An estimate of the impact of stratosphere-to-troposphere transport (STT) on the lower free tropospheric ozone over the Alps using ^{10}Be and ^{7}Be measurements

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[1] In the framework of the European project STACCATO, combined measurements of ^{10}Be and ^{7}Be were carried out regularly during a full year at the high-altitude stations, Jungfraujoch (JUN), Switzerland and Zugspitze (ZUG), Germany. Inspection of the variability of the ratio ^{10}Be/^{7}Be in relation to ^{10}Be, ^{7}Be, and relative humidity (RH) reveals that the ratio is independent from processes that have a clear effect on both radionuclides, such as wet scavenging. High ratio values are generally met under cyclonic or northerly advective conditions, which are the synoptic situations mostly related to stratosphere-to-troposphere transport (STT) events over central Europe, while the 10-day back trajectories indicate a stratospheric source for the majority of the cases within the upper 10% quantile of ^{10}Be/^{7}Be ratios. The monthly ^{10}Be/^{7}Be ratios show a clear May and June peak at JUN and a much weaker seasonality at ZUG. A simple mixing model is used for an independent estimate of the strength of STT throughout the year based on the ^{7}Be and ^{10}Be measurements. In spite of the various uncertainties, the results indicate a seasonal cycle of stratospheric ozone percentage contribution with an early spring maximum (3–11%) and autumn minimum (1–2%) at ZUG, while at JUN, a primary maximum in May and June (6–18%), a secondary maximum in March (4–13%), and a minimum again in autumn (1–4%) are revealed. Although the simple method applied here provides an independent estimate for the impact of STT to the lower troposphere, it nevertheless shows relatively good agreement with Lagrangian model calculations, especially for ZUG. *INDEX TERMS:* 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3329 Meteorology and Atmospheric Dynamics: Mesoscale meteorology; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; *KEYWORDS:* stratospheric intrusions, cosmogenic radionuclides, tropospheric ozone, ^{7}Be, ^{10}Be, Alps

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1. Introduction

[2] The cosmogenic radioisotopes ^{7}Be ($T_{1/2}$ = 53.3 days) and ^{10}Be ($T_{1/2} = 1.5 \times 10^{6}$ years) are produced by spallation reactions of primary (protons) and secondary (neutrons) cosmic ray particles with the atmospheric nuclei (nitrogen and oxygen), which take place mainly in the stratosphere [*Lal and Peters*, 1967]. About 67% of the ^{7}Be and ^{10}Be source is located in the stratosphere and the rest in the troposphere (particularly in the upper troposphere) [*Lal and Peters*, 1967]. The relatively high production rates of ^{7}Be and ^{10}Be in the upper troposphere, combined with transport from the lower stratosphere to the upper troposphere,

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normally maintain a steep vertical concentration gradient between the upper and the lower troposphere [*Feely et al.*, 1989]. The usefulness of cosmogenic radionuclides to trace the influx of stratospheric air into the troposphere is well established already from the 1960s [*Danielsen*, 1968; *Reiter et al.*, 1971]. Nevertheless, ^{7}Be and ^{10}Be cannot be considered as ideal stratospheric tracers, because they attach to aerosols and hence their tropospheric lifetime is primarily controlled by the wet scavenging of the carrier aerosol [*Feely et al.*, 1989].

[3] A way around the difficulties with wet deposition is to use the concentration ratio of the two beryllium radioisotopes because both species attach to the same aerosols and therefore are washed out in the same way [*Raisbeck et al.*, 1981; *Dibb et al.*, 1994]. Thus, the ratio of $^{10}Be/^{7}Be$ can be considered as a stratospheric tracer, like ^{10}Be and ^{7}Be independently, because their concentration ratios in the stratosphere are much higher than in the troposphere, due to the much longer radioactive half-life of ^{10}Be compared to ^{7}Be [*Koch and Rind*, 1998], which at the same time it is not affected by wet scavenging. Their production ratio is virtually constant throughout the atmosphere at a value of approximately 0.6 [*Kollar et al.*, 2000], but because of the much longer decay time of ^{10}Be, their concentration ratio is always larger than that. In the stratosphere, where wet and dry deposition are ineffective, $^{10}Be/^{7}Be$ ratios are much higher than in the troposphere and are controlled by the residence time (months to years) of the air in the stratosphere. *Raisbeck et al.* [1981] measured $^{10}Be/^{7}Be$ ratios ranging from 2.4 to 5.7 at 65°N in the lower stratosphere, while *Dibb et al.* [1994] measured $^{10}Be/^{7}Be$ ratios between 4.0 and 6.9 in the Arctic lower stratosphere, and $^{10}Be/^{7}Be$ ratios lower than 2.2 in stratospheric air in the midlatitudes. Typical $^{10}Be/^{7}Be$ ratios in the lower troposphere of the Northern Hemisphere range from 1.2 in winter to 2 in summer [*Nagai et al.*, 2000].

[4] One weakness of using the $^{10}Be/^{7}Be$ ratio as a stratospheric tracer to determine the stratospheric flux into the troposphere is that an important fraction of the production of both ^{10}Be and ^{7}Be occurs in the upper troposphere and hence surface concentrations of these radionuclides can be also influenced by downward mixing within the troposphere [*Feely et al.*, 1989; *Graustein and Turekian*, 1996; *Zanis et al.*, 1999].

[5] In contrast to ^{7}Be, which is measured regularly with high-resolution gamma spectrometry at Alpine peak stations and at many other sites in the world, regular ^{10}Be measurements are scarce, because its detection requires accelerator mass spectrometry (AMS), which is an expensive method for continuous monitoring. Hence, so far very few studies made use of both ^{7}Be and ^{10}Be data and the $^{10}Be/^{7}Be$ ratio [*Raisbeck et al.*, 1981; *Dibb et al.*, 1994]. *Dibb et al.* [1994] applied a simple model, introduced by *Raisbeck et al.* [1981], on one full year of ^{7}Be and ^{10}Be data at Alert, Canada to estimate a seasonal fraction of stratospheric air at the surface. Under some assumptions, the fraction of stratospheric air can also be used to derive the contribution of stratospheric ozone to the surface ozone. *Dibb et al.* [1994] found that stratosphere-to-troposphere (STT) can account for a maximum of 10–15% of the ozone at the surface in spring, and for less during the rest of the year.

[6] In the framework of STACCATO, combined measurements of ^{10}Be and ^{7}Be were carried out regularly during a full year at two high alpine peaks, Jungfraujoch (JUN) (3580 m asl), Switzerland, and Zugspitze (ZUG) (2962 m asl), Germany. In the present study, these measurements are interpreted in relation to the meteorological situation and atmospheric processes and an independent estimate of the seasonal impact of stratospheric air at the Earth's surface is performed.

2. Data and Methods

2.1. Measurements

[7] Continuous measurements of ozone and ^{7}Be as well as routine acquisition of meteorological data have been carried out regularly at the high-altitude stations JUN, Switzerland (46.53°N, 7.98°E, 3580 m asl), and ZUG, Germany (47.4°N, 11.0°E, 2962 m asl). Particle bound ^{7}Be and ^{10}Be are collected on glass fiber (or cellulose nitrate) filters using high volume air samplers with a time resolution of 24 hours at ZUG and 48 hours at JUN. Within about 50 days after the end of sampling half of the respective filter was measured for its ^{7}Be activity ($T_{1/2}$ = 53.3 days) in a well-type Ge-detector through its characteristic γ-radiation (477.6 keV). Details about the ^{7}Be measurements at both stations can be found in the study of *Gerasopoulos et al.* [2001]. In addition to the daily measurements of ^{7}Be (bidaily for JUN), regular measurements of ^{10}Be were performed with AMS. Two AMS facilities performed ^{10}Be measurements for STACCATO, the AMS facility of the Paul Scherrer Institute together with the Institute of Particle Physics of the ETH Zurich, Switzerland [*Synal et al.*, 1997], analyzing samples from JUN, and the Vienna Environmental Research Accelerator (VERA) of the University of Vienna, Austria [*Kutschera et al.*, 1997] analyzing samples from ZUG. The ^{10}Be activity in filters from ZUG was extracted using daily samples from every second day for the period January–December 2000, while at JUN the measurements were carried out using the bidaily samples or in some occasions 4-day samples or weekly samples from March 2000 to February 2001. Concentrations of ^{10}Be in the atmosphere can be enhanced locally by resuspension of dust from surface soils. Dust concentrations were measured at JUN in the year 2000 and found 56% of the samples to be below 2 $\mu g/m^3$. Assuming a value 5.0E − 8 atoms ^{10}Be/g dust [*Pavich et al.*, 1986], the dust correction is normally only 1% or less for ^{10}Be and it can be 5% if ^{10}Be concentration is extremely low. A direct comparison of the ^{10}Be measurements and the $^{10}Be/^{7}Be$ ratios between JUN and ZUG should be considered with caution because of the different measuring and sampling period.

2.2. Description of the Model

[8] Following the studies of *Raisbeck et al.* [1981] and *Dibb et al.* [1994] the general expression that describes the concentration ratio $^{10}Be/^{7}Be$ in a tropospheric air mass is given below:

$$\frac{[^{10}Be]}{[^{7}Be]} = \frac{P_{10} + Q_{10}}{P_7 + Q_7} \cdot \frac{\lambda_r + \lambda_7}{\lambda_r} \cdot \frac{1 - e^{-\lambda_r \cdot t}}{1 - e^{-(\lambda_r + \lambda_7) \cdot t}} \qquad (1)$$

where P_i and Q_i are the in situ production and injection of ^{i}Be (i = 7 or 10) in the tropospheric air mass, λ_7 is the

radioactive decay constant of ^{7}Be, and λ_r is the decay constant due to removal by wet scavenging and dry deposition. A rearrangement of expression (1) according to the study of *Dibb et al.* [1994] leads to expression (2) which can be evaluated by measured quantities taking also into account that the steady state value of Q_7/P_7 is obtained by letting the time t go to the limit of infinity.

$$\frac{Q_7}{P_7} = \frac{R \cdot \left(\frac{\lambda_r}{\lambda_r+\lambda_7}\right) - P_r}{S_r - R \cdot \left(\frac{\lambda_r}{\lambda_r+\lambda_7}\right)} \quad (2)$$

Here, R is the ratio $^{10}Be/^{7}Be$ measured at the surface, S_r is the ratio $^{10}Be/^{7}Be$ measured in the stratosphere, and P_r is the ratio of the production rates of ^{10}Be and ^{7}Be in the atmosphere.

[9] Using expression (2) the stratospherically derived ^{7}Be at the surface $S[^{7}Be]_{surf}$, can be obtained by expression (3) taking also into account the ^{7}Be concentration $[^{7}Be]_{surf}$ measured at the surface.

$$S\left[{}^{7}Be\right]_{surf} = \frac{Q_7}{Q_7 + P_7}\left[{}^{7}Be\right]_{surf} \quad (3)$$

The stratospherically derived ^{7}Be at the surface, $S[^{7}Be]_{surf}$, estimated from expression (3) can be used to estimate the volume fraction of stratospheric air at the surface, F_{sa}, if ^{7}Be concentrations in the stratosphere, $[^{7}Be]_{strat}$, are known assuming that the residence time $T_r(T_r = 1/\lambda_r)$ due to removal by wet scavenging and dry deposition in the troposphere is the time constant:

$$F_{sa} = \frac{S[{}^{7}Be]_{surf}}{[{}^{7}Be]_{strat}} \quad (4)$$

In general, this method requires measurements of both ^{7}Be and ^{10}Be at the surface and in the stratosphere, as well as an estimate of the atmospheric ratio of the production rate of ^{10}Be and ^{7}Be.

[10] For the application of this method in the current study, the ^{7}Be and ^{10}Be measurements carried out at ZUG and JUN were used, while for ^{7}Be and ^{10}Be measurements in the stratosphere the values reported by *Raisbeck et al.* [1981] and *Dibb et al.* [1994] were adopted. However, all the parameters involved in the calculations have their own uncertainties, and thus taking into account these uncertainties is essential. Considering the annual averages of ^{7}Be and ^{10}Be at ZUG a sensitivity analysis was therefore carried out of the volume fraction of stratospheric air at the surface F_{sa} in relation to P_r, λ_r, S_r, and $[^{7}Be]_{strat}$. *Dibb et al.* [1994] used in their calculations $P_r = 0.6 \pm 0.1$ as a weighted average from both proton and neutron induced reactions. More recent calculations of ^{7}Be and ^{10}Be production rates using improved neutron cross sections indicated a globally averaged production ratio of 0.6 by *Kollár et al.* [2000] and 0.52 by *Masarik and Beer* [1999], while *Nagai et al.* [2000] estimated a globally averaged $^{10}Be/^{7}Be$ production ratio of 0.44 in the stratosphere and 0.67 in the troposphere using the proton and neutron cross sections of ^{14}N and ^{16}O. Hence, in our sensitivity calculations a P_r value of 0.6 ± 0.1 was assumed. Concerning the decay constant λ_r ($\lambda_r = 1/T_r$) due to removal by wet scavenging and dry deposition in the troposphere we used in the sensitivity analysis residence times (T_r) ranging from 20 to 45 days with a step of 5 days. Finally, concerning the $^{10}Be/^{7}Be$ ratio values (S_r) and ^{7}Be concentrations in the stratosphere, we have to rely on the very few stratospheric samples measured by *Raisbeck et al.* [1981] and *Dibb et al.* [1994].

[11] Using back trajectories analysis *Gerasopoulos et al.* [2001] showed that the source region of the highest ^{7}Be concentrations at JUN and ZUG is the latitude band 52°–60°N over western Europe and the North Atlantic. Based on this result, three stratospheric samples measured from 47°N to 65°N at an altitude of approximately 10700 m asl were selected from the studies of *Raisbeck et al.* [1981] and *Dibb et al.* [1994]. The ratio values S_r in these samples range from 1.4 to 5.7 indicating large variability, while the ^{7}Be concentrations in the stratosphere $[^{7}Be]_{strat}$ range from 96×10^4 to 120×10^4 atoms/m^3. Hence, in the sensitivity analysis S_r was chosen to vary from 1.5 to 6. The results of the sensitivity analysis, shown in Figure 1, indicate that the stratospheric volume fraction at the surface decreases with increasing T_r, P_r, and S_r. The largest uncertainties, which can be as high as a factor of 5, are induced by the large uncertainties in S_r. The stratospheric volume fraction at the surface decreases also with increasing $[^{7}Be]_{strat}$, but the relatively small variations in the measurement of $[^{7}Be]_{strat}$ in the three stratospheric samples used here (about 12%) leads also to a similar uncertainty in F_{sa}. However, the scarceness of measurements in the lower stratosphere of ^{7}Be, ^{10}Be and their ratio is the most important limitation for the application of this methodology.

[12] The volume fraction of stratospheric air at the surface F_{sa} can be applied on ozone concentrations of the lower stratosphere $[O_3]_{strat}$ to estimate the surface ozone of stratospheric origin $S[O_3]_{surf}$ following expression (5) under the assumption that the tropospheric lifetime of ozone originating from STT is the same as the lifetime of the aerosols that carry the beryllium isotopes:

$$S[O_3]_{surf} = F_{sa} \cdot [O_3]_{strat} \quad (5)$$

The lifetime of tropospheric ozone ranges from a few days to a few months, with a mean lifetime in the free troposphere of about 1 month [*Liu*, 1987]. Thus, although removal of aerosols and ozone are controlled by different processes (washout and dry deposition versus chemical destruction and dry deposition), their lifetimes are rather similar, and both are lower in moist lower tropospheric air than in dry upper tropospheric air.

3. Results

3.1. Association of $^{10}Be/^{7}Be$ Ratios With Meteorological Conditions

[13] The ^{7}Be and ^{10}Be activity concentrations reveal a significant positive correlation at both stations (0.87 and 0.85 for ZUG and JUN, respectively), which is indicative of their similar sources and sinks in the atmosphere. The slope $\Delta(^{10}Be)/\Delta(^{7}Be)$ of a regression line forced to zero intercept, is 1.70 for ZUG and 1.96 at JUN. This is also reflected by the annual mean ratios $^{10}Be/^{7}Be$ of 1.82 at ZUG and 1.97 at JUN. The higher value at JUN than at ZUG is likely

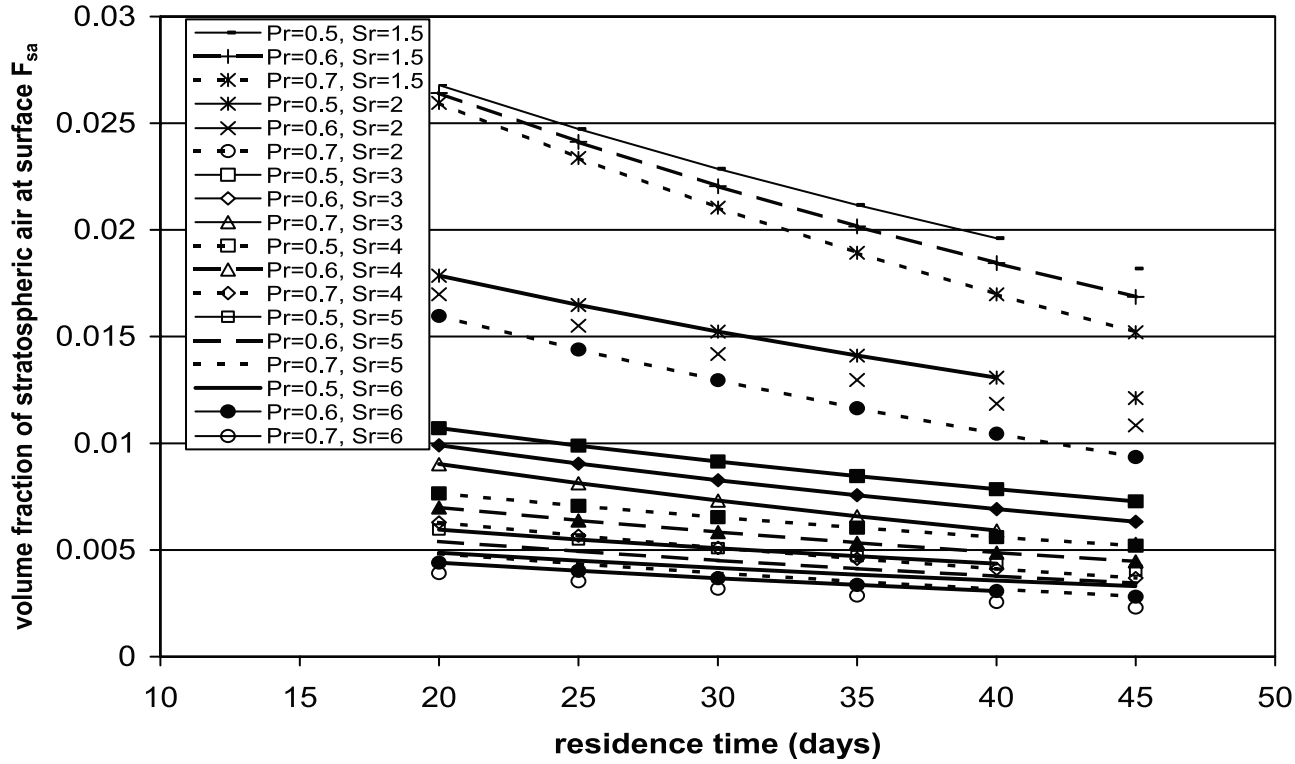

Figure 1. Calculated volume fraction of stratospheric air at the surface F_{sa} versus the residence time of the carrier aerosol with varying values for T_r, P_r, and S_r.

related to the different altitudes of the two stations, which leads to a stronger influence of STT at JUN than at ZUG.

[14] Multiple linear regression analysis reveals that 64% (n = 163) for ZUG and 76% (n = 110) for JUN of the $^{10}Be/^{7}Be$ ratio variability is explained by the variability in both ^{7}Be and ^{10}Be. In contrast, the explained variance of the ratio by ^{7}Be only is 7.0% for ZUG and 0.6% for JUN, and by ^{10}Be only is 1.9% for ZUG and 12.7% for JUN. Thus, the ratio is almost independent from processes that have a clear effect on both radionuclides, such as wet scavenging.

[15] At ZUG where the time resolution of ^{7}Be and ^{10}Be measurements is higher, the above conclusion is strengthened further by the fact that the correlation coefficients of ^{7}Be and ^{10}Be with relative humidity (RH) daily averages are -0.62 and -0.48, respectively, whereas the correlation between their ratio and RH is +0.32 indicating that the ratio is substantially relieved from the effect of wet scavenging. As RH can serve as a proxy for wet scavenging processes [*Gerasopoulos et al.*, 2001], at least such taking place close to the measurement site, this indicates that the ratio is virtually independent from wet scavenging. However, the question that arises is whether the ratio reflects mainly an effect from the unbalanced removal of ^{7}Be and ^{10}Be due to wet scavenging or if it also reflects intrusions from the stratosphere under certain synoptic situations.

[16] In order to investigate to what extent ^{7}Be, ^{10}Be, and $^{10}Be/^{7}Be$ trace intrusions of stratospheric air, data from ZUG (where daily values are available) were sorted according to Schüepp's weather classification [*Schüepp*, 1978]. According to this classification a region of 444 km in diameter over the central Alps is considered and each day is attributed to a specific synoptic weather type based on a number of meteorological parameters including the surface pressure and the 500 hPa heights. The Schüepp classification can be considered to be reliable for Swiss and Southern German weather conditions, since it includes most of the significant elements that determine the atmospheric conditions over a certain region, i.e., pressure, origin, and dynamics of air mass, dominant wind direction, etc. [*Beniston and Jungo*, 2002]. The eight main weather types (classes) were used for the present study: anticyclonic (A), indifferent (I), cyclonic (C), west (W), north (N), east (E), south (S), and a mixed one (M). For each class, median values of ^{7}Be, ^{10}Be, and their ratio were calculated, in order to avoid bias due to some extremely high or low values. Figure 2 shows that high ratio values occur under cyclonic and northerly advective conditions, which are the synoptic situations during which STT events occur most frequently over central Europe. High ^{7}Be and ^{10}Be concentrations, in contrast, are found under anticyclonic conditions. These are mostly fair weather conditions (no wet scavenging), when slow subsidence from middle or upper tropospheric levels occurs. High concentrations are also found for easterly winds, but due to the small number of cases, no firm conclusions can be drawn for this class.

[17] For a closer look, geopotential height charts at 500 hPa were inspected for all the days with $^{10}Be/^{7}Be$ within the upper 10% quantile ($^{10}Be/^{7}Be > 2.7$) at ZUG. Although not shown here, the vast majority of the synoptic patterns revealed a deep upper trough extending southwards, with strong northerly advection affecting the Alpine stations and there were also a few occasions with cutoff low systems affecting central Europe. These synoptic situations are known to be often related to stratospheric intrusion events

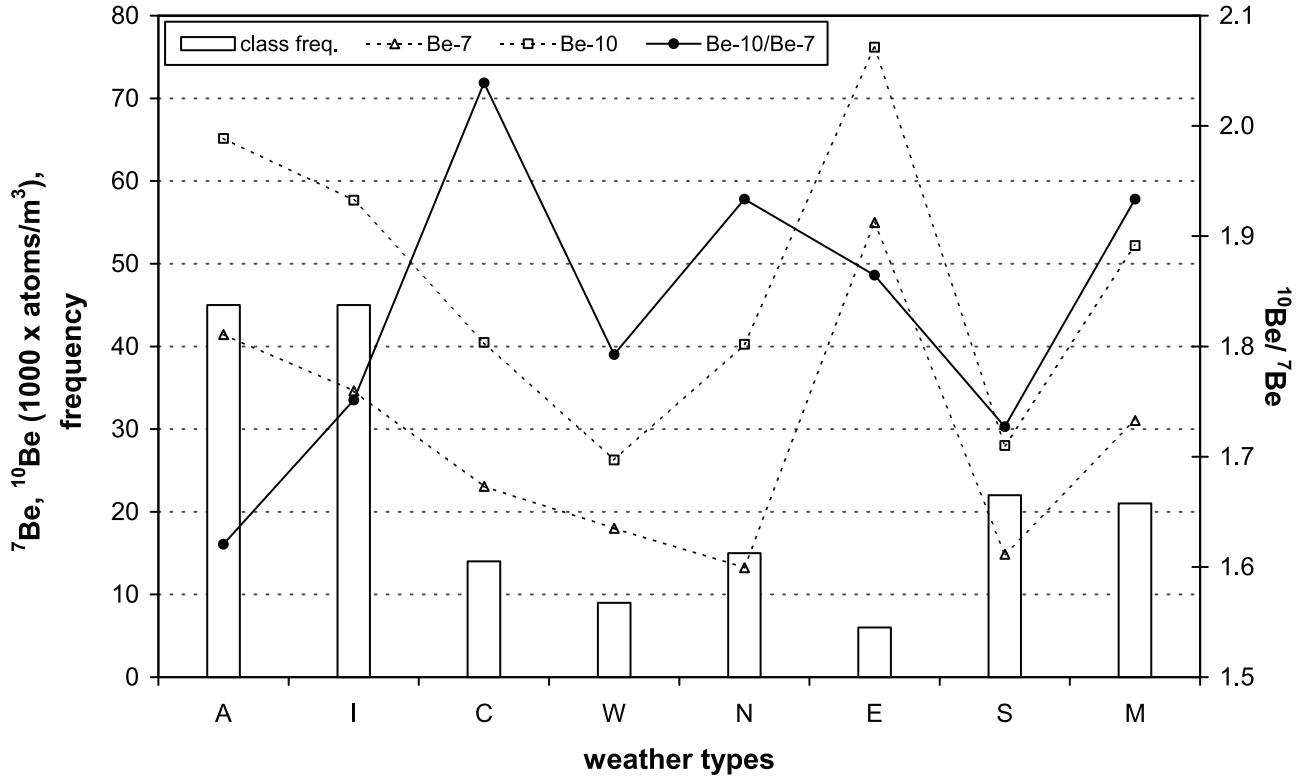

Figure 2. Medians of ^{7}Be, ^{10}Be, and the $^{10}Be/^{7}Be$ ratio for each of the eight main Schüepp weather type classes. The frequency of the events for each class is also shown.

[*Reiter et al.*, 1971; *Vaughan and Price*, 1989]. Back trajectory analysis for all these selected days (Table 1) indicated downward transport from the upper troposphere or lower stratosphere thus providing evidence for the use of the ratio as a stratospheric tracer and a confirmation that the ratio is mostly successful in identifying STT cases. Note that in 8 cases out of the 13 cases presented in Table 1, the highest potential vorticity (PV) reached a value higher than 2 pvu during the 10-day back trajectory, which is a value often selected as threshold value for stratospheric air (A. Stohl et al., A new concept of stratosphere-troposphere exchange, submitted to *Bulletin of the American Meteorological Society*, 2003, hereinafter referred to as Stohl et al., submitted manuscript, 2003), while in 4 cases there is descent from higher altitudes. It is only one case that the back trajectories indicate a low-level origin for the air mass. P. Zanis et al. (Forecast, observation and modeling of a deep stratospheric intrusion event over Europe, submitted to *Atmospheric Chemistry and Physics*, 2003) presented a stratospheric intrusion event affecting central Europe on 20 and 21 June 2001, where it was shown that at JUN the $^{10}Be/^{7}Be$ ratio increased by 23%, in contrast to ^{7}Be and ^{10}Be, which both decreased significantly. Thus, when wet scavenging plays a role, the $^{10}Be/^{7}Be$ ratio can still be a valid stratospheric tracer, although ^{7}Be and ^{10}Be alone cannot.

[18] However, when correlating the $^{10}Be/^{7}Be$ ratio with ozone, which is also expected to serve as an index for stratospheric intrusions, the interpretation of the correlation becomes a very complex task. At ZUG/JUN, the correlation coefficients of ^{7}Be and ^{10}Be with ozone daily averages are +0.50 and +0.53, respectively, whereas the correlation between the $^{10}Be/^{7}Be$ ratio and ozone is +0.04. After deseasonalizing the ozone daily averages by subtracting the respective monthly mean, the correlation coefficients of ^{7}Be, ^{10}Be, and $^{10}Be/^{7}Be$ ratio with the deseasonalized ozone daily averages are +0.50, +0.43, and −0.25. At JUN, the correlation coefficients of ^{7}Be, ^{10}Be, and $^{10}Be/^{7}Be$ ratio with ozone bidaily averages are +0.38, +0.58, and +0.54, while with the deseasonalized ozone bidaily averages, +0.40, +0.40, and +0.06, respectively. Hence, at both ZUG and JUN, the $^{10}Be/^{7}Be$ ratio is uncorrelated with the deseasonalized ozone, while the individual beryllium radiotopes are positively correlated with ozone, which is a complex result. Of course, an important limitation of ozone

Table 1. The Highest Altitude and PV Reached From 10-Day Back Trajectories for All the Days With $^{10}Be/^{7}Be$ Within the Upper 10% Quantile ($^{10}Be/^{7}Be > 2.7$)

Date	Highest Altitude Reached (m)	Highest PV Reached (pvu)
18 February 2000	7500	3.1
20 February 2000	5600	1.4
27 March 2000	7100	2.0
13 April 2000	7600	2.1
27 June 2000	8300	1.5
11 July 2000	5200	1.2
15 July 2000	3500	Low-level origin
17 July 2000	8100	1.3
3 September 2000	8500	3.3
21 September 2000	9200	6.5
3 October 2000	7600	3.9
7 November 2000	7100	2.6
15 December 2000	7900	2.5

as a stratospheric tracer is that the tropospheric ozone concentrations are also controlled by photochemical ozone production and loss processes to a great extent. For example, both ^{7}Be and ^{10}Be radioisotopes are higher during anticyclonic conditions due possibly to less removal of the carrier aerosol by wet scavenging (see in Figure 2), but at the same time these meteorological conditions favor the photochemical ozone production. Furthermore, the higher $^{10}Be/^{7}Be$ ratio values are associated with cyclonic conditions (see in Figure 2) which do not favor photochemical activity. Another limitation is that in daily or bidaily ozone averages the influence of a time limited stratospheric intrusion might be easily masked by other variability during the day and hence a correlation with daily or bidaily $^{10}Be/^{7}Be$ ratio values can be destroyed. Nevertheless, although in certain cases of deep STT the ratio can indeed be a very useful stratospheric tracer, from a climatological point of view, the $^{10}Be/^{7}Be$ ratio values are also influenced by other factors than deep STT (direct way). For example, downward transport from the upper troposphere which is a secondary source region of the cosmogenic radionuclides or shallow STT transporting stratospheric air of different stratospheric ages to the upper troposphere followed by subsequent downward transport to the lower troposphere within several days (indirect way) could be of importance.

3.2. Seasonal Estimate of the STT Impact Over the Alps

[19] At JUN, the $^{10}Be/^{7}Be$ ratio shows a clear seasonal cycle with a May and June peak (Figure 3). At ZUG the seasonal cycle of $^{10}Be/^{7}Be$ is less distinct, but a primary peak is revealed in March and April and a secondary peak in July (Figure 3). The reason for the different seasonalities is not clear, since both stations are located in the Alps. Part of the difference may be attributed to the different sampling intervals. Furthermore, January and February measurements of ^{10}Be at ZUG correspond to the year 2000 while at JUN they correspond to year 2001. Similar differences between JUN and ZUG were found by Stohl et al. (submitted manuscript, 2003) in the frequency of stratospheric intrusions, detected by a search algorithm using ^{7}Be, RH and ozone data. Partly, these could be explained by the higher altitude of JUN. As deep STT has a winter maximum, whereas more shallow STT has a spring maximum [*James et al.*, 2003], this may partly explain why the $^{10}Be/^{7}Be$ ratio peaks later at JUN than at ZUG. However, the differences are quite large, given the fact that JUN is only 620 m higher than ZUG.

[20] Given the monthly average values of ^{7}Be, ^{10}Be, and their ratio, we can calculate the seasonal cycle of the volume fraction of stratospheric air at the surface, F_{sa}, using expression (4). The uncertainties of P_r, T_r, S_r, and $[^{7}Be]_{strat}$ were considered for the calculation of F_{sa} for each month in the way discussed in section 2. Specifically, the values 0.5, 0.6, and 0.7 were used for P_r, 20, 25, 30, 35, 40, and 45 days for T_r, 1.5, 2, 3, 4, 5, and 6 for S_r, and 98×10^4, 111×10^4, and 124×10^4 atoms/m^3 for $[^{7}Be]_{strat}$. Hence, F_{sa} was calculated for each month based on the respective monthly values of ^{7}Be, ^{10}Be, their ratio with their respective ± 1 sigma included, and on multiple values for P_r, T_r, S_r, and $[^{7}Be]_{strat}$, which yielded 2916 solutions for each month.

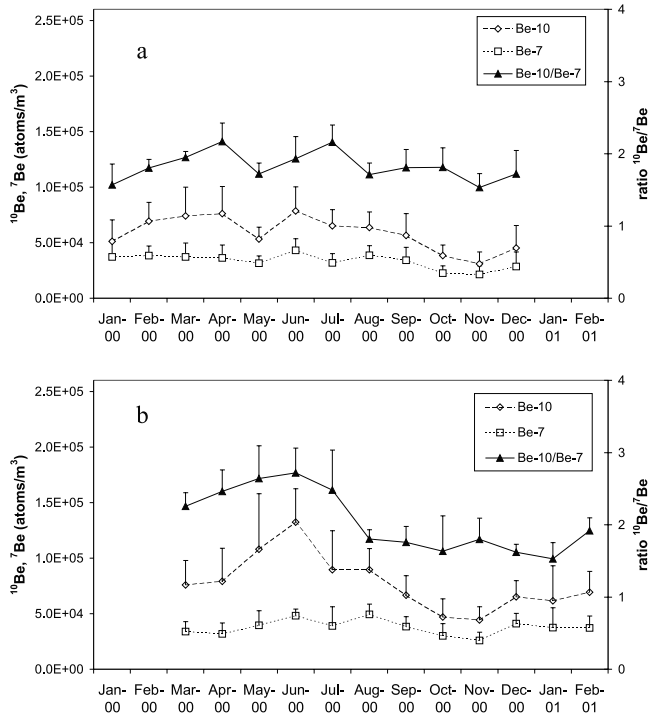

Figure 3. Seasonal cycle of ^{7}Be, ^{10}Be, and their ratio at (a) ZUG and (b) JUN. The error bars denote 95% confidence interval of the mean monthly values.

[21] Figure 4 shows the median, and the first and third quartiles of these solutions, thus reflecting the distribution and range of the monthly F_{sa} calculations. Differences between the first and the third quartiles are about a factor of 3 at both stations. At ZUG, F_{sa} shows a maximum in April and a minimum in November, whereas at JUN, F_{sa} shows a clear maximum in May and June and a minimum in October and November. The differences in the seasonal cycles of F_{sa} between JUN and ZUG are related only to the differences of the surface measurements of ^{7}Be, ^{10}Be, and their ratio as the other parameters involved in the calculations are the same. One has to be aware, though, that it is unlikely that stratospheric $^{10}Be/^{7}Be$ ratios are constant throughout the year, as the downwelling from higher levels in the stratosphere by the Brewer–Dobson circulation is most intense in winter and spring, thus delivering more older stratospheric air to the lowermost stratosphere, than in summer and fall.

[22] Applying the seasonal estimates of F_{sa} in expression (5) the stratospheric ozone at the mountain stations throughout the course of the year is estimated. We use for our calculations the monthly ozone concentrations of the lower stratosphere in this latitude–longitude band (52°–60°N/17.5°–12.5°W), which is a possible stratospheric source region, obtained from the gridded ozone climatology of *Logan* [1999]. This introduces additional uncertainties in our calculations, which we consider by using the monthly ozone values at 250 and 200 hPa, and the average of 250 and 200 hPa, which is about the altitude range from where stratospheric intrusions originate. Figure 5 shows the monthly ozone values at 250 and 200 hPa, as well as the mean between 200 and 250 hPa, for the grid 52°–60°N/

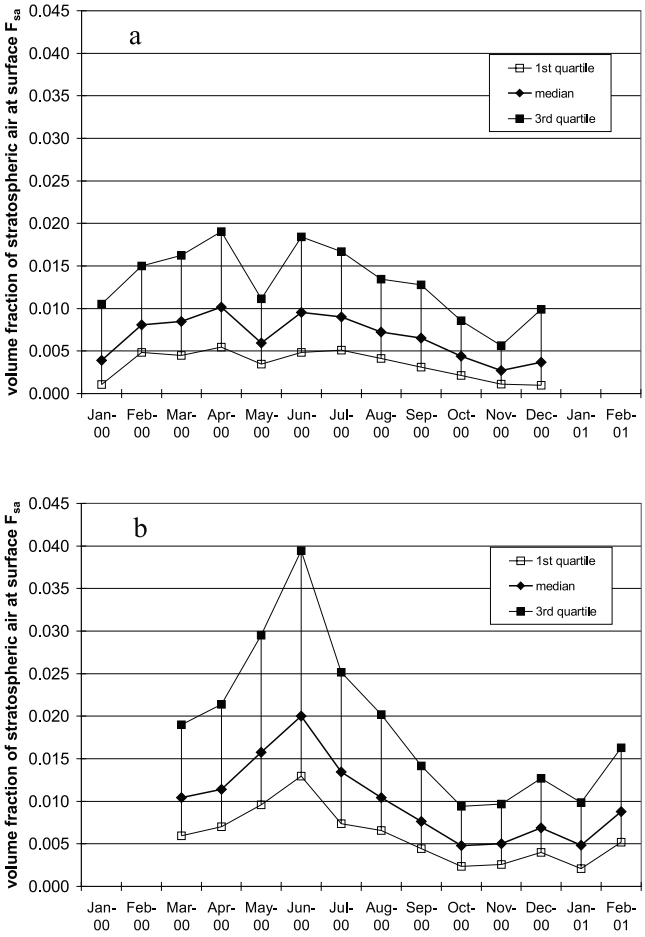

Figure 4. Seasonal cycle of the volume fraction of stratospheric air at the surface F_{sa} at (a) ZUG and (b) JUN.

17.5°–12.5°W according to the study of *Logan* [1999]. Hence, the estimation of surface ozone with stratospheric origin was based on 8748 (3 × 2916) solutions for each month. Figure 5 also shows the monthly surface ozone values throughout the course of a full year, from January to December 2000 at ZUG, and from March 2000 to February 2001 at JUN, which are then used to estimate the percent contribution of stratospheric ozone to surface ozone at ZUG and JUN, which is illustrated in Figure 6.

[23] At ZUG, the estimated percent contribution of stratospheric ozone to tropospheric surface ozone reveals a seasonal cycle with an early spring maximum and an autumn minimum. In spite of the large uncertainties of the estimates with the third quartile being 3 times higher than the first quartile, the stratospheric ozone contribution is in general relatively low, ranging from 3% (first quartile) to 11% (third quartile), with a median of around 5.5%, in February–April, the months with the highest values. In autumn, the median percentage contribution ranges from 1% to 2%. At JUN, we observe a rather different seasonal pattern with a late spring/early summer maximum peaking in June with a median percentage contribution of about 9%, and with an autumn minimum (2% median contribution). However, a secondary peak in March with a median percentage contribution of approximately 7% should be also noted. Hence, the main differences between the seasonal patterns of the stratospheric ozone contribution at ZUG and JUN are the much higher values in May and June at JUN, which arise from the differences of the surface measurements of ^{7}Be, ^{10}Be and their ratio at the two stations. The estimates throughout the year are somewhat higher at JUN than at ZUG. For example, the mean annual percentage stratospheric ozone contribution was estimated to be 5.0% (2.5 ppbv) at ZUG and 6.3% (3.3 ppbv) at JUN. As noted previously, a somewhat higher contribution can be expected for JUN, because of the station's higher altitude. This is also consistent with stratospheric tracer model calculations (Stohl et al., submitted manuscript, 2002). However, generally the estimated influence of stratospheric ozone at the surface is rather low at both stations.

4. Summary and Discussion

[24] Concurrent long-term measurements of ^{7}Be and ^{10}Be were carried out for the first time in Europe at two high Alpine stations JUN, Switzerland, and ZUG, Germany, throughout the course of a full year. The annual mean of the ratio $^{10}Be/^{7}Be$ is 1.82 for ZUG and 1.97 for JUN. Multiple linear and simple regression analysis of the ratio $^{10}Be/^{7}Be$ with ^{10}Be, ^{7}Be and RH revealed that the ratio is virtually independent from the effect of wet scavenging. Inspection of the weather patterns related to the highest ratios indicated that the highest values are associated with cyclonic conditions and northerly advection, which are both typical for stratospheric intrusions. In addition the 10-day back trajectories indicated a stratospheric source for the majority of the cases within the upper 10% quantile of $^{10}Be/^{7}Be$ ratios.

[25] The monthly ratio $^{10}Be/^{7}Be$ values show a clear seasonal cycle at JUN with a peak in May and June. At ZUG somewhat elevated ratios are seen during February–April and June and July, but the seasonal variation is much less pronounced than at JUN.

[26] A simple model was used for an estimate of the contribution of STT to ozone at the mountain stations, based on the ^{7}Be and ^{10}Be measurements. Our results for ZUG

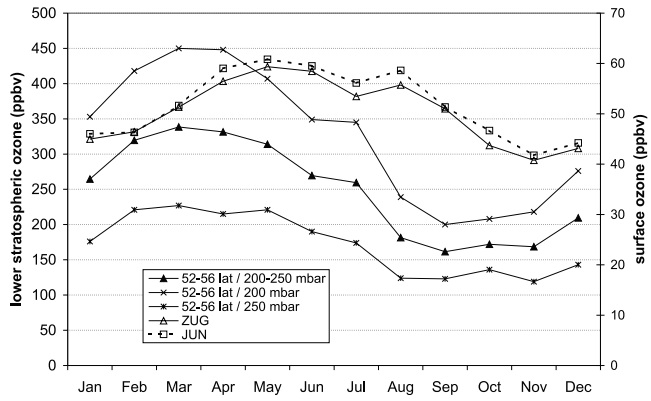

Figure 5. Monthly ozone concentrations at 250 and 200 hPa and the mean between 200 and 250 hPa for the grid 52°–60°N/17.5°–12.5°W obtained from the gridded ozone climatology of *Logan* [1999]. The monthly surface ozone values at ZUG (January and February 2000) and JUN (March 2000 to February 2001) are also shown.

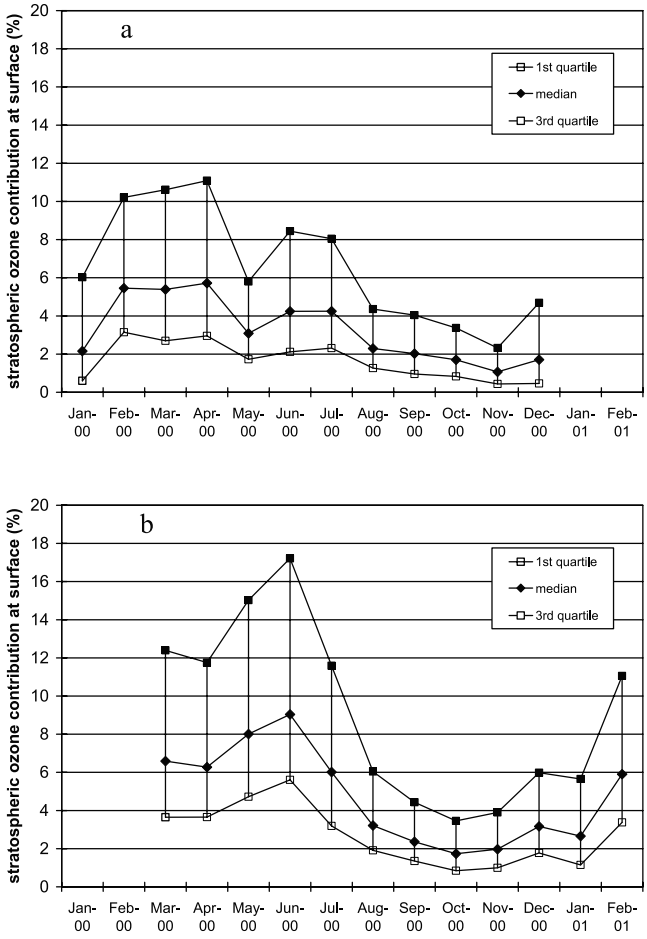

Figure 6. Seasonal cycle of the stratospheric ozone percentage contribution to surface ozone at (a) JUN and (b) ZUG based on the ^{10}Be and ^{7}Be measurements and their $^{10}Be/^{7}Be$ ratio during one full year.

indicate a seasonal cycle of the stratospheric ozone contribution with an early spring maximum (3–11%) and an autumn minimum (1–2%). At JUN, in contrast, a primary maximum in May and June (6–18%), a secondary maximum in March (4–13%) and a minimum in autumn (1–4%) was found. An ozone maximum is observed at many background surface measurement stations in the northern hemisphere in spring, typically in late April or May [*Monks*, 2000]. There has been much debate on the relative contribution from photochemistry and stratospheric intrusions to the origin of tropospheric ozone and its seasonal cycle [*Monks*, 2000]. Figure 5 shows that both ZUG and JUN display a broad spring–summer maximum peaking in May. Generally, the estimated influence of stratospheric ozone at both stations from our calculations is rather low in agreement with the current consensus view that photochemistry is the major contributor to the observed ozone levels [*Monks*, 2000].

[27] It should be noted that although the simple mixing model applied here provides an independent estimate for the impact of STT to the lower troposphere and has large uncertainties in the various parameters involved, the comparison with the Lagrangian model calculations from the studies of Stohl et al. (submitted manuscript, 2003) and *James et al.* [2003] for deep STT is relatively good, especially for ZUG. Based on the model climatology of *James et al.* [2003], we would expect a late winter maximum and a deep late summer minimum for rather short tropospheric lifetimes (order of 10 days), similar to what was found at ZUG in our study, while for longer tropospheric lifetimes times (order of 2 months) we would expect a flatter seasonal cycle and a maximum in spring. The respective calculations from the study of Stohl et al. (submitted manuscript, 2002) for deep STT assuming a tropospheric age of stratospheric air up to 8 days indicate a percentage contribution of stratospheric ozone to lower free troposphere in February up to 8%, which is within the range of our estimates. The lower limits of our estimates are close to the model calculations of *Follows and Austin* [1992], who found that stratospheric ozone contributes less than 5–6% in the lower free tropospheric ozone (620–790 hPa) at the latitudinal band 40°–50°N. The upper limits of our estimates are much lower than the Eulerian model calculations of *Roelofs and Lelieveld* [1997] who estimated that ozone originating from the stratosphere contributed about 40% on average to ozone in the troposphere.

[28] The differences in the seasonality of our estimates compared to the respective Lagrangian calculations from the studies of Stohl et al. (submitted manuscript, 2002) and *James et al.* [2003], can be attributed possibly to the fact that the monthly averages of ^{10}Be, ^{7}Be, and their ratio values do not reflect only the deep STT events but also other processes such as production of ^{10}Be, ^{7}Be in the upper troposphere, accompanied by vertical mixing within the troposphere which is a process that maximizes during the warm period of the year [*Feely et al.*, 1989]. Hence, the $^{10}Be/^{7}Be$ ratio is a difficult parameter for an automated stratospheric intrusion detection algorithm, because it is influenced also by other factors than STT. In spite of the fact that measurement of ^{10}Be with AMS is an expensive method, an extension of combined ^{10}Be and ^{7}Be measurements for more than 1 year in daily samples at surface stations but also in conjunction with more measurements of these radionuclides in the lower stratosphere and upper troposphere would help fill gaps in our understanding for the use of the ratio $^{10}Be/^{7}Be$ as an automated stratospheric intrusion index.

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