in the main to human activity resulting in a dramatic increase in background ozone concentrations (Volz and Kley, 1988). Ozone trends during the last 15–20 years appear less pronounced (Oltmans et al., 2006). In Northern mid-latitudes, a number of recent observational studies indicate slightly positive trends of background ozone from surface observations (Carslaw, 2005; Jaffe et al., 2003; Jenkin, 2008), ozonesonde (Naja et al., 2003) and airborne measurements from the MOZAIC (Measurement of ozone and water vapour by Airbus in service aircraft programme) (Marenco et al., 1998). However, a recent study of marine boundary layer concentrations in upwind European and American air found significant trends of about 0.5 ppbV $year^{-1}$ (see Fig. 20), a rate comparable to the average rate over the 20th Century (Parrish et al., 2009). In the tropics, measurements have also showed significant recent positive trends (Bortz and Prather, 2006).

At a regional scale contrasting trends have been reported from observations. In general, weak positive background ozone trends (Carslaw, 2005) compete with the effects of decreasing precursor emissions over continental areas (Jenkin, 2008; Jonson et al., 2006). High distribution percentiles decrease while low percentiles increase, as shown in Fig. 21 for the rural site of Lullington Heath in England (Jenkin, 2008). The decreasing trend of highest percentiles is compatible with the known emissions reductions since 1990 (Vautard et al., 2006a). In large cities the ozone trends can have a different behaviour, as ozone concentrations are largely limited by the presence of abundant NO. Mean ozone concentrations often have a positive trend in city centres owing to NO_x emission reductions (see Fig. 21). However, the decadal ozone trends in and around large cities have not yet seen much published work.

The regional structure of future ozone changes has been predicted in several modelling studies. Taking into account only emission control policies for the near future (2010 or 2020), several multi-model exercises have been conducted in support to the Clean Air For Europe programme (CAFE). The City Delta project (Cuvelier et al., 2007) aimed to predict the impact of emission reductions of several emission scenarios for 2010 and its uncertainty in several European cities. The same exercise was carried out at the larger scale of the European continent (EuroDelta: (van Loon et al., 2007)). At continental scale the efficiency of emission reductions was demonstrated but models provided a large spread of responses in city centres.

The impacts of two other major factors that influence future European ozone changes have also been investigated that is background ozone owing to global precursor emission increases and climate change. Background ozone increase leads to a rather

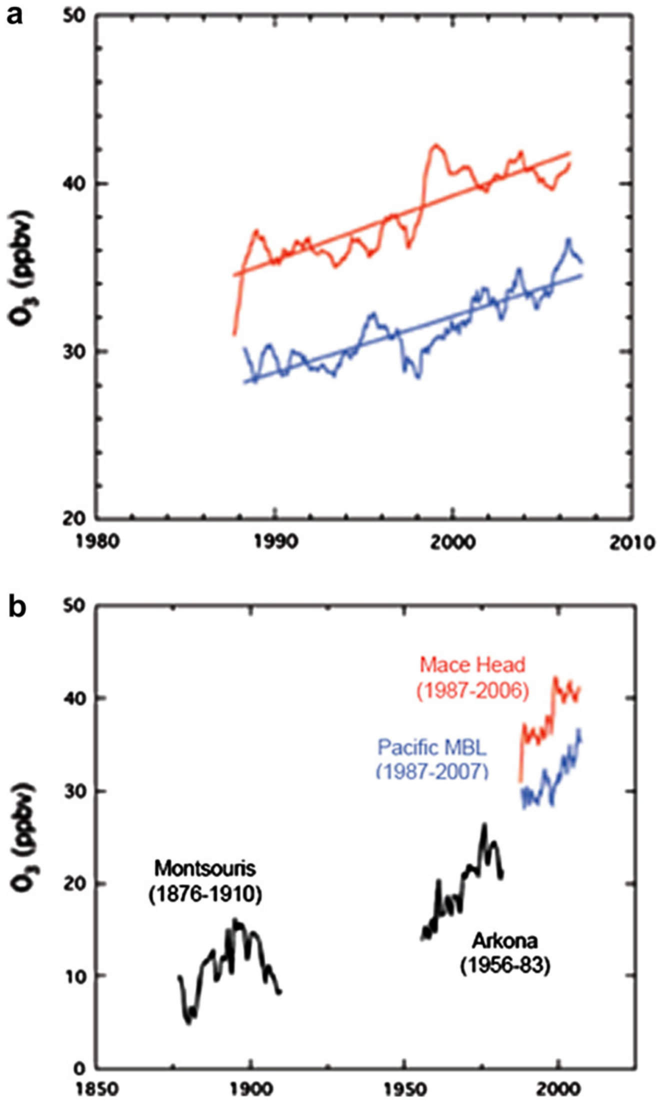


Fig. 20. (a) Comparison of the 12-month running mean O_3 concentrations from the Pacific MBL sites and Mace Head, Ireland. (b) Comparison of the running annual mean O_3 concentrations from this work with the annual averages of earlier measurements reported from two European sites by Volz and Kley (1988) (Parrish et al., 2009).

uniform regional surface ozone increase (see Fig. 35). The combination of this trend with the effect of European emission reductions leads to a divergent picture (Szopa et al., 2006). Several other studies focused on the regional impact of climate change only, and found a general increase of ozone concentrations owing to increasing biogenic emissions and shortwave radiation (Forkel and Knoche, 2005; Meleux et al., 2007; Mickley et al., 2004).

During the last ten years, the development of regional air quality models reached an operational or quasi-operational stage for ozone forecasting. After the pioneering experimental forecasts carried out by Tilmes et al. (2002) fully operational systems have been designed and evaluated over several years (Honoré et al., 2007). The GEMS European project also offered a framework to coordinate several European forecasting efforts and modelling groups. The simultaneous use of an ensemble of several regional air quality models for forecasting ozone concentrations has been evaluated (Delle Monache and Stull, 2003). For ozone simulation the use of ensembles seem to provide a fair representation of uncertainty, either using one model with perturbed parameters (Mallet and Sportisse, 2006) or using several different models developed independently (Vautard et al., 2006b). Uncertainty in emission scenario analysis at urban scale has also been tackled using Bayesian Monte-Carlo techniques (Deguillaume et al., 2008).

Effort has also been put on analysing the sensitivity of ozone production to factors like biogenic emissions using state of the art inventories and methodologies (Curci et al., 2009) or to the speciation of NO_x emissions and in particular the fraction of nitrogen dioxide and HONO (Jenkin et al., 2008).

Future global ozone changes will be driven by changes in precursor *global emissions* and by changes in *climate* (e.g. temperature, humidity, general circulation and mixing, clouds). Despite the fact there is now a significant body of literature on this subject, the future prediction of these drivers and their relative contributions to changes in atmospheric composition still have significant uncertainties (IPCC, 2007). A global increase of all primary emissions is predicted for the next decades, especially owing to the massive economic development and population increase in several developing countries (see Section 3.3.6). Without considering climate impacts, global air quality is predicted to worsen with the pollutant background concentrations increasing, in particular ozone.

The increase in temperature and water vapour tends to reduce the ozone burden, especially in tropical and equatorial areas. However, drought increase in sub-tropical and southern/central mid-latitudes should increase photochemistry and therefore ozone concentrations. Direct dynamical and chemical effects of climate change impact the concentration of ozone and primary pollutants

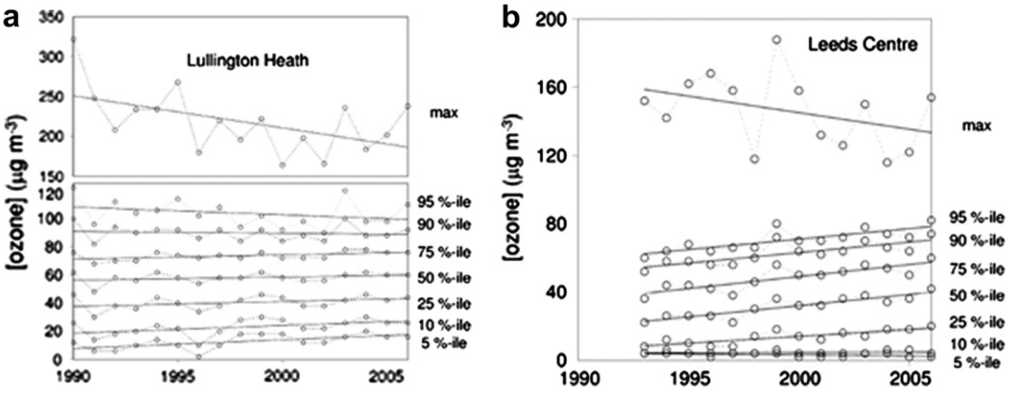


Fig. 21. Trend in hourly mean ozone distribution centiles at Lullington Heath (left) and Leeds Centre (right), based on data over the respective periods 1990–2006 and 1993–2006. Solid lines are linear regressions of data indicating the average trend over the period. After Jenkin (2008).

through changes in various other processes like atmospheric stability and stratospheric ozone intrusion (Hauglustaine et al., 2005; Rind et al., 2001; Zeng and Pyle, 2003). In addition to these processes involving changes and dynamics and atmospheric temperature, climate change can also affect atmospheric composition through perturbations of natural emissions of precursors. This is particularly the case for lightning NO_x, (Brasseur et al., 2006) biogenic emissions of volatile organic compounds (Lathiere et al., 2005; Sanderson et al., 2003) and emissions of nitrogen oxides by microbiological activity in soils. Even more indirect effects of climate change can influence future ozone concentrations like changes in methane emissions from flooded areas, changes in dry deposition owing to turbulence or vegetation evolution, changes in fire frequency. The proxy for climate change afforded by the recent studies of heat waves is discussed in Section 3.3.5.

3.1.5. Isotope chemistry

Measurement and modelling of isotopically-substituted molecules has become a major research area in atmospheric chemistry. The isotopic composition of trace gases and aerosols provides unique information on their origin, chemistry and transport, complementary to mere concentrations. Different isotopologues (molecules that differ only in their isotopic composition (Coplen, submitted for publication)) behave chemically in the same way, but their production and loss timescales vary by a few percent or less. This leads to small, but measurable changes in their characteristic isotopic composition (also known as "isotopic fingerprint" thanks to forensic applications including food authentication). Clearly, atmospheric isotope measurements are not restricted to the gas phase, but are increasingly used for particulates notably nitrate, sulphate and carbonaceous aerosols. Isotope measurements are not restricted to modern samples; rocks and other geological deposits as well as air and particles extracted from ice-core and firn samples offer a unique window into the climate and atmospheric chemistry of the past.

As noted by Brenninkmeijer et al. (2003), three main thrusts govern research in atmospheric isotope chemistry. Foremost, is the desire to obtain additional constraints on problems related to atmospheric chemistry itself. Secondly, atmospheric isotope measurements cross-fertilise discoveries in related fields, notably the strong anomalous isotope effect in ozone formation. Finally, methodological advances in measurement techniques often open up new scientific questions, for example the coupling of gas chromatography and isotope ratio mass spectrometry (Matthews and Hayes, 1978) or the development of position-dependent $^{15}N/^{14}N$ isotope ratio analysis in N_2O (Rockmann et al., 2000; Toyoda and Yoshida, 1999).

General reviews of the topic are available (Johnson et al., 2002; Brenninkmeijer et al., 2003; Gros et al., 2004) as well as reviews on volatile organic compounds (Goldstein and Shaw, 2003; Rudolph, 2007) and on non-mass dependent isotope effects (Mauersberger et al., 2003; Thiemens, 2006). Schinke et al. (2006) has reviewed progress in understanding the isotope effect in ozone formation. Atmospheric isotope measurement techniques are discussed in Laj et al. (2009). IUPAC has adopted a recommendation on isotope-related terms (Coplen, in press).

Atmospheric O_3 has large relative $^{17}O/^{16}O$ and $^{18}O/^{16}O$ enrichments ($>60‰$) compared to the source gas O_2, which is created by O_3 formation via $O + O_2 + M$ and O_3 photolysis. Since many atmospheric species (e. g., NO_x, NO_3^-, SO_4^{2-}, ClO_x, BrO_x, stratospheric CO_2, even O_2 itself) are formed or affected by reactions involving O_3, they inherit part of the "isotopic fingerprint" from O_3, which allows the tracing of these species through the atmosphere to study their reactions and transport. An important aspect of O_3 isotope chemistry is the non-mass dependent fractionation during its formation. Based on the mass differences between ^{17}O and ^{16}O and between ^{18}O and ^{16}O, one would expect to find approximately half the relative isotope ratio difference for $^{17}O/^{16}O$ ($^{17}\delta$) than for $^{18}O/^{16}O$ ($^{18}\delta$), using atmospheric O_2 as a reference. However, in O_3 and many other species, deviations from such a mass-dependent relationship occur. These deviations can be expressed as (Kaiser, 2008), but other definitions are also in use (Angert et al., 2003; Farquhar et al., 1998; Thiemens et al., 1995). The value of $l = 0.528$ is based on the meteoric water relationship between $^{17}\delta$ and $^{18}\delta$ (Barkan and Luz, 2005; Meijer and Li, 1998).

Fig. 22 shows measurements of the isotopic composition of many atmospheric species, most of which have non-zero $^{17}\Delta$ values

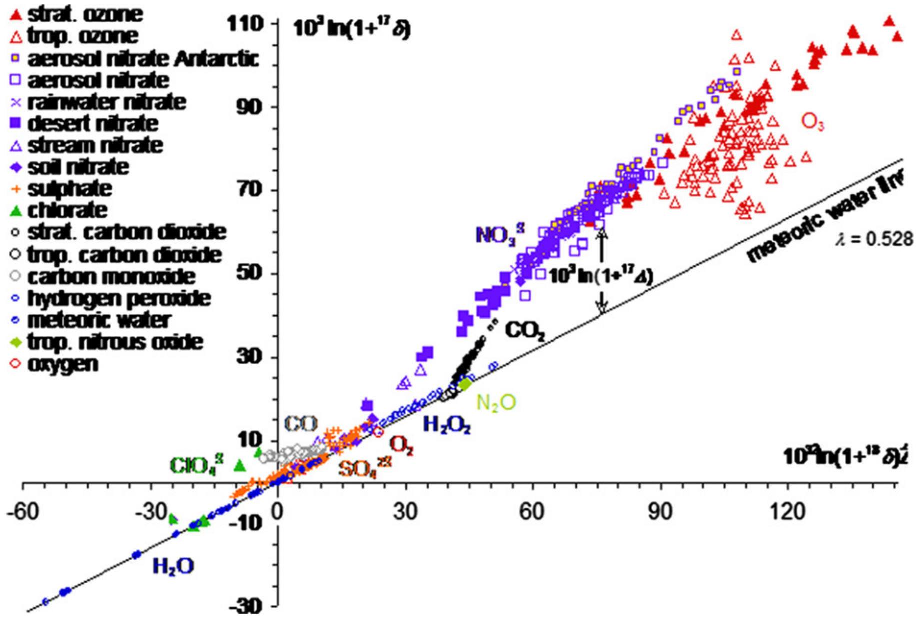


Fig. 22. Three-isotope plot of relative oxygen isotope ratio differences in atmospheric gases and aerosols, using Vienna Standard Mean Ocean Water (VSMOW) as a reference. Note that $\ln(1 + {}^{17}\delta) \approx {}^{17}\delta$, $\ln(1 + {}^{18}\delta) \approx {}^{18}\delta$ and $\ln(1 + {}^{17}\Delta) \approx {}^{17}\Delta$. The meteoric water line $\ln(1 + {}^{17}\delta) = l \ln(1 + {}^{18}\delta)$ with $l = 0.528$ (Meijer and Li, 1998; Barkan and Luz, 2005) is shown for comparison.

due to interaction with O_3. The only exceptions are water ($^{17}\Delta = 0$) and CO ($^{17}\Delta > 0$ due to reaction of CO + OH).

Stable sulphur isotopes ^{32}S, ^{33}S, ^{34}S and ^{36}S (Farquhar et al., 2000; Ono et al., 2006) can be used, as before the establishment of the stratospheric O_3 layer, shortwave UV radiation was responsible for non-mass dependent sulphur fractionation during SO_2 photolysis. The products of this reaction were partitioned into different sulphur species of sufficient lifetime that prevented immediate recycling to SO_2 and allowed incorporation into rocks. Sulphur isotope anomalies found in rocks therefore provide unique insights into O_2 and O_3 concentrations of the distant geological past (>2 Ga ago). The same partitioning can still occur even in the modern atmosphere during stratospheric volcanic eruptions (Baroni et al., 2007).

Many applications of isotope measurements involve using isotopic fingerprints of individual sources to improve budget estimates. For example, ^{14}C ("radiocarbon") is useful to distinguish fossil fuel emissions ("dead carbon" with no ^{14}C) from biomass burning or biogenic emissions (with "modern" ^{14}C abundance). Isotopic fingerprints of different sources often overlap, so that additional constraints are used or different isotopes are combined (e.g. in case of CO, ^{13}C, ^{14}C, ^{17}O and ^{18}O provide four independent constrains in addition to concentrations). However, it is important to realise that isotopes can tell us not only about sources and sinks, but also about atmospheric lifetimes, partitioning between atmospheric reactions, gas-to-aerosol conversion and the atmosphere in the recent and distant geological past, reaction kinetics, deficiencies of kinetic theories, etc. They are also useful to infer rates of atmospheric transport and mixing, e.g. stratosphere-troposphere exchange using $^{17}\Delta(CO_2)$ or water isotopes.

Several directions are evolving as foci of future isotope research in atmospheric chemistry. CO_2 isotope measurements can be expected to continue to grow as the number of monitoring stations around the globe operated by networks such as CARBO-EUROPE or the US NOAA laboratories is expanding. Only few groups currently analyse isotopes in VOCs, including formaldehyde, but this is likely to change and, arguably, may include more "exotic" isotope ratios such as $^{2}H/^{1}H$ and $^{37}Cl/^{35}Cl$. Work will increase on aerosols, especially nitrate, sulphate and carbonaceous aerosols, with the latter probably seeing more chemistry-related applications instead of just conventional budget calculations. Remote sensing of isotopic compounds, including satellite-based measurements, is an emerging field with the prospect of becoming to become a major player, especially in case of atmospheric water vapour (Herbin et al., 2007).

3.2. *Aerosol*

3.2.1. *Overview of aerosol types, sources, atmospheric burdens and processing*

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven, industrial or traffic-related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, micro-organisms, pollen, etc.). Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere and/or condensation of gaseous compounds on pre-existing aerosol particles.

As illustrated in Fig. 23, airborne particles undergo various physical and chemical interactions and transformations, that is, changes of particle size, structure, and composition (coagulation, restructuring, phase transitions, gas uptake, chemical reactions (Pöschl et al., 2007)). Many chemical reactions also occur in clouds, which are formed by condensation of water vapour on pre-existing aerosol particles (cloud condensation and ice nuclei, CCN and IN). Most clouds re-evaporate, and modified aerosol particles are again released from the evaporating cloud droplets or ice crystals (cloud processing). If, however, the cloud particles form precipitation that reaches the Earth's surface, not only the condensation nuclei but also other aerosol particles are scavenged on the way to the surface and removed from the atmosphere. This process, termed "wet deposition", is the main sink of atmospheric aerosol particles in the accumulation mode (ca. 0.1–1 μm). Particle deposition without precipitation of hydrometeors (airborne water particles), that is, "dry deposition" by convective transport, diffusion, and adhesion to the Earth's surface, is less important on a global scale, but is highly relevant with respect to local air quality and health effects (inhalation and deposition in the human respiratory tract). Depending on aerosol properties and meteorological conditions, the characteristic residence times (lifetimes) of aerosol particles in the atmosphere range from hours to weeks (Pöschl, 2005).

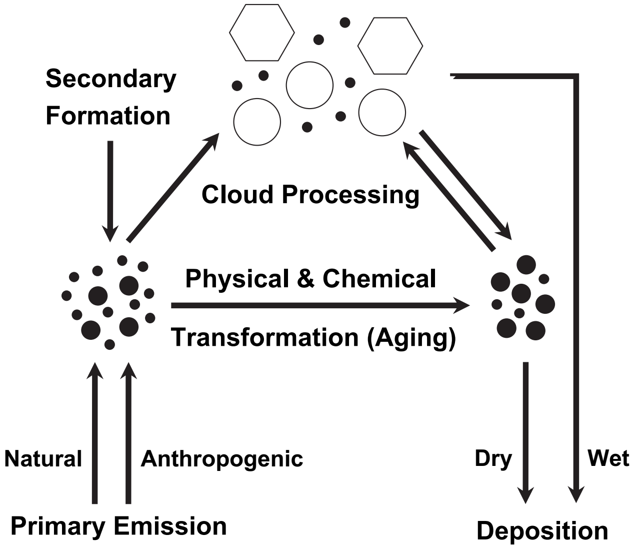


Fig. 23. Primary emissions, secondary formation, and atmospheric processing of natural and anthropogenic aerosols (Fuzzi et al., 2006; Pöschl, 2005).

An overview of major types, sources, emission rates and mass burdens of atmospheric aerosols is given in Tables 3 (adapted from (Andreae and Rosenfeld, 2008)). For all types of aerosols, except sea salt and mineral dust (desert/soil), the sources are mostly anthropogenic (i.e. directly related to human activities) or biogenic (i.e. related to the biosphere), although these categories are not mutually exclusive (e.g. biogenic SOA has an anthropogenic component (Kanakidou et al., 2000)). With respect to both sources and atmospheric burden, the best estimate values given in Table 3 are clearly higher for anthropogenic aerosols than for biogenic aerosols (ratios of 3:1 and 3:2, respectively) (See Section 3.2.3.2 for a discussion of recent, and much higher estimates of the BSOA contribution).

The concentration, composition, and size distribution of atmospheric aerosol particles are temporally and spatially highly variable. In the lower atmosphere (troposphere) the total particle number and mass concentrations typically vary in the range of about 10^2–10^5 cm^{-3} and 1–100 $\mu g\ m^{-3}$, respectively. In general, the predominant chemical components of air particulate matter (PM) are sulphate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon, each of which typically contribute about 10–30% of the overall mass load. At different locations, times, meteorological conditions, and particle size fractions, however, the relative abundance of different chemical components can vary by an order of magnitude or more (Fuzzi

Table 3
Major types, sources and mass burdens of atmospheric aerosols (adapted from (Andreae and Rosenfeld, 2008)).

	Mass emission	Mass emission	Mass emission	Mass Burden
	"Best"	Min	Max	
	Tg a^{-1}	Tg a^{-1}	Tg a^{-1}	Tg
Carbonaceous aerosols				
Primary organic (0–2 μm)	95	40	150	1.2
Biomass burning	54	26	70	–
Fossil fuel	4	3	9	–
Biogenic	35	15	70	0.2
Black carbon (0–2 μm)	10	8	14	0.1
Open burning & biofuel	6	5	7	–
Fossil fuel	4.5	3	6	–
Secondary organic	28	2.5	83	0.8
Biogenic	25	2.5	79	0.7
Anthropogenic	3.5	0.05	4.0	0.08
Sulphates	200	107	374	2.8
Biogenic	57	28	118	1.2
Volcanic	21	9	48	0.2
Anthropogenic	122	69	214	1.4
Nitrates	18	12	27	0.49
Industrial/Road Dust	100	40	130	1.1
Sea salt				
$d < 1$ μm	180	60	500	3.5
d=1–16 μm	9940	3000	20,000	12
Total	10,130	3000	20,000	15
Desert/Soil dust				
d <1 μm	165	–	–	4.7
d =1–2.5 μm	496	–	–	12.5
d =2.5–10 μm	992	–	–	6
Total	1600	1000	2150	18 ± 5
Anthropogenic total	312	158.1	467	3.1
Biogenic total	117	45.5	267	2.1

et al., 2006; Pöschl, 2005) In recent years, the widespread deployment of on-line instrumentation for aerosol composition measurement (see (Laj et al., 2009)) has led to the discovery that inorganic components (mostly sulphate, nitrate and ammonium) and a large variety of organic species dominate the mass of fine (sub-μm) particulate material. Assembling aerosol mass spectrometer (AMS) fine particulate mass data from 37 field campaigns in different parts of the world, Zhang et al. (2007) demonstrated that organic components always provided a significant fraction of the non-refractory aerosol mass at all locations that have been sampled (see Fig. 24).

3.2.2. Inorganic aerosol

Sulphate and nitrate are major constituents of the atmospheric aerosol. As an example, Fig. 25 shows the average chemical composition of PM_{10} in Zurich, Switzerland. Both components are formed i.e. not emitted in the atmosphere by oxidation of the gaseous precursors SO_2 and NO_x, respectively (exceptions are the emission of sea salt containing sulphate or of gypsum during construction activities).

For both nitrate and sulphate, there is a gas phase and multiphase route in the formation of sulphuric and nitric acid. As an example, gas phase sulphate formation contributes an average of 27% to the total sulphate production according to the AEROCOM comparison (Textor et al., 2007). While the gas phase reaction involves OH radicals, the multiphase reaction proceeds with various oxidation agents, most importantly H_2O_2 and O_3, after the uptake of SO_2 into cloud droplets, or the uptake and subsequent hydrolysis of N_2O_5 in the liquid phase. Sulphuric acid has a very low saturation vapour pressure and is therefore preferably found in the particulate phase. Depending on the availability of ammonia, sulphuric acid is neutralized to a variable extent (i.e. H_2SO_4, NH_4HSO_4, $(NH_4)_2SO_4$). The saturation vapour pressure of nitric acid is much higher, therefore the partitioning of nitric acid depends very much on the availability of NH_3 (formation of NH_4NO_3), the relative humidity, and temperature. For this reason, ammonium nitrate concentrations are typically substantially higher in winter, when

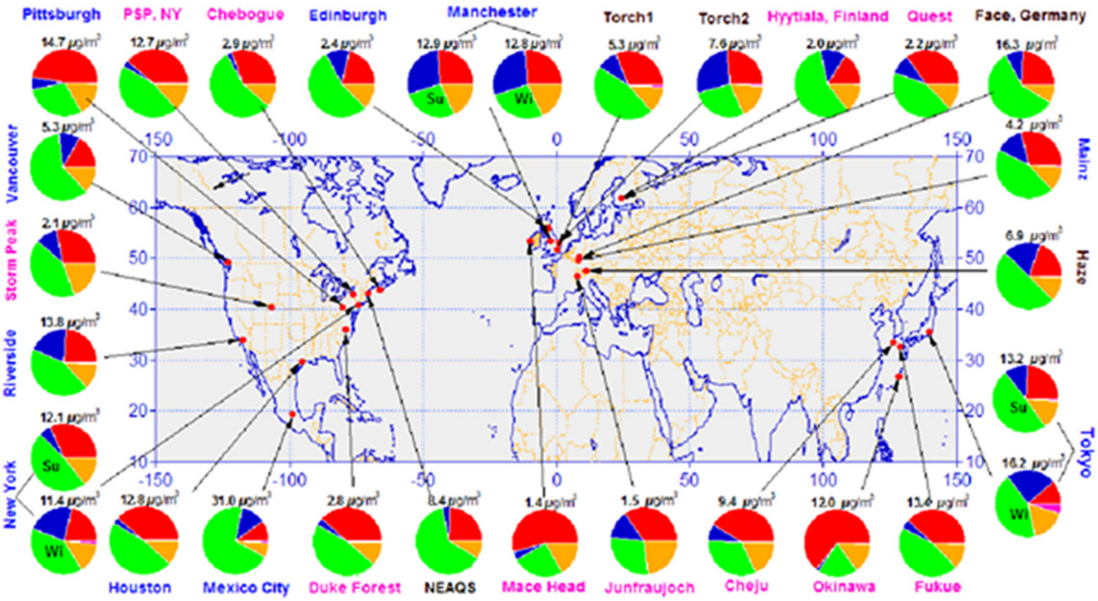


Fig. 24. Global map of aerosol mass spectrometer datasets of aerosol PM_1 composition. Colours for the study labels indicate the type of sampling location: urban areas (blue), <100 miles downwind of major cites (black), and rural/remote areas >100 miles downwind (pink). Pie charts show the average mass concentration and chemical composition: organics (green), sulphate (red), nitrate (blue), ammonium (orange), and chloride (purple). From (Zhang et al., 2007).

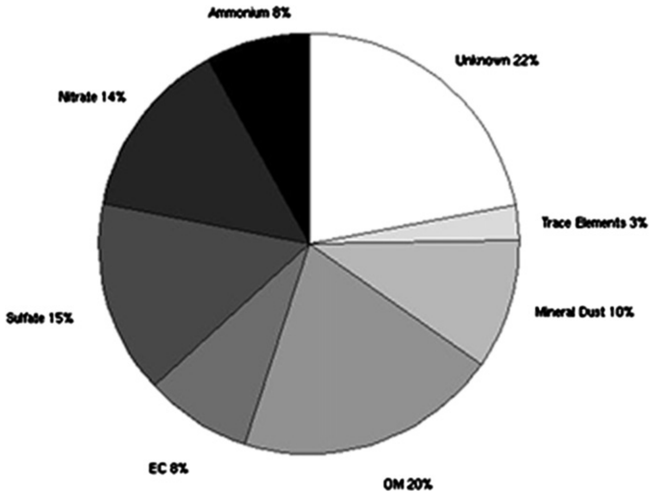


Fig. 25. Average chemical composition of PM_{10} from Zurich, Switzerland (from (Baltensperger and Prevot, 2008); data from (Hueglin et al., 2005)).

temperatures are lower, than in summer (Hueglin et al., 2005). Sulphuric acid is neutralized by ammonia always before nitric acid, therefore, nitric acid tends to remain in the gas phase at sites with limiting ammonia concentrations. On the other hand, nitric acid can also be neutralized by basic components in mineral dust, which is mainly found in the coarse mode. This nitrate is, unlike ammonium nitrate, non-volatile and therefore coarse mode nitrate is often found at dry places with considerable anthropogenic pollution. As an example, Perez et al. (2008) reported relatively high levels of mineral dust and a high proportion of coarse nitrate as PM patterns peculiar to Barcelona when compared with central and western European urban sites.

Putaud et al. (2004) reported a general decrease for sulphate at several European stations over the time periods from 1991 to 2001, with a considerable year-to-year variability (up to >30%). In contrast, there was no clear long-term trend in the concentrations of the sum of nitric acid and nitrate. In southern England the ratio of nitrate to sulphate increased over the years by a factor of 2.5 (Lee et al., 1999). In the Netherlands the change in the ratio, since 1980, is similar. The absolute change in sulphate levels since measurements started in the 1970’s is close to a factor of four (Janssen et al., 1998).

The decreasing sulphate trends are a direct result of the decrease in the precursor gas (SO_2) over the past few decades. This implies, however, that more ammonia ought to be available for the neutralization of nitric acid. This may result in increased ammonium nitrate concentrations as a result of decreased SO_2 emissions, even at constant NO_x emissions (Bauer et al., 2007). Ammonia concentrations can therefore be an important factor in determining the particulate nitrate concentrations. Deutsch et al. (2008) also stressed the importance of ammonia emissions in the formation of secondary particulate matter, and suggested that future emission abatement policy should consider more the role of ammonia in the formation of secondary particles. A decrease in the ammonia emissions, would not only result in a decrease of the particulate nitrate concentration, but also in a decrease of the total nitrate concentration: nitric acid has a higher dry deposition velocity, resulting in a shorter residence time in the atmosphere compared to particulate nitrate.

The same effects are seen in the vertical profiles of nitrate and sulphate: while the two components are available in similar concentrations at low altitude sites (Hueglin et al., 2005; Zhang et al., 2007), sulphate is by far more abundant than nitrate at higher elevation, owing to the strong decrease of the ammonia concentration with increasing altitude ((Cozic et al., 2008) and references therein).

3.2.3. Organic aerosol

Organic aerosol (OA) mass can contribute 30–70% to the total aerosol mass (Zhang et al., 2007), yet the exact sources, formation processes and composition are poorly understood. The organic component of aerosols can be emitted into the atmosphere directly as primary aerosol (POA) or formed by *in-situ* chemical reactions (secondary aerosol – SOA) of their precursor volatile organic compounds (VOC). SOA is an important fraction of organic aerosol that has recently been incorporated into global models and is relevant at both local and global scales.

Distinguishing between the POA and SOA is critical for the protection of the environment since primary emissions can be controlled, in contrast to the secondary sources that are influenced by biogenic emission and photochemistry and therefore are difficult to regulate. In addition, it is now recognized that a significant part of POA evaporates and reacts chemically in the gas phase leading to additional aerosol mass (Donahue et al., 2006; Robinson et al., 2007). This aged primary aerosol has secondary aerosol chemical characteristics since it contains oxygenated molecules although it is not part of what has been ‘traditionally’ referred to as SOA. This will be further referred to as aged POA.

3.2.3.1. Primary biogenic aerosols (PBA). One of the most uncertain aspects in current aerosol research is the abundance and effects of primary biogenic aerosols (PBA), which are emitted directly from the biosphere to the atmosphere. Examples of PBA particles are pollen, bacteria, fungal and fern spores, viruses, and fragments of animals and plants. PBA components comprise the non- or semi-volatile chemical substances contained in PBA particles as well as the biogenic substances contained in other types of aerosol particles such as soil dust, sea-spray, etc. Pollen grains, fern spores, large fungal spores, and other large PBA particles such as pollen typically belong to the coarse fraction of air particulate matter, with aerodynamic diameters up to one hundred micrometers. Such large particles can be particularly important as giant CCN and IN. PBA particles and components are, however, also found in intermediate and fine fractions of air particulate matter, with aerodynamic diameters less than 10 µm (PM_{10}), 2.5 µm ($PM_{2.5}$), and 1 µm (PM_1). Fungal spores, bacteria, viruses, carbohydrates, proteins, etc. are frequently detected in the micron and sub-micron size range, i.e. in the respirable fraction of air particulate matter which is most relevant for health effects and interactions with gaseous pollutants (Després et al., 2007; Franze et al., 2003; Pöschl, 2005; Pöschl et al., 2007). Marine primary biogenic particles are discussed in the companion paper by Fowler et al. (2009). In summary, marine primary biogenic particles result from the enrichment of the sea surface layer and resulting spray droplets in organic matter (O’Dowd et al., 2004). The enrichment is dominant in sub-micron sizes, increasing to greater than 80% for the smallest sizes of the order of 80–100 nm. Supermicron aerosol enrichment amounts to 3–4% of the sub-micron mass but account for approximately 50% of the total primary organic aerosol mass. Submicron organic matter was almost entirely water-insoluble and consisted of colloids and aggregates exuded by phytoplankton (Facchini et al., 2008).

The occurrence and dispersion of viable PBA particles like bacteria and spores in the air has been discussed and investigated very early in the history of aerosol science. Since then, aircraft, balloon, and rocket measurements have shown that PBA are not only ubiquitous over land and oceans but also transported to high altitudes (up to 80 km) and over long distances (Elbert et al., 2007). PBA were found to account for ~30% and more of fine and coarse particulate matter in rural continental air ($PM_{2.5}$; (Hock et al., 2008)) and in tropical rain forest air (PM_{10}, (Elbert et al., 2007)), where they dominate not only the organic fraction but also the abundance of certain inorganic species like potassium. Penner (1995) has estimated that plant fragments and micro-organisms contribute 56 Tg yr^{-1} to the global emission rate of fine particulate matter (<2.5 μm) and recently Janenicke (Jaenicke, 2005) has estimated that PBA emissions from the biosphere may amount to ∼1000 Tg yr^{-1}, which would be of the same order of magnitude as the emission estimates for mineral dust (∼2000 Tg yr^{-1}).

Several studies have shown that fungal spores account for a major fraction of PBA particles. They occur typically with number and mass concentrations on the order of 10^4 m^{-3} and 1 μg m^{-3} in continental boundary layer air (Elbert et al., 2007; Fröhlich-Nowoisky et al., 2009) and account for up to ∼10% of OC and ∼5% of PM_{10} at urban and sub-urban locations (Bauer et al., 2008). From spore counts and molecular tracers, Elbert et al. (2007) have derived a global emission rate of ∼50 Tg yr^{-1} for fungal spores, corresponding to an average emission flux of 200 m^{-2} s^{-1} over land surfaces. Comparison with estimated rates of emission and formation of other major types of organic aerosol (47 Tg yr^{-1} of anthropogenic primary organic aerosol; 12–70 Tg yr^{-1} of secondary organic aerosol; 3–25 Tg yr^{-1} for anthropogenic secondary organic aerosol; (Kanakidou et al., 2005; Volkamer et al., 2006)) shows that emissions from fungi should be taken into account as a significant global source of organic aerosol.

The atmospheric abundance and environmental effects of PBA particles are particularly pronounced in tropical regions, where both the biological activity at the Earth's surface and the physicochemical processes in the atmosphere are particularly intense and important for the Earth system and global climate (absorption and scattering of radiation, chemical reactions and oxidative self-cleaning of the atmosphere, formation of clouds and precipitation, etc.). The use of micro-organisms as biocontrol agents might lead to a man-made increase of PBA. Moreover, global warming and increasing CO_2 concentrations might enhance the emissions and abundance of PBA, influence cloud condensation, ice nucleation and the hydrological cycle, and provide a feedback to climate change (Deguillaume et al., 2008; Elbert et al., 2007; Fröhlich-Nowoisky et al., 2009; Junge and Swanson, 2008; Möhler et al., 2007; Morris et al., 2008).

3.2.3.2. Secondary organic aerosols. The emissions of VOC, mainly from terrestrial vegetation (biogenic VOC; BVOC), are 10 times larger than those of anthropogenic VOC (AVOC) (Heald et al., 2008a; Tsigaridis and Kanakidou, 2007). The gas phase emissions of reactive VOC exceed by more than a factor of 20 the amount of carbon that is directly emitted into the atmosphere in the form of particles. An unspecified part of the VOC emissions into the atmosphere is converted to semi-volatile organics that form secondary organic aerosol. Several studies pointed out the large number of detected organics in the troposphere and the potentially existing but still unknown compounds that could form significant amounts of SOA.

Goldstein and Galbally (2007) estimated a global SOA production of between 140 and 910 Tg C yr^{-1}, the wide range partly reflecting different methodologies. This estimate has recently been revised by Hallquist et al. (2009), with a new best estimate for SOA of 88 Tg C yr^{-1} (range 0–180). This is higher than the estimates presented previously for BSOA (Table 3), and higher than the 3–25 Tg C yr^{-1} Volkamer et al. (2006) estimated from anthropogenic VOC. A number of model simulations have reinforced this view of a dominant BSOA contribution (Gaydos et al., 2007; Kleeman et al., 2007). Although some studies, typically focused on densely populated areas, suggest that primary anthropogenic sources and ASOA may contribute substantially to summertime OC levels (Henze and Seinfeld, 2006), many other studies suggest that BSOA dominates strongly on the regional scale (at least in summertime) ((Kanakidou et al., 2005; Simpson et al., 2007a) and references therein), and many global model studies simply assume that all SOA is biogenic e.g. (Henze and Seinfeld, 2006). Recently, Goldstein et al. (2009) has revisited the distinction between biogenic and anthropogenic emissions proposing a link between them for the formation of SOA.

Probably the most reliable estimates of the biogenic contribution to OC comes from measurements of ^{14}C, in combination with other chemical markers. ^{14}C measurements, indicated by the 'fraction of modern carbon' (fM) ((Szidat et al., 2006) and references within), give an indication of the amount of 'modern' carbon in a sample, as opposed to the carbon associated with fossil fuels. The main complications in interpreting fM values are (a) to know whether the modern carbon is from primary (e.g. cooking, semi-volatile VOC from wood-burning, or BPAP discussed above), or from secondary sources (BSOA), (b) to account for the complications induced by the atomic bomb tests (which give a varying fM value for different ages of wood). Usage of chemical markers such as levoglucosan, cellulose, sugars, or GC/MS analysed VOC profiles are required to help resolve these issues.

Szidat et al. (2006) found that fossil fuel combustion accounts for ca.30% of OC in Zurich, Switzerland, throughout the year, even in the city centre. Biomass burning in wintertime and SOA in summertime seem to account for the majority of the remaining OC. At two Alpine valleys, the wintertime contribution of non-fossil sources to OC was 88% and 65% inside and outside of the villages, respectively, much of this attributed to wood-burning (Szidat et al., 2007). The EU CARBOSOL Project (Legrand and Puxbaum, 2007) combined weekly measurements of EC, OC, inorganic ions, elemental composition, levoglucosan, cellulose and radioactive tracers across a network of six sites in southern-central Europe. It was found that wintertime residential wood burning is a significant contributor to measured PCM levels at all CARBOSOL sites, whereas in summertime another modern-C source, likely biogenic SOA, is the dominant contributor (Gelencser et al., 2007; Simpson et al., 2007a).

In the United States, a recent study found that modern carbon accounted for about 50% of carbon at 2 urban sites, 70–97% of carbon at 4 near-urban sites, and 80–100% of carbon and six remote sites, as annual averages (Schichtel et al., 2008). Finally, some recent studies have suggested that BSOA may be linked to anthropogenic emissions. Both de Gouw et al. (2005) and Weber et al. (2007) found that signals of SOA formation correlated very well with anthropogenic markers, but that this finding conflicts with ^{14}C evidence that suggest a mainly biogenic origin for carbon at the study-locations. The authors suggested that the findings could be reconciled if SOA formation from biogenic VOC was enhanced by anthropogenic emissions.

The above studies highlight gaps in knowledge of chemical degradation pathways that is reflected in absence of mass closure and chemical characterization of all the products in chamber experiments. The state of the art of our understanding of secondary organic aerosol formation in the atmosphere has been recently reviewed (Fuzzi et al., 2006; Hallquist et al., 2009; Heald et al., 2008a,b,; Kanakidou et al., 2005). However, fast progress has been made in the past few years particularly with regard to the unidentified SOA precursors, to the NO_x dependence of aerosol yields from VOC oxidation, to oligomer formation (Jang et al., 2002; Kalberer et al., 2004) and to multiphase chemistry involvement in SOA build-up in the atmosphere.

Although isoprene and benzene are thought to be key to the SOA formation in the troposphere (Henze and Seinfeld, 2006; Henze et al., 2007; Jang et al., 2002), consideration of other precursor molecules such as semi-volatile compounds is needed to reconcile model results with observations. The non linearity in VOC oxidation and SOA formation promoted kinetic studies on the NO_x dependence of aerosol yields under ‘more realistic’ NO_x levels (Presto et al., 2005). These studies suggest classification of the NO_x dependence behaviour of various VOCs forming SOA into two main categories: i) those that show positive dependence (like n-alkanes: (Lim and Ziemann, 2005)); and sesquiterpenes (Ng et al., 2007a) owing to the formation of low volatility organic nitrates and/or the isomerisation of large alkoxy radicals leading to less volatile products under high NO_x conditions and ii) those that show negative dependence of aerosol yields to the NO_x levels, indicating formation of higher volatility organic products (nitrates) under high NO_x conditions (like monoterpenes, isoprene and aromatics; (Ng et al., 2007b; Presto et al., 2005)). Tsigaridis et al. (2006) found NO_x-dependent aerosol yields from VOC oxidation based on observations (Presto et al., 2005; Song et al., 2005) and calculated a reduction by about 20% in the chemical production of biogenic SOA whereas the NO_x dependence increased the anthropogenic SOA by about the same percentage. Sesquiterpenes are very reactive BVOC and, similarly to the high molecular weight n-alkanes, behave differently with regard to NO_x, and are thus more efficient SOA producers under polluted conditions. They have to be separately considered for SOA global modelling.

The chemical ageing of particles via multiphase reactions (Chen et al., 2007; Gelencser and Varga, 2005; Liggio et al., 2007; Lim et al., 2005; Lim and Ziemann, 2005; Loeffler et al., 2006; Rudich, 2003; Sorooshian et al., 2007; Zahardis and Petrucci, 2007) and evaporation and subsequent oxidation in the gas phase and condensation (Robinson et al., 2007) could significantly increase OA mass in the troposphere. The importance of these processes on global SOA budget estimates remains to be determined. It is a challenge to derive the SOA mass from field observations since *in-situ* measurements often do not discriminate between aged POA and SOA. In addition, atmospheric chemistry-transport models based on actual emission data and chemical kinetic knowledge underestimate OA observations (Heald et al., 2005; Volkamer et al., 2006). This could be attributed to an underestimation of POA emissions, of POA ageing, and of SOA formation.

3.2.3.3. Observational evidence of organic aerosol chemical processing. There are indirect methods to determine aged POA and SOA like the organic-to-elemental carbon ratio (OC/EC) method: The formation of SOA increases the ambient concentration of OC and the ambient OC/EC ratio. OC/EC ratios exceeding the expected primary emission ratio are an indication of SOA formation as well as of aged POA occurrence. Increases in the OC/EC ratio correlated to ozone episodes are indicative of chemical processing of organics.

The new observational data from AMS (Aerosol Mass Spectrometer) measurements (Jimenez et al., 2003) provide valuable information on the oxidation state of the organic particulate matter and allows simultaneous measurements of the other major aerosol components (Zhang et al., (2007) and references therein). In particular for organics, AMS measurements differentiate between the oxygenated part of the organic fraction of the aerosols (the so-called ‘OOA’) and the hydrocarbon-like part of it (termed ‘HOA’). There is increasing evidence that HOA is associated with the primary emitted organic aerosols whereas OOA results from chemical processing in the troposphere. Lanz et al. (2007) applied positive matrix factorization to the full organics mass spectrum to determine different sources of the organic aerosol in Zurich. This technique has proven to be successful in a number of follow-up studies.

SOA and aged POA are also linked to the water soluble organic carbon content of the aerosols (WSOC) since this part of the aerosol is chemically processed in the atmosphere. On the basis of the comparison of the WSOC concentrations with those of oxygenated organic carbon (OOC) derived from the AMS data. Kondo et al. (2007) conjectured that oxygenated organic aerosol (OOA) and WSOC were very similar in their chemical characteristics and approximately 88 ± 29% of OOA was water soluble.

OOA is ubiquitous in various atmospheric environments. Zhang et al. (2007) analysing AMS observations from 37 field campaigns providing significant global coverage (Fig. 26), found that OOA accounts for 64%, 83% and 95% of the total OA in urban, urban downwind and rural/remote sites, respectively and that OOA increases are mainly due to chemically formed organic aerosol. OOA is larger in summer, consistent with larger SOA precursor emission and enhanced photochemistry in summer. On the other hand, HOA is larger in winter, consistent with increased emissions from heating, reduced evaporation and reduced dilution.

Whilst developments of the broad chemical characterization from aerosol mass spectrometry have proven invaluable in teasing apart the broad nature and source of organic aerosol components, offline analyses based on proton nuclear magnetic resonance (^1H NMR)

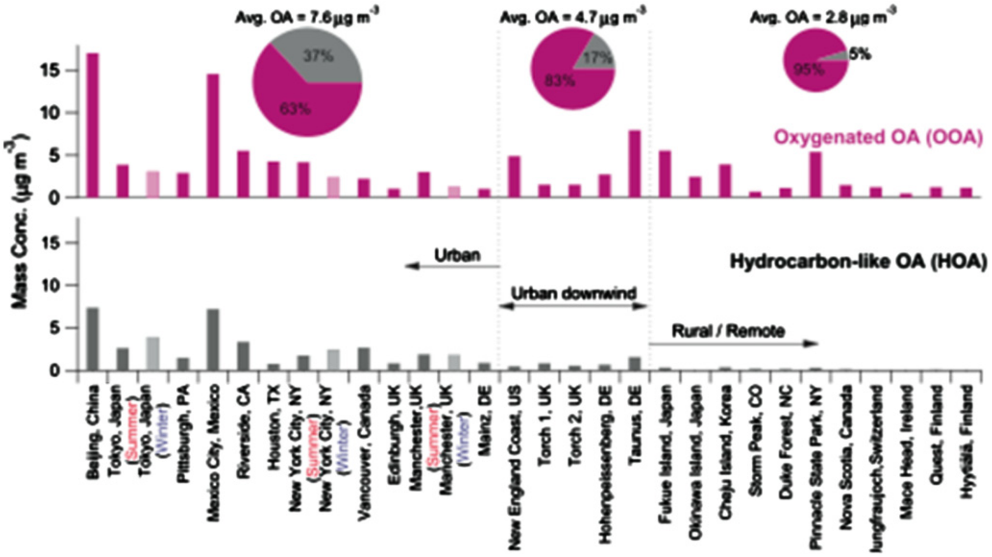


Fig. 26. Average mass concentrations of HOA and total OOA (sum of several OOA types) at sites in the Northern Hemisphere. The winter data of the three urban winter/summer pairs are placed to the right of the summer data and are shown in a lighter shade. Within each category, sites are ordered from left to right as Asia, North America, and Europe. From (Zhang et al., 2007).

spectroscopy have been developed by Decesari et al. (2000) for functional group analysis (Fuzzi et al., 2001) and source attribution of classes of organic components Decesari et al. (2007). These authors presented characteristic ^{1}H NMR fingerprints derived for three major aerosol sources: biomass burning, secondary formation from anthropogenic and biogenic VOCs, and emission from the ocean. Their analysis demonstrated the suitability of ^{1}H NMR spectroscopy for source identification. ^{1}H NMR is additionally able to relate the source fingerprints to the integral chemical functionality of the organic mixtures, which determine their reactivity, physicochemical properties, atmospheric impacts and ultimately their fate.

3.2.3.4. Aerosol ageing and organic aerosol mass changes. Aerosols are subject to ageing by chemical processes such as oxidation at the surface and bulk e.g. (Kanakidou et al., 2005; Rudich, 2003, 2007). It remains an open question how this mechanism proceeds and whether these reactions are increasing or reducing the organic aerosol mass. On the basis of observational growth rates of atmospheric particles, Maria et al. (2004) concluded that consideration of surface- and volume-limited chemical reactions should increase the computed carbonaceous particle burdens by 70%.

Chemical ageing of aerosols has been observed in the laboratory (Rudich, 2003, 2007; Zahardis and Petrucci, 2007) and in the field e.g. (de Gouw et al., 2005; Maria et al., 2004; Rinaldi et al., 2008; Takegawa et al., 2006) and can be followed by the change in the organic mass (OM) to organic carbon (OC) ratio of the aerosol. Observed OM to OC ratios vary between 1.4 ± 0.2 (samples collected in Asia and the Caribbean (Russell, 2003)), 1.6 ± 0.2 for urban aerosol (Turpin and Lim, 2001), 1.78 ± 0.13 for polluted marine NE US coast (de Gouw et al., 2005) and 2.1 ± 0.2 for non-urban aerosol (Turpin and Lim, 2001).

Chemical ageing of primary OA has been simulated by a global 3-dimensional model (Tsigaridis and Kanakidou, 2003), by assuming that O_3 reacts on OA surfaces, thereby resulting in an increase in the oxygenated content of the OA. The growth is parameterised in the model by a corresponding 26% increase in the OA molecular weight. According to TM4 model calculations by Myriokefalitakis et al. (2008), this chemical mechanism adds about 4 Tg year^{-1} of OA to the primarily emitted OA mass which corresponds to about 12% higher effective emissions. Kanakidou et al. (2008) and Robinson et al. (2007) suggest that the importance of chemical ageing of POA might be higher than the above estimate and that together with SOA formation from intermediate volatility organics it can counterbalance the modelled underestimation of observed OA. They estimate that these processes decrease predicted OA in urban areas by as much as 50% and increase it in many rural locations by 15–30% resulting in considerably better agreement with measured urban-to-regional OA. Zhang et al. (2007) pointed out that oxidation of the measured HOA cannot explain the observed increase in OOA with the photochemical age of the air masses. The oxidation of semi- or intermediate- volatility VOCs has been proposed to be at the origin of the observed OA increase during ageing. These suggestions require future model investigations.

3.2.3.5. Global modelling of organic aerosol. Owing to the above reported gaps in knowledge, large uncertainties are associated with tropospheric OA modelling. However, information on the secondary to the primary OA ratio can be derived from chemistry-transport models (CTMs). During the recent international global aerosol modelling exercise (AEROCOM: http://nansen.ipsl.jussieu.fr/AEROCOM (Textor et al., 2007)) the SOA source was simulated as a primary surface source equal to 15% of the monoterpenes emissions (Dentener et al., 2006), yielding 19 Tg year^{-1} which is in the range of actual global SOA chemistry-transport model estimates (Henze et al., 2007; Kanakidou et al., 2005; Tsigaridis et al., 2006). CTMs are the only modelling tools that have the ability to distinguish between fresh POA, aged POA and SOA. Note that these results depend strongly on the assumed aging turnover time of POA from insoluble to soluble (about 0.8 days) whereas the mean lifetime of the soluble POA is 5.9 days, well within the range of the AEROCOM results (Textor et al., 2007).

According to TM4 model calculations (Kanakidou et al., 2008), the global secondary source of OA is as important as its primary source (Fig. 27). Recent experimental data by O'Dowd et al. (2008) indicate the existence of an oceanic source of POA stronger than earlier reported by Duce et al. (1983). In addition, Spracklen et al. (2008) have evaluated the marine source of OA, both primary and secondary, at 8 Tg C yr^{-1} whereas Roelofs (2008) calculated a much larger source of OA up to 75 Tg C yr^{-1}. Following an updated version of the approach used by O'Dowd et al. (2008) to account for organic enrichment in sea-spray aerosol, the results of Vignati et al. (submitted for publication) and Myriokefalitakis et al. (2008) estimate an oceanic source of POA amounting to the order of 6–8 Tg yr^{-1} in sub-micron compared to the order of 24 Tg yr^{-1} sea-salt emissions. Myriokefalitakis et al. (2009) evaluated the SOA marine component production to be about 5 Tg yr^{-1} on a global scale.

3.2.4. New particle formation

An important phenomenon associated with the atmospheric aerosol system is the formation of new atmospheric aerosol particles. Atmospheric aerosol formation consists of a complicated set of processes that include the production of nanometre-size clusters from gaseous vapours, the growth of these clusters to detectable sizes, and their simultaneous removal by coagulation with the pre-existing aerosol particle population (e.g. (Kerminen et al., 2001; Kulmala, 2003)). Once formed, aerosol particles need to grow further to sizes >50–100 nm in diameter until they are able to influence climate, even though smaller particlse may have influences on human health and atmospheric chemistry. While aerosol formation has been observed to take place almost everywhere in the atmosphere (Kulmala et al., 2004), several gaps in our knowledge regarding this phenomenon still exist. These gaps range from the basic process-level understanding of atmospheric aerosol formation to its various impacts on atmospheric chemistry, climate, human health and the environment. However, significant progress has occurred to explain atmospheric nucleation and initial steps of the growth e.g. (Kulmala and Kerminen, 2008; Kulmala and Tammet, 2007). Regional and global models have been used to estimate the importance for climate-relevant particles e.g. (Spracklen et al., 2008).

3.2.4.1. Atmospheric observations of nucleation. Over the past decade or so, aerosol formation has been observed at a large number of sites around the world (Kulmala et al., 2004). Such observations have been performed on different platforms (ground, ships, and aircraft) and over different time periods (campaign or continuous-type measurements).

It appears that several types of atmospheric processes lead to aerosol formation. In the continental boundary layer so-called "regional nucleation events" are common (see Fig. 28). In such events the growth of nucleated particles continues throughout the day, increasing the particle number concentrations over distances of hundreds of kilometres.

In the marine boundary layer, intense yet highly-localized aerosol formation bursts have been reported over coastal environments around Europe and the United States e.g. (O'Dowd et al., 1999). In addition to coastal zones, localized aerosol formation has been observed in different kinds of plumes. Plumes capable of producing new aerosol particles range from large urban and industrial plumes containing SO_2 (Weber et al., 2003; Woo et al.,

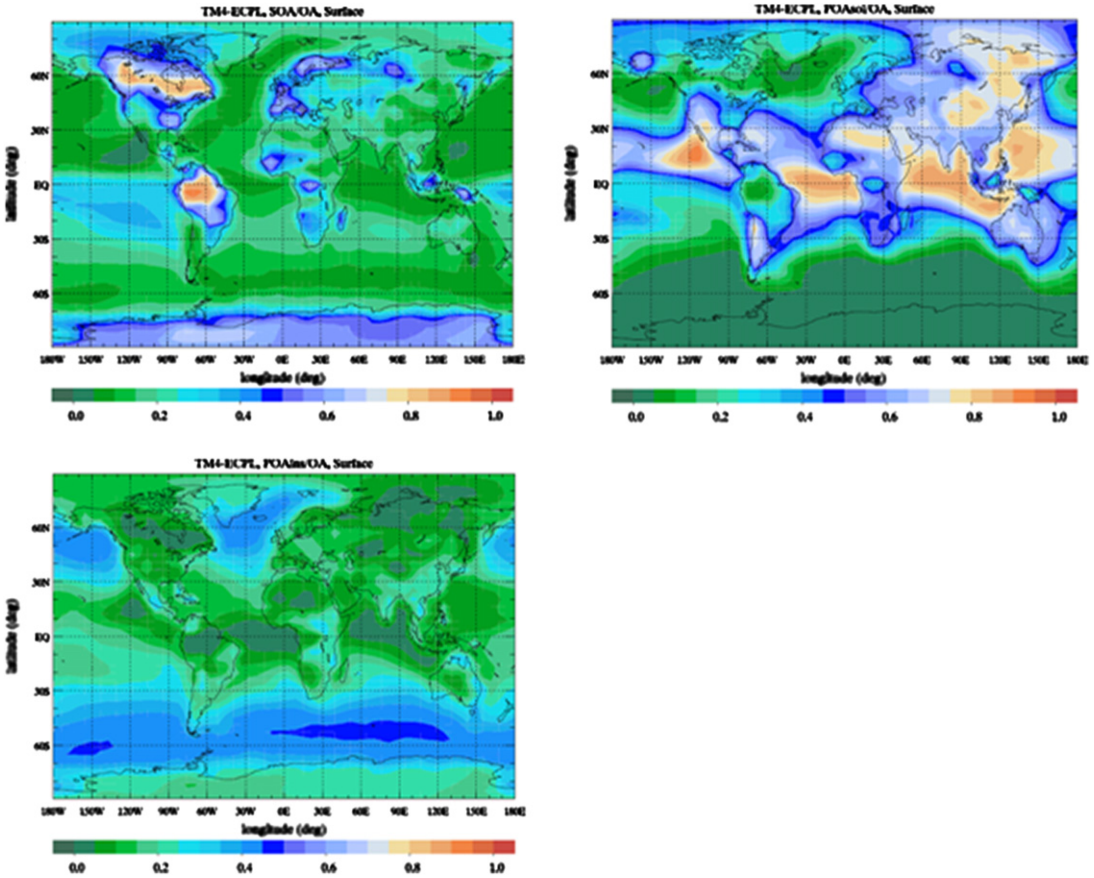


Fig. 27. Annual mean mass ratios of the SOA (top left), soluble POA including aged (top right) and fresh insoluble POA (bottom) to total OA for surface calculated by the TM4-ECPL model (Myriokefalitakis et al., 2008) for 2006 taking into account an oceanic source of organic aerosol.

2001) to small exhaust plumes associated with vehicles (Kittelson et al., 2004). Aerosol particles produced by plumes may be important locally or on regional scales. Aerosol formation has also been observed in the free troposphere, being a frequent phenomenon in the upper troposphere and in cloud-outflow regions (Singh et al., 2002; Twohy et al., 2002; Venzac et al., 2008).

With very few exceptions observed aerosol formation events occur during daytime, suggesting that photochemistry plays a central role in this process. Other factors that favour atmospheric aerosol formation include a sufficiently low pre-existing aerosol concentration, low relative humidity, high vapour source rate e.g. via biogenic emissions, and sometimes also a low temperature and weak mixing of air. The most important of these factors seem to be the high vapour source rate, typically via active photochemistry and biogenic source, and the low sink due to pre-existing particles.

Atmospheric nucleation is probably connected with ion and neutral clusters (Kulmala et al., 2004). The existence of ion clusters has been known for decades and recent observations support the idea that they are present always and everywhere (Kulmala and Tammet, 2007).

Typical observed formation rates of 3 nm particles associated with regional nucleation events are in the range 0.01–10 cm^{-3} s^{-1}, even though rates up to 100 cm^{-3} s^{-1} have been often been observed in urban areas. Locally, aerosol formation rates may be even higher, and rates as high as 10^4–10^5 cm^{-3} s^{-1} have been observed in coastal areas and industrial plumes.

The vast majority of reported particle growth rates lie in the range 1–10 nm $hour^{-1}$ (Kulmala et al., 2004), implying that it usually takes 0.5–3 days before the nucleated particles reach sizes at which they may act as cloud condensation nuclei. Growth rates in the range 0.1–1 nm $hour^{-1}$ have occasionally been observed in remote locations, whereas growth rates larger than 10 nm $hour^{-1}$ can be seen in polluted environments. Intermittently, very high

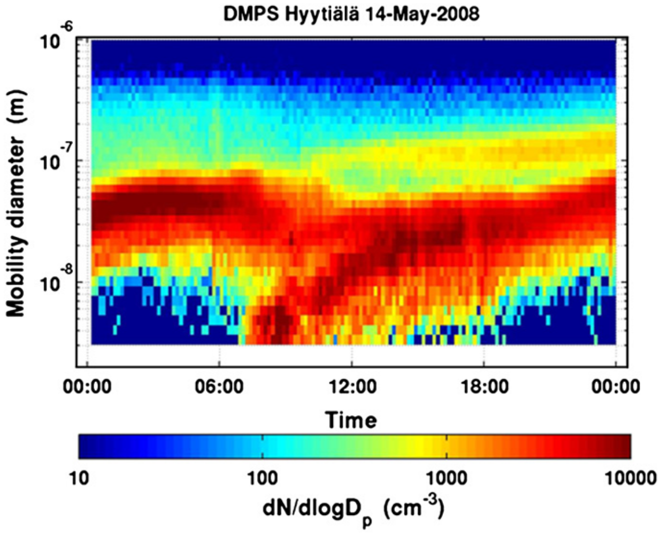


Fig. 28. A typical regional aerosol formation event observed at Hyytiälä, Finland. The continuous growth of newly formed particles is seen with a growth rate of ca 3 nm h^{-1}.

growth rates in excess of 100 nm $hour^{-1}$ can be reached in plumes and in coastal zones.

Recent observations have also shown the importance of sulphuric acid in atmospheric particle formation e.g. (Riipinen et al., 2007). However, sulphuric acid itself cannot explain the observed growth rate and a significant fraction of organic compounds in the particles is observed (Allan et al., 2006; O'Dowd et al., 2002; Tunved et al., 2006) during particle growth. Biogenic organic compounds may also influence the nucleation rate itself (Bonn et al., 2008). Airborne studies over forested regions confirm that the particle formation region is within the boundary layer and not in the free troposphere, at least for boreal forest nucleation events (O'Dowd et al., 2009).

Although atmospheric new particle formation has been observed to take place practically all over the world, our understanding of this phenomenon is still not complete. By summarising the major finding made during the recent years, it may be surmised that most field measurements support the idea that nucleation and subsequent particle growth are uncoupled under atmospheric conditions (Kulmala et al., 2000). The associations between the formation rate of 3 nm particles and H_2SO_4 vapour concentration are suggestive of the involvement of H_2SO_4 in atmospheric nucleation, yet the actual nucleation mechanism remains to be definitively identified. The few observations made in the free troposphere are consistent with binary homogeneous water-sulphuric acid nucleation (BHN), whereas in the boundary layer a third nucleating component (such as ammonia or some low volatility organics), or a totally different nucleation mechanism, is clearly needed (see e.g. (Kulmala et al., 2006a, 2007; Kulmala and Tammet, 2007)). It has been seen that ion-induced nucleation is taking place all the time but its contribution is usually limited (Kulmala et al., 2007; Kulmala and Tammet, 2007; Laakso et al., 2007), at least in the continental boundary layer. Observed growth rates of nucleated particles cannot usually be explained by the condensation of sulphuric and associated inorganic compounds (water and ammonia) alone. Organic compounds having a very low saturation vapour pressure would appear to be the most likely candidates for assisting the growth of nucleated particles, yet the identity of these compounds remains to be revealed (Laaksonen et al., 2008; O'Dowd et al., 2002).

3.2.4.2. Model studies of nucleation. Depending on the location, atmospheric aerosol formation is capable of increasing the concentrations of cloud condensation nuclei (CCN) by a factor more than two over the course of one day (e.g. Lihavainen et al., 2003) and ultimately lead to significant enhancements in cloud droplet concentrations (Kerminen et al., 2005). The production of new atmospheric aerosol particles is therefore an important process that must be understood and included in large-scale atmospheric models. The recent development of size-resolving microphysics models of regional and global aerosol has led to several attempts to include nucleation and to quantify its impact on observed aerosol properties. The wide range of mechanisms used in these modelling studies highlights the lack of consensus on which mechanisms are operating in various parts of the atmosphere.

The free troposphere (FT) and upper troposphere (UT) are recognized to be regions of significant new particle formation of importance to the global atmosphere (Raes et al., 2000), although the formation mechanism has not been confirmed. Binary water-sulphuric acid nucleation is predicted to be fast in the FT and UT and can explain high particle concentrations there, but global models suggest that the mean aerosol vertical profile is not very sensitive to the actual rate except in the UT (Liu et al., 2001).; Spracklen et al. (2006) used the MM5 model to show that BHN is likely to occur under preferential conditions such as above boundary layer clouds and in cloud outflow. Despite the apparent success of BHN in explaining FT aerosol, some UT observations have been interpreted in terms of ion-induced nucleation and models have been able to capture the observed number and size of particles using such a mechanism (Lee et al., 2003; Lovejoy et al., 2004). However, confirmation of the mechanism is difficult because of large uncertainties in nucleation rates and the difficulty in constraining important model quantities like humidity and sulphuric acid concentrations at appropriate time and space scales.

Mechanisms other than BHN are required to explain regional nucleation events in the continental boundary layer. Such events have been studied using box, column, regional and global models, and with a variety of mechanisms. Fan et al. (2006) used the EPA's Models-3 Community Multiscale Air Quality model (CMAQ) applying an organic-H_2SO_4 mechanism and were able to capture the diurnal variation and vertical profile of ultrafine aerosol. Sotiropoulou et al. (2006) used ternary nucleation of sulphuric acid, ammonia and water in the UAM-Aero regional model, as did Gaydos et al. (2005) and Jung et al. (2006) in box model studies of observed nucleation in the Eastern United States. Gaydos et al. (2005) and Jung et al. (2006) obtained very good agreement with observations and demonstrated the importance of ammonia and SO_2 in controlling the nucleation rate.

The first global study of nucleation in the continental boundary layer (Spracklen et al., 2006) used an empirical nucleation rate dependent on sulphuric acid concentrations. The model showed good agreement with observations at the Hyytiälä boreal forest site and predicted a global distribution of particle formation events broadly in agreement with what is expected from available observations. Monthly mean enhancements to boundary layer total particle concentrations of up to a factor of 8 over remote regions and a factor 2 over polluted regions are predicted by the model (Fig. 29).

With our present knowledge it is clear that nucleation can contribute to the atmospheric abundance of climate-relevant particles such as CCN and is therefore an important process to be included in large-scale models. A major challenge for the future is to understand how nucleation affects the response of global and regional aerosol to anthropogenic and biogenic changes.

3.2.5. Aerosol–water uptake

The gas/liquid/solid partitioning of atmospheric particles and precursor gases largely determine the composition and hygroscopicity of atmospheric aerosol particles, which affect human and ecosystem health, clouds and climate e.g. (IPCC, 2007). Overall, the most abundant aerosol species is water. Aerosol water governs the size distribution, the atmospheric lifetime of both the particles and the interacting gases, and the particle optical properties. For instance, sea salt particles can deliquesce at a very low relative humidity (RH) of ~32% since they contain a small amount of the very hygroscopic salt magnesium chloride ($MgCl_2$). Therefore, marine air is often much hazier than continental air at the same ambient temperature and relative humidity. The hygroscopic growth of the aerosol particles influences heterogeneous reactions, light extinction and visibility, whereby aerosol water is most relevant for the direct radiative forcing of Earth's climate (Pilinis et al., 1995). However, aerosol water depends, besides the meteorological conditions, on the ionic composition of the particles, which in turn depends on the aerosol water mass. Consequently, gas-aerosol partitioning and aerosol water mass are difficult to measure or predict numerically (by established methods), even if the complex gas-aerosol system is simplified by assuming thermodynamic gas/liquid/solid aerosol equilibrium.

3.2.5.1. Water uptake calculation and parameterization. The water associated with a certain amount and type of solute can be obtained

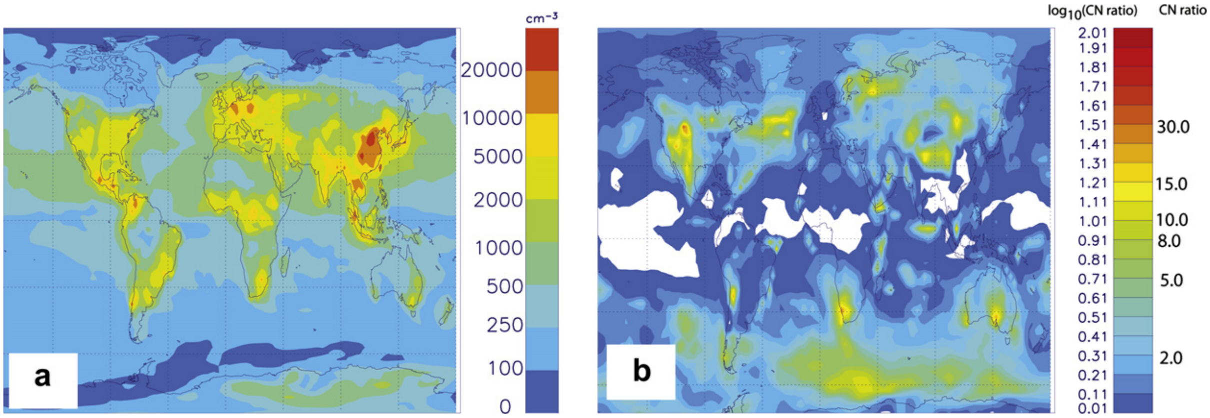


Fig. 29. Enhancement in surface level total particle number concentration (CN > 3 nm diameter) due to boundary layer nucleation. (a) CN concentration due to primary emissions only. (b) Increase in CN concentration when boundary layer nucleation is switched on in the model. Results are from the GLOMAP model and the figure is adapted from Spracklen et al. (2006).

from water activity measurements in the laboratory e.g. (Tang and Munkelwitz, 1994), or directly calculated from the vapour pressure reduction that occurs after dissolving a salt solute in water, known as Raoult's law, if solution non-idealities are taken into account. The so-called Raoult term considers the lowering of the equilibrium vapour pressure with increasing solute concentration at a given relative humidity. Complemented by the Kelvin term, which accounts for the increase in the water vapour pressure due to the curvature of the particle surface, one yields the Köhler theory. The Köhler theory determines the equilibrium size of an aerosol particle of given size and chemical composition at a given relative humidity.

An alternative approach recently introduced by Metzger and Lelieveld (2007), describes the water uptake of inorganic and organic salt compounds found in natural or man-made pollution aerosols more explicitly as a function of relative humidity, since the water mass consumed by solute hydration is explicitly taken into account dependent on the atmospheric conditions. Recently, Petters and Kreidenweis (2007) proposed a method to directly describe the relationship between the particle dry diameter and CCN activity using a single hygroscopicity parameter κ. Relatively low values of κ indicate less hygroscopic and less CCN active behaviour.

An advantage of this single parameter method obviously is its simplicity, though it must assume a constant value of κ throughout sub- and supersaturation conditions, which limits its use in interactive computations of atmospheric chemistry and particle composition and of the use of constant hygroscopic growth factors in the calculation of CCN properties (McFiggans et al., 2006). Water uptake measurements have also been used in the literature to infer the aerosol soluble fraction in various environments, which once parameterised, can be used in model calculations (Kandler and Schutz, 2007).

3.2.5.2. Hygroscopic growth factors (HGF) in natural environments. The hygroscopic growth of aerosol particles has been in the past classically studied using the tandem differential mobility analyzer (T-DMA) technique (see also (Laj et al., 2009)). Hygroscopic measurements reported in the literature have been performed during intensive campaigns over short periods (see Table 4). Because hygroscopicity is key information needed for a given air mass type at a given location with a seasonal and diurnal variability, a lot of efforts are being made for providing HGF on a continuous basis. Hygroscopicity Tandem Differential Mobility Analyzers (HTDMAs) of the new generation are meant to be autonomously run as monitoring instruments (http://www.eusaar.net). Technical challenges are also linked to fast hygroscopicity measurements for airborne applications in order to document high altitude hygroscopicity.

In marine environment, sub-micron aerosols show high hygroscopic growth factors that can witness the presence of partially neutralized sulphate aerosols (Massling et al., 2007), which can coexist with primary or aged sea salt in the accumulation mode (Sellegri et al., 2008). Typical sea salt HGF have been found down to the Aitken mode for diameters as low as 20 nm (Sellegri et al., 2008). In the micro-metric range, Massling et al. (2007) show that, aerosols sampled on board of a research vessels, have HGF of hydrophobic mineral dust for half of the population and HGF of sea salt particles for the rest of the population.

Urban aerosols usually show the contribution of two hygroscopic modes, one with a hydrophobic behaviour which is assumed to represent combustion sources from traffic and is enhanced during rush-hour periods and another one with a higher HGF, attributed to regional background aerosols (Baltensperger et al., 2002;Massling et al., 2005).

Table 4
Hygroscopic behaviour of accumulation mode particles in various environments (McFiggans et al., 2006).

		Lower accumulation mode size range (∼100–150 mm)				
		Dominant mode			Second mode	
	$GF_D(90\%)$	Frequency of occurrence	Fraction	$GF_D(90\%)$	Frequency of occurrence	Fraction
Urban	1.23–1.50	100%	16–90%	1.00–1.14	Up to 100%	10–84%
Continental polluted	1.41–1.64	100%	37–100%	1.03–1.18	10–90%	2–63%
Free troposphere	1.62	100%	∼85%	<1.3	–	∼15%
Biogenically dominated	1.20–1.25	>93%	90–96%	∼1.08	∼25%	<7%
Remote marine	1.47–1.78	100%	>80%	2.06–2.14	13–40%	<15%

New particle formation events have been usually found to produce either hygroscopic or non-hygroscopic particles. While in the coastal environment the non-hygroscopic property of freshly formed particles (the order of an hour) is clear (Väkevä et al., 2002), in the urban environment opposite hygroscopic behaviours can be found as well as in the boreal forest (Ehn et al., 2007). These findings imply that the species involved in the formation process of newly formed particles are variable and need to be further investigated using HTDMA studies. A review on HTDMA measurements has been recently published by Swietlicki et al. (2008).

Non-hygroscopic particles have been observed to gain hygroscopicity when aging while sea salt was observed to lose hygroscopicity when aging. As a result, HGF are frequently in the range 1.5–1.8 at RH=90%, when sampled away from fresh aerosol sources. The Volatility Hygroscopicity Tandem Differential Mobility Analyzer (VHTDMA) technique technique has shown that the 90 °C volatile fraction of the marine aerosol present in the accumulation mode slightly decreases its hygroscopicity compared to pure sea salt, indicating that a chemical ageing take place on marine aerosols over the ocean (Sellegri et al., 2008). In the natural free troposphere, sub-micron aerosols have been found with a rather constant moderately hygroscopic mode and a smaller fraction in the less hygroscopic mode (Sjögren et al., 2008). These results pose the question of the time scale needed for an aerosol sampled in the vicinity of its source to experience a significant change in hygroscopicity.

3.3. *Specific issues*

In a review of this scope it is impossible to deal with all the advances of the last decade. The following sub-sections deal with individual topics where significant progress or insight has been apparent in recent years.

3.3.1. *Halogen chemistry*

The relevance of halogen chemistry to the stratosphere, especially ozone destruction, is well known. However, reactive halogens play a role in tropospheric chemistry. The sources of reactive halogens in the troposphere are largely natural and to a large extent connected to the presence of halogens in ocean water (see Fig. 30). In this section recent research highlights, especially those affecting the global oxidizing capacity and hence the impacts of air pollution are focused on. In general, halogen compounds play a role in the destruction of ozone, changes in the OH/HO_2 and NO/NO_2 ratios, in the oxidation of DMS as well as that of elemental mercury. Under very specific conditions (high VOC and NO_x), chlorine chemistry can lead to ozone production. Details on the chemistry can be found, for example, in Platt and Hönninger (2003) and von Glasow and Crutzen (2007).

Halogen chemistry was first identified to be of importance for tropospheric chemistry in the polar boundary layer. Bromine is primarily responsible for the dramatic boundary layer ozone depletion events that are observed in both the Arctic and Antarctic (Barrie et al., 1988). The current state of knowledge of this field has been summarized by Simpson et al. (2007b). Elevated concentrations of reactive bromine compounds (BrO, Br_2, BrCl) have been observed on the ground and from satellite in many studies (e.g. (Foster et al., 2001; Saiz-Lopez et al., 2007b; Wagner and Platt, 1998 to name but a few) (see Fig. 31). There are strong indications that the source of bromine is closely linked to the presence of first-year sea ice and snow pack (e.g. Kaleschke et al., (2004)) but the exact details remain uncertain (see discussion in Simpson et al. (2007b)). Recent measurements have shown significant concentrations of iodine monoxide in the Antarctic boundary layer both from ground-based and satellite-based observations. (Saiz-Lopez et al., 2007a,b ; Schönhardt et al., 2008). These observations have revealed a seasonal maximum in spring, but with higher than expected concentrations sustained into the summer months. Although the source of iodine is not confirmed, it is postulated to originate from algae that colonise the underside of sea ice. Of major potential importance for polar ecosystems is the rapid oxidation of gaseous elemental mercury (Hg^0) by bromine to reactive gaseous mercury (Schroeder et al., 1998) which is readily deposited and transformed into toxic forms in a very sensitive ecosystem (see Steffen et al., 2007 for a recent review).

The extent of sea ice in summer in the Arctic has been dramatically decreasing in the last decades and it might be lost completely by the middle of this century (Simpson et al., 2007a). As the bromine release seems to be closely related to first-year sea ice, the extent and intensity of the area affected by bromine chemistry can be expected to increase in the future as the Arctic ocean will keep freezing over in winter, thereby producing an increasingly

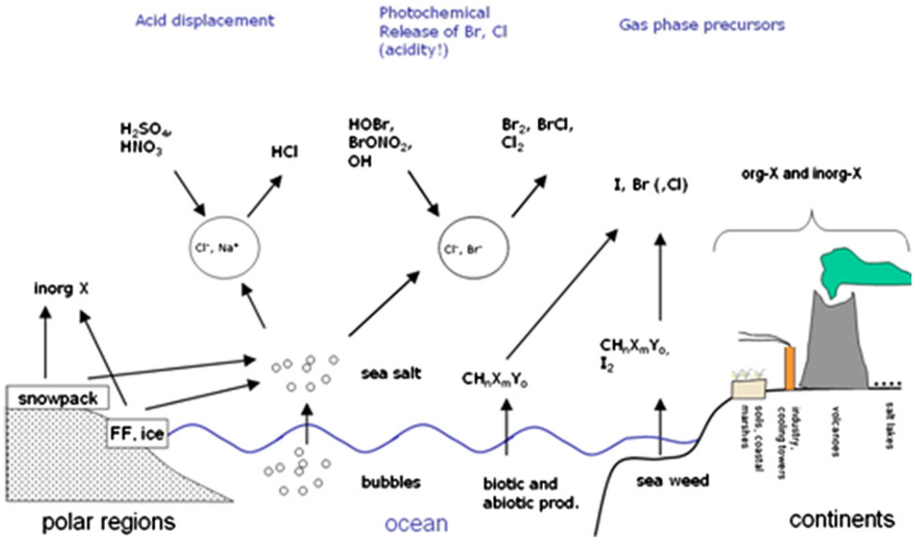


Fig. 30. Schematic depiction of the main release mechanisms for reactive halogens in the troposphere (including some not mentioned in the text).

large area of first-year sea ice. Therefore, the consequences for the ozone budget and mercury input into the Arctic ecosystem will likely be more important in the future.

The marine boundary layer (MBL) is in direct contact with the ocean, which is the largest reservoir for halogens. In general, the strongest source of bromine and chlorine in the MBL is through the production of sea salt aerosol upon bubble bursting, a smaller fraction is released from biogenic organic halogens. Iodine compounds on the other hand are largely released as organic compounds and molecular iodine from micro and macro algae that accumulate iodine from the ocean water. Measurements of halogen oxides in the open ocean MBL are very difficult and very few have been published so far. IO was measured on Tenerife and at Cape Grim by Allan et al. (2000) and it is likely that this is an open ocean signal but coastal effects cannot be excluded. Recently measurements at the UK-SOLAS observatory on the Cape Verde islands have shown very high levels of both BrO and IO of typical daytime maxima of 2.5 and 1.4 pptV which would indicate that ozone photochemistry in this area is dominated by halogen chemistry (Read et al., 2008) (see Fig. 32) and that DMS oxidation would be strongly affected by the presence of BrO. These BrO mixing ratios are consistent with the autocatalytic release from sea salt aerosol e.g. (Vogt et al., 1996; von Glasow et al., 2002). If the levels of reactive halogens as measured at Cape Verde were indeed a widespread phenomenon, our understanding of photochemical processes in the clean MBL needs to be completely re-assessed. Indirect evidence indeed suggests a widespread role of halogen chemistry in the clean MBL as so-called sunrise ozone destruction that have been observed in the West and North Pacific (Galbally et al., 2000; Nagao et al., 1999; Watanabe et al., 2005) could be due to bromine chemistry (von Glasow et al., 2002). Osthoff et al. (2008) detected for the first time nitryl chloride in the MBL under conditions with very high NO_x concentrations (continental outflow and ship plumes). At sunrise $ClNO_2$ photolyses rapidly releasing chlorine radicals which, in the presence of NO_x and VOC, could lead to enhanced ozone formation. As the global importance of outflow from coastal Megacities, as well as from ship plumes is projected to increase in the future, this chemistry could transform large ocean regions from a net ozone sink to a net ozone source. Furthermore, chlorine radical concentrations in the remote MBL have been estimated to be in the range of 10^3–10^5 in the MBL e.g. (Lowe et al., 1999; Wingenter et al., 1999, 1996) with relevance mainly for the methane budget. In the southern hemisphere Cl could account for about 3.3% of CH_4 destruction (Platt et al., 2004).

Bursts of new particles that were observed at Mace Head on the west coast of Ireland (O'Dowd et al., 1998, see also Section 3.2.4) were quickly associated with iodine chemistry owing to the detection of IO (Alicke et al., 1999). At Mace Head and other coastal sites where seaweeds are exposed at low tide, molecular iodine has been identified as the main precursor for iodine with nighttime mixing ratios of >10 pptV e.g. (Saiz-Lopez and Plane, 2004). Indeed, chamber studies using seaweeds at Mace Head illustrate a linear relationship between I_2 concentration and nanoparticle concentrations at sizes of 3–5 nm (Sellegri et al., 2005). The details of new particle formation

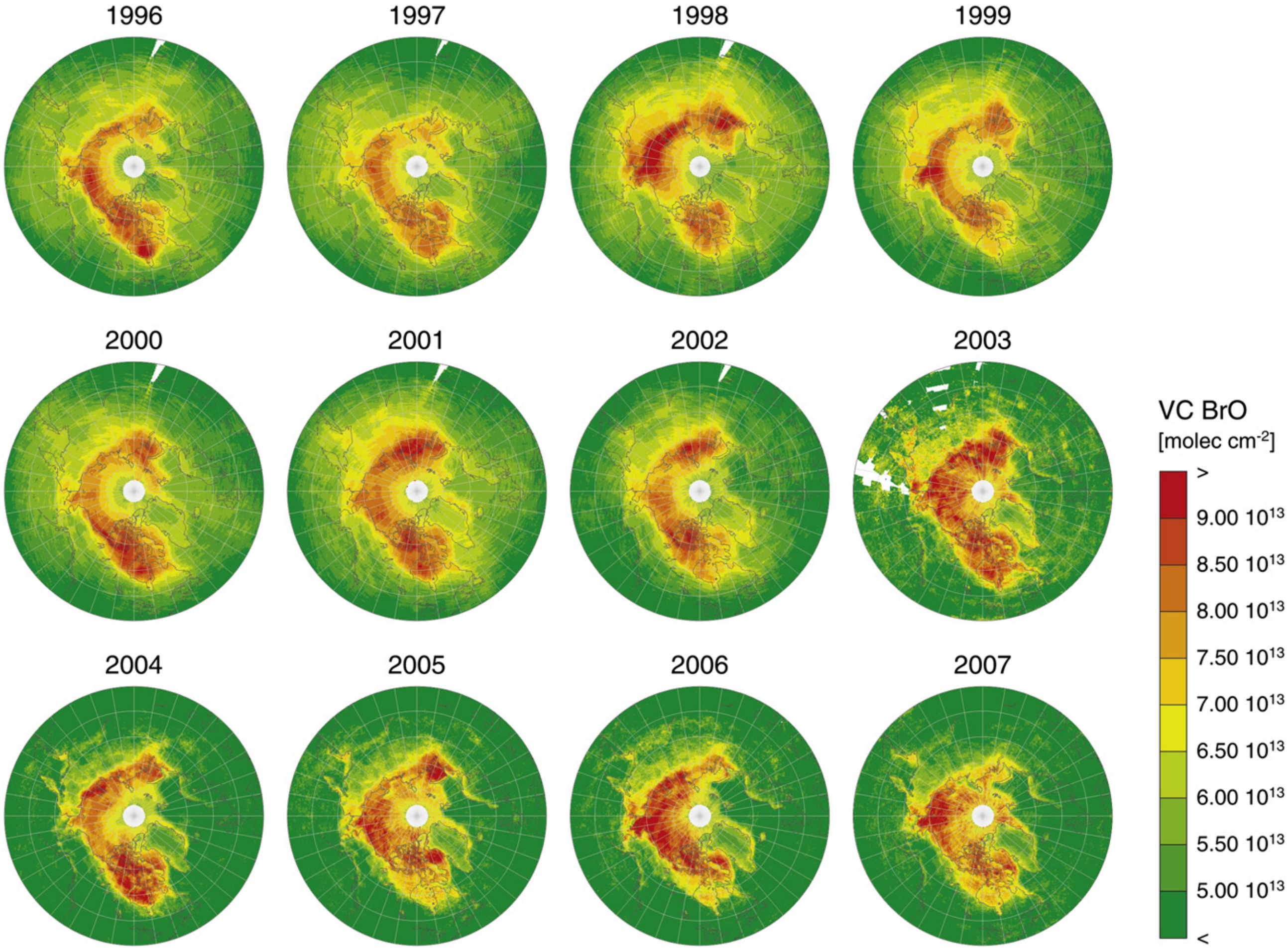


Fig. 31. BrO measured from space from GOME and SCIAMACHY (top panel Northern Hemisphere; bottom panel Southern Hemisphere) (Courtesy of A. Richter, M. Begoin, J.P. Burrows, U. Bremen).

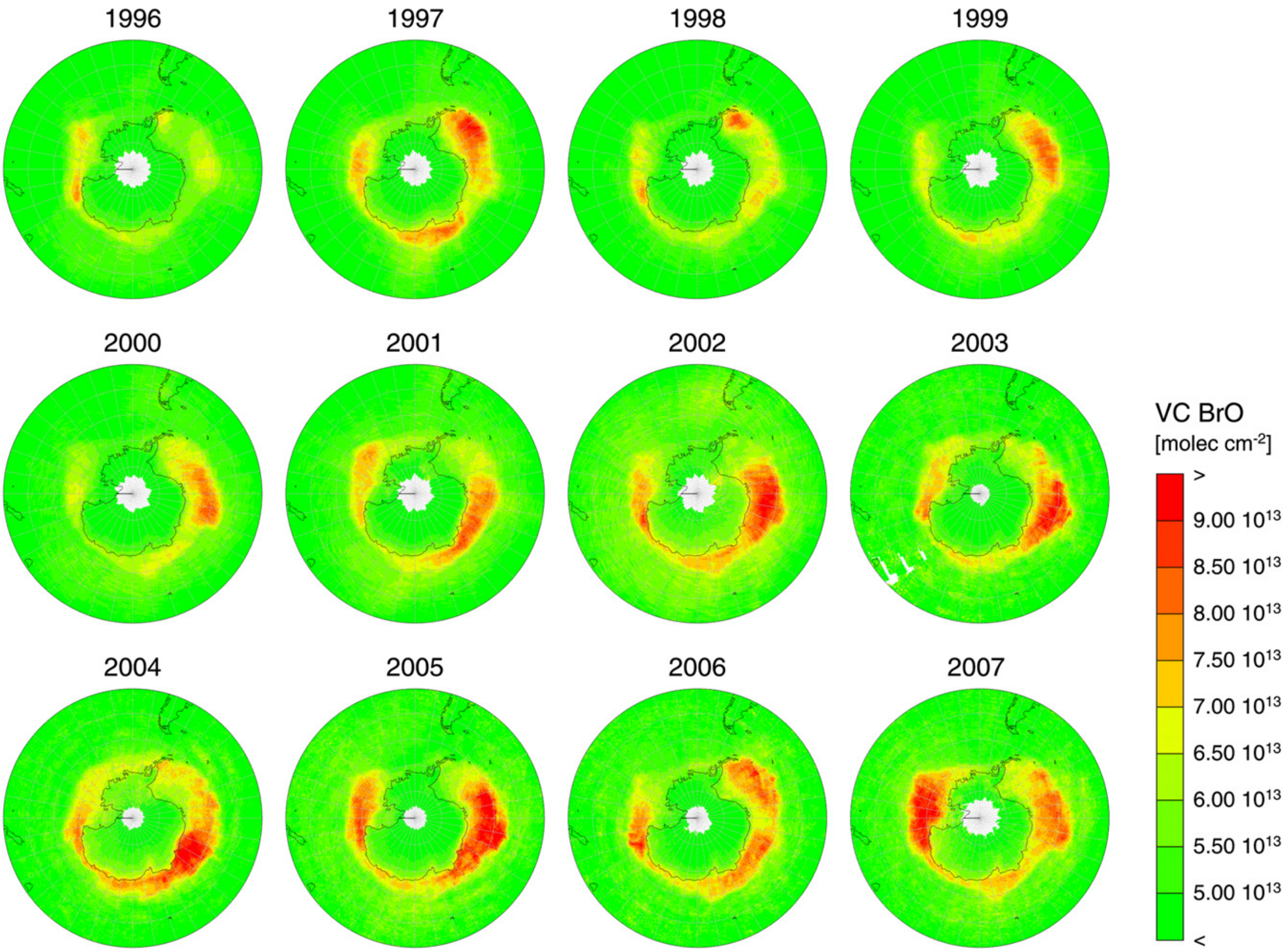


Fig. 31. (*continued*).

from iodine oxides are, however, not completely resolved yet. In terms of ozone destruction the relevance of these fairly local events of very high iodine loadings might be limited and although there are indications that the fine particles produced in these bursts can grow to CCN sizes (O'Dowd, 2001; O'Dowd et al., 2007), more studies are needed to test on what spatial scale this might be of relevance, especially in competition with other particle sources.

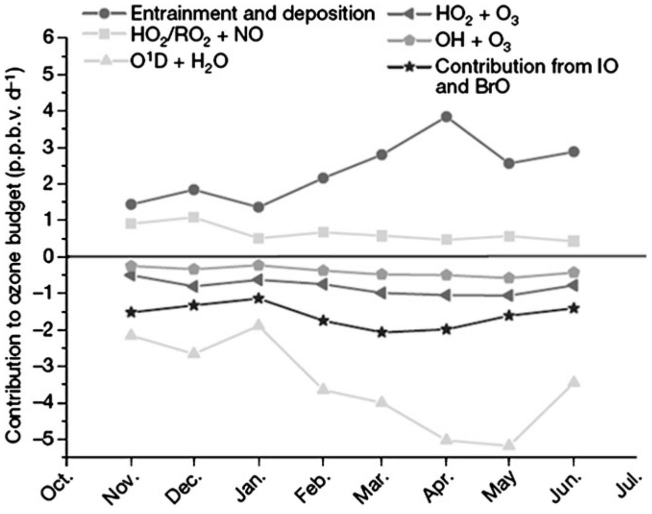


Fig. 32. Monthly averaged contributions to the daily ozone budgets between 09:00 and 17:00 UT for Cape Verde. The data shows the importance of halogen chemistry in this remote marine location in the ozone budget (Read et al., 2008). Reprinted by permission from Macmillan Publishers Ltd: Nature, copyright 2008.

The presence of reactive halogen compounds in the plumes of passively degassing volcanoes was discovered a few years ago (Bobrowski et al., 2003). Bobrowski et al. (2003) measured the highest BrO mixing ratios detected so far in the atmosphere with inferred values exceeding 1 ppbV. BrO has been identified at a number of other volcanoes e.g. (Bobrowski and Platt, 2007; Oppenheimer et al., 2006), as has OClO and ClO (Bobrowski et al., 2007; Lee et al., 2005). It has been known for a long time that very large amounts of halides are emitted from volcanoes but thermodynamic modelling suggests that other inorganic halogen compounds can be emitted from volcanoes (Gerlach, 2004). Measurements of the BrO:SO_2 ratio downwind of Mt Etna showed an increase with time of BrO concentrations and a comparison of these data with model calculations showed that the bromine explosion mechanism is sufficient to explain both the absolute amount of bromine as well as the rate of its formation (Bobrowski et al., 2007). As discussed previously, multiphase chemistry is the key to these reaction cycles. As most volcanoes emit directly into the free troposphere the potential for large-scale effects through long-range transport and extended lifetime of halogens through multiphase cycling is large. The expected effects include O_3 depletion and more rapid oxidation of S(IV) and, if Cl radical levels are sustained high enough, CH_4 oxidation.

From the comparison of ground-based, balloon and space-based measurements, the presence of 0.5–2 pptV BrO in the free troposphere has been suggested e.g. (van Roozendael et al., 2002). Recent long-term ground-based measurements are improving the fidelity of these numbers and suggest tropospheric columns of BrO of around 10^{13} molecule cm^{-2} with somewhat smaller values near the equator (Fietkau et al., 2007; Hendrick et al., 2007; Theys et al., 2007). Global model studies of tropospheric bromine chemistry indicate that these levels are enough to perturb the O_3 concentrations by 5–20% (Yang et al., 2005). The sources for bromine in the free troposphere are likely to be dominated by the breakdown of natural organic bromine gases and bromine released from sea salt (Yang et al., 2005) but bromine from volcanoes should also be considered.

Our knowledge about the relevance of halogen chemistry in the troposphere has increased dramatically in the last decade. The main implications of reactive halogens are a decrease of ozone in most regions but an increase in O_3 smog in densely populated coastal regions. Furthermore, the activation of elemental mercury and links with the sulphur cycle are of importance. It is interesting to note that the large majority of reactive halogen compounds in the troposphere are of natural origin and that basically all of them are related to the presence of halides in ocean water. This is true even for halogens in volcanic plumes as most of them originate from sea water that was, for example, included in subducted sediments.

3.3.2. *Night-time chemistry*

The nitrate radical, NO_3, is rapidly destroyed by daytime photochemistry (Wayne et al., 1991). It is mainly of importance in the nocturnal atmosphere. The nitrate radical is formed by the reaction of O_3 with NO_2. Through further reaction with NO_2, NO_3 subsequently can form N_2O_5, which can thermally degrade to NO_2 and NO_3, coupling NO_3 and N_2O_5. At colder temperatures degradation of N_2O_5 is very slow leading to an effective permanent sink for NO_3. NO_3 is lost from the gas phase both by gas phase reactions with *inter alia* NO, alkenes, organic nitrates, alkenes and di-methyl-sulphide (DMS) (Wayne et al., 1991). Both NO_3 and N_2O_5 can undergo heterogeneous uptake, a process which is known to be dependent on aerosol composition. NO_x can then be lost from the atmosphere system through wet/dry deposition of both gas phase and aerosol particles.

Ambient concentration levels of NO_3 are more uncertain than those of [OH]. New measurements (Allan et al., 2002; Brown et al., 2007b, 2006b) have shown that the concentrations measured at surface level tend to be significantly lower than concentrations higher up in the continental boundary layer, where sinks of NO_3 are less efficient (Geyer and Stutz, 2004a; Penkett et al., 2007).

NO_3 reacts with a variety of organic compounds in the atmosphere (Wayne et al., 1991). In particular, reactions with biogenic VOC, such as isoprene and terpenes, as well as the reactions with DMS, are of significance. NO_3 reactions with alkanes and aldehydes proceeds via H-abstraction

$$NO_3 + RH \rightarrow R + HNO_3 \tag{13}$$

The alkyl radicals produced in reaction (13) are transformed to peroxy radicals (RO_2) by reaction with O_2. Reactions with alkenes (including isoprene and terpenes) proceed via NO_3 addition to a C=C double bond. Further reaction steps are O_2 addition, followed by either reaction with other peroxy radicals or NO_2. Reasonably stable end products are organic nitrates and peroxy radicals (Monks, 2005; Wayne et al., 1991). A chamber investigation of the reaction of the NO_3 radical with isoprene showed a significant yield of aerosol. A "back-of –the-envelope" estimate of the global SOA formation from this reaction suggested an amount of 2–3 Tg yr^{-1} which is about 25% of the amount of SOA that is estimated to be formed from the reaction of isoprene with the OH radical (Ng et al., 2008). However, the actual SOA formation under ambient conditions from this as well as other NO_3 reactions with unsaturated organics is still uncertain.

Since most of the reactions of NO_3 with organic species appear to lead to the formation of peroxy radicals, an interesting consequence of the nighttime reaction of NO_3 with organic species is a considerable contribution to the HO_x budget (Carslaw et al., 1997; Geyer et al., 2003; Platt et al., 1990; Salisbury et al., 2001). When NO levels are very low, peroxy radicals can be converted to RO by reaction with other RO_2 radicals (in particular HO_2), NO_2 (see Section 3.1.1.3) O_3, or NO_3:

$$RO_2 + NO_3 \rightarrow RO + NO_2 + O_2 \tag{14}$$

In urban areas, where ubiquitous NO emissions and vertical transport can lead to an active mixing of NO_3, N_2O_5 and NO, the likely fate of RO_2 radicals, even at night, is reaction with NO (Geyer and Stutz, 2004a,b)

$$RO_2 + NO \rightarrow RO + NO_2 \tag{15}$$

This gives rise to a radical chemistry which is similar to that during the day and can include significant nighttime OH formation via:

$$HO_2 + NO \rightarrow OH + NO_2 \tag{16}$$

However, at night NO is irreversibly oxidized to NO_2 by O_3, therefore the region in which NO_3 and NO can coexist is often shallow and it moves vertically throughout depending on the NO emission strength and vertical stability (Geyer and Stutz, 2004b).

Homogeneous reactions of N_2O_5 with water vapour and other atmospheric trace gases are believed to be extremely slow (Mentel et al., 1996). However, heterogeneous reaction with water contained in aerosol or cloud particles will convert N_2O_5 to nitric acid:

$$N_2O_5 + H_2O\,(\mathrm{het}) \rightarrow HNO_3 \tag{17}$$

Uptake coefficients (γ) for N_2O_5 and NO_3 on water (droplet) surfaces are in the range of 0.04–0.1 (the higher values applying to water containing H_2SO_4) (Hallquist et al., 2003; Wahner et al., 1998a,b). If reaction (17) leads to accumulation of nitrate in the liquid phase, the accommodation coefficients can be considerably (by about one order of magnitude) reduced. For instance, Wahner et al. (1998b) find γ in the range of 0.002–0.023 at relative humidities of 48–88% for the accommodation of N_2O_5 on sodium nitrate aerosol. Recent studies (Brown et al., 2006a,b) find uptake coefficients of 0.017 and <0.0016, for situations with high (around 20 $\mu g\ m^{-3}$) and low aerosol sulphate contents, respectively. These reactions lead to non-photochemical NO_x to nitrate conversion and thus can strongly affect the daytime ozone formation (Brown et al., 2006a,b). Overall, a key question is the relative importance of the non-photochemical NO_3–N_2O_5 versus the photochemical $NO_2 + OH$ pathways in the conversion of NO_2-to-HNO_3 or nitrate (see also Section 3.1.2).

Further consequences of nighttime NO_3 are the oxidation of iodine species by NO_3, which can lead to nighttime formation of IO and OIO (Dillon et al., 2008), which was observed in various studies (Alicke et al., 1999; Allan et al., 2000; Peters et al., 2005; Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2006a,b). The proposed reaction scheme includes:

$$NO_3 + I_2 \rightarrow IONO_2 + I \tag{18}$$

followed by $I + O_3 \rightarrow IO + O_2$ and:

$$IO + NO_3 \rightarrow OIO + NO_2 \tag{19}$$

Recently, the oxidation of particulate chloride by N_2O_5 to form $ClNO_2$ (and in a further step Cl_2) was reported by (Roberts et al., 2008) and (Osthoff et al., 2008). These reactions could be an important source of Cl atoms in the lower atmosphere e.g. in polluted coastal areas (see also 3.3.1).

3.3.3. *Tropical chemistry – A driver for global oxidation*

The tropics are critical for climate because the high solar irradiance and humidity make this region important for determining the global oxidative capacity and hence the lifetime of greenhouse gases (see Fig. 33). Although the important processes controlling tropical chemistry have been known for some time, the major advancements in understanding in the last 5 or so years have come about through improved observations of the spatial and temporal distribution of trace gases and better model parameterizations. This has been enabled by data from a number of intensive measurement campaigns targeted at the tropics and improved instrumentation allowing the measurement of compounds previously not measured or at such high frequency and satellite observations. These data have allowed improvements in top-down emissions inventories, including better parameterizations of the lightning NO_x source (Schumann and Huntrieser, 2007). Better representations of convection in models have been vital for simulating tropical chemical composition. Comparing the new observations with improved model simulations has allowed the quantification of individual processes to be better constrained, their impact on tropical chemistry to be more accurately assessed e.g. (Sauvage et al., 2007b) and discrepancies to be identified for further study.

Tropical tropospheric ozone exhibits a number of features that are attributed to a combination of dynamics and chemistry. The climatological ozone profile is "S" shaped with a minimum at the surface, maximum around 6.5 km, another minimum at around 11 km and a subsequent increase towards the tropopause. The upper tropospheric minimum has largely been explained by outflow from deep convection lifting of ozone-poor air from near the surface (Folkins et al., 2002) and has also been shown to migrate meridionally over Africa with the passage of the ITCZ (Sauvage et al., 2007d). Away from this minimum, ozone increases in the poleward branches of the Hadley cell and this can largely be explained by ozone production promoted by NO_x from lightning. Generally lightning is considered to be very important for tropospheric chemistry, accounting for up to 70% of NO_x and 30–40% of ozone in the tropical UT (Grewe, 2007; Sauvage et al., 2007c).

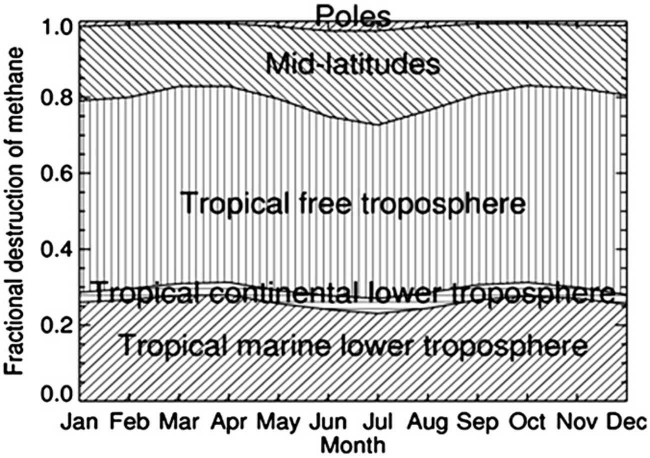


Fig. 33. Contribution of the different regions of the troposphere to the total removal of methane throughout the year calculated from a global CTM (Bloss et al., 2005c).

Two other features are a "zonal wave-one" pattern in the middle upper troposphere with a maximum over the Atlantic and Africa and the "Atlantic ozone paradox" with greater tropospheric ozone over the Southern rather than Northern tropical Atlantic during the boreal winter when biomass burning activity is greater in the northern hemisphere over Africa. These have been explained by combinations of dynamics, transported ozone from biomass burning, and ozone produced from lightning NO_x (Jenkins and Ryu, 2004a,b; Martin et al., 2002; Sauvage et al., 2006; Thompson et al., 2003) Not only has the transport of air impacted by biomass burning in northern Africa been linked to enhanced ozone in the southern hemisphere in boreal winter, but also air impacted by biomass burning in southern Africa has been linked to enhanced ozone in the northern hemisphere over West Africa in austral winter (Mari et al., 2007; Sauvage et al., 2007a, 2005).

A minimum in tropospheric ozone exists over the Pacific between the ITCZ and SPCZ as a result of this air having had a long residence time over the Pacific (Browell et al., 2001). Further, ozone and its precursors have been found in significantly higher concentrations in the southern Pacific during the dry season (as compared to the wet season) when biomass burning was more prevalent and when water vapour and hence ozone loss rates were greater (Browell et al., 2001).

The ENSO affects the intensity of biomass burning, lightning and the transport pathways that redistribute the pollutants over the Pacific and maritime continent. This can lead to, for example, local biomass burning pollution being confined to the boundary layer over northern Australia with elevated concentrations of NO_x and ozone aloft, which have been transported from Indonesia (Kondo et al., 2002) with the ozone having been produced enroute (Kita et al., 2002). During the wet season lightning was found to be a major source of NO_x over the tropical south Pacific (Wang et al., 2001) along with long-range transport of PAN (Staudt et al., 2001).

Measured latitude-altitude distributions of OH concentration have been compared to model estimates across the tropical Pacific and suggest that current model mechanisms provide a reasonably good representation of OH levels for tropical marine environments (Davis et al., 2001). Studies have shown convective uplift of CH_3OOH to be an important source of HO_x in the upper troposphere (Mari et al., 2003). In general, net loss of ozone was found across the tropical Pacific, (Olson et al., 2001) although pollution events were observed, including a river of low-altitude pollution from both Eurasia and America flowing south-westwards in the north-easterly trade winds (Raper et al., 2001). The composition of pollution from Asia flowing out into the Pacific has been extensively studied (Russo et al., 2003).

Near the surface biogenic emissions become relatively more important for the ozone budget e.g. (Aghedo et al., 2007). However, uncertainties as to their effect on the chemistry have been identified. Typically chemical models have calculated that VOCs, in particular isoprene and terpenes, that have been observed at high concentrations above tropical rain forests, (Warneke et al., 2001) lead to depleted boundary layer OH in low NO_x environments. However measurements have found OH concentrations to be higher than expected (Karl et al., 2007; Kuhn et al., 2007) and this is believed to be due to recycling of OH, via the reaction of HO_2 with organic peroxy radicals derived from isoprene (Lelieveld et al., 2008).

Terpenes react with ozone leading to OH, but their impact on the OH concentrations is highly uncertainty, largely owing to poorly quantified emission fluxes and ambient concentrations of these compounds. Observations also suggest large emissions of acetone, or its precursors, from South American rain forests, (Pöschl et al., 2001) whilst acetone and other oxygenated organics were found to be important for the HO_x and NO_x budgets over the tropical Pacific

(Singh et al., 2001). There is also considerable uncertainty over the yield of isoprene nitrates from the reaction of the isoprene peroxy radicals with nitrogen oxide (Chen et al., 1998; Sprengnether et al., 2002) as well as their fate, in particular whether NO_x is lost from the atmosphere (Chen et al., 1998). Global model studies show the impact of isoprene on ozone and PAN in tropical regions is dependent on this chemistry (von Kuhlmann et al., 2004) (see also Section 3.1.1.1).

Away from cities and active biomass burning, NO_x concentrations are low in many parts of the tropics, so natural sources, such as soils, are relatively important. The African Sahel has been identified as a particular important region, with emissions triggered by rain on dry soils. This source has been quantified by satellite observations of column NO_2 (Jaegle et al., 2004) and boundary layer aircraft observations where its impact on ozone has also been observed (Delon et al., 2008; Stewart et al., 2008). Studies in Amazonia have shown that NO_x emitted from forest soils is subject to chemical cycling within the canopy and subsequently re-uptake by the vegetation (Andreae et al., 2002). Tropical oceans have been shown to be a source of low molecular weight alkyl nitrates (Chuck et al., 2002; Dahl et al., 2005) leading to significant concentrations of reactive nitrogen (Blake et al., 2003) which can subsequently impact ozone both near the surface and in the upper troposphere following convective uplift (Neu et al., 2008).

3.3.4. *Heat waves*

Beyond the impact of emission and climate changes on mean ozone concentration, the recent occurrence of the deadly heat wave that struck Western Europe during the summer of 2003 raised several questions about photochemical oxidation processes in extreme weather. Several authors suggested that the 2003 summer is a premonitory picture of mean future European climate (Beniston, 2004; Schär et al., 2004). Deducing ozone concentrations in a warmer climate is however not a straightforward exercise as the effects of emissions and other factors (biogenic emissions and land use) most probably dominate the effect of climate (Vautard et al., 2007). This episode however taught us that the ozone "cloud" can have a large spatial extent over Europe owing to large-scale stagnation and recirculation (Vautard et al., 2005) (see Fig. 35). Large concentrations of many photochemical compounds were observed in different countries (Lee et al., 2006b; Ordonez et al., 2005). The large-scale nature of the episode was also confirmed by airborne MOZAIC measurements (Tressol et al., 2008). The 2003 heat wave was actually followed by other less extreme episodes, such as in 2006 over Central Europe (Struzewska and Kaminski, 2007).

The summer of 2003 also offered an excellent, albeit unfortunate, framework for the study of the combined impact of climate change and air quality on health. The heat wave period claimed about 35,000 extra deaths across Europe (WHO, 2005a). The largest death toll was in France with about 15000 excess deaths, an excess of 54% relative to normal. Although the dominant factor for extra mortality was undoubtedly temperature exposure to photo-oxidants such as ozone and related pollutants probably played a role.

The 2003 event was associated with a very robust and persistent high pressure system over Europe that blocked the flow of a rain-bearing low-pressure system at 700 mb and 500 mb (Lyamani et al., 2006). Some weather services suggested that this phenomenon might be a manifestation of an exceptional northward extension of the Hadley cell. Such synoptic conditions remained almost unchanged for the whole first half of August. Exceptionally high temperatures (often near 40 °C) and the stagnation of air masses over areas of high emissions caused a long-lasting, severe photochemical episode (Vautard et al., 2005). Very high ozone concentrations occurred mainly in the first half of August (see Fig. 35).

The spatial distribution of exceedances of the information threshold, a threshold that requires public information (180 μg m^{-3}) (EU Directive, 2002/3/EC, 2002) observed in summer 2003 was much more extensive than in previous periods. The averaged European daily 8 h ozone concentration for the period June–August 2003 was 87 μg m^{-3}, as compared to 71 μg m^{-3} in 2002 and 61 μg m^{-3} in 2000. In addition to enhanced photochemical pollution, Southern Europe also suffered from high concentrations of carbon monoxide and biomass burning particle aerosols emitted from wild fires in the Iberian Peninsula and mineral dust transported from the Sahara (Vautard et al., 2005). High temperatures and poor air quality resulted in increased mortality in many European countries.

In the Netherlands, 1000–1400 premature deaths were recorded in the 2003 summer period (Fischer et al., 2004). In the UK, an increase of about 2000 deaths during the same period was reported (Stedman, 2004). Mortality of an additional 28000 people was estimated for the southern part of Europe (Portugal, Balkans, Italy) and in France about 15000 excess deaths were recorded. It has been estimated that in the UK, between 423 and 769 of the excess deaths during the first 2 weeks of August 2003 were associated with the elevated ambient ozone and PM_{10} concentrations (Stedman, 2004). This represents 21–38% of the total excess deaths. In the Netherlands, air pollution is believed to have been responsible for 400–600 of the excess summer deaths (Fischer et al., 2004). Both the UK and Netherlands study demonstrate that many of the deaths that were being attributed to the abnormally high temperatures alone, may have been exacerbated by the concomitantly worsened air quality.

During the heatwave episode of 2003, a large atmospheric field measurement study was taking place at a sub-urban site in Writtle, approximately 25 miles North East of London. The observations made encompassed a wide range of gas phase species including O_3, NO, NO_2, CO, C_2–C_{10} non-methane hydrocarbons (NMHCs), C_2–C_7 carbonyl compounds, PAN, and peroxy radicals. Measurements were also made of a range of photolysis rates including $j(O^1D)$, $j(NO_2)$ and $j(HCHO)$ along with a large suite of aerosol number and composition measurements. All of these measurements allowed a unique study of the atmospheric chemistry of a European heatwave to be carried out (Lee et al., 2006b). Fig. 34 shows ozone and temperature data taken at the Writtle site in the southern UK during August 2003. It clearly shows the elevated levels of ozone during the high temperature period, particularly from 5th–11th August. A key part of understanding the 2003 highs is to determine the relative sources of ozone observed at the Writtle site and any potential non-linearities in this generation process.

For the longer-lived secondary products such as ozone (and also species such as acetone etc.), what is observed at this location during a heatwave is a combination of the general Northern

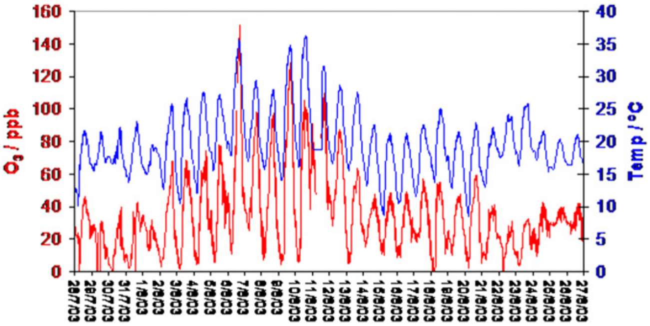


Fig. 34. Ozone and temperature measured in the southern UK through the 2003 heatwave adapted from (Lee et al., 2006b).

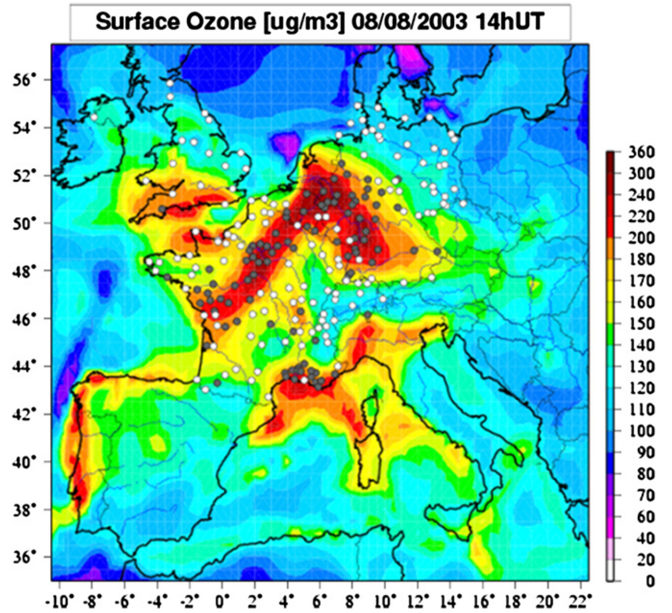


Fig. 35. Simulated surface ozone concentration field (in (μg m^{-3}) with the modified deposition on 8/8/2003 at 14 h UT, together with the station locations marked as empty circles when concentration at that time does not exceed 180 μg m^{-3} and shaded circles when it does (Vautard et al., 2005).

Hemisphere background and regionally produced products. During the heatwave of 2003, ozone data from other air quality monitoring sites in SE England (Harwell, Oxon; Wicken Fen, Cambs; Rochester, Kent and Lullington Heath, *E* Sussex) exhibited the same characteristics as the Writtle site, indicative of a regional scale phenomenon. Model studies such as that by Jenkin et al. (2002) point to Europe as a major source of ozone during such anticyclones and that will also hold true for this case. Measurements of the surface emissions tracers ethane, acetylene and isoprene also show significant enhancements during the heatwave period. Biogenic emissions of isoprene are dependent upon both light and temperature (Guenther et al., 2003) and consequently, atmospheric concentrations of isoprene exhibited a strong diurnal cycle with a maximum in the daytime falling to zero at night. Over the heatwave period in 2003 isoprene concentrations were seen to increase dramatically with a non-linear relationship to temperature, with a peak concentration of 1200 pptV observed on the hottest days. There is also evidence that the emission of additional isoprene during the heatwave was not limited solely to rural locations such as Writtle. Measurements taken at Marylebone Road in central London showed concentrations as high as 1600 pptV in August 2003. Photochemical products such as PAN, acetone and HCHO showed significant enhancement during the heatwave period, much greater than was seen in many of the precursor NMHCs, with peak daytime concentrations more than doubled. This behaviour was also seen in other secondary products such as the higher aldehydes and ketones. These species clearly show significant enhancement during the heatwave period, much greater than was seen in many of the precursor NMHCs, with peak daytime concentrations more than doubled. This behaviour was also seen in other secondary products such as the higher aldehydes and ketones.

An analysis of the OH reactivity of the measured species showed that in non-heatwave periods the largest contribution to VOC reactivity was from acetaldehyde, contributing 25% of the total VOC reactivity, with the total contribution from all oxygenated secondary species being 36%. Formaldehyde and isoprene were also significant, contributing 16% and 14% of the total reactivity, respectively. During the heatwave period, acetaldehyde contributed the most to total reactivity (25%). The total from oxygenated species and formaldehyde was very similar at 35% and 16%, respectively. However, the contribution from isoprene to the total reactivity during the heatwave period increases to 20%. The balance of reactivity between functional group types is broadly similar in the two periods, but absolute concentrations of organic compounds are generally higher. This data shows the extremely active local chemistry occurring during the 2003 heatwave period in the UK (through non-linear emissions of isoprene, elevated peroxy radical intermediates and labile products such as PAN) and therefore suggests a case for significant additional local (that is, within the boundary layer of the UK and on the day of observation) generation of ozone, to be added to an already enhanced regional background. A trajectory model run during the 2003 heatwave period showed that in general, tracers such as NMHCs could be well simulated for the 2003 heatwave, however the simulation of ozone was less successful (Utembe et al., 2005). It would appear from these results that the emissions inventory for anthropogenic VOCs and their chemistry within the trajectory model is well represented, but that estimation of ozone during the heatwave is not straightforward. The ability to correctly simulate ozone over this heatwave period using a trajectory model was closely tied to the biogenic emissions that were introduced by that model from the surface. Whilst biogenic emissions inventories exist for the UK, (Stewart et al., 2003), in general, it is not considered a geographic region which is strongly influenced by biogenic VOCs. There is also the possibility that other biogenic compounds such as monoterpenes have an important role in local ozone formation but are not well represented in emissions inventories.

It is clear that heatwave periods are accompanied by greatly increased levels of photochemical pollution. This, in turn, can cause severe public health effects, in addition to those caused directly by the high temperatures. Recent studies of the 2003 heatwave in the UK have shown the possibility that the abundance of ozone on the final day of an air mass trajectory arriving in the UK during an anticyclone may be influenced not only by longer range transport, but also by UK emissions including important biogenic species which have non-linear emissions and temperature-dependant chemistry. This has clear sensitivity to future changes in meteorology and climate. It is important to understand the chemical and physical processes occurring under such conditions, as climate models suggest that the occurrence of extreme high temperature periods are likely to significantly increase over the period to 2080 (Stott et al., 2004). The current probability in the UK of exceeding 35 °C is 0.6%, however by 2080 it is estimated to become 6%, (e.g. temperatures in excess of 35 °C currently occur roughly 1 day every two years whereas in 2080 we may expect 5 day yr^{-1}, or once every 2.5 weeks during summer.

3.3.5. *Megacities*

For the past few hundred years, human populations have been clustering in increasingly large settlements. It is estimated that in 2007, for the first time in history, the world's urban population exceeded the rural population (UN-HABITAT, 2006). At present, there are about 20 cities worldwide with a population of 10 million or greater and about 30 with a population of about 7 million or greater (see Fig. 36). Such coherent urban areas with more than about 5 or 10 million people are called megacities (there is no clear threshold or formal definition of a megacity at present). The rate of growth of megacities with populations exceeding 10 million has been tremendous, going from only 3 in 1975 to an anticipated 22 in 2015. These numbers are expected to continue to grow in the

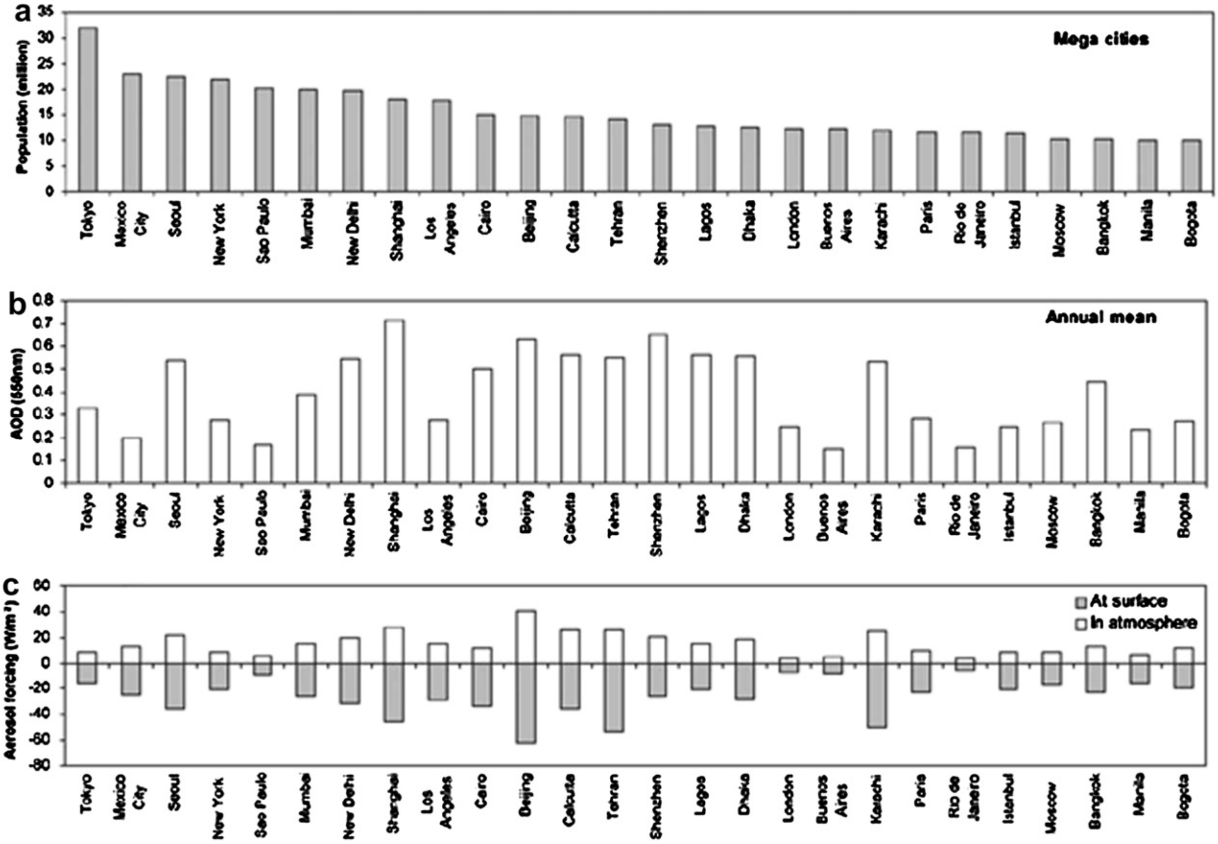


Fig. 36. (a) Population, (b) MODIS annual mean aerosol optical depths and (c) the annual mean aerosol forcing in the atmosphere and at the surface for the top 26 megacities (http://en.wikipedia.org/wiki/Megacity) in the world. The aerosol forcing is estimated by multiplying MODIS AOD with the MACR-modelled forcing efficiency. The AOD and forcing values are for 2001–2003 (Ramanathan et al., 2007).

future. In Europe, there are several major population centres that qualify as megacities, depending on the definition used, the source of data and the method of classifying urban and sub-urban populations.

Megacities and heavily urbanized regions produce large fractions of the national gross domestic product (GDP) (e.g. London, Paris and Mexico City account respectively of 19.9, 27.9 and 26.7% of national GDP (OECD, 2006)). The influence of human activity in megacities leads to serious issues in municipal management, such as housing, employment, provision of social and health services, the coordination of public and private transport, fluid and solid waste disposal, and local and regional air pollution (see Fig. 36). Research on the latter, the focus of this section, has spanned the range from emissions to air quality and effects on weather and climate, from urban to global scales. The general topic underlying this, namely the effects of emissions from large urban areas on remote environments have long been the subject of observational and modelling studies e.g. (Hov et al., 1978; White et al., 1976). Interest in this research has increased over the years owing to the recognition of the significant local and regional consequences which can be expected for human health and crop production e.g. (Chameides et al., 1994). A few representative examples of recent research focused on megacities and their air pollution effects are discussed below. A comprehensive review would be beyond the scope of this section and is not intended. Several good introductions and overviews of various aspects of this topic are available in the literature, for instance in, (Molina and Molina, 2004; Akimoto, 2003; Crutzen, 2004; Gurjar and Lelieveld, 2005), as well as the World Atlas of Atmospheric Pollution (Sokhi, 2008).

Research on emissions from megacities has included several studies of city-specific emissions, such as the collection of inventories for European cities created for use in the City Delta project, (Cuvelier et al., 2007) or various case studies on emissions from individual cities, for example Delhi (Gurjar et al., 2004). These have shown that the use of city-specific data can lead to differences in calculated emission trends compared with trends calculated by application of national policy data using a country-based method. A listing of emissions from a number of cities based on various studies is provided by Gurjar et al. (2008). Regional inventories can also provide significant insights into megacity emission, such as the regional emission inventory for Asia developed by (Streets et al., 2003) which was used for instance by (Guttikunda et al., 2005) to study the effects of Asian megacity emissions on regional air quality and by Streets et al. (2007) to examine the anticipated effectiveness of pollution control measures for the 2008 Summer Olympics in Beijing. In general, city-specific and specialized regional inventories can probably be considered more accurate than the global inventories; however, global inventories are the only ones that allow a cross-comparison of cities using the same underlying assumptions for each, and are the only emissions available for use in global chemistry-transport models. Butler et al. (2007) examine the megacity emissions in three widely-used global emissions datasets and find large differences (often a factor of two) between the emissions for individual cities, even when the total global emissions of gases like NO_X and CO are very similar.

In the global inventories, emissions from megacities in OECD countries are generally dominated by road transport, while in non-OECD countries, notably in Asia, megacity CO emissions are dominated by residential biofuel use, and industrial emissions predominate for NO_x. Non-methane hydrocarbon emissions in OECD megacities are found to be caused by industry and traffic, whereas in non-OECD countries residential biofuel use makes significant contributions. Future work on megacity emissions will include both greater refinements of the existing inventories, as well as scenario work on determining expected future impacts and the most effective mitigation measures.

The air pollution in megacities has long been of interest to researchers (Jacobson, 2002). Smog events in London date back at least to the 17th century, culminating in the week-long event in December, 1952, which caused about 12,000 deaths. Many other large cities, such as Los Angeles, have been renowned for their poor air, as well as for the substantial clean-ups over more recent years. Scientific research on the air quality (Haagen-Smit, 1952) in these cities has resulted in an increasing understanding of the complex interplay between emissions, gas and aerosol phase processes, urban-scale meteorology, regional meteorology and pollutant import.

For the specific sub-topic of megacities there have been far fewer publications, with the main overviews of the issue being those previously indicated. There are also many national and international research programs focusing in general on urban pollution. Amongst these, two which stand out as being sponsored by global organizations are the WMO GURME (GAW Urban Research Meteorology and Environment) program, and the UNEP Atmospheric Brown Clouds (ABC) program. From the European perspective, it is worth noting the City Delta project, (Cuvelier et al., 2007) mentioned above, along with others, e.g. the EU FP5 FUMAPEX (Forecasting Urban Meteorology, Air Pollution and Population Exposure) project (Baklanov et al., 2005). Again, there are far fewer international projects specific to the topic of megacities, though two European projects worth noting here are the new EU FP7 projects CityZen (megaCITY - Zoom for the ENvironment) and MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation), which will be delving deeper into these issues over the period 2008–2011.

Beyond urban pollution in the megacities themselves, the emissions from megacities can have significant effects on the atmospheric chemistry of downwind regions. The outflow, distribution and influence of pollutants on regional, continental and global scales have been examined in several previous studies using global models (e.g. Wild and Akimoto, 2001; Stohl et al., 2002; Lawrence et al., 2007, 2003). More detailed examinations of specific regions or individual megacities have been conducted using regional models e.g. (de Foy et al., 2006; Guttikunda et al., 2005). A good overview of this kind of research is provided by Akimoto (2003). On the whole, these studies have shown the substantial potential of the pollution from megacities to affect surrounding and downwind regions, including the upper troposphere, and that the effects depend strongly on the regional meteorological characteristics around the individual cities. Since most megacities are at or close to the coasts, much of this outflow (approximately half, according to Lawrence et al. (2007)) occurs over the oceans, with potential effects on elemental cycles (e.g. fixed nitrogen) in maritime surface waters. The outflow to surrounding continental regions can result in substantial impacts on health and agriculture, though this has yet to be characterized for megacities. It is also unclear whether the overall pollution levels and impacts would be greater or less if the total population were to be kept the same, but the population density were to be shifted from urban to surrounding regions. Other questions also remain open, such as whether the concentrated emissions of gases, aerosols and aerosol precursors in the megacities have a substantial impact on regional and global climate.

3.3.6. A regional hot spot – Mediterranean

The Mediterranean region consists of landmass surrounding a body of saline water (Mediterranean sea) that does not exchange very rapidly with the rest of the oceans. The Mediterranean climate is characterized by hot, dry summers and mild, rainy winters. Evaporation greatly exceeds precipitation and river runoff in this region, a fact that is central to water circulation within the basin.

The Mediterranean is a crossroad of air masses coming from Europe, Asia and Africa (see Fig. 37) (Lelieveld et al., 2002). At this crossroad, anthropogenic emissions, mainly from Europe, Balkans and the Black sea, meet with natural emissions from Saharan dust,

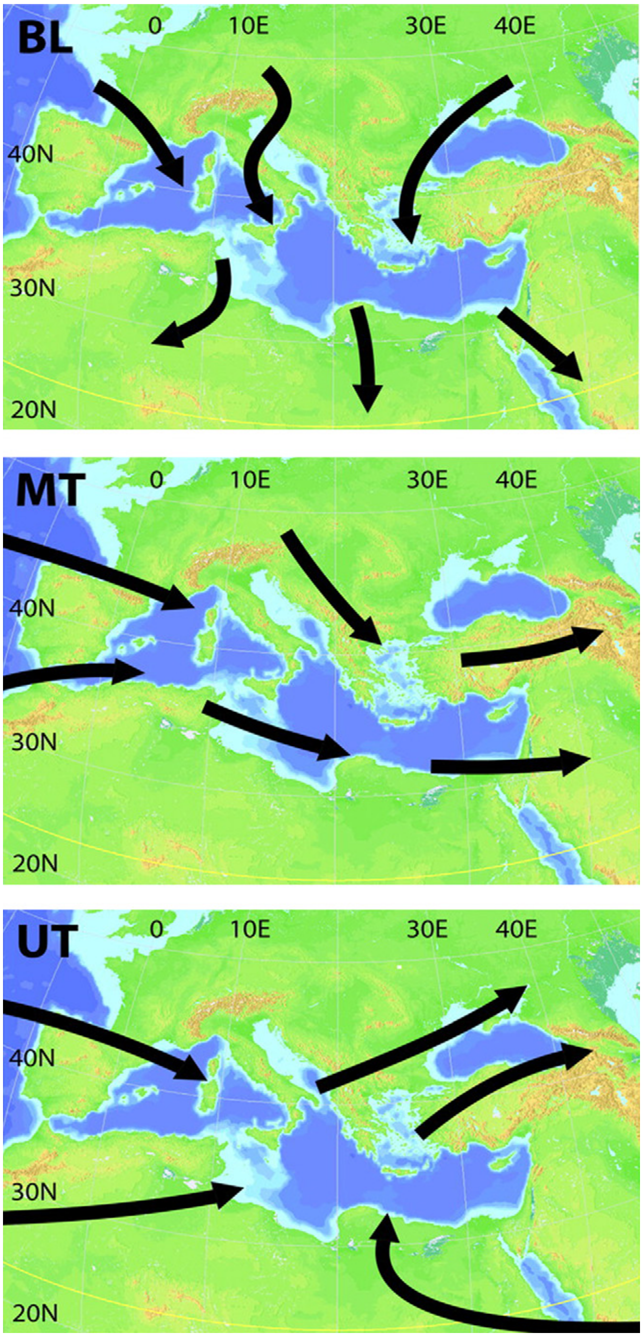


Fig. 37. Schematic air mass trajectories in the Mediterranean (during the MINOS campaign), representing transport during approximately 3 days in the lower, middle, and upper troposphere (from top to bottom, respectively). BL, boundary layer; MT, middle troposphere; UT, upper troposphere. The figure illustrates how the Mediterranean can be considered to be a cross roads for global air pollution (Lelieveld et al., 2002).

vegetation and the sea, as well as from biomass burning, which presents a strong seasonal pattern (Reneau et al., 2007). The transport of anthropogenic pollutants from America also exerts a significant influence in the free troposphere. As a consequence of its unique location and emissions, the Mediterranean region is often exposed to multiple stresses, such as a simultaneous water shortage and air pollution exposure. Pollution in this region has been high in the last couple of years, exacerbated by the Mediterranean climate and is likely to grow in the future owing to the rapid urbanization of the region. The meteorology and chemistry of the Mediterranean lead to two "distinct" but interlinked regions, the western and the eastern basins.

Ozone and aerosol air quality limits are often exceeded over the entire Mediterranean particular during the summer. The contribution of natural emissions to these exceedances seems significant but remains to be quantified. The Mediterranean, located at the boundary between the tropical and mid-latitudes, is subject to large (about 50%) changes in the total O_3 column (Ladstatter-Weissenmayer et al., 2007) which have been attributed to changes in the location of the sub-tropical front (Hudson et al., 2003). In summer, the total observed variability in tropospheric O_3 is about 5–10% of the total O_3 column, that is 25DU (Ladstatter-Weissenmayer et al., 2007). As Mediterranean background O_3 levels are high, particularly in spring or summer and depending on the meteorological conditions they are controlled by a combination of large-scale processes, long-range transport and photochemical formation, it makes it difficult to control ozone in urban and industrial areas.

In the eastern Mediterranean, experimental studies (Kourtidis et al., 2002; Kouvarakis et al., 2000) have demonstrated that transport from the European continent is the main mechanism controlling ozone levels in the eastern Mediterranean, especially in summer (or spring depending on the prevailing air transport patterns) when ozone presents a maximum of about 60 ± 10 ppbV (Gerasopoulos et al., 2005). However, both model results and observations have revealed a net photochemical ozone depletion over the eastern Mediterranean sea in summer. Gerasopoulos et al., (2006b) and Kalabokas et al. (2007) found that during the summer high tropospheric ozone values in the eastern basin were confined in the low troposphere whereas in the middle troposphere O_3 was only 5–10% higher than over Central Europe.

In the western Mediterranean, the highest ozone levels in the western basin are recorded in mid-spring and early fall, i.e. when the breezes oscillate the surface air mass between the sea and the mountain slopes, while still remaining mostly confined below approximately 300–700 m, or less. In summer, the O_3 production is higher but the vertical recirculations, described above, increase the overall mixing volume, so that average O_3 concentrations may actually be equal to or lower than in spring and early autumn (Millán, 2002).

Observations over the Mediterranean also show high concentrations of aerosols, both PM_{10} and $PM_{2.5}$. Chemistry-transport models successfully simulate the occurrence of high loadings of aerosols over the Mediterranean (Gangoiti et al., 2006; Kallos et al., 2007; Kanakidou et al., 2007; Nickovic et al., 2001). In the Mediterranean, PM_{10} has a similar seasonal behaviour to $PM_{2.5}$, which is marked by dust emission and transport, particularly in spring and fall in the eastern basin and in February–March and late spring-summer in the western basin (especially on regional background sites), whereas PM_1 behaves differently (Gerasopoulos et al., 2007; Koçak et al., 2008; Querol et al., 2008; Saliba et al., 2007). Mineral dust transport events that occur episodically over the area make a major contribution (more than 40%) to the PM_{10} exceedances of the EU limit of 50 $\mu g\ m^{-3}$ (Escudero et al., 2007; Gerasopoulos et al., 2006a; Koçak et al., 2008; Mitsakou et al., 2008). This is also evidenced by observations from lidar (Papayannis et al., 2008) and sun photometer (Fotiadi et al., 2006) networks and satellite observations (Kalivitis et al., 2007; Papayannis et al., 2005). Resuspension of dust is likewise a significant component of aerosols in the cities (Rodriguez et al., 2004). In industrial and urban areas, most exceedances (around 70–80%) are due almost exclusively to local anthropogenic source (Querol et al., 2008). During summer the persistent northerly winds carry large pollution loads from Europe that can deposit onto the Mediterranean sea, for instance, nitrate and phosphorus containing aerosols, which affect the water quality and could contribute to eutrophication (Kouvarakis et al., 2001).

The fine aerosol fraction (<1 μm) is mainly dominated by pollution components. In the eastern basin 60% of the total mass is due to ionic mass and about 30% to organics (Leung et al., 2007) (Bardouki et al., 2003; Koulouri et al., 2008). In the western basin the contribution of carbonaceous components increases (from about 10 to 40%) from the rural to the traffic locations (Querol et al., 2008). In the coarse mode in the eastern basin organics account for about 10% whereas ionic components and dust contribute about 50% and 40%, respectively (Koulouri et al., 2008); in western basin rural background areas these contributions are about 15%, 55% and 20%, respectively (Querol et al., 2008). Compared to the colder Central and North Europe, the high temperatures that impose a low thermal stability of ammonium nitrate in summer favour the formation of nitric acid rather than ammonium nitrate in the area (Mihalopoulos et al., 1997; Querol et al., 2008).

The Mediterranean atmosphere is a photochemical reactor with high levels of oxidants, particularly hydroxyl radicals, which have been measured to reach mid-day maxima of approximately 2×10^7 molecules cm^{-3} (Berresheim et al., 2003). These oxidants initiate reactions that form acids, including sulphuric and nitric acids, and secondary aerosols. The high sulphate loadings in the area are mostly attributed to the long-range transport of sulphurdioxide pollution (Zerefos et al., 2000). Significant interactions exist in the Mediterranean between natural and anthropogenic components in the atmosphere both in the gas and aerosol phases. Observations and modelling have shown that marine biogenic emissions contribute up to 20% of the total oxidized sulphur production (Kouvarakis and Mihalopoulos, 2002) and about 17% of the nitric acid plus particulate nitrate formation and thus the nutrient deposition to the sea (Vrekoussis et al., 2004, 2006) on a mean yearly basis.

Of particular interest for the sulphur abatement strategy is that during summer in the eastern Mediterranean, heterogeneous sulphate production on fine particles appears to be negligible whereas only about 10% of the supermicron non sea salt sulphate can be explained by condensation of gas phase sulphuric acid; the rest must be formed via heterogeneous pathways (Mihalopoulos et al., 2007). In addition, ageing of aerosols, such as coating of dust by pollution compounds (Falkovich et al., 2004) or chemical trapping of nitrogen on pollen particles, can be harmful for human health. Franze et al. (2005) found that proteins including the birch pollen allergen Bet v1 are efficiently nitrated by polluted urban air, and he suggested that this post translational modification of proteins might promote allergies by traffic-related air pollution. The observed rates of nitration were governed by the abundance of nitrogen oxides and ozone, and concentration levels typical for summer smog conditions led to substantial nitration within a few hours to days. During spring and summer, the Mediterranean subject to intensive pollen emissions is a favourable area for such interactions.

3.3.7. *Impacts of biomass and waste burning*

Biomass burning (BB) has an ongoing role in determining the composition of the Earth's surface and atmosphere. The representation of biomass burning emissions in models has been dealt with in Section 2.3. Biomass burning affects terrestrial vegetation dynamics (Houghton et al., 2000), soil erosion (and subsequent movement of organic carbon with implications for carbon dynamics) e.g. (Reneau et al., 2007), hemispheric atmospheric composition e.g. (Leung et al., 2007) and air quality e.g. (Stohl et al., 2007a; Wotowa and Trainer, 2000) and more broadly provides important contributions to radiative forcing via emissions of trace gases and aerosols, surface albedo changes owing to burn scars e.g. (Myhre et al., 2005), and associated climate feedbacks e.g. (Charney, 1975). Consequently, quantifying all impacts of biomass burning is integral to better understanding past, current, and future climate.

As discussed in Section 2.3, biomass burning represents a significant percentage of the global budget of many trace gases and particulates. The atmospheric impact of these emissions is controlled by the type, location, strength and duration of the burning source, and also by their subsequent vertical distribution with implications for their atmospheric transport and chemistry. There have only been a few studies of atmospheric chemistry within biomass burning plumes, reflecting the complexity and uncertainty of the associated chemistry. Space-borne observations of land-surface and tropospheric chemistry provide the only large-scale constraint on our current understanding. Linking these relatively new, large-scale measurements with more detailed *in-situ* observations is an ongoing scientific challenge. In this subsection, some recent work that helps to elucidate the role of BB in determining atmospheric composition is reviewed.

A topic that is receiving progressively more attention is the rapid vertical mixing of biomass burning emissions owing to intense surface heating from the fires, so-called pyroconvection. Pyroconvection of short-lived pollutants, which would otherwise be photochemically removed in the boundary layer, can significantly perturb chemistry in the free and upper troposphere and in some cases the stratosphere. Modelling pyroconvection is a difficult computational fluid dynamics problem that involves describing the response of the atmosphere to intense surface heating, often on spatial scales that are not captured by the current generation of CTMs. Historically, CTMs have treated BB the same way as other surface emissions by assuming they are well-mixed instantaneously in the boundary layer. But data from aircraft campaigns and satellite data provide mounting evidence that BB plumes can reach the free and upper troposphere, and in some circumstances reach the stratosphere e.g. (Damoah et al., 2006; Fromm et al., 2006; 2000, 2005; Fromm and Servranckx, 2003; Jost et al., 2004; Livesey et al., 2004; Myhre et al., 2005).

Recent work has highlighted that not considering pyroconvection has serious implications for our understanding of the atmospheric transport and fate of BB emissions (Colarco et al., 2004; Freitas et al., 2006; Turquety et al., 2007). Errors in vertically distributing BB emissions will also affect, to an unknown degree, top-down emission estimates e.g. (Hyer et al., 2007), based on optimally fitting model sources to trace gas measurements. Unfortunately, the sparse nature of the detailed aircraft campaign data precludes development of robust parameterizations based on these data, so the frequency at which plumes rise above the boundary layer is a subject of active research.

Only a few studies have attempted to model the first few hours of chemistry within BB plumes e.g. (Mason et al., 2001; Trentmann et al., 2003, 2005). As simultaneous measurements of biomass burning trace gases and aerosol properties become more comprehensive e.g. (Hobbs et al., 2003) so does our ability to test current understanding of resulting atmospheric chemistry. Even including a small subset of oxygenated volatile organic compounds (OVOCs, e.g. formaldehyde, acetic acid, formic acid, methanol, phenol, and hydroxyacetaldehyde) significantly improves the ability of chemistry models to reproduce observed concentrations of ozone and radical species in burning plumes (Mason et al., 2001; Trentmann et al., 2003, 2005). Including these OVOCs increases the abundance of radicals via photolysis leading to a significant decrease in NO_x lifetime, with the formation of HNO_3 more important early on and the formation of PAN progressively more important as the plume ages, with implications for long-range transport (LRT) of pollutants (Mason et al., 2001; Trentmann et al., 2003). Photolysis of HCHO represents the largest source of radicals, with related impacts for net O_3 productions, nitrogen reservoir species, and the oxidation of alkenes (Mason et al., 2001; Trentmann et al., 2003). Any processes that slow down the photochemistry of HCHO can effectively determine the speed of photochemistry within the BB plume. Young biomass plumes (less than 1 day old), very close to the point of emission, are depleted in O_3 via $O_3 + NO$ reaction (negative $\Delta O_3/\Delta CO$ ratios) but subsequent rapid production ($\sim$25 ppbV h^{-1}), largely via $HO_2 + NO$, increases O_3 concentrations to above ambient levels (positive $\Delta O_3/\Delta CO$ ratios) (Trentmann et al., 2003), a similar situation is reported in field campaigns e.g. (Goode et al., 2000; Hobbs et al., 1996; Yokelson et al., 2003). Model and observed O_3 concentrations within a small subset of young BB plumes, accounting for the photochemistry of OVOCs, generally show agreement within a few percent. Comparison of different chemistry models (Mason et al., 2006) agreed within a few percent for contrasting boreal and savannah burning environments, much less that the errors associated with field measurements or the photochemical data used to constrain the models. Differences between the models were largest when studying the boreal fire, associated with the higher VOC loading owing to direct and variable secondary sources. For instance, large secondary production of other atmospheric trace gases, such as methanol and acetone, has been inferred from burning plumes e.g. (Holzinger et al., 2005b) but they are not consistently reproduced e.g. (de Gouw et al., 2006), reflecting the large variations in local fuel sources and photochemical environments. Given the model sensitivity to VOCs and that only 70% of VOC present within smoke plumes can be readily identified suggests that better VOC speciation be a priority for future measurement campaigns (Mason et al., 2006).

Presence of aerosols affects the oxidizing efficiency of the plumes by altering the actinic flux available for photochemistry and providing surfaces for heterogeneous reactions but the magnitude of these effects is highly variable in space and time. Calculations based on upward and downward irradiances (integrated between 350 and 450 nm), converted into actinic flux by a radiative transfer model, concluded that the actinic flux is decreased by 30% in the plume core but increased the flux by 10% in the upper part of the plume owing to scattering (Trentmann et al., 2003). The resulting model calculation underestimated observed O_3 concentrations in the plume core, owing to reduced production of radical from the photolysis of OVOCs. An additional model calculation that enhanced the photolysis frequency and decreased plume dilution (core to ambient levels) did not significantly increase model O_3 concentrations in the upper part of the plume and the work concluded that model error was not entirely because of the effect of smoke aerosol on actinic flux (Trentmann et al., 2005). These results are qualitatively consistent with model calculations associated with long-range transport of pollutants discussed below. The importance of smoke aerosol also lies in their role in providing surfaces for heterogeneous reactions (e.g. $CH_3OH + NO_2$, (Tabazedeh et al., 2004; Trentmann et al., 2005)). The importance of indirect effects of BB aerosol on atmospheric composition via cloud processing (e.g. (Tabazedeh et al., 2004; Yokelson et al., 2003)) and eventual scavenging of soluble species has also been studied.

The advent of satellite observations first drew attention to the LRT of biomass burning pollutants (e.g. (Thompson et al., 2001)).

There are very few places on Earth that are not impacted directly by biomass burning via air pollutants (e.g. (Bertschi and Jaffe, 2005; Edwards et al., 2006; Holzinger et al., 2005b; Honrath et al., 2004; Lelieveld et al., 2004; Mari et al., 2007; Morris et al., 2006; Thompson et al., 2001)) or indirectly via deposition of absorbing aerosol that decrease albedo over the particularly sensitive polar regions e.g. (Park et al., 2005). The fire and atmospheric chemistry modelling communities have tended to focus mainly on using ground, aircraft and satellite observations of land-surface and atmospheric constituents *over* regions of burning to quantify the magnitude and spatial and temporal distribution of burning emissions (Turquety et al., 2007). Model calculations based on aircraft vertical profiles of biomass burning tracers (see above) suggest a significant fraction of emitted mass is injected directly into the free troposphere via fire-related convective processes and transported away from the emission region impact chemistry on a hemispheric-scale e.g. (Cook et al., 2007; Honrath et al., 2004; Leung et al., 2007; Pfister et al., 2006; Val Martin et al., 2006), and in some instances be responsible for a large percentage of observed year-to-year variations in observed concentrations of biomass burning tracers ((Spichtinger et al., 2004; Szopa et al., 2007; Honrath et al., 2004)). In some instances, the impact of biomass burning emissions of O_3 precursors is enhanced by concurrent increases in anthropogenic emissions of NO_x in relatively pristine regions (Lelieveld et al., 2004).

In some cases, LRT of air quality pollutants from biomass burning can rival those from local anthropogenic emissions (Morris et al., 2006; Real et al., 2007; Stohl et al., 2007a; Wotowa and Trainer, 2000). Meteorology also plays an important role: slight changes in the timing of burning when meteorological conditions are favourable for air quality exceedances can lead to unforeseen implications. For example, a shift in the burning season over Eastern Europe owing to late snowmelt led to air laden with biomass burning emissions being rapidly transported (few days) to Iceland causing the worst air quality episode in its history with surface ozone concentration exceeding 80 ppbV for a 1 h period (Stohl et al., 2007a).

4. The impact of atmospheric transport on composition

In order to establish the source–receptor relationships of air pollutants it is important to consider atmospheric transport processes and the chemical conversions and deposition processes occurring enroute across all the spatial scales. Depending on the lifetime and properties of a pollutant, it can be transported on scales ranging from the street level to the global scale. As the processes controlling the transport are scale-dependent, this chapter is structured according to the scales and relevant processes. In Section 4.1, processes in the atmospheric boundary layer (ABL) and on the urban scale are described. In Sections 4.2 and 4.3, thermally-induced circulation systems and convection are discussed which occur on the mesoscale. In Section 4.4, pollution transport on the synoptic scale, in particular as related to cyclones, are described. Finally, in Section 4.5, phenomena occurring on the hemispheric and global scale are examined. It must be noted that the different scales are not strictly separated and pollution transport occurring on one scale can influence the pollution transport on another scale. For instance, pollution lifted up from the ABL by small-scale circulation systems or deep convection can be transported by the fast winds in the free troposphere (FT) on the synoptic and hemispheric scale.

4.1. Transport in and export from the atmospheric boundary layer, including urban effects

During the last decade, mesoscale meteorological modelling for air quality purpose has been developed and applied both in research and operational practice (see e.g. an overview of European models in Baklanov et al., 2008). Advanced CTMs are nowadays coupled offline to or are integrated on-line with high-resolution meteorological or numerical weather prediction (NWP) models that contain ABL schemes which include advanced parameterization of stably-stratified ABLs, interaction of ABL with the free troposphere, and the representation of gravity waves (see an overview of recently published papers in Baklanov and Grisogono (2008). However, the description of the atmospheric pollution transport over strongly heterogeneous terrain, like mountain areas, coastal zones, and urban areas is still problematic. The Monin–Obukhov similarity theory, a standard theory for describing turbulence near the Earth's surface, is not applicable over complex terrain and does not realistically reproduce strongly stable or strongly unstable stratification regimes.

Air pollution episodes occurring during adverse meteorological conditions (e.g. stable ABLs under stagnant conditions) are presently one of the major concerns for the protection of human health in the urban environment as they can cause exceedances of short-term air quality standards. A reliable description and prediction of the urban-scale wind field and other meteorological parameters is also of utmost importance for urban emergency management systems for accidental (or purposeful) releases of toxic, radioactive or biological material.

The urban ABL presents a challenge to atmospheric scientists, both from the experimental and modelling point of view as typically urban areas have high roughness elements penetrating well above the surface layer and heterogeneous distribution of surface features with wide variation in surface fluxes of heat, moisture, momentum and pollutants. These urban features, some of which are summarized in Fig. 38, can influence the atmospheric flow and turbulence, the microclimate and, accordingly, modify the transport, dispersion and deposition of atmospheric pollutants within urban areas. Additionally, the structure of the conurbation may trigger local meteorological processes e.g. urban heat island owing to radiation trapping and anthropogenic heat fluxes, enhanced production of condensation nuclei and effects on clouds and precipitation owing to increased aerosol concentrations as well as enhanced vertical motions that can change the residence time of trace substances in the atmosphere (Hidalgo et al., 2008). During the last decade, several measurement campaigns have studied the urban boundary layer and air pollution processes in the urban areas of Europe and America e.g. BUBBLE (Rotach et al., 2005), ESCOMPTE (Mestayer et al., 2005), CAPITOUL (Masson et al., 2008) and MILAGRO (Molina et al., 2008).

Incorporation of the urban effects into CTMs should be accomplished first of all via improvements of the meteorological fields (wind velocity, temperature, humidity, etc.) over urban areas. Recent developments in the European project FUMAPEX on integrated systems for forecasting urban meteorology and air pollution (Baklanov et al., 2005) and by the US EPA and NCAR communities with the MM5 (Dupont et al., 2004; Taha, 2008) and WRF (Chen et al., 2006) models, as well as other relevant studies (Baklanov et al., 2009), show many opportunities for the "urbanization" of NWP and mesoscale meteorological models.

Simulating urban canopy effects in urban-scale NWP and meso-meteorological models use, in the main, three approaches:

1. Modifying existing non-urban approaches for urban areas by finding proper values for the effective roughness length, displacement height and heat fluxes (accounting for the anthropogenic heat flux, heat storage capacity and albedo change).
2. Augmenting the momentum, energy and turbulent kinetic energy equations by additional source and sink terms

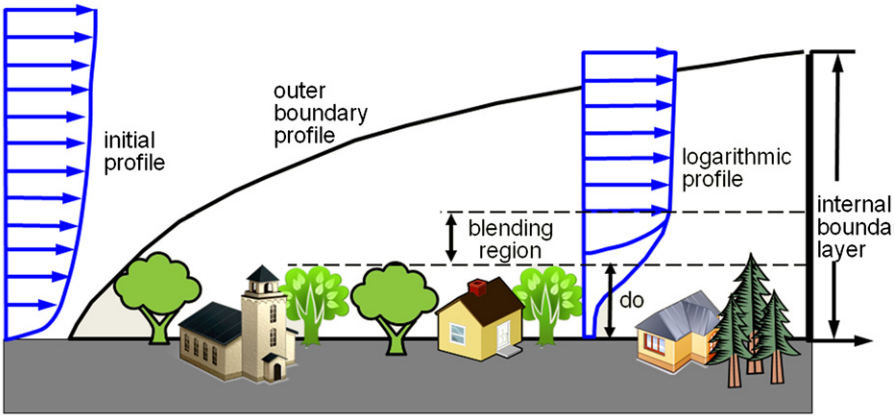


Fig. 38. Schematic development of an urban boundary layer.

representing the effects of buildings on radiation balance, heat and turbulence (Dupont et al., 2004; Hamdi and Masson, 2008; Kusaka et al., 2001; Martilli et al., 2002; Masson, 2000; Masson et al., 2008).

3. Two-way coupling of mesoscale NWP models with microscale/CFD models that operate in the urban- or street-scales. Interpolation metamodels have been suggested as a computationally affordable means to implement an effective on-line coupling).

The urbanization of urban air pollution (UAP) models has specific additional requirements compared to NWP models, as the vertical structure of the urban ABL is very important. Thus, vertical profiles of the main meteorological fields and turbulence characteristics within the urban canopy are much more important than for meteorological modelling alone. Another important characteristic for turbulent mixing of pollutants is the mixing height, which is very inhomogeneous over urban areas owing to the internal boundary layers, blending heights from different urban roughness elements. Other specific urban features, which need to be incorporated in UAP models, include pollutant deposition on urban surfaces, chemical transformation specifics (e.g. different photolysis rates owing to street shadows), specific aerosol dynamics in street canyons (e.g. resuspension of aerosols) and the heterogeneous emissions of pollutants. With the ultimate aim of quantifying air pollution health effects, it is also important to integrate the UAP and population exposure modelling, using high-resolution databases of urban morphology, population distribution and activities.

While urban-scale processes determine pollution transport from the urban area to the regional scales, regional-scale processes also affect air pollution on the urban scale, for instance by determining the inflow of pollution into an urban area. Therefore, the new generation of CTMs use nesting techniques for down- and upscaling (Fernando et al., 2001; Moussiopoulos, 1995), ideally in a two-way nesting approach allowing feedbacks in both directions.

4.2. *Small-scale thermally-induced circulation systems*

The influence of complex orography (mountainous and/or coastal terrain) on vertical transport and mixing within so-called thermally-induced circulation systems is discussed in this section. Although the influence of mountainous terrain on the synoptic flow by Rossby wave forcing, mountain waves, downward wind storms, foehn etc. can significantly contribute to or trigger vertical transport and mixing, it is not covered in detail here. The term “thermally-induced circulations” (TIC) here comprises flow systems that occur owing to the diurnal course of differential heating on the meso-γ- and meso-β-scale, and range from slope wind systems over valleys and land-sea breezes (including lake breezes) to plain-to-mountain flows (see Fig. 40). These flow systems arise from differential solar heating during the day (radiative cooling during night) causing horizontal temperature and pressure gradients that are counteracted by direct flow from the colder (higher pressure) to the warmer (lower pressure) region with minor influence of Coriolis forces. The pioneering work on TIC has been summarized by several authors (Barry, 1992; Sturman, 1987; Whiteman, 1990, 2000).

Thermally-induced flow systems were once thought to be closed circulations with upward motion in the low pressure region, a return flow aloft and sinking motion in the high pressure region of the system but with little net export of near surface air. However, it has since been determined that TIC can strongly contribute to net vertical transport and export of ABL air masses. Vertical mass export in TIC from the ABL to the FT was categorized into two types: “mountain venting”, describing direct export owing to thermal plumes above lines of flow convergence along slopes or over ridges that penetrate the ABL inversion and “advective venting” owing to advection of ABL air from elevated terrain or regions with increased ABL depth over the ABL top of less elevated terrain or regions with suppressed ABL (Kossmann et al., 1999). The more general term “topographic venting” was used by Henne et al. (2004) to describe all situations where TIC induces export of ABL air to the FT (also over coastal terrain) (see Fig. 39). Vertical transport in TIC often manifests itself in the formation of elevated pollution layers in the lower FT (McKendry and Lundgren, 2000). The lifetime of species that are subject to surface deposition is increased in such layers. Furthermore, owing to dilution with FT air during transport, O_3 production efficiency per molecule NO_x is increased (Henne et al., 2005a) because of the more efficient catalytic production at lower NO_x concentrations and the longer lifetime of NO_x.

Recent advances in computational capacity allow for the simulation of TIC in mesoscale models at sub-kilometre grid resolution. However, the quality of such simulations can only be validated if measurement data with high spatial resolution are available. Improved possibilities for ground-based remote sensing of the lower troposphere using various lidar, radar and acoustic techniques together with extensive surface measurement networks are able to deliver the necessary validation data sets. A number of extensive campaigns on TIC and its influence on pollutant dispersion were conducted around the world in the last decade. The Meso-scale Alpine Programme (MAP) (Bougeault et al., 2001) aimed to close the gaps in the understanding of the turbulence structure of the ABL over complex terrain. Key findings of several campaigns within the Alps are summarized by Rotach and Zardi

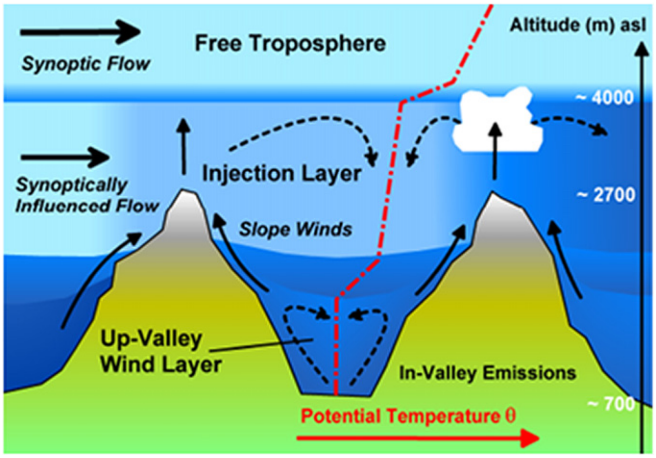


Fig. 39. Schematic of the daytime atmospheric structure and vertical pollution transport in and above deep Alpine valleys as described by Henne et al. (2005b). Altitudes given represent typical values for the cases studied. Typical potential temperature profile is indicated by dashed-dotted red line. See text for details.

(2007). The Pollution des Vallées Alpines (POVA) field studies in two Alpine valleys in the French Alps (Chamonix and Maurienne valleys) focused on the diurnal flow patterns and the evolution of air pollutants from road traffic during the morning and evening transition phases of the valley wind system (Chemel and Chollet, 2006). During October 2000 the Vertical Transport and Mixing (VTMX) campaign, taking place in the Salt Lake Valley, Utah, investigated vertical transport and mixing within nighttime stable boundary layers in an urban environment (Doran et al., 2002). An extensive field campaign yielding new insights into the meteorology, primary pollutant emissions, ambient secondary pollutant precursor concentrations, photochemical oxidant production and secondary aerosol particle formation in the Mexico City Metropolitan Area (MCMA-2003) took place in April 2003 (Molina et al., 2007). The ESCOMPTE (Expérience sur Site pour Contraindre less Modèles de Pollution atmosphérique et de Transport d'Émissions) field study (Cros et al., 2004) took place in the Marseille metropolitan area to analyse the interaction of the sea breeze with up-valley winds and also with the down-valley mistral flow. All these studies indicate that: (1) TIC has a strong influence on local pollution concentrations; (2) vertical transport occurs at convergence lines of the surface flow, and is most pronounced during daytime (up-slope convergence over ridges, sea breeze front especially when interacting with opposing synoptic flow), but can also occur within nighttime drainage flow; (3) pollutants lifted in TIC can influence regions down-stream by advection aloft and subsequent down-mixing; (4) operational NWP models and CTMs underestimate pollution transport in TIC despite improved grid resolution.

Zhong and Fast (2003) evaluated three different mesoscale models (RAMS, MM5, Meso-Eta) with sub-kilometre horizontal grid resolution for thermally- and synoptically-driven weather situations during the VTMX observation period. While all the models reproduced the general flow structure, a more in-depth analysis revealed a negative temperature bias of all models within the valley atmosphere. The models were not able to represent the shallow nighttime boundary layer and underestimated the temperature inversion in the lowest 100 m above ground even when the number of vertical model levels was doubled. The models

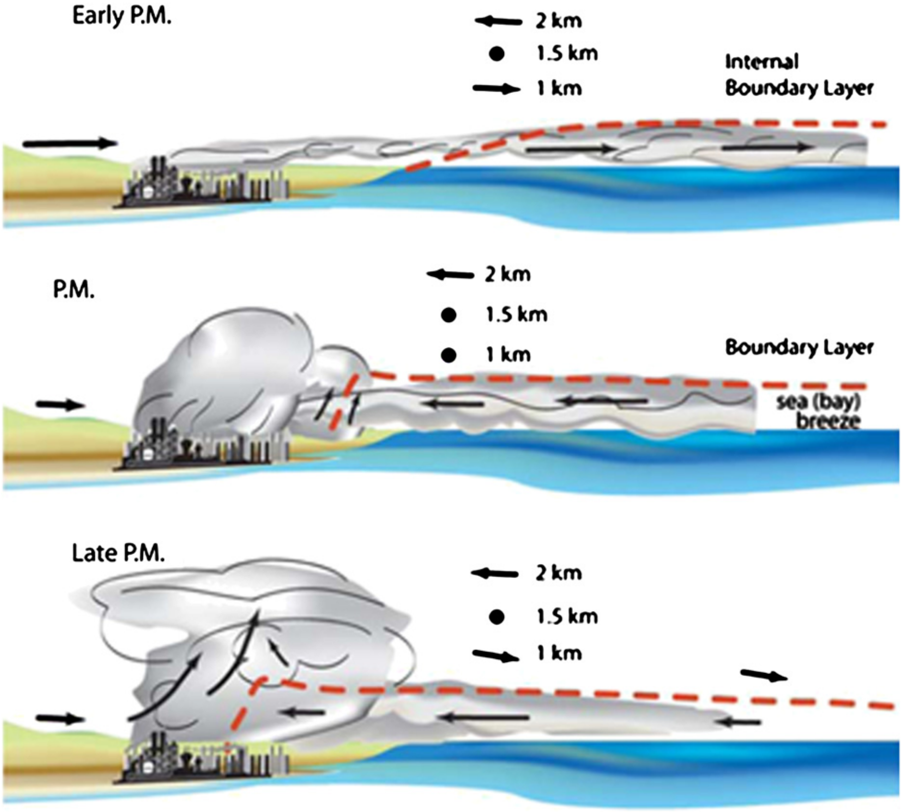


Fig. 40. Schematic vertical cross section along the west-east line from Houston city centre to Galveston Bay, (Banta et al., 2005) showing (top) early day offshore flow taking pollutants outward over Galveston Bay, (middle) the incipient bay-breeze producing a convergence zone of light and variable surface winds just onshore over the source regions, and (bottom) a more fully developed onshore flow producing stronger convergence, lofting pollutants high over the coastal zone. Arrows represent direction and relative speed of wind component, and dots represent layers of light flow. Heavy red dashed line indicates top of mixing layer over the bay and of bay-breeze layer over land.

overestimated the vertical eddy exchange, resulting in excessive vertical mixing compared to observations. The authors conclude that an increase in horizontal resolution will only yield improved small-scale forecasts when parameterizations of longwave radiation and turbulent mixing are improved. Rotach and Zardi (2007) conclude from their studies in the Alps that traditional ABL scaling theory, which was derived for flow over homogeneous terrain, cannot simply be applied over complex terrain owing to the large spatial variability of surface characteristics. However, they note that suitable extensions of those scaling relations might be applicable to different conditions over complex terrain. De Wekker et al. (2005) emphasize the importance of correctly simulating soil moisture and latent heat fluxes.

Only a small number of observations of TIC and the resulting pollution export on the meso-β-scale were conducted. Lugauer and Winkler (2005) analysed the plain-to-mountain flow towards the Alps in southern Bavaria as observed in surface meteorological measurements. They observed that on 42% of all days between April and August a northerly flow towards the Alps develops over Southern Bavaria extending ~100 km north of the Alpine margin. The depth of this inflow ranged from ~1 km at the foot of the Alps to ~2 km in the valleys in the northern Alps. A 1500 m thick inflow layer towards the Alps with wind speeds between 1 and 4 m s^{-1} and a maximal northward extent of 80 km were observed on a typical fair-weather day (Weissmann et al., 2005). Simulations with operational NWP models using grid sizes of 3 km could reproduce the larger scale advection towards the mountains.

Climatological studies of TIC are essential to understand the frequency and necessary conditions for the development of TIC. For the summer months of the period 1997 to 2000 Stewart et al. (2002) selected days with fair-weather conditions based on strong irradiation and weak synoptic flow to separate the characteristics of TIC within four regions in the North American inter-mountain west. They observed strong day-to-day similarity of TIC as indicated by high day-to-day wind consistency for nighttime flow (90%), moderate values for daytime flow (60%) and low values (20%) during the transition period. Convergence zones of TIC during both day- and night-time were observed in all four areas. The development of larger scale TIC lagged that of smaller scale TIC and often overwhelmed the latter during the course of the day. From 11 years of surface observations within Switzerland, Henne et al. (2005b) estimated that, depending on the selection criteria, on 23–39% of all days between March and September TIC develops within the Swiss Alps. This is similar to the 42% of all days between April and August derived by Lugauer and Winkler (2005) for southern Bavaria. Kar et al. (2006) present a study of carbon monoxide (CO) over the Zagros Mountains in the Middle East as retrieved by the MOPITT (Measurements of Pollution in the Troposphere, (Deeter et al., 2003)) instrument onboard NASA satellite Terra. They observed increased daytime CO mixing ratios up to the 350 hPa level for the months of April to June and ascribe the increase to vertical transport within the mountain range followed by topographic venting.

A step forward in deriving parameterizations of topographic venting for larger scale models is the quantification of the air mass exchanged vertically on a sub-grid scale. The exchange of the ABL of the valley wind systems of two narrow valleys in southern Switzerland was estimated from airborne flow measurements on eight, typical, strong irradiation, weak synoptic forcing days. Thirty to forty percent of the ABL air mass was found to be exported to the “injection layer” per hour during up-valley flow (Henne et al., 2004).

Vertical transport and mixing through TIC was identified as an important process altering small-scale air pollutant distribution but also through vertical export influencing long-range transport. In addition, TIC might trigger deep convective systems and therefore be the reason for even more rapid vertical transport to the upper troposphere (see Section 4.3). Currently, most CTMs still operate on grid scales much coarser than 1 km, which seems to be a necessary grid size to resolve small-scale TIC. While increasing resolution of operational models will sooner or later reach 1 km, sub-grid parameterizations are needed in the meantime to include the effect of TIC in global models.

4.3. Convective transport

In this section vertical transport in deep convection (known as thunderclouds or cumulonimbus clouds) is discussed. This transport pathway is the most rapid way that trace species from the ABL can reach the upper troposphere (UT) or even lower stratosphere (LS). Within few tens of minutes up to 1 h, trace species in the ABL may reach altitudes above 10 km and change the UT/LS composition and chemistry (e.g. Jaegle, 2007; Lelieveld and Crutzen, 1994 and references therein). In the colder and dryer environment of the UT, the lifetime of trace species increases since chemical destruction is slower. In the main updraft region, trace species may be transported upward almost undiluted and unaffected. Though, in the surrounding downdrafts soluble chemical species, such as nitric acid and hydrogen peroxides, can be scavenged by precipitation. The convective transport of radical precursors such as e.g. hydroperoxides, may increase the photochemical activity in the UT. Besides the upward transported species, an additional UT source is the *in-situ* production of nitrogen oxides ($NO_x = NO + NO_2$) by lightning, an important ozone precursor (Schumann and Huntrieser, 2007). Furthermore, the ozone (O_3) production efficiency per NO_x molecule typically increases with height, as already discussed in Section 4.2. The final stage in the development of a cumulonimbus cloud is the rapid spread of an anvil just below cloud top. This widespread cirrus cloud reflects solar radiation upwards. As a result chemical photolytic reaction rates increase above the anvil and at cloud top (scattering) and decrease inside. Owing to the longer lifetime and higher wind speed in the UT, trace species may be transported over long distances, affecting photochemistry and O_3 concentrations far downwind (Dickerson et al., 1987).

Preferred regions for the development of thunderstorms in Europe in summer are the foothills in vicinity of mountain ranges (orographic lifting). An evaluation of synoptic reports of thunderstorms from 1996 to 1999 shows that local maxima of thunderstorm frequency can be found north and south of the Alps (van Delden, 2001). An evaluation of data from the ATD-lightning detection system furthermore indicates preferred thunderstorm regions in the vicinity of the Alps and the Pyrenees (Holt et al., 2001). The type of thunderstorms with the highest mass flux from the ABL to the UT on a global-annual basis is mesoscale convective systems (MCSs) (Cotton et al., 1995; Houze, 2004). A climatology of MCSs for Europe was published by (Morel and Senesi, 2002). Orographic lifting (Alps and Pyrenees) combined with diurnal heating is the dominant source of European MCS triggering. The majority of these MCS moves to the east-north-east and frequently occurs in the vicinity of convergence lines or frontal zones. Results from a CTM (GEOS-CHEM) by Duncan and Bey (2004) confirm that convection over Germany and the Ural Mountains in Russia is an important export pathway for European pollution to the middle and upper troposphere in summer even though the main export pathway of European pollution is at low altitudes all times of the year, e.g. (Wild and Akimoto, 2001). Model studies by Wild et al. (2004) and Wild and Akimoto (2001) show that European emissions have the smallest effects on downwind continents and their O_3 mixing ratios because of less active vertical transport compared to other continents, predominantly because of less convection (see also Section 4.5).

It has been stated that large uncertainties of the emission rates from deep convective events at mid-latitudes still exist (IPCC, 1999).

The first airborne observations of pollutants (CO and NMHCs) uplifted by thunderstorms from the ABL to the anvil outflow region were reported from the U.S. by Dickerson et al. (1987). Furthermore, the enhanced NO_x mixing ratios in the anvil outflow compared to the ABL suggested that NO_x production by lightning was important (Hauf et al., 1995; Holler et al., 1999; Huntrieser et al., 1998). A larger field campaign was conducted in summer 1998 over southern Germany within the European Lightning Nitrogen Oxides Experiment (EULINOX) (Huntrieser et al., 2002). The polluted air masses in the UT were found to originate mainly from a height close to the top of the ABL (about 1.5 km above the ground). Cases with both high and low CO_2 mixing ratios in the ABL compared to the FT were observed and these especially high or low mixing ratios were reflected in the anvil outflow, indicating almost undiluted transport. Enhanced NO_x mixing ratios on the micro- to mesoscale (300 m to several 100 km) were observed, owing to both lightning and uplift from the ABL. In addition to chemical species small particles (condensation nuclei, CN, >10 nm) were observed. CN concentrations in the anvil outflow were distinctly higher than in the polluted ABL below, indicating production of new particles. Recently, Kumala et al. (2006b) suggested that convectively uplifted water-insoluble trace gases (organic vapours) can produce new particles at low temperatures near the tropopause. Fehr et al. (2004) used a three-dimensional cloud model combined with a Lagrangian particle model for the lightning-NO_x emissions and found that 50–80% of total lightning NO_x is transported into the anvil.

In the summer of 1999, the field experiment KONVEX probed a large number of thunderclouds with and without lightning and a mean convective mass flux of NO_x into the UT was determined per cloud type (50 and 8 g (N) s^{-1}, respectively) (Schlager et al., 2003). In the following summer 2000, the DLR Falcon aircraft performed joint flights together with UK Hercules C-130 aircraft over Central Europe within the European Export of Particulates and Ozone by Long-Range Transport (EXPORT) project. On the 2nd August 2000 a warm conveyor belt (WCB, see Section 4.4) slanted between Geneva (3–5 km) and Hannover (6–7 km) with embedded convection was probed by both aircraft. CO mixing ratios were slightly enhanced (90-100 ppbV) in the WCB and strong pollution ($CO > 130$ ppbV) could be found inside a convective cell embedded within the WCB (Schlager et al., 2003). The measurements from the C-130 aircraft of reactive NMHCs with different lifetimes (1–15 h) showed which regions of the WCB system had convective transport rather than large-scale, slantwise advection along the WCB (Purvis et al., 2003). Much higher ratios of alkenes and acetylene (similar to ABL) were measured within the embedded convection.

Within the Mediterranean Oxidant Study (MINOS) field experiment in August 2001, the Falcon aircraft ascended into the LS above a cumulonimbus cloud during one flight. In this region influenced by stratospheric air masses ($O_3 > 200$ ppbV), CO increased from 60 to 90 ppbV, acetone and methanol increased from 0.7 to 1.8 and from 0.4 to 1.4 ppbV, respectively, and benzene and acetonitrile were enhanced (Fischer et al., 2003). These observations where the first evidence that polluted ABL air can be directly mixed into the LS over Europe. It was estimated that LS air can contain up to 50% ABL air in such convective events. Within the SPURT campaign (trace gas measurements in the tropopause region) an air mass with unexpectedly high NO_y and H_2O mixing ratios was observed in the LS over the western Mediterranean on 10 November 2001 (Hegglin et al., 2004).

A combination of satellite brightness temperature and lightning strokes along backward trajectories ("convective influence") has been used to trace air masses back to a large convective system over Spain and Algeria. Results from model studies have suggested that the breaking of gravity waves at the top of deep convective systems in mid-latitudes can inject trace species into the LS (Wang, 2003). Forward trajectories indicate that this convectively influenced air mass remains in the LS for the next 10 days, impacting chemistry and radiation over a wide region. The same convective plume was observed from space (Thomas et al., 2003).

The projects CONTRACE (Convective Transport of Trace Gases into the Middle and Upper Troposphere over Europe) and UTOPIHAN (Upper Tropospheric Ozone Processes Involving HO_x and NO_x) focused on the vertical transport of European pollutants by deep convection and performed joint flights with the Falcon and Learjet aircraft. A case with convectively uplifted emissions from Germany transported towards the northwest (North Sea and North Atlantic) and re-imported to Western Europe 5 days later in the LT was probed by the Falcon (Huntrieser et al., 2005). The pollution circulated around a stationary low-pressure system over the British Islands and distinctly enhanced CO and peroxide mixing ratios were still observed in the aged plume. Within UTOPIHAN, airborne measurements of formaldehyde (HCHO) combined with model simulations indicate that deep convection plays an important role in the chemistry and budget of HCHO in the UT (Stickler et al., 2006). Though, the upward transport of precursor gases of both HCHO and HO_x (e.g. methanol and acetone, isoprene) seem to be more important than the direct convective transport of HCHO from the ABL. In the case of convectively uplifted air masses, HCHO was found to be the most important source for HO_x production in the UT (Colomb et al., 2006).

In addition to these selective observations of convectively influenced air masses, aged plumes influenced by convection have occasionally been probed by trace gas instruments onboard commercial airliners within the framework of NOXAR (Measurements of Nitrogen Oxides and Ozone Along Air Routes), MOZAIC (Measurement of Ozone and Water Vapour by Airbus In-service Aircraft) and CARIBIC (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrumented Container). Within NOXAR 1995–1997, (Brunner et al., 2001) found that the UT-NO_x budget in summer over Europe is dominated by large-scale NO_x plumes, (Grewe et al., 2001) originating from convectively uplifted ABL air and lightning production. However, coupled chemistry–climate models have difficulties to simulate these widespread NO_x plumes. Furthermore, Brunner et al. (2001) pointed out that a broad UT-NO_x maximum extends from Europe to Siberia in summer. Measurements from CARIBIC also indicate that especially high particle number concentrations are observed in the UT over Europe in summer, partly due to convective uplift of polluted BL air (Hermann et al., 2003). Tulet et al. (2002) used MOZAIC measurements combined with model simulations to study the impact of deep convection upon the redistribution of O_3. They concluded that deep convection might also have a significant effect at the surface due to both up- and downward fluxes (change in surface O_3 mixing ratios up to ±30 ppbV). The anvil outflow from deep convection often spreads laterally in the UT over large distances (>100 km). This layered structure of TS in the FT was first observed during airborne measurements by Newell et al. (1999, 1996). They found that a large fraction of the FT is occupied by such quasi-horizontal layers (up to 20%), mainly between 5 and 7 km, and with a mean thickness of the order of 1 km. An evaluation of MOZAIC measurements over Europe indicates that these kind of layers called "pollution with a stratospheric cap" (mean thickness 600–800 m) frequently occupy the FT (6–7 km) in summer (17%) (Thouret et al., 2000). A climatological analysis of ozone sounding data from Europe over the past 30 years also confirms that 10% of the ozone-rich layers in the FT was exported recently from the BL owing to convective uplift (Colette et al., 2005).

Observations of trace species transport in deep convective clouds are numerous. However, the simulation of these small-scale processes by models is still a challenge since the first attempts by e.g. Gidel, (1983). The spatial and temporal resolution in the models is in most cases not as high as required. Therefore these processes are parameterised and the result depends a lot on the choice of convective-transport parameterization, e.g. (Collins et al., 2002). Lawrence and Rasch (2005) pointed out that for the transport of short-lived TS (couple of days or less) the convective mass flux parameterization based on the plume ensemble formulation (PEF) instead of the bulk formulation (BF) improves the results of a three-dimensional global chemistry-transport model compared to measurements. Furthermore, such rapid transport processes as convection and turbulent mixing are not represented by the large-scale analyses used to drive Lagrangian trajectory models (Lawrence and Salzmann, 2008). During the EXPORT field experiment in summer 2000 it was found that the Lagrangian chemistry-transport model used could not reproduce the observed pollutant enhancements owing to convective ascent (Arnold et al., 2003; Purvis et al., 2003). However, in one Lagrangian particle dispersion model, a convective transport parameterization has been included (Forster et al., 2007).

Several three-dimensional global model studies have focused on the role of deep convection in the O_3 budget of the troposphere. Lelieveld and Crutzen (1994) found a net reduction of 20% in total tropospheric ozone burden owing to convective upward transport and compensating mesoscale subsidence and a net increase in the atmospheric oxidation efficiency by 10–20%. However, Lawrence et al. (2003) also pointed out the importance of O_3 precursors and computed that the net effect of convectively transported O_3 and its precursors is a 12% increase in total tropospheric O_3. In contrast, results from runs with a coupled chemistry–climate model by Doherty et al. (2005) indicate that convective transport at mid-latitudes reduces UT O_3 resulting in a 13% decrease in the global tropospheric ozone burden, since convective overturning of O_3 itself dominates over changes in ozone chemistry. The net effect on O_3 directly in the convective outflow has been investigated with high-resolution cloud models such as the three-dimensional Goddard Cumulus Ensemble (GCE) model for the 21 July 1998 EULINOX thunderstorm (Fehr et al., 2004). The inclusion of lightning-produced NO_x resulted in a small increase in the net production of ozone at most levels, max. $\sim$5 ppbV per day at 5.5 km, except between 8 and 10.5 km (highest concentration of lightning-produced NO_x) where the net ozone production decreased. It was concluded that the net O_3 production rate during the first 24 h in the outflow of storms with large flash rates over polluted regions may be less than in the outflow of storms with moderate flash rates over cleaner regions. Furthermore, a better description of the NO_x and NO_y chemistry, their sources and sinks is thought to be essential for future model improvements with respect to the representation of chemistry in the UT/LS region (Brunner et al., 2005).

It has been predicted that a changing climate in future will also impact the occurrence of thunderstorms. The frequency, intensity and distribution of deep convection will be affected, which in turn impact the trace gas composition in the UT/LS region (Schultz et al., 2002). Most climate models indicate that heat waves will become more frequent, intense and longer lasting during the second half of this century, especially over the Mediterranean, France, Germany, and Balkans (Meehl and Tebaldi, 2004; Schär et al., 2004). Heat waves and droughts may enhance the occurrence of extreme wildfire episodes (Hodzic et al., 2007). Dispersing smoke layers in turn may enhance the atmospheric stability and prohibit the initiation of thunderstorms. On the other hand, it was recently also found that the extreme convection directly over the fires (so-called pyroconvection) can transport pollutants directly into the lower stratosphere (Fromm and Servranckx, 2003). In one case, (Jost et al., 2004) pollution lifted in a pyro-cumulonimbus cloud was even observed in the stratospheric overworld (potential temperatures greater than $\sim$380 K).

4.4. *Synoptic-scale transport*

The synoptic scale applies to weather systems ranging in size from several hundred kilometres to several thousand kilometres, such as migratory high and low-pressure systems (frontal cyclones) of the lower troposphere (Glickman, 2000). With respect to the import of pollution to Europe the most important synoptic scale features are the mid-latitude cyclones that form above eastern North America and follow the North Atlantic storm track to western Europe. These systems export large quantities of trace gases and particulate matter from the east coast of North America throughout the year, even in summer when these weather systems are weaker (Cooper et al., 2002b; Merrill and Moody, 1996; Stohl et al., 2002).

Each mid-latitude cyclone contains a moisture-laden airstream referred to as the warm conveyor belt (WCB), an important mechanism for rapid intercontinental pollutant transport (Bader et al., 1995; Carlson, 1998; Cooper et al., 2001; Stohl and Trickl, 1999). The WCB originates in the atmospheric boundary layer within the warm sector of the cyclone which lies between the surface cold front and warm front. The cyclonic motion forces the warm sector air to rise out of the boundary layer, as it travels poleward, ascending into the mid- and upper troposphere. The water vapour within this air mass condenses into droplets, resembling in satellite imagery a broad river of cloud (or conveyor belt) flowing northward until it reaches the jet stream where it takes a turn towards the east. If boundary layer air within the warm sector contains North American emissions then these trace gases and particulate matter will also be transported with the water vapour along the pathway of the WCB, less the fraction that is water soluble and removed by precipitation. An example of a large pollution plume exported from eastern North America by a WCB is illustrated in Fig. 41.

Following the mid-latitude cyclone storm tracks, the WCB air is carried by the jet stream, rapidly transporting the pollutants downwind. Transport times from the moment North American atmospheric boundary layer air is lifted within the WCB until it reaches the European FT are typically 3–4 days (Eckhardt et al., 2004; Stohl et al., 2002) and in some cases less than 2 days (Stohl et al., 2003c). Several additional days are required for the North American emissions to reach the European surface with the greatest influence over the Mediterranean owing to trapping and anticyclonic descent of the emissions through the Azores' high (Stohl et al., 2002).

Mid-latitude cyclones can also export pollutants from North America at low altitudes, either when the warm sector of the cyclone pushes offshore and the WCB is too weak to loft the pollutants (Owen et al., 2006), or when the cold stable air behind the cyclone's surface cold front quickly advects fresher emissions offshore (Cooper et al., 2002a). Once the low-level export has occurred the pollutants can be transported across the Atlantic with the geostrophic wind that flows eastward between the Azores/Bermuda High to the south and the Icelandic Low to the north (Owen et al., 2006).

Over the past 10–12 years many studies have appeared in the peer-reviewed literature documenting the transport of North American emissions to Europe, originating from both anthropogenic and biomass burning sources. The transport mechanisms fall into three general categories: 1) export of anthropogenic emissions from eastern North America into a WCB followed by rapid transport to Europe in the mid- and upper troposphere, with impact limited to either the European FT or high mountaintop monitoring stations; 2) export of anthropogenic emissions from eastern North America at low altitude followed by slow low-level transport across the Atlantic with minor or imperceptible influence at low altitude monitoring stations; 3) emissions from boreal fires transported

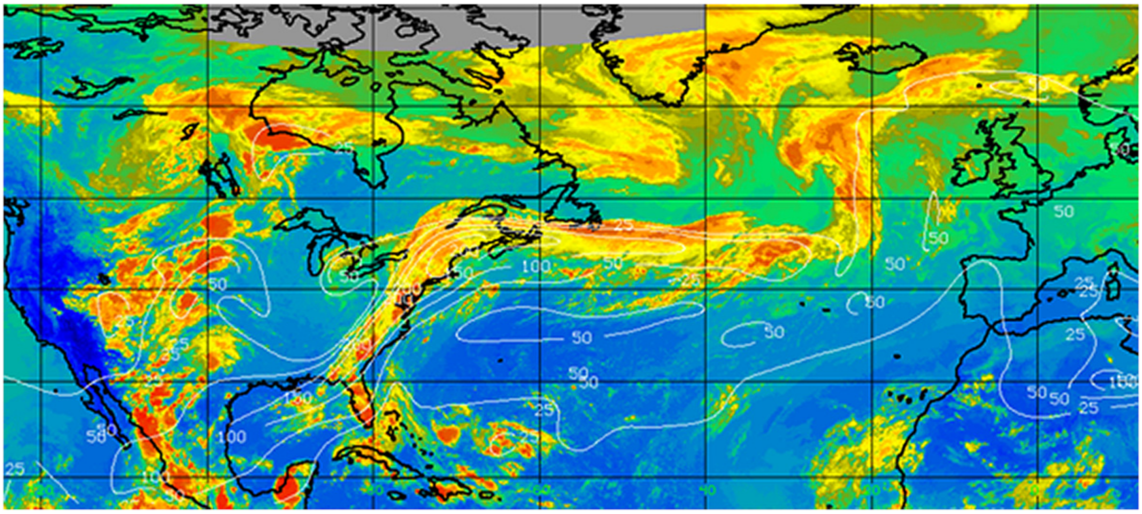


Fig. 41. Infrared satellite image at 1:00 UTC, July 28, 2004, showing high, cold cloud tops in reds and yellows, mid-level clouds in greens and the warm surface of the earth in blues. The white contours show the location of an anthropogenic carbon monoxide tracer in the mid- and upper troposphere, expressed as column values (mg m^{-2}). The concentrated plume above eastern North America and extending into the North Atlantic Ocean is being exported by a WCB, visible as the co-located band of high-level cloud tops. This plume crossed the western boundary of Europe 24 h later.

across the Atlantic in the lower or mid-troposphere at higher latitudes and/or colder potential temperatures than typically associated with anthropogenic emissions. Much of this work has been overviewed as part of the HTAP process (Keating and Zuber, 2007).

Stohl and Trickl (1999) using a trajectory model and lidar measurements of ozone above southern Germany were the first to demonstrate that anthropogenic emissions could be transported from North America to the European FT via a WCB. Further case studies of transport to the European FT were documented by Stohl et al. (2003b,c) and Trickl et al. (2003). Importantly, Huntrieser et al. (2005) showed that pollutant transport via a WCB could also be detected at the surface, but so far this has only been clearly demonstrated for high altitude sites in the Alps. With regard to low altitude trans-Atlantic transport and impact at European surface sites. Derwent et al. (1997) found five probable cases of North American emissions influencing Mace Head on the west coast of Ireland, but the pollutant concentrations were quite low. Methven et al. (2006) show that during July, 2004, the New York City plume was exported from North America behind a cold front and crossed the North Atlantic at low altitude. While the plume was not detected at the surface it was measured by an aircraft in the lower FT off the coast of Ireland.

The only major North American export event to show a strong impact on low altitude European surface sites involved smoke plumes from the widespread boreal forest fires in Canada that caused CO mixing ratios to reach 175 ppbV at Mace Head during August 1998 (Forster et al., 2001b). Anthropogenic pollution from eastern North America generally travels from a warmer lower-latitude regime to a colder, higher latitude regime, increasing the likelihood that quasi-isentropic transport will loft the pollutants into the FT above Europe. In contrast boreal fires occur at higher latitudes where potential temperatures are more likely to be similar to those of Europe allowing the plumes to intersect the European surface. Boreal forest fire plumes also impact the European FT and this has been dealt with in detail in Section 3.3.9.

Synoptic-scale transport also affects the export of pollutants from Europe. High-latitude Europe and Siberia are cold enough to allow direct transport of air pollution from these regions into the Arctic lower troposphere (Barrie, 1986; Stohl et al., 2006) contributing to Arctic Haze, a mixture of sulphate and particulate organic matter and, to a lesser extent, ammonium, nitrate, black carbon, and dust aerosols (Quinn et al., 2007). Typically, this pollution from Europe and Asia traverses the polar region of the Arctic and reaches high-latitude North America (Sharma et al., 2006).

Only a few studies have examined the transport of European pollution to Asia (Duncan and Bey, 2004; Newell and Evans, 2000; Pochanart et al., 2003; Wild et al., 2004). Newell and Evans (2000) estimated that, on an annual basis, 24% of the air parcels arriving over Central Asia have previously crossed over Europe, and some 4% have originated in the European atmospheric boundary layer. Pochanart et al. (2003) have shown that average ozone and CO concentrations in East Siberia are enhanced in air masses transported from Europe. Over Japan, impacts of North American and European emissions are similar (Wild et al., 2004).

European pollution is also exported southwards in the lower troposphere across the Mediterranean Sea to North Africa year round although the strongest events occur during summer (Lelieveld et al., 2002; Stohl et al., 2002). The transport of many species and particulate matter from Europe to Africa during summer can be very efficient due to the diminished impact of wet removal processes (Kallos et al., 1998). A modelling study by Duncan and Bey (2004) indicates the exported European pollution is responsible for 5–40% of the lower tropospheric ozone above North Africa during summer.

Synoptic scale mid-latitude cyclones also impact the chemical composition of the European troposphere by injecting large quantities of stratospheric ozone into the mid- and upper troposphere with subsequent descent into the lower troposphere (Monks, 2000; Stohl et al., 2003a). The ozone descends from the stratosphere into the troposphere in what is known as a stratospheric intrusion, a component of every mid-latitude cyclone that descends isentropically and equatorward along the western edge of the cyclone's WCB (Cooper et al., 2001; Danielsen, 1968; Johnson and Viezee, 1981). Stratospheric intrusions occur all year round, typically in mid-latitudes, and follow the seasonal cycle of the mid-latitude cyclone tracks, with a higher latitude origin in summer and a lower-latitude origin in winter. Once an intrusion has been irreversibly transported into the troposphere it can be advected more-or-less intact for several days (Bithell et al., 2000), with some intrusions reaching the lower troposphere and even the marine boundary layer of the tropics (Cooper et al., 2005). The intrusions make their strongest impact on lower tropospheric ozone in winter and spring when the associated cyclones are stronger, allowing for deeper descent, and when ozone in the lowermost stratosphere is more plentiful. Focusing on the lower troposphere of the northern hemisphere during winter, the regions most heavily impacted by stratospheric intrusions are the sub-tropical regions of the North Pacific Ocean, the southeastern USA, North Africa and the Middle East. In summer the most impacted regions are mid-latitude North America, the Middle East and the Tibetan Plateau (James et al., 2003). Europe is located north of the main belt of influence of stratospheric intrusions with the Mediterranean region receiving the strongest impact.

Several studies over the past fifteen years have provided firm evidence that stratospheric intrusions impact ozone mixing ratios at mountain top sites in Europe. For example, stratospheric intrusions have contributed to ozone peaks of 92 ppbV at Jungfraujoch, Switzerland (3580 m elevation) in January (Davies and Schuepbach, 1994); ~70 ppbV at Sonnblick, Austria (3106 m), Zugspitze, Germany (2962 m), and Jungfraujoch in a single event in October (Stohl et al., 2000); 70–90 ppbV at Sonnblick, Zugspitze, Jungfraujoch and Mt. Cimone, northern Italy (2165 m) in a multi-day event in May–June (Stohl et al., 2000) and 69 ppbV at Zugspitze and 85 ppbV at Jungfraujoch in a single event in June (Zanis et al., 2003). In general, modelling studies of the frequency of stratospheric intrusions at Zugspitze, Sonnblick and Mt. Cimone indicate a summertime minimum and a wintertime maximum, whereas no clear seasonal cycle was found for the higher elevation site of Jungfraujoch (Cristofanelli et al., 2006; Stohl et al., 2000).

In conjunction with the detection of stratospheric ozone at Alpine mountaintop sites, moderate increases in ozone mixing ratios in the nearby valleys have also been detected (Stohl et al., 2000). Furthermore, aircraft measurements have been used to demonstrate mixing between stratospheric intrusions and polluted air in the mid- and lower free troposphere above the UK in winter and spring (Esler et al., 2003). However, for low elevation sites in Europe attribution of ozone fluctuation to stratospheric intrusions has proven to be more difficult because the intrusions are diluted once they enter the atmospheric boundary layer, and the stratospheric ozone can often be masked by moderate to high levels of photochemically produced ozone at the surface. For example, Davies and Schuepbach (1994) describe transport conditions in March 1988, that would have allowed stratospheric ozone to contribute to an exceptionally high ozone peak of 75 ppbV at a surface measurement site on the Dutch coast, although they could not rule out the possibility that photochemistry also contributed substantially to the event. Similarly, Kunz and Speth (1997) showed that 20–30% of the time during the year 1990, surface ozone monitoring stations in Germany showed an average ozone increase of 4–8 ppbV after the passage of a cold front with conditions favourable for the descent of stratospherically enhanced ozone. Finally, Klaić et al. (2003) show that hourly ozone mixing ratios of 70–80 ppbV in Zagreb, Croatia during February 1990, occurred in conjunction with air mass transport from the lower stratosphere. However, in none of these studies were quantitative estimates made of the contribution of stratospheric ozone to the surface ozone measurements (Monks, 2000).

4.5. Hemispheric- and global scale transport

Although local and regional emissions significantly contribute to the level and occurrence of episodes of degraded air quality there is an increasing body of evidence that shows hemispheric transport of ozone, fine particles, and their precursors contributes to the degradation of air quality and impacts climate. During the past 5–7 years, scientific investigations related to long-range pollution transport have focused on the northern hemisphere mid-latitudes because most of the anthropogenic emissions are released there, over three main source regions (i.e. Europe, Asia, and North America) (Keating and Zuber, 2007). The long-range transport of pollution may have some implications for the design and efficiency of local air pollution control policies e.g. (Jacob et al., 1999; Li et al., 2002). Currently, increasing interest is being devoted to the long-range transport of pollution towards the high latitudes, as the Arctic region experiences the fastest environmental changes. A better quantitative understanding of the hemispheric-scale transport can be achieved by combining observations from different platforms with numerical tools (including Lagrangian particle dispersion model models, photochemical box models, and global CTMs). This section presents the most recent scientific highlights related to the hemispheric-scale transport.

4.5.1. Ozone and trace gases

Owing to their relatively long lifetime (up to several weeks in the FT), ozone, its precursors and related compounds (e.g. acyl peroxynitrates) experience long-range transport of pollution. Export of ozone-related pollution not only leads to frequent, episodic pollution export events but also contributes significantly to the overall increase of the background ozone concentrations (Derwent et al., 2004). Evidence for the frequent occurrence of pollution export events is provided by ground-based observations collected downwind of and relatively close to the source regions e.g. (Millet et al., 2006) or further away e.g. (Owen et al., 2006; Wolfe et al., 2007). Large-scale experiments using research aircraft such as the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) off the California coast, the Pacific Exploration of Asian Continental Emission–B (PEACE-B) over the northwest Pacific (Parrish et al., 2004) and the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) over the North Atlantic (Fehsenfeld et al., 2006) provided further proof of the mechanisms and impacts of long-range transport. In addition, satellites can now provide a global view of the atmospheric composition and are therefore becoming useful to examine long-range pollution transport e.g. (Guerova et al., 2006; Martin et al., 2006; Pfister et al., 2006).

The pathways for the pollution transport in the mid-latitudes are now relatively well documented e.g. (Cooper et al., 2004; 2002a, 2001; Li et al., 2002; Stohl and Trickl, 1999; Trickl et al., 2003). Vertical transport from the boundary layer to the FT occurs through deep convection and in mid-latitude cyclones, as described in Sections 4.3 and 4.4. It has been suggested that the East Asian region has the greatest potential to affect tropospheric ozone because the vertical transport is more efficient and stronger there (Stohl et al., 2002; Wild and Akimoto, 2001). In contrast, Europe is more likely to be affected by long-range transport of pollution because of the short-distance transport from North America (Wild and Akimoto, 2001).

In the framework of the ICARTT campaign, air masses were intercepted and sampled several times as they are travelling across the North Atlantic using aircraft based over the eastern coast of the U.S., on the Azores and on the western coast of Europe e.g. (Methven et al., 2006), allowing for detailed process studies. Analyses of ICARTT observations in conjunction with photochemical trajectory or box models highlight the role of PAN chemistry, the influence of high aerosol loading on photolysis rates (and thus ozone production) in the plumes and characterized the O_3/CO correlations as a function of chemical processing in the plumes e.g. (Hudman et al., 2004; Real et al., 2007; Reeves et al., 2007) also suggested that PAN decomposition represents a major and possibly dominant component of the ozone enhancement in transpacific Asian pollution plumes. Significant effort was also devoted to the determination of the relative magnitude of mixing versus chemistry in travelling plumes using for instance the relative concentrations of different hydrocarbons in plumes, thus providing a benchmark for evaluating global chemical transport models e.g. (Arnold et al., 2007; Parrish et al., 2007).

As a consequence of emission regulation, ozone precursor emissions in western Europe and North America have significantly decreased since the early 1990s, leading to a decrease in maximum ozone concentrations in some urban areas e.g. (Brönnimann et al., 2002). In contrast, ozone concentrations at mountain sites and background concentrations at several sites at lower elevations in Europe increased significantly e.g. (Brönnimann et al., 2002; Simmonds et al., 2004). Numerical simulations using global chemical models indicate that the increase during the last two decades in ozone precursors from anthropogenic emissions in Asia may have counter-balanced to some extent the decrease in tropospheric ozone levels over Europe and that this is likely to continue in the future e.g. (Auvray and Bey, 2005; Auvray et al., 2007; Szopa et al., 2006). More recently, it was shown that biomass burning plumes transported from Alaska can also significantly impact ozone concentrations over Europe (Pfister et al., 2006; Ravetta et al., 2007). Fewer studies have examined the export of European pollution. Observations and modelling studies indicated however that European pollution mainly affects Asia (Duncan and Bey, 2004; Newell and Evans, 2000; Pochanart et al., 2003; Wild et al., 2004) and the Mediterranean Basin up to North Africa (Duncan and Bey, 2004; Lelieveld et al., 2002; Stohl et al., 2002).

4.5.2. *Aerosols*

Aerosols have a much shorter lifetime (a few days) than ozone, so the concept of an increasing background does not stand for most aerosols. There is however strong evidence that aerosols can be transported on intercontinental distances as shown by a number of measurements taken from satellites, ground and space-based lidars. A number of specific events have been documented in the literature for various types of aerosols, including mineral dust, biomass burning and more recently aerosols of anthropogenic origins.

The long-range transport of dust has been documented over several decades. Throughout the year African desert dust is transported westward to the North Atlantic mostly under the influence of trade winds e.g. (Chiapello and Moulin, 2002; Swap et al., 1996; Zhu et al., 2007). Spaceborne measurements indicate that the aerosol optical depth over the North Atlantic Ocean is influenced by Saharan dust up to distances of 5000 km and more off the African west coast (Prospero et al., 2002). Trans-Pacific transport of dust originating from the Chinese desert also takes place frequently e.g. (Darmenova et al., 2005; Fairlie et al., 2007; Grousset et al., 2003). As a result of long-range transport, mineral dust from the Sahara and from the Asian desert can contribute to the degradation of air quality over Europe and North America, respectively e.g. (Heald et al., 2006; Prospero, 1999). During dust storm events, mass concentrations of up to 380 $\mu g\ m^{-3}$ are reported even for marine locations like Tenerife which are far away from source regions (Duce, 1995). On the Cape Verde islands in the outflow region of the Sahel zone, aerosol optical depths ($\lambda = 0.5\ \mu m$) ≥ 0.8 are not uncommon in summer with maximum values exceeding unity optical depth quite frequently (Holben et al., 2001).

The currently ongoing Saharan Mineral Dust Experiment SAMUM (Heintzenberg, 2009) is expected to improve the understanding of Saharan dust transport across the North Atlantic and towards Europe. In the framework of SAMUM, intense studies using airborne and spaceborne platforms as well as ground-based observations were conducted in Morocco near the desert in May and June 2006 and on the Cape Verde Islands in January and February 2008. First analyses of a regional-scale transport event from Morocco to Western Europe demonstrate a serious impact on air quality over Portugal with dust loadings up to 150 $\mu g\ m^{-3}$ at ground and dust layers being observed up to an altitude of 4 km above sea level (Wagner et al., 2009). Over the desert, dust layers reached 5 km above sea level, corresponding to an absolute layer thickness of approximately 4 km (Tesche et al., 2008). Detailed analyses of dust particle size distributions show the transport of particles up to sizes of 40 μm in diameter over distances larger than 1000 km (Weinzierl et al., 2009). Observations from Puerto Rico confirm the presence of dust particles in the far supermicron size range, when the plumes reach the American west coast (Maring et al., 2003; Reid et al., 2003). Aerosol emissions from large boreal fires in Alaska, Canada, and Siberia are another source of particles which are transported very efficiently over long distances. In some cases, aerosol plumes from fires have been monitored over many days by several instruments (Damoah et al., 2006; Forster et al., 2001a; Mattis et al., 2003; Müller and Stavrakou, 2005). Aerosols originating from biomass burning can be found even in the most remote parts of the Arctic (Stohl, 2006; Stohl et al., 2006; 2007a,b). Recent results from the EARLINET lidar network show that for about 30% of the year, lofted aerosol layers are observed in the Central European free troposphere between 2.0 and 6.0 km above sea level (Müller et al., 2008).

The largest Alaskan fires appear to impact the European atmosphere, as the maximum aerosol absorption coefficient values were 7–8 Mm^{-1} which is about two orders of magnitude above the average European free tropospheric background value (Petzold et al., 2007; Witham and Manning, 2007). Russian fires may influence the European air quality. The impact of wildfire emissions in Russia and Eastern Europe in 2002 on the $PM_{2.5}$ aerosol load over Finland is discussed by Niemi et al. (2005).The authors reported an increase of particle number concentrations in the diameter range 90–500 nm, but a decrease of Aitken and nucleation mode particles with $D_p < 90$ nm. The modification of forest fire aerosol properties during transport was investigated by *in-situ* measurements (Petzold et al., 2007) and by lidar observations (Müller et al., 2007). The results consistently show that the effective diameter of the smoke particles increases from 0.2 μm at a travel time of 1 day to a value of 0.7 μm for an approximate plume age of 10–15 days. Then, a steady state of the aerosol size distribution is reached. The AeroCom data set described by Dentener et al. (2006) for the use in global climate models uses a parameterization of modal diameter and width of the size distribution with plume age which extents only to a maximum plume age of 5 days. The new data reported by Müller et al. (2007) and Petzold et al. (2007) extend the applicability of this relationship to plume ages of 10 days and demonstrate the transition into a steady state size distribution after approximately 15 days.

The altitude at which aerosols are emitted is an important parameter as it determines their lifetime and thus the distance over which they can be transported e.g. (Generoso et al., 2007). The long-range transport efficiency of Black Carbon from forest fires and from anthropogenic sources was investigated, based on the evolution of the ratio of Black Carbon mass to a chemically inert gaseous tracer CO from the source to the transport regime. Following, Park et al. (2005) the ratio $[BC_e/\Delta CO]_{far\ field}$ observed in the far field to $[BC_e/\Delta CO]_{source}$ determined near the source can be interpreted as a measure for the efficiency of the atmospheric export of BC from a source region. Wet removal processes mainly influence the particle phase (BC) while ΔCO remains almost unaffected.

For North American forest fires, an export efficiency, as defined above, of >70% was found with only minor altitude dependence up to 7 km above sea level (Petzold et al., 2007). In contrast, Park et al. (2005) report a significant decrease in the ratio $[BC_e/\Delta CO]_{far}$

$_{\text{field}} \times [BC_e/\Delta CO]^{-1}{}_{\text{source}}$ with altitude from close to 100% at < 1 km above sea level to 30% at 5 km above sea level for anthropogenic Black Carbon emissions in the Asian outflow region. The interpretation suggests that the removal of BC during uplifting reduces the efficiency of the transport of anthropogenic BC to altitudes which are relevant for intercontinental transport, while forest fire BC is lifted very efficiently into the free troposphere. Thus, aerosols from fires are more likely to be injected at higher altitudes, which in turn imply that they are more likely to experience long-range transport than anthropogenic sources.

Finally, there are indications that anthropogenic aerosols, particularly sulphate, can be transported long distances over the Pacific and Atlantic e.g. (Brock et al., 2004). One case of aerosol transport from Asia across the North Pacific, North America and the North Atlantic to Europe has also been documented (Stohl et al., 2007a,b). The impact of that transport on the load of aerosols on the downwind continent is still poorly quantified, although a recent multi-model exercise provided some first estimates (Keating and Zuber, 2007).

5. Conclusions and future perspectives

This section attempts to draw out some of the more important policy-related conclusions from the work described in the previous sections. In particular, it consolidates the implications of the earlier sections for policy and strategy as well as looking forward to the implications of climate change for air quality.

5.1. Emissions

Accurate and reliable emission inventories are essential for good model performance, which in turn underpins the analysis and assessment of policy options and scenarios. Many advances have been made in recent years but much remains to be done. Some policy relevant issues discussed in Section 2 are highlighted here. Spatial resolution has in general improved but spatial and temporal variability still needs more quantification. There has been overall a reasonable correlation between trends in emissions and in measured concentrations, although very recently discrepancies have been noted in NO_x trends in urban areas, where concentrations in some areas, notably roadside locations, do not appear to have been reducing as quickly as emission inventories would predict. Aerosol (see for example (Cuvelier et al., 2007)) and VOC inventories need further speciation. In particular, biogenic VOC inventories still need much development in terms of better quantification of species currently reported such as isoprene and also the inclusion of more species in inventories, although much progress has been made in the representation of processes controlling biogenic VOC emissions (Arneth et al., 2008; Zimmer et al., 2003). This facet will become increasingly important as the effects of climate change become more apparent. Knowledge of the emissions of relevant organic species and their atmospheric chemistry is still limiting the understanding of secondary organic aerosols in the atmosphere, of importance for both air quality and climate change.

Further work is needed to improve the relationship between global and regional inventories, and in developing countries, little is known about industrial emissions. Recent work by Hoor et al. (2009) indicate that on global annual average lower tropospheric ozone responds most sensitively to ship emissions (50.6% ± 10.9% of the total traffic induced perturbation), followed by road (36.7% ± 9.3%) and aircraft exhaust (12.7% ± 2.9%), respectively. The emissions of NO_x from lightning are particularly uncertain. Models currently do not agree on the sign of the change of these emissions with climate change, a key topic if aircraft emissions of NO_x increase as forecast (Schumann and Huntrieser, 2007).

One very significant development in recent years has been the use of satellite observations in estimating emissions. These techniquesc offer exciting new opportunities for semi-empirical verification of emission inventories, and particularly temporal trends, not least in verifying or otherwise national emission trends reported by countries as part of their obligations under international emission legislation (Konovalov et al., 2008).

5.2. Aerosols

From an air quality point of view, the adverse health effects from particulate matter are the biggest driver of policies to improve air quality. This is because of the large amount of health effect evidence, which began to emerge in the 1990s with the epidemiological work of Dockery, Schwartz et al. and by Pope and co-workers in the US and more recently in Europe (Dockery et al., 1993; Pope et al., 2002). Early studies showed associations between daily concentrations of aerosols and daily mortality; more recently studies have shown associations between long-term exposure and mortality (Hoek et al., 2002; Pope et al., 2002) and these have allowed particulate matter concentrations to be related to life expectancy (WHO, 2003). The resulting monetisation and cost-benefit analyses based on these studies have been the main driving force of legislation to control PM concentrations in the past five years or so (Amann et al., 2005). Although the associations between concentrations of particles-usually as PM_{10} or $PM_{2.5}$ and adverse health effects were established and quantified, there was little known about possible mechanisms of damage, or the most toxic component of what is a heterogeneous mixture of pollutants in the particle mix. Many studies have sought to identify the key components or sources of particulate aerosol which lead to adverse effects. Traffic emissions have been identified in epidemiological studies (see for example (Hoek et al., 2002)), and also in toxicological studies (Mills et al., 2005), but other stationary sources have also been implicated as noted in a recent review (Grahame and Schlesinger, 2007).

Toxicological studies have begun to emerge which have now reached the stage where plausible mechanisms for health damage have been proposed (WHO, 2007). Perhaps the most widely accepted and researched is the concept of oxidative stress (Donaldson and Borm, 2007) where components of the particle mix can take part in the redox reactions known as Fenton chemistry. The key step in the process of causing damage is the depletion of antioxidants via the oxidative stress reactions.

The species identified in studies to date are mostly, but not exclusively, transition metals (Duvall et al., 2008), but other species such as quinones have also been shown to be active in this process. Another significant finding from a policy point of view is that some species which have been identified as possible toxic agents in the oxidative stress process are found in the coarse fraction of particle sizes, from 2.5 μm to 10 μm.

Other possible toxic components have been suggested, notably the ultrafine fraction in the nanoparticle size range and vehicle emissions in general. Regarding ultrafines or nanoparticles, there has been speculation as to whether the important property is the surface area, or simply the number of particles. It is interesting that many epidemiological studies of vehicle emissions use the distance of residence from roads as a measure of exposure rather than identifying specific chemical or physical properties or components which might be responsible for the adverse effects. However, in several studies in Europe, the relatively crude measure of 'black smoke' emerges as an important pollutant (Hoek et al., 2002). This metric is a measure of the reflectivity of a particle sample with a size range of around 4 μm and below and is probably an effective indicator of diesel emissions. Epidemiological studies have begun to emerge using more sophisticated measures of particles and components, beyond the straightforward $PM_{2.5}$ and PM_{10}, but as yet there has been no widespread consensus for other metrics in the same way as there has for $PM_{2.5}$ and PM_{10} where quantitative exposure–response relationships can be derived, forming the basis for the assessment of control policies and enabling cost-benefit analyses to be carried out on potential policies, when combined with economic studies on the valuation of life years lost and other adverse effects.

The role of aerosols in climate change is extremely important, as discussed further below (see also Isaksen et al., 2009). The fundamental atmospheric science of aerosols in recent years has been driven largely by climate change concerns rather than air quality and public health concerns. Nonetheless there is a considerable amount of knowledge, expertise and analytical techniques deployed on the study of aerosols which have yet to find full application in the air quality community, addressing policy concerns. There is potentially much to be gained by encouraging closer links between the fundamental aerosol science and the air quality community, particularly on questions of policy relevance and the ACCENT network is well placed to foster this. Key areas for further exploration would be in compositional studies using advanced instrumentation, mechanisms of formation of particles both primary and secondary (and by implication the response of concentrations to reductions in emissions) and if surface properties of particles are important the surface chemistry and physics could be a fruitful area of study. Studies relevant to the air quality community should be clearly guided by the most recent thinking on the likely toxic components or properties of the aerosol, further information on which will enable more specific and focused control strategies to be developed. Or alternatively, given that there are already policy measures in place on many components of the aerosol mix, more detailed information will give policy makers the opportunity to press harder and drive forward the more effective ones.

5.3. *Ozone*

It has been known for some time that ozone concentrations can damage human health, and over the past three decades guidelines and standards relating to health effects have been developed (WHO, 2003, 2005b, 2008). Historically, these have largely been based on direct exposure studies and have used the concept of a threshold level below which effects were not observed. More recently, epidemiological studies have been used to inform standards and guidelines and these studies can cover much larger populations, with a wider range of sensitivities and susceptibilities than can be used in chamber exposure studies. Findings from these more recent studies have begun to question the existence of a threshold concentration for effects at the population level. The task of identifying clearly the existence or otherwise of a threshold is difficult and no completely unambiguous conclusions have yet emerged. At lower concentrations, relationships between adverse effects and concentrations tend to show more variability. A recent report on the health effects of ozone has however questioned the existence of a threshold (or at least the likelihood of a threshold being detectable) in epidemiological studies at the population level (WHO, 2008). Risk estimates are generally carried out using no threshold assumptions but also using thresholds in the range of ~35–50 ppbV as 1–8 h averages. A precautionary approach would suggest a no threshold assumption at the population level.

This has profound implications for control strategies and abatement policies. Whereas the peak ozone levels experienced in the classical summer smog episodes are determined largely by emissions of precursors over regional scales up to about 1000 km or so, the absence of a threshold brings the extremes of spatial scales into play. If there is no threshold for effect, and if one assumes a linear exposure–response relationship, then the total annual health effect is proportional to the annual mean ozone concentration. This means that global ozone concentrations and the future behaviour of tropospheric baseline/background concentrations are important, so on the one hand global scales now become important for health effects. On the other hand, in urban areas in the developed world, emission controls on NO_x already achieved and still in the pipeline are leading to increased average ozone concentrations where most people live. Therefore, urban scales of the order of 1 km or less are also important. These considerations change significantly the nature of the policy response to ozone control and also pose significant challenges for the research community, not least in integrating the range of spatial and temporal scales in ozone models.

The behaviour of baseline ozone concentrations is therefore crucially important in assessing future impacts on health and on plants, crops and vegetation (Sitch et al., 2007). It has been known for some time that ozone levels near the baseline level can damage plants and this has been embodied in metrics such as AOT40 but the scope of control strategies to mitigate plant effects will also need to be extended to the global scale as peak episode levels continue to reduce.

The recent report on ozone by the Royal Society (2008) addressed issues regarding future baseline concentrations and their relationship to global emissions of ozone precursors, demonstrating the particular importance of emission trends in the developing countries in Asia. This work complemented the work of the UNECE Task Force on Hemispheric Transport of Air Pollution within the Convention on Long Range Transboundary Air Pollution (Keating and Zuber, 2007) and a report of an expert group in the UK (AQEG, 2009).

The Royal Society report also addressed the problem of ozone damage to crops and the implications for food security. The study made the point that impacts of ozone on vegetation could lead to long-term effects on ecosystem structure and impacts on the carbon cycle. Ozone can also affect the yield and nutritional quality of major crop species, including wheat, rice and soybean. Global yields of staple crops are reduced as a consequence of current ozone exposures and this impact may even increase in future as a consequence of current legislation. The economic impacts of the loss of arable crops can be large. In the USA in the 1980s this was estimated at $2–4 billion per annum while in the EU in 2000 the corresponding estimate of the loss was €6.7 billion. For the same year, global losses were estimated at $14–26 billion for rice, soybean, maize and wheat combined. The Royal Society (2008) concluded that in some rapidly developing countries such as South Asia the impact of ozone on some staple crops such as wheat and rice could present a significant threat to food security.

At present, there are long-term trend data on baseline ozone concentrations available from several sites in Europe for the past two decades or so. These generally show increasing trends over the period of measurements but the increases are not uniform in time, and the detailed behaviour is difficult to rationalise (see Section 3.1.5). It is therefore difficult to project concentrations forward without a degree of uncertainty, but there is also uncertainty about future emissions from developing countries, especially China and India. The degree of abatement applied in these countries could significantly affect future emissions, particularly of NO_x, and hence could determine future changes in baseline ozone levels. These considerations pose questions over what optimal global abatement strategies might look like-where are the most cost effective reductions of NO_x to be made-does convective lifting mean that a tonne of NO_x reduction in south Asia has more of an impact on global ozone levels than does the same amount in northern Europe? What is the role of NO_x reduction compared with reductions in methane?

There are also uncertainties about the influence of climate change on future ozone concentrations. Current modelling suggests that on current projections, European temperatures like those observed in 2003 could become the norm in 2050 rather than being a significant outlier as was the case in 2003. This could have significant implications for the frequency and intensity of ozone episodes, but could also have important influences on control strategies and policies. Of great importance here is the role of biogenic vis-a-vis man-made emissions. Current views of the temperature dependence of some biogenic emissions suggests a very rapid increase with temperatures above about 20 °C, so the balance between biogenic and man-made VOC emissions in future could change significantly. The role of the developing countries coupled with the comments above regarding health effect and crop effect thresholds suggest that there is a very strong case for a global approach to ozone control strategies.

5.4. Climate change and air quality

The scientific problems and the policy issues linking climate change and air quality are complex. The scientific issues are discussed elsewhere in this report, and have been the subject of much recent work (see for example, (AQEG, 2007), and (N.C.f.E. Assessment, 2007)) and this section explores the issues emerging from the science which present opportunities and pose challenges to the policy maker. There are policies which will improve both air quality and reduce greenhouse gas emissions, but there are also policies which will improve one but make the other worse. Fig. 42 illustrates this with some examples. The win–win policies generally involve measures which reduce energy consumption and travel-or at least in the latter case encourage modal shifts to forms of travel which use less energy per passenger kilometre. Energy efficiency measures are the obvious place to start in implementing measures which improve both air quality and climate change, not least because the economic case is generally very strong (assuming one can overcome the entry barriers of installing low-energy goods and appliances for example). Other win-wins involve increased use of non-combustion renewables like wind, tidal and solar power. Nuclear power also must clearly be considered in this context; there are problems to be addressed over waste disposal of course, but in the context of climate change and air quality, it is a clear win–win option.

There are however trade-offs in both directions, as noted above, and the challenge to the policy maker is to steer a path through the complexities. The role of the research community here is to understand the problems and to quantify the effects. The majority of the important trade-offs concern aerosols in some form (see Fig. 42). One pollutant of particular importance in several situations is black carbon (BC). Globally, there are major sources of BC from biomass burning-forest fires, or when used for heating or cooking in poorly ventilated homes, which can cause health effects as well as add to global warming. In these instances there are no trade-offs. However, in Europe in the past few years there have been measures proposed to reduce BC emissions from diesel vehicles, to reduce the air quality and public health impacts referred to in the previous section. These measures require the use of particulate filters on the vehicles which lead to increased fuel consumption and hence increased CO_2 emissions, so it is clear that one is immediately faced with the conflict of reducing particle emissions to improve public health, or foregoing these benefits to keep GHG emissions lower than they would otherwise have been. The problem in quantifying the climate impacts of BC revolve around quantifying the radiative forcing and then in modelling the impact on global temperature compared with that of CO_2 given that the atmospheric lifetime of BC is very much shorter than CO_2 and the other Kyoto GHGs. These issues have already begun to be addressed in the IPCC process, but other key papers have made some recent progress, notably the work of Boucher and Reddy (2008) who specifically addressed the

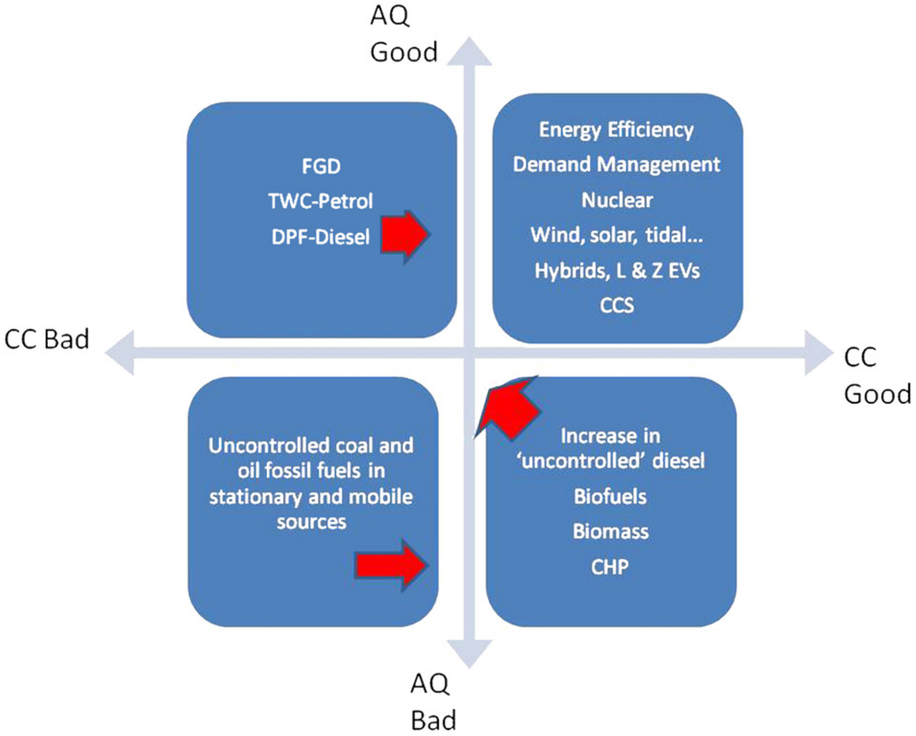


Fig. 42. The synergies and trade-offs between policies to improve air quality and to reduce greenhouse gas emissions.

quantification of the trade-off between BC and CO_2. One clear conclusion is that time horizons other than 100 years will need to be considered in making quantitative comparisons between the Kyoto GHGs and the climate effects of the 'air quality' pollutants which in general have very much shorter atmospheric lifetimes so that one is typically looking at decadal timescales (or shorter) in addressing the health, environmental and climate impacts of air pollutants, while the 'traditional' GHGs have lifetimes of the order of 100s of years. A related issue is the use of biomass and biofuels in place of the non-combustion renewables. Depending on the fossil fuels which are replaced by an increasing use of biomass or biofuels, and the type of combustion system they are used in, air quality could be made worse.

The other major trade-off issue regarding aerosols, climate and air quality concerns sulphate and nitrate. The overall effect of these aerosols on climate, from the direct and indirect effects, is a negative radiative forcing (i.e. a cooling effect). Reducing the concentrations of these aerosols in the troposphere will therefore lead to a warming additional to that of the GHGs in the atmosphere. This effect is potentially large, the direct plus indirect aerosol radiative forcing from the most recent IPCC report is 1.2 W m^{-2} compared with 1.66 W m^{-2} for CO_2, while those for methane and nitrous oxide are 0.48 W m^{-2} and 0.16 W m^{-2} respectively. But as noted above, the effect of specific reductions in aerosol concentrations will depend on the amount of the reduction and particularly the time horizon over which the temperature change is assessed. The research community has a clear responsibility to quantify these issues as accurately as possible and set out the implications for global temperatures and air quality and environmental effects for policy makers. Ultimately, to achieve air quality goals as well as climate change targets, society will need to reduce GHGs and air pollutants, including the radiatively active aerosols (Raes and Seinfeld, in press). While the long-term target of limiting temperature rises to 2 °C, or major reductions in GHGs of around 80% and equally large reductions in air pollutants should mitigate the worst effects, in the shorter term the effects on global temperatures may result in larger short term increases, owing partly to the fact that significant amounts of long-lived GHGs are already in the atmosphere but also because reductions in atmospheric aerosols in the next decade or so will add to the positive radiative forcing of the earth's climate, as illustrated in Fig. 43. One current issue is the extent to which immediate reductions in shorter lifetime pollutants like BC and ozone can offset the increases in radiative forcing resulting from the reductions in sulphate aerosol and also therefore maintain a downward pressure on temperature increases until the large reductions in the long-lived GHGs begin to take effect.

In managing the air quality/climate change trade-offs, it is unlikely that in the "real world" policy makers will be able to achieve simple optimal solutions which address both climate change and air quality in one easy step. In practice, progress is generally made through a series of steps which address one or the other problems in turn. In Europe for example, sulphate aerosols have been reduced over the past fifty years or so, initially to resolve the problem of urban smogs and then to reduce acidification. The definition of 'best available techniques' currently require abatement technology to reduce sulphur emissions from coal and oil fired power plants in the EU, and in developing countries who will potentially increase their use of coal for power generation there will be trade-offs to be managed between local air quality and climate change mitigation.

In terms of black carbon and diesel vehicles, in Europe, there has been a significant increase in the diesel car fleet over the past fifteen years or so, and policies to incentivise the purchase of cars with lower CO_2 emissions are common. Although emission standards were improving over this time, they were not always improving quickly enough to overcome the increase in diesel cars with the result that urban particulate concentrations have not reduced as fast as they otherwise would. The impact of this effect on premature mortality in the UK was studied recently with the conclusion that the increase in diesel cars in the fleet lead to 20–300 premature deaths per year over the period 2001–2020 (central estimate 90 deaths per year), but with simultaneous improvements in carbon emissions (Mazzi and Dowlatabadi, 2007). By contrast, in the last few years with the agreement of the Euro 5 and 6 emission standards for cars the EU has tacitly accepted a small 'hit' on carbon emissions through the use of the particle filters required by the new standards as the consequence of reducing the impact on mortality and morbidity from the particle emissions. The 'real-world' path taken to achieve optimal policies on diesel vehicle emissions, from the bottom left quadrant in Fig. 42 to the top right hand quadrant is shown by the red arrows in Fig. 42.

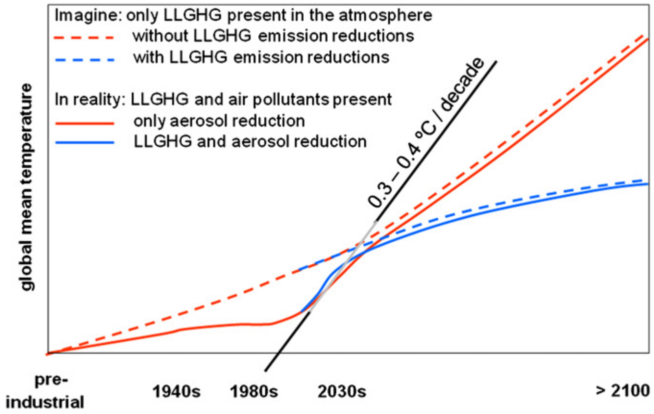


Fig. 43. The figure shows schematically the climate consequences of climate change and air pollution abatement strategies. The only way to reach global temperature stabilization is through LLGHG reductions. Such stabilization would be achieved according to the timescales mainly related to the several decade lifetime of LLGHG in the atmosphere. Reduction of air pollution (including that resulting from LLGHG emission reductions) would have a more immediate impact on global warming. Air pollutants have lifetimes of weeks to months, and the climate system would realize, in about 5 years, 50% of the global warming caused by their reduction. Air pollutant reductions are expected to accelerate the increase in global mean temperature in the short term (<30 year), on the way to eventual long-term (>100 year) climate stabilization (Raes and Seinfeld, in press).

Policies on air quality and climate change then often proceed in the real world in a more pragmatic and *ad-hoc* way than might be considered ideal from a theoretical point of view. Nonetheless it is now becoming clear that there are sufficiently large benefits to be gained from pursuing optimal co-benefits policies that efforts should continue in this direction. However, policies are agreed and implemented by governments who make decisions in the light of scientific, economic, social and political considerations. The current high political profile of climate change must be recognised in attempting to design and implement optimal strategies for air quality and climate change mitigation. However, policy makers should take into account the fact that there may be several options for achieving targets for greenhouse gas reductions and wherever possible should choose the options that minimise the impact on air quality, public health and the wider environment.

Acknowledgements

The authors would like to thank the EU ACCENT project. We would also like to thank Laura Dini and the ACCENT project office for the logistical support in assembling this review.

References

Acker, K., Moeller, D., Wieprecht, W., Meixner, F.X., Bohn, B., Gilge, S., Plass-Duelmer, C., Berresheim, H., 2006. Strong daytime production of OH from HNO_2 at a rural mountain site. Geophysical Research Letters 33, L02809.

Aghedo, A.M., Schultz, M.G., Rast, S., 2007. The influence of African air pollution on regional and global tropospheric ozone. Atmospheric Chemistry and Physics 7, 1193–1212.

Akimoto, H., 2003. Global air quality and pollution. Science 302, 1716–1719.

Akimoto, H., Ohara, T., Kurokawa, J., Horii, N., 2006. Verification of energy consumption in China during 1996–2003 by using satellite observational data. Atmospheric Environment 40, 7663–7667.

Alicke, B., Hebestreit, K., Stutz, J., Platt, U., 1999. Iodine oxide in the marine boundary layer. Nature 397, 572–573.

Alicke, B., Platt, U., Stutz, J., 2002. Impact of nitrous acid photolysis on the total hydroxyl radical budget during the limitation of oxidant production/pianura padana produzione di ozono study in Milan. Journal of Geophysical Research-Atmospheres 107 (D22), 8196. doi:10.1029/2000JD000075.

Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Patz, H.W., Schafer, J., Stutz, J., Volz-Thomas, A., Platt, U., 2003. OH formation by HONO photolysis during the BERLIOZ experiment. Journal of Geophysical Research-Atmospheres 108 (D4), 8247. doi:10.1029/2001JD000579.

Allan, B.J., McFiggans, G., Plane, J.M.C., Coe, H., 2000. Observation of iodine oxide in the remote marine boundary layer. Journal of Geophysical Research 105, 14363–314370.

Allan, B.J., Plane, J.M.C., Coe, H., Shillito, J., 2002. Observations of NO_3 concentration profiles in the troposphere. Journal of Geophysical Research-Atmospheres 107 (D21), 4588. doi:10.1029/2002JD002112.

Allan, J.D., Alfarra, M.R., Bower, K.N., Coe, H., Jayne, J.T., Worsnop, D.R., Aalto, P.P., Kulmala, M., Hyötyläinen, T., Cavalli, F., Laaksonen, A., 2006. Size and composition measurements of backround aerosol and new particle growth in a Finnish forest during QUEST 2 using an aerodyne aerosol mass spectrometer. Atmospheric Chemistry and Physics 6, 315–327.

Allen, D., Pickering, K., Stenchikov, G., Thompson, A., Kondo, Y., 2000. A three-dimensional total odd nitrogen (NO_y) simulation during SONEX using a stretched-grid chemical transport model. Journal of Geophysical Research 105, 3851–3876.

Allen, D.J., Pickering, K.E., 2002. Evaluation of lightning flash rate parameterizations for use in a global chemical transport model. Journal of Geophysical Research 107, 4711.

Alvarez, E.G., Viidanoja, J., Munoz, A., Wirtz, K., Hjorth, J., 2007. Experimental confirmation of the dicarbonyl route in the photo-oxidation of toluene and benzene. Environmental Science and Technology 41, 8362–8369.

Amann, M., Bertok, I., Cabala, R., Cofala, J., Heyes, C., Gyarfas, F., Klimont, Z., Schöpp, W., Wagner, F., 2005. Target Setting Approaches for Cost-effective Reductions of Population Exposure to Fine Particulate Matter in Europe. CAFE Report 4. International Institute for Applied Systems Analysis (IIASA), Laxenburg, Austria.

Andreae, M.O., Artaxo, P., Brandao, C., Carswell, F.E., Ciccioli, P., da Costa, A.L., Culf, A.D., Esteves, J.L., Gash, J.H.C., Grace, J., Kabat, P., Lelieveld, J., Malhi, Y., Manzi, A.O., Meixner, F.X., Nobre, A.D., Nobre, C., Ruivo, M., Silva-Dias, M.A., Stefani, P., Valentini, R., von Jouanne, J., Waterloo, M.J., 2002. Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: the LBA-EUSTACH experiments. Journal of Geophysical Research-Atmospheres 107 (D20), 8066. doi:10.1029/2001JD000524.

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochemical Cycles 15, 955–966.

Andreae, M.O., Rosenfeld, D., 2008. Aerosol–cloud precipitation interactions. Part 1. The nature and sources of cloud active aerosols. Earth Science Revision 89, 13–41.

Angert, A., Rachmilevitch, S., Barkan, E., Luz, B., 2003. Effects of photorespiration, the cytochrome pathway, and the alternative pathway on the triple isotopic composition of O_2. Global Biogeochemical Cycles 17, 1030, doi: 10.1029/2002GB001933.

Anttilla, T., Kiendler-Scharr, A., Tillmann, R., Mentel, T., 2006. On the reactive uptake of gaseous compounds by organic-coated aerosols: theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5. Journal of Physics and Chemistry A 110, 10435–10443. 2006.

AQEG, 2007. Air Quality Expert Group, Air Quality and Climate Change: a UK Perspective. HMSO, London.

AQEG, 2009. Air Quality Expert Group, Ozone in the United Kingdom. HMSO, London.

Arellano, A.F., Kasibhatla, P.S., Giglio, L., van der Werf, G.R., Randerson, J.T., 2004. Top-down estimates of global CO sources using MOPITT measurements. Geophysical Research Letters 31, L01104.

Arneth, A., Schurgers, G., Hickler, T., Miller, P.A., 2008. Effects of species composition, land surface cover, CO_2 concentration and climate on isoprene emissions from European forests. Plant Biology 10, 150–162.

Arnold, S., Chipperfield, M., ÓConnor, F., Law, K., Pyle, J., Methven, J., 2003. Investigating ozone production downwind of the European region using a Lagrangian chemistry-transport model. In: Penkett, S.A., Law, K.S., Platt, U., Volz-Thomas, A. (Eds.), EXPORT-E2: European Export of Particulates and Ozone by Long-range Transport. International Scientific Secretariat (ISS), GSF - National Research Center for Environment and Health, Munich, pp. 23–29.

Arnold, S.R., Chipperfield, M.P., Blitz, M.A., 2005. A three-dimensional model study of the effect of new temperature-dependent quantum yields for acetone photolysis. Journal of Geophysical Research-Atmospheres 110, D22305. doi:10.1029/2005JD005998.

Arnold, S.R., Methven, J., Evans, M.J., Chipperfield, M.P., Lewis, A.C., Hopkins, J.R., McQuaid, J.B., Watson, N., Purvis, R.M., Lee, J.D., Atlas, E.L., Blake, D.R., Rappenglück, B., 2007. Statistical inference of OH concentrations and air mass dilution rates from successive observations of nonmethane hydrocarbons in single air masses. Journal of Geophysical Research 112, D10S40.

Aschmann, S.M., Arey, J., Atkinson, R., 2004. Products and mechanism of the reaction of OH radicals with 2,3,4-trimethylpentane in the presence of NO. Environmental Science Technology 38, 5038–5045.

Aschmann, S.M., Long, W.D., Atkinson, R., 2006. Pressure dependence of pentyl nitrate formation from the OH radical-initiated reaction of n-pentane in the presence of NO. Journal of Physics and Chemistry A 110, 6617–6622. 2006.

Ashmore, M., 2005. Assessing the future global impacts of ozone on vegetation. Plant, Cell and Environment 28, 949–964.

Atkinson, R., 2007. Rate constants for the atmospheric reactions of alkoxy radicals: a revised estimation method. Atmospheric Environment 41, 8468–8485.

Atkinson, R., Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. Atmospheric Environment 37, S197–S219.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J., 2006. Evaluated kinetic and photochemical data for atmospheric chemistry: volume II – reactions of organic species. Atmospheric Chemistry and Physics 6, 3625–4055.

Aumont, B., Szopa, S., Madronich, S., 2005. Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: development of an explicit model based on a self generating approach. Atmospheric Chemistry and Physics 5, 2497–2517.

Auvray, M., Bey, I., 2005. Long-range transport to Europe: seasonal variations and implications for the European ozone budget. Journal of Geophysical Research 110 (D11) D11303.1-D11303.22, doi: 10.1029/2004JD005503.

Auvray, M., Bey, I., Llull, E., Schultz, M.G., Rast, S., 2007. A model investigation of tropospheric ozone chemical tendencies in long-range transported pollution plumes. Journal of Geophysical Research 112, D05304.

Bader, M.J., Forbes, G.S., Grant, J.R., Lilley, R.B.E., Waters, A.J., 1995. A Practical Guide for Interpreting Satellite and Radar Imagery. University Press, Cambridge.

Bakeas, E.B., Argyris, D.I., Siskos, P.A., 2003. Carbonyl compounds in the urban environment of Athens, Greece. Chemosphere 52, 805–813.

Baker, A.K., Beyersdorf, A.J., Doezema, L.A., Katzenstein, A., Meinardi, S., Simpson, I.J., Blake, D.R., Rowland, F.S., 2008. Measurements of nonmethane hydrocarbons in 28 United States cities. Atmospheric Environment 42, 170–182.

Baklanov, A., Joffre, S., Galmarini, S., 2005. Urban meteorology and atmospheric pollution (EMS-FUMAPEX).

Baklanov, A., Fay, B., Kaminski, J., Sokhi, R., 2008. COST-WMO: Overview of Existing Integrated (Off-line and On-line) Mesoscale Meteorological and Chemical Transport Modelling Systems in Europe, WMO GAW Report No. 177, Joint Report of COST Action 728 and GURME. 107 pp. Available from: http://www.cost728.org.

Baklanov, A., Grisogono, B., 2008. Atmospheric Boundary Layers: Nature, Theory and Applications to Environmental Modelling and Security. Springer, pp. 244.

Baklanov, A., Grimmond, S., Mahura, A., Athanassiadou, M. (Eds.), 2009. Meteorological and Air Quality Models for Urban Areas. Springer, Berlin, Heidelberg, ISBN 978-3-642-00297-7. doi:10.1007/978-3-642-00298-4.

Baltensperger, U., Prevot, A.S.H., 2008. Chemical analysis of atmospheric aerosols. Analytical and Bioanalytical Chemistry 390, 277–280.

Baltensperger, U., Streit, N., Weingartner, E., Nyeki, S., Prévôt, A.S.H., van Dingenen, R., Virkkula, A., Putaud, J.-P., Even, A., ten Brink, H., Blatter, A., Neftel, A., Gäggeler, H.W., 2002. Urban and rural aerosol characterization of summer smog events during the PIPAPO field campaign in Milan, Italy. Journal of Geophysical Reserach 107 (D22), 8193, doi:10.1029/2001JD001292.

Banta, R.M., Senff, C.J., Nielsen-Gammon, J., Ryerson, T.B., Darby, L.S., Alvarez, R.J., Sandberg, S.P., Williams, E.J., Trainer, M., 2005. A bad air day in Houston. Bulletin of the American Meteorological Society 86, 657–669.

Barbosa, P.M., Gregoire, J.M., Pereira, J.M.C., 1999. An algorithm for extracting burned areas from time series of AVHRR GAC data applied at a continental scale. Remote Sensing Environment 69, 253–263.

Bardouki, H., Liakakou, H., Economou, C., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Mihalopoulos, N., 2003. Chemical composition of size resolved atmospheric aerosols in the Eastern mediterranean during summer and winter. Atmospheric Environment 37, 195–208.

Barkan, E., Luz, B., 2005. High precision measurements of O-17/O-16 and O-18/O-16 of O2 in H2O. Rapid Communications in Mass Spectrometry 19, 3737–3742.

Baroni, M., Thiemens, M.H., Delmas, R.J., Savarino, J., 2007. Mass-independent sulfur isotopic compositions in stratospheric volcanic eruptions. Science 315, 84–87.

Barrie, L.A., 1986. Arctic air pollution – an overview of current knowledge. Atmospheric Environment 20, 643–663.

Barrie, L.A., Bottenheim, J.W., Schnell, R.C., Crutzen, P.J., Rasmussen, R.A., 1988. Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. Nature 334, 138–140.

Barry, R.G., 1992. Mountain Weather and Climate, second ed. Routledge.

Bauer, S.E., Koch, D., Unger, N., Metzger, S.M., Shindell, D.T., Streets, D.G., 2007. Nitrate aerosols today and in 2030: a global simulation including aerosols and tropospheric ozone. Atmospheric Chemistry and Physics 7, 5043–5059.

Bauer, H., Schueller, E., Weinke, G., Berger, A., Hitzenberger, R., Marr, I.L., Puxbaum, H., 2008. Significant contributions of fungal spores to the organic carbon and to the aerosol mass balance of the urban atmospheric aerosol. Atmospheric Environment 42, 5542–5549.

Beirle, S., Platt, U., Wenig, M., Wangner, T., 2003. Weekly cycle of NO_2 by GOME measurements: a signature of anthropogenic sources. Atmospheric Chemistry and Physics 3, 2225–2232.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., Benter, T., 2007. Investigations on the gas-phase photolysis and OH radical kinetics of methyl-2-nitrophenols. Physical Chemistry Chemical Physics 9 (42), 5686–5692.

Bell, M.L., Peng, R.D., Domenici, F., 2006. The exposure–response curve for ozone and risk of mortality and the adequacy of current ozone regulations. Environmental Health Perspective 114, 532–536.

Beniston, M., 2004. The 2003 heat wave in Europe: a shape of things to come? An analysis based on Swiss climatological data and model simulations. Geophysical Research Letters 31, L01812.

Berresheim, H., Elste, T., Tremmel, H.G., Allen, A.G., Hansson, H.-C., Rosman, K., Dal Maso, M., Mäkelä, J.M., Kulmala, M., O'Dowd, C.D., 2002. Gas-aerosol relationship of H_2SO_4, MSA and OH: observations in the coastal marine boundary layer at Mace Head, Ireland. Journal Geophysical Research 107, 8100.

Berresheim, H., Plass-Dulmer, C., Elste, T., Mihalopoulos, N., Rohrer, F., 2003. OH in the coastal boundary layer of Crete during MINOS: measurements and relationship with ozone photolysis. Atmospheric Chemistry and Physics 3, 639–649.

Bertschi, I.T., Jaffe, D.A., 2005. Long-range transport of ozone, carbon monoxide, and aerosols to the NE Pacific troposphere during the summer of 2003: observations of smoke plumes from Asian boreal fires. Journal of Geophysical Research 110, D05303.

Bishop, G.A., Stedman, D.H., 2008. A decade of on-road emissions measurements. Environmental Science Technology 42, 1651–1656.

Bithell, M., Vaughan, G., Reid, S.J., 2000. Persistence of stratospheirc ozone layers in the troposphere. Atmospheric Environment 34, 2563–2570.

Blake, N.J., Blake, D.R., Swanson, A.L., Rowland, F.S., Atlas, E., Flocke, F., 2003. Latitudinal, vertical, and seasonal variations of C_1–C_4 alkyl nitrates in the troposphere over the Pacific Ocean during PEM-tropics A and B: oceanic and continental sources. Journal of Geophysical Research 108.

Blitz, M.A., Heard, D.E., Pilling, M.J., Arnold, S.R., Chipperfield, M.P., 2004. Pressure and temperature-dependent quantum yields for the photodissociation of acetone between 279 and 327.5 nm. Geophysical Research Letters 31.

Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M., Pilling, M.J., 2005a. Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data. Atmospheric Chemistry and Physics 5, 623–639.

Bloss, C., Wagner, V., Jenkin, M.E., Volkamer, R., Bloss, W.J., Lee, J.D., Heard, D.E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J.C., Pilling, M.J., 2005b. Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. Atmospheric Chemistry and Physics 5, 641–644.

Bloss, W.J., Lee, J.D., Johnson, G.P., Sommariva, R., Heard, D.E., Saiz-Lopez, A., Plane, J.M.C., McFiggans, G., Coe, H., Flynn, M., Williams, P., Rickard, A.R., Fleming, Z.L., 2005c. Impact of halogen monoxide chemistry upon boundary layer OH and HO_2 concentrations at a coastal site. Geophysical Research Letters 32, L06814. doi:10.1029/2004GL022084.

Bloss, W.J., Lee, J.D., Heard, D.E., Salmon, R.A., Baugitte, S.J.-B., Roscoe, H.K., Jones, A.E., 2007. Observations of OH and HO_2 radicals in coastal Antarctica. Atmospheric Chemistry and Physics 7, 4171–4185.

Bobrowski, N., Hönninger, G., Galle, B., Platt, U., 2003. Detection of bromine monoxide in a volcanic plume. Nature 423, 273–276.

Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O.W., Platt, U., 2007. Reactive halogen chemistry in volcanic plumes. Journal of Geophysical Research 112, 206.

Bobrowski, N., Platt, U., 2007. SO_2/BrO ratios studied in five volcanic plumes. Journal of Volcanology and Geothermal Research 166, 147–160.

Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.-H., Klimont, Z., 2004. A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research 109, D14203.

Bonn, B., von Kuhlmann, R., Lawrence, M.G., 2004. High contribution of organic hydroperoxides to secondary organic aerosol formation. Geophysical Research Letters 31, L10108.

Bonn, B., Kulmala, M., Riipinen, I., Sihto, S.-L., Ruuskanen, T.M., 2008. How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation. Journal of Geophysical Research 113, D12209.

Bortz, S.E., Prather, M.J., 2006. Ozone, water vapor, and temperature in the upper tropical troposphere: variations over a decade of MOZAIC measurements. Journal of Geophysical Research 111, D05305.

Boucher, O., Reddy, M.S., 2008. Climate trade-off between black carbon and carbon dioxide emissions. Energy Policy 36, 193–200.

Bougeault, P., Binder, P., Buzzi, A., Dirks, R., Houze, R., Kuettner, J., Smith, R.B., Steinacker, R., Volkert, H., 2001. The MAP special observing period. Bulletin of the American Meteorological Society 82, 433–462.

Brasseur, G.P., Prinn, R.G., Pszenny, A.A.P., 2003. Atmospheric Chemistry in a Changing World. Springer.

Brasseur, G.P., Schultz, M., Granier, C., Saunois, M., Diehl, T., Botzet, M., Roeckner, E., Walters, S., 2006. Impact of climate change on the future chemical composition of the global troposphere. Journal of Climatology 19, 3932–3951.

Brauers, T., Hausmann, M., Bister, A., Kraus, A., Dorn, H.-P., 2001. OH radicals in the boundary layer of the Atlantic Ocean 1. Measurements by long-path laser absorption spectroscopy. Journal of Geophysical Research 106, 7399–7414.

Brenninkmeijer, C.A.M., Janssen, C., Kaiser, J., Röckmann, T., Rhee, T.S., Assonov, S.S., 2003. Isotope effects in the chemistry of atmospheric trace compounds. Chemical Reviews 103, 5125–5162.

Brinkop, S., 2002. Aspects of convective activity and extreme events in a transient climate change simulation. Meteorology Z 11, 323–333.

Brock, C., Hudson, P.K., Lovejoy, E.R., Sullivan, A., Nowak, J.B., Huey, L.G., Cooper, O.R., Cziczo, D.J., de Gouw, J., Fehsenfeld, F.C., Hollaway, J.S., Hübler, G., Lafleur, B.G., Murphy, D.M., Neuman, J.A., Nicks Jr., D.K., Orsini, D.A., Parrish, D.D., Ryerson, T.B., Tanner, D.J., Warneke, C., Weber, R.J., Wilson, J.C., 2004. Particle characteristics following cloud-modified transport from Asia to North America. Journal of Geophysical Research 109, D23S26.

Brönnimann, S., Buchmann, B., Wanner, H., 2002. Trends in near-surface ozone concentrations in Switzerland: the 1990s. Atmospheric Environment 36, 2841–2852.

Browell, E.V., Fenn, M.A., Butler, C.F., Grant, W.B., Ismail, S., Ferrare, R.A., Kooi, S.A., Brackett, V.G., Clayton, M.B., Avery, M.A., Barrick, J.D.W., Fuelberg, H.E., Maloney, J.C., Newell, R.E., Zhu, Y., Mahoney, M.J., Anderson, B.E., Blake, D.R., Brune, W.H., Heikes, B.G., Sachse, G.W., Singh, H.B., Talbot, R.W., 2001. Large-scale air mass characteristics observed over the remote tropical Pacific Ocean during March–April 1999: results from PEM-tropics B field experiment. Journal of Geophysical Research-Atmospheres 106, 32481–32501.

Brown, S.S., Neuman, J.A., Ryerson, T.B., Trainer, M., Dube, W.P., Holloway, J.S., Warneke, C., De Gouw, J.A., Donnelly, S.G., Atlas, E., Matthew, B., Middlebrook, A.M., Peltier, R., Weber, R.J., Stohl, A., Meagher, J.F., Fehsenfeld, F.C., Ravishankara, A.R., 2006a. Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere. Geophysical Research Letters 33, L08801.

Brown, S.S., Ryerson, T.B., Wollny, A.G.C., Brock, A., Peltier, R., Sullivan, A.P., Weber, R.J., Dube, W.P., Trainer, M., Meagher, J.F., Fehsenfeld, F.C., Ravishankara, A.R., 2006b. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. Science 311, 67–70.

Brown, S.G., Frankel, A., Hafner, H.R., 2007a. Source apportionment of VOCs in the Los Angeles area using positive matrix factorization. Atmospheric Environment 41, 227–237.

Brown, S.S., Dube, W.P., Osthoff, H.D., Wolfe, D.E., Angevine, W.M., Ravishankara, A.R., 2007b. High resolution vertical distributions of NO_3 and N_2O_5 through the nocturnal boundary layer. Atmospheric Chemistry and Physics 7, 139–149.

Brunner, D., Staehelin, J., Jeker, D., Wernli, H., Schumann, U., 2001. Nitrogen oxides and ozone in the tropopause region of the Northern hemisphere: measurements from commercial aircraft in 1995/1996 and 1997. Journal of Geophysical Research-Atmospheres 106, 27673–27699.

Brunner, D., Staehelin, J., Rogers, H.L., Kohler, M.O., Pyle, J.A., Hauglustaine, D.A., Jourdain, L., Berntsen, T.K., Gauss, M., Isaksen, I.S.A., Meijer, E., van Velthoven, P., Pitari, G., Mancini, E., Grewe, V., Sausen, R., 2005. An evaluation of the performance of chemistry transport models – part 2: detailed comparison with two selected campaigns. Atmospheric Chemistry and Physics 5, 107–129.

Butkovskaya, N., Kukui, A., Le Bras, G., 2007. HNO_3 forming channel of the $HO_2 + NO$ reactions as a function of pressure and temperature in the ranges of 72–600 Torr and 223–323 K. Journal of Physics and Chemistry A 111, 9047–9053.

Butler, T.M., Lawrence, M.G., Gurjar, B.R., van Aardenne, J., Schultz, M., Lelieveld, J., 2007. The representation of emissions from megacities in global emissions inventories. Atmospheric Environment 42, 703–719.

Butler, T.M., Taraborrelli, D., Brühl, C., Fischer, H., Harder, H., Martinez, M., Williams, J., Lawrence, M.G., Lelieveld, J., 2008. Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign. Atmospheric Chemistry and Physics 8, 4529–4546.

Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., Yarwood, G., 2002. The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons. Oxford University Press, New York.

Cariolle, D., Evans, M.J., Chipperfield, M.P., Butkovskaya, N., Kukui, A., Le Bras, G., 2008. Impact of the new HNO_3 forming channel of the $HO_2 + NO$ reaction on tropospheric HNO_3, NO_X, HO_X and ozone. Atmospheric Chemistry and Physics Discussions 8, 2695–2713.

Carlson, T.N., 1998. Midlatitude Weather Systems. American Meteorological Society, Boston.

Carr, S., Heard, D.E., Blitz, M.A., 2009. Comment on "Atmospheric hydroxyl radical production from electronically excited NO_2 and H_2O" Science 324, 2.

Carslaw, D.C., 2005. On the changing seasonal cycles and trends of ozone at mace head, Ireland. Atmospheric Chemistry and Physics 5, 3441–3450.

Carslaw, N., Carpenter, L.J., Plane, J.M.C., Allan, B.J., Burgess, R.A., Clemitshaw, K.C., Coe, H., Penkett, S.A., 1997. Simultaneous observations of nitrate and peroxy radicals in the marine boundary layer. Journal of Geophysical Research-Atmospheres 102, 18917–18933.

Carslaw, N., Creasey, D.J., Heard, D.E., Jacobs, P.J., Lee, J.D., Lewis, A.C., Bauguitte, S., Penkett, S.A., Monks, P.S., Salisbury, G., 2002. Eastern atlantic spring experiment 1997 (EASE97) 2. Comparisons of model concentrations of OH, HO_2, and RO_2 with measurements. Journal of Geophysical Research 107 (D14), 4190. doi:10.1029/2001JD001568.

Carter, W.P.L., 2000. Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment. Final Report to California Air Resources Board Contract 92–329 and Contract 95-308. Air Pollution Research Center and College of Engineering Center for Environmental Research and Technology University of California Riverside, California.

Carter, W.P.L., Atkinson, R., 1989. A computer modeling study of incremental hydrocarbon reactivity. Environmental Science Technology 23, 864–880.

Cassanelli, P., Johnson, D., Cox, R.A., 2005. A temperature-dependent relative-rate study of the OH initiated oxidation of n-butane: the kinetics of the reactions of the 1-and 2-butoxy radicals. Physical Chemistry. Chemical Physics 7, 3702–3710.

Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., 1988. The role of biogenic hydrocarbons in urban photochemical smog: atlanta as a case study. Science 241 (4872), 1473–1475. doi:10.1126/science.3420404.

Chameides, W.L., Kasibhatla, P.S., Yienger, J., Levy, H., 1994. Growth of continental-scale Metro-Agro-Plexes, regional ozone pollution, and world food-production. Science 264, 74–77.

Chameides, W.L., Walker, J.C.G., 1973. A photochemical theory for tropospheric ozone. Journal of Geophysical Research 78, 8751–8760.

Charney, J.G., 1975. Dynamics of deserts and droughts in the Sahel. Quarterly Journal of the Royal Meteorological Society 101, 193–202.

Chemel, C., Chollet, P., 2006. Observations of the daytime boundary layer in deep alpine valleys. Boundary-Layer Meteorology 119, 239–262.

Chen, Y., Penner, J.E., 2005. Uncertainty analysis for estimates of the first indirect aerosol effect. Atmospheric Chemistry and Physics 5, 2935–2948.

Chen, X.H., Hulbert, D., Shepson, P.B., 1998. Measurement of the organic nitrate yield from OH reaction with isoprene. Journal of Geophysical Research 103, 25563–25568.

Chen, F., Tewari, M., Kusaka, H., Warner, T.L., 2006. Current status of urban modeling in the community weather research and forecast (WRF) model. Sixth AMS Symposium on the urban environment, January 2006, Atlanta GA. Available at: http://ams.confex.com/ams/Annual2006/techprogram/paper_98678.htm.

Chen, J., Griffin, R.J., Tulet, P., 2007. Modeling secondary organic aerosol formation through cloud processing of organic compounds. Atmospheric Chemistry and Physics 7, 5343–5355.

Chiapello, I., Moulin, C., 2002. TOMS and METEOSAT satellite records of the variability of Saharan dust transport over the Atlantic during the last two decades (1979–1997). Geophysical Research Letters 29, 4.

China Energy Statistical Yearbook, 2006. National Bureau of Statistics of China. China Energy Statistical Yearbook. Available at: www.stats.gov.cn/tjsj/ndsj/2006/indexeh.htm.

Choi, Y., Wang, Y., Zeng, T., Martin, R.V., Kurosu, T.P., Chance, K., 2005. Evidence of lightning NO_x and convective transport of pollutants in satellite observations over North America. Geophysical Research Letters 32, L02805.

Chuck, A.L., Turner, S.M., Liss, P.S., 2002. Direct evidence for a marine source of C_1 and C_2 alkyl nitrates. Science 297, 1151–1154.

Chuong, B., Stevens, P.S., 2002. Measurements of the kinetics of the OH-initiated oxidation of isoprene. Journal of Geophysical Research 107, 4132.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. Science 303, 1173–1176.

Cofala, J., Amann, M., Klimont, Z., Kupiainen, K., Höglund-Isaksson, L., 2007. Scenarios of global anthropogenic emissions of air pollutants and methane until 2030. Atmospheric Environment 41 (38), 8486–8499. doi:10.1016/j.atmosenv.2007.07.010.

Colarco, P.R., Schoeberl, M.R., Doddridge, B.G., Marufu, L.T., Torres, O., Welton, E.J., 2004. Transport of smoke from Canadian forest fires to the surface near Washington D.C.: injection height, entrainment and optical properties. Journal of Geophysical Research 109, D06203.

Colette, A., Ancellet, G., Borchi, F., 2005. Impact of vertical transport processes on the tropospheric ozone layering above Europe. Part I: study of air mass origin using multivariate analysis, clustering and trajectories. Atmospheric Environment 39, 5409–5422.

Collins, W.J., Derwent, R.G., Johnson, C.E., Stevenson, D.S., 2002. A comparison of two schemes for the convective transport of chemical species in a Lagrangian global chemistry model. Quarterly Journal of the Royal Meteorological Society 128, 991–1009.

Colomb, A., Williams, J., Crowley, J., Gros, V., Hofmann, R., Salisbury, G., Klupfel, T., Kormann, R., Stickler, A., Forster, C., Lelieveld, J., 2006. Airborne measurements of trace organic species in the upper troposphere over Europe: the impact of deep convection. Environmental Chemistry 3, 244–259.

Cook, P.A., Savage, N.H., Turquety, S., Carver, G.D., O'Connor, F.M., Heckel, A., Stewart, D., Whalley, L.K., Parker, A.E., Schlager, H., Singh, H.B., Avery, M.A., Sachse, G.W., Brune, W., Richter, A., Burrows, J.P., Purvis, R., Lewis, A.C., Reeves, C.E., Monks, P.S., Levine, J.G., Pyle, J.A., 2007. Forest fire plumes over the North Atlantic: p-TOMCAT model simulations with aircraft and satellite measurements from the ITOP/ICARTT campaign. Journal of Geophysical Research 112, D10S43.

Cooke, W.F., Wilson, J.J.N., 1996. A global black carbon aerosol model. Journal of Geophysical Research 101, 19185–19369.

Cooper, O.R., Moody, J.L., Parrish, D.D., Trainer, M., Ryerson, T.B., Hollaway, J.S., Hubler, G., Fehsenfeld, F.C., Oltmans, S.J., Evans, M.J., 2001. Trace gas signatures of the airstreams within North Atlantic cyclones – case studies from the NARE'97 aircraft intensive. Journal of Geophysical Research 106, 5437–5456.

Cooper, O.R., Moody, J.L., Parrish, D.D., Trainer, M., Holloway, J.S., Hubler, G., Fehsenfeld, F.C., Stohl, A., 2002a. Trace gas composition of midlatitude cyclones over the western North Atlantic Ocean: a seasonal comparison of O_3 and CO. Journal of Geophysical Research 107, 4057–4070.

Cooper, O.R., Moody, J., Parrish, D.D., Trainer, M., Ryerson, T.B., Holloway, J.S., Hubler, G., Fehsenfeld, F.C., Evans, M.J., 2002b. Trace gas composition of mid-latitude cyclones over the western North Atlantic Ocean: a conceptual model. Journal of Geophysical Research 107, 4056.

Cooper, O.R., Forster, C., Parrish, D.D., Trainer, M., Dunlea, E., Ryerson, T., Hübler, G., Fehsenfeld, F., Nicks, D., Holloway, J., de Gouw, J., Warneke, C., Roberts, J.M., Flocke, F., Moody, J., 2004. A case study of trans-Pacific warm conveyor belt transport: the influence of merging airstreams on trace gas import to North America. Journal of Geophysical Research 109, D23S08.

Cooper, O.R., Stohl, A., Hübler, G., Hsie, E.Y., Parrish, D.D., Tuck, A.F., Kiladis, G.N., Oltmans, S.J., Johnson, B.J., Shapiro, M., Moody, J.L., Lefohn, A.S., 2005. Direct transport of midlatitude stratospheric ozone into the lower troposphere and marine boundary layer of the tropical Pacific Ocean. Journal of Geophysical Research 110, D23310.

Coplen, T.B. Explanatory glossary of terms used in expression of relative isotope ratios and gas ratios. Pure and Applied Chemistry submitted for publication.

Correa, S.M., Martins, E.M., Arbilla, G., 2003. Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil. Atmospheric Environment 37, 23–29.

Cotton, W.R., Alexander, G.D., Hertenstein, R., Walko, R.L., McAnelly, R.L., Nicholls, M., 1995. Cloud venting – a review and some new global annual estimates. Earth Science Reviews 39, 169–206.

Cozic, J., Verheggen, B., Weingartner, E., Crosier, J., Bower, K., Flynn, M., Coe, H., Henning, S., Steinbacher, M., Collaud Coen, M., Petzold, A., Baltensperger, U., 2008. Chemical composition of free tropospheric aerosol for PM_1 and coarse mode at the high alpine site Jungfraujoch. Atmospheric Chemistry and Physics 8, 407–423.

Creasey, D.J., Evans, G.E., Heard, D.E., Lee, J.D., 2003. Measurements of OH and HO_2 concentrations in the Southern Ocean marine boundary layer. Journal of Geophysical Research 108, 4475.

Cristofanelli, P., Bonasoni, P., Tositti, L., Bonafe, U., Calzolari, F., Evangelisti, F., Sandrini, S., Stohl, A., 2006. A 6-year analysis of stratospheric intrusions and their influence on ozone at Mt. Cimone (2165 m above sea level). Journal of Geophysical Research-Atmospheres 111, 11.

Cros, B., Durand, P., Cachier, H., Drobinski, P., Frejafon, E., Kottmeier, C., Perros, P.E., Peuch, V.H., Ponche, J.L., Robin, D., Said, F., Toupance, G., Wortham, H., 2004. The ESCOMPTE program: an overview. Atmospheric Research 69, 241–279.

Crowley, J.N., Carl, S.A., 1997. OH formation in the Photoexcitation of NO_2 beyond the dissociation threshold in the presence of water vapor. Journal of Physics and Chemistry 101, 4178–4184.

Crutzen, P.J., 1973. Photochemical reactions initiated by and influencing ozone in the unpolluted troposphere. Tellus 26, 47–57.

Crutzen, P.J., 2004. New directions: the growing urban heat and pollution "island" effect-impact on chemistry and climate. Atmospheric Environment 38, 3539–3540.

Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R., Theloke, J., Friedrich, R., 2009. Modeling study of the impact of isoprene and terpene emissions on European ozone levels. Atmospheric Environment 43, 1380–1391.

Cuvelier, C., Thunis, P., Vautard, R., Amann, M., Bessagnet, B., Bedogni, M., Berkowicz, R., Brandt, J., Brocheton, F., Builtjes, P., Coppalle, A., Denby, B., Douros, J., Graf, A., Hellmuth, O., Honoré, C., Hodzic, A., Jonson, J., Kerschbaumer, A., de Leeuw, F., Minguzzi, E., Moussiopoulos, N., Pertot, C., Pirovano, G., Rouil, L., Schaap, M., Stern, R., Tarrason, L., Vignati, E., Volta, M., White, L., Wind, P., Zuber, A., 2007. CityDelta: a model intercomparison to explore the impact of emission reductions in 2010 in European cities in 2010. Atmospheric Environment 41, 189–207.

Dahl, E.E., Saltzman, E.S., Yvon-Lewis, S.A., 2005. Saturation anomalies of alkyl nitrates in the tropical Pacific Ocean. Geophysical Research Letters 32, 1–4.

Damoah, R., Spichtinger, N., Servranckx, R., Fromm, M., Eloranta, E.W., Razenkov, I.A., James, P., Shulski, M., Forster, C., Stohl, A., 2006. A case study of pyro-convection using transport model and remote sensing data. Atmospheric Chemistry and Physics 6, 173–185.

Danielsen, E.F., 1968. Stratospheirc-tropospheirc exchange based on radioactivity, ozone and potential vorticity. Journal of Atmospheric Science 25, 502–518.

Darmenova, K., Sokolik, I.N., Darmenov, A., 2005. Characterization of east Asian dust outbreaks in the spring of 2001 using ground-based and satellite data. Journal of Geophysical Research 110, D02204.

Davies, T.D., Schuepbach, E., 1994. Episodes of high ozone concentrations at the Earth's surface resulting from transport down from the upper troposphere/lower stratosphere: a review and case studies. Atmospheric Environment 28, 53–68.

Davis, D., Grodzinsky, G., Chen, G., Crawford, J., Eisele, F., Mauldin, L., Tanner, D., Cantrell, C., Brune, W., Tan, D., Faloona, I., Ridley, B., Montzka, D., Walega, J., Grahek, F., Sandholm, S., Sachse, G., Vay, S., Anderson, B., Avery, M., Heikes, B., Snow, J., O'Sullivan, D., Shetter, R., Lefer, B., Blake, D., Blake, N., Carroll, M., Wang, Y., 2001. Marine latitude/altitude OH distributions: comparison of Pacific Ocean observations with models. Journal of Geophysical Research-Atmospheres 106, 32691–32707.

De Wekker, S.F.J., Steyn, D.G., Fast, J.D., Rotach, M.W., Zhong, S., 2005. The performance of RAMS in representing the convective boundary layer structure in a very steep valley. Environmental Fluid Mechanics 5, 32–62.

Decesari, S., Facchini, M.C., Fuzzi, S., Tagliavini, E., 2000. Characterization of water soluble organic compounds in atmospheric aerosol: a new approach. Journal of Geophysical Research 105, 1481–1489.

Decesari, S., Mircea, M.C., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., Facchini, M.C., 2007. Source attribution of water-soluble organic aerosol by nuclear magnetic resonance spectroscopy. Environmental Science Technology 41, 2479–2484.

Deeter, M.N., Emmons, L.K., Francis, G.L., Edwards, D.P., Gille, J.C., Warner, J.X., Khattatov, B., Ziskin, D., Lamarque, J.F., Ho, S.P., Yudin, V., Attie, J.L., Packman, D., Chen, J., Mao, D., Drummond, J.R., 2003. Operational carbon monoxide retrieval algorithm and selected results for the MOPITT instrument. Journal of Geophysical Research 108.

Deguillaume, L., Leriche, M., Amato, P., Ariya, P.A., Delort, A.-M., Pöschl, U., Chaumerliac, N., Bauer, H., Flossmann, A.I., Morris, C.E., 2008. Microbiology and atmospheric processes: chemical interactions of primary biological aerosols. Biogeosciences 5, 1073–1084.

Del Genio, A.D., Yao, M.-S., Jonas, J., 2007. Will moist convection be stronger in a warmer climate? Geophysical Research Letters 34, L16703.

van Delden, A., 2001. The synoptic setting of thunderstorms in western Europe. Atmospheric Research 56, 89–110.

Delle Monache, L., Stull, R.B., 2003. An ensemble air quality forecast over western Europe during an ozone episode. Atmospheric Environment 37, 3469–3474.

Delon, C., Reeves, C.E., Stewart, D.J., Serca, D., Dupont, R., Mari, C., Chaboureau, J.P., Tulet, P., 2008. Biogenic nitrogen oxide emissions from soils - impact on NO_x and ozone over West Africa during AMMA (African Monsoon Multidisciplinary Experiment): modelling study. Atmospheric Chemistry and Physics 8, 2351–2363.

DeMott, P., Sassen, K., Poellot, M., Baumgardner, D., Rogers, D., Brooks, S., Prenni, A., Kreidenweis, S., 2003. African dust aerosols as atmospheric ice nuclei. Geophysical Research Letters 30, 1732.

Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global atmosphere. Journal of Geophysical Research 101, 22869–22890.

Dentener, F.J., Kinne, S., Bond, T., Boucher, O., Cofala, J., Generoso, S., Ginoux, P., Gong, S., Hoelzemann, J.J., Ito, A., Marelli, L., Penner, J.E., Putaud, J.-P., Textor, C., Schulz, M., van der Werf, G.R., Wilson, J., 2006. Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom. Atmospheric Chemistry and Physics 6, 4321–4344.

Derognat, C., Beekmann, M., Baeumle, M., Martin, D., Schmidt, H., 2003. Effect of biogenic volatile organic compound emissions on tropospheric chemistry during the atmospheric pollution over the Paris area (ESQUIF) campaign in the Ile-de-France region. Journal of Geophysical Research 108, 8560.

Derwent, R.G., Simmonds, P.G., Seuring, S., Dimmer, C., 1997. Observation and interpretation of the seasonal cycles in the surface concentrations of ozone and carbon monoxide at Mace Head, Ireland, from 1990 to 1994. Atmospheric Environment 32, 145–147.

Derwent, R.G., Stevenson, D.S., Collins, W.J., Johnson, C.E., 2004. Intercontinental transport and the origins of the ozone observed at surface sites in Europe. Atmospheric Environment 38, 1891–1901.

Derwent, R.G., Jenkin, M.E., Passant, N.R., Pilling, M.J., 2007. Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a master chemical mechanism. Atmospheric Environment 41, 2570–2579.

Després, V.R., Nowoisky, J.F., Klose, M., Conrad, R., Andreae, M.O., Pöschl, U., 2007. Characterization of primary biogenic aerosol particles in urban, rural, and high-alpine air by DNA sequence and restriction fragment analysis of ribosomal RNA genes. Biogeosciences 4, 1127–1141.

Deutsch, F., Vankerkom, J., Janssen, L., Janssen, S., Bencs, L., van Grieken, R., Fierens, F., Dumont, G., Mensink, C., 2008. Modelling concentrations of airborne primary and secondary PM_{10} and $PM_{2.5}$ with the BelEUROS-model in Belgium. Ecological Modelling 217, 230–239.

Di Carlo, P., Brune, W.H., Martinez, M., Harder, H., Lesher, R., Ren, X.R., Thornberry, T., Carroll, M.A., Young, V., Shepson, P.B., Riemer, D., Apel, E., Campbell, C., 2004. Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOCs. Science 304, 722–725.

Dickerson, R.R., Huffman, G.J., Luke, W.T., Nunnenmacker, L.J., Pickering, K.E., Leslie, A.C.D., Lindsey, C.G., Slinn, W.G.N., Kelly, T.J., Daum, P.H., Delany, A.C., Greenberg, J.P., Zimmerman, P.R., Boatman, J.F., Ray, J.D., Stedman, D.H., 1987. Thunderstorms: an important mechanism in the transport of air pollutants. Science 235, 460–465.

Dillon, T.J., Crowley, J.N., 2008. Direct detection of OH formation in the reactions of HO_2 with $CH_3C(O)O_2$ and other substituted peroxy radicals. Atmospheric Chemistry and Physics 8, 4877–4889.

Dillon, T.J., Tucceri, M.E., Sander, R., Crowley, J.N., 2008. LIF studies of iodine oxide chemistry. Physical Chemistry Chemical Physics 10, 1540–1554.

Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air pollution and mortality in six US cities. New England Journal of Medicine 29, 1753–1759.

DoE, 1997. Ozone in the United Kingdom 1997. Fourth Report of the United Kingdom Photochemical Oxidants Review Group. Department of the Environment, London.

Doherty, R.M., Stevenson, D.S., Collins, W.J., Sanderson, M.G., 2005. Influence of convective transport on tropospheric ozone and its precursors in a chemistry–climate model. Atmospheric Chemistry and Physics 5, 3205–3218.

Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M.R., Gascho, A., Weingarner, E., Prevot, A.S.H., Verheggen, B., Baltensperger, U., 2006. Laboratory observation of oligomers in the aerosol from isoprene/NO_x photooxidation. Geophysical Research Letters 33, L13805, doi:10.1029/2006GL026523.

Donahue, N., Robinson, A.L., Stanier, C.O., Pandis, S.N., 2006. The coupled partitioning, dilution, and chemical aging of semivolatile organics. Environmental Science Technology 40, 2635.

Donaldson, K., Borm, P. (Eds.), 2007. Particle Toxicology. CRC Press, Boca Raton, USA.

Doran, J.C., Fast, J.D., Horel, J., 2002. The VTMX 2000 campaign. Bulletin of American Meteorological Society 83, 537–551.

Dozier, J., 1981. A method for satellite identification of surface temperature fields of Subpixel resolution. Remote Sensing Environment 11, 221–229.

Dubovik, O., Holben, B., Eck, T., Smirnov, A., Kaufman, Y.J., King, M.D., Tanre, D., Slutsker, I., 2002. Variability of absorption and optical properties of key aerosol types observed in worldwide locations. Journal of Atmospheric Sciences 59, 590–608.

Duce, R.A., 1995. Sources, distributions and fluxes of mineral aerosols and their relationship to climate. In: Charlson, R.J., Heintzenberg, J. (Eds.), Aerosol Forcing of Climate. John Wiley, New York 43–72.

Duce, R.A., Mohnen, V.A., Zimmerman, P.R., Grosjean, D., Cautreels, W., Chatfield, R.B., Jaenicke, R., Ogren, J.A., Pellizzari, E.D., Wallace, G.T., 1983. Organic material in the global troposphere. Reviews of Geophysics 21, 921–952.

Duncan, B.N., Bey, I., 2004. A modeling study of the export pathways of pollution from Europe: seasonal and interannual variations (1987–1997). Journal of Geophysical Research 109, D08301.

Dupont, S., Otte, T.L., Ching, J.K.S., 2004. Simulation of meteorological fields within and above urban and rural canopies with a mesoscale model (MM5). Boundary-Layer Meteorology 113, 111–158.

Durbin, T.D., Miller, J.W., Younglove, T., Huai, T., Cocker, K., 2007. Effects of fuel ethanol content and volatility on regulated and unregulated exhaust emissions for the latest technology gasoline vehicles. Environmental Science & Technology 41, 4059–4064.

Duvall, R.M., Norris, G.A., Dailey, L.A., Burke, J.M., McGee, J.K., Gilmour, M.I., Gordon, T., Devlin, R., 2008. Source apportionment of particulate matter in the US and associations with lung inflammatory markers. Inhalation Toxicology 20, 671–683.

Eckhardt, S., Stohl, A., Wernli, H., James, P., Forster, C., Spichtinger, N., 2004. A 15-year climatology of warm conveyor Belts. Journal of Climate 17, 20.

Edney, E.O., Kleindeinst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Wang, W., Claeys, M., 2005. Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiate isoprene/NO_X/SO_2/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States. Atmospheric Environment 39, 5281–5289.

Edwards, D.P., Emmons, L.K., Gille, J.C., Chu, A., Attié, J.-L., Giglio, L., Wood, S.W., Haywood, J., Deeter, M.N., Massie, S.T., Ziskin, D.C., Drummond, J.R., 2006. Satellite-observed pollution from Southern Hemisphere biomass burning. Journal of Geophysical Research 111, D14312.

EEA, 2007. Air Pollution in Europe 1990–2004. EEA Report No2/2007. European Environment Agency, Copenhagen.

Ehhalt, D.H., 1999. Photooxidation of trace gases in the troposphere. Physical Chemistry Chemical Physics 1, 5401–5408.

Ehhalt, D.H., Rohrer, F., 2000. Dependence of the OH concentration on solar UV. Journal of Geophysical Research 105, 3565–3571.

Ehn, M., Petaja, T., Aufmhoff, H., Aalto, P., Hameri, K., Arnold, F., Laaksonen, A., Kulmala, M., 2007. Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid. Atmospheric Chemistry and Physics 7, 211–222.

Eisele, F., Mount, G.H., Tanner, D.J., Jefferson, A., Shetter, R., Harder, J.W., Williams, E.J., 1997. Understanding the production and interconversion of the hydroxyl radical during the tropospheric OH photochemistry experiment. Journal of Geophysical Research 102, 6457–6465.

Elbert, W., Taylor, P.E., Andreae, M.O., Pöschl, U., 2007. Contribution of fungi to primary biogenic aerosols in the atmosphere: wet and dry discharged spores, carbohydrates, and inorganic ions. Atmospheric Chemistry and Physics 7, 4569–4588.

Elrod, M.J., Ranschaert, D.L., Schneider, N.J., 2001. Direct kinetics study of the temperature dependence of the CH_2O branching channel for the $CH_3O_2 + HO_2$ reaction. International Journal of Chemical Kinetics 33, 363–376.

Elshorbany, Y.F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A.R., Pilling, M.J., Kleffmann, J., 2008. Oxidation capacity of the city of Santiago, Chile. Atmospheric Chemistry and Physics 9, 2257–2273.

Emmerson, K.M., Carslaw, N., Carpenter, L.J., Heard, D.E., Lee, J.D., Pilling, M.J., 2005. Urban atmospheric chemistry during the PUMA campaign 1: comparison of modelled OH and HO_2 concentrations with measurements. Journal of Atmospheric Chemistry 52, 143–164.

Emmerson, K.M., Carslaw, N., Carlaw, D.C., Lee, J.D., McFiggans, G., Bloss, W.J., Gravestock, T., Heard, D.E., Hopkins, J., Ingham, T., Pilling, M.J., Smith, S.C., Jacob, M., Monks, P.S., 2007. Free radical modelling studies during the UK TORCH Campaign in Summer 2003. Atmospheric Chemistry and Physics 7, 167–181.

EPA, 1990. National Air Quality and Emission Trends Report, 1988, EPA-450/4-90-002. U.S. Environmental Protection Agency, Washington, DC.

EPA, 1995. National Air Pollutant Emission Trends Report, 1900–1994, EPA-454/R-95-011. U.S. Environmental Protection Agency, Washington, DC.

EPA, 2000. National Air Pollutant Emission Trends: 1900–1998, EPA 454/R-00-002. U.S. Environmental Protection Agency, Washington, DC.

EPA, 2003. National Air Quality and Emission Trends Report: 2003 Special Studies Edition, EPA 454/R-03-005. U.S. Environmental Protection Agency, Washington, DC.

Escudero, M., Querol, X., Avila, A., Cuevas, E., 2007. Origin of the exceedances of the European daily PM limit value in regional background areas of Spain. Atmospheric Environment 41, 730–744.

Esler, J.G., Haynes, P.H., Law, K.S., Barjat, H., Dewy, K., Schmitgen, S., Brough, N., 2003. Transport and mixing between airmasses in cold frontal regions during Dynamics and Chemistry of Frontal Zones (DCFZ). Journal of Geophysical Research 108, 4142.

Facchini, M.C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E.D., de Leeuw, G., Martino, M., Woeltjen, J., O'Dowd, C.D., 2008. Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. Geophysical Research Letters 35, 5.

Fagerli, H., Legrand, M., Preunkert, S., Vestreng, V., Simpson, D., Cerquira, M., 2007. Modeling historical long-term trends of sulfate, ammonium and elemental carbon over Europe: a comparison with ice core records in the Alps. Journal of Geophysical Research 112, D23S13, doi: 10.1029/2006JD008044.

Fairlie, T.D., Jacob, D.J., Park, R.J., 2007. The impact of transpacific transport of mineral dust in the United States. Atmospheric Environment 41, 1251–1266.

Falkovich, A.H., Schkolnik, G., Ganor, E., Rudich, Y., 2004. Adsorption of organic compounds pertinent to urban environments onto mineral dust particles. Journal of Geophysical Research 109, D02208, doi: 10.1029/2003JD003919.

Faloona, I., Tan, D., Brune, W., Hurst, J., Baker Jr., D., Couch, T.L., Shepson, P., Apel, E., Riemer, D., Thornberry, T., Carroll, M.A., Sillman, S., Keeler, G.J., Sagady, J., Hooper, D., Paterson, K., 2001. Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy. Journal of Geophysical Research 106, 24315–24333.

Fan, J.-W., Zhang, R.-Y., Collins, D., Li, G.-H., 2006. Contribution of secondary condensable organics to new particle formation: a case study in Houston, Texas. Geophysical Research Letters 33, L15802.

Fantechi, G., Vereecken, L., Peeters, J., 2002. The OH-initiated atmospheric oxidation of pinonaldehyde: detailed theoretical study and mechanism construction. Physical Chemistry. Chemical Physics 4, 5795–5805.

Farmer, D.K., Cohen, R.C., 2008. Observations of HNO_3, PAN, PPN and fluxes: evidence for rapid HO_x chemistry within a pine forest canopy. Atmospheric Chemistry and Physics 8, 3899–3917.

Farquhar, J., Thiemens, M.H., Jackson, T., 1998. Atmosphere-surface interactions on Mars: $\Delta^{17}O$ measurements of carbonate from ALH 84001. Science 280, 1580–1582.

Farquhar, J., Savarino, J., Jackson, T.L., Thiemens, M.H., 2000. Evidence of atmospheric sulphur in the martian regolith from sulphur isotopes in meteorites. Nature 404, 50–52.

Fehr, T., Höller, H., Huntrieser, H., 2004. Model study on production and transport of lightning-produced NO_x in a EULINOX supercell storm. Journal of Geophysical Research 109, D09102.

Fehsenfeld, F.C., Ancellet, G., Bates, T.S., Goldstein, A.H., Hardesty, R.M., Honrath, R., Law, K.S., Lewis, A.C., Leaitch, R., McKeen, S., Meagher, J., Parrish, D.D., Pszenny, A.A.P., Russell, P.B., Schlager, H., Seinfeld, J., Talbot, R., Zbinden, R., 2006. International Consortium for atmospheric research on transport and transformation (ICARTT): north America to Europe – overview of the 2004 summer field study. Journal of Geophysical Research-Atmospheres 111, 36.

Felzer, B., Cronin, T., Reilly, J.M., Wang, X., 2007. Impact of ozone on trees and crops. Comptes Rendus Geoscience 339, 784–798.

Fernando, H.J.S., Lee, S.M., Anderson, J., Princevac, M., Pardyjak, E., Grossman-Clarke, S., 2001. Urban fluid mechanics: air circulation and contaminant dispersion in cities. Journal of Environmental Fluid Mechanics 1, 107–164.

Fietkau, S., Medeke, T., Richter, A., Sheode, N., Sinnhuber, B.-M., Wittrock, F., Theys, N., Roozendael, M.v., Burrows, J.P., 2007. Ground-based measurements of tropospheric and stratospheric bromine monoxide above Nairobi (1°S, 36°E). Atmospheric Chemistry and Physics Discussions 7, 6527–6555.

Fiore, A.M., Horowitz, L.W., Purves, D.W., Levy II, H., Evans, M.J., Wang, Y., Li, Q., Yantosca, R.M., 2005. Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States. Journal of Geophysical Research 110, D12303.

Fischer, H., de Reus, M., Traub, M., Williams, J., Lelieveld, J., de Gouw, J., Warneke, C., Schlager, H., Minikin, A., Scheele, R., Siegmund, P., 2003. Deep convective injection of boundary layer air into the lowermost stratosphere at midlatitudes. Atmospheric Chemistry and Physics 3, 739–745.

Fischer, P.H., Brunekreef, B., Lebret, E., 2004. Air pollution related deaths during the 2003 heat wave in the Netherlands. Atmospheric Environment 38, 1083–1085.

Fiscus, E.L., Fitzgarrald, L.B., Burkey, K.O., 2005. Crop responses to ozone: uptake, modes of action, carbon assimilation and partitioning. Plant, Cell and Environment 28, 997–1011.

Flatøy, F., Hov, Ø., 1997. NO_x from lightning and the calculated chemical composition of the free troposphere. Journal of Geophysical Research 102, 21373–21381.

Fleming, Z.L., Monks, P.S., Rickard, A.R., Bandy, B.J., Brough, N., Green, T.J., Reeves, C.E., Penkett, S.A., 2006a. Seasonal dependence of peroxy radical concentrations at a Northern hemisphere marine boundary layer site during summer and winter: evidence for radical activity in winter. Atmospheric Chemistry and Physics 6, 5415–5433.

Fleming, Z.L., Monks, P.S., Rickard, A.R., Heard, D.E., Bloss, W.J., Seakins, P.W., Still, T.J., Sommariva, R., Pilling, M.J., Morgan, R., Green, T.J., Brough, N., Mills, G.P., Penkett, S.A., Lewis, A.C., Lee, J.D., Saiz-Lopez, A., Plane, J.M.C., 2006b. Peroxy radical chemistry and the control of ozone photochemistry at Mace Head, Ireland during the summer of 2002. Atmospheric Chemistry and Physics 6, 2193–2214.

Folkins, I., Braun, C., Thompson, A.M., Witte, J., 2002. Tropical ozone as an indicator of deep convection. Journal of Geophysical Research-Atmospheres 107.

Forkel, R., Knoche, R., 2005. Regional climate change and its impact on photooxidant concentrations in southern Germany: simulations with a coupled regional climate-chemistry model. Journal of Geophysical Research 111, D12302.

Forster, C., Wandinger, U., Wotawa, G., James, P., Mattis, I., Althausen, D., Simmonds, P., O'Doherty, S., Jennings, S.G., Kleefeld, C., Schneider, J., Trickl, T., Kreipl, S., Jäger, H., Stohl, A., 2001a. Transport of boreal forest fire emissions from Canada to Europe. Journal of Geophysical Research 106, 22887–22906.

Forster, C., Wandinger, U., Wotawa, G., James, P., Mattis, I., Althausen, D., Simmonds, P., O'Doherty, S., Jennings, S.G., Kleefeld, C., Schneider, J., Trickl, T., Kreipl, S., Jäger, H., Stohl, A., 2001b. Transport of boreal forest fire emissions from Canada to Europe. Journal of Geophysical Research 106 (D19), 22887–22906.

Forster, C., Stohl, A., Seibert, P., 2007. Parameterization of convective transport in a Lagrangian particle dispersion model and its evaluation. Journal of Applied Meteorology and Climatology 46, 403–422.

Foster, K.L., Plastridge, R.A., Bottenheim, J.W., Shepson, P.B., Finlayson-Pitts, B.J., Spicer, C.W., 2001. The role of Br_2 and BrCl in surface ozone destruction at polar sunrise. Science 291, 471–474.

Fotiadi, A., Hatzianastassiou, N., Drakakis, E., Matsoukas, C., Pavlakis, K.G., Hatzidimitriou, D., Gerasopoulos, E., Mihalopoulos, N., Vardavas, I., 2006. Aerosol physical and optical properties in the Eastern Mediterranean Basin, Crete, from Aerosol Robotic Network data. Atmospheric Chemistry and Physics 6, 5399–5413.

Fowler, D., Pilegaard, K., Sutton, M.A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Schjoerring, J.K., Neftel, A., Burkhardt, J., Daemmgen, U., Neiyrink, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J.P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T.N., Ro-Poulsen, H., Cellier, P., Cape, J.N., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P.I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M.W., Vesala, T., Skiba, U., Brüeggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M.C., de Leeuw, G., Flossman, A., Chaumerliac, N., Erisman, J.W., 2009. Atmospheric composition change: ecosystems and atmosphere exchange 43, 5192–5263.

de Foy, B., Varela, J.R., Molina, L.T., Molina, M.J., 2006. Rapid ventilation of the Mexico city basin and regional fate of the urban plume. Atmospheric Chemistry and Physics 6, 2321–2335.

Franze, T., Weller, M.G., Niessner, R., Pöschl, U., 2003. Enzyme immunoassays for the investigation of protein nitration by air pollutants. Analyst 128, 824–831.

Franze, T., Weller, M.G., Niessner, R., Pöschl, U., 2005. Protein nitration by polluted air. Environment Science Technology 39, 1673–1678.

Fraser, R.H., Li, Z., Cihlar, C., 2000. Hot spot and NDVI differencing synergy (HANDS): a new technique for burned area mapping over boreal forest. Remote Sensing of Environment 74, 362–376.

Freitas, S.R., Longo, K.M., Andreae, M.O., 2006. Impact of including the plume rise of vegetation fires in numerical simulations of associated atmospheric pollutants. Geophysical Research Letters 33, L17808.

Frey, H.C., Zheng, J., 2002. Quantification of variability and uncertainty in utility NO_x emission inventories. Journal of Air & Waste Management Association 52, 1083–1095.

Fröhlich-Nowoisky, J., Després, V.R., Andreae, M.O., Pöschl, U., 2009. Diversity of fungi in continental air determined by DNA analysis of fine and coarse aerosol particle samples. Proceedings of the National Academy of Science, 106, 12814-12819, doi: 10.1073/pnas.0811003106.

Fromm, M.D., Alfred, J., Hoppel, K., Hornstein, J., Bevilacqua, R., Shettle, E., Servranckx, R., Li, Z., Stocks, B., 2000. Observations of boreal forest fire smoke in the stratosphere by POAMIII, SAGEII, and lidar in 1998. Geophysical Research Letters 27, 1407–1410.

Fromm, M.D., Bevilacqua, R., Servranckx, R., Rosen, J., Thayer, J.P., Herman, J., Larko, D., 2005. Pyro-cumulonimbus injection of smoke to the stratosphere: observations and impact of a super blowup in northwestern Canada on 3–4 August 1998. Journal of Geophysical Research 110, D08205.

Fromm, M., Tupper, A., Rosenfeld, D., Servranckx, R., McRae, R., 2006. Violent pyro-convective storm devastates Australia's capital and pollutes the stratosphere. Geophysical Research Letters 33, L05815.

Fromm, M.D., Servranckx, R., 2003. Transport of forest fire smoke above the tropopause by supercell convection. Geophysical Research Letters 30, 1542.

Frost, G.J., McKeen, S.A., Trainer, M., Ryerson, T.B., Neuman, J.A., Roberts, J.M., Swanson, A.L., Holloway, J.S., Sueper, D.T., Fortin, T., Parrish, D.D., Fehsenfeld, F.C., Flocke, F., Peckham, S.E., Grell, G.A., Kowal, D., Cartwright, J., Auerbach, N., Habermann, T., 2006. Effects of changing power plant NO_x emissions on ozone in the eastern United States: proof of concept. Journal of Geophysical Research 111, D12306.

Fuzzi, S., Decesari, S., Facchini, M.C., Matta, E., Mircea, M., Tagliavini, E., 2001. A simplified model of the water soluble organic component of atmospheric aerosols. Geophysical Research Letters 28, 4079–4082.

Fuzzi, S., Andreae, M., Huebert, B.J., Kulmula, M., Bind, T.C., Doherty, S.J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Pöschl, U., Russell, L.M., 2006. Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. Atmospheric Chemistry and Physics 6, 2017–2038.

Galbally, I.E., Bentley, S.T., Meyer, C.P.M., 2000. Mid-latitude marine boundarylayer ozone destruction at visible sunrise observed at Cape Grim, Tasmania, 41°S. Geophysical Research Letters 27, 3841–3844.

Gangoiti, G., Alonso, L., Navazo, M., Garcia, J.A., Millan, M., 2006. North African soil dust and European pollution transport to America during the warm Seaton: hidden links shown by a passive tracer simulation. Journal of Geophysical Research 111, D10109.

Gaydos, T.M., Stanier, C.O., Pandis, S.N., 2005. Modeling of in situ ultrafine atmospheric particle formation in the eastern United States. Journal of Geophysical Research 110, D07S12.

Gaydos, T.M., Pinder, R., Koo, B., Fahey, K.M., Yarwood, G., Pandis, S.N., 2007. Development and application of a three-dimensional aerosol chemical transport model, PMCAMx. Atmospheric Environment 41, 2594–2611.

Gelencser, A., May, B., Simpson, D., Sanchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., Legrand, M., 2007. Source apportionment of $PM_{2.5}$ organic aerosol over Europe: primary/secondary, natural/anthropogenic, fossil/biogenic origin. Journal of Geophysical Research 112, D23S04, doi: 10.1029/2006JD008094 .

Gelencser, A., Varga, Z., 2005. Evaluation of the atmospheric significance of multiphase reactions in atmospheric secondary organic aerosol formation. Atmospheric Chemistry and Physics 5, 2823–2831.

Generoso, S., Bey, I., Attié, J.-L., Bréon, F.-M., 2007. A satellite- and model-based assessment of the 2003 Russian fires: impact on the Arctic region. Journal of Geophysical Research 112, D15302.

George, C., Strekowski, R.S., Kleffmann, J., Stemmler, K., Ammann, M., 2005. Photoenhanced uptake of gaseous NO_2 on solid organic compounds: a photochemical source of HONO? Faraday Discussions 130, 195–210.

Gerasopoulos, E., Kouvarakis, G., Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., 2005. Ozone variability in the marine boundary layer of the Eastern Mediterranean based on 7-year observations. Journal of Geophysical Research 110, D15309.

Gerasopoulos, E., Kouvarakis, G., Babasakalis, P., Vrekoussis, M., Putaud, J.-P., Mihalopoulos, N., 2006a. Origin and variability of particulate matter (PM_{10}) mass concentrations over the Eastern Mediterranean. Atmospheric Environment 40, 4679–4690.

Gerasopoulos, E., Kouvarakis, G., Vrekoussis, M., Donoussis, C., Mihalopoulos, N., Kanakidou, M., 2006b. Photochemical ozone production in the Eastern Mediterranean. Atmospheric Environment 40, 3057–3069.

Gerasopoulos, E., Koulouri, E., Kalivitis, N., Kouvarakis, S., Makela, T., Hillamo, R., Mihalopoulos, N., 2007. Size-segregated mass distributions of aerosols over Eastern Mediterranean: seasonal variability and comparison with AERONET columnar size-distributions. Atmospheric Chemistry and Physics 7, 2551–2561.

Gerlach, T.M., 2004. Volcanic sources of tropospheric ozone-depleting trace gases. Geochemistry Geophysics Geosystems 5 Q09007.

Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Klüpfel, T., Pätz, H.-W., Perner, D., Schäfer, H.-J., Volz-Thomas, A., Platt, U., 2003. Nighttime production of peroxy and hydroxyl radicals during the BERLIOZ campaign. Observations and modeling studies. Journal of Geophysical Research 108, 8249.

Geyer, A., Stutz, J., 2004a. Vertical profiles of NO_3, N_2O_5, O_3, and NO_x in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry. Journal of Geophysical Research 109.

Geyer, A., Stutz, J., 2004b. The vertical structure of $OH–HO_2–RO_2$ chemistry in the nocturnal boundary layer: a one-dimensional model study. Journal of Geophysical Research 109, D16301.

Giacopelli, P., Ford, K., Espada, C., Shepson, P.B., 2005. Comparison of the measured and simulated isoprene nitrate distributions above a forest canopy. Journal of Geophysical Research 110, D01304.

Gidel, L.T., 1983. Cumulus cloud transport and transient tracers. Journal of Geophysical Research 88, 6587–6599.

Giglio, L., Descloitres, J., Justice, C., Kaufman, Y., 2003. An enhanced contextual fire detection algorithm for MODIS. Remote Sensing of Environment 87, 273–282.

Ginoux, P., Chin, M., Tegen, I., Prospero, J.M., Holben, B., Dubrovik, O., Lin, S., 2001. Sources and distributions of dust aerosols simulated with the GOCART model. Journal of Geophysical Research 106, 20255–220273.

von Glasow, R., Crutzen, P.J., 2007. Tropospheric halogen chemistry. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry. Elsevier-Pergamon, Oxford, pp. 1–67.

von Glasow, R., Sander, R., Bott, A., Crutzen, P.J., 2002. Modeling halogen chemistry in the marine boundary layer. 1. Cloud-free MBL. Journal of Geophysical Research 107 (D17), 4323.

Glickman, T.S., 2000. Glossary of Meterology. American Meterology Society, Boston.

Goldstein, A.H., McKay, M., Kurpius, M.R., Schade, G.W., Lee, A., Holzinger, R., Rasmussen, R.A., 2004. Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs. Geophysical Research Letters 31, L22106.

Goldstein, A.H., Koven, C.D., Heald, C.L., Fung, I.Y., 2009. Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States. Proceedings of the National Academy of Science U.S.A. 106, 8835–8840.

Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the Earth's atmosphere. Environmental Science and Technology, 1515–1521. 1 March.

Goldstein, A.H., Shaw, S.L., 2003. Isotopes of volatile organic compounds: an emerging approach for studying atmospheric budgets and chemistry. Chemical Reviews 103, 5025–5048.

Goode, J.G., Yokelson, R.J., Ward, D.E., Susott, R.A., Babbitt, E.R., Davies, M.A., Hao, W.M., 2000. Measurements of excess O_3, CO_2, CO, CH_4, C_2H_4, C_2H_2, HCN, NO, NH_3, HCOOH, CH_3COOH, HCHO, and CH_3OH in 1997 Alaskan biomass burning plumes by airborne Fourier transform infrared spectroscopy (AFTIR). Journal of Geophysical Research 105, 22147–22166.

de Gouw, J.A., Middlebrook, A.M., Warneke, C., Goldan, P.D., Kuster, W.C., Roberts, J.M., Fehsenfeld, F.C., Worsnop, D.R., Canagaratna, M.R., Pszenny, A.A.P., Keene, W.C., Marchewka, M., Bertman, S.B., Bates, T.S., 2005. Budget of organic carbon in a polluted atmosphere: results from the new England air quality study in 2002. Journal of Geophysical Research 110, D16305.

de Gouw, J., Warneke, C., Stohl, A., Wollny, A.G., Brock, C.A., Cooper, O.R., Holloway, J.S., Trainer, M., Fehsenfeld, F.C., Atlas, E.L., Donnelly, S.G., Stroud, V., Leub, A., 2006. Volatile organic compounds composition or merged and aged forest fire plumes from Alaska and western Canada. Journal of Geophysical Research 111, D10303.

Graedel, T.E., Bates, T.S., Bouwman, A.F., Cunnold, D., Dignon, J., Fung, I., Jacob, D.J., Lamb, B.K., Logan, J.A., Marland, G., Middleton, P., Pacyna, J.M., Placer, M., Veldt, C., 1993. A Compilation of inventories of emissions to the atmosphere. Global Biogeochemical Cycles 7 (1993), 1–26.

Grahame, T.J., Schlesinger, R.B., 2007. Health effects of airborne particulate matter: do we know enough to consider regulating specific particle types or sources? Inhalation Toxicology 19, 457–481.

Grégoire, J.-M., Tansey, K., Silva, J.M.N., 2003. The GBA2000 initiative: developing a global burned area database from SPOT-VEGETATION imagery. International Journal of Remote Sensing 24, 1369–1376.

Grell, G., Emeis, S., Stockwell, W.R., Schoenemeyer, T., Forkel, R., Michalkes, U., Knoche, R., Seidl, W., 2000. Application of a multiscale, coupled MM5/chemistry model to the complex terrain of the VOTALP valley campaign. Atmospheric Environment 34, 1435–1453.

Grennfelt, P., Hov, Ø., 2005. Regional air pollution at a turning point. Ambio 34, 2–10.

Grewe, V., 2007. Impact of climate variability on tropospheric ozone. Science of the Total Environment 374, 167–181.

Grewe, V., 2008. Impact of lightning on air chemistry and climate. In: Betz, H.D., Schumann, U., Laroche, P. (Eds.), Lightning Principles, Instruments and Applications: Review of Modern Lightning Research. Springer–Verlag, Berlin Germany.

Grewe, V., Brunner, D., Dameris, M., Grenfell, J.L., Hein, R., Shindell, D., Staehelin, J., 2001. Origin and variability of upper tropospheric nitrogen oxides and ozone at northern mid-latitudes. Atmospheric Environment 35, 3421–3433.

Gros, V., Brenninkmeijer, C.A.M., Jockel, P.J., Kaiser, J., Lowry, D., Nisbet, E.G., O'Brian, P., Rockmann, T., Warwick, N., 2004. Isotope signatures of trace gas sources. In: Granier, C., Artaxo, P., Reeves, C.E. (Eds.), Emissions of Atmospheric Trace Compounds. Kluwer Academic Pub., Paris.

Grousset, F.E., Ginoux, P., Bory, A., Biscaye, P.E., 2003. Case study of a Chinese dust plume reaching the French Alps. Geophysical Research Letters 30.

Grutter, M., Flores, E., Andraca-Ayala, G., Baez, A., 2005. Formaldehyde levels in downtown Mexico City during 2003. Atmospheric Environment 39, 1027–1034.

Gryparis, A., Forsberg, B., Katsouyanni, K., Analitis, A., Touloumi, G., Schwartz, J., Samoli, E., Medina, S., Anderson, H.R., Niciu, E.M., Wichmann, H.-E., Kriz, B., Kosnik, M., Skorkovsky, J., Vonk, J.M., Dortbudak, Z., 2004. Acute effects of ozone on mortality from the "Air pollution and health: a European approach" project. American Journal of Respiratory and Critical Care Medicine 170, 1080–1087.

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., Scholes, R., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100, 8873–8892.

Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 2003. Isoprene and monoterpene emission ratevariability-model evaluations and sensitivity analyses. Journal Geophysical Research 9, 12609–12617.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature. Atmospheric Chemistry and Physics 6, 3181–3210.

Guerova, G., Bey, I., Attié, J.-L., Martin, R.V., Cui, J., Sprenger, M., 2006. Impact of transatlantic transport episodes on summertime ozone in Europe. Atmospheric Chemistry and Physics 6, 2057–2072.

Gurjar, B.R., van Aardenne, J.A., Lelieveld, J., Mohan, M., 2004. Emission estimates and trends (1990–2000) for megacity Delhi and implications. Atmospheric Environment, 5663–5681.

Gurjar, B.R., Butler, T.M., Lawrence, M.G., Lelieveld, J., 2008. Evaluation of emissions and air quality in megacities. Atmospheric Environment 42, 1593–1606.

Gurjar, B.R., Lelieveld, J., 2005. New directions: megacities and global change. Atmospheric Environment 39, 391–393.

Gustafsson, R.J., Orlov, A., Griffiths, P.T., Cox, R.A., Lambert, R.M., 2006. Reduction of NO_2 to nitrous acid on illuminated titanium dioxideaerosol surfaces: implications for photocatalysis and atmospheric chemistry. Chemical Communications, 3936–3938.

Guttikunda, S.K., Tang, Y., Carmichael, G.R., Kurata, G., Pan, L., Streets, D.G., Woo, J.H., Thongboonchoo, N., Fried, A., 2005. Impacts of Asian megacity emissions on regional air quality during spring 2001. Journal of Geophysical Research 110, D20301.

Haagen-Smit, A.J., 1952. Chemistry and physiology of Los Angeles smog. Industrial & Engineering Chemistry 44, 1342.

Hak, C., Pundt, I., Trick, S., Kern, C., Platt, U., Dommen, J., Ordonez, C., Prevot, A.S.H., Junkermann, W., Astorga-Llorens, C., Larsen, B.R., Mellqvist, J., Strandberg, A., Yu, Y., Galle, B., Kleffmann, J., Lorzer, J.C., Braathen, G.O., Volkamer, R., 2005. Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air. Atmospheric Chemistry and Physics 5, 2881–2900.

Hallquist, M., Stewart, D.J., Stephenson, S.K., Cox, R.A., 2003. Hydrolysis of N_2O_5 on sub-micron sulfate aerosols. Physical Chemistry Chemical Physics 5, 3453–3463.

Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmospheric chemistry and physics 9, 5155–5235.

Hamdi, R., Masson, V., 2008. Inclusion of a drag approach in the Town Energy Balance (TEB) scheme: offline 1D evaluation in a street canyon. Journal of Applied Meteorology and Climatology 47, 2627–2644, doi: 10.1175/2008JAMC1865.1

Hamilton, J.F., Webb, P.J., Lewis, A.C., Hopkins, J.R., Smith, S., Davy, P., 2004. Partially oxidised organic components in urban aerosol using GCXGC-TOF/MS. Atmospheric Chemistry and Physics 4, 1279–1290.

Hao, W.M., Liu, M.H., 1994. Spatial and temporal distribution of tropical biomass burning. Global Biogeochemical Cycles 8, 495–504.

Harley, R.A., Marr, L.C., Lehner, J.K., Giddings, S.N., 2005. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition. Environmental Science and Technology 39, 5356–5362.

Hasson, A.S., Tyndall, G.S., Orlando, J.J., 2004. A product yield study of the reaction of HO_2 radicals with ethyl peroxy ($C_2H_5O_2$), acetyl peroxy ($CH_3C(O)O_2$) and acetonyl peroxy ($CH_3C(O)CH_2O_2$) radicals. Journal of Physics and Chemistry A 108, 5979–5989.

Hauf, T., Schulte, P., Alheit, R., Schlager, H., 1995. Rapid vertical trace gas transport by an isolated midlatitude thunderstorm. Journal of Geophysical Research 100, 22957–22970.

Hauglustaine, D.A., Madronich, S., Ridley, B.A., Flocke, S.J., Cantrell, C.A., Eisele, F.L., Shetter, R.E., Tanner, D.J., Ginoux, P., Atlas, E.L., 1999. Photochemistry and budget of ozone during the Mauna Loa observatory photochemistry experiment (MLOPEX 2). Journal of Geophysical Research 104, 30275–30307.

Hauglustaine, D.A., Lathiere, J., Szopa, S., Folberth, G.A., 2005. Future tropospheric ozone simulated with a climate-chemistry-biosphere model. Geophysical Research Letters 32, L24807.

Heald, C.L., Jacob, D.J., Park, R.J., Russell, L.M., Huebert, B.J., Seinfeld, J.H., Liao, H., Weber, R.J., 2005. A large organic aerosol source in the free troposphere missing from current models. Geophysical Research Letters 32, L18809.

Heald, C.L., Jacob, D.J., Turquety, S., Hudman, R.C., Weber, R.J., Sullivan, A.P., Peltier, R.E., Atlas, E.L., de Gouw, J.A., Warneke, C., Holloway, J.S., Neuman, J.A., Flocke, F.M., Seinfeld, J.H., 2006. Concentrations and sources of organic carbon aerosols in the free troposphere over North America. Journal of Geophysical Research 111, D23S47.

Heald, C.L., Heald, C.L., Henze, D.K., Horowitz, L.W., Feddema, J., Lamarque, J.-F., Guenther, A., Hess, P.G., Vitt, F., Seinfeld, J.H., Goldstein, A.H., Fung, I., 2008a. Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change. Journal of Geophysical Research 113, D05211.

Heald, C.L., Goldstein, A.H., Allan, J.D., Aiken, A.C., Apel, E., Atlas, E.L., Baker, A.K., Bates, T.S., Beyersdorf, A.J., Blake, D.R., Campos, T., Coe, H., Crounse, J.D., DeCarlo, P.F., de Gouw, J.A., Dunlea, E.J., Flocke, F.M., Fried, A., Goldan, P., Griffin, R.J., Herndon, S.C., Holloway, J.S., Holzinger, R., Jimenez, J.L., Junkermann, W., Kuster, W.C., Lewis, A.C., Meinardi, S., Millet, D.B., Onasch, T., Polidori, A., Quinn, P.K., Riemer, D.D., Roberts, J.M., Salcedo, D., Sive, B., Swanson, A.L., Talbot, R., Warneke, C., Weber, R.J., Weibring, P., Wennberg, P.O., Worsnop, D.R., Wittig, A.E., Zhang, R., Zheng, J., Zheng, W., 2008b. Total observed organic carbon (TOOC) in the atmosphere: a synthesis of North American observations. Atmospheric Chemistry and Physics 8, 2007–2025.

Healy, R.M., Wenger, J.C., Metzger, A., Duplissy, J., Kalberer, M., Dommen, J., 2008. Gas/particle partitioning of carbonyl in the photooxidation of isoprene and 1,3,5-trimethylbenzene. Atmospheric Chemistry and Physics 8, 3215–3230.

Heard, D.E., Carpenter, L.J., Creasey, D.J., Hopkins, J.R., Lee, J.D., Lewis, A.C., Pilling, M.J., Seakins, P.W., 2004. High levels of the hydroxyl radical in the winter urban atmosphere. Geophysical Research Letters 31, L1812.

Heard, D.E., Pilling, M.J., 2003. Measurement of OH and HO_2 in the troposphere. Chemical Reviews 103, 5163–5198.

Hegglin, M.I., Brunner, D., Wernli, H., Schwierz, C., Martius, O., Hoor, P., Fischer, H., Parchatka, U., Spelten, N., Schiller, C., Krebsbach, M., Weers, U., Staehelin, J., Peter, T., 2004. Tracing troposphere-to-stratosphere transport above a mid-latitude deep convective system. Atmospheric Chemistry and Physics 4, 741–756.

Heikes, B.G., Chang, W.N., Pilson, M.E.Q., Swift, E., Singh, H.B., Guenther, A., Jacob, D.J., Field, B.D., Fall, R., Riemer, D., Brand, L., 2002. Atmospheric methanol budget and ocean implication. Global Biogeochemical Cycles 16, 1133.

Heintzenberg, J., 2009. The SAMUM-1 experiment over Southern Morocco: overview and introduction. Tellus 61, 2–11.

Hély, C., Caylor, K., Alleaume, S., Swap, R.J., Shugart, H.H., 2003. Release of gaseous and particulate carbonaceous compounds from biomass burning during the SAFARI 2000 dry season field campaign. Journal of Geophysical Research 108, 8470.

Hendrick, F., van Roozendael, M., Chipperfield, M.P., Dorf, M., Goutail, F., Yang, X., Fayt, C., Hermans, C., Pfeilsticker, K., Pommereau, J.-P., Pyle, J.A., Theys, N., Mazière, M.D., 2007. Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60_N. Atmospheric Chemistry and Physics 7, 4869–4885.

Henne, S., Furger, M., Nyeki, S., Steinbacher, M., Neininger, B., De Wekker, S.F.J., Dommen, J., Spichtinger, N., Stohl, A., Prevot, A.S.H., 2004. Quantification of topographic venting of boundary layer air to the free troposphere. Atmospheric Chemistry and Physics 4, 497–509.

Henne, S., Dommen, J., Neininger, B., Reimann, S., Staehelin, J., Prevot, A.S.H., 2005a. Influence of mountain venting in the Alps on the ozone chemistry of the lower free troposphere and the European pollution export. Journal of Geophysical Research 110, D22307. doi:10.1029/2005JD005936.

Henne, S., Furger, M., Prévôt, A.S.H., 2005b. Climatology of mountain venting induced moisture layers in the lee of the Alps. Journal of Applied Meteorology 44, 620–633.

Henze, D.K., Seinfeld, J.H., Ng, N.L., Kroll, J.H., Fu, T.-M., Jacob, D.J., Heald, C.L., 2007. Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs low-yield pathways. Atmospheric Chemistry and Physics 8, 2405–2420.

Henze, D.K., Seinfeld, J.H., 2006. Global secondary organic aerosol from isoprene oxidation. Geophysical Research Letters 33, L09812.

Herbin, H., Hurtmans, D., Turquety, S., Wespes, C., Barret, B., Hadji-Lazaro, J., Clerbaux, C., Coheur, P.F., 2007. Global distributions of water vapour isotopologues retrieved from IMG/ADEOS data. Atmospheric Chemistry and Physics 7, 3957–3968.

Herman, J.R., Bhartia, P.K., Torres, O., Hsu, C., Seftor, C., Celarier, E., 1997. Global distribution of UV-absorbing aerosols from Nimbus 7/TOMS data: passive remote sensing of tropospheric aerosol and atmospheric corrections from the new generation of satellite sensors. Journal of Geophysical Research 102, 16911–16922.

Hermann, M., Heintzenberg, J., Wiedensohler, A., Zahn, A., Heinrich, G., Brenninkmeijer, C.A.M., 2003. Meridional distributions of aerosol particle number concentrations in the upper troposphere and lower stratosphere obtained by Civil Aircraft for Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) flights. Journal of Geophysical Research 108, 4114.

Hidalgo, J., Pigeon, G., Masson, V., 2008. Urban-breeze circulation during the CAPITOUL experiment: experimental data analysis approach. Meteorology and Atmospheric Physics 102, 223–241.

Hobbs, P.V., Reid, J.S., Herring, J.A., Nance, J.D., Weiss, R.E., Ross, J.L., Hegg, D.A., Ottmar, R.D., Liousse, C., 1996. Particle and trace gas measurements in the smoke from prescribed burns of forest products in the Pacific Northwest. In: Levine, J.S. (Ed.), Biomass Burning and Global Change. MIT Press, Cambridge, Mass, pp. 697–715.

Hobbs, P.V., Sinha, P., Yokelson, R.J., Christian, T.J., Blake, D.R., Gao, S., Kirchstetter, T.W., Novakov, T., Pilewskie, P., 2003. Evolution of gases and particles from a savanna fire in South Africa. Journal of Geophysical Research 108, 8485.

Hock, N., Schneider, J., Borrmann, S., Römpp, A., Moortgat, G., Franze, T., Schauer, C., Pöschl, U., Plass-Dülmer, C., Berresheim, H., 2008. Rural continental aerosol properties and processes observed during the Hohenpeissenberg Aerosol Characterization Experiment (HAZE2002). Atmospheric Chemistry and Physics 8, 603–623.

Hodzic, A., Madronich, S., Bohn, B., Massie, S., Menut, L., Wiedinmyer, C., 2007. Wildfire particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions, transport and radiative effects. Atmospheric Chemistry and Physics 7, 4043–4064.

Hoek, G., Brunekreef, B., Goldbohm, S., Fischer, P., van den Brandt, P.A., 2002. Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. The Lancet 360, 1203–1209.

Hoelzemann, J.J., Schultz, M.G., Brasseur, G.P., Granier, C., Simon, M., 2004. Global Wildland Fire Emission Model (GWEM): evaluating the use of global area burnt satellite data. Journal of Geophysical Research 109, D14504.

Hofzumahaus, A., Lefer, B.L., Monks, P.S., Hall, S.R., Kylling, A., Mayer, B., Shetter, R.E., Junkermann, W., Bais, A., Calvert, J.G., Cantrell, C.A., Madronich, S., Edwards, G.D., Kraus, A., Muller, M., Bohn, B., Schmitt, R., Johnston, P., McKenzie, R., Frost, G.J., Griffioen, E., Krol, M., Martin, T., Pfister, G., Roth, E.P., Ruggaber, A., Swartz, W.H., Lloyd, S.A., Van Weele, M., 2004. Photolysis frequency of O_3 to $O(^1D)$: measurements and modeling during the international photolysis frequency measurement and modeling intercomparison (IPMMI). Journal of Geophysical Research A 109, D08S90.

Hofzumahaus, A., Rohrer, F., Lu, K.D., Bohn, B., Brauers, T., Chang, C.C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S.R., Shao, M., Zeng, L.M., Wahner, A., Zhang, Y.H., 2009. Amplified trace gas removal in the troposphere. Science 324, 1702–1704.

Holben, B.N., Tanré, D., Smirnov, A., Eck, T., Slutsker, I., Abuhassan, N., Newcomb, W.W., Schafer, J.S., Chatenet, B., Lavenu, F., Kaufman, Y.J., Vande Castle, J., Setzer, A., Markham, B., Clark, D., Frouin, R., Halthore, R., Karneli, A., O'Neill, N.T., Pietras, C., Pinker, R.T., Voss, K., Zibordi, G., 2001. An emerging ground-based aerosol climatology: aerosol optical depth from AERONET. Journal of Geophysical Research 106, 12067–12097.

Holland, F., Hofzumahaus, A., Schäfer, J., Kraus, A., Pätz, H.-W., 2003. Measurements of OH and HO_2 radical concentrations and photolysis frequencies during BERLIOZ. Journal of Geophysical Research 108, 8246.

Holler, H., Finke, U., Huntrieser, H., Hagen, M., Feigl, C., 1999. Lightning-produced NO_x (LINOX): experimental design and case study results. Journal of Geophysical Research 104, 13911–13922.

Holt, M.A., Hardaker, P.J., McLelland, G.P., 2001. A lightning climatology for Europe and the UK, 1990–99. Weather 56, 290–296.

Holzinger, R., Lee, A., Paw, K.T., Goldstein, A.H., 2005a. Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds. Atmospheric Chemistry and Physics 5, 67–75.

Holzinger, R., Williams, J., Salisbury, G., Klüpfel, T., de Reus, M., Traub, M., Crutzen, P.J., Lelieveld, J., 2005b. Oxygenated compounds in aged biomass burning plumes over the Eastern Mediterranean: evidence for strong secondary production of methanol and acetone. Atmospheric Chemistry and Physics 5, 39–46.

Honoré, C., Rouil, L., Vautard, R., Beekmann, M., Bessagnet, B., Dufour, A., Elichegaray, C., Flaud, J.-M., Malherbe, L., Meleux, F., Menut, L., Martin, D., Peuch, A., Peuch, V.-H., Poisson, N., 2007. Predictability of European air quality: the assessment of three years of operational forecasts and analyses. Journal of Geophysical Research 113, D04301.

Honrath, R.E., Owen, R.C., Val Martìn, M., Reid, J.S., Lapina, K., Fialho, P., Dziobak, M.P., Kleissl, J., Westphal, D.L., 2004. Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O_3 in the North Atlantic lower free troposphere. Journal of Geophysical Research 109, D24310.

Hoor, P., Borken-Kleefeld, J., Caro, D., Dessens, O., Endresen, O., Gauss, M., Grewe, V., Hauglustaine, D., Isaksen, I.S.A., Jockel, P., Lelieveld, J., Myhre, G., Meijer, E., Olivie, D., Prather, M., Poberaj, C.S., Shine, K.P., Staehelin, J., Tang, Q., van Aardenne, J., van Velthoven, P., Sausen, R., 2009. The impact of traffic emissions on atmospheric ozone and OH: results from QUANTIFY. Atmospheric Chemistry and Physics 9, 3113–3136.

Horowitz, L.W., Liang, J., Gardner, G.M., Jacob, D.J., 1998. Export of reactive nitrogen from North America during summertime: sensitivity to hydrocarbon chemistry. Journal of Geophysical Research 103, 13451–13476.

Horowitz, L.W., Fiore, A.M., Milly, G.P., Cohen, R.C., Perring, A., Wooldridge, P.J., Hess, P.G., Emmons, L.K., Lamarque, J.-F., 2007. Observational constraints on the chemistry of isoprene nitrates over the eastern United States. Journal of Geophysical Research 112, D12S08.

Hoshi, J.-y., Amanoa, S., Sasakia, Y., Korenaga, T., 2008. Investigation and estimation of emission sources of 54 volatile organic compounds in ambient air in Tokyo. Atmospheric Environment 42, 2383–2393.

Houghton, R.A., Skole, D.L., Nobre, C.A., Hackler, J.L., Lawrence, K.T., Chomentowski, W.H., 2000. Annual fluxes of carbon from deforestation and regrowth in the Brazilian Amazon. Nature 403, 301–304.

Houze, R.A., 2004. Mesoscale convective systems. Reviews of Geophysics 42, RG4003.

Hov, Ø., Hesstveldt, E., Isaksen, I.S.A., 1978. Long-range transport of tropospheric ozone. Nature 273, 341–344.

Hudman, R.C., Jacob, D.J., Cooper, O.R., Evans, M.J., Heald, C.L., Park, R.J., Fehsenfeld, F., Flocke, F., Holloway, J., Hübler, G., Kita, K., Koike, M., Kondo, Y., Neuman, A., Nowak, J., Oltmans, S., Parrish, D., Roberts, J.M., Ryerson, T., 2004. Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California. Journal of Geophysical Research 109, D23S10.

Hudson, R.D., Frolov, A.D., Andrade, M.F., Follette, M.B., 2003. The total ozone field separated into meteorological regimes. Part I: defining the regimes. Journal of Atmospheric Science 60, 1669–1677.

Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C., Vonmont, H., 2005. Chemical characterisation of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment 39, 637–651.

Huntrieser, H., Schlager, H., Feigl, C., Holler, H., 1998. Transport and production of NO_x in electrified thunderstorms: survey of previous studies and new observations at midlatitudes. Journal of Geophysical Research 103, 28247–28264.

Huntrieser, H., Feigl, C., Schlager, H., Schröder, F., Gerbig, C., van Velthoven, P., Flatoy, F., Théry, C., Petzold, A., Höller, H., Schumann, U., 2002. Airborne measurements of NO_x, tracer species, and small particles during the European lightning nitrogen oxides experiment. Journal of Geophysical Research 107, 4113.

Huntrieser, H., Schlager, H., Arnold, F., Forster, C., Junkermann, W., Stohl, A., 2005. CONTRACE – Convective transport of trace gases into the middle and upper troposphere over Europe: budget and impact on chemistry. AFO2000 Newsletter, GSF – Forschungszentrum für Umwelt und Gesundheit. GmbH, 3–6.

Hurley, M.D., Ball, J.C., Wallington, T.J., Toft, A., Nielsen, O.J., Bertman, S., Perkovic, M., 2007. Atmospheric chemistry of a model biodiesel fuel, $CH_3C(O)O(CH_2)(2)OC(O)CH_3$: kinetics, mechanisms, and products of Cl atom and OH radical initiated oxidation in the presence and absence of NO_x. Journal of Physics and Chemistry A 111, 2547–2554.

Hyer, E.J., Allen, D.J., Kasischke, E.S., 2007. Examining injection properties of boreal forest fires using surface and satellite measurements of CO transport. Journal of Geophysical Research 112, D18307.

Ichoku, C., Kaufman, Y.J., 2005. A method to derive smoke emission rates from MODIS fire radiative energy measurements. IEEE Transactions on Geoscience and Remote Sensing 43, 2636–2649.

IPCC, 1999. Aviation and the global atmosphere. In: Penner, J.E., Lister, D.H., Griggs, D.J., Dokken, D.J., McFarland, M. (Eds.), Intergovernmental Panel on Climate Change Report. Cambridge University Press, New York, pp. 29–64. Available at: http://www.grida.no/climate/ipcc/aviation/index.htm.

IPCC, 2007. The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, New York, USA. Available at: http://www.ipcc.ch.

Isaksen, I.S.A., Benestad, R., Berntsen, T.K., Bosquet, P., Collins, W., Cox, T., Dalsoren, S.B., Eyring, V., Fowler, D., Fuzzi, S., Gauss, M., Granier, C., Joeckel, P., Klimont, Z., Laj, P., Lohmann, U., Maione, M., Monks, P.S., Myhre, G., Prevot, A.S.H., Raes, F., Richter, A., Rognerud, B., Schulz, M., Shindell, D., Stevenson, D., Storelvmo, T., Wang, W.-C., van Weele, M., Wild, M., Wuebbles, D., 2009. Atmospheric Composition Change: Climate–Chemistry Interaction 43, 5138–5191.

Ito, A., Penner, J.E., 2004. Global estimates of biomass burning emissions based on satellite imagery for the year 2000. Journal of Geophysical Research 109, D14S05.

Ito, A., Sillman, S., Penner, J.E., 2007. Effects of additional nonmethane volatile organic compounds, organic nitrates, and direct emissions of oxygenated organic species on global tropospheric chemistry. Journal of Geophysical Research 112, D06309.

Jacob, D.J., Logan, J.A., Murti, P.P., 1999. Effect of rising Asian emissions on surface ozone in the United States. Geophysical Research Letters 26, 2175–2178.

Jacob, D.J., Field, B.D., Jin, E.M., Bey, I., Li, Q.B., Logan, J.A., Yantosca, R.M., Singh, H.B., 2002. Atmospheric budget of acetone. Journal of Geophysical Research-Atmospheres 107.

Jacob, D.J., Field, B.D., Li, Q.B., Blake, D.R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H.B., Guenther, A., 2005a. Global budget of methanol: constraints from atmospheric observations. Journal of Geophysical Research-Atmospheres 110.

Jacob, D.J., Field, B.D., Li, Q.B., Blake, D.R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H.B., Guenther, A., 2005b. Global budget of methanol: constraints from atmospheric observations. Journal of Geophysical Research 110, D08303.

Jacobson, M.Z., 2002. Atmospheric Pollution: History, Science and Regulation. Cambridge University Press.

Jaegle, L., 2007. Pumping up surface air. Science 315, 772–773.

Jaegle, L., Jacob, D.J., Brune, W.H., Wennberg, P.O., 2001. Chemistry of HO_x radicals in the upper troposphere. Atmospheric Environment 35, 469–489.

Jaegle, L., Martin, R.V., Chance, K., Steinberger, L., Kurosu, T.P., Jacob, D.J., Modi, A.I., Yoboue, V., Sigha-Nkamdjou, L., Galy-Lacaux, C., 2004. Satellite mapping of rain-induced nitric oxide emissions from soils. Journal of Geophysical Research-Atmospheres 109.

Jaenicke, R., 2005. Abundance of cellular material and proteins in the atmosphere. Science 308, 73.

Jaffe, D., Anderson, T., Covert, D., Kotchenruther, R., Trost, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D., Harris, J., Carmichael, G., Uno, I., 1999. Transport of Asian air pollution to north America. Geophysical Research Letters 26 (6), 711–714.

Jaffe, D., Price, H., Parrish, D., Goldstein, A., Harris, J., 2003. Increasing background ozone during spring on the west coast of North America. Geophysical Research Letters 30, 1613.

Jagiella, S., Zabel, F., 2007. Reaction of phenylperoxy radicals with NO_2 at 298 K. Physical Chemistry Chemical Physics 9, 5036–5051.

James, P., Stohl, A., Forster, C., Eckhardt, S., Seibert, P., Frank, A., 2003. A 15-year climatology of stratosphere-troposphere exchange with a Lagrangian particle dispersion model 2. Mean climate and seasonal variability. Journal of Geophysical Research 108, 8522.

Jang, M.S., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814–817.

Janssen, L.H.J.M., Visser, H., Romer, F.G., 1998. Analysis of large scale sulphate, nitrate, chloride and ammonium concentrations in The Netherlands using an aerosol measuring network. Atmospheric Environment 23, 2783–2796.

Jaoui, M., Leungsakul, S., Kamens, R.M., 2003. Gas and particle products distribution from the reaction of b-caryophyllene with O_3. Journal of Atmospheric Chemistry 45, 261–287.

Jaoui, M., Sexton, K.G., Kamens, R.M., 2004. Reaction of α-cedrene with ozone: mechanism, gas and particulate products distribution. Atmospheric Environment 38, 2709–2725.

Jaoui, M., Kamens, R.M., 2003. Gas and particulate products distribution from the photooxidation of a-humulene in the presence of NO_x, natural atmospheric air and sunlight. Journal of Atmospheric Chemistry 46, 29–54.

Jefferson, A., Tanner, D.J., Eisele, F.L., Davis, D.D., Chen, G., Crawford, J., Huey, J.W., Torres, A.L., Berresheim, H., 1998. OH Photochemistry and methane sulphonic acid formation in the coastal Antarctic boundary layer. Journal of Geophysical Research 103, 1647–1656.

Jenkin, M.E., 2004. Modelling the formation and composition of secondary organic aerosol from alpha and beta- pinene ozonolysis using MCM v3. Atmospheric Chemistry Physics 4, 1741.

Jenkin, M.E., 2008. Trends in ozone concentration distributions in the UK since 1990: local, regional and global influences. Atmospheric Environment 42, 5434–5445.

Jenkin, M.E., Clemitshaw, K.C., 2000. Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. Atmospheric Environment 34, 2499–2527.

Jenkin, M.E., Davies, T.J., Stedman, J.R., 2002. The origin and day-of-week dependence of photochemical ozone episodes in the UK. Atmospheric Environment 36, 999–1012.

Jenkin, M.E., Saunders, S.M., Wagner, V., Pilling, M.J., 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. Atmospheric Chemistry and Physics 3, 181–193.

Jenkin, M.E., Hurley, M.D., Wallington, T.J., 2007. Investigation of the radical product channel of the $CH_3C(O)O_2 + HO_2$ reaction in the gas phase. Physical Chemistry Chemical Physics 9, 3149–3162.

Jenkin, M.E., Utembe, S.R., Derwent, R.G., 2008. Modelling the impact of elevated primary NO_2 and HONO emissions on regional scale oxidant formation in the UK. Atmospheric Environment 42, 323–336.

Jenkins, G.S., Ryu, J.H., 2004a. Linking horizontal and vertical transports of biomass fire emissions to the tropical Atlantic ozone paradox during the Northern Hemisphere winter season: climatology. Atmospheric Chemistry and Physics 4, 449–469.

Jenkins, G.S., Ryu, J.H., 2004b. Space-borne observations link the tropical Atlantic ozone maximum and paradox to lightning. Atmospheric Chemistry and Physics 4, 361–375.

Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X., Smith, K.A., Morris, J.W., Davidovits, P., 2003. Ambient aerosol sampling using the Aerodyne aerosol mass spectrometer. Journal of Geophysical Research 108 (D7), 13–21. doi:10.1029/2001JD001213 2003. 8425.

Johnson, M.S., Feilberg, K.L., von Hessberg, P., Nielsen, O.J., 2002. Isotopic processes in atmospheric chemistry. Chemical Society Review 31, 313–323.

Johnson, D., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M., 2005. Simulating the formation of secondary organic aerosol from the photooxidation of aromatic hydrocarbons. Environmental Chemistry 2, 35–48.

Johnson, D., Marston, G., 2008. The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere. Chemical Society Reviews, 37, 699–716, doi: 10.1039/b704260b.

Johnson, W.B., Viezee, W., 1981. Stratospheric ozone in the lower troposphere, I, presentation and interpretation of aircraft measurements. Atmospheric Environment 15, 1309–1323.

Jonson, J.E., Simpson, D., Fagerli, H., Solberg, S., 2006. Can we explain the trends in European ozone levels? Atmospheric Chemistry and Physics 313, 51–66.

Jost, H.-J., Drdla, K., Stohl, A., Pfister, L., Loewenstein, M., 2004. In-situ observations of mid-latitude forest fire plumes deep in the stratosphere. Geophysical Research Letters 31, L11101.

Jung, J.G., Adams, P.J., Pandis, S., 2006. Simulating the size distribution and chemical composition of ultrafine particles during nucleation events. Atmospheric Environment 40, 2248–2259.

Junge, K., Swanson, B.D., 2008. High-resolution ice nucleation spectra of sea-ice bacteria: implications for cloud formation and life in frozen environments. Biogeosciences 5, 865–873.

Junker, C., Liousse, C., 2008. A global emission inventory of carbonaceous aerosol including fossil fuel and biofuel sources for the period 1860–1997. Atmospheric Chemistry and Physics 8, 1–13.

Kahn, R.A., Chen, Y., Nelson, D.L., Leung, F.-Y., Li, Q., Diner, D., Logan, J.A., 2008. Wildfire smoke injection heights: two perspectives from space. Geophysical Research Letters 35, L04809.

Kaiser, J., 2008. Reformulated ^{17}O correction of mass spectrometric stable isotope measurements in carbon dioxide and a critical appraisal of historic 'absolute' carbon and oxygen isotope ratios. Geochimica et Cosmochimica Acta 72, 1312–1334.

Kalabokas, P.D., Volz-Thomas, A., Brioude, J., Thouret, V., Cammas, J.-P., Repapis, C.C., 2007. Vertical ozone measurements in the troposphere over the Eastern Mediterranean and comparison with Central Europe. Atmospheric Chemistry and Physics 7, 3783–3790.

Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U., 2004. Identification of polymers as major components of atmospheric organic aerosols. Science 303, 1659–1662.

Kaleschke, L., Richter, A., Burrows, J., Afe, O., Heygster, G., Notholt, J., Rankin, A.M., Roscoe, H.K., Hollwedel, J., Wagner, T., Jacobi, H.-W., 2004. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. Geophysical Research Letters 31, L16114.

Kalivitis, N., Gerasopoulos, E., Vrekoussis, M., Kouvarakis, G., Kubilay, N., Hatzianastassiou, N., Vardavas, I., Mihalopoulos, N., 2007. Dust transport over the Eastern Mediterranean from TOMS, AERONET and surface measurements. Journal of Geophysical Research 112, D03202.

Kallos, G., Kotroni, V., Lagouvardos, K., Papadopoulos, A., 1998. On the long-range transport of air pollutants from Europe to Africa. Geophysical Research Letters 25, 619–622.

Kallos, G., Astitha, M., Katsafados, P., Spyrou, C., 2007. Long-range transport of anthropogenically and naturally produced particulate matter in the Mediterranean and North Atlantic: current state of knowledge. Journal of Applied Meteorology and Climatology 46, 1230–1251.

Kanakidou, M., Tsigaridis, K., Dentener, F.J., Crutzen, P., 2000. Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation. Journal of Geophysical Research 105, 9243–9254.

Kanakidou, M., Seinfeld, J.H., Pandis, S., Barnes, I., Dentener, F.J., Facchini, M.C., van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J.C., 2005. Organic aerosol and global climate modelling: a review. Atmosphere Chemistry Physics 5, 1053–1123.

Kanakidou, M., Mihalopoulos, N., Kalivitis, N., Tsigaridis, K., Kouvarakis, G., Koulouri, E., Gerasopoulos, E., Vrekoussis, M., Myriokefalitakis, S., 2007. Natural contributions to particulate matter levels over Europe - the experience from Greece. In: Proceedings of the 10th International Conference on Environmental Science and Technology, Kos Island, Greece 5–7 September 2007 CEST2007: A-585–592. Available at: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=9717.

Kanakidou, M., Tsigaridis, K., Myriokefalitakis, S., 2008. Global modeling of secondary organic aerosol (SOA) formation: knowledge and challenges. In: Barnes, I. (Ed.), Simulation and Assessment of Chemical Processes in a Multiphase Environment. Springer.

Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Kamazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., Kondo, Y., 2007a. Urban photochemistry in central Tokyo: 1. Observed and modelled OH and HO$_2$ radical concentrations during the winter and summer of 2004. Journal of Geophysical Research 112, D21312.

Kanaya, Y., Cao, R., Kato, S., Miyakawa, Y., Kajii, Y., Tanimoto, H., Yokouchi, Y., Mochida, M., Kawamura, K., Akimoto, H., 2007b. Chemistry of OH and HO$_2$ radicals observed at Rishiri Island, Japan, in September 2003: missing daytime sink of HO$_2$ and positive nighttime correlations with monoterpenes. Journal of Geophysical Research 112, D11308.

Kandler, K., Schutz, L., 2007. Climatology of the average water-soluble volume fraction of atmospheric aerosol. Atmospheric Research 83, 77–92.

Kar, J., Drummond, J.R., Jones, D.B.A., Liu, J., Nichitiu, F., Zou, J., Gille, J.C., Edwards, D.P., Deeter, M.N., 2006. Carbon monoxide (CO) maximum over the Zagros mountains in the Middle East: signature of mountain venting? Geophysical Research Letters 33, L15819.

Karl, T., Guenther, A., Yokelson, R.J., Greenberg, J., Potosnak, M., Blake, D.R., Artaxo, P., 2007. The tropical forest and fire emissions experiment: emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia. Journal of Geophysical Research 112, D18302.

Kasischke, E.S., Hyre, E.P., Novelli, P.C., Bruhwiler, L.P., French, N.H.F., Sukhinin, A., Hewson, J., Stocks, B.J., 2005. Influences of boreal fire emissions on Northern Hemisphere atmospheric carbon and carbon monoxide. Global Biogeochemical Cycles 19, GB1012.

Keating, T., Zuber, A., 2007. Hemispheric Transport of Air Pollution 2007. Air Pollution Studies No. 16, UNECE, Geneva.

Kerminen, V.-M., Pirjola, L., Kulmala, M., 2001. How significantly does coagulational scavenging limit atmospheric particle production? Journal of Geophysical Research 106, 24119–24126.

Kerminen, V.-M., Lihavainen, H., Komppula, M., Viisanen, Y., Kulmala, M., 2005. Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation. Geophysical Research Letters 32, L14803.

Kim, S.-W., Heckel, A., McKeen, S.A., Frost, G.J., Hsie, M.K., Trainer, M., Richter, A., Burrows, J., Peckham, S.E., Grell, G., 2006. Satellite-observed US power plant NO$_x$ emission reductions and their impact on air quality. Geophysical Research Letters 33, L22812.

Kirchstetter, T.W., Harley, R.A., Littlejohn, D., 1996. Measurement of nitrous acid in motor vehicle exhaust. Environmental Science and Technology 30, 2843–2849.

Kita, K., Kawakami, S., Miyazaki, Y., Higashi, Y., Kondo, Y., Nishi, N., Koike, M., Blake, D.R., Machida, T., Sano, T., Hu, W., Ko, M., Ogawa, T., 2002. Photochemical production of ozone in the upper troposphere in association with cumulus convection over Indonesia. Journal of Geophysical Research-Atmospheres 108.

Kittelson, D.B., Watts, W.F., Johnson, J.P., 2004. Nanoparticle emissions on Minnesota highways. Atmospheric Environment 38, 9–19.

Klaić, Z.B., Belušić, D., Bulić, I.H., Hrust, L., 2003. Mesoscale modeling of meteorological conditions in the lower troposphere during a winter stratospheric ozone intrusion over Zagreb, Croatia. Journal of Geophysical Research 108, 4720.

Kleeman, M.J., Ying, Q., Lu, J., Mysliwiec, M.J., Griffin, R.J., Chen, J., Clegg, S., 2007. Source apportionment of secondary organic aerosol during a severe photochemical smog episode. Atmospheric Environment 41, 576–591.

Kleffmann, J., 2007. Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer. Chemical Physics and Chemistry 8, 1137–1144.

Kleffmann, J., Gavriloaiei, T., Hofzumahaus, A., Holland, F., Koppmann, R., Rupp, L., Schlosser, E., Siese, M., Wahner, A., 2005. Daytime formation of nitrous acid: A major source of OH radicals in a forest. Geophysical Research Letters 32, L05818. doi:10.1029/2005GL022524.

Klimont, Z., Streets, D.G., 2007. Emissions inventories and projections for assessing hemispheric or intercontinental transport. In: Keating, T., Zuber, A. (Eds.), Hemispheric Transport of Air Pollution 2007. Atmospheric Pollution Studies No. 16, ECE/EB.AIR/94, United Nations, Geneva.

Kondo, Y., Koike, M., Kita, K., Ikeda, H., Takegawa, N., Kawakami, S., Blake, D., Liu, S.C., Ko, M., Miyazaki, Y., Irie, H., Higashi, Y., Liley, B., Nishi, N., Zhao, Y., Ogawa, T., 2002. Effects of biomass burning, lightning, and convection on O$_3$, CO, and NO$_y$ over the tropical Pacific and Australia in August–October 1998 and 1999. Journal of Geophysical Research-Atmospheres 108.

Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R.J., Jimenez, J.L., Zhang, Q., Worsnop, D.R., 2007. Oxygenated and water-soluble organic aerosols in Tokyo. Journal of Geophysical Research 112, D01203.

Konovalov, I.B., Beekmann, M., Richter, A., Burrows, J.P., 2006. Inverse modelling of the spatial distribution of NO$_x$ emissions on a continental scale using satellite data. Atmospheric Chemistry and Physics 6, 1747–1770.

Konovalov, I.B., Beekmann, M., Burrows, J.P., Richter, A., 2008. Satellite measurement based estimates of decadal changes in European nitrogen oxides emissions. Atmospheric Chemistry and Physics Discussions 8, 2013–2059.

Kormann, R., Fischer, H., de Reus, M., Lawrence, M., Brühl, Ch., von Kuhlmann, R., Holzinger, R., Williams, J., Lelieveld, J., Warneke, C., de Gouw, J., Heland, J., Ziereis, H., Schlager, H., 2003. Formaldehyde over the Eastern Mediterranean during MINOS: Comparison of airborne in-situ measurements with 3D-model results. Atmospheric Chemistry and Physics 3, 851–861.

Kossmann, M., Corsmeier, U., De Wekker, S., Fiedler, F., Vögtlin, R., Kalthoff, N., Güsten, H., Neininger, B., 1999. Observations of handover processes between the atmospheric boundary layer and the free troposphere over mountainous terrain. Contribution to Atmospheric Physics 72, 329–350.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., Mihalopoulos, N., 2008. Chemical Composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean. Atmospheric Environment, 42, 6542–6550, doi: 10.1016/J.ATMOSENV.2008.04.010

Kourtidis, K., Zerefos, C., Rapsomanikis, S., Simeonov, V., Balis, D., Perros, P.E., Thompson, A.M., Witte, J., Calpini, B., Sharobiem, W.M., Mihalopoulos, N., Drakou, R., 2002. Regional levels of ozone in the troposphere over eastern Mediterranean. Journal of Geophysical Research 107, 8140.

Kouvarakis, G., Tsigaridis, K., Kanakidou, M., Mihalopoulos, N., 2000. Temporal variations of surface regional background ozone over Crete Island in the southeast Mediterranean. Journal of Geophysical Research 105, 4399–4407.

Kouvarakis, G., Mihalopoulos, N., Tselepides, T., Stavrakakis, S., 2001. On the importance of atmospheric nitrogen inputs on the productivity of Eastern Mediterranean. Global Biogeochemical Cycles 15, 805–818.

Kouvarakis, G., Mihalopoulos, N., 2002. Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere. Atmospheric Environment 36, 929–938.

Kovacs, T.A., Brune, W.H., 2001. Total OH loss rate measurement. Journal of Atmospheric Chemistry 39, 105–122.

Koçak, M., Mihalopoulos, N., Kubilay, N., 2008. Contributions of natural sources to high PM$_{10}$ and PM$_{2.5}$ events in the eastern Mediterranean. Atmospheric Environment 41, 3806–3818.

Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., Seinfeld, J.H., 2005. Secondary organic aerosol formation from isoprene photooxidation under high-NO$_x$ conditions. Geophysical Research Letters 32, L18808.

Krupa, S.V., Manning, W.J., 1988. Atmospheric ozone: formation and effects on vegetation. Environmental Pollution 50, 101–137.

Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdekens, G., Fischer, H., Gurk, C., Klupfel, T., Konigstedt, R., Parchatka, U., Schiller, C.L., Stickler, A., Taraborrelli, D., Williams, J., Lelieveld, J., 2008. Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA. Atmospheric Chemistry and Physics Discussions 8, 15239–15289.

von Kuhlmann, R., Lawrence, M.G., Poschl, U., Crutzen, P.J., 2004. Sensitivities in global scale modeling of isoprene. Atmospheric Chemistry and Physics 4, 1–17.

Kuhn, U., Andreae, M.O., Ammann, C., Araujo, A.C., Brancaleoni, E., Ciccioli, P., Dindorf, T., Frattoni, M., Gatti, L.V., Ganzeveld, L., Kruijt, B., Lelieveld, J., Lloyd, J., Meixner, F.X., Nobre, A.D., Poschl, U., Spirig, C., Stefani, P., Thielmann, A., Valentini, R., Kesselmeier, J., 2007. Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget. Atmospheric Chemistry and Physics 7, 2855–2879.

Kulmala, M., 2003. How particles Nucleate and grow? Science 302, 1000–1001.

Kulmala, M., Pirjola, L., Mäkelä, J.M., 2000. Stable sulphate clusters as a source of new atmospheric particles. Nature 404, 66–69.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., McMurry, P.H., 2004. Formation and growth rates of ultrafine atmospheric particles: a review of observations. Journal of Aerosol Science 35, 143–176.

Kulmala, M., Lehtinen, K.E.J., Laaksonen, A., 2006a. Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration. Atmospheric Chemistry and Physics 6, 787–793.

Kulmala, M., Reissell, A., Sipila, M., Bonn, B., Ruuskanen, T.M., Lehtinen, K.E.J., Kerminen, V.M., Strom, J., 2006b. Deep convective clouds as aerosol production engines: role of insoluble organics. Journal of Geophysical Research-Atmospheres 111.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H.E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R.M., Hanson, I., Leung, C., Lehtinen, K.E.J., Kerminen, V.-M., 2007. Toward direct measurement of atmospheric nucleation. Science 318, 89–92.

Kulmala, M., Kerminen, V.-M., 2008. On the formation and growth of atmospheric nanoparticles. Atmospheric Research, 90, 132–150

Kulmala, M., Tammet, H., 2007. Finnish-Estonian air ion and aerosol workshops. Boreal Environment Research 12, 237–245.

Kunz, H., Speth, P., 1997. Variability of near-ground ozone concentrations during cold front passages – a possible effect of tropopause folding events. Journal of Atmospheric Chemistry 28, 77–95.

Kupiainen, K., Klimont, Z., 2007. Primary emissions of fine carbonaceous particles in Europe. Atmospheric Environment 41, 2156–2170.

Kurpius, M., Goldstein, A.H., 2003. Gas-phase chemistry dominates O$_3$ loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere. Geophysical Research Letters 30, 1371. doi:10.1029/2002GL016785.

Kurtenbach, R., Becker, K.H., Gomes, J.A.G., Kleffmann, J., Lorzer, J.C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., Platt, U., 2001. Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel. Atmospheric Environment 35, 3385–3394.

Kusaka, H., Kondo, H., Kikegawa, Y., Kimura, F., 2001. A simple single-layer urban canopy model for atmospheric models: comparison with multi-layer and SLAB models. Boundary Layer Meteorology 101, 329–358.

Kwok, E.S.C., Atkinson, R., Arey, J., 1995. Observation of hydroxycarbonyls from the OH radical-initiated reaction of isoprene. Environmental Science Technology 29, 2467–2469.

Laakso, L., Gagne, S., Petäjä, T., Hirsikko, A., Aalto, P.P., Kulmala, M., Kerminen, V.-M., 2007. Detecting charging state of ultrafine particles: instrumental development and ambient measurements. Atmospheric Chemistry and Physics 7, 1333–1345.

Laaksonen, A., Kulmala, M., O'Dowd, C.D., Joutsensaari, J., Vattovaara, P., Mikkonen, S., Lehtinen, K.E.J., Sogacheva, L.S., Dal Maso, M., Aalto, P., Petäjä, T., Sogachev, A., Yoon, Y.J., Lihavainen, H., Nilsson, D., Facchini, M.C., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J.D., Alfarra, M.R., Worsnop, D.R., Riekkola, M.-L., Hyötyläinen, T., Viisanen, Y., 2008. The role of VOC oxidation products in continental new particle formation. Atmospheric Chemistry and Physics 8, 2657–2665.

Labonne, M., Breon, F.-M., Chevallier, F., 2007. Injection height of biomass burning aerosols as seen from a spaceborne lidar. Geophysical Research Letters 34, L11806.

Ladstatter-Weissenmayer, A., Kanakidou, M., Meyer-Arnek, J., Dermitzaki, E.V., Richter, A., Vrekoussis, M., Wittrock, F., Burrows, J.P., 2007. Pollution events over the East Mediterranean: synergistic use of GOME, ground-based and sonde observations and models. Atmospheric Environment 41, 7262–7273.

Laj, P., Klausen, J., Bilde, M., Plaβ-Duelmer, C., Pappalardo, G., Clerbaux, C., Baltensperger, U., Hjorth, J., Simpson, D., Reimann, S., Coheur, P.-F., Richter, A., De Mazière, M., Rudich, Y., McFiggans, G., Torseth, K., Wiedensohler, A., Morin, S., Schulz, M., Allan, J., Attié, J.-L., Barnes, I., Birmilli, W., Cammas, P., Dommen, J., Dorn, H.-P., Fowler, D., Fuzzi, J.-S., Glasius, M., Granier, C., Hermann, M., Isaksen, I., Kinne, S., Koren, I., Madonna, F., Maione, M., Massling, A., Moehler, O., Mona, L., Monks, P.S., Müller, D., Müller, T., Orphal, J., Peuch, V.-H., Stratmann, F., Tanré, D., Tyndall, G., Riziq, A.A., Van Roozendael, M., Villani, P., Wehner, B., Wex, H., Zardini, A.A., 2009. Measuring Atmopsheric composition change 43, 5345–5406.

Lamb, B., Guenther, A., Gay, D., Westberg, H., 1987. A national inventory of biogenic hydrocarbon emissions. Atmospheric Environment 21, 1695–1705.

Lammel, G., Cape, J.N., 1996. Nitrous acid and nitrite in the atmosphere. Chemical Society Reviews 25, 361–369.

Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C., Prevot, A.S.H., 2007. Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra. Atmospheric Chemistry and Physics 7, 1503–1522.

Lathiere, J., Hauglustaine, D.A., De Noblet-Ducoudre, N., Krinner, G., Folberth, G.A., 2005. Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model. Geophysical Research Letters 32, L20818.

Lavoué, D., Liousse, C., Cachier, H., Stocks, B.J., Goldammer, J.G., 2000. Modelling of carbonaceous particles emitted by boreal and temperate wildfires at northern latitudes. Journal of Geophysical Research 105 26, 871–826, 890.

Lawrence, M.G., von Kuhlmann, R., Salzmann, M., Rasch, P.J., 2003. The balance of effects of deep convective mixing on tropospheric ozone. Geophysical Research Letters 30 (18), 1940. doi:10.1029/2003GL017644.

Lawrence, M.G., Butler, T.M., Steinkamp, J., Gurjar, B.R., Lelieveld, J., 2007. Regional pollution potentials of megacities and other major population centers. Atmospheric Chemistry and Physics 7, 3969–3987.

Lawrence, M.G., Rasch, P.J., 2005. Tracer transport in deep convective updrafts: plume ensemble versus bulk formulations. Journal of Atmospheric Science 62, 2880–2894.

Lawrence, M.G., Salzmann, M., 2008. On interpreting studies of tracer transport by deep cumulus convection and its effects on atmospheric chemistry. Atmospheric Chemistry and Physics 8, 6037–6050.

Lee, D.S., Dollard, G.J., Derwent, R.G., Pepler, S., 1999. Observations on gaseous and aerosols components of the atmosphere and their relationships. Water, Air, & Soil Pollution 113, 175–202.

Lee, S.H., Reeves, J.M., Wilson, J.C., Hunton, D.E., Viggiano, A.A., Miller, T.M., Ballenthin, J.O., Lait, L.R., 2003. Particle formation by ion nucleation in the upper troposphere and lower stratosphere. Science 301, 1886–1889.

Lee, C., Kim, Y.J., Tanimoto, H., Bobrowski, N., Platt, U., Mori, T., Yamamoto, K., Hong, C.S., 2005. High ClO and ozone depletion observed in the plume of Sakurajima volcano, Japan. Geophysical Research Letters 32, 21809.

Lee, A., Goldstein, A.H., Kroll, J.H., Ng, N.L., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., 2006a. Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes. Journal of Geophysical Research 111, D17305.

Lee, J.D., Lewis, A.C., Monks, P.S., Jacob, M., Hamilton, J.F., Hopkins, J.R., Watson, N.M., Saxton, J.E., Ennis, C., Carpenter, L.J., Carslaw, N., Fleming, Z., Bandy, B.J., Oram, D.E., Penkett, S.A., Slemr, J., Norton, E., Rickard, A.R., Whalley, L.K., Heard, D.E., Bloss, W.J., Gravestock, T., Smit, S.C., Stanton, J., Pilling, M.J., Jenkin, M.E., 2006b. Ozone photochemistry and elevated isoprene during the UK heatwave of August 2003. Atmospheric Environment 40, 7598–7613.

Legrand, M., Puxbaum, H., 2007. Summary of the CARBOSOL project: present and retrospective state of organic versus inorganic aerosol over Europe. Journal of Geophysical Research 112, D23S01.

Legreid, G., Reimann, S., Steinbacher, M., Staehelin, J., Young, D., Stemmler, K., 2007. Measurements of OVOCs and NMHCs in a swiss highway tunnel for estimation of road transport emissions. Environmental Science & Technology 41, 7060–7066.

Legreid, G., Reimann, S., Folini, D., Staehelin, J., Balzani, J., Steinbacher, M., Vollmer, K.M., 2008. Measurements of organic trace gases including OVOCs at the high alpine site Jungfraujoch (Switzerland): seasonal variation and source allocations. Journal of Geophysical Research 113, D05307.

Lelieveld, J., Crutzen, P.J., 1994. Role of deep cloud convection in the ozone budget of the troposphere. Science 264, 1759–1761.

Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P.J., Dentener, F.J., Fischer, H., Feichter, J., Flatau, P.J., Heland, J., Holzinger, R., Korrmann, R., Lawrence, M.G., Levin, Z., Markowicz, K.M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G.J., Scheeren, H.A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stephanou, E.G., Stier, P., Traub, M., Warneke, C., Williams, J., Ziereis, H., 2002. Global air pollution crossroads over the Mediterranean. Science 298, 794–799.

Lelieveld, J., van Aardenne, J., Fischer, H., de Reus, M., Williams, J., Winkler, P., 2004. Increasing ozone over the Atlantic ocean. Science 304, 1483–1487.

Lelieveld, J., Butler, T.M., Crowley, J.N., Dillon, T.J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.G., Martinez, M., Taraborrelli, D., Williams, J., 2008. Atmospheric oxidation capacity sustained by a tropical forest. Nature 452, 737–740.

Lemieux, P.M., Lutes, C.C., Santoianni, D.A., 2004. Emissions of organic air toxics from open burning: a comprehensive review. Progress in Energy and Combustion Science 30, 1–32.

Leung, F.-Y.T., Logan, J.A., Park, R., Hyer, E., Kasischke, E., Streets, D., Yuganov, L., 2007. Impacts of enhanced biomass burning in the boreal forests in 1998 on tropospheric chemistry and the sensitivity of model results to the injection height of emissions. Journal of Geophysical Research 112, D10313.

Lewis, A.C., Hopkins, J.R., Read, K.A., Carpenter, L.J., Pilling, M.J., Stanton, J., 2005. Sources and sinks of acetaldehyde, acetone and methanol in north Atlantic marine boundary layer air. Atmospheric Chemistry and Physics 5, 1963–1974.

Lewis, A.C., Evans, M.J., Methven, J., Watson, N.M., Lee, J.D., Hopkins, J.R., Purvis, R.M., Arnold, S.R., McQuaid, J.B., Whalley, L.K., Pilling, M.J., Heard, D.E., Monks, P.S., Parker, A.E., Reeves, C.E., Oram, D.E., Mills, G., Bandy, B.J., Stewart, D., Coe, H., Williams, P., Crosier, J., 2007. Chemical composition observed over the mid-Atlantic and the detection of pollution signatures far from source regions. Journal of Geophysical Research 112, D10S39.

Li, Q.B., Jacob, D.J., Bey, I., Palmer, P.I., Duncan, B.N., Field, B.D., Martin, R.V., Fiore, A.M., Yantosca, R.M., Parrish, D.D., Simmonds, P.G., Oltmans, S.J., 2002. Transatlantic transport of pollution and its effects on surface ozone in Europe and North America. Journal of Geophysical Research 107 (D13), 4166.

Li, S., Matthews, J., Sinha, A., 2008. Atmospheric hydroxyl radical production from electronically excited NO_2 and H_2O. Science 319, 1657–1660.

Li, S.P., Matthews, J., Sinha, A., 2009. Response to comment on "Atmospheric hydroxyl radical production from electronically excited NO_2 and H_2O" Science 324, 2.

Liang, J.Y., Horowitz, L.W., Jacob, D.J., Wang, Y.H., Fiore, A.M., Logan, J.A., Gardner, G.M., Munger, J.W., 1998. Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere. Journal of Geophysical Research 103, 13435–13450.

Liao, H., Seinfeld, J.H., 2005. Global impacts of gas-phase chemistry–aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone. Journal of Geophysical Research 110, 18208.

Liggio, J., Li, S.-M., Brook, J.R., Mihele, C., 2007. Direct polymerization of isoprene and α-pinene on acidic aerosols. Geophysical Research Letters 34, L05814.

Lihavainen, H., Kerminen, V.-M., Komppula, M., Hatakka, J., Aaltonen, V., Kulmala, M., Viisanen, Y., 2003. Production of "potential" cloud condensation nuclei associated with atmospheric new particle formation in northern Finland. Journal of Geophysical Research 108, 4782.

Lim, H.J., Carlton, A.G., Turpin, B.J., 2005. Isoprene forms secondary organic aerosol through cloud processing: model simulations. Environmental Science & Technology 39, 4441–4446.

Lim, Y.B., Ziemann, P.J., 2005. Products and mechanism of secondary organic aerosol formation form reactions of n-alkanes with OH radicals in the presence of NO_x. Environmental Science & Technology 39, 9229–9236.

Liousse, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., Cachier, H., 1996. A global three-dimensional model study of carbonaceous aerosols. Journal of Geophysical Research 101, 19411–19432.

Liousse, C., Andreae, M.O., Artaxo, P., Barbosa, P.M., Cachier, H., Gregoire, J.M., Hobbs, P.V., Lavoué, D., Mouillot, F., Penner, J., Scholes, R., Schultz, M.G., 2004. Deriving global quantitative estimates for spatial and temporal distributions of biomass burning emissions. In: Granier, C., Artaxo, P., Reeves, C.E. (Eds.), Emissions of Atmospheric Trace Compounds. Springer, New York, pp. 71–114.

Liousse, C., Brivio, P.A., Grégoire, J.M., Stroppiana, D., Zambiano, C., Guillaume, B., Granier, C., Mieville, A., 2008. How to Access Global and Regional Burnt Biomass from Satellite Observations to Derive gases and Particle Emission Inventories? IGAC Conference, Annecy, France. September 2008.

Liu, X.H., Hegg, D.A., Stoelinga, M.T., 2001. Numerical simulation of new particle formation over the northwest Atlantic using the MM5 mesoscale model coupled with sulfur chemistry. Journal of Geophysical Research 106, 9697–9715.

Liu, L., Andreani-Aksoyoglu, S., Keller, J., Ordonez, C., Junkermann, W., Hak, C., Braathen, G.O., Reimann, S., Astorga-Llorens, C., Schultz, M., Prevot, A.S.H., Isaksen, I.S.A., 2007. A photochemical modeling study of ozone and formaldehyde generation and budget in the Po basin. Journal of Geophysical Research 112, D22303.

Livesey, N.J., Fromm, M.D., Waters, J.W., Manney, G.L., Santee, M.L., Read, W.G., 2004. Enhancements in lower stratospheric CH_3CN observed by the upper atmosphere research satellite microwave limb Sounder following boreal forest fires. Journal of Geophysical Research 109, D06308.

Loeffler, K.W., Koehler, C.A., Paul, N.M., De Haan, D.O., 2006. Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions. Environmental Science & Technology 40, 6318–6323.

van Loon, M., Vautard, R., Schaap, M., Bergström, R., Bessagnet, B., Brandt, J., Builtjes, P.J.H., Christensen, J.H., Cuvelier, K., Graf, A., Jonson, J.E., Krol, M., Langner, J., Roberts, P., Rouil, L., Stern, R., Tarrasón, L., Thunis, P., Vignati, E., White, L., Wind, P., 2007. Evaluation of long-term ozone simulations from seven regional air quality models and their ensemble average. Atmospheric Environment 41, 2083–2097.

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.C., Fuchs, H., Häseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., Hofzumahaus, A., 2009. Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results. Atmospheric Chemistry and Physics Discussions 9, 17035–17072.

Lovejoy, E.R., Curtius, J., Froyd, K.D., 2004. Atmospheric ion-induced nucleation of sulfuric acid and water. Journal of Geophysical Research 109, D08204.

Lowe, D.C., Allan, W., Manning, M.R., Bromley, T., Brailsford, G., Ferretti, D., Gomez, A., Knobben, R., Martin, R., Mei, Z., Moss, R., Koshy, K., Maata, M., 1999. Shipboard determinations of the distribution of ^{13}C in atmospheric methane in the Pacific. Journal of Geophysical Research 104, 26125–126135.

Lugauer, M., Winkler, P., 2005. Thermal circulation in South Bavaria – climatology and synoptic aspects. Meteorologische Zeitschrift 14, 15–30.

Lyamani, H., Olmo, F.J., Alcantara, A., Alados-Arboledas, L., 2006. Atmospheric aerosols during the 2003 heat wave in southeastern Spain I: spectral optical depth. Atmospheric Environment 40, 6453–6464.

Ma, Y., Luciani, T., Porter, R.A., Russell, A.T., Johnson, D., Marston, G., 2007a. Organic acid formation in the gas-phase ozonolysis of alpha-pinene. Physical Chemistry Chemical Physics 9, 5084–5087.

Ma, Y., Willcox, T.R., Russell, A.T., Marston, G., 2007b. Pinic and pinonic acid formation in the reaction of ozone with alpha-pinene. Chemical Communications 13, 1328–1330.

Ma, Y., Russell, A.T., Marston, G., 2008. Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of a-pinene. Physical Chemistry Chemical Physics 10, 4294–4312.

MacKenzie, A.R., Harrison, R.M., Colbeck, I., Hewitt, N., 1991. The role of biogenic hydrocarbons in the production of ozone in urban plumes in Southeast England. Atmospheric Environment 25A, 351–359.

Mahowald, N., Kiehl, L., 2003. Mineral aerosols and cloud interactions. Geophysical Research Letters 30, 10.

Mahowald, N., Luo, C., 2003. A less dusty future? Geophysical Research Letters 301, 1903.

Mallet, V., Sportisse, B., 2006. Uncertainty in a chemistry-transport model due to physical parameterizations and numerical approximations: an ensemble approach applied to ozone modeling. Journal of Geophysical Research 111, D01302.

Mao, J., Ren, X., Brune, W.H., Olson, J.R., Crawford, J.H., Fried, A., Huey, L.G., Cohen, R.C., Heikes, B., Singh, H.B., Blake, D.R., Sachse, G.W., Diskin, G.S., Hall, S.R., Shetter, R.E., 2008. Airborne measurement of OH reactivity during INTEX-B. Atmospheric Chemistry and Physics 9, 163–173.

Marenco, A., Thouret, V., Nedelec, P., Smit, H., Helten, M., Kley, D., Karcher, F., Simon, P., Law, K., Pyle, J., Poschmann, G., Von Wrede, R., Hume, C., Cook, T., 1998. Measurement of ozone and water vapor by Airbus in-service aircraft: the MOZAIC airborne program, an overview. Journal of Geophysical Research 103, 25631–25642.

Mari, C., Saut, C., Jacob, D.J., Ravetta, F., Anderson, B., Avery, M.A., Blake, D.R., Brune, W.H., Faloona, I., Gregory, G.L., Heikes, B.G., Sachse, G.W., Sandholm, S.T., Singh, H.B., Talbot, R.W., Tan, D., Vay, S., 2003. Sources of upper tropospheric HO_x over the South Pacific Convergence Zone: a case study. Journal of Geophysical Research 107, 8229 [printed 108(D2), 2003].

Mari, C., Caillet, G., Corre, L., Saunois, M., Attié, J.L., Thouret, V., Stohl, A., 2007. Tracing biomass burning plumes from the Southern Hemisphere during the AMMA 2006 wet season experiment. Atmospheric Chemistry and Physics 8, 3951–3961.

Maria, S.F., Russell, L.M., Gilles, M.K., Myneni, S.C.B., 2004. Organic aerosol growth mechanism and their climate-forcing implications. Science 306, 1921–1924.

Maring, H., Savoie, D.L., Izaguirre, M.A., Custals, L., Reid, J.S., 2003. Vertical distributions of dust and sea-salt aerosols over Puerto Rico during PRIDE measured from a light aircraft. Journal of Geophysical Research 108, 8587.

Martilli, A., Clappier, A., Rotach, M.W., 2002. An urban surface exchange parameterization for mesoscale models. Boundary-Layer Meteorology 104, 261–304.

Martin, J.H., 1990. Glacial-interglacial CO_2 change: the iron hypothesis. Paleoceanography 5, 1–13.

Martin, R.V., Jacob, D.J., Logan, J.A., Bey, I., Yantosca, R.M., Staudt, A.C., Li, Q.B., Fiore, A.M., Duncan, B.N., Liu, H.Y., Ginoux, P., Thouret, V., 2002. Interpretation of TOMS observations of tropical tropospheric ozone with a global model and in situ observations. Journal of Geophysical Research 107 (D18), 4351.

Martin, R.V., Jacob, D.J., Yantosca, R.M., Chin, M., Ginoux, P., 2003. Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols. Journal of Geophysical Research 108, 4097.

Martin, R.V., Sioris, C.E., Chance, K., Ryerson, T.B., Bertram, T.H., Wooldridge, P.J., Cohen, R.C., Newuman, J.A., Swanson, A., Flocke, F.M., 2006. Evaluation of space-based constraints on global nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America. Journal of Geophysical Research 111, D15308.

Martinez, M., Harder, H., Kovacs, T.A., Simpas, J.B., Bassis, J., Lesher, R., Brune, W.H., Frost, G.J., Williams, E.J., Stroud, C.A., Jobson, B.T., Roberts, J.M., Hall, S.R., Shetter, R.E., Wert, B., Fried, A., Alicke, B., Stutz, J., Young, V.L., White, A.B., Zamora, R.J., 2003. OH and HO_2 concentrations, sources, and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999. Journal of Geophysical Research 108, 4617.

Martins, E.M., Arbilla, G., 2003. Computer modeling study of ethanol and aldheyde reactivities in Rio de Janeiro urban air. Atmospheric Environment 37, 1715–1722.

Mason, S.A., Field, R.J., Yokelson, R.J., Kochivar, M.A., Tinsley, M.R., Ward, D.E., Hao, W.M., 2001. Complex effects arising in smoke plume simulations due to include of direct emissions of oxygenated organic species from biomass combustion. Journal of Geophysical Research 106, 12527–512539.

Mason, S.A., Trentmann, J., Winterrath, T., Yokelson, R.J., Christain, T.J., Carlson, L.J., Warner, T.R., Wolfe, L.C., Andreae, M.O., 2006. Intercomparison of two box models of the chemical evolution in biomass burning plumes. Journal of Atmospheric Chemistry 55, 272–297.

Massling, A., Stock, M., Wiedensohler, A., 2005. Diurnal, weekly, and seasonal variation of hygroscopic properties of submicrometer urban aerosol particles. Atmospheric Environment 39, 3911–3922.

Massling, A., Leinert, S., Wiedensholer, A., Covert, D., 2007. Hygroscopic growth of sub-micrometer and one-micrometer aerosol particles measured during ACE-Asia. Atmospheric Chemistry and Physics 7, 3249–3259.

Masson, V., 2000. A Physically-based scheme for the urban energy budget in atmospheric models. Boundary Layer Meteorology 98, 357–397.

Masson, V., Gomes, L., Pigeon, G., Liousse, C., Lagouarde, J.-P., Voogt, J., Salmond, J., Oke, T., Legain, D., Garrouste, O., Lac, C., Connan, O., Briottet, X., 2008. The canopy and aerosol particles interactions in Toulouse urban layer (CAPITOUL) experiment. Meteorology and Atmospheric Physics, 102, 135–157, doi: 10.1007/s00703-008-0289-4.

Matson, M., Dozier, J., 1981. Identification of subresolution high temperature sources using a thermal IR sensor. Photogrammetric Engineering and Remote Sensing 47, 1311–1318.

Matsumi, Y., Comes, F.J., Hancock, G., Hofzumahaus, A., Hynes, A.J., Kawasaki, M., Ravishankara, A.R., 2002. Quantum yields for production of O(^{1}D) in the ultraviolet photolysis of ozone: recommendation based on evaluation of laboratory data. Journal of Geophysical Research 107 (D3), 4024.

Matthews, D.E., Hayes, J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. Analytical Chemistry 50, 1465–1473.

Mattis, I., Ansmann, A., Wandinger, U., Müller, D., 2003. Unexpectedly high aerosol load in the free troposphere over central Europe in spring/summer 2003. Geophysical Research Letters 30, 2178.

Mauersberger, K., Krankowsky, D., Janssen, C., 2003. Oxygen isotope processes and transfer reactions. Space Science Reviews 106, 265–279.

Mauldin, R.L.I., Kosciuch, E., Henry, B., Eisele, F.L., Shetter, R., Lefer, B., Chen, G., Davis, D., Huey, G., Tanner, D., 2004. Measurements of OH, $HO_2 + RO_2$, H_2SO_4 and MSA at the south Pole during ISCAT 2000. Atmospheric Environment 38, 5423–5437.

Mazzi, E.A., Dowlatabadi, H., 2007. Air quality impacts of climate mitigation: UK policy and passenger vehicle choice. Environmental Science Technology 41, 387–392.

Mazzoni, D., Logan, J.A., Diner, D., Kahn, R.A., Tong, L.-L., Li, Q.-B., 2007. A data-mining approach to associating MISR smoke plume heights with MODIS fire measurements. Remote Sensing of Environment 107, 138–148.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M.C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T.F., Murphy, D.M., O'Dowd, C.D., Snider, J.R., Weingartner, E., 2006. The effect of physical and chemical aerosol properties on warm cloud droplet activation. Atmospheric Chemistry and Physics 6, 2593–2649.

McKendry, I.G., Lundgren, J., 2000. Tropospheric layering of ozone in regions of urbanized complex and/or coastal terrain: a review. Progress in Physical Geography 24, 329–354.

Meehl, G.A., Tebaldi, C., 2004. More intense, more frequent, and longer lasting heat waves in the 21st century. Science 305, 994–997.

Meijer, H.A.J., Li, W.J., 1998. The use of electrolysis for accurate δ^{17}O and δ^{18}O isotope measurements in water. Isotopes in Environmental and Health Studies 349–369.

Meijer, E.W., van Velthoven, P.F.J., Brunner, D.W., Huntrieser, H., Kelder, H., 2001. Improvement and evaluation of the parameterisation of nitrogen oxide production by lightning. Physics and Chemistry of the Earth C 26, 557–583.

Meleux, F., Solmon, F., Giorgi, F., 2007. Increase in summer European ozone amounts due to climate change. Atmospheric Environment 41, 7577–7587.

Mentel, T.F., Bleilebens, D., Wahner, A., 1996. A study of nighttime nitrogen oxide oxidation in a large reaction chamber- the fate of NO_2, N_2O_5, HNO_3, and O_3 at different humidities. Atmospheric Environment 30, 4007–4020.

Merrill, J.T., Moody, J.L., 1996. Synoptic meterology and transport during the north atlantic regional experiment (NARE) intensive: overview. Journal of Geophysical Research 101, 19.

Mestayer, P.G., Durand, P., Augustin, P., Bastin, S., Bonnefond, J.-M., Bénech, B., Campistron, B., Copalle, A., Delbarre, A., Dousset, H., Drobinski, P., Druilhet, A., Fréjafon, E., Grimmond, S., Groleau, D., Irvine, M., Kergomard, C., Kermadi, S., Lagouarde, J.-P., Lemonsu, A., Lohou, F., Long, N., Masson, V., Moppert, C., Noilhan, J., Offerle, B., Oke, T., Pigeon, G., Puygrenier, V., Roberts, S., Rosant, J.-M., Said, F., Salmond, J., Talbaut, M., Voogt, J., 2005. The urban boundary layer field experiment over Marseille, UBL/CLU-ESCOMPTE: experimental set-up and first results. Boundary-Layer Meteorology 114, 315–365.

Methven, J., Arnold, S.R., Stohl, A., Evans, M.J., Avery, M., Law, K., Lewis, A.C., Monks, P.S., Parrish, D.D., Reeves, C.E., Schlager, H., Atlas, E., Blake, D.R., Coe, H., Crosier, J., Flocke, F.M., Holloway, J.S., Hopkins, J.R., McQuaid, J., Purvis, R., Rappenglück, B., Singh, H.B., Watson, N.M., Whalley, L.K., Williams, P.I., 2006. Establishing Lagrangian connections between observations within air masses crossing the atlantic during the international Consortium for atmospheric research on transport and transformation experiment. Journal of Geophysical Research 111, D23S62.

Metzger, A., Dommen, J., Gaeggeler, K., Duplissy, J., Prevot, A.S.H., Kleffmann, J., Elshorbany, Y., Wisthaler, A., Baltensperger, U., 2008. Evaluation of 1,3,5 trimethylbenzene degradation in the detailed tropospheric chemistry mechanism, MCMv3.1, using environmental chamber data. Atmospheric Chemistry and Physics 8, 6453–6468.

Metzger, S., Lelieveld, J., 2007. Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into fog, haze and clouds. Atmospheric Chemistry and Physics 7, 3163–3193.

Michel, C., Liousse, C., Grégoire, J.-M., Tansey, K., Carmichael, G.R., Woo, J.-H., 2005. Biomass burning emissions inventory from burnt area data given by SPOT-Vegetation satellite for TRACE-P and ACE-Asia case studies. Journal of Geophysical Research 110, D09304.

Mickley, L.J., Jacob, D.J., Field, B.D., Rind, D., 2004. Effects of future climate change on regional air pollution episodes in the United States. Geophysical Research Letters 31, L24103.

Mieville, A., Granier, C., Liousse, C., Guillaume, B., Mouillot, F., Lamarque, J.-F., Gregoire, J.-M., Petron, G. Emissions of gases and particles from biomass burning during the 20th century using satellite data and an historical reconstruction. Atmospheric Environment, submitted for publication.

Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., Bousquet, P., 1997. Tropospheric aerosol ionic composition above the eastern Mediterranean area. Tellus B 49, 314–326.

Mihalopoulos, N., Kerminen, V.M., Kanakidou, M., Berresheim, H., Sciare, J., 2007. Formation of particulate sulfur species (sulfate and methanesulfonate) during summer over the Eastern Mediterranean: a modelling approach. Atmospheric Environment 41, 6860–6871.

Millán, M. (Ed.), 2002. Ozone Dynamics in the Mediterranean Basin: A Collection of Scientific Papers Resulting from the MECAPIP, RECAPMA and SECAP Projects. Air Pollution Research Report 78. European Commission and CEAM, La ImprentaComunication Grafica, Spain.

Miller, C.A., Hidy, G., Hales, J., Kolb, C.E., Werner, A.S., Haneke, B., Parrish, D., Frey, H.C., Rojas-Bracho, L., 2006. Air emission inventories in north America: a critical assessment. Journal of the Air & Waste Management Association 56, 1115–1129.

Miller, R., Tegen, I., 1998. Climate response to soil dust aerosols. American Meteorological Society 11, 3247–3267.

Millet, D.B., Goldstein, A.H., Holzinger, R., Williams, B.J., Allan, J.D., Jimenez, J.L., Worsnop, D.R., Roberts, J.M., White, A.B., Hudman, R.C., Bertschi, I.T., Stohl, A., 2006. Chemical characteristics of north American surface layer outflow: insights from Chebogue point, Nova Scotia. Journal of Geophysical Research 111, D23S53.

Mills, N.L., Tornquist, H., Robinson, S.D., Gonzalez, M., Darnley, K., MacNee, W., Boon, N.A., Donaldson, K., Blomberg, A., Sandstrom, T., Newby, D.E., 2005. Diesel exhaust inhalation causes vascular dysfunction and impaired endogenous fibrinolysis. Circulation 112, 3930–3936.

Mitsakou, C., Kallos, G., Papantoniou, N., Spyrou, C., Solomos, S., Astitha, M., Housiadas, C., 2008. Saharan dust levels in Greece and received inhalation doses. Atmospheric Chemistry and Physics Discussions 8, 11967–11996.

Miyoshi, A., Hatakeyama, S., Washida, N., 1994. OH radical-initiated photooxidation of isoprene - an estimate of global CO production. Journal of Geophysical Research 99, 18779–18787.

Möhler, O., DeMott, P.J., Vali, G., Levin, Z., 2007. Microbiology and atmospheric processes: the role of biological particles in cloud physics. Biogeosciences 4, 1059–1071.

Molina, L.T., Kolb, C.E., de Foy, B., Lamb, B.K., Brune, W.H., Jimenez, J.L., Ramos-Villegas, R., Sarmiento, J., Paramo-Figueroa, V.H., Cardenas, B., Gutierrez-Avedoy, V., Molina, M.J., 2007. Air quality in North America's most populous city – overview of the MCMA-2003 campaign. Atmospheric Chemistry and Physics 7, 2447–2473.

Molina, L.T., Madronich, S., Gaffney, J.S., Singh, H.B., 2008. Overview of the MILAGRO/INTEX-B campaign. IGACtivities Newsletter 38, 2–15.

Molina, M.J., Molina, L.T., 2004. Megacities and atmospheric pollution. Journal of the Air & Waste Management Association 54, 644–680.

Monks, P.S., 2000. A review of the observations and origins of the spring ozone maximum. Atmospheric Environment 34, 3545–3561.

Monks, P.S., 2005. Gas-phase radical chemistry in the troposphere. Chemical Society Reviews 34, 376–395.

Monks, P.S., Carpenter, L.J., Penkett, S.A., Ayers, G.P., Gillett, R.W., Galbally, I.E., Meyer, C.P., 1998. Fundamental ozone photochemistry in the remote marine boundary layer: the SOAPEX experiment, measurement and theory. Atmospheric Environment 32, 3647–3664.

Morel, C., Senesi, S., 2002. A climatology of mesoscale convective systems over Europe using satellite infrared imagery. II: characteristics of European mesoscale convective systems. The Quarterly Journal of the Royal Meteorological Society 128, 1973–1995.

Morris, G.A., Hersey, S., Thompson, A.M., Pawson, S., Nielsen, J.E., Colarco, P.R., McMillan, W.W., Stohl, A., Turquety, S., Warner, J., Johnson, B.J., Kucsera, T.L., Larko, D.E., Oltmans, S.J., Witte, J.C., 2006. Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004. Journal of Geophysical Research 111, D24S03.

Morris, C.E., Sands, D.C., Bardin, M., Jaenicke, R., Vogel, B., Leyronas, C., Ariya, P.A., Psenner, R., 2008. Microbiology and atmospheric processes: an upcoming era of research on bio-meteorology. Biogeosciences Discussions 5, 191–212.

Moussiopoulos, N., 1995. The EUMAC Zooming Model, a tool for local-to-regional air quality studies. Meteorology and Atmospheric Physics 57, 115–133.

Mozurkewich, M., McMurry, P.H., Gupta, A., Calvert, J.G., 1987. Mass Accomodation coefficient for HO_2 radicals on aqueous particles. Journal of Geophysical Research 92, 4163–4170.

Müller, D., Mattis, I., Ansmann, A., Wandinger, U., Ritter, C., Kaiser, D., 2007. Multiwavelength Raman lidar observations of particle growth during long-range transport of forest-fire smoke in the free troposphere. Geophysical Research Letters 34, L05803.

Müller, J.F., Stavrakou, T., Wallens, S., De Smedt, I., van Roozendael, M., Potosnak, M.J., Rinne, J., Munger, B., Goldstein, A., Guenther, A.B., 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. Atmospheric Chemistry and Physics 8, 1329–1341.

Müller, J.-F., Stavrakou, T., 2005. Inversion of CO and NO_x emissions using the adjoint of the IMAGES model. Atmospheric Chemistry and Physics 5, 1157–1186.

Myhre, G., Govaerts, Y., Haywood, J.M., Bernsten, T.K., 2005. Radiative effect of surface albedo change from biomass burning. Geophysical Research Letters 32, L20812.

Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Brühl, C., Volkamer, R., Burrows, J.P., Kanakidou, M., 2008. The influence of natural and anthropogenic secondary sources on the glyoxal global distribution. Atmospheric Chemistry and Physics 8, 4965–4981.

Nagao, I., Matsumoto, K., Tanaka, H., 1999. Sunrise ozone destruction found in the sub-tropical marine boundary layer. Geophysical Research Letters 26, 3377–3380.

Naja, M., Akimoto, H., Staehelin, J., 2003. Ozone in background and photochemically aged air over central Europe: analysis of long-term ozonesonde data from Hohenpeissenberg and Payerne. Journal of Geophysical Research 108, 4063.

N.C.f.E. Assessment, 2007. Assessment of the Impacts of Global Change on Regional US Air Quality U.S. Environmental Protection Agency, Washington, D.C.

Ndour, M., D'Anna, B., George, C., Ka, O., Balkanski, Y., Kleffmann, J., Stemmler, K., Ammann, M., 2008. Photoenhanced uptake of NO_2 on mineral dust: laboratory experiments and model simulations. Geophysical Research Letters 35, 5.

Neu, J.L., Lawler, M.J., Prather, M.J., Saltzman, E.S., 2008. Oceanic alkyl nitrates as a natural source of tropospheric ozone. Geophysical Research Letters 35, L13814.

Newell, R.E., Wu, Z.X., Zhu, Y., Hu, W., Browell, E.V., Gregory, G.L., Sachse, G.W., Collins, J.E., Kelly, K.K., Liu, S.C., 1996. Vertical fine-scale atmospheric structure measured from NASA DC-8 during PEM-West A. Journal of Geophysical Research 101, 1943–1960.

Newell, R.E., Thouret, V., Cho, J.Y.N., Stoller, P., Marenco, A., Smit, H.G., 1999. Ubiquity of quasi-horizontal layers in the troposphere. Nature 398, 316–319.

Newell, R.E., Evans, M.J., 2000. Seasonal changes in pollutant transport to the North Pacific: the relative importance of Asian and European sources. Geophysical Research Letters 27, 4.

Ng, N.L., Chhabra, P.S., Chan, A.W.H., Surratt, J.D., Kroll, J.H., Kwan, A.J., McCabe, D.C., Wennberg, P.O., Sorooshian, A., Murphy, S.M., Dalleska, N.F., Flagan, R.C., Seinfeld, J.H., 2007a. Effect of NO_x level on sec-ondary organic aerosol (SOA) formation from the photooxidation of terpenes. Atmospheric Chemistry and Physics 7, 5159–5174.

Ng, N.L., Kroll, J.H., Chan, A.W.H., Chhabra, P.S., Flagan, R.C., Seinfeld, J.H., 2007b. Secondary organic aerosol formation from m-xylene, toluene, and benzene. Atmospheric Chemistry and Physics 7, 3909–3922.

Ng, N.L., Kwan, A.J., Surratt, J.D., Chan, A.W.H., Chhabra, P.S., Sorooshian, A., Pye, H.O.T., Crounse, J.D., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2008. Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3). Atmospheric Chemistry and Physics 8, 4117–4140.

Nickovic, S., Kallos, G., Papadopoulos, A., Kakaliagou, O., 2001. A model for prediction of desert dust cycle in the atmosphere. Journal of Geophysical Research 106, 18113–18130.

Nielsen, O.-K., Winther, M., Hjorth Mikkelsen, M., Hoffmann, L., Nielsen, M., Gyldenkærne, S., Frauser, P., Tranekjær Jensen, M., Plejdrup, M.S., Boll Illerup, J., 2008. Denmark's National Inventory Report 2008-Emission Inventories 1990–2006-Submitted under the United Nations Framework Convention on Climate Change. National Environmental Research Institute, University of Aarhus. NERI Technical Report no. 667. Available at: http://www.dmu.dk/Pub/FR667.pdf.

Niemi, J.V., Tervahattu, H., Vehkamäki, H., Martikainen, J., Laakso, L., Kulmala, M., Aarnio, P., Koskentalo, T., Sillanpää, M., Makkonen, U., 2005. Characterisation of aerosol particle episodes in Finland caused by wildfires in Eastern Europe. Atmospheric Chemistry and Physics 5, 2299–2310.

Niven, R.K., 2005. Ethanol in gasoline: environmental impacts and sustainability review article. Renewable & Sustainable Energy Reviews 9, 535–555.

Northway, M.J., de Gouw, J.A., Fahey, D.W., Gao, R.S., Warneke, C., Roberts, J.M., Flocke, F., 2004. Evaluation of the role of heterogeneous oxidation of alkenes in the detection of atmospheric acetaldehyde. Atmospheric Environment 38, 6017–6028.

O'Dowd, C.D., 2001. Biogenic coastal aerosol production and its influence on aerosol radiative properties. Journal of Geophysical Research 106, 1545–1549.

O'Dowd, C.D., Geever, M., Hill, M.K., Smith, M.H., Jennings, S.G., 1998. New particle formation: nucleation rates and spatial scales in the clean marine coastal environment. Geophysical Research Letters 25, 1661–1664.

O'Dowd, C.D., McFiggans, G., Greasey, D.J., Pirjola, L., Hoell, C., Smith, M.H., Allan, B.J., Plane, J.M.C., Heard, D.E., Lee, J.D., Pilling, M.J., Kulmala, M., 1999. On the photochemical production of new particles in the coastal boundary layer. Geophysical Research Letters 26, 1707–1710.

O'Dowd, C.D., Aalto, P., Hameri, K., Kulmala, M., Hoffmann, T., 2002. Aerosol formation – atmospheric particles from organic vapours. Nature 416, 497–498.

O'Dowd, C.D., Facchini, M.C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y.J., Putaud, J.P., 2004. Biogenically driven organic contribution to marine aerosol. Nature 431, 676–680.

O'Dowd, C.D., Yoon, Y.J., Junkerman, W., Aalto, P., Kulmala, M., Lihavainen, H., Viisanen, Y., 2007. Airborne measurements of nucleation mode particles I: coastal nucleation and growth rates. Atmospheric Chemistry and Physics 7, 1491–1501.

O'Dowd, C.D., Langmann, B., Varghese, S., Scannell, C., Cebernus, D., Facchini, M.C., 2008. A combined organic-inorganic sea-spray source function. Geophysical Research Letters 35, L01801.

O'Dowd, C.D., Yoon, Y.J., Junkermann, W., Aalto, P., Kulmala, M., Lihavainen, H., Viisanen, Y., 2009. Airborne measurements of nucleation mode particles II: boreal forest nucleation events. Atmospheric Chemistry and Physics 9, 937–944.

OECD, 2006. Competitive Cities in a Global Economy. OECD, ISBN 92-64-02709-2.

Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., Hayasaka, T., 2007. An Asian emission inventory of anthropogenic emission sources for the period 1980–2020. Atmospheric Chemistry and Physics 7, 4419–4444.

Olariu, R.I., Barnes, I., Becker, K.H., Klotz, B., Mocanu, R., 2002. FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, p-cresol. Atmospheric Environment 36, 3685–3697.

Olson, J.R., Crawford, J.H., Davis, D.D., Chen, G., Avery, M.A., Barrick, J.D.W., Sachse, G.W., Vay, S.A., Sandholm, S.T., Tan, D., Brune, W.H., Faloona, I.C., Heikes, B.G., Shetter, R.E., Lefer, B.L., Singh, H.B., Talbot, R.W., Blake, D.R., 2001. Seasonal differences in the photochemistry of the South Pacific: a comparison of observations and model results from PEM-tropics A and B. Journal of Geophysical Research 106, 32749–32766.

Oltmans, S.J., Lefohn, A.S., Harris, J.M., Galbally, I., Scheel, H.E., Bodeker, G., Brunke, E., Claude, H., Tarasick, D., Johnson, B.J., Simmonds, P., Shadwick, D., Anlauf, K., Hayden, K., Schmidlin, F., Fujimoto, T., Akagi, K., Meyer, C., Nichol, S., Davies, J., Redondas, A., Cuevas, E., 2006. Long term changes in tropospheric ozone. Atmospheric Environment 40, 3156–3173.

Ono, S., Wing, B., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. Geochimica et Cosmochimica Acta 70, 2238–2252.

Oppenheimer, C., Tsanev, V.I., Braban, C.F., Cox, R.A., Adams, J.W., Aiuppa, A., Bobrowski, N., Delmelle, P., Barclay, J., McGonigle, A.J., 2006. BrO formation in volcanic plumes. Geochimica et Cosmochimica Acta 70, 2935–2941.

Ordonez, C., Mathis, H., Furger, M., Henne, S., Huglin, C., Staehelin, J., Prevot, A.S.H., 2005. Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003. Atmospheric Chemistry and Physics 5, 1187–1203.

Orlando, J.J., Tyndall, G.S., 2001. The atmospheric chemistry of the HC(O)CO radical. International Journal of Chemical Kinetics 33, 149–156.

Ortega, J., Helmig, D., Guenther, A., Harley, P., Pressley, S., Vogel, C., 2007. Flux estimates and OH reaction potential of reactive biogenic volatile organic compounds (BVOCs) from a mixed northern hardwood forest. Atmospheric Environment 41, 5479–5495.

Ortega, J., Helmig, D., Daly, R.W., Tanner, D.M., Guenther, A.B., Herrick, J.D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – part B: applications. Chemosphere 72, 365–380.

Ortega, J., Helmig, D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – part A. Chemosphere 72, 343–364.

Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva, R., Bates, T.S., Coffman, D., Quinn, P.K., Dibb, J.E., Stark, H., Burkholder, J.B., Talukdar, R.K., Meagher, J., Fehsenfeld, F.C., Brown, S.S., 2008. High levels of nitryl chloride in the polluted subtropical marine boundary layer. Nature Geoscience 1, 324–328.

Owen, R.C., Cooper, O.R., Stohl, A., Honrath, R.E., 2006. An analysis of the mechanisms of North American pollutant transport to the central North Atlantic lower FT. Journal of Geophysical Research 111, D23S58.

Palmer, P.I., Jacob, D.J., Fiore, A.M., Martin, R.V., Chance, K., Kurosu, T.P., 2003. Mapping isoprene emissions over North America using formaldehyde column observations from space. Journal of Geophysical Research-Atmospheres 108 (D6), 4180. doi:10.1029/2002JD002153.

Papayannis, A., Balis, D., Amiridis, V., Chourdakis, G., Tsaknakis, G., Zerefos, C., Castanho, A.D.A., Nickovic, S., Kazadzis, S., Grabowski, J., 2005. Measurements of Saharan dust aerosols over the Eastern Mediterranean using elastic backscatter-Raman lidar, spectrophotometric and satellite observations in the frame of the EARLINET project. Atmospheric Chemistry and Physics 5, 2065–2079.

Papayannis, A., Amiridis, V., Mona, L., Tsaknakis, G., Balis, D., Bösenberg, J., Chaikovski, A., de Tomasi, F., Grigirov, I., Mattis, I., Mitev, V., Müller, D., Nickovic, S., Pérez, C., Peitruczuk, A., Pisani, G., Ravetta, F., Rizi, V., Sicard, M., Trickl, T., Wiegner, M., Gerding, M., Mamouri, R.E., D'Amico, G., Pappalardo, G., 2008. Systematic lidar observations of Saharan dust over Europe in the frame of EARLINET (2000–2002). Journal of Geophysical Research 113, D10204.

Park, R.J., Jacob, D.J., Palmer, P.I., Clarke, A.D., Weber, R.J., Zondlo, M.A., Eisele, F.L., Bandy, A.R., Thornton, D.C., Sachse, G.W., Bond, T.C., 2005. Export efficiency of black carbon aerosol in continental outflow: global implications. Journal of Geophysical Research 110, D11205.

Parrish, D., 2006a. Top-Down assessments of emission inventories. In: T.N.E.I.A. Team (Ed.), Improving Emission Inventories for Effective Air Quality Management Across North America – A NARSTO Assessment, pp. 197–219.

Parrish, D., 2006b. Critical evaluation of US on-road vehicle emission inventories. Atmospheric Environment 40, 2288–2300.

Parrish, D.D., Kondo, Y., Cooper, O.R., Brock, C.A., Jaffe, D.A., Trainer, M., Ogawa, T., Hübler, G., Fehsenfeld, F.C., 2004. Intercontinental transport and chemical transformation 2002 (ITCT 2K2) and pacific exploration of Asian continental emission (PEACE) experiments: an overview of the 2002 winter and spring intensives. Journal of Geophysical Research 109, D23S01.

Parrish, D.D., Stohl, A., Forster, C., Atlas, E.L., Blake, D.R., Goldan, P.D., Kuster, W.C., de Gouw, J.A., 2007. Effects of mixing on evolution of hydrocarbon ratios in the troposphere. Journal of Geophysical Research 112, D10S34.

Parrish, D.D., Millet, D.B., Goldstein, A.H., 2009. Increasing ozone concentrations in marine boundary layer air inflow at the west coasts of North America and Europe. Atmospheric Chemistry and Physics 9, 1303–1323.

Patchen, A.K., Pennino, M.J., Kiep, A.C., Elrod, M.J., 2007. Direct kinetics study of the product-forming channels of the reaction of isoprene-derived hydroxyperoxy radicals with NO. International Journal of Chemical Kinetics 39, 353–361.

Pathak, R.K., Presto, A.A., Lane, T.E., Stanier, C.O., Donahue, N.M., SPandis., N., 2007. Ozonolysis of alpha-pinene: parameterization of secondary organic aerosol mass fraction. Atmospheric Chemistry and Physics 7, 3811–3821.

Pathak, R.K., Donahue, N.M., Pandis, S.N., 2008. Ozonolysis of b-pinene: temperature dependence of secondary organic aerosol mass fraction. Environmental Science & Technology 42, 5081–5086.

Peeters, J., Vereecken, L., Fantechi, G., 2001. The detailed mechanism of the OH-initiated atmospheric oxidation of α-pinene: a theoretical study. Physical Chemistry Chemical Physics 3, 5489–5504.

Peeters, J., Nguyen, T.L., Vereecken, L., 2009. HO_x radical regneration in the oxidation of isoprene. Physical Chemistry Chemical Physics 11, 5935–5939.

Penkett, S.A., Burgess, R.A., Coe, H., Coll, I., Hov, O., Lindskog, A., Schmidbauer, N., Solberg, S., Roemer, M., Thijsse, T., Beck, J., Reeves, C.E., 2007. Evidence for large average concentrations of the nitrate radical (NO_3) in Western Europe from the HANSA hydrocarbon database. Atmospheric Environment 41, 3465–3478.

Penner, J.E., 1995. Carbonaceous aerosols influencing atmospheric radiation: black and organic carbon. In: Charlson, R.J., Heintzenberg, J. (Eds.), Aerosol Forcing of Climate. Wiley and Sons, Chichester, pp. 91–108.

Penner, J.E., Andreae, M.O., Annegam, H., Barrie, J., Feichter, J., Hegg, D., Jayaraman, A., Leaitch, R., Murphy, D., Nganga, J., Pitari, G., 2001. Aerosols, their direct and indirect effects. In: Houghton, J.T., et al. (Eds.), Climate Change 2001: The Scientific Basis. Cambridge University Press, Cambridge, p. 881.

Pérez, N., Pey, J., Querol, X., Alastuey, A., Lopez, J.M., Viana, M., 2008. Partitioning of major and trace components in PM_{10}–$PM_{2.5}$–PM_1 at an urban site in Southern Europe. Atmospheric Environment 42, 1677–1691.

Peters, C., Pechtl, S., Stutz, J., Hebestreit, K., Hönninger, G., Heumann, K.G., Schwarz, A., Winterlik, J., Platt, U., 2005. Reactive and organic halogen species in three different European coastal environments. Atmospheric Chemistry and Physics 5, 3357–3375.

Petters, M.D., Kreidenweis, M., 2007. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. Atmospheric Chemistry and Physics 7, 1961–1971.

Petzold, A., Weinzierl, B., Huntrieser, H., Stohl, A., Real, E., Cozic, J., Fiebig, M., Hendricks, J., Lauer, A., Law, K., Roiger, A., Schlager, H., Weingartner, E., 2007. Perturbation of the European FT aerosol by North American forest fire plumes during the ICARTT-ITOP experiment in summer 2004. Atmospheric Chemistry and Physics 7, 5105–5127.

Pfister, G.G., Emmons, L.K., Hess, P.G., Honrath, R., Lamarque, J.-F., Val Martin, M., Owen, R.C., Avery, M.A., Browell, E.V., Holloway, J.S., Nedelec, P., Purvis, R., Ryerson, T.B., Sachse, G.W., Schlager, H., 2006. Ozone production from the 2004 North American boreal fires. Journal of Geophysical Research 111, D24S07.

Pfister, G.G., Emmons, L.K., Hess, P.G., Lamarque, J.-F., Orlando, J.J., Walters, S., Guenther, A., Palmer, P.I., Lawrence, P.J., 2008. Contribution of isoprene to chemical budgets: a model tracer study with the NCAR CTM MOZART-4. Journal of Geophysical Research 113, D02204.

Pierce, T., Waldruff, P., 1991. PC-BEIS: a personal computer version of the biogenic emissions inventory system. Journal of the Air & Waste Management Association 41, 937–941.

Pilinis, C., Pandis, S.N., Seinfeld, J.H., 1995. Sensitivity of direct climate forcing by atmospheric aerosols to aerosol-size and composition. Journal of Geophysical Research 100, 18739–18754.

Pinho, P.G., Pio, C.A., Jenkin, M.E., 2005. Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data. Atmospheric Environment 39, 1303–1322.

Pinho, P.G., Pio, C.A., Carter, W.P.L., Jenkin, M.E., 2006. Evaluation of alkene degradation in the detailed tropospheric chemistry mechanism, MCM v3, using environmental chamber data. Journal of Atmospheric Chemistry 55, 55–79.

Pinho, P.G., Pio, C.A., Carter, W.P.L., Jenkin, M.E., 2007. Evaluation of a- and b-pinene degradation in the detailed tropospheric chemistry mechanism, MCM v3.1, using environmental chamber data. Journal of Atmospheric Chemistry 57, 171–202.

Platt, U., LeBras, G., Poulet, G., Burrows, J.P., Moortgat, G., 1990. Peroxy radicals from night-time reaction of NO_3 with organic compounds. Nature 348, 147–149.

Platt, U., Allan, W., Lowe, D., 2004. Hemispheric average Cl atom concentration from $^{13}C/^{12}C$ ratios in atmospheric methane. Atmospheric Chemistry and Physics 4, 2393–2399.

Platt, U., Hönninger, G., 2003. The role of halogen species in the troposphere. Chemosphere 52, 325–338.

Pochanart, P., Akimoto, H., Kajii, Y., Potemkin, V.M., Khodzher, T.V., 2003. Regional background ozone and carbon monoxide variations in remote Siberia/East Asia. Journal of Geophysical Research 108 (D1), 4028.

Pope, C.A., Burnett, R., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, Cardiopulmonary mortality and long-term exposure to fine particulate air pollution. Journal of the American Medical Association 287, 1132–1141.

Poppe, D., Zimmermann, J., Bauer, R., Brauers, T., Brüning, D., Callies, J., Dorn, H.-P., Hofzumahaus, A., Johnen, F.-J., Khedim, A., Koch, H., Koppmann, R., London, H., Müller, K.-P., Neuroth, R., Plass-Dülmer, C., Platt, U., Rohrer, F., Röth, E.-P., Rudolph, J., Schmidt, U., Wallasch, M., Ehhalt, D.H., 1994. Comparison of measured OH concentrations with model calculations. Journal of Geophysical Research 99, 16633–16642.

Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angewandte Chemie – International Edition 44, 7520–7540.

Pöschl, U., Williams, J., Hoor, P., Fischer, H., Crutzen, P.J., Warneke, C., Holzinger, R., Hansel, A., Jordan, A., Lindinger, W., Scheeren, H.A., Peters, W., Lelieveld, J., 2001. High acetone concentrations throughout the 0–12 km altitude range over the tropical rainforest in Surinam. Journal of Atmospheric Chemistry 38, 115–132.

Pöschl, U., Rudich, Y., Ammann, M., 2007. Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions – part 1: general equations, parameters, and terminology. Atmospheric Chemistry and Physics 7, 5989–6023.

Presto, A.A., Hartz, K.E.H., Donahue, N.M., 2005. Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NO_x concentration. Environmental Science & Technology 39, 7046–7054.

Price, C., Asfur, M., 2006. Can lightning observations be used as an indicator of upper-tropospheric water vapor variability? Bulletin of the American Meteorological Society 87, 291–298.

Price, C., Rind, D., 1992. A simple lightning parameterization for calculating global lightning distributions. Journal of Geophysical Research 97, 9919–9933.

Prospero, J.M., 1999. Long-term measurements of the transport of African mineral dust to the southeastern United States: implications for regional air quality. Journal of Geophysical Research 104 (D13), 15917–15,927.

Prospero, J.M., Ginoux, P., Torres, O., Nicholson, S.E., Gill, T.E., 2002. Environmental characterization of global sources of atmospheric soil dust identified with the NIMBUS 7 total ozone mapping spectrometer (TOMS) absorbing aerosol product. Reviews of Geophysics 40, 1002.

Prospero, J.M., Lamb, P.J., 2003. African droughts and dust transport to the Caribbean: climate change implications. Science 302 1,024–021,027.

Purvis, R.M., Lewis, A.C., Carney, R.A., McQuaid, J.B., Arnold, S.R., Methven, J., Barjat, H., Dewey, K., Kent, J., Monks, P.S., Carpenter, L.J., Brough, N., Penkett, S.A., Reeves, C.E., 2003. Rapid uplift of nonmethane hydrocarbons in a cold front over central Europe. Journal of Geophysical Research 108, 4224.

Putaud, J.-P., Raes, F., van Dingenen, Baltensperger, J.P.U., Brüggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.C., Hüglin, C.R., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K., Wehner, B., Wiedensohler, A., 2004. A European aerosol phenomenology. 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579–2595.

Querol, X., Alastuey, A., Moreno, T., Viana, M.M., Castillo, S., Pey, J., Rodriguez, S., Artinano, B., Salvador, P., Sanchez, M., Dos Santos, S.G., Garraleta, M.D.H., Fernandez-Patier, R., Moreno-Grau, S., Negral, L., Minguillon, M.C., Monfort, E., Sanz, M.J., Palomo-Marin, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., de la Campa, A.S., 2008. Spatial and temporal variations in airborne particulate matter (PM_{10} and $PM_{2.5}$) across Spain 1999–2005. Atmospheric Environment 42, 3964–3979.

Quinn, P.K., Shaw, G., Andrews, E., Dutton, E.G., Ruoho-Airola, T., Gong, S.L., 2007. Arctic haze: current trends and knowledge gaps. Tellus 59B, 99–114.

Raes, F., Van Dingenen, R., Vignati, E., Wilson, J., Putaud, J.P., Seinfeld, J.H., Adams, P., 2000. Formation and cycling of aerosols in the global troposphere. Atmospheric Environment 34, 4215–4240.

Raes, F., Seinfeld, J.H. New directions: climate change and air pollution abatement: A bumpy road. Atmospheric Environment, in press, doi:10.1016/j.atmosenv.2009.06.001.

Ramanathan, V., Li, F., Ramana, M.V., Praveen, P.S., Kim, D., Corrigan, C.E., Nguyen, H., Stone, E.A., Schauer, J.J., Carmichael, G.R., Adhikary, B., Yoon, S.C., 2007. Atmospheric brown clouds: Hemispherical and regional variations in long-range transport, absorption, and radiative forcing. Journal of Geophysical Research 112, D22S21, doi:10.1029/2006JD008124.

Raper, J.L., Kleb, M.M., Jacob, D.J., Davis, D.D., Newell, R.E., Fuelberg, H.E., Bendura, R.J., Hoell, J.M., McNeal, R.J., 2001. Pacific exploratory mission in the tropical pacific: PEM-Tropics B, March-April 1999. Journal of Geophysical Research-Atmospheres 106, 32401–32425.

Ravetta, F., Ancellet, G., Colette, A., Schlager, H., 2007. Long-range transport and tropospheric ozone variability in the western Mediterranean region during the Intercontinental Transport of Ozone and Precursors (ITOP-2004) campaign. Journal of Geophysical Research 112, D10S46.

Read, K.A., Mahajan, A.S., Carpenter, L.J., Evans, M.J., Faria, B.V.E., Heard, D.E., Hopkins, J.R., Lee, J.D., Moller, S.J., Lewis, A.C., Mendes, L., McQuaid, J.B., Oetjen, H., Saiz-Lopez, A., Pilling, M.J., Plane, J.M.C., 2008. Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. Nature 453, 1232–1235.

Real, E., Law, K.S., Weinzierl, B., Fiebig, M., Petzold, A., Wild, O., Methven, J., Arnold, S., Stohl, A., Huntrierser, H., Roiger, A., Schlager, H., Stewart, D., Avery, M., Sachse, G., Browell, E., Ferrare, R., Blake, D., 2007. Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic. Journal of Geophysical Research 112, D10S41.

Reeves, C.E., Slemr, J., Oram, D.E., Worton, D., Penkett, S.A., Stewart, D.J., Purvis, R., Watson, N., Hopkins, J., Lewis, A., Methven, J., Blake, D.R., Atlas, E., 2007. Alkyl nitrates in outflow from north America over the north atlantic during intercontinental transport of ozone and precursors 2004. Journal of Geophysical Research 112, D10S37.

Reich, P.B., Amundson, R.G., 1985. Ambient levels of ozone reduce net photosynthesis in tree and crop species. Science 230, 566–570.

Reid, J.S., Kinney, J.E., Westphal, D.L., Holben, B., Welton, E.J., Tsay, S., Eleutero, D.P., Campbell, J.R., Christopher, S.A., Colarco, P.R., Jonsson, H.H., Livingston, J.M., Maring, H.B., Meier, M.L., Pilewskie, P., Prospero, J.M., Reid, E.A., Remer, L.A., Russell, P.B., Savoie, D.L., Smirnov, A., Tanré, D., 2003. Analysis of measurements of Saharan dust by airborne and ground-based remote sensing methods during the Puerto Rico Dust Experiment (PRIDE). Journal of Geophysical Research 108 (D19), 8586.

Reisen, F., Aschmann, S.M., Atkinson, R., Arey, J., 2005. 1,4-hydroxycarbonyl products of the OH radical initiated reactions of C_5–C_8 n-alkanes in the presence of NO. Environmental Science & Technology 39, 4447–4453.

Ren, X., Harder, H., Martinez, M., Lesher, R.L., Oliger, A., Simpas, J.B., Brune, W.H., Schwab, J.J., Demerjian, K.L., He, Y., Zhou, X., Gao, H., 2003. OH and HO_2 chemistry in urban atmosphere of new York city. Atmospheric Environment 37, 3639–3651.

Ren, X., Brune, W.H., Oliger, A., Metcalf, A.R., Simpas, J.B., Shirley, T., Schwab, J.J., Bai, C., Roychowdhury, U., Li, Y., Cai, C., Demerjian, K.L., He, Y., Zhou, X., Gao, H., Hou, J., 2006a. OH, HO_2, and OH reactivity during the PTMACS-NY Whiteface Mountain 2002 campaign: observations and model comparisons. Journal of Geophysical Research 111, D10S03.

Ren, X., Brune, W.H., Mao, J., Mitchell, M.J., Lesher, R.L., Simpas, J.B., Metcalf, A., Schwab, J.J., Cai, C., Li, Y., Demerjian, K.L., Felton, H.D., Boynton, G., Adams, A., Perry, J., He, Y., Zhou, X., Hou, J., 2006b. Behavior of OH and HO_2 in the winter atmosphere in new York city. Atmospheric Environment 40, S252–S263.

Ren, X., Olson, J.R., Crawford, J.H., Brune, W.H., Mao, J., Long, R.B., Chen, G., Avery, M.A., Sachse, G.W., Barrick, J.D., Diskin, G.S., Huey, L.G., Fried, A., Cohen, R.C., Heikes, B., Wennberg, P., Singh, H.B., Blake, D.R., Shetter, R.E., 2008. HO_x chemistry during INTEX-A 2004: observation, model calculation, and comparison with previous studies. Journal of Geophysical Research 113, D05310.

Reneau, S.L., Katzman, D., Kuyumjian, G.A., Lavine, A., Malmon, D., 2007. Sediment delivery after a wildfire. Geological Society of America 2, 151–154.

Richter, A., Burrows, J.P., Nuss, H., Granier, C., Niemeier, U., 2005. Increase in tropospheric nitrogen dioxide over China observed from space. Nature 437, 129–132.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., Lehtinen, K.E.J., 2007. Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Hyytiälä and Heidelberg. Atmospheric Chemistry and Physics 7, 1899–1914.

Rinaldi, M., Facchini, M.C., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Ehn, M., Kulmala, M., de Leeuw, G., O'Dowd, C.D., 2008. Coastal and open ocean aerosol characteristics: investigating the representativeness of coastal aerosol sampling over the North-East Atlantic Ocean. Atmospheric Chemistry and Physics Discussions 8, 19035–19062.

Rind, D., Lerner, J., McLinden, C., 2001. Changes of tracer distribution in the doubled CO_2 climate. Journal of Geophysical Research 106, 28061.

Roberts, J.M., Osthoff, H.D., Brown, S.S., Ravishankara, A.R., 2008. N_2O_5 Oxidizes chloride to Cl_2 in acidic atmospheric aerosol. Science 321, 1059.

Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E., Pierce, J.R., Pandis, S.N., 2007. Rethinking organic aerosols: semivolatile emissions and photochemical aging. Science 315, 1259–1262.

Rockmann, T., Brenninkmeijer, C.A.M., Wollenhaupt, M., Crowley, J.N., Crutzen, P.J., 2000. Measurement of the isotopic fractionation of (NNO)-N-15-N-14-O-16, (NNO)-N-14-N-15-O-16 and (NNO)-N-14-N-14-O-18 in the UV photolysis of nitrous oxide. Geophysical Research Letters 27, 1399–1402.

Rodríguez, S., Querol, X., Alastuey, A., Viana, M.M., Alarcón, M., 2004. Comparative PM10-PM2.5 source contribution study at rural, urban and industrial sites during PM episodes in Eastern Spain. Science of Total Environment 328, 95–113.

Roelofs, G.J., 2008. A GCM study of organic matter in marine aerosol and its potential contribution to cloud drop activation. Atmospheric Chemistry and Physics 8, 709–719.

Rohrer, F., Berresheim, H., 2006. Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. Nature 442, 184–187.

Rohrer, F., Bohn, B., Brauers, T., Bruning, D., Johnen, F.J., Wahner, A., Kleffmann, J., 2005. Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR. Atmospheric Chemistry and Physics 5, 2189–2201.

van Roozendael, M., Wagner, T., Richter, A., Pundt, I., Arlander, D.W., Burrows, J.P., Chipperfield, M., Fayt, C., Johnston, P.V., Lambert, J.-C., Kreher, K., Pfeilsticker, K., Platt, U., Pommereau, J.-P., Sinnhuber, B.-M., Tørnkvist, K.K., Wittrock, F., 2002. Intercomparision of BrO measurements from ERS-2 GOME, ground-based and balloon platforms. Advances in Space Research 29, 1661–1666.

Rosenfeld, D., Rudich, Y., Lahav, R., 2001. Desert dust suppressing precipitation: a possible desertification feedback loop. Proceedings of the National Academy of Sciences 98, 5975–5980.

Rotach, M.W., Vogt, R., Bernhofer, D., Batchvarova, E., Christen, A., Clappier, A., Fedderson, B., Grynning, S.-E., Martucci, G., Mayer, H., Mitev, V., Oke, T.R., Parlow, E., Richner, H., Roth, M., Roulet, Y.A., Ruffieux, D., Salmond, J., Schatzmann, M., Voogt, J., 2005. BUBBLE – an urban boundary layer meteorology project. Theoretical and Applied Climatology 81, 231–261.

Rotach, M.W., Zardi, D., 2007. On the boundary-layer structure over highly complex terrain: key findings from MAP. The Quarterly Journal of the Royal Meteorological Society 133, 937–948.

Roy, D.P., Boschetti, L., Justice, C.O., Ju, J., 2008. The collection 5 MODIS burned area product - Global evaluation by comparison with the MODIS active fire product. Remote Sensing of Environment 112, 3690–3707.

Royal Society, 2008. Ground-Level Ozone in the 21st Century: Future Trends, Impacts and Policy Implications: Science Policy Report 15/08. The Royal Society, London.

Rudich, Y., 2003. Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles. Chemical Reviews 103, 5097–5124.

Rudich, Y., 2007. Aging of organic aerosol: bridging the gap between laboratory and field studies. Annual Review of Physical Chemistry 58, 321–523.

Rudolph, J., 2007. Gas chromatography–isotope ratio mass spectrometry. In: Koppmann, R. (Ed.), Volatile Organic Compounds in the Atmosphere. Blackwell Publishing, Oxford, pp. 388–466.

Russell, L.M., 2003. Aerosol organic-mass to organic-carbon ratio measurements. Environmental Science & Technology 37, 2982–2987.

Russo, R.S., Talbot, R.W., Dibb, J.E., Scheuer, E., Seid, G., Jordan, C.E., Fuelberg, H.E., Sachse, G.W., Avery, M.A., Vay, S.A., Blake, D.R., Blake, N.J., Atlas, E., Fried, A., Sandholm, S.T., Tan, D., Singh, H.B., Snow, J., Heikes, B.G., 2003. Chemical composition of Asian continental outflow over the western pacific: results from transport and chemical evolution over the pacific (TRACE-P). Journal of Geophysical Research 108, 8804.

Sadanaga, Y., Yoshino, A., Watanabe, K., Yoshioka, A., Wakazono, Y., Kanaya, Y., Kajii, Y., 2004. Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique. Review of Scientific Instruments 75, 2648–2655.

Saeger, M., Langstaff, J., Waiters, R., Modica, L., Zimmerman, D., Fratt, D., Dulleba, D., Ryan, R., Demmy, J., Tax, W., Sprague, D., Mudgett, D., Werner, A.S., 1989. The 1985 NAPAP Emissions Inventory (Version 2): Development of the Annual Data and Modelers' Tapes. Technical Report EPA-600/7-89-012a. U.S. Environmental Protection Agency, Washington, D.C.

Saiz-Lopez, A., Plane, J.M.C.P., McFiggans, G., Williams, P.I., Ball, S.M., Bitter, M., Jones, R.L., Hongwei, C., Hoffmann, T., 2006a. Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation. Atmospheric Chemistry and Physics 6, 883–895.

Saiz-Lopez, A., Shillito, J.A., Coe, H., Plane, J.M.C., 2006b. Measurements and modelling of I_2, IO, OIO, BrO and NO_3 in the mid-latitude marine boundary layer. Atmospheric Chemistry and Physics 6, 1513–1528.

Saiz-Lopez, A., Chance, K., Liu, X., Kurosu, T.P., Sander, S.P., 2007a. First observations of iodine oxide from space. Geophysical Research Letters 34, L12812.

Saiz-Lopez, A., Mahajan, A.S., Salmon, R.A., Bauguitte, S.J.-B., Jones, A.E., Roscoe, H.K., Plane, J.M.C., 2007b. Boundary layer halogens in coastal Antarctica. Science 317, 348–351.

Saiz-Lopez, A., Plane, J.M.C., 2004. Novel iodine chemistry in the marine boundary layer. Geophysical Research Letters 31 L04112.

Saliba, N.A., Kouyoumdjian, H., Roumie, M., 2007. Effect of local and long-range transport emissions on the elemental composition of $PM_{10-2.5}$ and $PM_{2.5}$ in Beirut. Atmospheric Environment 41, 6497–6509.

Salisbury, G., Rickard, A.R., Monks, P.S., Allan, B.J., Bauguitte, S., Penkett, S.A., Carslaw, N., Lewis, A.C., Creasey, D.J., Heard, D.E., Jacobs, P.J., Lee, J.D., 2001. Production of peroxy radicals at night via reactions of ozone and the nitrate radical in the marine boundary layer. Journal of Geophysical Research 106, 12669–12687.

Salisbury, G., Williams, J., Holzinger, R., Gros, V., Mihalopoulos, N., Vrekoussis, M., Sarda-Est'eve, R., Berresheim, H., vonKuhlmann, R., Lawrence, M., Lelieveld, J., 2003. Ground-based PTR-MS measurements of reactive organic compounds during the MINOS campaign in Crete, July–August 2001. Atmospheric Chemistry and Physics Discussions 3, 925–940.

Sanderson, M.G., Jones, C.D., Collins, W.J., Johnson, C.E., Derwent, R.G., 2003. Effect of climate change on isoprene emissions and surface ozone levels. Geophysical Research Letters 30, 1936.

Saunders, S.M., Jenkin, M.E., Derwent, R.G., Pilling, M.J., 2003. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. Atmospheric Chemistry and Physics 3, 161–180.

Sauvage, B., Thouret, V., Cammas, J.P., Gheusi, F., Athier, G., Nedelec, P., 2005. Tropospheric ozone over Equatorial Africa: regional aspects from the MOZAIC data. Atmospheric Chemistry and Physics 5, 311–335.

Sauvage, B., Thouret, V., Thompson, A.M., Witte, J.C., Cammas, J.P., Nedelec, P., Athier, G., 2006. Enhanced view of the "tropical Atlantic ozone paradox" and "zonal wave one" from the in situ MOZAIC and SHADOZ data. Journal of Geophysical Research 111, D01301.

Sauvage, B., Gheusi, F., Thouret, V., Cammas, J.P., Duron, J., Escobar, J., Mari, C., Mascart, P., Pont, V., 2007a. Medium-range mid-tropospheric transport of ozone and precursors over Africa: two numerical case studies in dry and wet seasons. Atmospheric Chemistry and Physics 7, 5357–5370.

Sauvage, B., Martin, R.V., van Donkelaar, A., Liu, X., Chance, K., Jaegle, L., Palmer, P.I., Wu, S., Fu, T.M., 2007b. Remote sensed and in situ constraints on processes affecting tropical tropospheric ozone. Atmospheric Chemistry and Physics 7, 815–838.

Sauvage, B., Martin, R.V., van Donkelaar, A., Ziemke, J.R., 2007c. Quantification of the factors controlling tropical tropospheric ozone and the South Atlantic maximum. Journal of Geophysical Research 112, D11309.

Sauvage, B., Thouret, V., Cammas, J.P., Brioude, J., Nedelec, P., Mari, C., 2007d. Meridional ozone gradients in the African upper troposphere. Geophysical Research Letters 34, L03817.

Saylor, R., 1997. An estimate of the potential significance of heterogenous loss to aerosols as an additional sindk for hydroperoxy radicals in the troposphere. Atmospheric Environment 31, 3653–3658.

Schade, G.W., Goldstein, A.H., 2006. Seasonal measurements of acetone and methanol: abundances and implications for atmospheric budgets. Global Biogeochemical Cycles 20, GB1011.

Schär, C., Vidal, P.L., Lüthi, D., Frei, C., Häberli, C., Liniger, M.A., Appenzeller, C., 2004. The role of increasing temperature variability in European summer heatwaves. Nature 427, 332–336.

Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2002. Source reconciliation of atmospheric gas-phase and particlephase pollutants during a severe photochemical smog episode. Environmental Science & Technology 36, 3806–3814.

Schichtel, B.A., Malm, W.C., Bench, G., Fallon, S., McDade, C.E., Chow, J.C., Watson, J.G., 2008. Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States. Journal of Geophysical Research 113, D02311.

Schinke, R., Grebenshchikov, S.Y., Ivanov, M.V., Fleurat-Lessard, P., 2006. Dynamical studies of the ozone isotope effect: a status report. Annual Review of Physical Chemistry 57, 625–661.

Schlager, H., Huntrieser, H., Heland, J., Ziereis, H., 2003. Analysis of convective and long-range transport of reactive nitrogen species over Europe using aircraft observations. In: Penkett, S.A., Law, K.S., Platt, U., Volz-Thomas, A. (Eds.), EXPORT-E2: European Export of Particulates and Ozone by Long-range Transport. International Scientific Secretariat (ISS), GSF – National Research Center for Environment and Health, Munich, pp. 151–155.

Schönhardt, A., Richter, A., Wittrock, F., Kirk, H., Oetjen, H., Roscoe, H.K., Burrows, J.P., 2008. Observations of iodine monoxide columns from satellite. Atmospheric Chemistry and Physics 8, 637–653.

Schroeder, W.H., Anlauf, K.G., Barrie, L.A., Lu, J.Y., Steffen, A., Schneeberger, D.R., Berg, T., 1998. Arctic springtime depletion of mercury. Nature 394, 331–332.

Schultz, M.G., Brasseur, G.P., Granier, C., 2002. The global tropospheric ozone budget - Review and outlook. In: Midgley, P.M., Reuther, M. (Eds.), EUROTRAC-2 Proceedings: Transport and Chemical Transformation in the Troposphere. Margraf Verlag, Weikersheim, Germany, pp. 133–138.

Schultz, M.G., Heil, A., Hoelzemann, J.J., Spessa, A., Thonicke, K., Goldammer, J., Held, A.C., Pereira, J.M., 2008. Global emissions from Wildland fires from 1960 to 2000. Global Biogeochemical Cycles 22, GB2002.

Schumann, U., Huntrieser, H., 2007. The global lightning-induced nitrogen oxides source. Atmospheric Chemistry and Physics Discussions 7, 2623–2818.

Seco, R., Penuelas, J., Filella, I., 2007. Short-chain oxygenated VOCs: emission and uptake by plants and atmospheric sources, sinks, and concentrations. Atmospheric Environment 41, 2477–2499.

Seiler, W., Crutzen, P.J., 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. Climatic Change 2, 207–248.

Sellegri, K., Loon, Y.J., Jennings, S.G., O'Dowd, C.D., Pirjola, L., Cautenet, S., Chen, H.W., Hoffmann, T., 2005. Quantification of coastal new ultra-fine particles formation from in situ and chamber measurements during the BIOFLUX campaign. Environmental Chemistry 2, 260–270.

Sellegri, K., Villani, P., Picard, D., Dupuy, R., O'Dowd, C., Laj, P., 2008. Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties. Atmospheric Research 90, 272–277, doi: 10.1019/j.atmosres.2008.04.004.

Sharma, S., Andrews, E., Barrie, L.A., Ogren, J.A., Lavoue, D., 2006. Variations and sources of the equivalent black carbon in the high Arctic revealed by long-term observations at Alert and Barrow: 1989–2003. Journal of Geophysical Research 111, D14208.

Shim, C., Wang, Y., Choi, Y., Palmer, P., Abbot, D., Chance, K., 2005. Constraining global isoprene emissions with global ozone monitoring experiment (GOME) formaldehyde column measurements. Journal of Geophysical Research 110, D24301.

Shim, C.S., Wang, Y.H., Singh, H.B., Blake, D.R., Guenther, A.B., 2007. Source characteristics of oxygenated volatile organic compounds and hydrogen cyanide. Journal of Geophysical Research 112, D10305.

Shirley, T.R., Brune, W.H., Ren, X., Mao, J., Lesher, R., Cardenas, B., Volkamer, R., Molina, L.T., Molina, M.J., Lamb, B., Velasco, E., Jobson, T., Alexander, M., 2006. Atmospheric oxidation in the Mexico city Metropolian Aerea (MCMA) during April 2003. Atmospheric Chemistry and Physics 6, 2753–2765.

Simmonds, P.G., Derwent, R.G., Manning, A.L., Spain, G., 2004. Significant growth in surface ozone at Mace Head, Ireland, 1987–2003. Atmospheric Environment 38, 4769–4778.

Simpson, D., 1995. Biogenic emissions in Europe 2. Implications for ozone control strategies. Journal of Geophysical Research 100, 22891–22906.

Simpson, D., Yttri, K., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencs'er, A., Pio, C., Legrand, M., 2007a. Modeling carbonaceous aerosol over Europe. Analysis of the CARBOSOL and EMEP EC/OC campaigns. Journal of Geophysical Research 112, D23S14. doi: 10.1029/2006JD008158.

Simpson, W.R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L.J., Frieß, U., Goodsite, M.E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, A., Wolff, E., 2007b. Halogens and their role in polar boundary-layer ozone depletion. Atmospheric Chemistry and Physics 7, 4375–4418.

Singh, H.B., Kanakidou, M., Crutzen, P.J., Jacob, D.J., 1995. High-Concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere. Nature 378, 50–54.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., Snow, J., 2001. Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds. Nature 410, 1078–1081.

Singh, H.B., Anderson, B.E., Avery, M.A., Viezee, W., Chen, Y., Tabazadeh, A., Hamill, P., Pueschel, R., Fuelberg, H.E., Hannan, J.R., 2002. Global distribution and sources of volatile and nonvoloatile aerosol in the remote troposphere. Journal of Geophysical Research 107 (D11), 4121.

Singh, H.B., Salas, L.J., Chatfield, R.B., Czech, E., Fried, A., Walega, J., Evans, M.J., Field, B.D., Jacob, D.J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J.H., Avery, M.A., Sandholm, S., Fuelberg, H., 2004. Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. Journal of Geophysical Research 109, D15S07.

Sinha, V., Williams, J., Crowley, J.N., Levlieveld, J., 2008. The Comparative Reactivity Method - a new tool to measure total OH Reactivity in ambient air. Atmospheric Chemistry and Physics 8, 2213–2227.

Sitch, S., Cox, P.M., Collins, W.J., Huntingford, C., 2007. Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. Nature 448, 791–U794.

Sjögren, S., Gysel, M., Weingartner, E., Alfarra, M.R., Duplissy, J., Cozic, J., Crosier, J., Coe, H., Baltensperger, U., 2008. Hygroscopicity of the submicrometer aerosol at the high-alpine site Jungfraujoch, 3580 m a.s.l., Switzerland. Atmospheric Chemistry and Physics 8, 5715–5729.

Sjostedt, S.J., Huey, L.G., Tanner, D.J., Peischl, J., Chen, G., Dibb, J.E., Lefer, B., Hutterli, M.A., Beyersdorf, A.J., Blake, N.J., Sueper, D., Ryerson, T., Burkhardt, J., Stohl, A., 2007. Observations of hydroxyl and the sum of peroxy radicals at Summit, Greenland during summer 2003. Atmospheric Environment 41, 5122–5137.

Slemr, J., Junkermann, W., VolzThomas, A., 1996. Temporal variations in formaldehyde, acetaldehyde and acetone and budget of formaldehyde at a rural site in southern Germany. Atmospheric Environment 30, 3667–3676.

Sokhi, R. (Ed.), 2008. World Atlas of Atmospheric Pollution. Anthem Press, London, UK.

Solberg, S., 2006. VOC measurements 2004. EMEP/CCC Report 8/2006. Available at: http://www.nilu.no/projects/ccc/reports/cccr8-2006.doc.

Solberg, S., Dye, C., Schmidbauer, N., Herzog, A., Gehrig, R., 1996. Carbonyls and nonmethane hydrocarbons at rural European sites from the Mediterranean to the Arctic. Journal of Atmospheric Chemistry 25, 33–66.

Sommariva, R., Haggerstone, A.L., Carpenter, L.J., Carslaw, N., Creasey, D.J., Heard, D.E., Lee, J.D., Lewis, A.C., Pilling, M.J., Zador, J., 2004. OH and HO_2 chemistry in clean marine air during SOAPEX-2. Atmospheric Chemistry and Physics 4, 839–856.

Sommariva, R., Bloss, W.J., Brough, N., Carslaw, N., Flynn, M., Haggerstone, A.-L., Heard, D.E., Hopkins J.RLee, J.D., Lewis, A.C., McFiggans, G., Monks, P.S., Penkett, S.A., Pilling, M.J., Plane, J.M.C., Read, K.A., Saiz-Lopez, A., Rickard, A.R., Williams, P.I., 2006. OH and HO_2 chemistry during NAMBLEX: roles of oxygenates, halogen oxides and heterogeneous uptake. Atmospheric Chemistry and Physics 6, 1135–1153.

Song, C., Na, K., Cocker Jr., D.R., 2005. Impact of hydrocarbon to NO_x ratio on secondary organic aerosol formation. Environmental Science & Technology 39, 3143–3149.

Sorooshian, A., Lu, M.-L., Brechtel, F.J., Jonsson, H., Feingold, G., Flagan, R.C., Seinfeld, J.H., 2007. On the Source of organic acid aerosol layer above clouds. Environmental Science & Technology 41, 4647–4654.

Sotiropoulou, R.E.P., Tagaris, E., Pilinis, C., Anttilla, T., Kulmala, M., 2006. Modeling new particle formation during air pollution episodes: impacts on aerosol and cloud condensation nuclei. Aerosol Science and Technology 40, 557–572.

Spichtinger, N., Damoah, R., Eckhartdt, S., Forster, C., James, P., Beirlie, S., Marbach, T., Wagner, T., Novelli, P.C., Stohl, A., 2004. Boreal forest fires in 1997 and 1998: a seasonal comparison using transport model simulations and measurement data. Atmospheric Chemistry and Physics 4, 1857–1868.

Spittler, M., Barnes, I., Becker, K.H., Wallington, T.J., 2000. Product study of the $C_2H_5O_2 + HO_2$ reaction in 760 Torr of air at 284–312 K. Chemical Physics Letters 321, 57–61.

Spracklen, D.V., Carslaw, K.S., Kulmala, M., Kerminen, V.M., Mann, G.W., Sihto, S.-L., 2006. The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales. Atmospheric Chemistry and Physics 6, 5631–5648.

Spracklen, D.V., Carslaw, K.S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G.W., Chipperfield, M.P., Wiedensohler, A., Birmili, W., Lihavainen, H., 2008. Contribution of particle formation to global cloud condensation nuclei concentrations. Geophysical Research Letters 35, L06808.

Sprengnether, M., Demerjian, K.L., Donahue, N.M., Anderson, J.G., 2002. Product analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO. Journal of Geophysical Research 107, 4268.

Staudt, A.C., Jacob, D.J., Logan, J.A., Bachiochi, D., Krishnamurti, T.N., Sachse, G.W., 2001. Continental sources, transoceanic transport, and interhemispheric exchange of carbon monoxide over the Pacific. Journal of Geophysical Research 106, 32571–32589.

Stedman, J.R., 2004. The predicted number of air pollution related deaths in the UK during the August 2003 heatwave. Atmospheric Environment 3, 1087–1090.

Steffen, A., Douglas, T., Amyot, M., Ariya, P., Aspmo, K., Berg, T., Bottenheim, J., Brooks, S., Cobbett, F., Dastoor, A., Dommergue, A., Ebinghaus, R., Ferrari, C., Gardfeldt, K., Goodsite, M.E., Lean, D., Poulain, A.J., Scherz, C., Skov, H., Sommar, J., Temme, C., 2007. A synthesis of atmospheric mercury depletion even chemistry linking atmosphere, snow and water. Atmospheric Chemistry and Physics 8, 1445–1482.

Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Curci, G., 2009. Intra- and Inter-annual variability VOC emissions from natural and semi-natural vegetation for Europe and neighbouring countries. Atmospheric Environment, 43, 1380–1391.

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., George, C., 2006. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. Nature 440, 195–198.

Stern, A.C. (Ed.), 1968. Air Pollution, second ed. Academic Press, New York.

Stern, D.I., 2005. Global sulphur emissions from 1850 to 2000. Chemosphere 58, 163–175.

Stewart, J.Q., Whiteman, C.D., Steenburgh, W.J., Bian, X.D., 2002. A climatological study of thermally driven wind systems of the US Intermountain West. Bulletin of the American Meteorological Society 83, 699–708.

Stewart, H.E., Hewitt, C.N., Bunce, R.G.H., Steinbrecher, R., Smiatec, G., Schoenemeyer, T., 2003. A highly spatially and temporally resolved inventory for biogenic isoprene and monoterpene emissions: model description and application to Great Britain. Journal of Geophysical Research 108 (D20), 4644.

Stewart, D.J., Taylor, C.M., Reeves, C.E., McQuaid, J.B., 2008. Biogenic nitrogen oxide emissions from soils: impact on NO_x and ozone over west Africa during AMMA (African Monsoon Multidisciplinary Analysis: observational study). Atmospheric Chemistry and Physics 8, 2285–2297.

Stickler, A., Fischer, H., Williams, J., de Reus, M., Sander, R., Lawrence, M.G., Crowley, J.N., Lelieveld, J., 2006. Influence of summertime deep convection on formaldehyde in the middle and upper troposphere over Europe. Journal of Geophysical Research 111, D14308.

Stohl, A., 2006. Characteristics of atmospheric transport into the Arctic troposphere. Journal of Geophysical Research 111, D11306.

Stohl, A., Spichtinger-Rakowsky, N., Bonasoni, P., Feldmann, H., Memmesheimer, M., Scheel, H.E., Trickl, T., Hübener, S.H., 2000. The influence of stratospheric intrusions on alpine ozone concentrations. Atmospheric Environment 34, 1323–1354.

Stohl, A., Eckhardt, S., Forster, C., James, P., Spichtinger, N., 2002. On the pathways and timescales of intercontinental air pollution transport. Journal of Geophysical Research 107 (D23), 4684.

Stohl, A., Bonasoni, P., Cristofanelli, P., Collins, W.J., Feichter, J., Frank, A., Forster, C., Gerasopoulos, E., Gäggeler, H., James, P., Kentarchos, T., Kromp-Kalb, H., Krüger, B., Land, C., Meloen, J., Papayannis, A., Priller, A., Seibert, P., Sprenger, M., Roelofs, G.J., Scheel, H.E., Schnabel, C., Siegmund, P., Tobler, L., Trickl, T., Wernli, H., Wirth, V., Zanis, P., Zerefos, C., 2003a. Stratosphere-troposphere exchange: a review, and what we have learned from STACCATO. Journal of Geophysical Research 108 (D12), 8516.

Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F., Cooper, O., 2003b. A backward modeling study of intercontinental pollution transport using aircraft measurements. Journal of Geophysical Research 108 (D12), 4370.

Stohl, A., Huntrieser, H., Richter, A., Beirle, S., Cooper, O.R., Eckhardt, S., Forster, C., James, P., Spichtinger, N., Wagner, T., Wenig, M., Burrows, J., Platt, U., 2003c. Rapid intercontinental air pollution transport associated with a meterological bomb. Atmospheric Chemistry and Physics 3, 969–986.

Stohl, A., Andrews, E., Burkhart, J.F., Forster, C., Herber, A., Hoch, S.W., Kowal, D., Lunder, C., Mefford, T., Ogren, J.A., Sharma, S., Spichtinger, N., Stebel, K., Stone, R., Ström, J., Torseth, K., Wehrli, C., Yttri, K., 2006. Pan-Arctic enhancements of light absorbing aerosol concentrations due to North American boreal forest fires during summer 2004. Journal of Geophysical Research 111, D22214.

Stohl, A., Berg, T., Burkhart, J.F., Fjaeraa, A.M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W.W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., Yttri, K., 2007a. Arctic smoke – record high air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring 2006. Atmospheric Chemistry and Physics 7, 511–534.

Stohl, A., Forster, C., Huntrieser, H., Mannstein, H., McMillan, W.W., Petzold, A., Schlager, H., Weinzierl, B., 2007b. Aircraft measurements over Europe of an air pollution plume from Southeast Asia – aerosol and chemical characterization. Atmospheric Chemistry and Physics 7, 913–937.

Stohl, A., Trickl, T., 1999. A text book example of long range transport: simultaneous observation of ozone maxima of stratospheric and North American origin in the FT over Europe. Journal of Geophysical Research 104, 30445–430462.

Stott, P.A., Stone, D.A., Allen, M.R., 2004. Human contribution to the European heatwave of 2003. Nature 432, 610–614.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandez, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.H., Yarber, K.F., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. Journal of Geophysical Research 108 (D21), 8809.

Streets, D.G., Zhang, Q., Wang, L., He, K., Hao, J., Wu, Y., Tang, Y., Carmichael, G.R., 2006. Revisiting China's CO emissions after the Transport and Chemical Evolution over the Pacific (TRACE-P) mission: synthesis of inventories, atmospheric modeling, and observations. Journal of Geophysical Research 111, D14306.

Streets, D.G., Fu, J.S., Jang, C.J., Hao, J., He, K., Tang, X., Zhang, Y., Wang, Z., Li, Z., Zhang, Q., Wang, L., Wang, B., Yu, C., 2007. Air quality during the 2008 Beijing Olympic Games. Atmospheric Environment 41, 480–492.

Stroppiana, D., Pinnoch, S., Gregoire, J.-M., 2000. The global fire product: daily fire occurrence from April 1992 to December 1993 derived from NOAA AVHRR data. International Journal of Remote Sensing 21, 1279–1288.

Struzewska, J., Kaminski, J., 2007. Interactive comment on formation and transport of photooxidants over Europe during the July 2006 heat wave – observations and GEM-AQ model simulations. Atmospheric Chemistry and Physics Discussions 7, S5805–S5810.

Sturman, A.P., 1987. Thermal influence on Airflow in mountainous terrain. Progress in Physical Geography 11, 183–206.

Stutz, J., Alicke, B., Neftel, A., 2002. Nitrous acid formation in the urban atmosphere: gradient measurements of NO_2 and HONO over grass in Milan, Italy. Journal of Geophysical Research 107 (D22), 8192.

Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. The Journal of Physical Chemistry A 110, 9665–9690.

Swap, R., Ulanski, S., Cobbett, M., Garstang, M., 1996. Temporal and spatial characteristics of Saharan dust outbreaks. Journal of Geophysical Research 101, 4205–4220.

Swietlicki, E., Hansson, H.-C., Hameri, K., Svenningson, B., Massling, A., McFiggans, G., McMurry, P.H., Petaja, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., Kulmala, M., 2008. Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments-a review. Tellus 60B, 432–469.

Szidat, S., Jenk, T.M., Synal, H.A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., Baltensperger, U., 2006. Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C. Journal of Geophysical Research 111, D07206, doi:10.1029/2005JD006590.

Szidat, S., Prévôt, A.S.H., Sandradewi, J., Alfarra, M.R., Synal, H.-A., Wacker, L., Baltensperger, U., 2007. Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophysical Research Letters 34, L05820, doi:10.1029/2006GL028325.

Szopa, S., Hauglustaine, D.A., Vautard, R., Menut, L., 2006. Future global tropospheric ozone changes and impact on European air quality. Geophysical Research Letters 33, L14805.

Szopa, S., Hauglustaine, D.A., Ciais, P., 2007. Relative contributions of biomass burning emissions and atmospheric transport to carbon monoxide interannual variability. Geophysical Research Letters 34, L18810.

Tabazedeh, A., Yokelson, R.J., Singh, H.B., Hobbs, P.V., Crawford, J.H., Iraci, L.T., 2004. Heterogeneous chemistry involving methanol in tropospheric clouds. Geophysical Research Letters 31, L06114.

Taha, H., 2008. Sensitivity of the urbanized MM5 (uMM5) to perturbations in surface properties in Houston Texas. Boundary-Layer Meteorology 127, 193–218.

Takegawa, N., Miyakawa, T., Kondo, Y., Blake, D.R., Kanaya, Y., Koike, M., Fukuda, M., Komazaki, Y., Miyazaki, Y., Shimono, A., Takeuchi, T., 2006. Evolution of submicron organic aerosol in polluted air exported from Tokyo. Geophysical Research Letters 33, L15814.

Taketani, F., Kanaya, Y., Akimoto, H., 2008. Kinetics of heterogeneous reactions of HO_2 radical at ambient concentration levels with $(NH_4)_2SO_4$ and NaCl aerosol particles. The Journal of Physical Chemistry A 112, 2370–2377.

Tan, D., Faloona, I., Simpas, J.B., Brune, W., Shepson, P.B., Couch, T.L., Sumner, A.L., Carroll, M.A., Thornberry, T., Apel, E., Riemer, D., Stockwell, W., 2001. HO_x budgets in a deciduous forest: results from the PROPHET summer 1998 campaign. Journal of Geophysical Research 106, 24407–24427.

Tang, I.N., Munkelwitz, H.R., 1994. Aerosol phase-transformation and growth in the atmosphere. Journal of Applied Meteorology 33, 791–796.

Tansey, K., Gregoire, J.M., Defourny, P., Leigh, R., Pekel, J.F., van Bogaert, E., Bartholome, E., 2008. A new, global, multi-annual (2000–2007) burnt area product at 1 km resolution. Geophysical Research Letters 35, L01401.

Tarrasón, L. 2007. Transboundary acidification, eutrophication and ground level ozone in Europe. EMEP Status Report 1/2007, ISSN 1504–6109.

Tegen, I., 2003. Modeling the mineral dust aerosol cycle in the climate system. Quaternary Science Reviews 22, 1821–1834.

Tegen, I., Harrison, S.P., Kohfeld, K., Prentice, I.C., Coe, M., Heimann, M., 2002. Impact of vegetation and preferential source areas on global dust aerosol: results from a model study. Journal of Geophysical Research 107 (D21), 4576.

Tesche, M., Ansmann, A., Müller, D., Althausen, D., Heese, B., Freudenthaler V., Wiegner M., Esselborn M., Pisani G., Knippertz P., 2008. Vertical profiling of Saharan dust with Raman lidars and airborne high-spectral-resolution lidar during SAMUM. Tellus 60B,61, 144–164.

Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, H., Berntsen, T., Berglen, T., Boucher, O., Chin, M., Dentener, F., Diehl, T., Feichter, J., Fillmore, D., Ginoux, P., Gong, S., Grini, A., Hendricks, J., Horowitz, L., Huang, P., Isaksen, I.S.A., Iverson, T., Kloster, S., Koch, D., Kirkevåg, A., Kristjansson, J.E., Krol, M., Lauer, A., Lamarque, F., Liu, X., Montanaro, V., Myhre, G., Penner, J.E., Pitari, G., Reddy, M.S., Seland, Ø., Stier, P., Takemura, T., Tie, X., 2007. The effect of harmonized emissions on aerosol properties in global models – an AeroCom experiment. Atmospheric Chemistry and Physics 7, 4489–4501.

Theys, N., van Roozendael, M., Hendrick, F., Fayt, C., Hermans, C., Baray, J.-L., Goutail, F., Pommereau, J.-P., Mazière, M.D., 2007. Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21°S, 56°E). Atmospheric Chemistry and Physics 7, 4733–4749.

Thiemens, M.H., 2006. History and applications of mass-independent isotope effects. Annual Review of Earth and Planetary Sciences 34, 217–262.

Thiemens, M.H., Jackson, T.L., Brenninkmeijer, C.A.M., 1995. Observation of a mass-independent oxygen isotopic composition in terrestrial stratospheric CO_2, the link to ozone chemistry, and the possible occurrence in the martian atmosphere. Geophysical Research Letters 22, 255–257.

Thomas, W., Baier, F., Erbertseder, T., Kastner, M., 2003. Analysis of the Algerian severe weather event in November 2001 and its impact on ozone and nitrogen dioxide distributions. Tellus Series B-Chemical and Physical Meteorology 55, 993–1006.

Thompson, A.M., Witte, J.C., Hudson, R.D., Guo, H., Herman, J.R., Fujiwara, M., 2001. Tropical tropospheric ozone and biomass burning. Science 291, 2128–2132.

Thompson, A.M., Witte, J.C., Oltmans, S.J., Schmidlin, F.J., Logan, J.A., Fujiwara, M., Kirchhoff, V., Posny, F., Coetzee, G.J.R., Hoegger, B., Kawakami, S.J., Ogawa, T., Fortuin, J.P.F., Kelder, H.M., 2003. Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2000 tropical ozone climatology – 2. Tropospheric variability and the zonal wave-one. Journal of Geophysical Research 108 (D2), 8241.

Thornton, J.A., Wooldridge, P.J., Cohen, R.C., Martinez, M., Harder, H., Brune, W.H., Williams, E.J., Roberts, J.M., Fehsenfeld, F.C., Hall, S.R., Shetter, R.E., Wert, B.P., Fried, A., 2002. Ozone production rates as function of NO_x abundances and HO_x production rates in the Nashville urban plume. Journal of Geophysical Research 107 (D12), 4146.

Thouret, V., Cho, J.Y.N., Newell, R.E., Marenco, A., Smit, H.G.J., 2000. General characteristics of tropospheric trace constituent layers observed in the MOZAIC program. Journal of Geophysical Research 105 (D13), 17379–17392.

Tilmes, S., Brandt, J., Flatoy, F., Bergstrom, R., Flemming, J., Langner, J., Christensen, J.H., Frohn, L.M., Hov, O., Jacobsen, I., Reimer, E., Stern, R., Zimmermann, J., 2002. Comparison of five eulerian air pollution forecasting systems for the summer of 1999 using the German ozone monitoring data. Journal of Atmospheric Chemistry 42, 91–121.

Tobias, H.J., Ziemann, P.J., 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O_3 in the presence of alcohols and carboxylic acids. Environmental Science & Technology 34, 2105–2115.

Toyoda, S., Yoshida, N., 1999. Determination of nitrogen isotopomers of nitrous oxide on a modified isotope ratio mass spectrometer. Analytical Chemistry 71, 4711–4718.

Trainer, M., Williams, E.J., Parrish, D.D., Buhr, M.P., Allwine, E.J., Westberg, H.H., Fehsenfeld, F.C., Liu, S.C., 1987. Models and observations of the impact of natural hydrocarbons on rural ozone. Nature 329, 705–707.

Trentmann, J., Andreae, M.O., Graf, H.-F., 2003. Chemical processes in a young biomass-burning plume. Journal of Geophysical Research 108 (D22), 4705.

Trentmann, J., Yokelson, R.J., Hobbs, P.V., Winterrath, T., Christian, T.J., Andreae, M.O., Mason, S.A., 2005. An analysis of the chemical processes in the smoke plume from a savanna fire. Journal of Geophysical Research 110, D12301.

Trentmann, J., Luderer, G., Winterrath, T., Fromm, M.D., Servranckx, R., Textor, C., Herzog, M., Graf, H.-F., Andreae, M.O., 2006. Modeling of biomass smoke injection into the lower stratosphere by a large forest fire (Part I): reference simulation. Atmospheric Chemistry and Physics 6, 5247–5260.

Tressol, M., Ordonez, C., Zbinden, R., Brioude, J., Thouret, V., Mari, C., Nedelec, P., Cammas, J.-P., Smit, H., Patz, H.-W., Volz-Thomas, A., 2008. Air pollution during the 2003 European heat wave as seen by MOZAIC airliners. Atmospheric Chemistry and Physics 8, 2133–2150.

Trickl, T., Cooper, O.R., Eisele, H., James, P., Mucke, R., Stohl, A., 2003. Intercontinental transport and its influence on the ozone concentrations over central Europe: three case studies. Journal of Geophysical Research 108 (D12), 8530.

Tsigaridis, K., Krol, M., Dentener, F.J., Balkanski, Y., Lathière, J., Metzger, S., Hauglustaine, D.A., Kanakidou, M., 2006. Change in global aerosol composition since preindustrial times. Atmospheric Chemistry and Physics 6, 5143–5162.

Tsigaridis, K., Kanakidou, M., 2003. Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis. Atmospheric Chemistry and Physics 3, 1849–1869.

Tsigaridis, K., Kanakidou, M., 2007. Secondary organic aerosol importance in the future atmosphere. Atmospheric Environment 41, 4682–4692.

Tsyro, S., Simpson, D., Tarrasón, L., Klimont, Z., Kupiainen, K., Pio, C., Yttri, K.E., 2007. Modeling of elemental carbon over Europe. Journal of Geophysical Research 112, D23S19, doi: 10.1029/2006JD008164.

Tuazon, E.C., Atkinson, R., 1990. A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x. International Journal of Chemical Kinetics 22, 1221–1235.

Tulet, P., Suhre, K., Mari, C., Solmon, F., Rosset, R., 2002. Mixing of boundary layer and upper tropospheric ozone during a deep convective event over Western Europe. Atmospheric Environment 36, 4491–4501.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P.P., Komppula, M., Kulmala, M., 2006. High natural aerosol loading over boreal forests. Science 312, 261–263.

Turpin, B.J., Lim, H.J., 2001. Species contributing to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Science and Technology 35, 602–610.

Turquety, S., Logan, J.A., Jacob, D.J., Hudman, R.C., Leung, F.Y., Heald, C.L., Yantosca, R.M., Wu, S.L., Emmons, L.K., Edwards, D.P., Sachse, G.W., 2007. Inventory of boreal fire emissions for North America in 2004: the importance of peat burning and pyroconvective injection. Journal of Geophysical Research 112, D12S03.

Twohy, C.H., Clement, C.F., Gandrud, B.W., Weinheimer, A.J., Campos, T.L., Baumgardner, D., Brune, W.H., Faloona, I., Sachse, G.W., Vay, S.A., Tan, D., 2002. Deep convection as a source of new particles in the midlatitude upper troposphere. Journal of Geophysical Research 107 (D21), 4560.

UNECE, 2004. Handbook for the 1979 Convention on Long-Range Transboundary Air Pollution and its Protocols. United Nations, New York and Geneva. ECE/EB.AIR.5, ISBN 92-1-116895-32004. http://www.unece.org/env/lrtap/ (including amendment of December 2005).

UN-HABITAT, 2006. State of the World's Cities 2006/7. The Millennium Development Goals and Urban Sustainability: 30 Years of Shaping the Habitat Agenda. Earthscan, London, UK.

Utembe, S.R., Jenkin, M.E., Derwent, R.G., Lewis, A.C., Hopkins, J.R., Hamilton, J.F., 2005. Modelling the ambient distribution of organic compounds during the August 2003 ozone episode in the southern UK. Faraday Discussion 130, 311–326.

Väkevä, M., Hämeri, K., Aalto, P.P., 2002. Hygroscopic properties of nucleatin mode and aitken mode particles during nucleation bursts and in background air on the west coast of Ireland. Journal of Geophysical Research 107 (D19), 8104.

Val Martin, M., Honrath, R.E., Owen, R.C., Pfister, G., Fialho, P., Barata, F., 2006. Significant enhancements of nitrogen oxides, black carbon and ozone in the North Atlantic lower free troposphere resulting from North American boreal wildfires. Journal of Geophysical Research 111, D23S60.

van Aardenne, J.A., Dentener, F.J., Olivier, J.G.J., Klein Goldewijk, C.G.M., Lelieveld, J., 2001. A 1° × 1° resolution dataset of historical anthropogenic trace gas emissions for the period 1890–1990. Global Biogeochemical Cycles 15, 909–928.

Vautard, R., Honore, C., Beekmann, M., Rouil, L., 2005. Simulation of ozone during August 2003 heat wave and emission control scenarios. Atmospheric Environment 39, 2957–2967.

Vautard, R., Szopa, S., Beekmann, M., Menut, L., Hauglustaine, D.A., Rouil, L., Roemer, M., 2006a. Are decadal anthropogenic emission changes in Europe consistent with surface ozone observations? Geophysical Research Letters 33, L13810.

Vautard, R., Van Loon, M., Schaap, M., Bergström, R., Bessagnet, B., Brandt, J., Builtjes, P.J.H., Christensen, J.H., Cuvelier, K., Graf, A., Jonson, J.E., Krol, M., Langner, J., Roberts, P., Rouil, L., Stern, R., Tarrasón, L., Thunis, P., Vignati, E., White, L., Wind, P., 2006b. Is regional air quality model diversity representative of uncertainty for ozone simulation? Geophysical Research Letters 33, L24818.

Vautard, R., Beekmann, M., Desplats, J., Hodzic, A., Morel, S., 2007. Air quality in Europe during the summer of 2003: a prototype of air quality in a warmer climate. Comptes Rendus Geoscience 339, 747–763.

Venzac, H., Sellegri, K., Laj, P., Villani, P., Bonasoni, P., Marinoni, A., Cristofanelli, P., Calzolari, F., Fuzzi, S., Decesari, S., Facchini, M.C., Vuillermoz, E., Verza, G.P., 2008. High frequency new particle formation in the Himalayas. Proceedings of the National Academy of Science U.S.A. 105, 15666–15671.

Vereecken, L., Müller, J.F., Peeters, J., 2007. Low-volatility poly-oxygenates in the OH-initiated oxidation of a-pinene: impact of non-traditional peroxyl radical chemistry. Physical Chemistry Chemical Physics 9, 5241–5248.

Vereecken, L., Peeters, J., 2004. Nontraditional (per)oxy ring-closure paths in the atmospheric oxidation of isoprene and monoterpenes. The Journal of Physical Chemistry A 108, 5197–5204.

Vestreng, V., Myhre, G., Fagerli, H., Reis, S., Tarrasón, L., 2007. Twenty-five years of continuous sulphur dioxide emission reduction in Europe. Atmospheric Chemistry and Physics 7, 3663–3681.

Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I.S.A., Tarrasón, L., 2009. Evolution of NO_x emissions in Europe with focus on road transport control measures. Atmospheric Chemistry and Physics 9, 1503–1520.

Vignati, E., Facchini, M.C., Rinaldi, M., Scannell, C., Ceburnis, D., Sciare, J., Kanakidou, M., Myriokefalitakis, S., Dentener, F., O'Dowd, C.D. Global scale emission and distribution of sea spray aerosol: sea-salt and organic enrichment. Atmospheric Environment, submitted for publication.

Vogt, R., Crutzen, P.J., Sander, R., 1996. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. Nature 383, 327–330.

Volkamer, R., Platt, U., Wirtz, K., 2001. Primary and secondary glyoxal formation from aromatics: experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene and p-xylene. The Journal of Physical Chemistry A 105, 7865–7874.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K.H., Platt, U., 2002. OH-initiated oxidation of benzene – part I. Phenol formation under atmospheric conditions. Physical Chemistry Chemical Physics 4, 1598–1610.

Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R., Molina, M.J., 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. Geophysical Research Letters 33, L17811.

Volkamer, R., Martini, F.S., Molina, L.T., Salcedo, D., Jimenez, J.L., Molina, M.J., 2007a. A missing sink for gas-phase glyoxal in Mexico City: formation of secondary organic aerosol. Geophysical Research Letters 34, L19807.

Volkamer, R., Sheehy, P.M., Molina, L.T., Molina, M.J., 2007b. Oxidative capacity of the Mexico City atmosphere – part 1: a radical source perspective. Atmospheric Chemistry and Physics Discussions 7, 5365–5412.

Volz, A., Kley, D., 1988. Evaluation of the Montsouris series of ozone measurements made in the 19th-Century. Nature 332, 240–242.

Volz-Thomas, A., Geiss, H., Hofzumahaus, A., Becker, K.H., 2003. Introduction to special section: photochemistry experiment in BERLIOZ. Journal of Geophysical Research 108 (D4), 8252.

Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., Crutzen, P.J., Lelieveld, J., Perner, D., Berresheim, H., Baboukas, E., 2004. Role of the NO_3 radicals in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign. Atmospheric Chemistry and Physics 4, 169–182.

Vrekoussis, M., Liakakou, E., Mihalopoulos, N., Kanakidou, M., Crutzen, P.J., Lelieveld, J., 2006. Formation of HNO_3 and NO_3- in the anthropogenically-influenced eastern Mediterranean marine boundary layer. Geophysical Research Letters 33, L05811.

Wagner, V., Jenkin, M.E., Saunders, S.M., Stanton, J., Wirtz, K., Pilling, M.J., 2003. Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms. Atmospheric Chemistry and Physics 3, 89–106.

Wagner F., Bortoli D., Pereira S., Costa M.J., Silva A.M., Weinzierl B., Esselborn M., Petzold, Andreas, Rasp K., Heinold B., Tegen I., 2009. Properties of dust aerosol particles transported to Portugal from the Sahara desert. Tellus B 61, 297–306.

Wagner, T., Platt, U., 1998. Satellite mapping of enhanced BrO concentrations in the troposphere. Nature 395, 486–490.

Wahner, A., Mentel, T.F., Sohn, M., 1998a. Gas-phase reaction of N_2O_5 with water vapor: importance of heterogeneous hydrolysis of N_2O_5 and surface desorption of HNO_3 in a large Teflon chamber. Geophysical Research Letters 25, 2169–2172.

Wahner, A., Mentel, T.F., Sohn, M., Stier, J., 1998b. Heterogeneous reaction of N_2O_5 on sodium nitrate aerosol. Journal of Geophysical Research 103, 31103–31112.

Wallington, T.J., 1991. Fourier-transform infrared product study of the reaction of $CH_3O_2 + HO_2$ over the pressure range 15–700 Torr at 295 K. Journal of the Chemical Society, Faraday Transactions 87, 2379–2382.

Wang, P.K., 2003. Moisture plumes above thunderstorm anvils and their contributions to cross-tropopause transport of water vapor in midlatitudes. Journal of Geophysical Research 108 (D6), 4194.

Wang, Y.H., Liu, S.C., Wine, P.H., Davis, D.D., Sandholm, S.T., Atlas, E.L., Avery, M.A., Blake, D.R., Blake, N.J., Brune, W.H., Heikes, B.G., Sachse, G.W., Shetter, R.E., Singh, H.B., Talbot, R.W., Tan, D., 2001. Factors controlling tropospheric O_3, OH, NO_x and SO_2 over the tropical Pacific during PEM-Tropics B. Journal of Geophysical Research 106, 32733–32747.

Warneke, C., Holzinger, R., Hansel, A., Jordan, A., Lindinger, W., Poschl, U., Williams, J., Hoor, P., Fischer, H., Crutzen, P.J., Scheeren, H.A., Lelieveld, J., 2001. Isoprene and its oxidation products methyl vinyl ketone, methacrolein, and isoprene related peroxides measured online over the tropical rain forest of Surinam in March 1998. Journal of Atmospheric Chemistry 38, 167–185.

Watanabe, A., Nojiria, Y., Kariyab, S., 2005. Measurement on a commercial vessel of the ozone concentration in the marine boundary layer over the northern North Pacific Ocean. Journal of Geophysical Research 110 (D11), 310.

Watson, J.G., Chow, J.C., Fujita, E.M., 2001. Review of volatile organic compound source apportionment by chemical mass balance. Atmospheric Environment 35, 1567–1584.

Wayne, R.P., Barnes, I., Biggs, P., Burrows, J.P., Canosamas, C.E., Hjorth, J., Lebras, G., Moortgat, G.K., Perner, D., Poulet, G., Restelli, G., Sidebottom, H., 1991. The nitrate radical – physics, chemistry, and the atmosphere. Atmospheric Environment Part a – General Topics 25, 1–203.

Weber, R.J., Sullivan, A.P., Peltier, R.E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J.S., Atlas, E.L., Edgerton, E., 2007. A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. Journal of Geophysical Research 112, D13302.

Weber, R.J., Lee, S., Chen, G., Wang, B., Kapustin, V., Moore, K., Clarke, A.D., Mauldin, L., Kosciuch, E., Cantrell, C., Eisele, F., Thornton, D.C., Bandy, A.R., Sachse, G.W., Fuelberg, H.E., 2003. New particle formation in anthropogenic plumes advecting from Asia observed during TRACE-P. Journal of Geophysical Research, 8814. D21.

Weinzierl, B., Petzold, A., Esselborn, M., Wirth, M., Rasp, K., Kandler, K., Schutz, L., Koepke, P., Fiebig, M., 2009. Airborne measurements of dust layer properties, particle size distribution and mixing state of Saharan dust during SAMUM 2006. Tellus B 61, 96–117.

Weissmann, M., Braun, F.J., Gantner, L., Mayr, G.J., Rahm, S., Reitebuch, O., 2005. The Alpine mountain-plain circulation: airborne Doppler lidar measurements and numerical simulations. Monthly Weather Review 133, 3095–3109.

Wennberg, P.O., Dabdub, D., 2008. Rethinking ozone production. Science 319, 1624–1625.

Went, F., 1960. Blue haze in the atmosphere. Nature 187, 641–643.

van der Werf, G.R., Randerson, J.T., Collatz, G.J., Giglio, L., 2003. Carbon emissions from fires in tropical and subtropical ecosystems. Global Change Biology 9, 547–562.

van der Werf, G.R., Randerson, J.T., Giglio, L., Collatz, G.J., Kasibhatla, P.S., Arellano Jr., A.F., 2006. Interannual variability of global biomass burning emissions from 1997 to 2004. Atmospheric Chemistry and Physics 6, 3423–3441.

White, W.H., Anderson, J.A., Blumenthal, D.L., Husar, R.B., Gillani, N.V., Husar Jr., J.D.W.E.W., 1976. Formation and transport of secondary air pollutants: ozone and aerosols in the St. Luis urban plume. Science 194, 187–189.

Whiteman, C.D., 1990. Observation of thermally developed wind systems in mountainous terrain. In: Blumen, W. (Ed.), Atmospheric Processes over Complex Terrain. American Meteorological Society, Boston, Massachusetts, p. 323.

Whiteman, C.D., 2000. Mountain Meteorology Fundamentals and Applications. Oxford University Press, New York.

WHO, 2002. World Health Report: Reducing Risks, Promoting Healthy Life. World Health Organization, Geneva, Switzerland.

WHO, 2003. Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide. Report on a WHO working group. Bonn, Germany. 13–15 January.

WHO, 2005a. Health and Climate Change: the "now and How". A Policy Action Guide. WHO Regional Office for Europe, Copenhagen, Denmark.

WHO, 2005b. Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide. World Health Organization, Geneva, Switzerland.

WHO, 2007. Health Relevance of Particulate Matter from Various Sources. WHO Regional Office for Europe, Copenhagen, Denmark. Report on a WHO Workshop Bonn, Germany, 26–27 March 2007.

WHO, 2008. Health Risks of Ozone from Long-range Transboundary Air Pollution. WHO Regional Office for Europe, Copenhagen, Denmark.

Wild, O., Akimoto, H., 2001. Intercontinental transport of ozone and its precursors in a three-dimensional global CTM. Journal of Geophysical Research 106, 27729–27744.

Wild, O., Pochanart, P., Akimoto, H., 2004. Trans-Eurasian of ozone and its precursors. Journal of Geophysical Research 109, D11302.

Wingenter, O.W., Kubo, M.K., Blake, N.J., Smith Jr., T.W., Blake, D.R., Rowland, F.S., 1996. Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights. Journal of Geophysical Research 101, 4331–4340.

Wingenter, O.W., Blake, D.R., Blake, N.J., Sive, B.C., Rowland, F.S., Atlas, E., Flocke, F., 1999. Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean. Journal of Geophysical Research 104, 21819–21828.

Witham, C., Manning, A., 2007. Impacts of Russian biomass burning on UK air quality. Atmospheric Environment 41, 8075–8090.

Wittrock, F., Richter, A., Oetjen, H., Burrows, J.P., Kanakidou, M., Myriokefalitakis, S., Volkamer, R., Beirle, S., Platt, U., Wagner, T., 2006. Simultaneous global observations of glyoxal and formaldehyde from space. Geophysical Research Letters 33, L16804.

Wolfe, G.M., Thornton, J.A., McNeill, V.F., Jaffe, D.A., Reidmiller, D., Chand, D., Smith, J., Swartzendruber, P., Flocke, F., Zheng, W., 2007. Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundances and speciation at Mount Bachelor Observatory during INTEX-B. Atmospheric Chemistry and Physics 20, 5309–5325.

Woo, K.S., Chen, D.R., Pui, D.Y.H., McMurry, P.H., 2001. Measurements of Atlanta aerosol size distributions: observations of ultrafine Particle events. Aerosol Science and Technology 34, 75–87.

Wood, E.C., Bertram, T.H., Wooldridge, P.J., Cohen, R.C., 2005. Measurements of N_2O_5, NO_2, and O_3 east of the San Francisco bay. Atmospheric Chemistry and Physics 5, 483–491.

Wooster, M.J., 2002. Small-scale experimental testing of fire radiative energy for quantifying mass combusted in natural vegetation fires. Geophysical Research Letters 29 (21), 2027.

Wotowa, G., Trainer, M., 2000. The influence of Canadian forest fires on pollutant concentrations in the United States. Science 288, 324–328.

Wu, S., Mickley, L.J., Jacob, D.J., Logan, J.A., Yantosca, R.M., Rind, D., 2007. Why are there large differences between models in global budgets of tropospheric ozone? Journal of Geophysical Research 112, D05302.

Wyche, K.P., Monks, P.S., Ellis, A.M., Cordell, R.L., Parker, A.E., Whyte, C., Metzger, A., Dommen, J., Duplissy, J., Prevot, A.S.H., Baltensperger, U., Rickard, A.R., Wulfert, F., 2009. Gas phase precursors to anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation. Atmospheric Chemistry and Physics 9, 635–665.

Xie, Y., Berkowitz, C.M., 2006. The use of positive matrix factorization with conditional probability functions in air quality studies: an application to hydrocarbon emissions in Houston, Texas. Atmospheric Environment 40, 3070–3091.

Yang, X., Cox, R.A., Warwick, N.J., Pyle, J.A., Carver, G.D., O'Connor, F.M., Savage, N.H., 2005. Tropospheric bromine chemistry and its impacts on ozone. Journal of Geophysical Research 110, D23311.

Yokelson, R.J., Bertschi, I.T., Christian, T.J., Hobbs, P.V., Ward, D.E., Hao, W.M., 2003. Trace gas measurements in nascent, aged and cloud processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy. Journal of Geophysical Research 08 (D13), 8478.

Yoshino, A., Sadanaga, Y., Watanabe, K., Kato, S., Miyakawa, Y., Matsumoto, J., Kajii, Y., 2006. Measurements of total OH reactivity by laser-induced pump and probe technique – comprehensive observations in the urban atmosphere of Tokyo. Atmospheric Environment 40, 7869–7881.

Yu, J., Jeffries, H.E., Le Lacheur, R.M., 1995. Identifying airborne carbonyl compounds in isoprene atmospheric photooxidation products by their PFBHA oximes using gas chromatography/ion trap mass spectrometry. Environmental Science & Technology 29, 1923–1932.

Zahardis, J., Petrucci, G., 2007. The oleic acid-ozone heterogeneous reaction system: products, kinetics, secondary chemistry, and atmospheric implications of a model system – a review. Atmospheric Chemistry and Physics 7, 1237–1274.

Zanis, P., Trickl, T., Stohl, A., Wernli, H., Cooper, O., Zerefos, C., Gaeggeler, H., Schnabel, C., Tobler, L., Kubik, P.W., Priller, A., Scheel, H.E., Kanter, H.J., Cristofanelli, P., Forster, C., James, P., Gerasopoulos, E., Delcloo, A., Papayannis, A., Claude, H., 2003. Forecast, observation and modeling of a deep stratospheric intrusion event over Europe. Atmospheric Chemistry and Physics 3, 763–777.

Zender, C.S., Newman, D., Torres, O., 2002. Spatial heterogeneity in Aeolian erodibility: uniform, topographic, geomorphic, and hydrologic hypotheses. Journal of Geophysical Research 108 (D17), 4543.

Zeng, G.J., Pyle, J.A., 2003. Changes in tropospheric ozone between 2000 and 2100 modeled in a chemistry-climate model. Geophysical Research Letters 30 (7), 1392.

Zerefos, C., Ganev, K., Kourtidis, K., Tzortziou, M., Vasaras, A., Syrakov, E., 2000. On the origin of SO_2 above northern Greece. Geophysical Research Letters 27 (3), 365–368.

Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Allan, J.D., Coe, H., Ulbrich, I., Alfarra, M.R., Takami, A., Middlebrook, A.M., Suni, Y.L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P.F., Salcedo, D., Onasch, T., Jayne, J., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R.J., Rautiainen, J., Sun, J.Y., Zhang, Y.M., Worsnop, D.R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. Geophysical Research Letters 34, L13801.

Zhao, J., Zhang, R.Y., Fortner, E.C., North, S.W., 2004. Quantification of hydroxycarbonyls from OH-isoprene reactions. Journal of the American Chemical Society 126, 2686–2687.

Zhong, S.Y., Fast, J., 2003. An evaluation of the MM5, RAMS, and Meso-Eta models at subkilometer resolution using VTMX field campaign data in the Salt Lake Valley. Monthly Weather Review 131, 1301–1322.

Zhou, X., Beine, H.J., Honrath, R.E., Fuentes, J.D., Simpson, W., Shepson, P.B., Bottenheim, J.W., 2001. Snowpack photochemical production of HONO: a major soure of OH in the Arctic boundary layer in springtime. Geophysical Research Letters 28, 4087–4090.

Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J., Demerjian, K., 2002. Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York state. Journal of Geophysical Research 107, 4590.

Zhu, A., Ramanathan, V., Li, F., Kim, D., 2007. Dust plumes over the Pacific, Indian, and Atlantic oceans: climatology and radiative impact. Journal of Geophysical Research 112, D16208.

Zimmer, W., Steinbrecher, R., Körner, C., Schnitzler, J.-P., 2003. The recently developed process-based model SIM-BIM realistically predicts isoprene emissions from adult Quercus petraea forest trees. Atmospheric Environment 37, 1665–1671.

Zimmerman, P.R., 1979. Testing of Hydrocarbon Emissions from Vegetation, Leaf Litter and Aquatic Surfaces, and Development of a Methodology for Compiling Biogenic Emission Inventories. Report EPA-450-4-70-004. US Environmental Protection Agency, Washington, DC.