Atmos. Chem. Phys. Discuss., 11, 27107–27137, 2011
www.atmos-chem-phys-discuss.net/11/27107/2011/
doi:10.5194/acpd-11-27107-2011
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Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Impact of sampling frequency in the analysis of tropospheric ozone observations

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Received: 8 July 2011 – Accepted: 9 September 2011 – Published: 4 October 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

## Abstract

The measurements of the ozone vertical profiles are valuable for the evaluation of atmospheric chemistry models and contribute to the understanding of the processes controlling the distribution of tropospheric ozone. The longest record of the ozone vertical profiles is provided by ozone sondes, which have a low time resolution with a typical frequency of 12 or 4 profiles a month. Here we discuss and quantify the uncertainty in the analysis of such data sets using high frequency MOZAIC (Measurements of OZone, water vapor, carbon monoxide and nitrogen oxides by in-service AIrbus airCraft) profiles data sets, such as the one over Frankfurt. We subsampled the MOZAIC data set at the two typical ozone sonde frequencies. We find that the uncertainty introduced by the coarser sampling is around 8 % for a 12 profiles a month frequency (14 % for a 4 profiles a month frequency) in the free troposphere over Frankfurt. As a consequence, this uncertainty at the lowest frequency is higher than the typical 10 % accuracy of the ozone sondes and should be carefully considered for observation comparison and model evaluation. We found that the average intra-seasonal variability represented in the samples is similar to the sampling uncertainty and could also be used as an estimate of the sampling error in some Northern Hemisphere cases. The sampling impacts substantially the inter annual variability and the trend derived over the period 1995–2008 both in magnitude and in sign throughout the troposphere. Therefore, the sampling effect could be part of the observed discrepancies between European sites. Similar results regarding the sampling uncertainty are found at five other Northern Hemispheric sites. Also, a tropical case is discussed using the MOZAIC profiles taken over Windhoek, Namibia between 2005 and 2008.






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## 1 Introduction

Tropospheric ozone is an important trace gas because of its role in the oxidative capacity of the global atmosphere, its climate effect and its impact on air quality. This trace gas is monitored worldwide on various platforms (surface stations, balloons, aircraft, satellites) with diverse instruments (electronic cells, UV absorption instruments, Brewer-Dobson instruments, infrared spectrometers). After the continuous increase of ozone concentrations over Europe until the 1980s or 1990s (e.g., Logan, 1999; Naja et al., 2003; Ordóñez et al., 2005; Oltmans et al., 2006; Zbinden et al., 2006; Parrish et al., 2009), a levelling-off has been observed over the past decade. Since the 1980s, the global anthropogenic emissions of ozone precursors increased due to rapid economic development in Asia, while European and North American emissions have been decreasing (Vestreng et al., 2007; Monks et al., 2009). Tropospheric ozone is also influenced by the high variability of biomass burning emissions (Koumoutsaris et al., 2008), changes in atmospheric circulation (Eckhardt et al., 2003) and transport from the stratosphere (Fusco and Logan, 2003).

Due to high temporal and spatial variability of ozone, long term measurements (15 years or longer) are usually necessary to determine changes in ozone concentrations with some measure of significance. While the surface stations provide extensive datasets of surface ozone measurements, the ozone in-situ measurements in the free troposphere on a regular basis (i.e., not dedicated aircraft campaigns) were limited to the soundings until the MOZAIC (Measurements of OZone, water vapor, carbon monoxide and nitrogen oxides by in-service AIrbus airCraft) program was launched in 1994. The measurements of the ozone vertical profiles are useful for the evaluation of numerical models (e.g., Logan, 1999; Emmons et al., 2000) and contribute to the understanding of the processes controlling the distribution of tropospheric ozone (e.g., Lamarque and Hess, 2004; Koumoutsaris et al., 2008).

However, the observational data that can be used for model evaluation, for example, in the framework of international projects such as ACC-MIP (Atmospheric Chemistry





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and Climate – Model Intercomparison Project), HTAP (Hemispheric Transport of Air Pollution), CCMVAL2 (Chemistry-climate Model Validation Activity), and comparison to other observations, need to be provided in a format comparable with model output, that is generally based on monthly means. Averaging the observational data on a monthly-mean time scale facilitates the comparison of model to observation and reduces the effort required in data exchange. However, the sampling frequency of the soundings are typically of 4 or 12 profiles per month. Thus, the monthly mean derived from those observational data will depend on how typical were the days sampled and thus, may be biased due to the sampling.

The objective of this paper is to discuss and quantify the uncertainty in the analysis of low sampling frequency measurements like ozone sondes. For that purpose, we subsample the high frequency MOZAIC data over Frankfurt at typical sonde frequencies to study to what extent time resolution can influence seasonal estimates, as if they were derived from different data sets. The data and the subsampling methodology are described in Sect. 2. Section 3 presents the effect of sampling derived from the ozone vertical profiles over Frankfurt as well as the definition of the metric used to discuss this issue. A generalisation of the results for the Northern Hemisphere midlatitudes is presented in Sect. 4 and a tropical case study is discussed in Sect. 5. Conclusions are given in Sect. 6.

## 2 Observations

### 2.1 MOZAIC data

We focus on the period 1995–2008 which is documented by the MOZAIC program (http://mozaic.aero.obs-mip.fr, Marenco et al., 1998), and essentially on the vertical profiles collected over Frankfurt, Germany. This airport is the most frequently sampled by MOZAIC with a total of 11,623 vertical profiles between January 1995 and December 2008. On average, 77 profiles per month, i.e. more than two profiles a day, are





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provided. The ozone measurement is made by a dual beam UV absorption instrument with a detection limit of 2 ppbv and overall precision of ±(2 ppbv + 2 %) (Thouret et al., 1998).

The detailed discussion in Sect. 3 includes only profiles taken between 05:00 and 13:00 UT. This choice is made to avoid the effect of a strong diurnal cycle in the lowest levels and matches the time window of the balloon launch in Central Europe. Indeed, sondes are launched generally at 11:30 UT or 12:00 UT in five of the six ozone sonde stations located in Central Europe (Debilt, Lindenberg, Payerne, Praha and Uccle) and around 05:30 UT at the Hohenpeissenberg station. Figure 1 shows the number of profiles available within this time window. The morning subset of ozone profiles over Frankfurt represents 79 % of the whole dataset and includes often more than 100 profiles per season. Thus the morning profiles are numerous enough to be subsampled at the two typical ozone sonde frequencies: 4 profiles and 12 profiles a month.

The vertical profiles are binned by 100 hPa thick levels around the following mid-level pressures: 1000, 900, 800, 700, 600, 500, 400 and 300 hPa.

The MOZAIC measurements made over Vienna, Paris, New-York, Boston, Osaka and Tokyo are also used to generalise our results to the Northern Hemisphere mid-latitudes in Sect. 4. The data collected in Namibia over Windhoek between 2005 and 2008 are used for the tropical case study presented in Sect. 5.

## 2.2 Ozone sondes and surface stations

A discussion about ozone trends is made using MOZAIC, ozone sounding and surface measurements in Sect. 3.5. The area of interest, referenced hereafter Central Europe, is defined as the region between 44° N and 55° N latitude, and 3° W and 18° W longitude, which encompasses Frankfurt and several sounding stations. Figure 2 shows a map of this region and the measurement sites considered in Sect. 3.5. Frankfurt is presented as a black diamond on the map. Six ozone sonde stations located near Frankfurt provided data over the period 1995–2008: Debilt, Hohenpeissenberg, Lindenberg, Payerne, Praha and Uccle (blue stars). The sounding data are available through the





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World Ozone and Ultraviolet Radiation Data Center (WOUDC, http://www.woudc.org). A column ozone filter is applied for all ozone sonde profiles to avoid single profile to exceed unreasonable column ozone values of more than 700 DU. We do not correct profiles based on the corrections factor provided. The correction factor was scaled to the entire column. The impact of an applied correction factor to averaged ozone profiles between 1995–2008 is small for most stations considered Tilmes et al. (2011). The surface layer (1050–950 hPa) of the sonde profile is considered for all of these stations. For the mountain sites Hohenpeissenberg and Payerne, the surface layer is 950–850 hPa.

More than 180 EMEP (European Monitoring and Evaluation Program) surface stations provide measurements of ozone concentrations. However we only keep the EMEP stations located within our Central Europe region and with continuous measurements over the period 1995–2008. The data of the 36 remaining sites are filtered to keep morning measurements only. The surface stations appear as the green plus markers on the map (Fig. 2).

### 2.3 Subsampling methodology

In order to mimic the regular sampling of the soundings, we subsampled the MOZAIC morning dataset using a "regular" sampling method. Figure 3 illustrates how the profiles are picked for a month documented with 24 profiles, when we want to create subsamples of 4 profiles. The first subsample (S1) includes the profiles: #1, #6, #11 and #16; the second subsample (S2) includes the #2, #7, #12 and #17; and so on for the other subsamples. In this example we are able to create 5 independent subsamples but the last 4 profiles will not be used as we do not allow multiple uses of profiles. This method avoids picking sequential days, which is consistent with the sampling frequency of ozone sondes, even though some MOZAIC profiles are discarded in this way. Following this method, there are usually less than 10 subsamples created with 12 profiles for each month. As a compromise between representativity and data availability, we limit the number of monthly subsamples to 10 for both frequencies.





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The seasonal subsamples are derived from the monthly subsamples. If there are $n1$, $n2$ and $n3$ subsamples for month 1, month 2 and month 3 respectively, then we derive $n = n1 \times n2 \times n3$ seasonal subsamples. Consequently, a monthly subsample may be used in several seasonal subsamples. The number of created subsamples per season and per year are given in Fig. 1. As there are up to 10 monthly subamples, the maximum number of seasonal subsamples is 1000. This value is often reached for the 4 profiles a month frequency. As there are generally less than 10 monthly subsamples of 12 profiles that could be created, the maximum of seasonal subsamples at this frequency is around 120. Using this "regular" sampling method, the number of subsamples is highly dependent on the number of available profiles. In particular, fewer profiles are available for the years 2002 and 2005, especially in spring and summer (Fig. 1). In order to keep a minimum of two subsamples per season, per year and for each frequency we discard spring 2005 and summer 2002 and 2005. Discarding those particular years does not significantly affect the results regarding the trends presented in Sect. 3.5.

We also tried a "random" sampling method, illustrated in Fig. 3, which gives similar results to those presented hereafter. A random sampling allows to eventually consider any profiles and to create 10 subsamples whatever the number of profiles available and the frequency. However profiles from sequential days might be selected, giving more weight to a particular time/event in the monthly mean. The results obtained with this "random" sampling method are compared to those from the "regular" method.

## 3 Effect of the sampling over Frankfurt

In this section we discuss to what extent the sampling impacts the observed means and the annual and inter annual variabilities.





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## 3.1 Definition of the metric called sampling uncertainty

In this study, we aim to give quantitative estimates of the uncertainties that arise from low time resolution, depending on season, altitude level and sampling frequency. Here we explain how we defined the metric used as an estimate of the sampling uncertainty.

First, we define, for each season and each year, the true value as the overall mean of the morning profiles, $\overline{x}$. We named $x_i^{\text{samp}}$ the seasonal mean derived from one subsample. For each subsampling frequency, each season and each year, there are $n$ possible values of $x_i^{\text{samp}}$ $(i = 1, n)$. We considered the distributions of the $\{x_i^{\text{samp}} - \overline{x}\}$, differences between the true value and the biased seasonal means, and defined $\sigma_{\text{yr}}^{\text{samp}}$ the standard deviation of this distribution.

Then, the $x_i^{\text{samp}} - \overline{x}$ values of approximatly 11 000 (1500) seasonal subsamples of 4 (12) profiles a month were gathered over the period 1995–2008 in order to obtain the probability density functions of the biased seasonal means. We defined the uncertainty due to a low sampling frequency as three times the standard deviation $\sigma^{\text{samp}}$ of these distributions. This value ensures that 99 % of the seasonal means derived from the subsamples are within $\pm 3 \times \sigma^{\text{samp}}$ of their true value.

## 3.2 Sampling effect on the seasonal means

Figure 4 presents the seasonal variations of ozone concentrations from the MOZAIC morning subset (in blue) between 1995 and 2008 at four pressure levels (1000, 800, 600 and 400 hPa) over Frankfurt. The confidence limits on the ozone mean ($\overline{x}$) correspond to $\pm 3\overline{\sigma}$ where $\overline{\sigma} = \sigma / \sqrt{N-1}$ with $\sigma$ the standard deviation and $N$ the number of profiles of the morning MOZAIC data set. The shaded areas represent the range of the seasonal means at 4 and 12 profiles a month frequencies (in orange and red respectively), defined as $\pm 3\sigma_{\text{yr}}^{\text{samp}}$ around the true value. This means that 99 % of the seasonal biased means lie within this range. Table 1 summarises the values of $3 \times \sigma^{\text{samp}}$ for each season at both frequencies in percentage relative to the seasonal mean at four pressure levels.





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The uncertainty due to low frequency sampling derived from the "random" sampling method is generally similar however slightly higher to that from the "regular" sampling method. The $3 \times \sigma^{samp}$ values from this method are generally within 15 % of the values presented for the "regular" method in Table 1, with exceptions in the lowest levels for the $N_f = 12$ profiles a month samples where the differences can reach 50 %.

As expected, the uncertainty due to time resolution increases when the sampling frequency decreases. The sampling uncertainty ranges between 11 to 44 % for a 4 profile a month dataset compared to 7–27 % for the 12 profile a month dataset. For surface ozone, the narrowest ranges in ppbv are observed in the winter and fall seasons due to a lower day-to-day variability in winter and fall (Fig. 4); however as these months have lower ozone concentrations, the uncertainty represents up to 27 and 44 % of the true value, respectively. In the free troposphere, the lowest uncertainty is found in winter. Also due to higher day-to-day variability in the boundary layer and in the upper troposphere (high impact of stratospheric intrusions), the distributions are larger at these levels compared to the ones in the middle troposphere.

As a result, different low time frequency samples may show substantially different seasonal means and may partly mask the annual and inter annual variabilities. This uncertainty needs to be quantified and taken into account for further observation comparison or model evaluation.

### 3.3 Sampling effect on annual and inter annual variabilities

The seasonal cycle is well marked in the whole morning data set in Fig. 4. The seasonal differences of the long-term means between the cold and the warm months (DJF vs. JJA) are 44, 28, 29 and 85 % relative to the cold month concentrations, respectively to the four pressure levels considered (from top to the surface). These differences are higher than the sampling uncertainty (Table 1), meaning that the seasonal cycle can be distinguished even by the low frequency measurements.

The variability of ozone concentration from one year to another is calculated as $(\overline{x_{yr+1}} - \overline{x_{yr}})/\overline{x_{yr}}$. On average, the inter annual variability (IAV) never exceeds 6 % in



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the free troposphere and ranges between 7 and 20 % in the two lowest levels. The observed IAV signal is generally similar to the confidence limits of the overall morning data set means and much lower than the sampling uncertainty. Consequently, except for extreme events, the IAV signal might possibly be masked by the sampling effect when using low time resolution data sets and the observed IAV signal will be highly dependent on the sampling, especially at the lowest time resolution.

### 3.4 Sampling uncertainty versus measurement uncertainties

Figure 5 shows the vertical profiles of the uncertainty introduced by sampling, as defined by $3 \times \sigma^{\text{samp}}$ (solid lines). The sampling uncertainty is systematically higher than 10 % at the lowest time resolution, while at a 12 profiles a month frequency, this uncertainty generally drops below 10 % in the free troposphere. The lowest uncertainty is observed in the free troposphere at 700 hPa. This result suggests that over Frankfurt the 700 hPa level is the best candidate for comparing observations or model with observation and limiting the bias due to different samplings. At this level, the sampling uncertainty is 6.6, 6.5, 7.6, 7.9 % for winter, spring, summer and fall respectively for a 12 profile a month dataset (13.3, 13.9, 15.2, 14.0 % for 4 profile a month). The C-shape reflects the occurence of stratospheric influence and the boundary layer variability as discussed above. The "random" sampling method shows similar profiles in shape (orange and red dashed lines in Fig. 5). It is worth noting that the MOZAIC instrument uncertainty is typically 2–3 ppbv for a concentration lower than 50 ppb, which is not significant compared to the sampling uncertainty.

The sampling uncertainty is compared to the average standard deviation of a subsample, as this latter value can be easily determined when using any data set. The standard deviation of the seasonal subsample mean is calculated as $\overline{\sigma^{\text{s}}} = \sigma^{\text{s}} / \sqrt{(N_{\text{s}} - 1)}$ where $N_{\text{s}}$ is the number of profiles in the subsample and the average values of $3 \times \overline{\sigma^{\text{s}}}$ are overplotted in Fig. 5 (orange and red dot-dashed lines). We observed that the $3 \times \overline{\sigma^{\text{s}}}$ values are generally higher or similar to the sampling uncertainty we derived




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in this study (within $3\times\sigma^{samp}\pm 8\,\%$ on average over the season and altitudes). The $3\times\overline{\sigma^{s}}$ values reflect the intra-seasonal variability (variation within each season) of ozone concentrations in a subsample. The blue dot-dashed line represents the true intra-seasonal variability, which is much lower than the sampling uncertainty. As a result, this intra-seasonal variability is masked by the sampling.

The accuracy of ozone sonde measurements is often quoted as ±5 % (Smit and Kley, 1998). A series of experiments evaluated the sonde performance and indicated a precision of better than ±(3–5) % and an accuracy of about ±(5–10) % up to 30 km altitude if standard operating procedures for ECC sondes are used (Smit et al., 2007). Those values are represented on Fig. 5 in dotted lines and are generally lower than the sampling uncertainty, except in the free troposphere for the 12 profile a month frequency.

The results, regardless of the method, show that deriving seasonal means from low time resolution measurements leads to a significant uncertainty. We found that:

1. the sampling uncertainty is generally higher than the accuracy of the ozone sondes, suggesting that the uncertainty on the seasonal means is probably underestimated when considering only the accuracy of the sonde.

2. the true intra-seasonal variability is masked by the sampling

3. the sampling uncertainty is similar to the biased intra-seasonal variability detected by a subsample. As a consequence, we suggest that the uncertainty on the seasonal means of ozone concentrations *f* rom sonde measurements should take into account the sampling resolution. Thus the $3\times\sigma^{samp}$ values presented in Table 1 and Fig. 5 should be used as an estimate of the uncertainty of measurements made at low time frequency and especially for the 4 profile a month data sets, when compared to other observations or model on a seasonal basis. The statistical uncertainty derived with the standard deviation of the sample mean ($3\times\overline{\sigma^{s}}$) might also be used as estimates of the sampling uncertainty.





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### 3.5 Sampling effect on ozone trends

Seasonal trends in ozone over the period 1995–2008 are derived from the whole morning MOZAIC data set using a linear regression with points weighted by $\overline{\sigma}$ (defined in Sect. 3.1). The linear trends are also derived from the measurements made at the six European sonde sites and the 36 EMEP surface stations. Weighting the points allows taking into account the uncertainty we have on each yearly seasonal mean. The weighting greatly raises the uncertainty estimate of the trend but the trend magnitude remains unchanged. As a consequence, the standard error of the slope is highly dependent on the standard deviation $\overline{\sigma}$ used for the weighting, and therefore dependent on the number of data. Figure 6 displays the distribution of the trends and their uncertainty estimates.

The MOZAIC morning subset shows the highest positive trends in winter and fall in the lowest level, while the surface ozone trend in summer is negative ($-0.4\,\text{ppbv}\,\text{yr}^{-1}$). Those results for surface ozone are in agreement with previous studies (Ordóñez et al., 2005; Zbinden et al., 2006; Jonson et al., 2006; Oltmans et al., 2006; Jeannet et al., 2007; Gilge et al., 2010). They result from a decrease of nitrogen oxide emissions during this period. In the cold months, the loss of ozone decreases due to reduced NO titration, and during summer pollution episodes, the photo-chemical ozone production is weaker. In the free troposphere and the upper troposphere, the trends are weaker and not statistically significant.

Surface stations give the lowest uncertainty in the slope due to their large amount of data. Most of them suggest a positive trend in all seasons, except in summer when trends are more scattered around zero. The seasonal trends vary with the altitude of the stations (not shown). Above 1 km, the results suggest a negative trend in summer, positive in winter and spring and a near-zero trend during the fall season, in agreement with MOZAIC measurements in Frankfurt.

To quantify the effect of a low frequency sampling on the linear trend in ozone concentrations, we selected 200 random time series within each ensemble of Frankfurt





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subsamples and calculated the associated trends. These low frequency MOZAIC trends are overplotted in Fig. 6 in red and orange diamonds for the 12 and 4 profiles a month frequencies respectively. The true value of the trend at Frankfurt is defined as the trend derived from the full MOZAIC morning subset (black diamond). The mean values of the trends derived from the ensembles are generally similar to the true value (within 0.2 ppbv $yr^{-1}$). As expected, the variance of the trends is greater at a frequency of 4 profiles a month than of 12 profiles a month. Winter and fall trends from the MOZAIC morning subset being well pronounced in the lowest levels, the distribution of the subsample trends remains in the positive quadrant. The narrowest scattering in the cold months is due to a lower variability of ozone (see Sect. 3.2). In summer and spring, the higher variability and the less marked trend result in a larger scattering around a null trend.

The trends derived from the ozone sondes (blue stars) are generally highly uncertain due to their low time resolution. Comparing the sonde data points with the Frankfurt subsamples, we observe that the uncertainty estimate of the slope of each sounding station is close to those of the ensemble at similar sampling frequency. Obviously this results from measurement frequency at each station (close to 4–7 profiles a month for Debilt, Lindenberg and Praha and around 12 times a month over Hohenpeissenberg, Payerne and Uccle). The sonde data fall surprisingly well within the Frankfurt subsamples except for the winter season. This discrepancy can be explained by the different variations observed at the beginning of the time period when MOZAIC ozone increases while the sonde time series are flat (Tilmes et al., 2011). The reason for this difference is not understood yet, and could be due to measurement issues or sampling effect.

We applied the same approach using the subsamples created with the "random" sampling method. The main characteristics of the distributions obtained from the 200 random time series are generally similar to those using the "regular" sampling method, showing that both sampling methods lead to similar conclusions regarding the effect of sampling frequency on the trend (not shown).



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To conclude, this study suggests that low sampling frequency data sets may show significant differences in trend over the period 1995–2008. It is worth noting that ozone concentrations do not show significant variations over this period. This explains why the sonde trends are found both positive and negative over this period. We show that the trends extracted from the subsamples can be highly biased and not representative even if apparently significative. As a consequence, our study suggests that apparent discrepancies between stations may be attributed to the low sampling frequency, in addition to specific conditions at each station.

## 4 Generalisation to the Northern Hemisphere midlatitudes

In this paragraph, we aim to generalise our results to the Northern Hemisphere mid-latitudes. The Frankfurt data set was the best candidate to start this study since there were more than two profiles per day collected. However others cities in the Northern Hemisphere are well documented, such as Vienna, Paris, New-York, Boston, Tokyo and Osaka. The number of profiles collected per season over these cities are summarised in Table 2.

Over Frankfurt, Vienna, Paris and New York, the average number of profiles collected per season and per year allows subsampling of these data sets at the two typical ozonesonde frequencies. The data sets over Boston, Tokyo and Osaka have a lower frequency sampling and thus can be subsampled only at the 4 profiles a month frequency. In order to have more subsamples, we considered all the profiles without time restrictions and used the "random" sampling method. As the sampling method had no significant impact on the results obtained for Frankfurt in Sect. 3, we argue applying this method here is appropriate. As for Frankfurt, the time filtering affects only the lowest levels and has no influence in the free troposphere.

For the seven cities we derived the values of the uncertainty of sampling defined as $3 \times \sigma^{\text{samp}}$ (see Sect. 3.1) and plotted these values against pressure levels on Fig. 7, color coded by cities. The vertical profiles for Vienna, Paris, New-York and Boston are





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similar to those for Frankfurt in regards of the shape and the order of magnitude. As expected, the sampling uncertainty is higher at the lowest frequency for all the sites. Except Paris in MAM, they all show that the sampling uncertainty at 12 profiles a month is lower than the 10 % measurement error in the free troposphere (around 8 %), while the sampling uncertainty at 4 profile a month is systematically larger than the measurement accuracy. For $N_f = 4$ profiles a month, the uncertainty due to sampling is around 10–18 % in the free troposphere. The results suggest a greater sampling uncertainty for Tokyo and Osaka (20 to 30 % in JJA and SON) than for Europe and North America in all seasons except in winter. From spring to fall, the troposphere over Japan is under the influence of the pollution emitted by biomass burning in Siberia and China (Streets et al., 2003). Also the dynamics can influence the ozone distribution depending on the regime under which the site is from one day to another (tropical dynamics with influence of monsoon circulation and convective systems, transport of midlatitude air masses). This leads to a greater day-to-day variability of ozone concentrations in the Japanese free troposphere which largely impacts the $\{x_i^{\text{samp}} - \overline{x}\}$ distributions.

We also compared the vertical profiles of $3 \times \sigma^{\text{samp}}$ with the vertical profiles of $3 \times \overline{\sigma^{\text{s}}}$ as in Fig. 5 for all these cities. We did not overplot these profiles on Fig. 7 for clarity. As for Frankfurt in Sect. 3.3, we found that the sampling uncertainty is similar to the intra-seasonal variability depicted by a subsample for all stations in the Northern Hemisphere. However, the difference between these two metrics relative to $3 \times \sigma^{\text{samp}}$ (between 10 and 18 %, except for Boston (47 %) and Osaka (24 %)) is larger than the difference calculated for Frankfurt due to fewer profiles available.

To conclude, the results derived from the detailed study done for Frankfurt in Sect. 3 can be extended to other northern midlatitude sites without a strong influence of biomass burning pollution or tropical dynamics. For sites more similar to Tokyo and Osaka in terms of fire pollution impact and dynamics the intra-seasonal variability is higher, leading to an enhanced sampling uncertainty. As a consequence, we suggest a careful interpretation of the observed means over Japan.





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## 5 Tropical case: Windhoek, Namibia

In order to extend our discussion to the tropics, we use here the daily data collected over Windhoek, Namibia by the MOZAIC aircraft under the carrier Air Namibia between December 2005 and November 2008. During this three year period, there were 250, 262, 267 and 263 profiles collected over Windhoek in winter, spring, summer and fall respectively (leading to around one profile per day). The random sampling method was applied to the Windhoek data set. The time period recorded over Windhoek is shorter than for Frankfurt, however the frequency of the sampling is high enough for the results to be reliable.

The results are presented in Fig. 8 similar to Fig. 5 for Frankfurt. Over Windhoek, there is less variation in altitude compared to the C-shape profiles shown for Frankfurt in Fig. 5. The tropopause being much higher in altitude in the tropics, there is no influence of stratospheric mixing up to 300 hPa over Windhoek. In the lowest levels, the vicinity of Windhoek airport presents lower anthropogenic pollution than in the Northern Hemisphere airports. As a consequence, there is less variability due to local anthropogenic ozone pollution.

The sampling uncertainty calculated for Windhoek is around 10 % and 15 % for the 12 and 4 profiles a month frequencies respectively. These values are similar to what was found in the free troposphere at the Northern Hemisphere midlatitudes.

Compared to Frankfurt and the other Northern Hemispheric cities, the differences between the sampling uncertainty and the intra-seasonal variability depicted by the subsamples are much higher. These differences range from 10 to 40 % on average over the column, depending on the season. The highest difference is reached during the JJA, which are the peak months of the burning season of southern Africa. Compared to Japan during the Asian biomass burning season, the sampling uncertainty seems to have a lesser importance over Windhoek. This could be explained by more regular biomass burning pollution events and also a more regular dynamics over Windhoek than over Japan, leading to high intra-seasonal variability but close seasonal means





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among the subsamples. As a consequence the intra-seasonal variability is not masked by the sampling.

## 6 Conclusions

We have used high frequency MOZAIC data sets to discuss the effect of sampling in the analysis of ozone vertical profiles in order to estimate the uncertainty that arises when using low time resolution data sets such as the ozone sondes. We subsampled the MOZAIC profiles at the two typical ozone sounde frequencies, which are 4 and 12 profiles a month, and combined the monthly subsamples into seasonal subsamples. We did a detailed analysis using the Frankfurt dataset as this is the best documented airport by MOZAIC. Also we used other northern midlatitude sites to generalise our findings, and the Windhoek, Namibia dataset to discuss a tropical case.

We defined the sampling uncertainty as $3 \times \sigma^{\text{samp}}$ where $\sigma^{\text{samp}}$ is the standard deviation of the distribution of the differences between the biased seasonal means and the overall mean. This metric has been derived per season and per pressure levels. As expected the sampling uncertainty is higher at the lower time resolution.

The vertical profiles of the sampling uncertainty have a C-shape for all the Northern Hemisphere sites. The lowest and highest levels present higher uncertainty due to higher day-to-day variability causes by local anthropogenic pollution events and stratospheric intrusions respectively. The lowest uncertainty is found in the free troposphere at 700 hPa with values around 7 and 14 % for the 12 and 4 profile a month frequencies respectively over Frankfurt. As a consequence this level is the best candidate for observation comparison and model evaluation purpose.

We compared the sampling uncertainty to the measurement accuracy and the intra-seasonal variability detected by a subsample, we found that:

1. At a 12 profile a month frequency, the sampling uncertainty drops below the measurement accuracy in the free troposphere, while at 4 profile a month the sampling uncertainty is higher than the measurement accuracy and should be considered carefully.





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2. The true intra-seasonal variability is masked by the sampling.

3. The sampling uncertainty is lower or similar to the biased intra-seasonal variability detected by a subsample when no biomass burning pollution import is involved. In case of biomass burning pollution, as for Japan in the summer season, we found that the sampling uncertainty is much higher than the intra-seasonal variability. This could reflect the irregularity of the pollution import events. However the small amount of profiles available for the two Japanese sites could also lead to this effect.

We discussed how accurate the low time resolution measurements are to detect ozone variations at different time scales. We concluded that:

1. The seasonal cycle is well observed.

2. The IAV signal is generally too low, consequently masked by the sampling effect.

3. The trend derived over the 14 year period 1995–2008 varies significantly in magnitude and even in sign with the samples. As a consequence, apparent discrepancies between sites might be attributed to a low frequency sampling in some cases.

We used the Windhoek ozone profiles as a tropical case study. The sampling uncertainty in the free troposphere is similar to the one found for Frankfurt, around 10 and 15 % at 12 and 4 profiles a month respectively. However we found larger differences between the sampling uncertainty and the average intra-seasonal variability within a sample, especially during the fire season.

To conclude, this study highlights the significant effect of sampling when using low time resolution measurements. We provided estimates of the sampling uncertainty that arises from such data sets, and we believe these estimates should be considered for observation comparison and model evaluation. Also, this study strengthens the need for regular and high frequency measurements of tropospheric ozone to obtain





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accurate observations of the inter annual variability and decadal changes in ozone concentrations and to better understand changes in ozone concentrations.

*Acknowledgements.* The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation. The authors acknowledge the strong support of the European Commission, Airbus, and the Airlines (Lufthansa, Austrian, Air France) who carry free of charge the MOZAIC equipment and perform the maintenance since 1994. MOZAIC is presently funded by INSU-CNRS (France), Météo-France, and Forschungszentrum (FZJ, Jülich, Germany). The MOZAIC data based is supported by ETHER (CNES and INSU-CNRS). The authors are grateful to all the agencies that provide ozonesonde data to the World Ozone and Ultraviolet Radiation Data Centre (WOUDC): German Weather Service – Meteorological Observatory at Hohenpeissenberg and Lindenberg, the National Meteorological Institute of the Netherlands, MeteoSwiss, the Royal Meteorological Institute of Belgium and the Czech HydroMeteorlogical Institute.

## References

Eckhardt, S., Stohl, A., Beirle, S., Spichtinger, N., James, P., Forster, C., Junker, C., Wagner, T., Platt, U., and Jennings, S. G.: The North Atlantic Oscillation controls air pollution transport to the Arctic, Atmos. Chem. Phys., 3, 1769–1778, doi:10.5194/acp-3-1769-2003, 2003. 27109

Emmons, L. K., Hauglustaine, D., Muller, J.-F., Caroll, M., Brasseur, G. P., Brunner, D., Staehelin, J., Thouret, V., and Marenco, A.: Data composites of airborne observations of tropospheric ozone and its precursors, J. Geophys. Res., 105, 20497–20538, 2000. 27109

Fusco, A. C. and Logan, J. A.: Analysis of 1970–1995 trends in tropospheric ozone at Northern Hemisphere midlatitudes with the GEOS-CHEM model, J. Geophys. Res., 108, 4449, doi:10.1029/2002JD002742, 2003. 27109

Gilge, S., Plass-Duelmer, C., Fricke, W., Kaiser, A., Ries, L., Buchmann, B., and Steinbacher, M.: Ozone, carbon monoxide and nitrogen oxides time series at four alpine GAW mountain stations in central Europe, Atmos. Chem. Phys., 10, 12295-12316, doi:10.5194/acp-10-12295-2010, 2010. 27118

Jeannet, P., Stübi, R., Levrat, G., Viatte, P., and Staehelin, J.: Ozone balloon soundings at Payerne (Switzerland): Reevaluation of the time series 1967–2002 and trend analysis, J. Geophys. Res., 112,D11302, 2007. 27118





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Jonson, J. E., Simpson, D., Fagerli, H., and Solberg, S.: Can we explain the trends in European ozone levels?, Atmos. Chem. Phys., 6, 51–66, doi:10.5194/acp-6-51-2006, 2006. 27118
Koumoutsaris, S., Bey, I., Generoso, S., and Thouret, V.: Influence of El Niño Southern Oscillation on the interannual variability of tropospheric ozone in the northern midlatitudes, J. Geophys. Res., 113, D19301, doi:10.1029/2007JD009753, 2008. 27109
Lamarque, J.-F. and Hess, P. G.: Arctic Oscillation modulation of the Northern Hemisphere spring tropospheric ozone, Geophys. Res. Lett., 31, 6127, doi:10.1029/2003GL019116, 2004. 27109
Logan, J.: An Analysis of Ozonesonde Data for the Lower Stratosphere: Recommendations for Testing Models, J. Geophys. Res., 104, 16151–16170, 1999. 27109
Marenco, A., Thouret, V., Nédélec, P., Smit, H., Helten, M., Kley, D., Karcher, F., Simon, P., Law, K., Pyle, J., Poschmann, G., Von Wrede, R., Hume, C., and Cook, T.: Measurement of ozone and water vapor by Airbus in-service aircraft: The MOZAIC airborne program, An overview, J. Geophys. Res., 103, 25631–25642, 1998. 27110
Monks, P. S., Granier, C., Fuzzi, S., Stohl, A., Williams, M.L., Akimoto, H., Amann,M., Baklanov, A., Baltensperger, U., Bey, I., Blake, N., Blake; R.S., Carslaw, K., Cooper, O.R., Dentener, F., Fowler, D., Fragkou, E., Frost, G.J., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hansson, H.C., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I.S.A, Jenkin, M.E., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M.G., Lee, J.D., Liousse, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Moussiopoulos, N., Orlando, J.J., O'Dowd, C.D., Palmer, P.I., Parrish, D.D., Petzold, A., Platt, U., Pschl, U., Prvt, A.S.H., Reeves, C.E., Reimann, S., Rudich, Y., Sellegri, K., Steinbrecher, R., Simpson, D., Brink, H. ten, Theloke, J., van der Werf, G.R., Vautard, R., Vestreng, V., Vlachokostas, Ch., von Glasow, R.: Atmospheric composition change – global and regional air quality, Atmos. Environ., 43, 5268–5350, doi:10.1016/j.atmosenv.2009.08.021, 2009. 27109
Naja, M., Akimoto, H., and Staehelin, J.: Ozone in background and photochemically aged air over central Europe: Analysis of long-term ozonesonde data from Hohenpeissenberg and Payerne, J. Geophys. Res., 108, 4063, doi:10.1029/2002JD002477, 2003. 27109
Oltmans, S., Lefohn, A., Harris, J., Galbally, I., Scheel, H., Bodeker, G., Brunke, E., Claude, H., Tarasick, D., Johnson, B., Simmonds, P., Shadwick, D., Anlauf, K., Hayden, K., Schmidlin, F., Fujimoto, T., Akagi, K., Meyer, C., Nichol, S., Davies, J., Redondas, A., and Cuevas, E.: Long-term changes in tropospheric ozone, Atmos. Environ., 40, 3156–3173, doi:10.1016/j.atmosenv.2006.01.029, 2006. 27109, 27118





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Ordóñez, C., Mathis, H., Furger, M., Henne, S., Hüglin, C., Staehelin, J., and Prévt̂, A. S. H.: Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003, Atmos. Chem. Phys., 5, 1187–1203, doi:10.5194/acp-5-1187-2005, 2005. 27109, 27118

Parrish, D. D., Millet, D. B., and Goldstein, A. H.: Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe, Atmos. Chem. Phys., 9, 1303–1323, doi:10.5194/acp-9-1303-2009, 2009. 27109

Smit, H. G. J. and Kley, D.: The 1996 WMO International intercomparison ozonesondes under quasi flight conditions in the environmental chamber at Jülich, report, World Meteorol. Organ., Geneva, Switzerland, 1998. 27117

Smit, H. G. J., Straeter, W., Johnson, B.J., Oltmans, S.J., Davies, J., Tarasick, D.W., Hoegger, B., Stubi, R., Schmidlin, F.J., Northam, T., Thompson, A.M., Witte, J.C., Boyd, I., Posny, F.: Assessment of the performance of ECCozonesondes under quasiflight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE), J. Geophys. Res., 112, D19306, 2007. 27117

Streets, D. G., Yarber, K. F., Woo, J., and Carmichael, G.: Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions, Global Biogeochem. Cy., 17, 1099, doi:10.1029/2003GB002040, 2003. 27121

Thouret, V., Marenco, A., Logan, J. A., Nédélec, P., and Grouhel, C.: Comparisons of ozone measurements from the MOZAIC airborne program and the ozone sounding network at eight locations, J. Geophys. Res., 103, 25,695–25,720, doi:10.1029/98JD02243, 1998. 27111

Tilmes, S., Lamarque, J.-F., Emmons, L. K., Conley, A., Saunois, M., Thouret, V., Thompson, A.M., Oltmans, S.J., Johnson, B., Tarasick, D.: Updated ozonesonde cimatology for model evaluation, to be submitted to Geoscientific Model Development, 2011. 27112, 27119

Vestreng, V., Mareckova, K., Kakareka, S., Malchykhina, A., and Kukharchyk, T.: Inventory Review 2007; Emission Data reported to LRTAP Convention and NEC Directive, Tech. Rep. MSC-W Technical Report 1/07, Norw. Meteorol. Inst., Oslo, 2007. 27109

Zbinden, R. M., Cammas, J.-P., Thouret, V., Nédélec, P., Karcher, F., and Simon, P.: Mid-latitude tropospheric ozone columns from the MOZAIC program: climatology and interannual variability, Atmos. Chem. Phys., 6, 1053–1073, doi:10.5194/acp-6-1053-2006, 2006. 27109, 27118





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**Table 1.** Percentage uncertainty due to low time resolution, defined as the $3 \times \sigma^{samp}$ (see text for details). Values are given for the "regular" sampling method in percentage relative to the overall seasonal mean at both sampling frequencies ($N_f = 4$ and 12 profiles a month) and at four pressure levels.

| | Frequency | Winter | Spring | Summer | Fall |
|---|---|---|---|---|---|
| 400 hPa | $N_f = 4$ | 25.3 | 31.5 | 21.3 | 27.3 |
| | $N_f = 12$ | 13.2 | 13.4 | 11.3 | 14.5 |
| 600 hPa | $N_f = 4$ | 11.1 | 13.8 | 15.7 | 16.5 |
| | $N_f = 12$ | 7.1 | 8.3 | 8.5 | 10.1 |
| 800 hPa | $N_f = 4$ | 14.1 | 16.4 | 18.7 | 16.9 |
| | $N_f = 12$ | 8.2 | 8.4 | 8.1 | 9.6 |
| 1000 hPa | $N_f = 4$ | 43.5 | 35.7 | 36.4 | 44.0 |
| | $N_f = 12$ | 17.0 | 15.2 | 19.6 | 26.8 |





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**Table 2.** Number of profiles collected per season over the 14 year period 1995–2008 by the MOZAIC aircraft over Frankfurt, Vienna, Paris, New-York, Boston, Tokyo and Osak. Numbers in bracket are the average number of profiles collected per season per year.

| City (Period) | DJF | MAM | JJA | SON | Total |
|---|---|---|---|---|---|
| Frankfurt (1995–2008) | 3010 (215) | 3026 (216) | 3406 (243) | 3231 (231) | 12 676 |
| Vienna (1995–2006) | 867 (62) | 1136 (81) | 1517 (108) | 1245(89) | 4765 |
| Paris (1995–2004) | 1040 (74) | 961 (69) | 1062 (76) | 1090 (78) | 4153 |
| New-York (1995–2006) | 762 (54) | 778 (56) | 846 (60) | 863 (62) | 3249 |
| Boston (1995–2006) | 198 (14) | 190 (14) | 332 (24) | 298 (21) | 1018 |
| Tokyo (1995–2006) | 307 (22) | 410 (29) | 455 (33) | 346 (25) | 1518 |
| Osaka (1995–2006) | 293 (21) | 349 (25) | 400 (29) | 409 (29) | 1451 |





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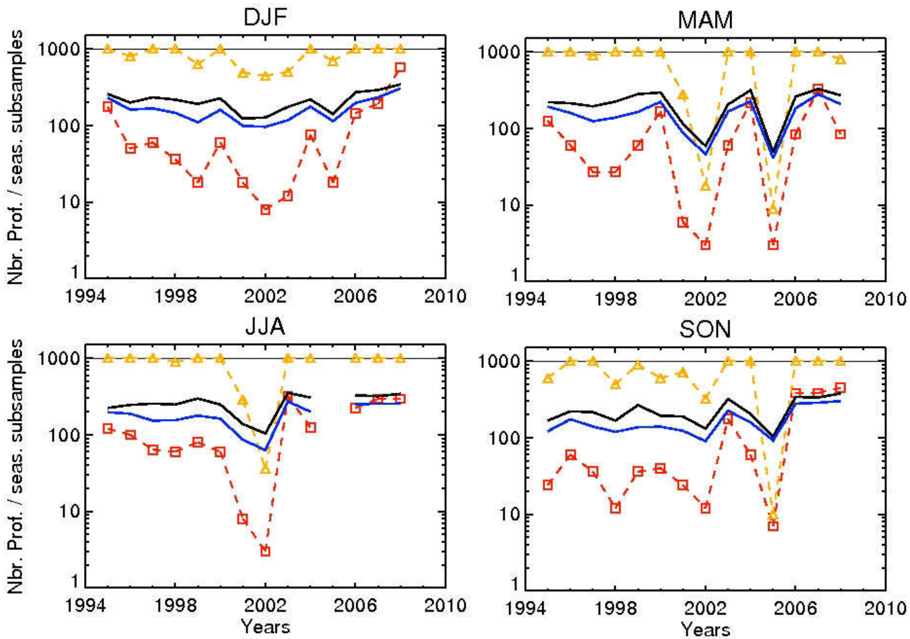


**Fig. 1.** Time record of the number of vertical profiles taken over Frankfurt between 1995 and 2008, in the whole data set (black) and in the morning (blue) subset in solid lines. The number of seasonal subsamples created with a frequency of 4 (orange) and 12 (red) profiles a month using the "regular" sampling method is shown by the dashed line.

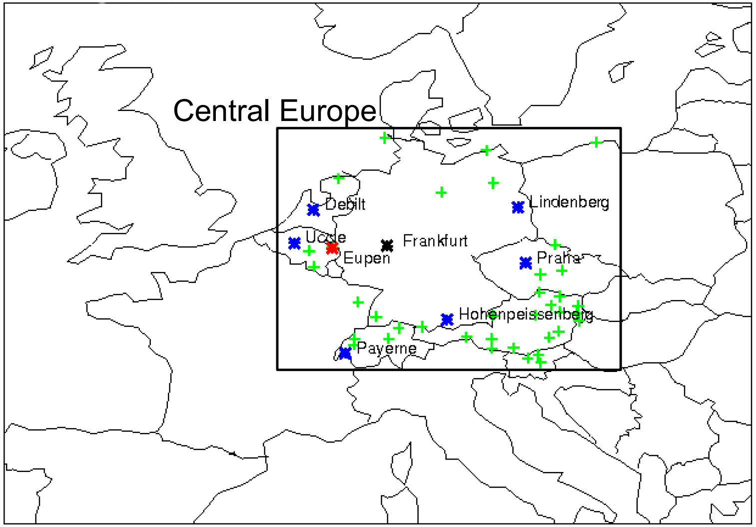


**Fig. 2.** Map of Europe. The Central Europe region defined by the area between 44° N and 55° N latitude, and 3° W and 18° W longitude is within the black rectangle. The sites used in Sect. 3.4.2 are shown with different markers: the MOZAIC city, Frankfurt (black diamond), the six ozone sounding sites (blue stars) and the EMEP surface stations (green plus and Eupen, Belgium as the red star).





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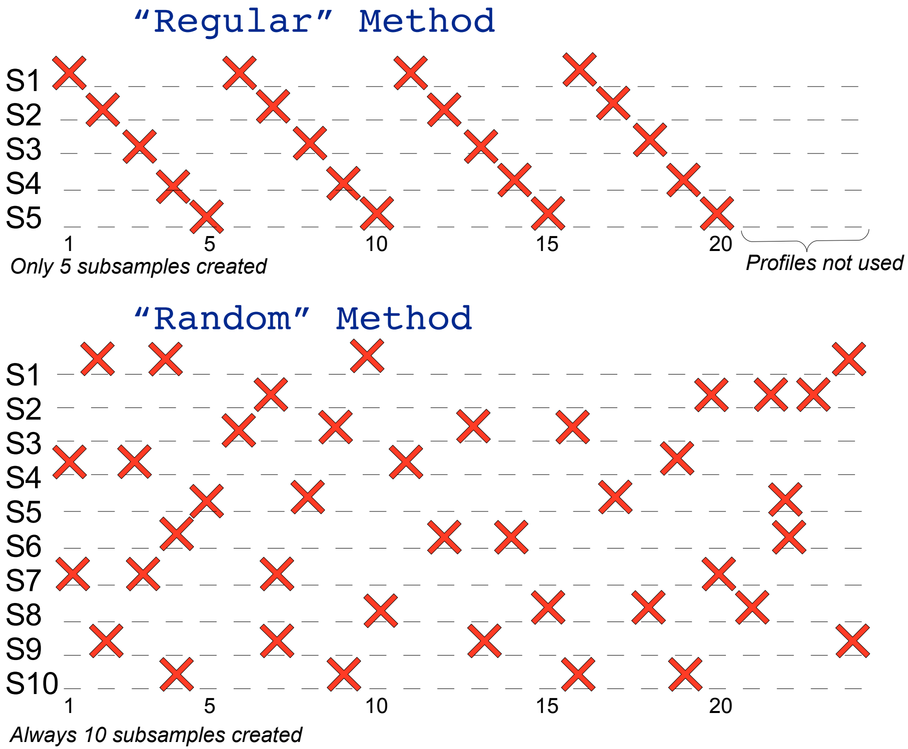


**Fig. 3.** Illustration of the "regular" and the "random" sampling methods. Here we subsample a month, for which 24 profiles are available, at a 4 profiles per month frequency using both methods. Each line represents one subsample (S1 to S5 or S10). Each small thin horizontal line represents a profile, if the profile is picked a red cross is on it.



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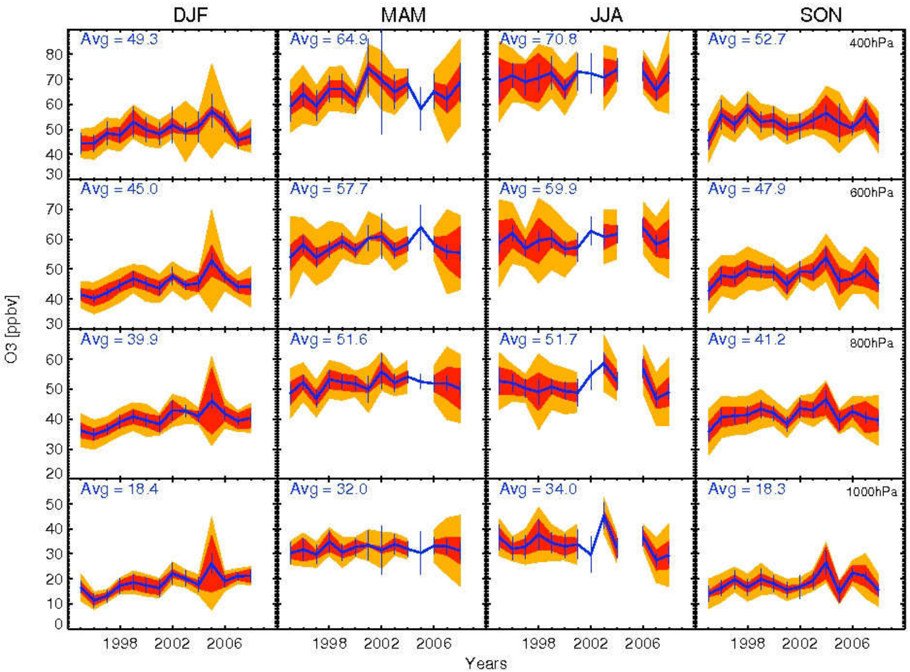


**Fig. 4.** Time evolution of the ozone seasonal means over Frankfurt between 1995 and 2008 as observed by MOZAIC aircraft at four pressure levels (1000, 800, 600, 400 hPa). Overall means ($\overline{x}$) from the morning data set is shown in blue with the 99 % confidence limit error bars ($3 \times \overline{\sigma}$). The shaded areas represent the range $[\overline{x} - 3 \times \sigma_{\text{yr}}^{\text{samp}}, \overline{x} + 3 \times \sigma_{\text{yr}}^{\text{samp}}]$ derived from the ensemble at a 4 (orange) and 12 (red) profiles a month frequency. $\sigma_{\text{yr}}^{\text{samp}}$ is the standard deviation of the distribution of the seasonal mean of the subsamples for each year. On the top left corner, the average seasonal means over the entire period is shown.





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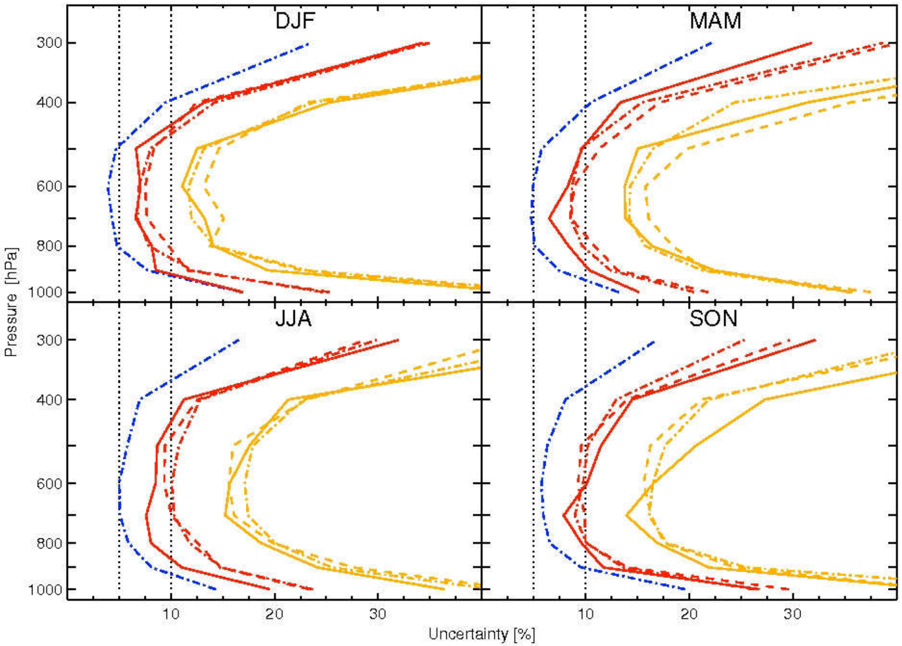


**Fig. 5.** Vertical profiles of the uncertainty due to low time resolution, defined as $3 \times \sigma^{samp}$, derived from Frankfurt MOZAIC data. The solid lines corresponds to the "regular" sampling method and the dashed lines to the "random" sampling method. The dot-dashed lines represent the average values of $3 \times \overline{\sigma}^{s}$ (orange and red) and $3 \times \overline{\sigma}$ (blue) where $\overline{\sigma}^{s}$ is the standard deviation of a subsample and $\overline{\sigma}$ the standard deviation sing the whole morning data set (see texte for details). The $N_f = 4$ profile a month values are shown in orange and $N_f = 12$ in red. The vertical dotted lines are the 5 and 10 % value lines, uncertainty commonly quoted for error measurements of ozone sondes.

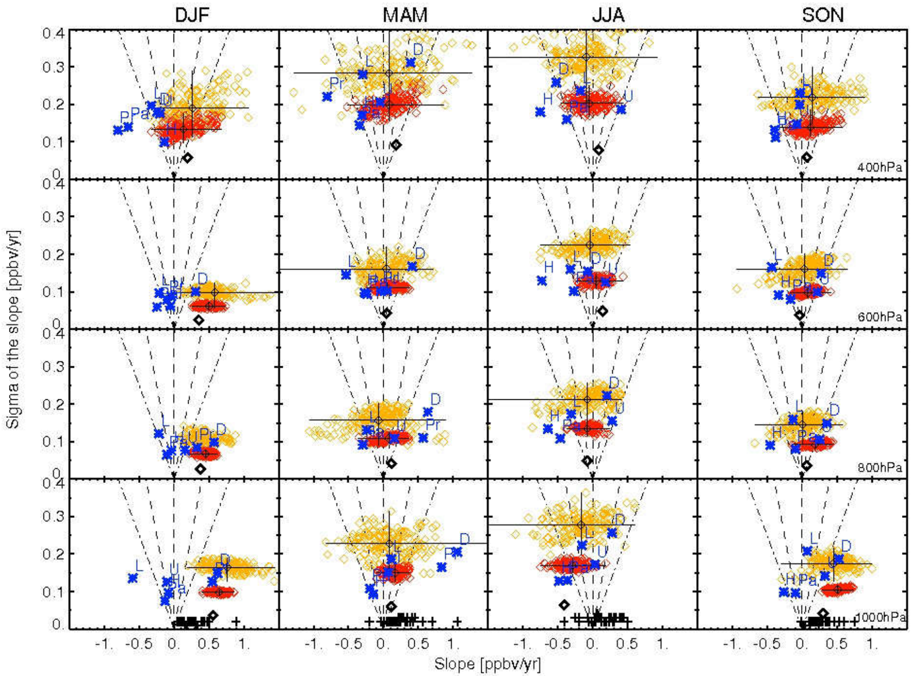


**Fig. 6.** Slope of the linear trend against the 1-sigma uncertainty estimate of this slope. Black plus symbols give the trends at the 36 surface stations. Blue stars give the trends derived from ozone sondes at the six stations (D = Debilt, H = Hohenpeissenberg, L = Lindenberg, Pa = Payerne, Pr = Praha, U = Uccle) at 1000 hPa except for H and Pa, value at 900h Pa. The black diamond corresponds to the trends derived from whole morning MOZAIC data set in Frankfurt. 200 random time series were created from the ensemble of Frankfurt subsamples. The resulting trends are given by the cloud of diamonds in red (frequency of 12 profiles a month) and orange (4 profiles a month). The mean, minimum and maximum of the distributions are shown with the vertical and horizontal black thin lines. The dashed and dot-dashed lines show the 67 % and 95 % confidence limit lines.





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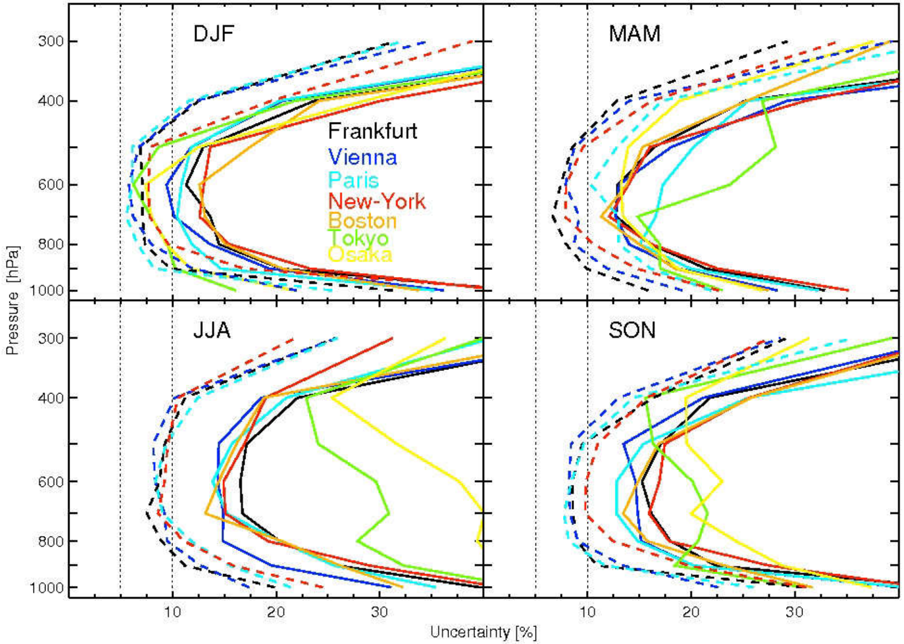


**Fig. 7.** Vertical profiles of the uncertainty due to low time resolution, defined as $3 \times \sigma^{samp}$, colored by cities. The $N_f = 4$ profile a month values are shown in solid lines and $N_f = 12$ in dashed lines for the seven cities. The vertical dotted lines are the 5 and 10 % value lines, uncertainty commonly quoted for error measurements of ozone sondes.





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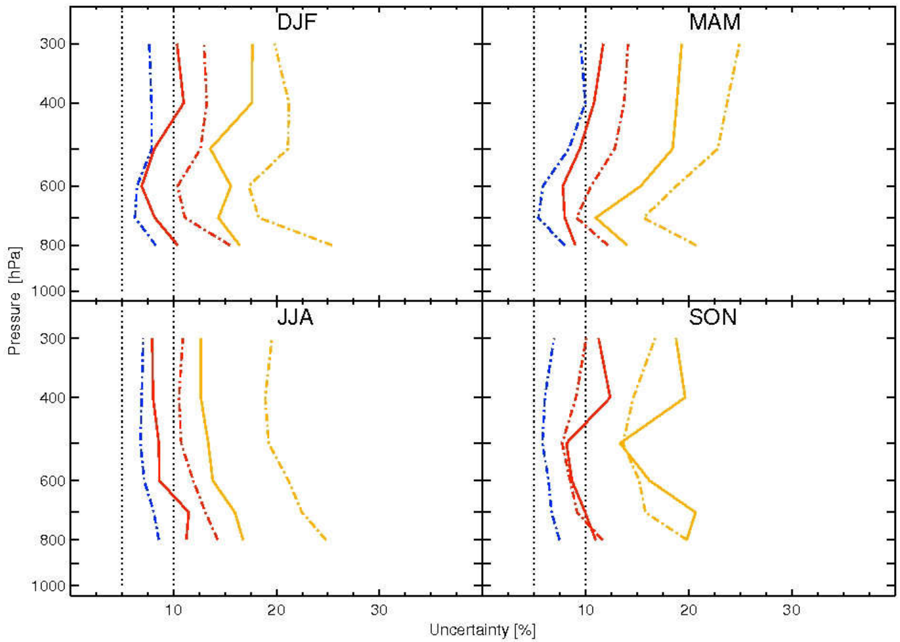


**Fig. 8.** Vertical profiles of the uncertainty due to low time resolution, defined as $3 \times \sigma^{\text{samp}}$, derived from Windhoek MOZAIC data. Only the "random" sampling method results are shown in solid lines. The dot-dashed lines represent the average values of $3 \times \overline{\sigma^{\text{s}}}$ (orange and red) and $3 \times \overline{\sigma}$ (blue) where $\overline{\sigma^{\text{s}}}$ is the standard deviation of a subsample and $\overline{\sigma}$ the standard deviation using the full Windhoek data set. The $N_f = 4$ profile a month values are shown in orange and $N_f = 12$ in red. The vertical dotted lines are the 5 and 10 % value lines, uncertainty commonly quoted for error measurements of ozone sondes.





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