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Have primary emission reduction measures reduced ozone across Europe? An analysis of European rural background ozone trends 1996–2005

R. C. Wilson[1], Z. L. Fleming[2], P. S. Monks[1], G. Clain[3,4], S. Henne[5], I. B. Konovalov[6,7], S. Szopa[4], and L. Menut[3]

[1]Department of Chemistry, University of Leicester, University Road, Leicester, UK
[2]National Centre for Atmospheric Science, Department of Chemistry, University of Leicester, University Road, Leicester, UK
[3]Laboratoire de Météorologie Dynamique, École Polytechnique, 91128 Palaiseau, France
[4]Laboratoire de Sciences du Climat et de l'Environnement, Gif-sur-Yvette, 91191 France
[5]Empa, Swiss Federal Laboratories for Materials Testing and Research, Dübendorf, Switzerland
[6]Institute of Applied Physics, Russian Academy of Sciences, Nizhniy Novgorod, Russia
[7]Laboratoire Inter-Universitaire de Systèmes Atmosphériques, CNRS, Université Paris-Est and Université Paris 7, Créteil, France

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Correspondence to: P. S. Monks (p.s.monks@le.ac.uk)

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Abstract

National and European legislation over the past 20 years, and the modernisation or removal of industrial sources, have significantly reduced European ozone precursor emissions. This study quantifies observed and modelled European ozone annual and seasonal linear trends from 158 harmonised rural background monitoring stations over a constant time period of a decade (1996–2005). Mean ozone concentrations are investigated, in addition to the ozone 5th percentiles as a measure of the baseline or background conditions, and the 95th percentiles that are representative of the peak concentration levels. This study aims to characterise and quantify surface European ozone concentrations and trends and assess the impact of the changing anthropogenic emission tracers on the observed and modelled trends.

Significant ($p < 0.1$) positive annual trends in ozone mean, 5th and 95th percentiles are observed at 54 %, 52 % and 45 % of sites respectively (85 sites, 82 sites and 71 sites). Spatially, sites in Central and Northwestern Europe tend to display positive annual ozone trends in mean, 5th and 95th percentiles. Significant negative annual trends in ozone mean 5th and 95th percentiles are observed at 11 %, 12 % and 12 % of sites respectively (18 sites, 19 sites and 19 sites) which tend to be located in the eastern and south-western extremities of Europe. European-averaged annual trends have been calculated from the 158 sites in this study. Overall there is a net positive annual trend in observed ozone mean (0.16 ± 0.02 ppbv yr^{-1} (2σ error)), 5th (0.13 ± 0.02 ppbv yr^{-1}) and 95th (0.16 ± 0.03 ppbv yr^{-1}) percentiles, representative of positive trends in mean, baseline and peak ozone. Assessing the sensitivity of the derived overall trends to the constituent years shows that the European heatwave year of 2003 has significant positive influence and 1998 the converse effect; demonstrating the masking effect of inter-annual variability on decadal based ozone trends.

The European scale 3-D CTM CHIMERE was used to simulate hourly O_3 concentrations for the period 1996–2005. Comparisons between the 158 observed ozone trends to those equivalent sites extracted from regional simulations by CHIMERE better match

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the observed increasing annual ozone (predominantly in Central and Northwestern Europe) for 5th percentiles, than for mean or 95th ozone percentiles. The European-averaged annual ozone trend in CHIMERE 5th percentiles (0.13 ± 0.01 ppbv yr^{-1}) matches the corresponding observed trend extremely well, but displays a negative trend for the 95th percentile (-0.03 ± 0.02 ppbv yr^{-1}) where a positive ozone trend is observed. Inspection of the EU-averaged monthly means of ozone shows that the CHIMERE model is overestimating the summer month O_3 levels.

In comparison to trends in EMEP emissions inventories, with the exception of Austria-Hungary, we find anthropogenic NO_x and VOC reductions do not appear to have a substantial effect on observed annual mean O_3 trends in the rest of Europe.

1 Introduction

Ozone is central to the chemistry of the troposphere owing to its role in the initiation of photochemical oxidation processes via photolysis and subsequent reactions of the photo-products to form the hydroxyl radical (Monks, 2005). Tropospheric ozone is also recognised to be a threat to human health (WHO, 2003), have a deleterious impact on vegetation (Fowler et al., 1999, 2009) as well as being an important tropospheric greenhouse gas (IPCC, 2007). Tropospheric ozone is a secondary pollutant formed from the chemistry of the nitrogen oxides and volatile organic compounds (VOCs) (Monks, 2005).

Throughout the whole troposphere the concentrations of ozone have changed in the modern era characterised by the enhanced emissions of precursors from industrialisation. Analysis of historical ozone records indicate that tropospheric ozone levels in both hemispheres have increased by a factor of 3 to 4 over the recent centuries (Anfossi et al., 1991; Pavelin et al., 1999; Sandroni et al., 1992; Staehelin et al., 1994; Volz and Kley, 1988).

The tropospheric ozone budget at any given place is a complex combination of photochemical processes and physical processes, i.e. photochemical production or

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destruction of ozone, stratospheric-tropospheric exchange (STE) and destruction of ozone at the Earth's surface.

Quantitative establishment of temporal ozone trends is important for quantifying the impact of changing precursor emissions and also from the perspective of local and regional air quality control in terms of import/export of ozone and the amount that is locally or regionally controllable. Observed ozone trends are a challenge to interpret as there are a number of possible factors responsible (Cape, 2008) such as (a) changes in anthropogenic emissions of precursors (both regional and global), (b) effects of variable precursor emissions from biomass burning (both regional and global), (c) changes in stratosphere-troposphere exchange trends, (d) changes in geographical emission patterns and (e) changes in air-mass transport patterns. Long-term series of high quality data are required in order to detect the trend amongst the large inter annual variation. Jonson et al. (2006) have discussed many of these effects in relation to ozone trends.

Within ozone trend work there has been substantial focus to date on quantifying hemispheric "background" trends in ozone (The Royal Society, 2008). There are different definitions of background (Chan and Vet, 2010; Parrish et al., 2009; The Royal Society, 2008) but a pragmatic definition is that it is ozone measured at a site without the influence of strong local effects. This leads to a hierarchy of background measurements from hemispheric background, to regional, rural and urban. Much of the focus in hemispheric background trends has been on the detection and attribution of ozone trends in marine air entering the western seaboards of the USA/Canada and Europe (Carslaw, 2005; Chan and Vet, 2010; Derwent et al., 2007a; Jaffe and Ray, 2007; Oltmans et al., 2006; Parrish et al., 2009; Simmonds et al., 2004). Measurements of marine inflow provide the opportunity to sample ozone in an environment without the confounding influence of continental emissions while at the same time having acted as an integrator of upwind continental-scale emissions. There remains some discussion as to the attribution of the observed trends (Oltmans et al., 2006, 2008; Parrish et al., 2009; Cooper et al., 2010).

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A review of Northern Hemisphere ground-based "background" ozone trends (including several European sites) has shown a slowly increasing average ozone concentration in the Northern Hemisphere of 0.5–2 % yr^{-1} (Vingarzan, 2004). Long-term European background ozone trends of 1.5 ppbv yr^{-1} at Hohenpeissenberg (1971–1983) (Logan, 1985), 1.2 ppbv yr^{-1} at Zugspitze (1978–2005) (Oltmans et al., 2006), 0.31 ppbv yr^{-1} at Mace Head (1987–2007) (Derwent et al., 2007b) have been observed, with more recent annual ozone trends at background European sites summarised by country in Table 1. The period of trend analysis varies in each case study, rendering it difficult to compare all sites in a uniform manner. Despite the increasing ozone trends in the Northern Hemisphere, the upward trends appear to be continuing at a reduced rate since the 1980s (Guicherit and Roemer, 2000).

In many respects continental/regional trends are more difficult to characterise owing to a greater number of competing effects. Jenkin (2008) concluded from an analysis of UK ozone data that the observations at a given location where influenced by a combination of global/hemispheric-, regional- and local-scale effects with the net trend being dependent on the relative influence of these contributions which can vary spatially and temporally. For the UK, he noted three major influences (i) a gradual increase in the hemispheric baseline ozone concentration resulting from global-scale effects, thereby influencing the baseline levels of ozone brought into the UK from the Atlantic Ocean; (ii) substantial short-term elevations in ozone concentrations during summertime episodes, resulting from the formation of additional ozone from regional-scale photochemical processing of emitted VOC and NO_x over Northwest Europe, and (iii) local-scale removal of ozone by direct reaction with emitted NO has gradually decreased, as a result of the control of NO_x emissions.

Much legislation over the past 20 yr, for example the European Directive 2008/50/EC (2008), has focused on the reduction of ozone precursor emissions in Europe. Emission inventories (Monks et al., 2009; Vestreng et al., 2009) show a downward trend in emissions (Fig. 1) in Europe which seems to be matched on the whole by observations of the precursor species (Derwent et al., 2003; EEA, 2007; von Schneidemesser et al.,

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2010). The mapping of these emission trends to models and observations remains a challenge (Jonson et al., 2006), particularly the ability to pull out relatively smaller trends from inter-annual variability (Koumoutsaris et al., 2008; Voulgarakis et al., 2010). Derwent et al. (2010) carried out sensitivity studies with a photochemical trajectory model to show how European reductions in VOC and NO_x levels would have been the cause of reductions in episodic peak ozone levels. Models (Derwent et al., 2010; Szopa et al., 2006) have also shown that the benefit of European emission control measures can be significantly counterbalanced by increasing background ozone levels and subsequent long range transport, as both are of the same magnitude (up to 4 ppbv) but opposite in sign coupled to non-linearities in the photochemical ozone formation. The impact of long-range transport of ozone and its precursors on European ozone concentrations are of significant policy concern (Keating and Zuber, 2007).

The amount of regional-scale work on ozone trends is substantially smaller than that on hemispheric trends. There has been regional-scale work in the USA and Canada (Chan and Vet, 2010; Cooper et al., 2010; Fiore et al., 2002; Jaffe and Ray, 2007) Japan (Tanimoto et al., 2009), China (Xu et al., 2008) and often on a country-scale within Europe based on a representative site (recent examples in Table 1). There are few studies that have investigated regional scale trends in a self-consistent manner across Europe (see Jonson et al., 2006; Solberg et al., 2009; Vautard et al., 2006).

The work in this paper details observed and modelled regional European ozone trends. A harmonised observational ozone data set from a constant time period of a decade (1996–2005) is used for trend calculation using consistent data analysis techniques. Not only are mean ozone concentrations investigated, but also the ozone 5th percentiles which can be a measure of the baseline or background conditions, in addition to the 95th percentiles that are representative of the peak concentration levels. Both the annual and seasonal variability are explored to decompose potential photochemical and non-photochemical influences. The study aims to characterise and quantify surface European ozone concentrations and trends and assess the impact of the changing anthropogenic emission tracers on the observed and modelled trends.

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2 Data selection and methodology

The data used in the trend analysis originates from the the GEOmon project (Global Earth Observation and MONitoring, http://www.geomon.eu/) harmonised data set of trace gases from 397 ground-based measurement stations representative of rural, suburban and urban European environments. These stations belong to a variety of regional, national and European air quality networks (e.g. EMEP, GAW, Airbase and some national network stations).

The harmonised trace gas data set, available from the GEOmon distributed database, provides one ASCII file per site of hourly O_3, NO_2 and CO data covering the time period of 1996–2006 inclusive (http://geomon.nilu.no/). Each file has unified and consistent time stamps in UTC, the conversion of data to units of volume mixing ratio (ppbv), a uniform data flagging system for quality assurance, details of the data source and consistent data formatting to facilitate site comparisons across Europe.

158 sites categorised as rural/background (not directly impacted by nearby precursor emissions), with O_3 data available between 1996–2006, were selected for analysis from the overall data set (see Fig. 2 and Table 2). The majority of these sites have a continuous time series for the 1996–2005 inclusive period. The selection criteria was a maximum of one year with less than 75 % of data and more than 75 % of the data for all other years. These sites have been assessed in terms of their representativeness and recategorised accordingly (Henne et al., 2010), allowing a characterisation of continental-scale O_3 trends. The advantage of this approach at the continental-scale, is the use of a large number of sites which are less influenced by measurement/sampling bias of any single site.

A variety of tools have been developed to assess the ozone trends using the statistical programming language R (R Development Core Team, 2009). Decadal and seasonally disaggregated O_3 trends have been characterised using the non-parametric loess regression (Cleveland, 1979) to fit more complex trends of daily and monthly O_3 concentrations with at least 75 % data coverage. To identify changes in mean, background

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and peak O_3, the openair package (Carslaw and Ropkins, 2009) was used to deseasonalise O_3 time series (using an stl-based method i.e. decomposing the time series into seasonal, trend and irregular components using loess regression, Cleveland et al., 1990), and quantify linear trends (combining the non-parametric Mann-Kendall analysis for trend (Hirsch et al., 1982) with Sen-Theil slope estimates) of monthly means, 5th and 95th percentiles, respectively. Linear trends were also quantified in units of % yr^{-1} from log-transformed (Parrish et al., 2002; Parrish, 2006) data. Annual and seasonal trends are reported including 95 % confidence intervals. The uncertainty of European-averaged annual trends in ozone are reported with 2σ errors (σ_T) calculated through error propagation from the individual trend uncertainties (σ_t) using Eq. (1), where N is the total number of observed sites in this study (158 sites).

$$\sigma_T = \frac{\sqrt{\Sigma\sigma_t^2}}{N} \tag{1}$$

3 Results

Methods of characterising and quantifying ozone trends vary owing to inter-annual and seasonal variations. Loess regression is a non-parametric method that can be used to derive a good fit and characterisation of complex ozone time-series that have a seasonal component, however the trend is not readily quantifiable. Consequently, a Mann-Kendall trend test is used to quantify linear trends over the ten year time period in this study.

3.1 Characterisation of annual European ozone trends

Visual inspection of the loess trends in monthly mean O_3 over the period of 1996–2005 (inclusive) show six different forms of temporal evolution (see Fig. 3) namely, (i) no trend, (ii) positive trend, (iii) negative trend, (iv) increasing then decreasing concentrations, (v) decreasing then increasing concentrations and (vi) complex behaviour.

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Individual plots for all sites are available in Fig. A1 of the Supplement. Each site was categorised accordingly (Table 3, summarised from Table A1 from the Supplement), with the majority (97 sites) exhibiting no apparent loess trends in O_3. 30 of the 158 sites exhibit positive O_3 loess trends, all of which show increasing annual O_3 5th and/or 95th percentiles. 8 sites, located in Eastern, Northeastern and Southwestern Europe, were characterised with negative O_3 loess trends all with declining annual 5th and/or 95th O_3 percentiles. A total of 14 sites were categorised with more complex O_3 loess trends, 4 of which are located in the UK.

Quantification of the more simplistic linear trend shows that 85 of the 158 sites, the majority of which are located in Northwestern and Central Europe, display significant ($p < 0.1$) positive linear trends in monthly mean O_3 (Fig. 4 and Table A2 in the Supplement), with a range of 0.11 to 1.05 ppbv yr^{-1} (0.34 to 6.05 % yr^{-1}). Especially high trends are noted in several Austrian sites, with trends of > 1 ppbv yr^{-1} for AT0154 (Wiesmath) and AT0167 (Payerbach). The largest linear trend as a percentage increase over the time period is observed at IT04 (Ispra) located within the Po Valley, a region of high anthropogenic emissions and static meteorology (Finzi and Lechi, 1991; Henne et al., 2010). Significant ($p < 0.1$) negative linear trends in mean O_3 are identified at 18 sites, with a range of −0.16 to −1.28 ppbv yr^{-1} (−0.45 to −4.11 % yr^{-1}). The greatest reduction is observed at HU0002R (K-puszta). The linear trends calculated for the remaining 55 sites, located throughout Europe, are not statistically significant ($p > 0.1$). The European-averaged annual trend in mean O_3 is 0.16 ± 0.02 ppbv yr^{-1} (2σ error), with a total range of −1.28 to 1.05 ppbv yr^{-1}.

The low percentiles in an ozone distribution can be representative of the influence of "background" ozone, or be a result from a decreasing trend in removal by reaction with locally emitted NO (for example see Jenkin, 2008). Often these two effects have different seasonal patterns as during winter shallow inversion layers can cause elevated NO_x concentrations, even at rural sites. Previous work (Lindskog et al., 2003) with NO_x integrated trajectories has shown a decrease in the winter ozone deficit across Europe. Examination of O_3 5th percentiles demonstrates that 82 of the 158 sites in Central

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and Northwestern Europe have significant ($p < 0.1$) positive linear trends. The range across those sites with a positive significant trends was > 0.00 to a maximum value of 0.98 ppbv yr^{-1} (> 0.00 to a maximum value of 20.02 % yr^{-1}, rounded to 2 decimal places) (see Fig. 4 and Table A3 in the Supplement). The highest trends in ozone 5th percentiles are seen in several Austrian sites, with trends of 0.98 ppbv yr^{-1} for AT0154 (Wiesmath) and AT0167 (Payerbach). These findings are similar to the increasing background trends identified in baseline O_3 in Northwest European and Alpine regions (including sites in Ireland, Scotland, Norway, Sweden, Finland and high altitude sites) between the early 1990s to early 2000s (Lindskog et al., 2003) and are consistent with observations across the Northern Hemisphere (Carslaw (2005); Vingarzan (2004) and references therein). Similar to the annual mean O_3 trends, the largest trends of the 5th percentiles in terms of percentage increase per year is observed at IT04 (Ispra), which is influenced by the extremely low O_3 levels (< 2 ppbv) at the beginning of the measurement period attributed to NO titration in stagnant air masses. Therefore, emission reductions most likely caused this trend.

19 of the 158 sites typically in the outermost locations of Europe, some near-coastal, display significant ($p < 0.1$) negative trends in O_3 5th percentiles, with a range of −0.03 to −0.88 ppbv yr^{-1} (−0.67 to −6.32 % yr^{-1}). A total of 57 of the 158 sites have linear trends that are not statistically significant, suggesting that low percentile O_3 may not have substantially changed at these sites between 1996–2005. The European annual trend in O_3 5th percentiles is 0.13 ± 0.02 ppbv yr^{-1} (2σ error), with a total range of −0.88 to 0.98 ppbv yr^{-1}.

Figure 4 (compiled from Table A4 within the Supplement) illustrates that significant ($p < 0.1$) 1996–2005 O_3 95th percentile linear trends are positive across 71 of the 158 sites predominantly in Central, Northwestern and Western Europe, with a range of 0.15 to 1.21 ppbv yr^{-1} (0.24 to 2.16 % yr^{-1}). Peak ozone values and their trends are often taken as evidence for the number and frequency of photochemically induced events (see for example Jenkin, 2008). Just 19 of the 158 sites scattered throughout Europe display negative linear trends ($p < 0.1$), with a range of −0.21 to −1.62 ppbv yr^{-1}

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(-0.38 to $-3.12\,\%\,yr^{-1}$), consistent with previous analyses of sites in the UK, Denmark, Norway, Sweden, Netherlands, Germany, Switzerland and Lithuania which showed a decrease in peak (95th or 98th percentiles) O_3 levels from the early 1990's to early 2000's (Lindskog et al., 2003; Jenkin, 2008; Brönnimann et al., 2002). Furthermore, 68 of the 158 sites throughout Europe display trends that were not statistically significant, suggesting that O_3 levels at these sites may not have substantially altered during the period. The European annual trend in O_3 95th percentiles is $0.16 \pm 0.03\,ppbv\,yr^{-1}$ (including 2σ error propagation), with a total range of -1.62 to $1.21\,ppbv\,yr^{-1}$. It is interesting to note that these observations on the surface seem to contradict the perceived wisdom that emission reductions across Europe have reduced peak ozone levels.

3.1.1 Testing the influence of individual years in the annual trend

To establish how the overall annual ozone trend calculated in this study is effected by the data from any given year, the influence of individual years on the the annual trend in the 1996–2005 time period has been investigated. Table 4 summarises the European-averaged trends (using all 158 sites, 2σ error) for O_3 mean, 5th and 95th percentiles when data from one year is systematically excluded. The deviation from the European-averaged annual trends for mean, 5th and 95th percentiles are given in Fig. 5. The removal of individual years 1997, 1998 and 1999 from the trend analysis result in higher magnitude overall positive trends, with a greater proportion of statistically significant ($p < 0.1$) sites showing positive trends. In contrast, the removal of data from 2003 or 2004 respectively from the trend analysis has a profound influence resulting in negative overall annual trends in O_3 95th percentiles. A lower number of sites exhibit significant trends, of these a higher proportion of sites exhibit negative annual trends in O_3 mean, 5th and 95th percentiles if 2003 or 2004 are excluded from analysis.

Despite using 10 yr time series for trend analysis, inter-annual and extreme variation of meteorological and climatological conditions can have a strong influence on trends during the selected time period (Jonson et al., 2006). Visual inspection of the

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O_3 time-series (available in the Supplement in Fig. A1) highlights that many sites exhibit unusually high O_3 levels in 1997–1998 and/or 2003. A number of phenomena occurred during these time periods that could have had a substantial influence on the observed O_3 concentrations. The relatively high O_3 monthly means in 1998/1999 have been linked to large-scale global biomass burning, in conjunction with an El Niño event between 1997–1998 (Simmonds et al., 2004). In contrast, the European heatwave during the summer of 2003 is a contributory factor leading to high O_3 levels that year (Solberg et al., 2008; Lee et al., 2006; Ordóñez et al., 2005). With European summer heat waves recorded more frequently in recent years (i.e. 2003, 2006, 2007 and 2010), these extreme meteorological/climatological conditions will influence O_3 levels and trends during this time period, potentially masking the effect of emissions reductions on the production of secondary pollutants such as O_3 (Solberg et al., 2008).

It is apparent that 1998 and 2003 are pivotal years during the 1996–2005 O_3 trend analysis period. Investigating trends in significantly longer time-series would be required to limit the effects of such years containing unusually high O_3 levels as a result of extreme meteorological/climatological conditions. There are only a limited number of European measuring sites with long O_3 time-series of 20 yr or more, these presently not temporally harmonised to offer spatial coverage across Europe. The continuation of trace gas measurements across Europe will eventually provide the lengthy time-series required for future trace gas trend analysis on a regional scale.

3.2 The characterisation and quantification of seasonal European ozone trends

In order to further investigate the different contributions to the observed ozone trends, seasonal variations of monthly mean, 5th and 95th percentiles of O_3 for 1996–2005 have been calculated for spring (MAM), summer (JJA), autumn (SON) and winter (DJF). Figure 6 shows typical seasonal cycles for 4 sites (available in full in Fig. A2 within the Supplement). The nature of the shape and form of ozone seasonal cycles has been discussed by Monks (2000). For example, the seasonal cycles in Northern, Northwestern and Western European sites (Great Britain, Ireland, Norway and

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Portugal) display a spring maximum (or summer minimum), with O_3 peaking typically in April or May. There has been much debate as to the controlling features of ozone seasonal cycles (see for example Monks (2000) and references therein) and the relative contributions of in-situ photochemistry, deposition, stratospheric/tropospheric exchange. Jonson et al. (2006) have also noted that Northwestern Europe is less influenced by emissions. The remaining European sites exhibit either a broad spring-summer maximum peaking between April and August, or a spring maximum followed by a secondary summer maximum, indicative of regional O_3 production following prevalent precursor emissions (Logan, 1985). This north-east and south-west dichotomy in European seasonal cycles has been previously noted (Esser, 2008).

In the case of O_3 5th percentiles, sites in peripheral Europe display a spring time maximum, whilst those in more central locations exhibit either a secondary summer maximum or a broad spring-summer maximum. GB0006R (Lough Navar) and IE31 (Mace Head) display spring maxima in O_3 95th percentiles, consistent with the clean Atlantic air received at these sites, which is not affected by locally emitted human-induced O_3 precursors. All other sites display either a secondary summer maximum or a broad spring-summer maximum in the 95th percentiles.

Relatively few sites display statistically significant ($p < 0.1$) linear trends in Winter (19 sites), spring (31 sites), summer (30 sites) or Autumn (10 sites) mean O_3. Of those that are statistically significant, many show positive trends in winter (17 sites), spring (27 sites) and summer (23 sites) (0.3 to 1.31 ppbv yr^{-1}, 0.28 to 1.65 ppbv yr^{-1} and 0.37 to 1.15 ppbv yr^{-1}, respectively). Additionally, there are negative trends at a small number of sites in winter (ES1437A (Coratxar) and ZUG (Zugspitze)), (spring EE0011R (Vilsandi), HU0002R (K-puszta) and NO01 (Birkenes)), summer (CZ0001R (Svratouch), DE0009R (Zingst), DE0684A (Schwarzwald Süd), DE0754A (B Grunewald), HU0002R (K-puszta) and LV0010R (Rucava)) and autumn (BE0033R (Moerkerke), HU0002R (K-puszta), LV0010R (Rucava), SI0008R (Iskrba) and ZUG (Zugspitze)) of -0.4 to -0.72 ppbv yr^{-1}, -0.15 to -1.88 ppbv yr^{-1}, -0.40 to -1.27 ppbv yr^{-1} and -0.46 to -1.60 ppbv yr^{-1}, respectively.

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A greater number of sites display statistically significant ($p < 0.1$) linear trends of O_3 5th percentiles in winter (43 sites), spring (34 sites), summer (44 sites) or autumn (26 sites) than for the respective seasonal mean O_3. Of these sites, many show positive trends in winter (33 sites), spring (29 sites) and summer (33 sites) (0.09 to 1.30 ppbv yr^{-1}, 0.06 to 1.65 ppbv yr^{-1} and 0.04 to 1.15 ppbv yr^{-1}, respectively). Negative trends are observed at a number of sites in winter (10 sites, 6 of which are in Spain), spring (5 sites), summer (11 sites) and autumn (19 sites) with a range of −0.12 to −1.01 ppbv yr^{-1}, −0.02 to −1.88 ppbv yr^{-1}, −0.20 to −1.27 ppbv yr^{-1} and −0.08 to −1.60 ppbv yr^{-1}, respectively. The seasonal linear trends in O_3 5th percentiles tend to be of the greatest magnitude during winter and spring, suggesting these have the most influence on the typically increasing annual trends in 5th percentiles of O_3.

Very few sites display statistically significant ($p < 0.1$) linear trends of O_3 95th percentiles in winter (18 sites), spring (19 sites), summer (28 sites) or autumn (11 sites) (available in full in Table A7 in Supplement). Of these, many show positive trends in winter (15 sites), spring (18 sites) and summer (18 sites) (0.25 to 1.30 ppbv yr^{-1}, 0.24 to 1.65 ppbv yr^{-1} and 0.26 to 1.15 ppbv yr^{-1}, respectively), with the highest magnitude often exhibited in summer at a time of maximum photochemistry, consequently having the largest influence on annual trends in 95th percentiles of O_3. Negative trends are observed at a number of sites in winter (3 sites), spring (2 sites), summer (10 sites) and particularly autumn (10 sites) with values of −0.41 to −0.70 ppbv yr^{-1}, −1.22 to −1.88 ppbv yr^{-1}, −0.07 to −0.1.30 ppbv yr^{-1} and −0.37 to −2.94 ppbv yr^{-1}, respectively.

An average European seasonal cycle 1996–2005 (inclusive), calculated using all sites from this study shows a broad spring-summer maximum in mean O_3 (Fig. 7), with a secondary summer maximum. This summer maximum is most dominant in the O_3 95th percentile seasonal cycle, peaking in August when there is increased photochemical activity. The European averages of both seasonal and annual trends have been calculated and included on Fig. 7 using the data from all 158 sites. Averaged across Europe, trends in O_3 5th and 95th percentiles are positive during

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winter, spring and summer. The greatest magnitudes are observed in winter 5th (0.26 ± 0.07 ppbv yr^{-1}, 2σ error) and spring for both O_3 5th and 95th percentiles, with values of 0.24 ± 0.05 ppbv yr^{-1} and 0.31 ± 0.09 ppbv yr^{-1}, respectively. Autumn trends in both 5th and 95th percentiles are negative with values of -0.05 ± 0.05 ppbv yr^{-1} and -0.20 ± 0.09 ppbv yr^{-1}, respectively.

4 Trends in emissions as represented in inventories

In order to explore the factors driving the observed ozone trends, the trends in the corresponding emission inventories for the anthropogenic ozone precursors have been examined. Trend analysis of EMEP anthropogenic NO_x and VOC emissions (Vestreng et al., 2006) (available at http://www.ceip.at/) for Europe during the observation period 1996–2005 are shown in Fig. 8. For scaling purposes, only statistically significant ($p < 0.1$) trends between -10 to 10 % yr^{-1} are displayed on the maps. In the emission inventory data the majority of Europe show negative trends in excess of -3.00 % yr^{-1} in NO_x and VOC emissions, consistent with with NO_x emissions trends calculated for 1996–2005 by Konovalov et al. (2008) who determined reductions of -4.7 ± 0.6 % yr^{-1}, -3.7 ± 0.7 % yr^{-1} and -2.8 ± 1.3 % yr^{-1} for Great Britain, Germany and France, respectively. These reductions are thought to be influenced by the introduction of European legislation and the mandatory use of catalytic converters in vehicles Monks et al. (2009); Vestreng et al. (2009). Spain and Portugal display positive trends in NO_x, with the Iberian and Italian coasts highlighting high positive NO_x trends of up to 10.00 % yr^{-1} ($p < 0.1$). These coastal regions are affected by the Atlantic and Mediterranean shipping tracks (Konovalov et al., 2008). Positive NO_x trends are also noted in Austria and Hungary which may be linked to the economic recovery of Eastern European countries since the late 1990's (Vestreng et al., 2009). VOC emissions across Europe have decreased with the exception of North Sea fossil fuel sites and the Iberian peninsula.

Trends in O_3 (% yr^{-1}) are also given in Fig. 8, including those from French sites between 1995–2003 (Sicard et al., 2009), which are consistent with trends from sites

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within this study. Comparing observed O_3 and anthropogenic emissions, the Austrian sites show a record of positive trends in NO_x and observed O_3 trends in addition to negative trends in VOC emissions between 1996–2005 (Fig. 8). In contrast, Spanish sites display positive trends in NO_x, whilst negative trends in VOCs and observed O_3. Anthropogenic NO_x (see Fig. 9) and VOC reductions appear to be uncorrelated to O_3 annual trends in the rest of Europe (Fig. 8), suggesting precursor emissions may not have as directly related an effect on O_3 formation at these sites. Consideration must also be given to meteorological conditions, chemical reactions (e.g. NO_x titration) and the trans-boundary transport of precursors to the measurement sites.

5 A comparison with a regional chemical transport model

In order to investigate the impact of emission reductions on a regional scale for comparison to observed measurements, simulated O_3 from the CHIMERE chemical transport model was analysed. CHIMERE (Schmidt et al., 2001) was used to generate simulated O_3 concentrations for a regional domain including Europe, with a horizontal resolution of $1^\circ \times 1^\circ$. The chemical boundary conditions were initialised with fixed climatologies calculated from long-term runs of LMDZ-INCA chemical transport models (CTMs). Emission inventories were taken from EMEP (Vestreng et al., 2006) (see Sect. 4 for details of trends in this emission inventory). Hourly concentrations of O_3 of each year 1996–2005 (inclusive) were extracted from grid squares closest to the site locations given in Table 2 and assigned to these sites.

Loess regression and linear regression (available in full in Appendix B Fig. B1 and Tables B1–B3 of the Supplement) of annual mean, 5th and 95th percentiles have characterised and quantified trends in CHIMERE simulated O_3 with data extracted for the 158 locations of measurement sites used in this study. Figure 10 gives examples of the CHIMERE monthly means from six sites, with the corresponding observed sites from Fig. 3. From a visual inspection, CHIMERE time-series are of the similar magnitude and variability as the observed O_3 time-series, with the exception of some high altitude sites. As CHIMERE O_3 concentrations were extracted from the surface layer of the model, this may explain the differences between the minimum O_3 levels in the model and observed time-series (Fig. 10) as a result of surface deposition in the model, but not at the elevated site. These six sites were representative of different loess trends categorised manually from a visual inspection of the observed data (Fig. 3). However, the loess trends of the CHIMERE monthly mean O_3 from equivalent sites are more static, showing no apparent trend.

Despite the limited sites with statistically significant trends ($p < 0.1$), annual trends in mean O_3 tend to be positive with a range of 0.09 to 0.32 ppbv yr^{-1} (37 sites) with just 5 sites displaying a negative trend with a range of −0.08 to −0.14 ppbv yr^{-1} (Fig. 11). Similarly, significant ($p < 0.01$) trends in annual 5th percentiles of O_3 are also positive, with a range of 0.09 to 0.56 ppbv yr^{-1} (74 sites). Annual trends ($p < 0.01$) in 95th percentiles of O_3 tend to be negative with a range of −0.11 to −0.46 ppbv yr^{-1} (20 sites). Comparing significant annual mean and 5th percentile trends in simulated and observed O_3, the trends in simulated O_3 lie within the broad range of observed trends. In the case of significant ($p < 0.1$) annual trends in 95th percentiles, contrary to the negative trends quantified from CHIMERE output, observed trends at almost half of the sites (71 sites) are positive. Inspection of the monthly mean O_3 levels from the observed and simulated sites (Fig. 12), show that the CHIMERE model configuration slightly underestimates the mean O_3 in winter and greatly over estimates the mean O_3 levels from May to August, leading to differences between daily observed and simulated O_3 annual trends in mean, 5th and 95th percentiles.

Frequency distributions of the observed and CHIMERE modelled annual O_3 trends in mean, 5th and 95th percentiles are given in Fig. 13 for i) all trends and ii) only those that are statistically significant ($p < 0.1$). It is clear that whilst the range of O_3 annual trends is the same when looking at only statistically significant trends or all trends, the distribution of trends is different. In the observed trends the distribution is unimodal for O_3 mean, 5th and 95th percentiles when accounting for all annual trends (with frequencies peaking at 0.1 to 0.2 ppbv yr^{-1}, 0.0 to 0.1 ppbv yr^{-1} and 0.2

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to 0.3 ppbv yr^{-1}, respectively). When just statistically significant ($p < 0.1$) trends are taken into account, unimodal distribution of trends is seen for 5th percentiles peaking at 0.2 to 0.3 ppbv yr^{-1}, but bimodal distributions are seen for both mean (with frequency peaking at −0.4 to −0.3 ppbv yr^{-1} and 0.2 to 0.3 ppbv yr^{-1}) and 95th percentiles (with frequency peaking at −0.4 to −0.3 ppbv yr^{-1} and 0.3 to 0.5 ppbv yr^{-1}).

In comparison, ranges of CHIMERE annual O_3 trends are similar for both mean and 5th percentiles whilst those for 95th percentiles are different. The CHIMERE annual O_3 trends in mean, 5th and 95th percentiles exhibit a unimodal distribution when considering all trends (peaking at 0.0 to 0.1 ppbv yr^{-1}, 0.0 to 0.1 ppbv yr^{-1} and −0.1 to 0.0 ppbv yr^{-1}, respectively). A unimodal distribution of the statistically significant trends of O_3 mean (with frequency peaking at 0.1 to 0.2 ppbv yr^{-1}), 5th (with frequency peaking at 0.1 to 0.2 ppbv yr^{-1}) and 95th (with frequency peaking at −0.2 to −0.1 ppbv yr^{-1}) percentiles is also observed, in contrast to the bimodal distribution in observed O_3 mean and 95th percentiles. The CHIMERE model distributions for annual trends in O_3 mean, 5th and 95th percentiles tend to have a peak frequency at a lower value than the observed data.

The average European trends for annual mean, 5th and 95th O_3 percentiles have been calculated, with 2σ errors, for all sites observed and those extracted from the CHIMERE regional model (see Table 5). There is good agreement between the observed and CHIMERE European-averaged 5th percentile trends (0.13 ± 0.02 ppbv yr^{-1} and 0.13 ± 0.01 ppbv yr^{-1}, respectively). However, there is poorer agreement between the observed and the CHIMERE European-average trends in an mean (0.16 ± 0.02 ppbv yr^{-1} and 0.05 ± 0.01 ppbv yr^{-1}, respectively) and the 95th percentiles (0.16 ± 0.03 ppbv yr^{-1} and -0.03 ± 0.02 ppbv yr^{-1}, respectively).

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6 Summary and conclusions

The establishment of temporal ozone trends is important for quantifying the impact of changing precursor emissions and also from the perspective of local and regional air quality control in terms of import/export of ozone and the amount that is locally or regionally controllable. Using ozone data from 158 European observation sites over the time period 1996–2005, the annual and seasonal trends have been determined. A paucity of monitoring sites in France, Spain and the Mediterranean area in the harmonised dataset used (owing to not being available through the monitoring networks used) may lead to a bias towards the ozone trends within Central/Northern Europe. Ozone time-series at each each station was manually characterised as having positive, negative, a combination of these increasing and decreasing concentrations, complex behaviour and static forms of temporal evolution.

Annual linear trends were calculated by de-seasonalising the ozone time series and using Mann-Kendall analysis of Sen-Theil slopes. The overall annual European-averaged trend was net positive, $0.16 \pm 0.02\,\mathrm{ppbv\,yr^{-1}}$ (2σ error). When the European-averaged annual trends are decomposed into percentiles, both the 5th (background) and the 95th percentiles (peak) show positive trends of $0.13 \pm 0.02\,\mathrm{ppbv\,yr^{-1}}$ and $0.16 \pm 0.03\,\mathrm{ppbv\,yr^{-1}}$, respectively ($2\sigma$ error).

Stations in south-western and Eastern Europe had negative trends in 5th and 95th percentiles and means, whereas most of the central and north-western stations had positive trends. Assessment of the sensitivity of the derived trends to the years includes in the decadal average show that the net positive trend is heavily weighted by the 2003 NW European "heatwave" year while the early part of the chosen decade is heavily influenced by 1997–1998 El Niño/biomass burning years. The dependency on the selection of the years highlights the role of variability driven by chemical and meteorological processes. The observed spatial variability of the trends could reflect the sphere of influence of the 2003 event (Vautard et al., 2005).

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European trends in NO_x and VOC emissions from the EMEP inventory show near uniform decrease in ozone precursor emissions (apart from increases in NO_x in south-western Europe) across Europe which are not directly reflected in the observed ozone trends.

The average ozone seasonal cycle over Europe (from these 158 stations as shown in Fig. 7) displays a spring maximum for the 5th percentile and both a high spring maximum with a secondary summer maximum for the mean and 95th percentiles. There are positive seasonal ozone trends in spring, summer and autumn in 5th and 95th percentiles. The highest magnitude trend in 5th percentile and mean O_3 are observed in winter (0.26 ± 0.07 ppbv yr^{-1}, 2σ error) and 0.26 ± 0.07 ppbv yr^{-1}, respectively. The highest trend out of all seasons was found in spring 95th percentiles (0.31 ± 0.09 ppbv yr^{-1}) and the summer 95th percentile was also high (0.24 ± 0.10 ppbv yr^{-1}) and these periods of high photochemical activity would suggest an increase in ozone precursor build up and photolysis over the years. Mean, 5th and 95th percentile autumn ozone trends are negative, with the greatest negative magnitude observed in the 95th percentile (-0.20 ± 0.09 ppbv yr^{-1}).

Simulated ozone was extracted at the coordinates of the 158 measurement stations from the CHIMERE regional chemistry transport model. The CHIMERE model displays small positive annual trends in European-averaged mean ozone (0.05 ± 0.01 ppbv yr^{-1}) and 5th percentiles (0.13 ± 0.01 ppbv yr^{-1}), with annual trends in 5th percentiles closely matching that of European-average observed trends. It is noted that CHIMERE tends to overestimate the ozone levels in summer months relative to observed ozone, consequently CHIMERE European-averaged trends in 95th percentiles (-0.03 ± 0.02 ppbv yr^{-1}, 2σ error) do not match those in observed ozone (0.16 ± 0.03 ppbv yr^{-1}).

The ensemble approach of using many regional background sites does seem a robust way of exploring regional ozone trends. The ability to use distribution statistics on

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these ensembles as a way of challenging models needs to be explored further.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/18433/2011/ acpd-11-18433-2011-supplement.pdf.

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Table 1. Mean trends by country from this study (bold) compared to literature values with 95 % confidence limits given, standard error given in square brackets. N = number of measurement sites used to calculate the average trend. Sig = significance of trend, where ⋄ statistically significant ($p < 0.1$), ⊕ not statistically significant ($p > 0.1$) and – not stated.

Country	Period	N	Trend (% yr^{-1})	Sig.	N	Trend (ppbv yr^{-1})	Sig.
Austria	1995–2004[1]				1	0.12 ± 0.34	⋄
	1994–2003[1]				1	0.25 ± 0.24	⋄
	1996–2005	**32**	**1.76**	⋄	**32**	**0.41**	⋄
Belgium	**1996–2005**	**7**	**0.23**	⋄	**8**	**0.14**	⋄
Czech Republic	**1996–2005**	**6**	**0.61**	⋄	**6**	**0.15**	⋄
Estonia	**1996–2005**	**1**	**−1.15**	⋄	**1**	**−0.38**	⋄
France	1995–2003[2]	9	0.6 ± 1.3	–			
	1997–2003[2]	1	2.00	⋄			
	1995–2003[2]	7	−0.48	⊕			
	1997–2005[3]	1	1.6	⊕			
	1996–2005	**1**	**0.95**	⋄	**1**	**0.29**	⋄
Germany	1995–2004[1]				1	0.03 ± 0.39	⋄
	1994–2003[1]				1	0.30 ± 0.38	⋄
	1978–2004[4]	1	12.6 [±0.8] %/decade	–			
	1996–2005	**24**	**1.27**	⋄	**21**	**0.25**	⋄
Great Britain	1990–2006[5]				12	0.56	-
	2000–2007[6]				1	0.07 [±0.15]	⊕
	1996–2005	**9**	**1.48**	⋄	**9**	**0.3**	⋄
Greece	1998–2002[7]				1	−3.4 ± [0.2]	⋄

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Table 1. Continued.

Country	Period	*N*	Trend (% yr^{-1})	Sig.	*N*	Trend (ppbv yr^{-1})	Sig.
Hungary	1990–2002[8]				1	0.32	-
	1996–2005	**1**	**–4.11**	⋄	**1**	**–1.28**	⋄
Ireland	1995–2007[6]				1	−0.12 [±0.07]	⋄
	2001–2007[6]				1	−0.05 [±0.15]	⊕
	2000–2007[6]				1	0.27 [±0.10]	not stated
	1995–2007[9]				1	0.31 ± 0.31	⋄
	1990–2004[10]				1	0.18 ± 0.04	⋄
	1996–2005	**1**	**–**	⊕	**1**	**–**	⊕
Italy	**1996–2005**	**1**	**6.05**	⋄	**1**	**0.23**	⋄
Lithuania	1988–2000[11]				1	0.56	–
	1996–2005	**1**	**1.14**	⋄	**1**	**0.31**	⋄
Latvia	**1996–2005**	**1**	**−1.92**	⋄	**1**	**−0.33**	⋄
Netherlands	**1996–2005**	**7**	**1.79**	⋄	**8**	**0.26**	⋄
Norway	**1996–2005**	**1**	**−0.87**	⋄	**1**	**−0.16**	⋄
Poland	**1996–2005**	**1**	**−1.38**	⋄	**1**	**−0.43**	⋄
Portugal	**1996–2005**	**1**	**–**	⊕	**1**	**–**	⊕
Slovenia	**1996–2005**	**1**	**−2.22**	⋄	**1**	**−0.24**	⋄
Spain	**1996–2005**	**5**	**−1.83**	⋄	**5**	**−0.54**	⋄
Switzerland	1995–2004[1]				1	0.34 ± 0.38	⋄
	1994–2003[1]				1	0.54 ± 0.36	⋄
	1991–1999[12]				4	0.58	–
	1996–2005	**5**	**1.76**	⋄	**5**	**0.21**	⋄

[1] Chevalier et al. (2007), [2] Sicard et al. (2009), [3] Sicard et al. (2010), [4] Oltmans et al. (2006), [5] Jenkin (2008), [6] Tripathi et al. (2010), [7] Gerasopoulos et al. (2005), [8] Haszpra et al. (2003), [9] Derwent et al. (2007b), [10] Carslaw (2005), [11] Gigzdiene and Girgzdys (2003), [12] Brönnimann et al. (2002)

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Table 2. Background sites selected from the GEOmon harmonised data set including their categorisation as per Henne et al. (2010).

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
AT0002R	Illmitz	16.77	47.77	117	rural
AT0004R	St. Koloman Kleinhorn	13.23	47.65	1005	rural
AT0005R	Vorhegg bei Kötschach-Mauthen	12.97	46.68	1020	valley/basin
AT0034R	Sonnblick	12.97	47.05	3106	elevated
AT0044A	Streithofen	15.94	48.28	220	rural
AT0052A	Piber	15.08	47.08	585	valley/basin
AT0054A	Schöneben	13.95	48.71	920	elevated
AT0058A	Zillertaler Alpen	11.87	47.14	1970	elevated
AT0064A	Innsbruck Nordkette	11.38	47.31	1910	elevated
AT0069A	Haunsberg	13.02	47.97	730	elevated
AT0073A	Grünbach bei Freistadt	14.57	48.53	918	elevated
AT0079A	Sonnblick	12.96	47.05	3106	elevated
AT0080A	St. Valentin Stein	14.56	48.23	242	rural
AT0086A	Kollmitzberg	14.87	48.18	465	rural
AT0089A	Karwendel West	11.23	47.34	1730	elevated
AT0094A	Hochgössnitz	15.02	47.06	900	rural
AT0095A	Mistelbach	16.58	48.58	250	rural
AT0096A	Forsthof am Schöpfl	15.92	48.11	581	rural/polluted
AT0101A	Heidenreichstein Thaures	15.05	48.88	560	rural
AT0102A	Wolkersdorf	16.52	48.39	190	rural/polluted
AT0103A	Stixneusiedl	16.68	48.05	210	rural/polluted
AT0105A	Irnfritz	15.5	48.72	556	rural
AT0108A	Masenberg	15.88	47.35	1137	elevated
AT0111A	Dunkelsteinerwald	15.55	48.37	305	rural/agricultural
AT0115A	Grundlsee	13.8	47.62	980	rural
AT0121A	Höfen Lächbichl	10.68	47.47	880	valley/basin
AT0122A	Kramsach Angerberg	11.91	47.46	600	valley/basin

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Table 2. Continued.

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
AT0124A	Gerlitzen Steinturm	13.90	46.68	1895	elevated
AT0128A	St. Georgen im Lavanttal-Herzogberg	14.89	46.71	540	rural
AT0134A	Annaberg-Joachimsberg	15.32	47.86	891	rural
AT0141A	Obervellach Schulzentrum	13.2	46.94	686	valley/basin
AT0143A	Bleiburg Koschatstrasse	14.8	46.59	480	rural
AT0146A	Stolzalpe bei Murau	14.2	47.13	1302	rural
AT0149A	Pillersdorf bei Retz	15.94	48.72	315	rural
AT0153A	Arnfels-Remschnigg	15.37	46.65	785	elevated
AT0154A	Wiesmath	16.29	47.61	738	elevated
AT0162A	Liezen	14.24	47.57	665	valley/basin
AT0164A	Oberwart-Brunnenfeld	16.19	47.3	330	rural
AT0166A	Zell am See Krankenhaus	12.81	47.34	770	valley/basin
AT0167A	Payerbach	15.85	47.67	890	rural
AT0175A	Klöch bei Bad Radkersburg	15.96	46.75	300	rural
AT0176A	Zöbelboden-Reichraminger Hintergebirge	14.44	47.84	899	elevated
AT0180A	Hochwurzen	13.63	47.36	1850	elevated
BE0032R	Eupen	6	50.63	295	rural/polluted
BE0033R	Moerkerke	3.36	51.26	3	rural/coastal
BE0035R	Vezin	4.99	50.5	160	rural/polluted
BE0211A	Gellik	5.62	50.88	70	suburban
BE0238A	Offagne	5.2	49.88	430	rural
BE0294A	Walshoutem	5.1	50.71	135	rural/polluted
BE0298A	Idegem	3.93	50.8	15	rural/polluted
BE0302A	Habay-la-n	5.63	49.72	375	rural
BE0304A	Dourbes	4.59	50.1	225	rural

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Table 2. Continued.

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
BE0311A	Saint-ode	5.59	50.03	510	rural
BE0345A	St.P.Leeuwg	4.23	50.77	20	suburban
CH0001R	Jungfraujoch	7.98	46.55	3573	elevated
CH0002R	Payerne	6.94	46.81	489	rural
CH0003R	Tänikon	8.9	47.48	539	rural/polluted
CH0004R	Chaumont	6.98	47.05	1137	elevated
CH0005R	Rigi-Seebodenalp	8.46	47.07	1031	elevated
CH0019A	St. Gallen Stuelegg	9.39	47.41	920	elevated
CH0024A	Saxon	7.15	46.14	460	valley/basin
CH0033A	Magadino-Cadenazzo	8.93	46.16	204	valley/basin
CMN	Monte Cimone	10.68	44.17	2165	elevated
CZ0001R	Svratouch	16.04	49.74	735	elevated
CZ0003R	Kosetice	15.08	49.57	535	rural
CZ0017A	Bily Kriz	18.54	49.5	890	elevated
CZ0030A	Sous	15.32	50.79	771	elevated
CZ0041A	Ondrejov	14.78	49.92	514	rural/polluted
CZ0045A	Kostelni Myslova	15.44	49.16	569	rural
CZ0049A	Churanov	13.61	49.07	1118	elevated
CZ0051A	Jesenik	17.19	50.24	625	elevated
CZ0055A	Krkonose-Rychory	15.85	50.66	1001	elevated
CZ0057A	Hojna Voda	14.72	48.72	818	elevated
CZ0062A	Rudolice v Horach	13.42	50.58	840	elevated
DE0003R	Schauinsland	7.91	47.91	1205	elevated
DE0007R	Neuglobsow	13.03	53.14	65	rural
DE0008R	Schmücke	10.77	50.65	937	elevated
DE0009R	Zingst	12.72	54.44	1	rural/coastal
DE0035R	Lückendorf	14.79	50.83	490	rural

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Table 2. Continued.

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
DE0422A	Riedstadt	8.52	49.83	87	rural/polluted
DE0510A	Neustadt a.d. Donau/Eining	11.78	48.85	359	rural
DE0514A	Mehring/Sportplatz	12.78	48.18	415	rural
DE0556A	Zinnwald	13.75	50.73	877	elevated
DE0649A	Grebenau	9.46	50.76	373	rural
DE0651A	Witzenhausen/Wald	9.77	51.29	610	elevated
DE0674A	Simmerath Eifel	6.28	50.65	572	elevated
DE0679A	Tiefenbach/Altenschneeberg	12.55	49.44	755	elevated
DE0680A	Horn-Bad Meinberg Egge	8.95	51.83	430	elevated
DE0684A	Schwarzwald Süd	7.76	47.81	920	elevated
DE0685A	Westpfalz-Waldmohr	7.29	49.42	455	elevated
DE0686A	Hunsrück-Leisel	7.19	49.74	650	elevated
DE0687A	Westeifel Wascheid	6.38	50.27	680	elevated
DE0688A	Westerwald-Herdorf	7.97	50.77	480	elevated
DE0699A	Welzheimer Wald	9.57	48.88	500	rural/polluted
DE0719A	Spessart	9.4	50.16	502	rural/polluted
DE0732A	Solling	9.58	51.76	500	elevated
DE0735A	Netphen Rothaargebirge	8.19	50.93	635	elevated
DE0737A	Pfälzerwald-Hortenkopf	7.83	49.27	606	elevated
DE0738A	Naila/Selbitzer Berg	11.72	50.32	534	rural
DE0739A	Fürth/Odenwald	8.82	49.65	484	rural/polluted
DE0754A	B Grunewald (3.5 m)	13.23	52.47	50	suburban
DE0844A	Bornhöved	10.24	54.09	45	rural/polluted
DE0874A	Soest-Ost	8.15	51.57	110	rural
DE0907A	Nidda	9	50.42	193	rural/polluted
DE0960A	Ueckermünde	14.07	53.74	1	rural/coastal
DE0996A	Wurmberg	10.61	51.76	930	elevated

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Table 2. Continued.

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
EE0011R	Vilsandi	21.85	58.38	6	remote
ES0007R	Viznar	−3.32	37.14	1265	elevated
ES1222A	Santa Maria de Palautordera	2.44	41.69	208	rural/polluted
ES1400A	Bujaraloz	−0.15	41.51	325	–
ES1435A	Vilafranca	−0.25	40.43	1125	rural
ES1437A	Coratxar	0.08	40.69	1200	rural
ES1441A	Morella	−0.09	40.64	1150	rural
FR08	Donon	7.13	48.5	775	elevated
GB0002R	Eskdalemuir	−3.21	55.32	269	rural
GB0006R	Lough Navar	−7.9	54.44	130	rural
GB0013R	Yarner Wood	−3.72	50.6	119	rural
GB0014R	High Muffles	−0.81	54.33	267	rural
GB0015R	Strath Vaich	−4.78	57.73	270	remote
GB0031R	Aston Hill	−3.33	52.5	370	rural
GB0033R	Bush Estate	−3.21	55.86	180	suburban
GB0036R	Harwell	−1.33	51.57	137	rural
GB0037R	Lady Bower	−1.75	53.4	420	rural/polluted
GB0038R	Lullington Heath	0.18	50.79	125	rural/coastal
GB0039R	Sibton	1.46	52.29	46	rural/coastal
GB0044R	Somerton	−2.74	51.04	55	rural
GB0045R	Wicken Fen	−0.29	52.3	5	rural/polluted
GB0617A	Rochester Stoke	0.63	51.46	14	rural/polluted
HPB	Hohenpeissenberg	11.02	47.8	985	elevated
HU0002R	K-puszta	19.55	46.97	125	rural/agricultural
IE31	Mace Head	−9.9	53.33	25	remote
IT04	Ispra	8.63	45.8	209	valley/basin
LT0015R	Preila	21.03	55.38	5	rural/coastal

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Table 2. Continued.

ID	Station	Longitude (°)	Latitude (°)	Altitude (m a.s.l.)	GEOmon Category
LV0010R	Rucava	21.17	56.16	18	rural
NL0007R	Eibergen-Lintveldseweg	6.61	52.09	19	rural
NL0009R	Kollumerwaard-Hooge Zuidwal	6.28	53.33	1	rural/coastal
NL0010R	Vredepeel-Vredeweg	5.85	51.54	28	rural/polluted
NL0196A	Budel-Toom	5.56	51.27	32	rural/polluted
NL0198A	Zierikzee-Lange Slikweg	3.92	51.64	−1	rural/coastal
NL0202A	Posterholt-Vlodropperweg	6.04	51.12	32	rural/polluted
NL0205A	Hellendoorn-Luttenbergerweg	6.4	52.39	7	rural
NL0207A	Balk-Trophornsterweg	5.57	52.92	0	rural/coastal
NL0209A	Cabauw-Zijdeweg	4.93	51.97	−1	rural/polluted
NL0220A	Philippine-Stelleweg	3.75	51.3	5	rural/coastal
NL0223A	Biest Houtakker-Biestsestraat	5.15	51.52	15	suburban
NL0226A	Westmaas-Groeneweg	4.45	51.79	0	rural/polluted
NL0227A	Wieringerwerf-Medemblikkerweg	5.05	52.8	−4	rural/coastal
NL0228A	Biddinghuizen-Hoekwantweg	5.62	52.45	−4	rural/coastal
NL0229A	Zegveld-Oude Meije	4.84	52.14	−2	rural/polluted
NL0231A	Barsbeek-De Veenen	6.02	52.66	0	rural
NL0232A	Huijbergen-Vennekenstraat	4.36	51.44	18	suburban
NL0250A	De Zilk-Vogelaarsdreef	4.51	52.3	4	rural/polluted
NO01	Birkenes	8.25	58.38	190	rural
PL03	Sniezka	15.74	50.74	1603	elevated
PT0004R	Monte Velho	−8.8	38.08	43	rural/coastal
PUY	Puy de Dome	3	45.75	1465	elevated
SI0008R	Iskrba	14.86	45.56	540	rural/agricultural
ZUG	Zugspitze	10.98	47.42	2950	elevated

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Table 3. Manual categorisation of O_3 time series by loess smoothing. NT – no trend, P – positive trend, N – negative trend, I + D increasing then decreasing levels, D + I – decreasing then increasing levels, C – complex behaviour.

O_3 Trends	NT	P	N	I + D	D + I	C	TOTAL
Austria (AT)	23	14	0	4	0	2	43
Belgium(BE)	8	2	0	1	0	0	11
Switzerland (CH)	7	0	0	0	0	1	8
Czech Republic (CZ)	7	3	0	0	0	1	11
Germany (DE, HPB, ZUG)	26	6	1	0	0	1	34
Estonia(EE)	0	0	1	0	0	0	1
France (FR, PUY)	1	0	0	0	0	1	2
Great Britain (GB)	4	3	0	2	1	4	14
Hungary (HU)	0	0	1	0	0	0	1
Ireland (IE)	1	0	0	0	0	0	1
Italy (IT, CMN)	2	0	0	0	0	0	2
Lithuania (LT)	0	1	0	0	0	0	1
Latvia (LV)	0	0	0	0	0	1	1
Netherlands (NL)	17	1	0	0	0	0	18
Norway (NO)	0	0	1	0	0	0	1
Poland (PL)	0	0	0	1	0	0	1
Portugal (PT)	0	0	0	0	0	1	1
Spain (ES)	1	0	3	0	0	2	6
Slovenia (SI)	0	0	1	0	0	0	1
TOTAL	97	30	8	8	1	14	158

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Table 4. A summary of European-averaged trends (where $N = 158$ sites) in O_3 mean, 5th and 95th percentiles during the period 1996–2005 with the exclusion of data from individual years. $N(+)$ and $N(-)$ the number of sites with significant ($p < 0.1$) positive and negative trends, respectively. Bold text highlights those years with high influence on trends during the overall 1996–2005 period, see text for details.

Excluded Year	Trend Mean	*N* (+)	*N* (−)	Trend 5th Percentile	*N* (+)	*N* (−)	Trend 95th Percentile	*N* (+)	*N* (−)
1996	0.14 ± 0.02	64	18	0.08 ± 0.02	56	21	0.18 ± 0.03	65	17
1997	**0.27 ± 0.02**	**104**	**15**	**0.24 ± 0.02**	**104**	**19**	**0.36 ± 0.03**	**101**	**11**
1998	**0.31 ± 0.02**	**109**	**4**	**0.26 ± 0.02**	**104**	**8**	**0.36 ± 0.03**	**96**	**4**
1999	**0.26 ± 0.02**	**107**	**11**	**0.20 ± 0.02**	**97**	**13**	**0.30 ± 0.03**	**95**	**6**
2000	0.19 ± 0.02	86	15	0.16 ± 0.02	84	16	0.21 ± 0.03	68	14
2001	0.14 ± 0.02	67	17	0.12 ± 0.02	72	22	0.13 ± 0.03	51	19
2002	0.09 ± 0.02	53	19	0.08 ± 0.02	62	23	0.05 ± 0.03	34	24
2003	**−0.04 ± 0.02**	**25**	**28**	**0.00 ± 0.02**	**38**	**33**	**−0.14 ± 0.03**	**13**	**44**
2004	**0.02 ± 0.02**	**41**	**25**	**0.03 ± 0.02**	**45**	**31**	**−0.07 ± 0.03**	**23**	**37**
2005	0.20 ± 0.02	91	16	0.16 ± 0.02	82	13	0.19 ± 0.03	16	17
none	0.16 ± 0.02	85	18	0.13 ± 0.02	82	19	0.16 ± 0.03	71	19

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Table 5. Summary of the average European annual trends (ppbv yr^{-1}, with 2σ error) from observations at all 158 sites in Table 2 and the CHIMERE simulation. N = number of sites used to calculate European average.

Source	Period	Mean (ppbv yr^{-1})	5th Percentile (ppbv yr^{-1})	95th Percentile (ppbv yr^{-1})
Observations annual trend	1996–2005	0.16 ± 0.02	0.13 ± 0.02	0.16 ± 0.03
CHIMERE annual trend	1996–2005	0.05 ± 0.01	0.13 ± 0.01	−0.03 ± 0.02

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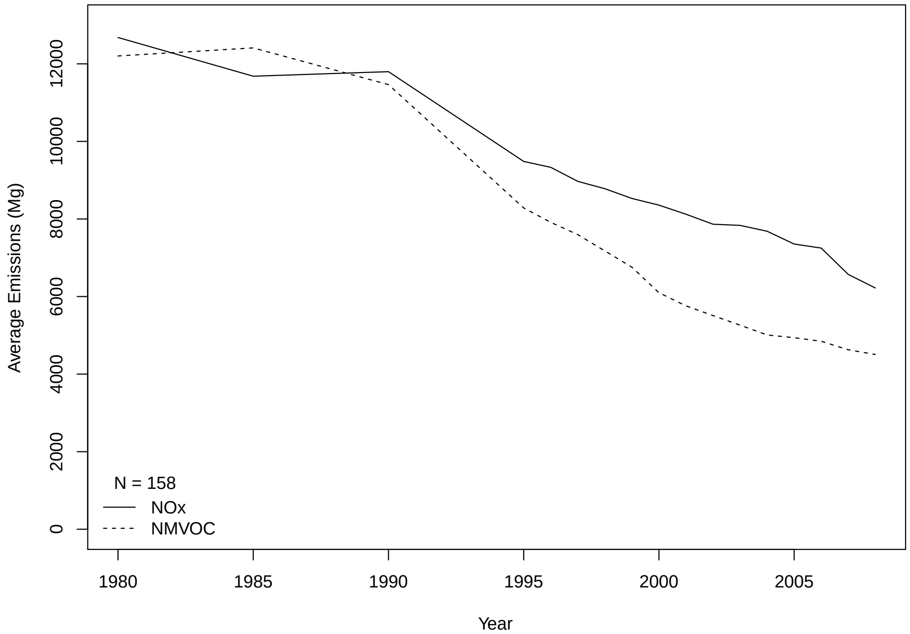

Fig. 1. The average anthropogenic NO_x and NMVOC emissions (from the EMEP emission inventory) 1980–2008 for the 158 sites used in this study.

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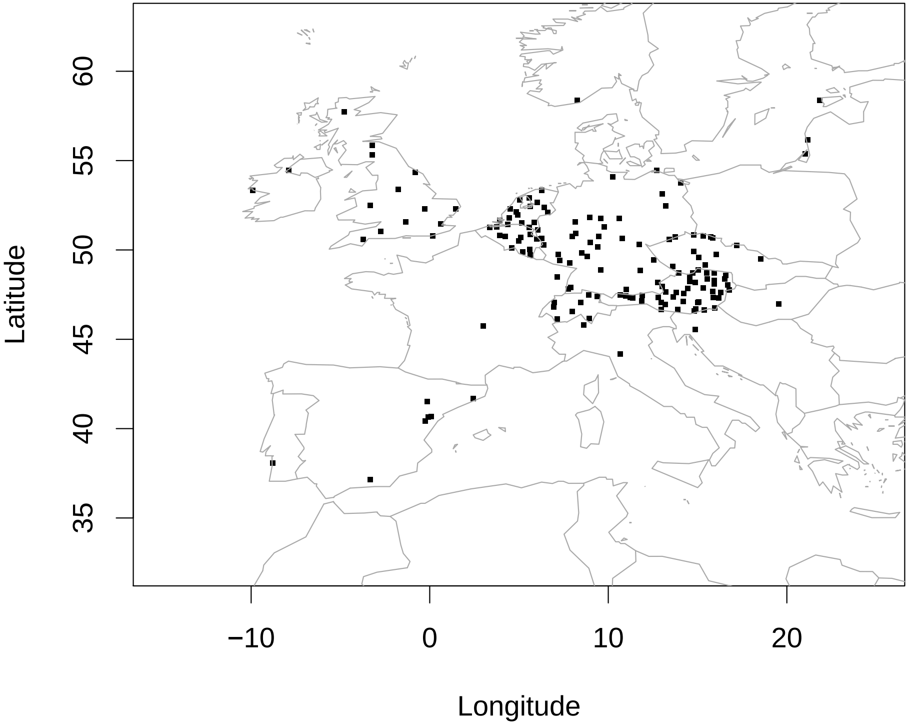

Fig. 2. Locations of the 158 measurement stations used in this study.

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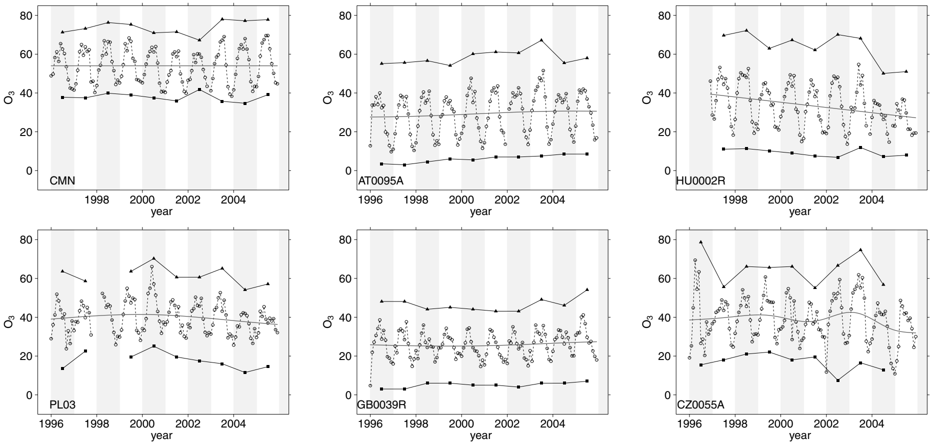

Fig. 3. Examples of categorised loess trends of observed monthly mean O_3 (ppbv yr^{-1}) (all sites available in Fig. A1 of the Supplement) displaying no trend (top left), increasing trend (top middle), decreasing trend (top right), increasing then decreasing trend (bottom left), decreasing then increasing trend (bottom middle right) and a complex trend (bottom right). Circles = monthly mean, squares = annual 5th percentile, triangle = annual 95th percentile, grey line = loess trend of monthly mean.

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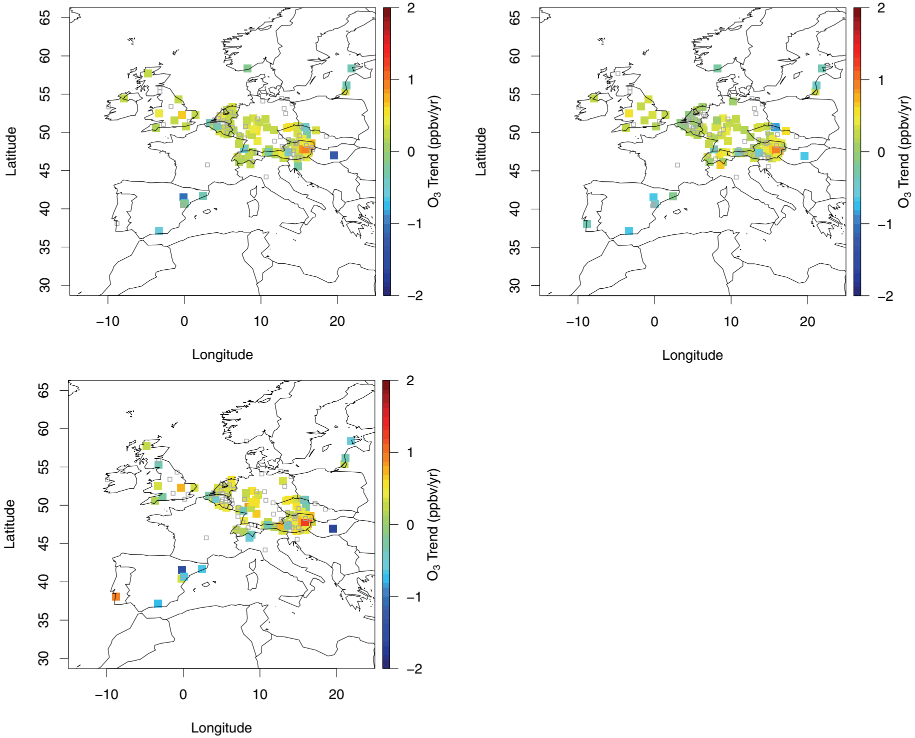

Fig. 4. Spatial distribution of statistically significant annual trends ($p < 0.1$) in observed O_3 mean (top left), 5th (top right) and 95th (bottom left) percentiles. Open squares represent sites with no statistically significant trends.

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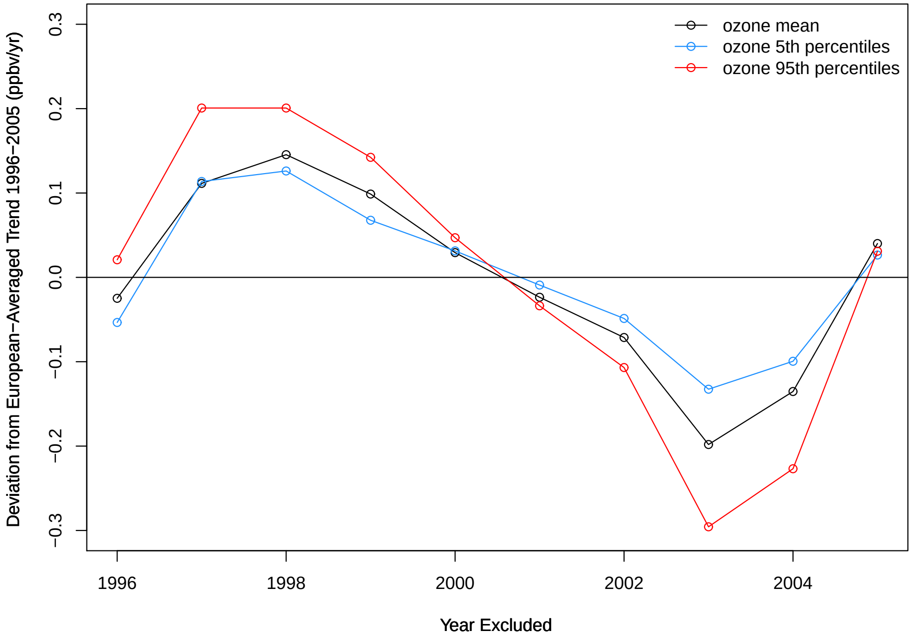

Fig. 5. The deviation from the 1996–2005 inclusive European-averaged annual trend in mean, 5th and 95thpercentiles when individual years are excluded from analysis.

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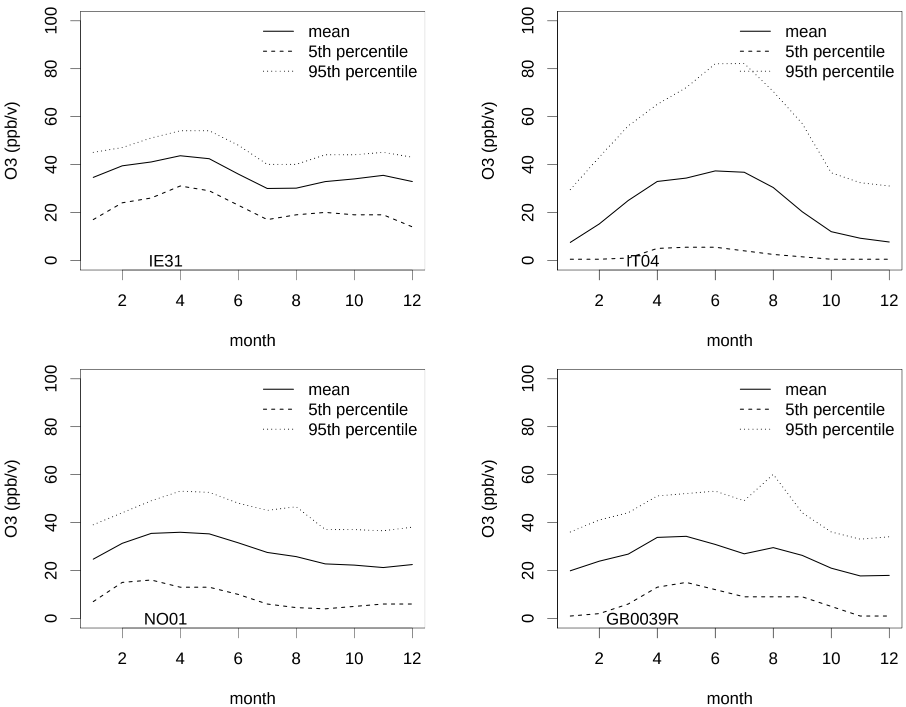

Fig. 6. Examples of seasonal cycles from IE31 (Mace Head), IT04 (Ispra), NO01 (Birkenes) and GB0039R (Sibton) showing (top left) spring maximum, (top right) broad spring-summer maximum, (bottom left) spring maximum with secondary summer maximum in 95th percentile and (bottom right) spring and summer maxima in mean, 5th and 95th percentiles. All sites are available in Fig. A2 of the Supplement.

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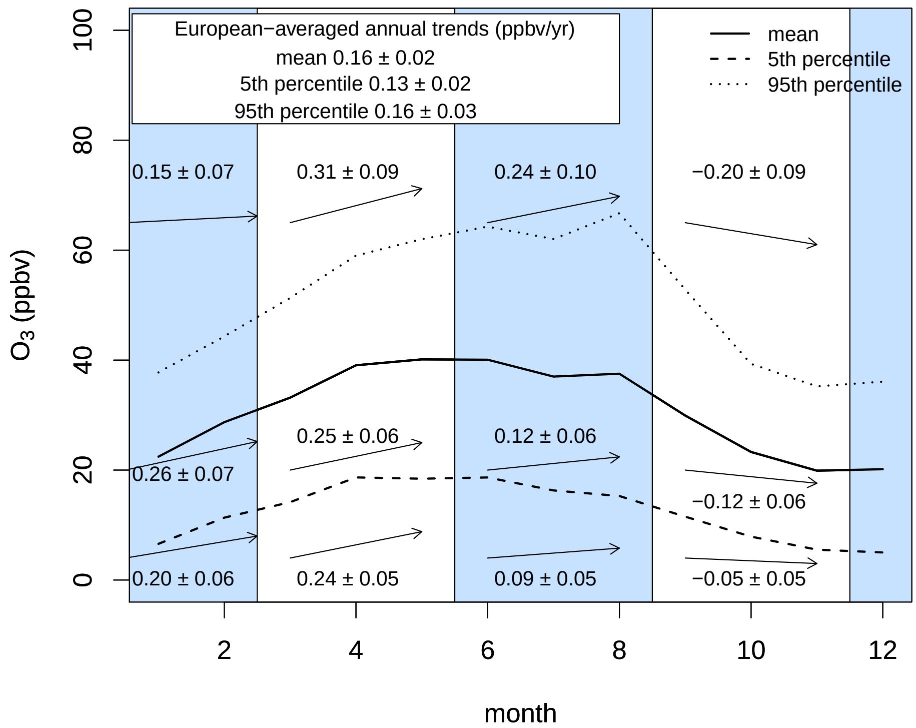

Fig. 7. The average European seasonal O_3 cycle for mean, 5th and 95th percentiles. Annotations display the statistically significant ($p < 0.1$) European-averaged seasonal (winter, spring summer, autumn) and annual trends in ppbv yr^{-1} (2σ errors).

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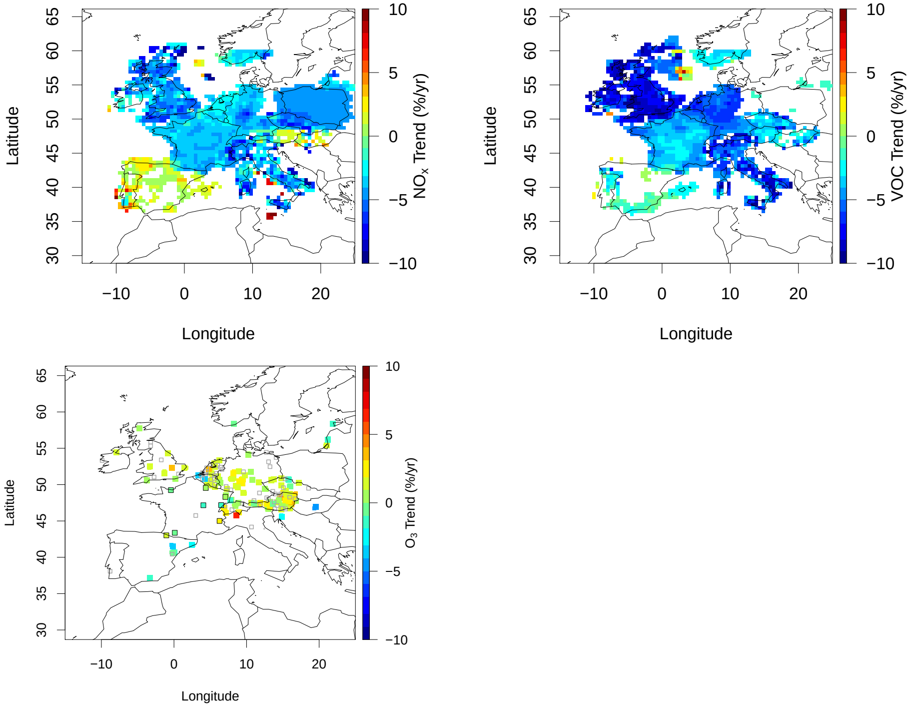

Fig. 8. Spatial distribution of significant ($p < 0.1$) annual trends (between −10 to 10 % yr^{-1}) in NO_x (top left), VOCs (top right) (both from the EMEP emission inventory, see text for details) and mean O_3 (bottom left) 1996–2005 inclusive. Open squares = sites with no statistically significant trends, black lined squares are O_3 surface data 1995–2003 inclusive from Sicard et al. (2009).

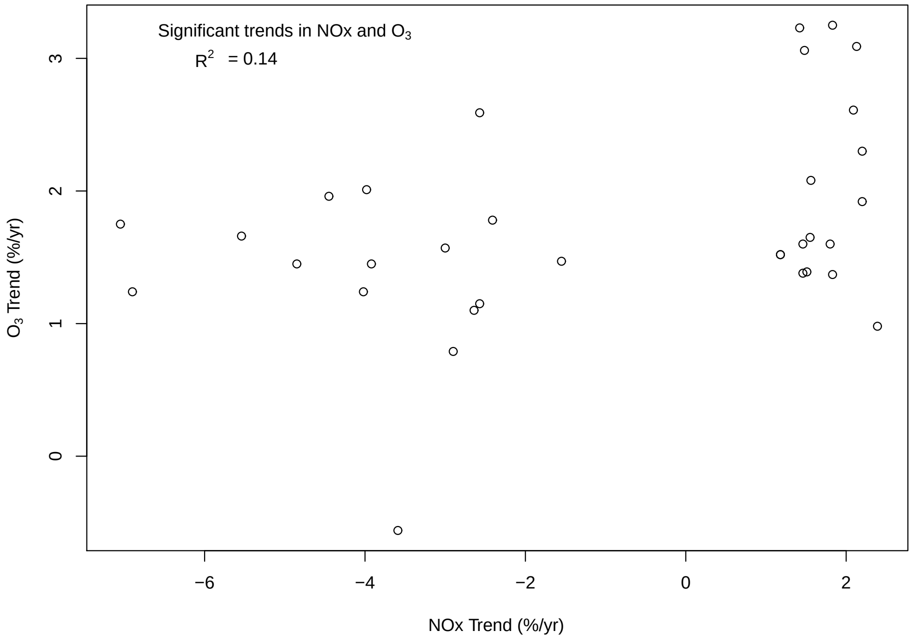

Fig. 9. Correlation of statistically significant annual trends in NO_x (from the EMEP emission inventory, see text for details) and observed O_3 (40 sites).

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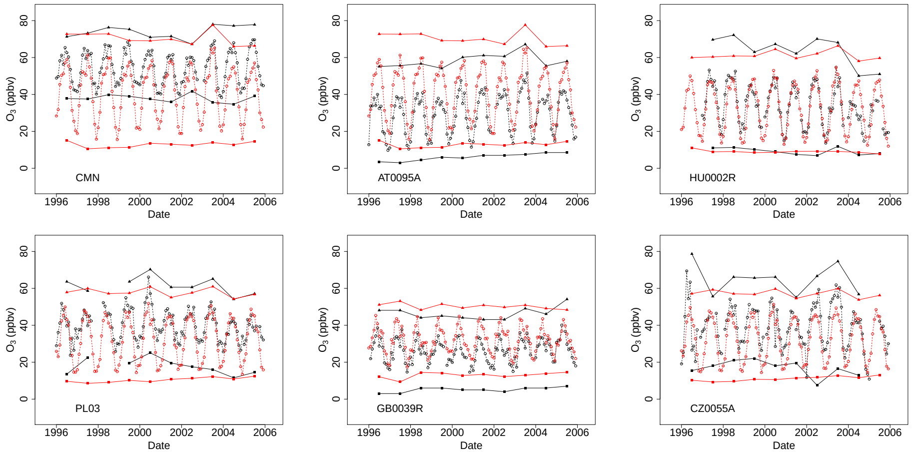

Fig. 10. Examples of loess trends of observed (black) and CHIMERE simulated (red) monthly mean O_3 (ppbv yr^{-1}) (Full observed sites given in Fig. A1 of the Supplement, full CHIMERE simulated sites given in Appendix B Fig. B1 of the Supplement). Circles = monthly mean, squares = annual 5th percentile, triangle = annual 95th percentile.

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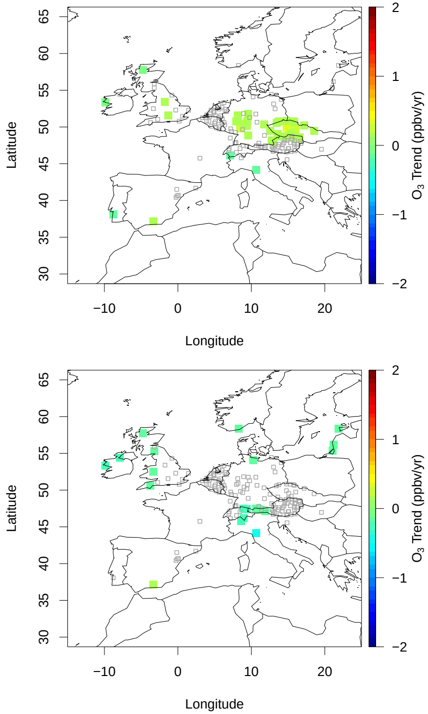

Fig. 11. Spatial distribution of significant ($p < 0.1$) annual CHIMERE modelled trends ($\mathrm{ppbv\,yr^{-1}}$) in O_3 mean (top left), 5th (top right) and 95th percentiles (bottom left) 1996–2005. Open squares = sites with no statistically significant trends.

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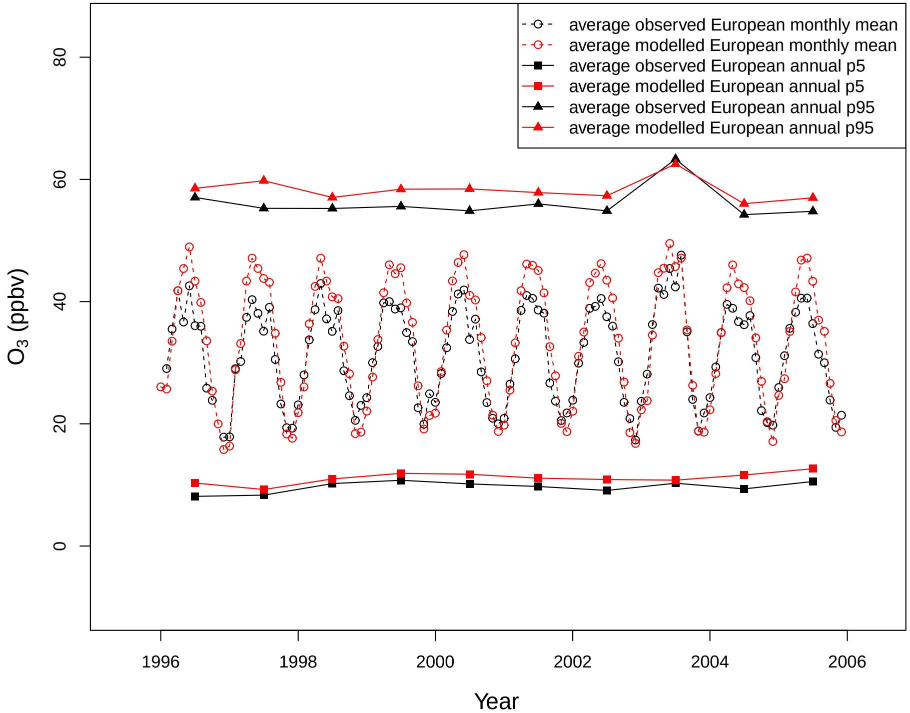

Fig. 12. A comparison of the European average O_3 observed monthly mean and annual 5th and 95th percentiles and the CHIMERE model output for all 158 site locations.

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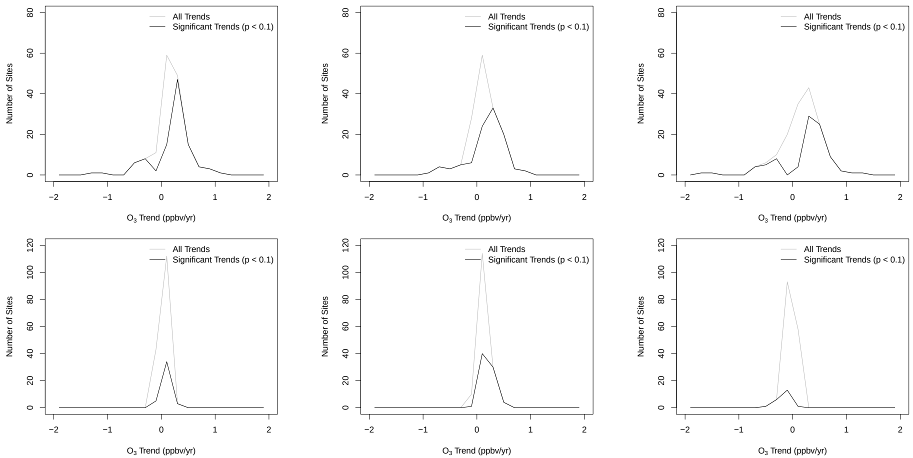

Fig. 13. A comparison of the frequency distribution of observed and CHIMERE annual O_3 trends.

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