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## Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites

J. A. Logan,<sup>1</sup> J. Staehelin,<sup>2</sup> I. A. Megretskaia,<sup>1</sup> J.-P. Cammas,<sup>3,4</sup> V. Thouret,<sup>3,4</sup> H. Claude,<sup>5</sup> H. De Backer,<sup>6</sup> M. Steinbacher,<sup>7</sup> H.-E. Scheel,<sup>8</sup> R. Stübi,<sup>9</sup> M. Fröhlich,<sup>10</sup> and R. Derwent<sup>11</sup>

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[1] We use ozone observations from sondes, regular aircraft, and alpine surface sites in a self-consistent analysis to determine robust changes in the time evolution of ozone over Europe. The data are most coherent since 1998, with similar interannual variability and trends. Ozone has decreased slowly since 1998, with an annual mean trend of  $-0.15$  ppb  $\text{yr}^{-1}$  at  $\sim 3$  km and the largest decrease in summer. There are some substantial differences between the sondes and other data, particularly in the early 1990s. The alpine and aircraft data show that ozone increased from late 1994 until 1998, but the sonde data do not. Time series of differences in ozone between pairs of locations reveal inconsistencies in various data sets. Differences as small as few ppb for 2–3 years lead to different trends for 1995–2008, when all data sets overlap. Sonde data from Hohenpeissenberg and in situ data from nearby Zugspitze show ozone increased by  $\sim 1$  ppb  $\text{yr}^{-1}$  during 1978–1989. We construct a mean alpine time series using data for Jungfrauoch, Zugspitze, and Sonnblick. Using Zugspitze data for 1978–1989, and the mean time series since 1990, we find that the ozone increased by 6.5–10 ppb in 1978–1989 and 2.5–4.5 ppb in the 1990s and decreased by 4 ppb in the 2000s in summer with no significant changes in other seasons. It is hard to reconcile all these changes with trends in emissions of ozone precursors, and in ozone in the lowermost stratosphere. We recommend data sets that are suitable for evaluation of model hindcasts.

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### 1. Introduction

[2] Ozone plays an important role in tropospheric chemistry and in the energy budget of the atmosphere, as well as having deleterious effects on human health and vegetation. Emissions of its precursors, nitrogen oxides ( $\text{NO}_x$ ), methane, carbon monoxide, and hydrocarbons increased dramatically after 1950 [e.g., *van Aardenne et al.*, 2001], leading to increases in tropospheric ozone [e.g., *Staehelin et al.*, 1994]. Efforts to improve air quality led to decreases in precursor emissions, particularly those of  $\text{NO}_x$ , from North America and Europe in the last 20 years, while  $\text{NO}_x$  emissions increased dramatically in Asia in the 21st century (<http://www.epa.gov/ttn/chief/trends>) [*Vestreng et al.*, 2009; *Zhang et al.*, 2009]. The lifetime of ozone is sufficiently long that

its burden over one continent is affected by emissions from the others [e.g., *Fiore et al.*, 2009; *Jonson et al.*, 2010], and there is great current interest in unraveling the effects of changes in precursor emissions, as well as changes in circulation, on the ozone distribution and its trends. Europe has a unique set of long-term ozone measurements above the boundary layer from balloon soundings, commercial aircraft, and alpine sites. We use these data to determine the robust changes in the temporal evolution of ozone above Europe and to recommend data sets to use for evaluation of model hindcasts.

[3] The first quantitative measurements of surface ozone were made from 1876 to 1910 at the Montsouris Observatory near Paris; ozone was about 10 ppb with a range of 6–15 ppb

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for annual mean values [Volz and Kley, 1988]. Ozone was measured continuously from 1956 to 1983 at Arkona, on the Baltic coast, and values increased from  $\sim 15$  ppb in the 1950s to 20–27 ppb in the last few years of the record [Feister and Warmbt, 1987]. Both sites used a wet chemical technique involving oxidation of ozone by the iodine ion, although the details differed. A disadvantage of both KI methods is that sulfur dioxide ( $\text{SO}_2$ ) interferes negatively with the measurement. Volz and Kley [1988] tried to remove data polluted by  $\text{SO}_2$  from nearby Paris by using local wind measurements.

[4] Ozone measurements at two sites in Arosa in the Swiss Alps in the 1950s showed annual mean values of  $\sim 20$  ppb, again using a KI method [Stahelin et al., 1994]. Ozone was also measured in Arosa during some clear nights in the 1930s, using long-path ultraviolet (UV) measurements. Ozone values were similar to those in the 1950s. The large increase in ozone precursor emissions in Europe (and elsewhere) took place after 1950 [e.g., Vestreng et al., 2009], so an increase in ozone prior to this would not be expected. Continuous measurements using UV-photometers (now the current standard method) started in Arosa in 1989, and showed an increase by about a factor of two between the 1950s and the early 1990s [Stahelin et al., 1994]. Similar increases were found in Europe when comparing measurements made until the end of the 1950s with measurements at similar altitudes in 1988–1991. The longest continuous surface ozone record at a rural site in central Europe started in 1971 at Hohenpeissenberg in southern Germany, and shows an increase for the first  $\sim 30$  years [Gilge et al., 2010]. The measurement technique changed from a KI method for the first 16 years to a chemiluminescence technique for 18 months, and then to UV instruments in mid-1988.

[5] In this study, we focus on ozone measurements above 2 km, in an effort to avoid sites that are influenced by local air pollution, and also to avoid the strong vertical gradient in ozone in the lowest kilometer of the atmosphere [e.g., Chevalier et al., 2007]. Thus we rely on measurements from ozonesondes, regular aircraft, and alpine stations. Previous studies have shown that the time series for profiles for European airports are similar to each other, with an increase from late 1994 until about 1998 [Zbinden et al., 2006], that mean profiles from aircraft at Frankfurt, Germany, and from sondes at Payerne, Switzerland, in the early 2000s are similar above the boundary layer [Chevalier et al., 2007] and that European alpine stations have similar time series since 1995 [Gilge et al., 2010]. The air masses above the sonde stations, airports, and alpine surface stations are not necessarily identical in their ozone content, and mountains sites are sometimes affected by boundary layer air and by local wind systems, but the data in Zbinden et al. [2006] and Gilge et al. [2010] suggest some degree of uniformity in ozone over central Europe on time scales of about a month.

[6] Three ozonesonde stations provide records of ozone over Europe since 1970: Hohenpeissenberg, Payerne, and Uccle (in Belgium). All show increases in ozone from 1970 to 1990, but there are large deviations in the temporal evolution at the different stations [Logan, 1994; Logan et al., 1999]. The Hohenpeissenberg record shows a decrease at 500 hPa since the mid-1980s [Oltmans et al., 2006]. The tropospheric part of the Payerne record has several inhomogeneities in the first three decades and is deemed unsuitable for deriving reliable trends in that period [Jeannot

et al., 2007]. The Uccle record required correction for  $\text{SO}_2$  interference until the mid-1980s [De Backer, 1999].

[7] The longest continuous surface ozone record at an alpine peak in Europe started at the Zugspitze, Germany, in 1978, and shows a large increase in the earliest years [Oltmans et al., 2006]. Continuous surface measurements at the alpine sites of Jungfraujoch, Switzerland, and Sonnblick, Austria, began around 1990. The early years of data at Jungfraujoch showed an increase of 0.5–1 ppb  $\text{yr}^{-1}$ , depending on the period chosen [Zanis et al., 1999; Brönnimann et al., 2002; Cui et al., 2011]. The general time evolution of ozone is similar at the three alpine sites, with an increase during the 1990s and stabilization after around 2000 [Ordóñez et al., 2007; Gilge et al., 2010]. Ozone at the marine site of Mace Head, on the west coast of Ireland, also shows increasing values from its inception in 1987 until the late 1990s, with no increase thereafter [Derwent et al., 2007]. The data from Zugspitze, Jungfraujoch, the Hohenpeissenberg surface site, and Arkona, along with more recent data from nearby Zingst, were used to evaluate trends in ozone over Europe in the recent HTAP (hemispheric transport of air pollution) assessment [Task Force on HTAP, 2010]. That study also found that ozone increased until about 2000 in central Europe and leveled off thereafter, with increases of 0.3–0.7 ppb  $\text{yr}^{-1}$  for the various sites.

[8] The main goal of this study is to use the data from sondes, aircraft, and alpine sites in a self-consistent analysis, to determine robust changes in the time evolution of ozone over Europe after 1990. We also address ozone trends in the preceding decade. We describe the data used in this study in Section 2. In Section 3 we discuss the different time series and their consistency, and present trends for various periods. We recommend which data sets to use for model evaluation. We discuss our results in the context of current understanding of influences on ozone trends in Section 4.

## 2. Data and Methodology

[9] Ozonesonde data were obtained from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC, <http://www.woudc.org>), and were current as of February, 2011. Details for the six stations in Europe are given in Table 1a, with their locations shown in Figure 1. We focus mainly on the stations that make measurements 2–3 times a week. Of these, Brewer Mast (BM) sondes were used for the entire record at Hohenpeissenberg. We note that revised data (for 1994 onwards) for this station were posted at WOUDC in July 2010, and are used here. Both Uccle and Payerne used BM sondes for many years, but changed to electrochemical concentration cell (ECC) sondes in March 1997 and August 2002 respectively. Both sonde types are based on the reaction of KI with ozone. The sonde techniques, data treatment, and errors are discussed in *World Meteorological Organization (WMO)* [1998], Logan [1999], Smit et al. [2007], and Schnadt Poberaj et al. [2009]. Jeannot et al. [2007] describe the quality of the Payerne BM record, and note problems with the data from April 1990 to March 1993 that were partially corrected using a statistical technique. Dual flights of BM and ECC sondes were made at Uccle and Payerne before changing sonde type, and showed mean differences of less than 3% in the mid-troposphere [De Backer et al., 1998; Stübi et al., 2008]. Comparisons of

**Table 1a.** Information About Ozone Sonde Stations

	Latitude	Longitude	Altitude (m)	Sonde Type	Number per Week	ECC Start Date	Scaled to Column
Hohenpeissenberg	47.8	11.0	960	BM	2–3 <sup>a</sup>		Yes
Payerne	46.7	6.6	486	BM/ECC	3	9/2/2002	BM: Yes ECC: No
Uccle	50.8	4.4	85	BM/ECC	3	4/5/1997	Yes
De Bilt	52.1	5.2	4	ECC	1	11/26/1997	No
Lindenberg	52.2	14.1	97	ECC	1	7/1/1992	Yes
Legionowo	52.4	21.0	81	ECC	1	6/9/1993	No

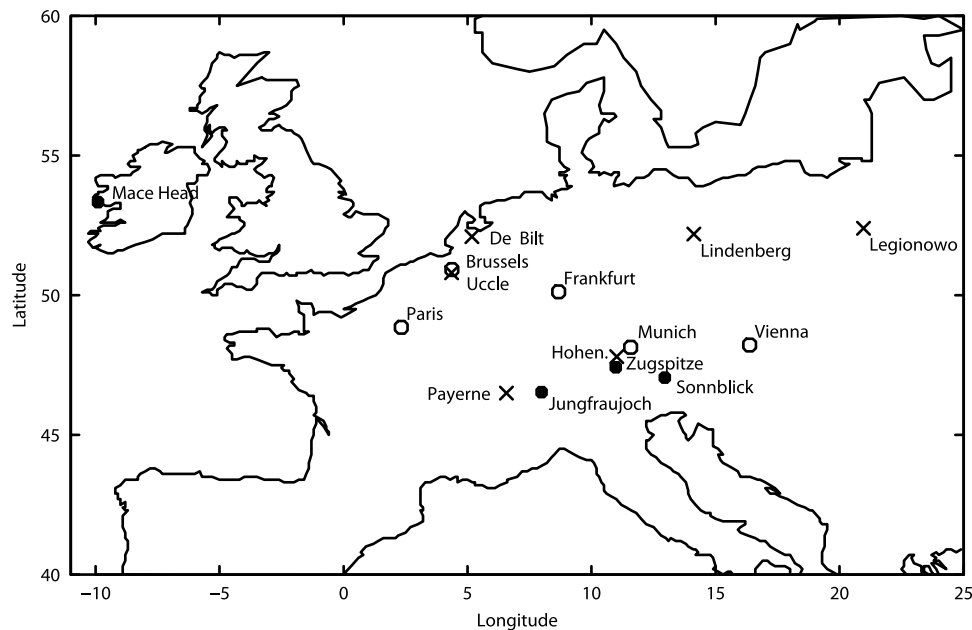
<sup>a</sup>Three per week in December to April, two per week in May to November.

ECC sondes with a UV photometer in an environmental chamber showed that the sondes were biased high compared to the UV measurement in the tropospheric part of the simulated profile [Smit *et al.*, 2007]. The mean bias was 3–8% at 0–5 km and 2–15% at 5–10 km for tests in 1996, 1998, and 2000, for the ENSI-Z sondes that are used at Payerne and Uccle. For BM sondes that were tested only in 1996, the sondes were biased low in the troposphere by ~2–3%, but with a larger scatter than for ECC sondes which had much better precision, about  $\pm(3\text{--}5)\%$  [Smit and Kley, 1998; Smit *et al.*, 2007]. Earlier intercomparisons held from 1970 to 1989 had shown that ECC sondes measured 15–20% more ozone than BM sondes in the middle troposphere, as reviewed by Logan [1999], but the tests in 1996 indicated differences of only ~5%, so there appears to have been changes in the response of at least one of the sonde types to tropospheric ozone. Vömel and Diaz [2010] show that the interpretation of the background current in ECC sondes may have an impact on the accuracy of the measurements at low ozone concentrations.

[10] It is standard practice at many sonde stations to scale the integrated ozone profile to a ground-based measurement of the ozone column (allowing for the ozone above the top of the sounding), and this is done at Hohenpeissenberg (all profiles), and for the BM profiles at Payerne. The

Payerne ECC data are not scaled to the ozone column. At Uccle, both for BM and ECC sondes, the correction factor is measured under laboratory conditions and the scaling is done by adjusting the pump efficiency profile [De Backer, 1999]. The scaling, or correction, factor (CF) is used as quality check, and we note that it is affected primarily by the ozone profile in the stratosphere. The CFs are provided with the data at WOUDC, even if they have not been applied. Here we use ECC profiles with a CF of 0.8–1.2, and BM profiles with a CF of 0.9–1.2 (Hohenpeissenberg) and 0.9–1.35 (Payerne and Uccle), with the larger range to accommodate higher mean values earlier in their records [Logan, 1994]. These requirements remove ~4% of the profiles at Hohenpeissenberg (75% before 1996), about 6% of the BM profiles at Uccle and Payerne, but only a few ECC profiles. Most CFs for ECC profiles from Payerne and Uccle are in the range 0.9–1.1.

[11] We also use data from stations that make weekly measurements with ECC sondes, Lindenberg, Legionowo, and De Bilt (Table 1a). The De Bilt data start in late 1992, while the other two stations used Brewer sondes made in the former East Germany in earlier years. The Brewer sondes were biased high in the troposphere by as much as 30% [e.g., Logan, 1994], so we do not consider them to be reliable and do not use them. The Lindenberg data are scaled to the



**Figure 1.** Locations of ozone measurement sites. Sonde locations are shown by a cross, MOZAIC airports by an open circle, and alpine and surface sites by a closed circle.

**Table 1b.** Information About Alpine/Surface Stations

	Latitude	Longitude	Altitude (m)	Start Date	UV Spectrometer Start Date
Jungfraujoch	46.5	8.0	3580	1/1/1988 <sup>a</sup>	start
Sonnblick	47.1	13.0	3106	10/1/1989	start
Zugspitze	47.4	11.0	2962	1/1/1978	1996 <sup>b</sup>
Hohenpeissenberg	47.8	11.0	985	- <sup>c</sup>	1988
Mace Head	53.3	-9.9	8	4/1/1987	start

<sup>a</sup>There are 3 months of data in 1986 and 2 months in 1987, but regular data with only small gaps starting in 1988. Ozone has been measured with two co-located instruments since March 1992.

<sup>b</sup>A chemiluminescence analyzer was used from 1978 to 1999, and UV spectrometers have been used since about 1996, with 2–3 instruments operated in parallel.

<sup>c</sup>Data are available from WDCGG for 1995–2007, but the surface site has operated since 1971.

ozone column data, but the profiles from the other two stations are not. The CF requirement removes 1% of profiles at Lindenberg, but only 0–1 at the other stations.

[12] Our analysis uses monthly means on a common vertical grid for the sonde and MOZAIC data. Both types of data are provided on a pressure grid, and we retain pressure as the vertical coordinate, noting that three-dimensional models also use a pressure grid. The profile data were averaged on 35 levels equally spaced in log pressure between 1000 and 5 hPa (~1 km apart). The mid-points of the pressure levels used in much of this work are 681, 584, 501, and 430 hPa, corresponding to altitudes of 3.23, 4.41, 5.55, and 6.66 km using the U.S. Standard Atmosphere; for these levels, the ozone data are averages for 2.6–3.8 km, 3.8–5 km, 5–6.1 km, and 6.1–7.2 km.

[13] We use the CFs as a filter to omit sonde profiles outside the selected ranges, and form monthly means for each level. For the stations with 2–3 profiles per week, we required 6 in a month to be included in the analysis, and for those with weekly profiles, we required 3 in a month. This requirement removes data for 13 months for Hohenpeissenberg (12 in 1990–1994 and one in 1995), 6 months for Payerne (all in 1990–1994), none for Uccle, and 2, 11, and 13 months for Lindenberg, Legionowo, and De Bilt, respectively.

[14] The MOZAIC profiles are provided on a flight by flight basis for ascents from and descents into airports, within ~400 km of the airport (<http://mozaic.aero.obs-mip.fr>). Ozone is measured using a dual-beam UV analyzer, with estimated accuracy of  $\pm[2 \text{ ppb}+2\%]$  [Thouret *et al.*, 1998]. The data are given as averages on a 150 m geopotential height grid for a standard atmosphere, so are on a pressure grid. The MOZAIC data start in August 1994, and we use data up to the end of 2008, as data for only 3 months of 2009 had been released when our analysis was done; also, there is a data gap of a year after October, 2009. There were instruments on five aircraft until 2005, and on three until 2008, and all the flights originated or ended in Europe. The most complete time series is for Frankfurt (1994–2008, with no data for 8 months, mainly in 2005), with shorter records for Vienna (1995–2006), Paris (1994–2004), Brussels (1997–2001), and Munich (2002–2005), with gaps of 13–24 months. The number of profiles per month is about 50–75 (or more) at Frankfurt except for 2001–2002, when there are often <50; there are about 25–45 profiles a month at Paris, Vienna, and Munich, except for 2001–2002 when there are often ~25 or less, and in 2005 there are ~40 to >100 at Munich; and there are about 35–55 profiles a month at Brussels. We required 20 ozone profiles in a month (10 days of data) for further analysis of individual stations. This

requirement removes 5–13 months with sparse data at individual airports, and 22 months at Vienna. Unlike the sonde data, which are distributed throughout a month, the months with very few MOZAIC profiles sometimes sample only a short part of the month.

[15] We formed a combined time series for Frankfurt and Munich (~300 km apart) for a more complete record in the period of overlap. This record has a gap of only 3 months, with 2 more months removed as they lacked 20 profiles. This is the most dense time series of ozone profiles in the world. Only 20 months in the 14 year record have <50 profiles, so most months have almost daily data. In addition we formed a European time series from the data for the 5 cities, weighted by the number of profiles at each in a given month. In this case only one month of data was removed because it lacked 20 profiles. Five months have <50 profiles, and almost 75% of months have over 100 profiles, but these cities cover a range of up to ~1000 km in some months, and the profiles may be further apart depending on the flight track.

[16] Surface data for two alpine sites, Jungfraujoch (1988–2009), and Sonnblick (1990–2009), were obtained from the World Data Centre for Greenhouse Gases (WDCGG, <http://gaw.kishou.go.jp/wdcgg>) as monthly means, while H. E. Scheel provided the monthly mean data from Zugspitze (1978–2009). We also obtained monthly mean surface data for Hohenpeissenberg Observatory (1995–2007) from WDCGG; these are used only for trend calculations, as the site at 985 m is in the planetary boundary layer and subject to local influences. These sites are part of the Global Atmosphere Watch (GAW) program of the WMO. Details about the alpine/surface sites are given in Table 1b. Ozone has been measured by UV absorption for the entire record at Jungfraujoch and Sonnblick. Two instruments have been operated in parallel at Jungfraujoch since March 1992. A chemiluminescence analyzer was used at Zugspitze until 1999, and UV absorption has been used since about 1996; two or three instruments are operated in parallel. The GAW stations have been audited regularly since 1996 by the World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide, hosted by Swiss Federal Laboratories for Materials Science and Technology (Empa). The audits determined that data quality at the alpine stations was “good” in terms of the WMO/GAW Data Quality Objectives (DQOs), 1.8 ppb +2% for ozone <20 ppb, and 1.4 ppb +2% for ozone >20 ppb [Klausen *et al.*, 2003; Buchmann *et al.*, 2009; Zellweger *et al.*, 2011]. We note that these are not particularly strict criteria. The audit at Hohenpeissenberg in 1997 revealed a discrepancy of 3%, which required an adjustment of the data. Calibration and audits

performed since the mid-1990s are also described in *Gilge et al.* [2010], which gives further details about these sites. A standard reference photometer was used in the Swiss network that includes Jungfraujoch starting in 1993, and prior to this the data were referenced to an ozone transfer instrument from Monitor Labs that was calibrated by the manufacturer. Quality assurance procedures were less sophisticated in the early years of operation of the Swiss network. *Zanis et al.* [1999] argued that ozone measurements at Jungfraujoch prior to fall 1989 are suspicious, based on a statistical analysis of differences with Zugspitze.

[17] The alpine sites are sometimes influenced by boundary layer air. Studies quantifying the boundary layer influence (or the influence of regional pollution) at Jungfraujoch conclude that it is smallest in winter (6–30% of the time) with synoptic lofting as the main cause, and largest in summer (48–60% of the time) with convection the main cause [*Zellweger et al.*, 2003; *Cui et al.*, 2011; *Collaud Coen et al.*, 2011]. These results were based on various types of meteorological analyses, including back trajectories. Such studies are not available for Zugspitze and Sonnblick.

[18] We did not attempt to filter the alpine data in any way. *Zellweger et al.* [2003] showed that the mean difference in ozone at Jungfraujoch for air they categorized as disturbed by regional pollution (as opposed to undisturbed) is 1–2 ppb, except in winter when ozone is ~5 ppb lower in disturbed air. *Cui et al.* [2011] find a difference of 1.8 ppb in winter and 3.8 ppb in summer. The region used in the analysis by *Collaud Coen et al.* [2011] included Payerne, Hohenpeissenberg, and Zugspitze, and the lofting mechanisms in the studies cited above would likely affect the alpine sonde data at 3 km. The diurnal variation of ozone at Jungfraujoch and Zugspitze is very small, 2–3 ppb in spring and summer, less in winter and autumn [*Zellweger et al.*, 2003; *Scheel et al.*, 1994], and we find a slightly larger diurnal amplitude at Sonnblick in summer only (~5 ppb). Ozone is slightly higher at night. There may be local topographic influences on ozone at the alpine peaks, but the small diurnal amplitudes and the comparisons to sonde data shown below suggest that these are not of great concern for our analysis. Any filtering of alpine surface data would have to be applied to profile data in the region at the same altitude.

[19] We also show data for Mace Head, a remote site on the west coast of Ireland. *Derwent et al.* [2007] derived “baseline” data for this site using coincident measurements of halocarbons and carbon monoxide to remove polluted air for 1989–1997, and a Lagrangian dispersion model thereafter. For this work, R. Derwent provided an updated time series for baseline data that were filtered using the dispersion model for 1989–2009. Unfiltered data for 1990 onwards were obtained from the European Monitoring and Evaluation Program (EMEP) data center (<http://www.nilu.no/projects/ccc/emepdata.html>), and earlier data from R. Derwent.

[20] This analysis focuses on observations above 2 km and below the tropopause. Time series for the profile data sets are shown for the average of two levels in the lower troposphere (681 and 584 hPa, 2.6–5 km) and the middle troposphere (500 and 430 hPa, 5–7.2 km). *Logan* [1999] shows that the relative variability of tropospheric ozone in a given month is smallest between 700 and 400 hPa, with higher variability at lower altitudes, and near the tropopause. The average tropopause over Central Europe is between about

270 and 200 hPa (9.8–11.5 km) [e.g., *Logan*, 1999; *Zbinden et al.*, 2006]. Comparisons between the alpine data sites and profile data use the 681 hPa pressure level, 2.6–3.8 km.

[21] Trends in ozone are computed for all the pressure levels (~1 km resolution), and for the surface data. The linear regression model includes 12 monthly means and four seasonal trends (for DJF, MAM, JJA, and SON) [e.g., *Miller et al.*, 1995], i.e., the annual cycle and four seasonal trends are fit simultaneously. The model is unweighted, and we do not account for autocorrelation in the monthly means. More formally: let  $Y_t$  represent the time series of monthly ozone values.

$$Y_t = \sum_{i=1}^{12} \mu_i I_{i,t} + \sum_{s=1}^4 \omega_s I_{s,t} X_t + N_t \quad (1)$$

where  $Y_t$  is the monthly mean ozone value for month  $t$ ;  $I_{i,t}$  is an indicator series for the  $i$ th month of the year which equals 1 if the month corresponds to month  $I$  and zero otherwise;  $\mu_i$  is the monthly intercept;  $I_{s,t}$  is an indicator series for season  $s$ ;  $\omega_s$  is the trend for season  $s$  (in ppb yr<sup>-1</sup>) from the start of the time series;  $X_t$  is the time in years since the first month in the time series,  $t_0$ , and is equal to  $t - t_0$ ; and  $N_t$  is the residual noise. This method accommodates missing months of data. Annual trends are calculated from the four seasonal trends, and their standard errors from the covariance matrix of the seasonal trend estimates. Two standard errors are given for the trends in the text and figures below. When we refer to the change in ozone in the text, we mean the trend times the number of years involved.

[22] To accommodate the case where there is a change in the slope of ozone over time, we also fit seasonal mean time series using a quadratic polynomial for each season separately. Here  $Y_t$  is a time series of seasonal means, and

$$Y_t = \alpha X_t + \beta X_t^2 + \text{constant} + N_t \quad (2)$$

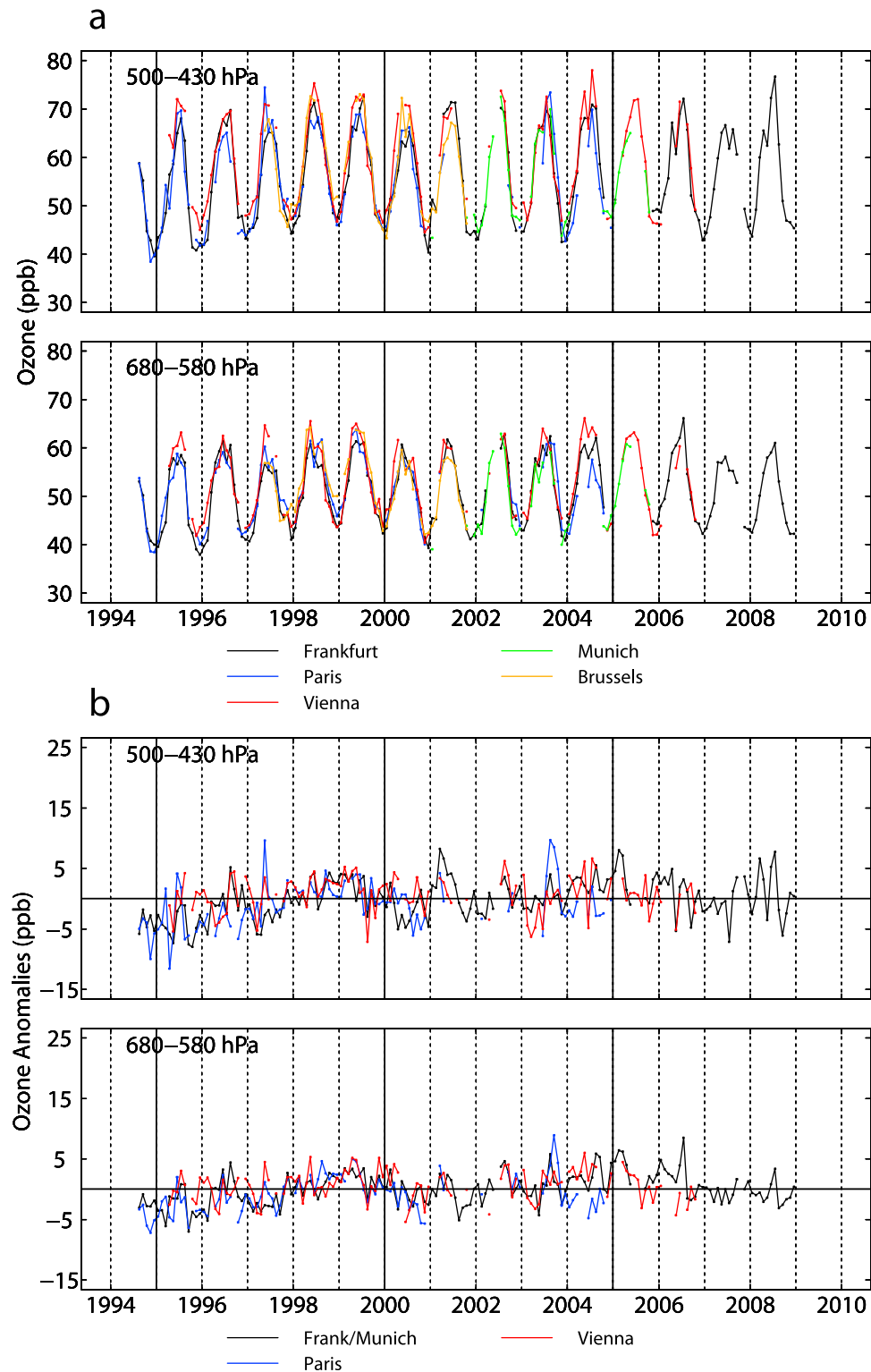
where  $X_t$  is time in years since the start of the time series and  $\alpha$  and  $\beta$  the respective coefficients for the linear and quadratic terms. We use the quadratic fit to compute the change in ozone between one year and another, and we compute the mean trend from the ozone change and the number of years.

### 3. Ozone Time Series and Trends

[23] The various alpine stations and profile sites are within a few hundred kilometers of each other, and many are closer (Figure 1). Distances between profile locations may change at higher altitudes, depending on the flight path of the aircraft or balloon. We first compare the time series of ozone for each measurement type, then make comparisons between measurement types, determine the robust features of the temporal evolution since 1990, and present trends in the data sets for various periods. We also discuss the behavior of ozone before 1990 using the early Zugspitze data and Hohenpeissenberg sonde data.

#### 3.1. Comparisons Within Measurement Types

[24] The monthly time series from the various MOZAIC airports in Europe are shown in Figure 2a for the lower and middle troposphere. Monthly differences between the various pairs of locations are usually <5 ppb, and the mean



**Figure 2.** (a) Time series of monthly mean ozone (in ppb) for MOZAIC data at European airports. (bottom) The mean of two layers centered at 681 and 584 hPa (2.6–5 km) and (top) the mean of layers centered at 501 and 430 hPa (5–7.2 km). (b) Monthly anomalies (in ppb), relative to the monthly means for January 1997 to December 2003.

biases are less than 1.9 ppb with a standard deviation ( $\sigma$ ) of 2.3–3.8 ppb for the lower troposphere as shown in Table 2. Biases in the middle troposphere are less than 3.4 ppb, with  $\sigma$  in the range 2.5–4.2 ppb. There is an increase in ozone for

both the winter minimum and summer maximum from 1994 until 1998 as shown by Zbinden *et al.* [2006], but ozone has been relatively constant since 1998. This is seen more clearly in Figure 2b, which shows the monthly anomalies

**Table 2.** Differences Between Pairs of Ozone Time Series (in ppb) for the Layers Shown in Figures 2–3, at 2.6–5 km and 5–7.2 km<sup>a</sup>

Station Pair	Period	681–580 hPa			501–430 hPa			n
		Mean Diff.	Std. Dev.	Std. Err.	Mean Diff.	Std. Dev.	Std. Err.	
<i>MOZAIC</i>								
Frankfurt-Vienna	1994–2006	–1.52	2.71	0.27	–2.57	3.17	0.32	100
Paris-Frankfurt	1994–2004	0.35	2.77	0.29	–0.62	3.86	0.41	90
Paris-Vienna	1995–2004	–1.51	3.44	0.4	–3.44	4.17	0.48	75
Brussels-Frankfurt	1997–2001	1.16	2.70	0.39	1.08	3.61	0.52	49
Brussels-Vienna	1997–2001	–0.24	3.84	0.59	–1.26	3.78	0.58	42
Brussels-Paris	1997–2001	0.48	2.40	0.39	1.16	3.68	0.60	38
Munich - Vienna	2001–2005	–1.49	2.43	0.52	–0.69	2.52	0.54	22
Frankfurt-Munich	2001–2004	1.88	2.29	0.50	–0.38	2.79	0.59	21
<i>Sondes</i>								
Payerne-Hohen.	1990–1992	–1.18	7.48	1.53	–5.61	8.44	1.80	24
	1993–2009	2.75	3.06	0.22	2.27	4.15	0.29	198
Uccle-Hohen.	1990–1992	0.70	4.99	0.96	–1.67	6.11	1.22	27
	1993–2006	3.53	4.06	0.32	2.80	5.02	0.39	164
	2007–2009	8.29	4.21	0.7	9.80	6.84	1.14	36
Uccle-Payerne	1990–1992	1.37	7.64	1.35	3.24	10.32	1.82	32
	1993–2006	0.50	3.78	0.29	–0.06	4.98	0.39	166
	2007–2009	6.84	3.35	0.56	10.0	6.71	1.12	36
<i>Sonde - MOZAIC</i>								
Payerne-Fran/Munich	1994–1996	6.37	2.20	0.41	9.87	3.56	0.66	29
	1997–1998	4.11	2.02	0.41	4.81	3.18	0.65	24
	1999–2008	0.94	2.84	0.26	1.65	3.77	0.35	115
Hohen.-Fran/Munich	1994–1996	4.11	2.04	0.39	6.51	2.87	0.54	28
	1997–2003	–0.27	2.92	0.32	1.02	3.73	0.41	83
	2004–2006	–4.37	2.89	0.50	–2.19	3.31	0.58	33
	2007–2008	–0.62	2.70	0.56	0.82	3.26	0.68	23
Uccle-Fran/Munich	1994–1996	5.69	4.75	0.88	8.30	7.04	1.31	29
	1997–2006	2.48	2.77	0.26	2.96	2.94	0.27	116
	2007–2008	7.7	3.53	0.74	10.28	6.67	1.39	23

<sup>a</sup>Biases for more than one period are given if time series plots of differences between the two time series showed a change in bias. The columns show the years, the mean bias, its standard deviation, and the standard error of the mean bias for both pairs of levels, with the number of paired months in the last column.

computed relative to the base period of January 1997 to December 2003, chosen to facilitate comparison to the anomalies for the sonde data; this figure uses the combined Frankfurt/Munich time series. The interannual variability of ozone is similar for 3–7 km. We describe the monthly MOZAIC time series as coherent because of the similarity of the time evolution at the various locations evident in Figure 2b and the small mean biases between locations, which for these data sets do not vary with time.

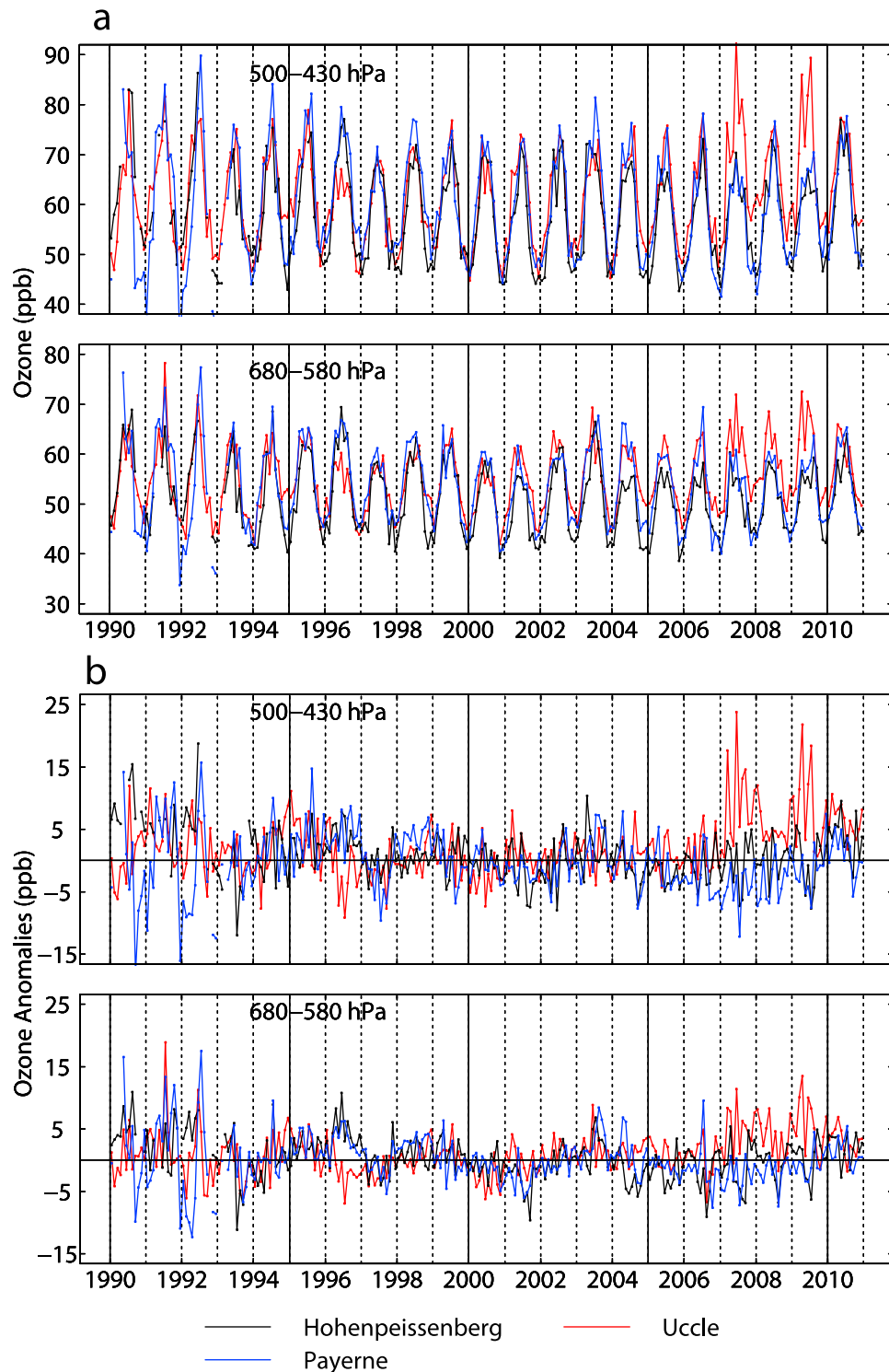
[25] Time series for the primary sonde stations since 1990 are shown in Figure 3. They are clearly less coherent than the MOZAIC locations, except for 1997–2003 when the interannual variability is similar to that in the MOZAIC data, with higher ozone in 1998–1999, lower ozone in 2000–2001, and highest ozone in mid-2003 (Figure 3b). Because of the similar temporal evolution, we show anomalies relative to 1997–2003 for the sonde and MOZAIC data. The sonde measurements are highly variable in much of 1990–1992 (see also Table 2). *Jeannot et al.* [2007] discuss the problems with the Payerne ozone data caused by a change in the meteorological sonde and electronic interface in April 1990. After 1992, the mean bias between Payerne and Hohenpeissenberg is 2.75 ppb ( $\sigma = 3.0$  ppb), only slightly larger than the biases between pairs of MOZAIC time series

in the lower troposphere (Table 2), and these two stations follow a similar time evolution. From 1993 to 1997, when all three stations were using BM sondes, Uccle is an outlier in mid-1996 in that ozone in the LT is lower than the other two sites by 5–13 ppb for 5 consecutive months, the only such occurrence. However, the mean bias between Uccle and the other two stations is small for 1993–2006, <3.5 ppb, with  $\sigma \approx 4.0$  ppb. None of the sonde stations show the increase in ozone between late 1994 and 1998 that is apparent in the MOZAIC data.

[26] Ozone is higher at Uccle in 2007–2009 than the other two stations by about 5–20 ppb, with mean biases of 7–10 ppb (Table 2), and it is higher also than measured at De Bilt which is only 155 km away (Figures 3 and 4), suggesting a problem with the data in this altitude range during those years. The procedures for the ozone sensor preparation at Uccle did not change during this time. The ground equipment for the reception of the radiosonde signals was upgraded in 2007, and the possible influence on the ozone measurements is under investigation by the station team in collaboration with the manufacturer.

[27] Figure 4 shows the time series for the weekly sonde stations since 1994, the first year for which they all have data. As expected, the time series are noisier than those for the sites



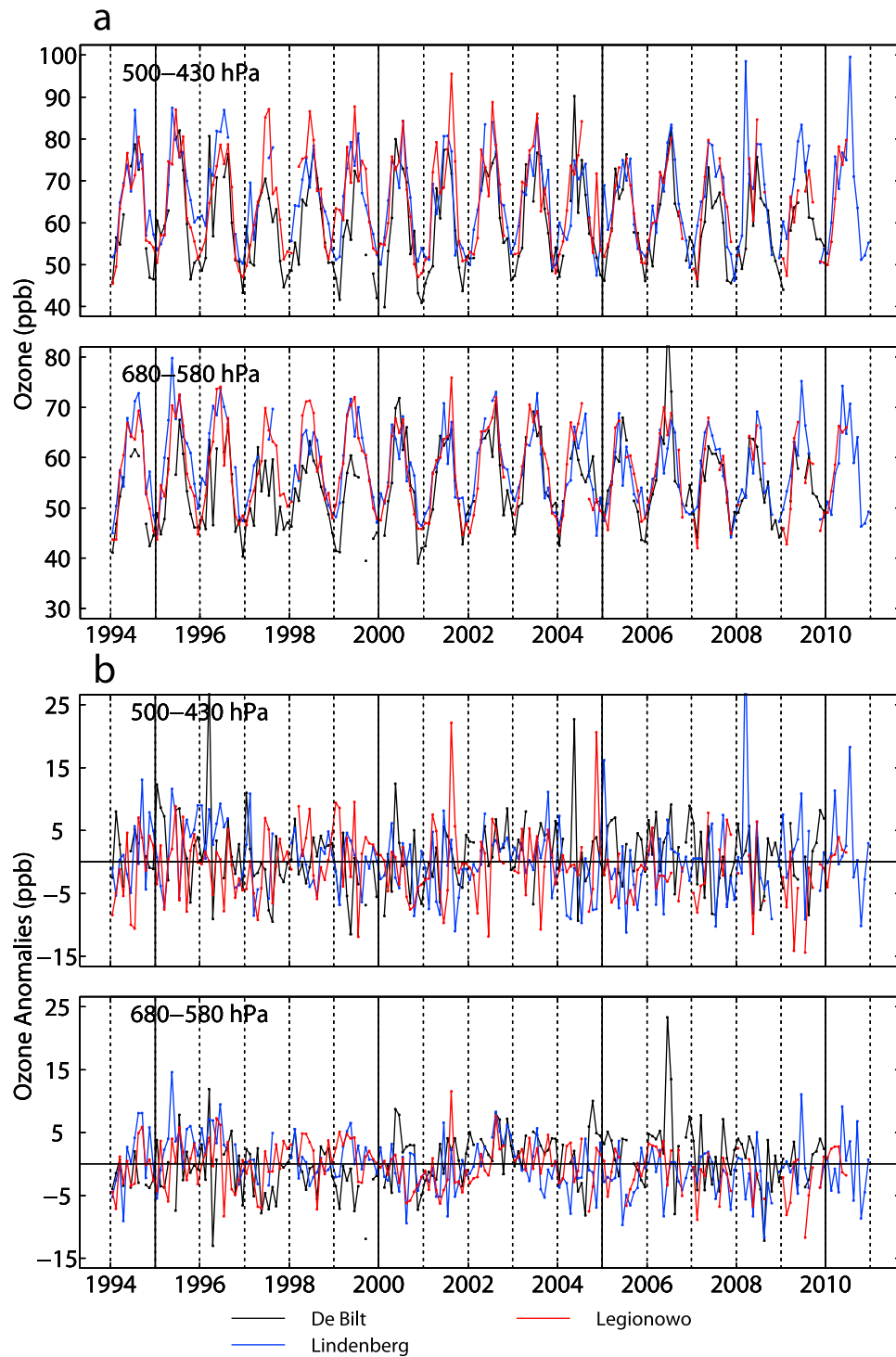


**Figure 3.** (a) Time series of monthly mean ozone (in ppb) for sonde stations with 2–3 profiles per week. (bottom) The mean of two layers centered at 681 and 584 hPa (2.6–5 km) and (top) the mean of layers centered at 501 and 430 hPa (5–7.2 km). (b) Monthly anomalies (in ppb) relative to the monthly means for January 1997 to December 2003.

with more frequent measurements. The ECC record from the weekly stations shows no evidence for an increase between 1994 and 1998, supporting the results from the BM stations.

Comparing Figures 3 and 4, none of the weekly sites show the anomalous behavior seen at Uccle in 2007–2009.

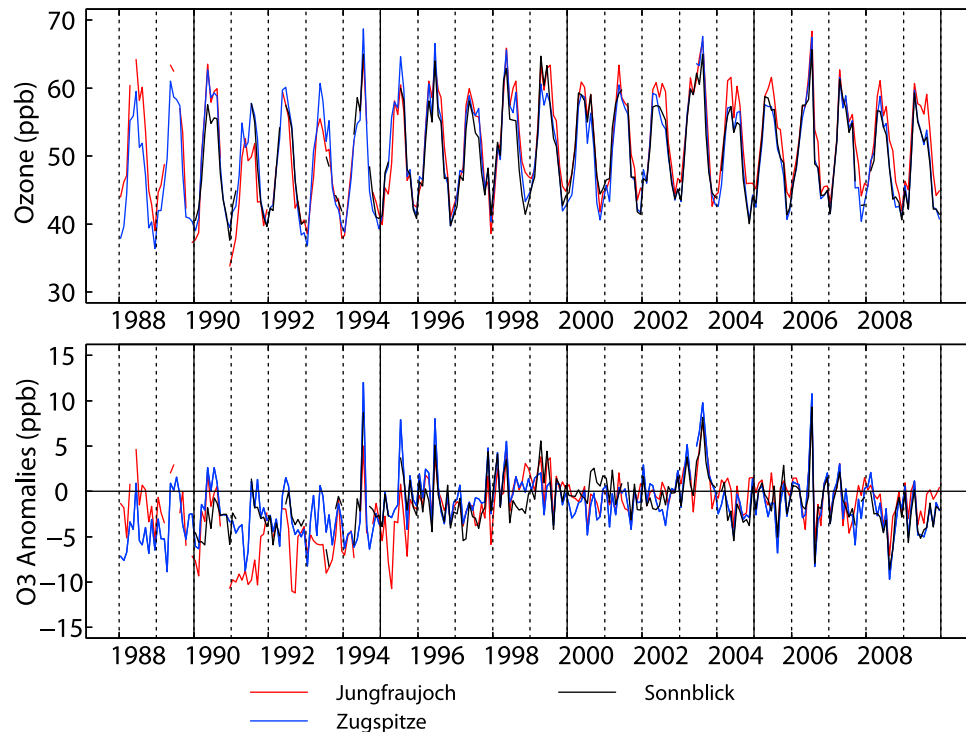
[28] Time series for the alpine sites are rather coherent since 1994 (Figure 5). *Zanis et al.* [1999] compared



**Figure 4.** (a) Time series of monthly mean ozone (in ppb) for sonde stations with weekly profiles. (bottom) The mean of two layers centered at 681 and 584 hPa (2.6–5 km) and (top) the mean of layers centered at 501 and 430 hPa (5–7.2 km). (b) Monthly anomalies (in ppb), relative to the monthly means for January 1997 to December 2003.

measurements from Jungfraujoch and Zugspitze for 1988–1996, and noted the differences in the early years that are evident in Figure 5; the ozone analyzer at Jungfraujoch was changed three times in 1991. Jungfraujoch is located at a higher elevation than the other two sites, so it is expected that the mixing ratios would be slightly higher given the

vertical gradient in ozone [e.g., Logan, 1999; Chevalier *et al.*, 2007]. This is the case mainly after about 1998 with a 2 ppb difference (Table 3). The anomaly time series is coherent from 1994 to 2008, except for early spring 1995 when ozone at Jungfraujoch is considerably lower than at Zugspitze. Ozone increased from 1994 to 1998, and was



**Figure 5.** (top) Monthly mean time series for ozone (in ppb) at the alpine sites. (bottom) Monthly anomalies (in ppb) relative to the monthly means for January 1997 to December 2003.

relatively constant from 1998 to 2006 with somewhat lower values in 2008 and 2009. Ozone is unusually high at all three sites in July of 1994 and 2006 and also in August 2003, three periods when there were record heat waves in Europe.

[29] The temporal behavior of ozone at the alpine sites is similar to that reported for Mace Head, with increases in ozone from 1988 to 1997 and relatively constant ozone since 1999 [Derwent *et al.*, 2007]. We compare the monthly anomalies from Mace Head to those for Zugspitze in Figure 6, for both filtered and unfiltered data. We use monthly anomalies because of the differences in the seasonal cycle at the two locations, a summer minimum at Mace Head and a summer maximum at Zugspitze [e.g., Oltmans *et al.*, 2006]. Figure 6 suggests two periods of relatively constant ozone at Mace Head, 1988–1995, and 1998–2009, with an increase in between. There is a change in the offset between the filtered and unfiltered data in 1997. The filtered data suggests the increase in ozone occurs 1–2 years later at Mace Head than at Zugspitze.

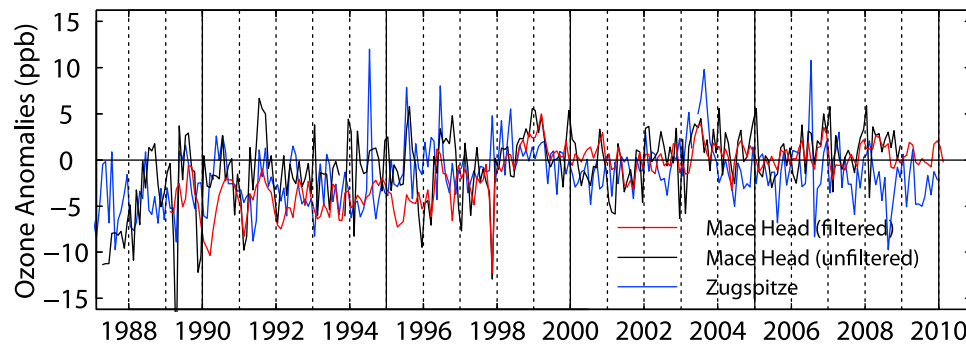
### 3.2. Comparisons Between Measurement Types

[30] The sonde measurements at Payerne are most similar to the MOZAIC time series at Frankfurt and Munich from 1999 to 2008 in the lower troposphere (usually within  $\pm 5$  ppb, with a mean bias of  $0.9 \pm 2.8$  ppb,  $1\sigma$  given), although there are some larger differences in the mid-troposphere (Figure 7 and Table 2). Payerne changed from BM to ECC sondes in September 2002, but this did not impact the consistency of its measurements with those of the MOZAIC profiles. Prior to 1999, the sonde measurements are 3–10 ppb higher than the aircraft data in the lower troposphere (mean biases of  $6.3 \pm 2.2$  and  $4.1 \pm 2.0$  ppb for 1994–1996 and 1997–1998), with a larger bias in the middle

**Table 3.** Differences in Ozone (ppb) Between Pairs of Time Series, Using the Layer Centered at 681 hPa (2.6–3.8 km) for the Profile Data<sup>a</sup>

	Period	Mean Diff.	Std. Dev.	Std. Err.	n
Jungfraujoch-Zugspitze	1988–1989	3.85	2.71	0.61	20
	1991–1995	−1.51	2.88	0.38	56
	1998–2009	2.07	1.67	0.14	142
Sonnblick-Zugspitze	1989–2009	−0.27	1.78	0.12	221
Jungfraujoch-Sonnblick	1990–1995	−0.53	3.06	0.44	49
	1996–2009	2.04	2.06	0.16	163
Payerne-Jungfraujoch	1989–1992	5.44	8.11	1.33	37
	1993–1996	3.57	2.81	0.42	44
	1997–2009	−1.41	2.27	0.18	155
Hohen.-Zugspitze	1978–1989	8.08	4.88	0.41	142
	1990–1992	3.36	3.26	0.57	33
	1993–1995	0.02	2.59	0.44	34
	1997–2007	−2.72	2.59	0.23	131
	2008–2009	−0.56	2.57	0.52	24
Fran/Munich-Jungfraujoch	1994–2008	−2.94	2.44	0.19	166
Fran/Munich-Zugspitze	1995–1998	−3.33	2.62	0.38	48
	1999–2008	−0.74	2.88	0.27	114

<sup>a</sup>Biases for more than one period are shown if time series plots of differences between the two time series showed a change in bias (see Figure 10). The columns show the years, the mean bias, its standard deviation, the standard error of the mean bias, and the number of paired months (n).



**Figure 6.** Monthly anomalies (in ppb) for Mace Head and Zugspitze. The anomalies are given relative to the period January 1997 to December 2003. The Mace Head data are shown for filtered and unfiltered data (see Section 2).

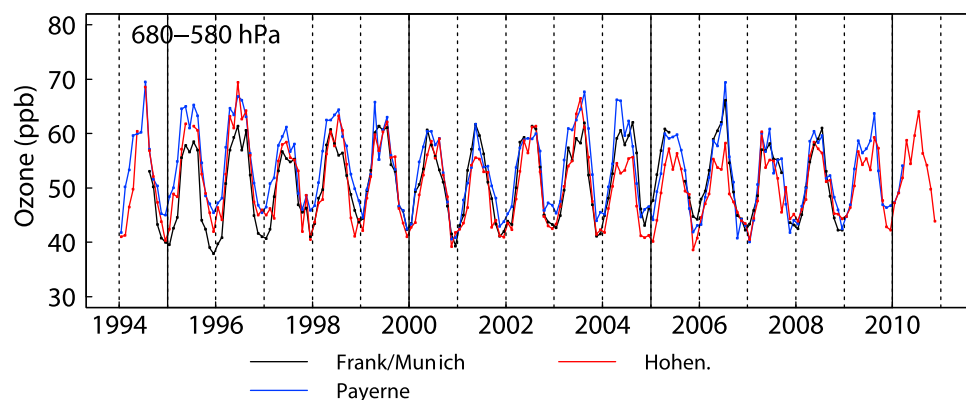
troposphere in 1994–1996,  $10 \pm 3.6$  ppb (Table 2). The Hohenpeissenberg sonde data are generally within  $\pm 5$  ppb of the MOZAIC data after 1997, with a mean bias of  $< 1$  ppb, except for a few months in 2004 and 2006, when the sonde data are 5–9 ppb lower (Figure 7). These are also the years when ozone at Hohenpeissenberg is lower than that at Payerne and Uccle (Figure 3). In 1994–1996, the sonde data are 4–6.5 ppb higher than the MOZAIC data (Table 2). The high bias was noted in the first analysis of MOZAIC ozone data by *Thouret et al.* [1998], who also found that the bias was significantly reduced if the sonde data were not scaled to the ozone column. As a result of the larger biases in 1994–1996 compared to later years, the sonde data do not show the increase from late 1994 to 1998 apparent in the MOZAIC record.

[31] The closest pairs of measurement locations are the sonde and alpine site pairs, Hohenpeissenberg and Zugspitze,  $\sim 40$  km apart, and Payerne and Jungfraujoch,  $\sim 100$  km apart. The German data sets are very similar in 1993–1996 and 2008–2009, but the sonde data are about 2–3 ppb lower than the Zugspitze data from 1997 to 2006, with differences as large as 10 ppb in mid-2006 (Figure 8). The most striking feature in Figure 8 is that the sonde data exceed the surface data by about 8 ppb from 1978 until 1989; we defer discussion of the early part of the sonde record until Section 3.6. The two Swiss data sets (Figure 9)

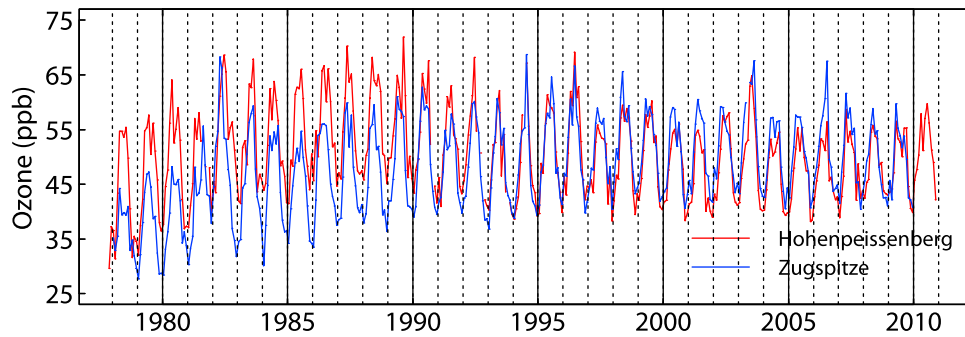
are most similar between 1997 and 2009. In what follows, we examine in more detail the consistency of the time series for ozone at 3–3.5 km over central Europe.

### 3.3. Robust Features of the Temporal Evolution of Ozone Since 1990

[32] In comparing ozone time series from the various locations, the question arises as to whether the differences are geophysical, caused by differences in sampling frequency or by measurement problems, or are statistically insignificant. Continuous monitoring is used at the alpine sites, while there are 1–3 profiles a week at the sonde stations, and 2 or more profiles a day at MOZAIC airports, sometime for the entire month. We sub-sampled the Frankfurt time series on the dates and near the time of the Hohenpeissenberg sondes, and determined that the relatively large differences between MOZAIC and sonde data in 1994–1996 are not caused by the lower sampling frequency of the sondes (not shown). Clearly real differences in ozone may be expected among the different locations, but we argue that temporal changes in the biases between pairs of sites reveal problems with one or other of the measurements. Ultraviolet absorption instruments are used almost universally at surface sites, and were used as a standard to evaluate ozone sondes in the chamber studies [e.g., *Smit et al.*, 2007]. They are



**Figure 7.** Comparison of monthly mean MOZAIC time series for Frankfurt/Munich with those for sondes at Payerne and Hohenpeissenberg, for the mean of two layers centered at 681 and 584 hPa (2.6–5 km).



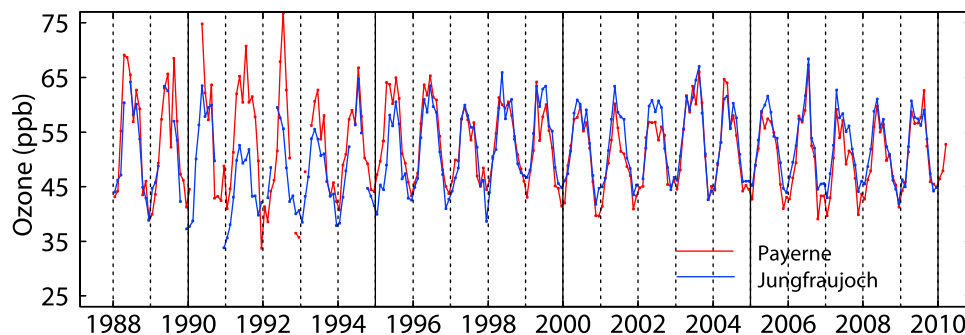
**Figure 8.** Comparison of time series for Zugspitze (2962 m) with sonde data from Hohenpeissenberg, for the layer centered at 681 hPa (2.6–3.8 km).

inherently the more accurate instrument, although this does not mean they never give erroneous measurements.

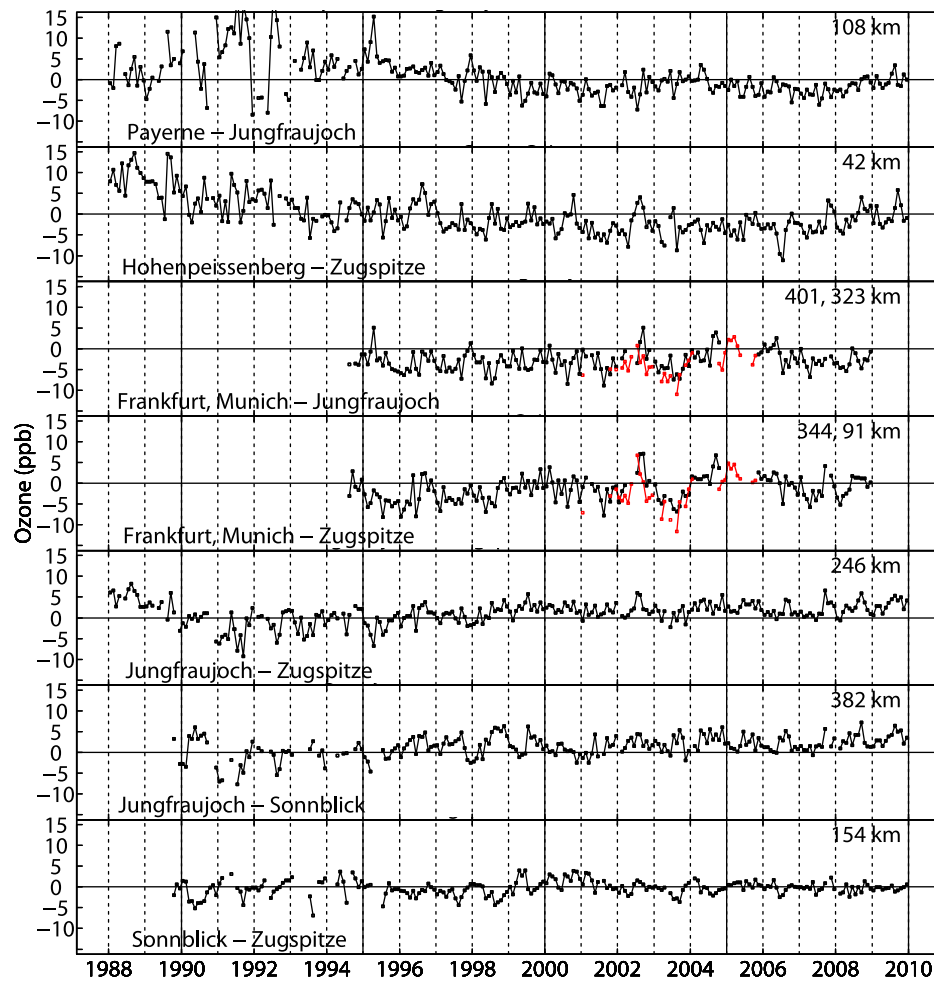
[33] We use difference plots of sondes with UV data and between pairs of UV data sets, and statistics of such differences (see Table 3) to quantify potential difficulties with various data sets and then to recommend robust time series for model evaluation and trend calculations. For the profile data we use the layer centered at 681 hPa (2.6–3.8 km) which spans the altitudes of the alpine stations (Table 1b). Figure 10 shows that differences in ozone are small between the alpine sites and have the lowest variability after 1998. Mean biases are  $2.1 \pm 1.7$  ppb (one  $\sigma$ ) for Jungfraujoch and Zugspitze for 1998–2009, and  $2.0 \pm 2.1$  ppb for Jungfraujoch and Sonnblick for 1996–2009 (Table 3). Higher ozone at Jungfraujoch is consistent with its higher elevation (by  $\sim 600$  m) as noted above. The mean bias is  $-0.3 \pm 1.8$  ppb for Sonnblick and Zugspitze for 1989–2009. Figure 10 suggests some systematic problems with the Jungfraujoch data at a level of several ppb for several months in 1991–1995, when Zugspitze and Sonnblick are more consistent. Indeed, ozone is  $1.5 \pm 2.9$  ppb lower on average at Jungfraujoch than at Zugspitze in these years, and  $3.9 \pm 2.7$  ppb higher in 1988–1989. The biases for both these periods are statistically significantly different from the positive bias after 1998, as determined using a Student's *t*-test. Likewise Jungfraujoch is  $0.5 \pm 3.0$  ppb lower than Sonnblick in 1990–1995, significantly different from the positive bias thereafter. We conclude that Zugspitze and Sonnblick are the more reliable records for 1990–1995. The

Jungfraujoch data are most problematic in 1991, when there was only one instrument and it was changed three times.

[34] The consistency between Payerne and Jungfraujoch since 1998, with the Payerne data about 1–4 ppb lower (mean bias =  $-1.4 \pm 2.3$  ppb), lends confidence to the sonde data for this period. The somewhat higher values of ozone at Payerne than at Jungfraujoch in 1993–1996, by about 1–5 ppb (mean bias =  $3.6 \pm 2.8$  ppb), may partly reflect too low ozone at Jungfraujoch in those years by  $\sim 2$  ppb (based on the alpine site comparisons), and partly too high ozone from the sondes, by  $\sim 2$  ppb. Differences between the Hohenpeissenberg sondes and Zugspitze for 1997–2007 are similar to those for the Swiss pair of sites ( $-2.7 \pm 2.6$  ppb). The largest discrepancy is in June and July 2006, with ozone at Zugspitze about 10 ppb higher. There is a small shift in the mean bias between the sonde data and the Zugspitze data around 1996 (mean bias =  $0 \pm 2.6$  ppb for 1993–1995), suggesting a change in the accuracy of the sondes of  $\sim 3$  ppb, since Sonnblick and Zugspitze agree well in these years. Thus both sonde/site comparisons indicate a change in the accuracy of BM sondes of 2–3 ppb between 1993–1996 and the data thereafter. The comparisons also indicate more serious problems with the sondes before 1993, and the problems with Payerne data in 1990–92 noted by Jeannot *et al.* [2007] are obvious. Mean biases between the Frankfurt/Munich time series and the alpine sites are similar to those between sonde and alpine pairs after 1998, even though Frankfurt is 340–400 km from the alpine sites, and distances at  $\sim 3$  km may be larger depending on the flight path of the aircraft. However, there is a significant change in the bias with respect to Zugspitze



**Figure 9.** Comparison of time series for Jungfraujoch (3580 m) with sonde data from Payerne for the layer centered at 681 hPa (2.6–3.8 km).



**Figure 10.** Difference of monthly mean values for ozone for pairs of locations. The level centered at 681 hPa (2.6–3.8 km) was used for the profile data sets. The distance between the locations at the surface is given in the upper right. Differences between the Munich and alpine data are given in red in the third and fourth panels, while those with Frankfurt are in black.

between 1995 and 1998 ( $-3.3 \pm 2.6$  ppb) and 1999–2008 ( $-0.7 \pm 2.9$  ppb) based on a t-test (see Table 3). Thus the Frankfurt/Munich time series is likely to give a more positive trend in ozone since 1995 than the Zugspitze data.

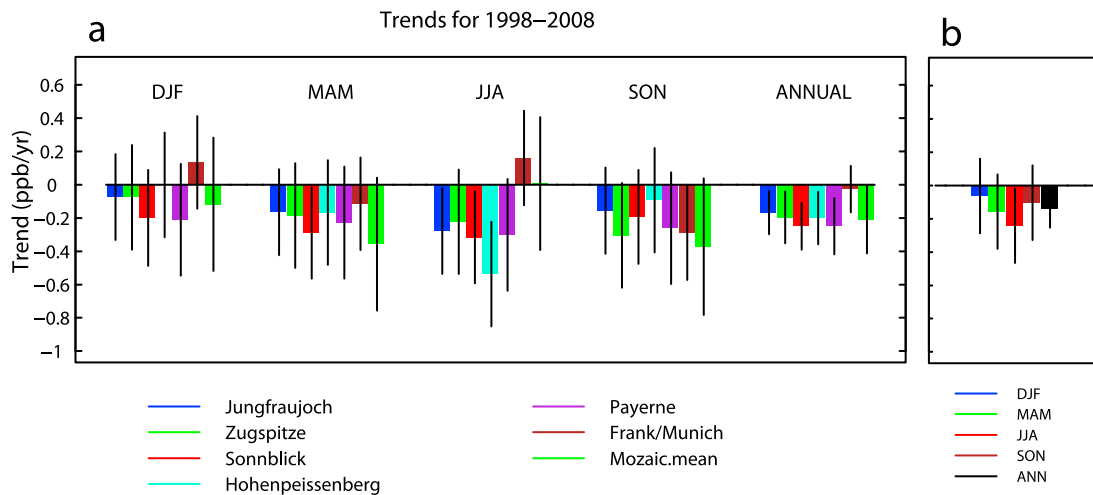
[35] Reliable ozone time series are needed to evaluate hindcast simulations of atmospheric composition, and the results in Figure 10 show that the alpine sites offer the most promise in this regard, with the caution that there appear to be some problems with the data from Jungfraujoch in the early years, particularly in 1991. The BM sonde data in 1990–1992 should not be used. The change in the bias of the sondes with respect to the alpine sites around 1997 argues for a decrease in the response of the BM sondes by  $\sim 3$  ppb as noted above. The MOZAIC data appear to be the better profile data set for late 1994 to 1997, but the increase in the bias of the Frankfurt/Munich time series with respect to Zugspitze by  $\sim 2.5$  ppb raises some concern. Whether this change is caused by true geophysical variations, by small biases in the MOZAIC spatial and temporal sampling, or even by changes in the accuracy of the instruments is unclear. After 1998, the alpine, MOZAIC, and sonde data from Payerne and Hohenpeissenberg are reasonably consistent, so

all appear suitable for model evaluation of interannual variability and trends.

### 3.4. Trends in Ozone in 1995–2008 and 1998–2008

[36] We computed linear trends from the monthly means (equation 1) for 1998–2008, and also for 1995–2008, when all data sets are available. The trends for 1998–2008 at 3–3.5 km agree within their errors for the alpine sites, Hohenpeissenberg, Payerne, Frankfurt/Munich, and the MOZAIC mean record, with each giving a small annual decrease of  $\sim 0.2 \pm 0.16$  ppb yr $^{-1}$  (Figure 11). The seasonal trends are less significant, with insignificant trends close to zero in winter for most locations, and decreases that are generally not significant in spring and autumn. In summer there are decreases of  $\sim 0.2$ – $0.5$  ppb yr $^{-1}$  that are significant (or close to it) at the alpine and sonde locations, and only the MOZAIC data give a zero trend. The similarity of the interannual variability of ozone after 1998 given by the three types of measurements is apparent in Figure 12, which shows the annual mean trends superimposed on the monthly anomalies.

[37] We computed mean trends at 3–3.5 km for 1998–2008 in two ways. We averaged six trends (those for three



**Figure 11.** (a) Seasonal and annual linear trends in ozone ( $\text{ppb yr}^{-1}$ ) for 1998–2008 for sondes and MOZAIC data (681 hPa, 2.6–3.8 km) and for alpine sites computed as described in the text using equation (1). Two standard errors are shown. (b) Trends for 1998–2008 for the mean time series composed of the three alpine sites, two sonde sites, and the mean MOZAIC data used in Figure 11a.

alpine sites, two sonde sites, and the mean MOZAIC time series in Figure 12). This gives an annual mean trend of  $0.21 \pm 0.07 \text{ ppb yr}^{-1}$  and seasonal trends of 0.11, 0.23, 0.27 and  $0.23 \text{ ppb yr}^{-1}$  (each with 2 standard errors of 0.13), for winter, spring, summer and autumn. This approach likely underestimates the trend error because of covariance of the time series. We also formed an average monthly time series for the alpine and sonde sites and the mean MOZAIC record, and computed trends from it, as shown in Figure 11b. The seasonal trends for the mean time series are smaller than the mean of the 6 trends because the average time series is smoother (see anomalies in Figure 12), and the trends are strongly influenced by deviations near the start and end. There is a significant decrease in summer,  $-0.24 \pm 0.22 \text{ ppb yr}^{-1}$ , close to the average of the 6 trends,  $-0.27 \text{ ppb yr}^{-1}$ . The trend in winter is close to zero and not significant, while the trends in spring and autumn are slightly larger ( $-0.16$  and  $-0.10 \text{ ppb yr}^{-1}$ ), but also not significant. The annual trend for the mean time series,  $-0.14 \pm 0.11 \text{ ppb yr}^{-1}$  is less negative than the mean of the 6 trends,  $-0.21 \text{ ppb yr}^{-1}$ . We consider the trends from the mean time series to be the more reliable, and note that they are within the errors of those for the six individual time series.

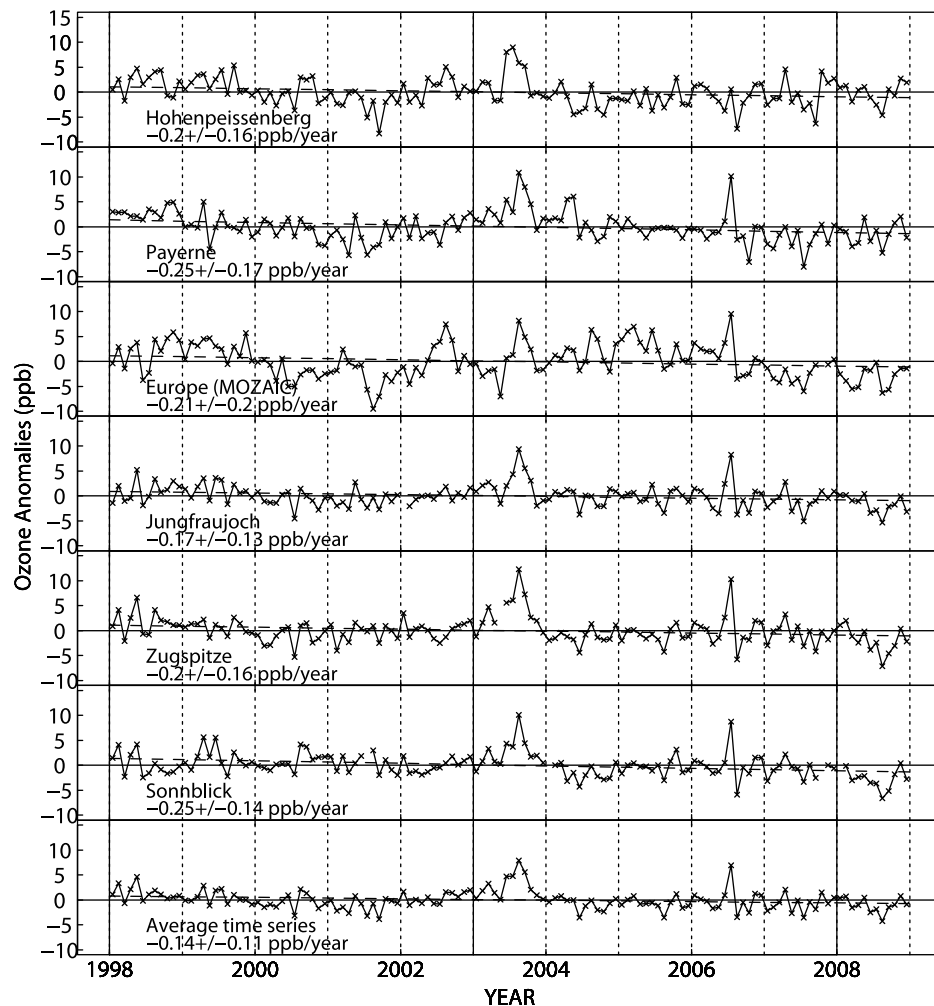
[38] Profile trends are shown in Figure 13, and here we include also results for Uccle and the weekly sonde stations, as well as the alpine surface sites, including Hohenpeissenberg surface data. For the ECC stations that provide data scaled to the overhead ozone column, Uccle and Lindenberg, we also show trends for unscaled data. The consistency among the trends for the MOZAIC mean, Hohenpeissenberg, Payerne, and Lindenberg extends from  $\sim 900$  hPa to  $\sim 600$  hPa (1–4.25 km), with a decrease of 0.15–0.3  $\text{ppb yr}^{-1}$ . The Frankfurt/Munich record gives zero trend, while De Bilt gives positive trends, as does Uccle. At Uccle the positive trend results from the unusually high ozone in 2007 and 2008 that is not seen in any other record, including nearby De Bilt (Figures 3 and 4), while at De Bilt it results from relatively

low values in 1998 and 1999 and high values in 2006 (Figure 4).

[39] As might be expected from the offsets between the sonde and MOZAIC data in 1995–1998, the trends for 1995–2008 from these two sets of measurements do not agree (Figures 14 and 15). The MOZAIC data give an increase in ozone ( $\sim 0.2 \text{ ppb yr}^{-1}$ ), largest in winter, while the Payerne and Hohenpeissenberg sonde data give a decrease ( $\sim -0.3 \text{ ppb yr}^{-1}$ ), largest in summer. The Uccle and De Bilt sonde data give similar trends to those for the MOZAIC data (Figure 15), but as shown in Figures 2–4 the time series are very different, with the increase in the MOZAIC data resulting from lower ozone in 1995–1998, and that in the Uccle data from the high values in 2007–2008. Clearly, caution is required in interpreting trends alone, without consideration of the time series. Of the alpine sites, only Jungfraujoch gives a small increase, less than half of that given by Frankfurt/Munich. The other alpine sites give smaller decreases than the sonde stations, as does the Hohenpeissenberg surface data. We showed above that the bias between the alpine sites and both the sondes and Frankfurt/Munich change by 2–3 ppb before and after  $\sim 1997$ , and these small changes give rise to trends that differ in magnitude and even sign. As noted above, the trends are strongly influenced by the data near the start and end of the record, explaining the differing results for the two time periods. There are MOZAIC time series at three airports for 1995–2004, and trends at Frankfurt are larger than those at Paris and Vienna, 0.7, 0.5, and  $0.3 \text{ ppb yr}^{-1}$  at  $\sim 700$  hPa (not shown), explaining why the Frankfurt/Munich trends for 1995–2008 are larger than those for the MOZAIC mean. The magnitude of the increase at Frankfurt/Munich for 1995–2008 is not supported by the alpine site data.

### 3.5. Temporal Behavior of Ozone Before 1990

[40] Earlier studies have shown that the three long-term sonde stations imply an increase in ozone between the late 1960s and 1990, but there are differences in the temporal



**Figure 12.** Annual trends in ozone ( $\text{ppb yr}^{-1}$ ) for the alpine sites and for Hohenpeissenberg, Payerne, and the MOZAIC mean time series at 681 hPa (2.6–3.8 km), and for a time series composed of the average of the monthly mean time series for these six locations (bottom panel). The annual trends are superimposed on monthly anomalies computed relative to monthly means for 1998–2008. The trend regression model is described in the text, equation (1). Two standard errors are shown.

evolution at each, and in the magnitude of the increase [Logan, 1994; Logan *et al.*, 1999; Jeannot *et al.*, 2007]. Ozone difference plots at 500 hPa are shown in Logan *et al.* [1999], while Jeannot *et al.* [2007] show 12 month running means up to 2002. There are concerns about the reliability of the earlier sonde data in the lower troposphere because of interference from  $\text{SO}_2$ , titration of ozone by  $\text{NO}_x$ , poisoning of the sonde by pollutants (including smoke), in addition to the effects of the sonde preparation procedure, as discussed by De Muer and De Backer [1992], Logan [1994], Tarasick *et al.* [2002] and Jeannot *et al.* [2007]. A comparison of aircraft data for the upper troposphere from 1975 to 1978 [Nastrom, 1979] with MOZAIC data for 1994–2001 implied an increase over Europe of  $\sim 10\%$  only in spring, much smaller than implied by the sonde data for the same two periods [Schnadt Poberaj *et al.*, 2009].

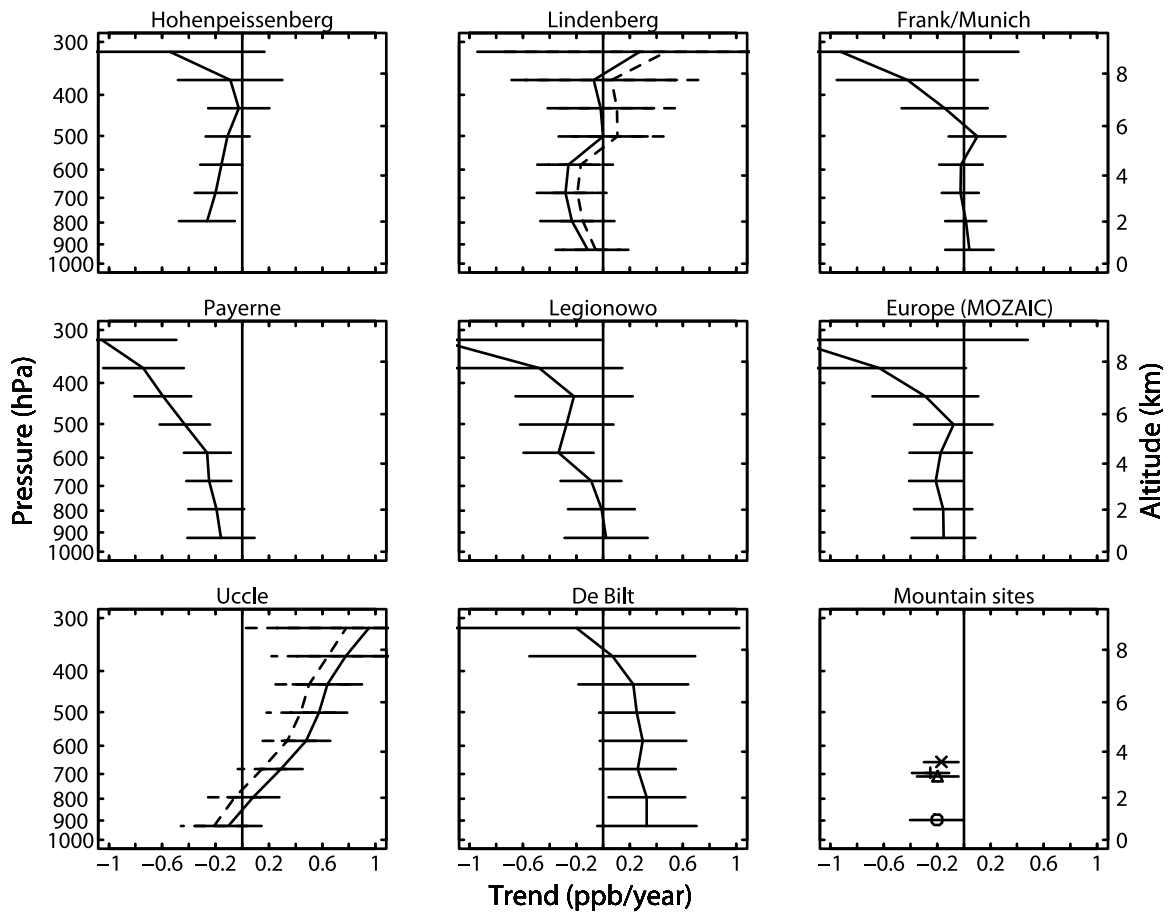
[41] Our analysis here relies on the contemporaneous data from Hohenpeissenberg and Zugspitze. The same procedures have been used for the sondes at Hohenpeissenberg since the 1970s. The method changed from

chemiluminescence to UV absorption in  $\sim 1996$  at Zugspitze, and both methods were used until 1999. The sonde data are systematically higher than the surface data from 1978 to 1989 (except for early 1982), and the two time series converge 2–3 years later, as shown in Figure 8. There appear to be problems with the Zugspitze data in January to May, 1982, when values are 10–15 ppb higher than highest value in the corresponding months in other years from 1979 to 1986, a difference that exceeds the range for each of these months; after May, the monthly means for 1982 are within the range of the other means for 1979–86. We excluded Zugspitze data for these five months in 1982 when computing trends. The annual trends in the sonde and Zugspitze data for 1978–1989 are very similar,  $1 \pm 0.2 \text{ ppb yr}^{-1}$  (Figure 16), although there are differences in their seasonality.

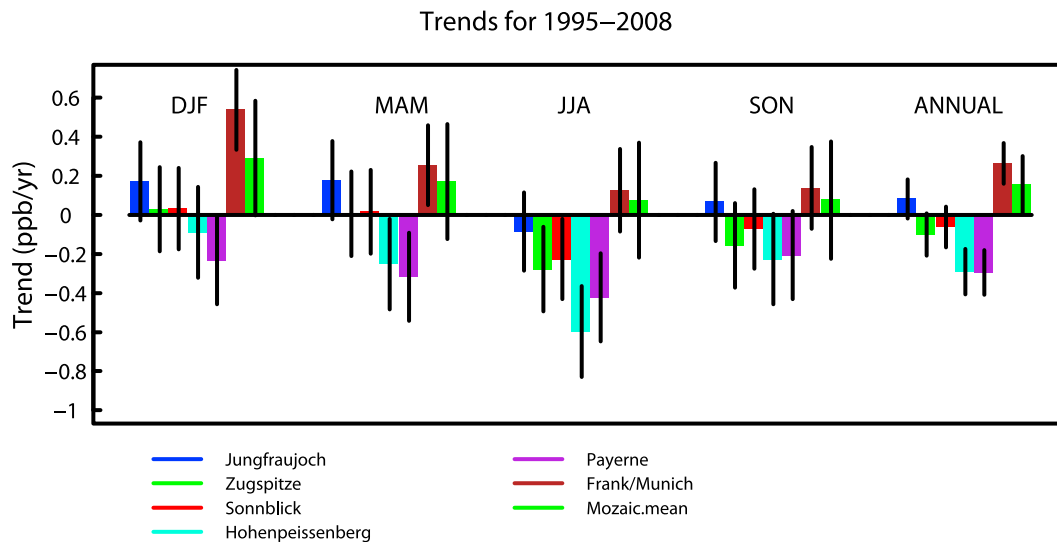
[42] The high bias of the BM sondes compared to Zugspitze in the early years is puzzling. Removing the CFs from the sonde data would reduce the bias in the early years but would not remove it: the mean CF was  $\sim 1.1$  at the time. Laboratory tests conducted in 2000 of BM sondes from the



Annual trends for 1998 – 2008 .

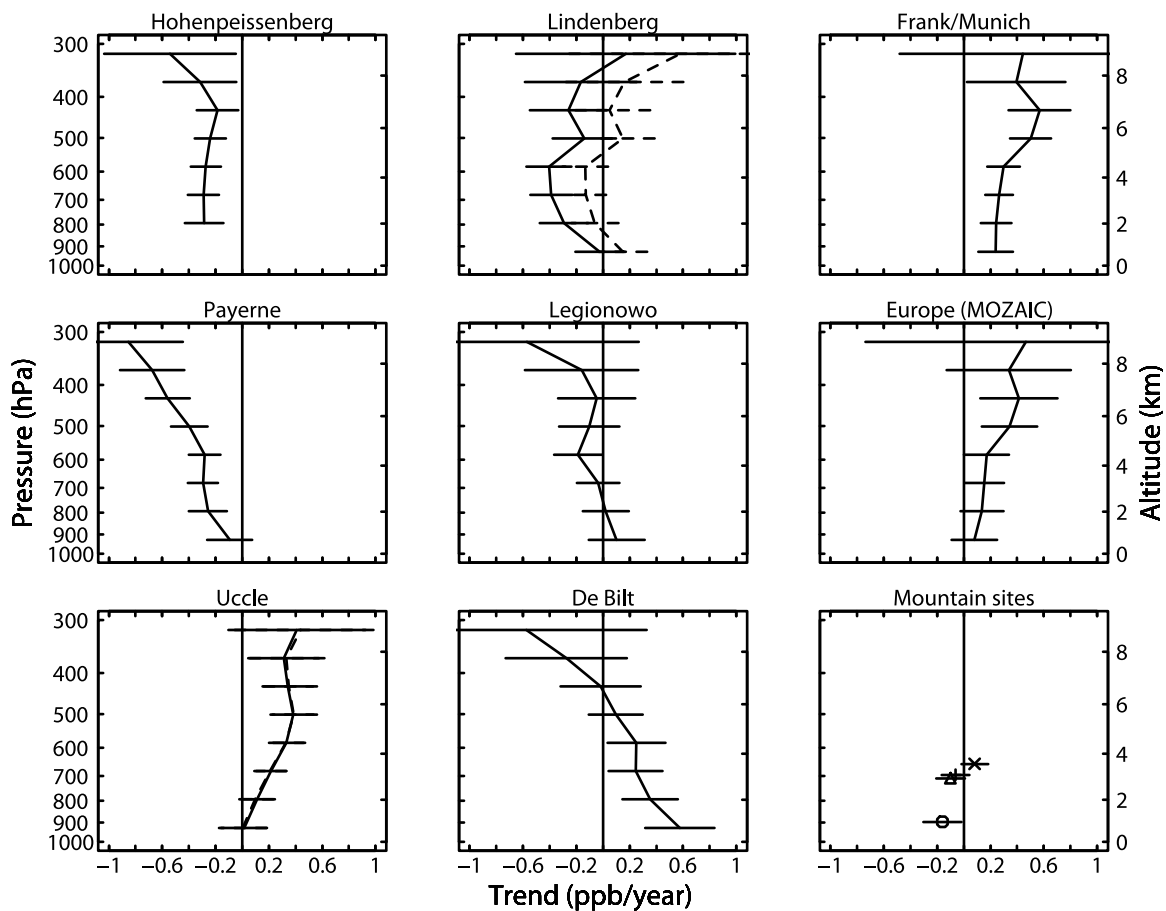


**Figure 13.** Annual profile trends in ozone ( $\text{ppb yr}^{-1}$ ) for 1998–2008 for sondes, MOZAIC data, and mountain sites: Jungfraujoch (cross), Sonnblick (plus), Zugspitze (triangle), and the Hohenpeissenberg surface site (circle). The dashed lines show trends for ECC data divided by the CF for the two sites that provide them scaled to the CF. The other sites provide the ECC data unscaled to the CFs (see Section 2). Two standard errors are shown.



**Figure 14.** Seasonal and annual linear trends in ozone ( $\text{ppb yr}^{-1}$ ) for 1995–2008 for sondes and MOZAIC data (681 hPa) and for alpine sites computed as described in the text. Two standard errors are shown.

## Annual trends for 1995 – 2008.



**Figure 15.** Annual profile trends in ozone ( $\text{ppb yr}^{-1}$ ) for 1995–2008 for sondes, MOZAIC data, and mountain sites: Jungfraujoch (cross), Sonnblick (plus), Zugspitze (triangle), and the Hohenpeissenberg surface site (circle). The dashed lines show trends for ECC data divided by the CF for the two sites that provide them scaled to the CF. The other sites provide the ECC data unscaled to the CFs (see Section 2). Two standard errors are shown.

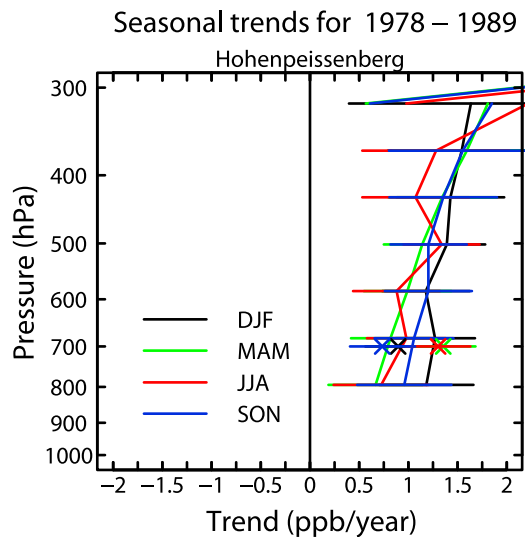
1970s showed that the sondes always measured less ozone than an accurate ozone calibrator by at least 10%, even when prepared according to the methods used at Hohenpeissenberg [Tarasick *et al.*, 2002]. This result is consistent with having to scale the sonde data up by 10% to match ozone column data. Earlier intercomparisons had shown that BM sondes measured 15–20% less ozone in the troposphere than ECC sondes, but differences were less than 5% by mid-1990s as noted in Section 2, so the response of the BM sondes appears to have changed. The fact that every intercomparison of BM sondes before 1989 showed that they underestimated ozone makes it all the more difficult to explain the high bias with respect to the Zugspitze data evident in Figure 8, assuming that the Zugspitze data are the more reliable. Nevertheless, the two independent data sets give the same mean linear trend in ozone for 1978–1989.

### 3.6. Changes in Ozone From 1978 to 2009

[43] Based on the analysis presented above, the alpine sites provide the best representation of the time evolution of ozone over central Europe since 1978. Here we determine changes in ozone using seasonal mean time series composed of

Zugspitze for 1978–1989 (omitting January–May 1982) and the mean of the Zugspitze, Jungfraujoch, and Sonnblick for 1990–2009, as shown in Figure 17. We adopted a quadratic fit to the time series, given the obvious change in the gradient of ozone; the quadratic term is highly significant in all seasons for 1978–2009. Using the quadratic fit and the standard errors shown in Figure 17, we computed the change in ozone from 1978 to 1989, 1990 to 1999, 2000–2009, and from 1990 to 2009, and compare these changes as the mean trend per year in Figure 18. The error in the change in ozone was calculated by summing the errors for the fit at the start and end of each period. With this approach, the mean annual trend in ozone is  $0.87 \pm 0.13 \text{ ppb yr}^{-1}$  for 1978–1989, and exceeds  $0.9 \text{ ppb yr}^{-1}$  except in autumn ( $0.65 \pm 0.24 \text{ ppb yr}^{-1}$ ). It is substantially smaller,  $0.33 \pm 0.10 \text{ ppb yr}^{-1}$  for 1990–1999, and largest in winter and spring. In marked contrast, there is a decrease in ozone of  $0.16 \pm 0.14 \text{ ppb yr}^{-1}$ , largest in summer ( $-0.40 \pm 0.40$ ), for 2000–2009. Between 1990 and 2009, there was a significant increase in ozone only in winter, and an annual mean increase of  $0.09 \pm 0.08 \text{ ppb yr}^{-1}$ .

[44] From the quadratic fit, ozone increased by  $\sim 15 \text{ ppb}$  from 1978 to 2000 in winter, spring, and summer, and by



**Figure 16.** Seasonal profile trends in ozone ( $\text{ppb yr}^{-1}$ ) for 1978–1989 for Hohenpeissenberg and Zugspitze (crosses). Data for January to May 1982 were omitted for Zugspitze in calculating trends. Two standard errors are shown. Winter trends are in black, spring in green, summer in red, and autumn in blue.

11 ppb in autumn, with more than 70% of the increase occurring before 1990. We note that the fit has its largest errors at the start and end of the time series, and has the smallest residuals in winter and the largest in summer.

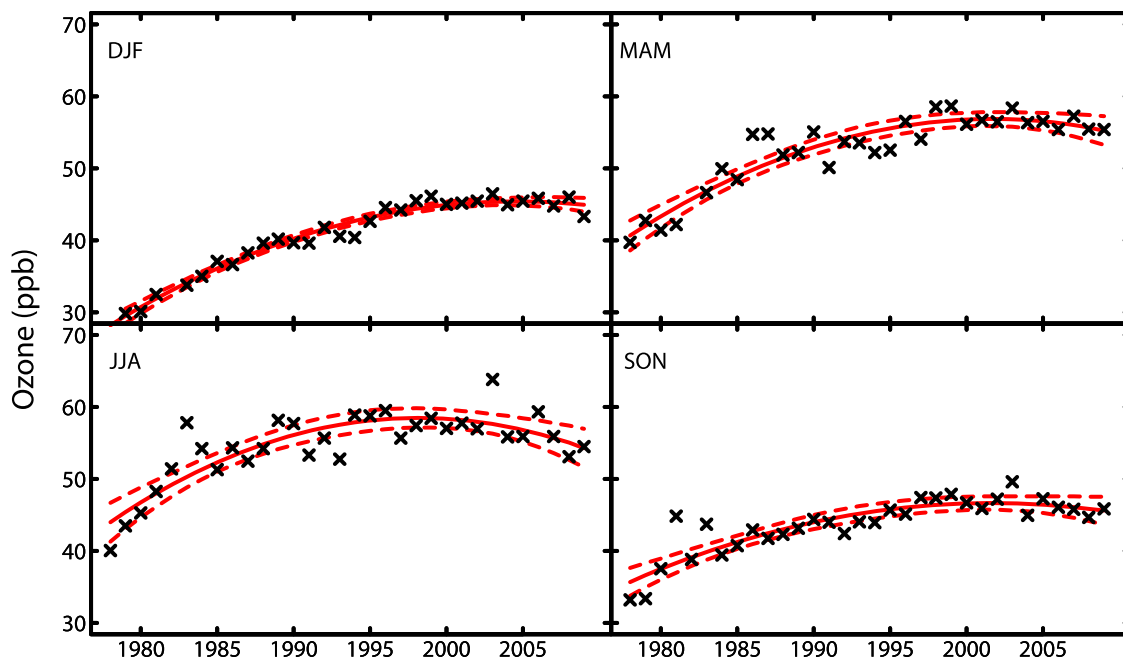
[45] The analysis here did not filter Jungfraujoch data in the early years. We found that omitting the data from 1991 had a negligible effect on the fit for 1978–2009, but it

impacts linear trends calculated for 1990–1999. The mean trends for the individual decades in Figure 18 derived from the quadratic fit for 1978–2009 are somewhat smaller in magnitude than linear trends calculated for the same periods, but have similar seasonal behavior in each decade.

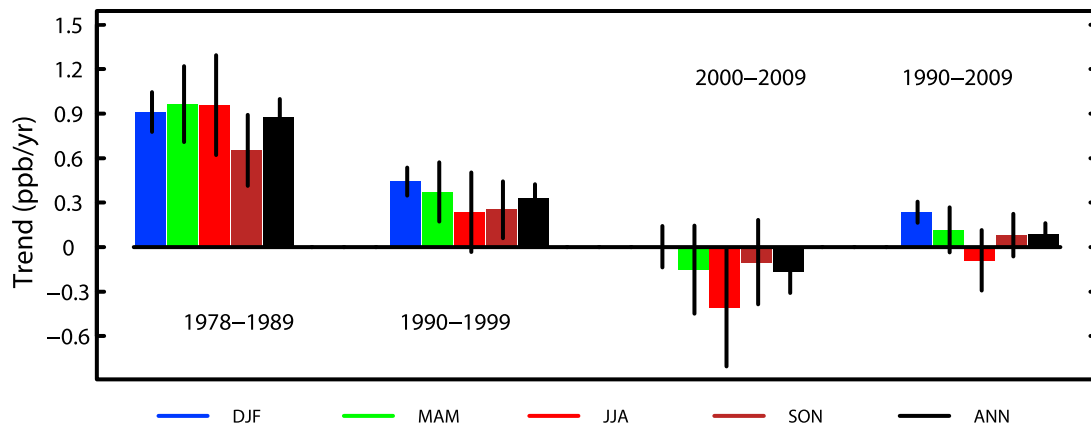
#### 4. Discussion and Conclusions

[46] The results presented here confirm that the increase in ozone in the 1990s seen in the alpine data and at Mace Head has stopped, and show that ozone decreased in the decade of the 2000s in summer. The trends for the mean alpine time series for 2000–2009 are similar to those for 1998–2008 for the mean time series that includes concurrent alpine, sonde, and MOZAIC data, with the same annual trend ( $-0.15 \text{ ppb yr}^{-1}$ ), and a significant decrease only in summer (Figures 11b and 18). The increase in ozone over central Europe was largest in the 1980s, and slowed down in the 1990s.

[47] The homogeneity of the three measurement types for about a decade is reassuring for continuity of these climate-relevant records, but caution is always needed with sondes as shown by the inconsistencies noted in Sections 3.1–3.3. For profile trends, the MOZAIC record is the more reliable from late 1994 onwards, with the sonde data converging to the alpine data by 1998, particularly in terms of interannual variability. The BM sonde data are not useful for deriving reliable tropospheric trends prior to about 1998, but we note that the change in their accuracy in the mid-late 1990s appears to be small, about 3 ppb. The only exception is the Hohenpeissenberg sonde record that overlaps with the early Zugspitze data, where both give the about same trend,  $1 \pm 0.2 \text{ ppb yr}^{-1}$  for 1978–1989, even though the reliability of the absolute values of ozone from the sondes is questionable. The stratospheric data from the BM sondes do not



**Figure 17.** Seasonal means for Zugspitze (1978–1989) and for the mean of Jungfraujoch, Sonnblick, and Zugspitze (1990–2009) (crosses). The solid line shows a quadratic fit for each season (equation (2)), and the dashed lines show two standard errors of the fit.



**Figure 18.** Seasonal and annual trends in ozone ( $\text{ppb yr}^{-1}$ ) for Zugspitze (1978–1989) and for the mean alpine time series for the more recent decades and for 1990–2009 as indicated. Trends and errors were computed from the quadratic fit as described in Section 3.5.

appear to have problems in 1980–1998 [e.g., *Terao and Logan, 2007*].

[48] The utility of independent data sets to check for consistency is evident in this study, allowing identification of problems with some of the earlier Jungfraujoch data, and with the sonde data at Uccle since 2007. We identified changes in bias between the alpine site data and both sonde and Frankfurt data of about 3 ppb in the mid-late 1990s. Biases as small as a few ppb for a few years lead to very different trends for relatively short periods such as 1995–2008.

[49] Given the interannual variability in ozone, trends depend on the exact time period chosen. *Cui et al.* [2011] illustrate this with data from Jungfraujoch, showing trends for a sequence for moving 10 year periods, with one year spacing. It is thus important to compare trends from different data sets using the same time period.

[50] The contrast between the changes in ozone over recent decades is stark, from seasonal increases of 6.5–10 ppb in the 1980s and 2.5–4.5 ppb in the 1990s to a decrease of 1–4 ppb in the 2000s at 3–3.5 km (Figure 18). Here we consider some of the factors that may have contributed to these changes in ozone, including changes in stratospheric input and in ozone precursors. *Ordóñez et al.* [2007] argued that the variability and increase in ozone at the alpine sites from 1992 to 2004 in winter and spring were caused largely by increases in stratospheric input of ozone. They found significant correlations between ozone in the lowermost stratosphere and the troposphere, as did *Tarasick et al.* [2005] for the Canadian sonde stations and *Terao et al.* [2008] for the northern extratropics. The variability in the lower stratosphere explained about 45% of the variance in the Zugspitze data in winter and spring in 1992–2004 [*Ordóñez et al.*, 2007].

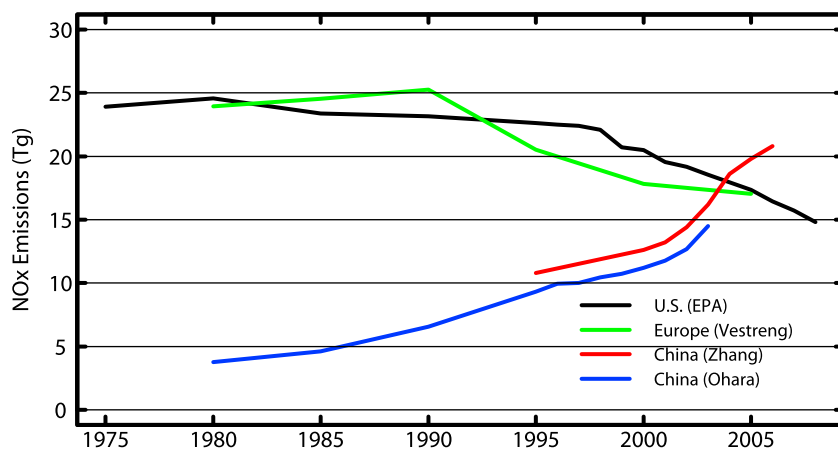
[51] Ozone was relatively constant in the lowermost stratosphere over Europe in the 1980s and the 2000s, and the largest changes occurred in the 1990s when ozone increased after record low values in early 1993 [e.g., *WMO, 2011, Figure 2.6*]. Using the same data as *Ordóñez et al.* [2007] for the lowermost stratosphere, the mean of Hohenpeissenberg and Payerne at 150 hPa, we found that there were no trends in ozone for the three decades shown in Figure 18, except for

a marginally significant decrease in winter for 1978–1989,  $-1.12 \pm 1.14\% \text{ yr}^{-1}$ , driven by very low values in early 1989, and an increase in winter,  $3.3 \pm 2.2\% \text{ yr}^{-1}$  and in spring,  $1.5 \pm 1.8\% \text{ yr}^{-1}$ , for 1990–1999. None of the other seasonal trends were even close to statistical significance. Stratospheric input from other regions could influence ozone over Europe, but there is no evidence in the time series for the lowermost stratosphere from either sondes over North America [*Tarasick et al.*, 2005] or from satellite data [*WMO, 2007*] to suggest that changes in stratospheric input can explain the increase in ozone over Europe in the 1980s. Input from the stratosphere is expected to have the largest effect on tropospheric ozone in spring [e.g., *Hsu et al.*, 2005]. Increases in stratospheric ozone after 1993 may have contributed to the increase in tropospheric ozone in the 1990s as noted above.

[52] In summer, unusually high temperatures and the associated circulation patterns are responsible for the highest ozone observed at  $\sim 3$  km in central Europe. Analysis of the Frankfurt profiles during the heat wave of August 2003 by *Tressol et al.* [2008] shows that ozone was elevated throughout the boundary layer, and ozone at surface monitoring stations in central Europe was unusually high [*Ordóñez et al.*, 2005; *Solberg et al.*, 2008]. Our analysis found that the heat waves of July of 1994 and 2006 [*Fischer et al.*, 2007; *Rebetez et al.*, 2009] also caused unusually high ozone at 3 km at the alpine sites.

[53] *Solberg et al.* [2008] argued that emissions from major forest fires in Portugal in August 2003 may have contributed to the peak values in surface ozone observed in northern Europe, on the basis of back trajectory calculations. We are not aware of any indication that fires contributed to the high ozone in July of 1994 and 2006. A few case studies have shown that ozone is sometimes enhanced in biomass burning plumes over Europe that originated from severe fires in North America, and sometimes is not [e.g., *Forster et al.*, 2001; *Real et al.*, 2007; *Task Force on HTAP, 2010*]. The influence of fires on ozone over Europe is highly episodic, and not well quantified.

[54] Trends in  $\text{NO}_x$  emissions from the northern extratropics are shown in Figure 19. Changes in domestic emissions should have the largest effect on ozone in summer,



**Figure 19.** Emissions of  $\text{NO}_x$ , given as Tg  $\text{NO}_2$ . Emissions for Europe are from Vestreng *et al.* [2009] and include Eastern Europe and the Russian Federation. Emissions for the United States are from the Environmental Protection Agency (<http://www.epa.gov/ttn/chief>, accessed in June, 2011). Emissions for China are from Ohara *et al.* [2007] for the earlier period (in blue) and from Zhang *et al.* [2009] for the later period (in red).

while changes in emissions in North America and Asia should have the largest effect on ozone over Europe in spring and late autumn, according to model studies [Fiore *et al.*, 2009; Jonson *et al.*, 2010]. Emissions of  $\text{NO}_x$  from both the United States and Europe were almost constant in the 1980s, when the ozone increases over Europe were largest. Emissions of reactive hydrocarbons in North America and in western Europe have been decreasing since 1980 [Environmental Protection Agency (EPA), 2002; Pulles *et al.*, 2007]. The smaller ozone increases in the 1990s occurred when  $\text{NO}_x$  emissions from these two continents were decreasing, albeit slowly in the United States. Emissions were increasing in China in this decade, but were less than a third of those from each of the other continents in 1990. When ozone in central Europe was decreasing in summer in the 2000s,  $\text{NO}_x$  emissions were declining in Europe and the United States, and rising steeply in China, becoming similar on the three continents by around 2004. The increase in ozone precursors in Asia influenced trends in spring time ozone over western North America, according to Cooper *et al.* [2010]. They report an increase in median ozone in April–May of  $0.63 \pm 0.34$  ppb  $\text{yr}^{-1}$  for 1995–2008 at 3–8 km, based on relatively sparse measurements (MOZAIC, research aircraft, sonde and lidar data) compared to the abundant measurements available for central Europe.

[55] Jonson *et al.* [2010] present results from a multimodel comparison of the effects on ozone above the boundary layer of 20% decreases in precursor emissions in 2001. They found that decreases in European, North American, and East Asian emissions caused reductions in ozone of 1–1.5 ppb, 0.5–1 ppb, and 0.2–0.3 ppb respectively at  $\sim 700$  hPa over Europe in summer. If we extrapolate from these results using the last 10 years of emissions in Figure 19, the decreases in emissions of  $\text{NO}_x$  in Europe and the U.S. would cause a decrease in ozone of 2–3 ppb. This would be offset by the effects of the increase in Asian emissions of potentially over 1 ppb. These simple scaling arguments are not inconsistent with the observed trend in summer, although it appears to be dominated by trends in emissions outside Asia. The effects of changes in emissions from a given continent have more

effect on surface ozone for that continent than on ozone above the boundary layer [Fiore *et al.*, 2009; Jonson *et al.*, 2010].

[56] Fusco and Logan [2003] simulated the effects of changes in ozone precursors from 1970 to 1994 using one year of model meteorology, and found an increase of about 3–4 ppb and 5–6 ppb over Europe at 700–500 hPa in January and July, most of which occurred by 1985. Most of the increase in  $\text{NO}_x$  emissions was between 1970 and 1980. The change in methane from 1970 to 1994 contributed about 1 ppb to the change in January and 2 ppb to the change in July. The growth rate of  $\text{CH}_4$  slowed considerably after the mid-1990s [Dlugokencky *et al.*, 2011], so should not have had much influence on ozone in the past 15 years. Carbon monoxide increased slightly in the 1980s but has slowly decreased since about 1990 in the extratropics [Khalil and Rasmussen, 1994; Novelli *et al.*, 2003] so should have had only a minor effect on ozone trends.

[57] Recent simulations with two chemistry climate models for 1960–2000 underestimate the increase in ozone at Zugspitze in the 1980s by at least a factor of two, and give a slower rate of growth, or no growth in ozone at all, in the 1990s [Lamarque *et al.*, 2010]. A simulation for 1987–2005 with assimilated meteorology, varying emissions up to 1998, but a parameterized stratospheric ozone source, was unable to match the observed interannual variability of extratropical ozone [Koumoutsaris *et al.*, 2008]. However, they found an influence of El Niño on ozone over Europe, with an enhancement in the spring following an El Niño year (e.g., in early 1998), which they attributed an increase in the source from the stratosphere and enhanced transport of ozone originating over Asia and North America. Other model studies have shown an increase in stratospheric input following an El Niño year [Zeng and Pyle, 2005; Voulgarakis *et al.*, 2010], and the observations show that ozone was anomalously high over Europe in spring 1998 (as well as 1999, Figure 17), as discussed in the context of the MOZAIC data by Thouret *et al.* [2006] and Zbinden *et al.* [2006]. Ozone was anomalously high also in the lower stratosphere in 1998 and 1999.

[58] The ozone increase from the 1950s to the early 1990s at  $\sim 1850$  m in Switzerland, from  $\sim 20$  ppb to  $\sim 40$  ppb [Staehelin *et al.*, 1994], took place during the steepest increase in ozone precursor emissions in both North America and Western Europe, prior to 1970 and 1975, respectively. Between 1950 and 1975, emissions of  $\text{NO}_x$  from Western Europe increased from 4 Tg to 14 Tg [Vestreng *et al.*, 2009], while those in the U.S. increased from 9 Tg to 24 Tg [EPA, 2002], and then were relatively constant for about 15 years.

[59] The existing data do not provide useful information on details of the time evolution of ozone over central Europe between 1950 and about 1980, but that is not the case for the period after 1980. While the data from the 1980s are less robust than we would wish, there is now reliable alpine data since 1990, reliable MOZAIC data since late 1994, and reliable sonde data since 1998 that document how ozone has changed. Thus we recommend that hindcast simulations of ozone are evaluated with the alpine time series, the MOZAIC time series and the Payerne and Hohenpeissenberg sondes from 1998 onwards. It is important to evaluate the ability of the models to match the interannual variability of the observations, rather than just to examine linear trends for selected periods. Any comparisons between model and observed trends should use identical time periods. It is also important to evaluate temporal behavior in different seasons, given the seasonality of photochemical production, long range transport, and stratospheric input. Modelers concerned about local topographic effects on ozone at the alpine stations may wish to use nighttime data to sample data above the boundary layer.

[60] The most reliable longer term data sets discussed here are all in central Europe, with several in or near the Alps. However, the shorter-term MOZAIC records from Paris, Vienna, and Brussels show that the temporal variability of ozone is similar on spatial scales of 500–1000 km in the lower and middle troposphere. The similarity of the temporal behavior of ozone at Zugspitze and the Mace Head on the west coast of Ireland also demonstrates the large spatial scale of the processes affecting ozone.

[61] Intercomparisons among the ozone data sets should continue, as they provide an easy check on consistency of the various records. The audit process in place for the GAW stations had clearly improved the consistency of the alpine records. The existing data provide a serious challenge to current understanding of the processes that control tropospheric ozone, particularly the increases year-round in the 1980s and in summer in the 1990s when emissions of the key precursor,  $\text{NO}_x$ , were constant or decreasing over North America and Europe, and Chinese emissions were relatively low.

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