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$^{10}Be/^{7}Be$ implies the contribution of stratosphere-troposphere transport to the winter-spring surface O_3 variation observed on the Tibetan Plateau

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$^{10}Be/^{7}Be$ is a stratospheric sensitive tracer. In this paper, measurements of $^{10}Be/^{7}Be$ and surface O_3 from October 2005 to May 2006 at Mt. Waliguan (hereafter WLG, 100.898°E, 39.287°N, 3810 m, a.s.l.), China global atmospheric watch (GAW) observatory, are introduced and used to investigate the stratosphere-troposphere transport (STT) and its impact on surface O_3 on the Tibetan Plateau. The results show that the magnitude of STT is weak in winter, followed by strengthening from the end of winter to the middle of spring (from mid February to mid April) with large increases in ^{10}Be,^{7}Be,$^{10}Be/^{7}Be$ and surface O_3. At the end of spring (from the end of April to mid May in this paper), the STT weakened, and the continuous increase of surface O_3 at WLG is produced by tropospheric photochemistry reactions.

$^{10}Be/^{7}Be$, stratosphere-troposphere transport, surface O_3, Mt. Waliguan

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^{7}Be and ^{10}Be are produced mainly from collisions of cosmic rays with oxygen and nitrogen atoms in the upper atmosphere, including the upper troposphere and stratosphere. Both ^{7}Be and ^{10}Be are absorbed easily by sub-micrometer-size aerosol particles once produced. ^{7}Be as a natural tracer of downward transport from the upper atmosphere had been gradually established since the 1960s, and the first application of $^{10}Be/^{7}Be$ as a stratospheric tracer was addressed by Rasebeck et al. [1] in 1981. The half -lives of ^{7}Be and ^{10}Be are 53.3 d and 1.5×10^{6} a, respectively, while the average age of the stratospheric air mass is ~1.5 a. In the stratosphere, although the initial production rate of ^{10}Be is lower than that of ^{7}Be, $^{10}Be/^{7}Be$ increases as the ^{7}Be isotope naturally decays to a lower concentration until reaching its equilibrium concentration, resulting in higher $^{10}Be/^{7}Be$. In the troposphere, the ratio of $^{10}Be/^{7}Be$ is little influenced by wet deposition scavenging of aerosol particles because they are from the same source, making the ratio a more sensitive tracer of stratosphere than using ^{7}Be or ^{10}Be alone. Research on ^{10}Be measurements is mainly conducted in the field of paleoclimatology. However, as a natural stratospheric tracer, $^{10}Be/^{7}Be$ effectively indicates the contribution of Stratosphere-Troposphere Transport (STT) to surface-level O_3 variations as observed in the European Alps and Arctic regions [2,3]. Jordan et al. [4] reported latitudinal distribution of $^{10}Be/^{7}Be$ values in the upper troposphere and lower stratosphere over several regions through analysis of extensive aircraft aerosol samples. However, publications of at-

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mospheric ^{10}Be measurements are still limited because of the complexities in ^{10}Be target preparation and ^{10}Be detection by Accelerator Mass Spectrometry (AMS). Shen et al. [5] reported short-term ^{10}Be concentrations in dust deposition sampled in Beijing and Ningbo. Measurements of ^{10}Be/^{7}Be in atmospheric aerosol samples have not yet been reported in China.

Tropospheric O_3 is a significant trace gas due its oxidation and greenhouse characteristics. Tropospheric photochemical production and the direct or indirect STT are the two primary sources of tropospheric O_3. The debate on which source is dominant is ongoing, especially on the extensive spring peaks in surface O_3 in the northern hemisphere [6]. With respect to atmospheric circulation, the seasonally intensified downward transport branch (presented as STT) of the stratospheric Brewer-Dobson circulation in the northern hemisphere increases the fraction of stratosphere O_3 in troposphere, contributing to the rise of surface O_3 [7]. However, atmospheric chemistry suggests that as the solar radiation seasonally increases in spring, tropospheric O_3 may be largely produced in the short-term through photochemical reactions with precursors, such as NO_x, which are emitted in significant amounts in winter [8].

Mt. Waliguan (hereafter WLG) is located on the northeast margin of the Tibetan Plateau. It was selected as a site for China's Global Atmospheric Watch (GAW) observatory. Long-term observations reveal that surface O_3 at WLG increases from winter to spring, reaching its maximum in June. There are several publications presenting possible mechanisms of the summer O_3 maximum at WLG [9–13]. However, the mechanisms for winter and spring surface variations at WLG require elucidation. In this paper, weekly concentrations of ^{7}Be and ^{10}Be measured on aerosol samples obtained from October 2005 to May 2006 at WLG are presented, and ^{10}Be/^{7}Be is used as a sensitive stratospheric tracer to investigate the STT and its contribution to winter-spring variation in surface O_3.

1 Measurements and data set

Measurements of ^{7}Be and ^{210}Pb analysis were described in an earlier study [14]. Every aerosol particle sample was continuously collected over one week by a pump with flow rate of ~1.3 m^3 min^{-1}. The collector is a three-layered polypropylene filter. The sampled filters were then sent to the State Key Laboratory of Earth Geochemistry (SKLEG), Chinese Academy of Sciences, to measure ^{7}Be and ^{210}Pb. The total relative measurement errors are from ±1.4% to ±6.4% [14]. Complying with the standard operation procedures issued by the World Meteorological Organization (WMO), surface O_3 at WLG is routinely measured by UV absorption analyzers (Thermal Environment, Model 49C) with a precision of $\pm 2\times10^{-9}$ volume mixing ratio [15]. The long-term surface O_3 data is also periodically audited by the assigned WMO laboratory with stringent inter-comparison measurements [16].

After ^{7}Be and ^{210}Pb were analyzed, the aerosol samples were sent to the Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, for target preparation for AMS ^{10}Be analysis. The detailed procedures for making ^{10}Be targets have been described in other references [5,17]. Briefly, the filters were alternately pulverized and leached to extract final ^{10}Be residues in BeO. The ^{10}Be AMS target was made by mixing Nb powder with the BeO. These targets were sent to the 6 MeV EN tandem AMS system, National Key Laboratory of Nuclear Physics and Technology, Peking University for ^{10}Be measurements. The detection limit of ^{10}Be in the AMS system is 6×10^{-15}. The standard, ^{10}Be/^{9}Be, is 2.67×10^{-11} with a precision higher than 5‰, and was imported from the US National Institute of Standards and Technology [18]. The total relative error for the ^{10}Be determination is estimated to within ±5%, including errors caused by the efficiency of leaching filters and ^{10}Be measurements [17].

2 Results and analysis

Figure 1 shows the weekly concentrations of ^{7}Be, ^{10}Be and ^{210}Pb at WLG from October 2005 to May 2006. Because precipitation is the most significant sink for the Be and Pb isotopes, weekly precipitation and occurrence fog are also shown in Figure 1. The variations in ^{7}Be and ^{10}Be concentrations are generally consistent. ^{10}Be concentration was lower than that of ^{7}Be before February 2006, and then rose, exceeding ^{7}Be concentration. After mid April, both ^{10}Be and ^{7}Be concentrations began to decrease. The weekly variations in Be isotope concentration are somewhat associated with synoptic processes indicated by precipitation and fog records. Be isotope concentration increased almost continuously during two periods with little precipitation, one was from circa December 2005 to February 2006, another was from circa mid of March to mid of April in 2006. However, in the second dry period, Be concentrations increased as a result of STT (Figure 2). Be isotope concentrations began to reduce after mid April as precipitation increased.

The main source of ^{210}Pb is from land surface emission. Figure 1 shows that ^{210}Pb concentration in the spring did not increase as did Be isotopes. When maximum ^{210}Pb concentrations occurred in winter, concentrations of Be isotope did not rise correspondingly. These comparisons suggest that dust or soil emissions have little impact on variation in Be isotope concentration at WLG, and the cause of spring ^{10}Be and ^{7}Be enhancement is only the intensified STT. The temporal increases of ^{210}Pb, ^{10}Be and ^{7}Be concentration during the two non-precipitation periods are due to weak wet scavenging. To some extent, the general decreasing trend of ^{210}Pb concentration from winter to spring is associated with

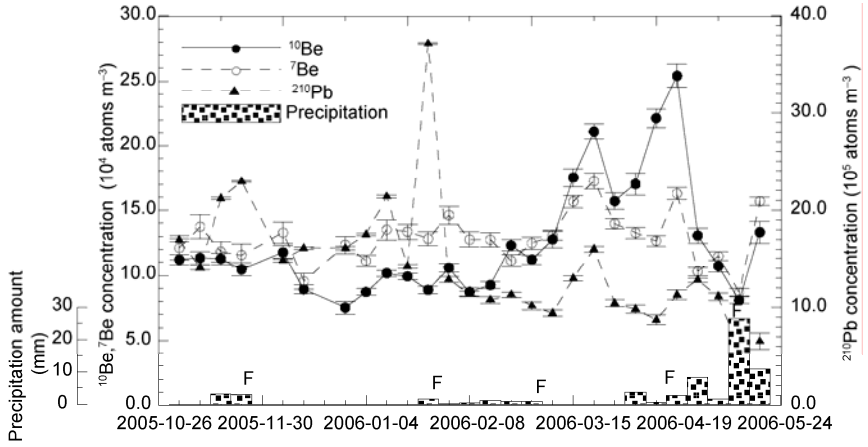

Figure 1 Weekly concentrations of ^{10}Be,^{7}Be and ^{210}Pb measured in aerosol samples obtained at WLG from October 2005 to May 2006. Weekly precipitation (vertical bars) and fog occurrence (F) are also shown.

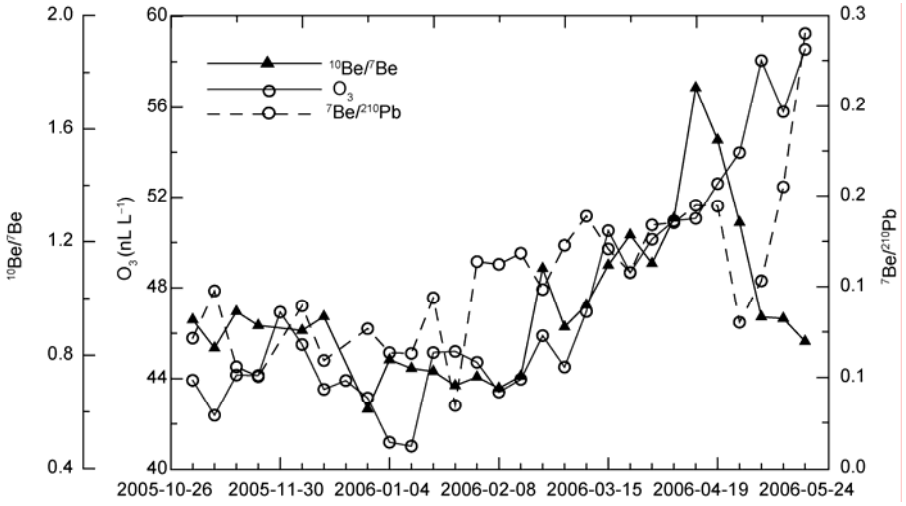

Figure 2 Weekly variation in ^{10}Be/^{7}Be, ^{7}Be/^{210}Pb and surface O_3 concentration at WLG.

seasonal increase in precipitation.

Figure 2 presents weekly variations of surface O_3 concentration, ^{10}Be/^{7}Be, and ^{7}Be/^{210}Pb. ^{7}Be/^{210}Pb is considered to be a tracer unaffected by wet scavenging processes. The STT during the period from 15 February to the end of April is evidenced by the simultaneous elevations of surface O_3 and ^{10}Be/^{7}Be. However, for the last five samples starting from the end of April, the clear reductions of ^{10}Be/^{7}Be reveal a weakening of STT. At the same time, the continuous increase of surface O_3 at WLG supports dominant tropospheric photochemical O_3 production. This transfer is consistent with estimations of monthly average surface O_3 budget using the ^{7}Be observation alone. In that study, the contribution from STT to the surface O_3 budget in May 2003 was concluded to be less than that in April and June, and the input from tropospheric chemical production was dominant for the surface O_3 budget [19].

Using high values of ^{7}Be/^{210}Pb, studies have plausibly interpreted that summer surface O_3 at WLG is influenced by downward transport from the upper atmosphere [12,13]. However, the last four samples in Figure 2 demonstrate the different physical processes implied by ^{7}Be/^{210}Pb, and ^{10}Be/^{7}Be. Obviously, the implication of strengthening downward transport from the stratosphere is not reasonable based on the observed increase of ^{7}Be/^{210}Pb alone. Due to differences in the source distribution, ^{210}Pb is more sensitive to wet scavenging than Be isotopes [20], and this caused a higher ^{7}Be/^{210}Pb ratio at the end of spring and even throughout the summer at WLG, but a corresponding strengthening STT did not occur.

The inter-comparisons of ^{10}Be, and ^{10}Be/^{7}Be ratio between WLG and the other sites are given in Table 1. It has been noted that ^{7}Be concentrations tend to have the highest values in comparisons with data obtained at the sites with elevations or latitudes similar to WLG [23]. In Table 1, ^{10}Be also tends to have the highest concentration at WLG, but the case for ^{10}Be/^{7}Be is much different given the fact that WLG is located at lower latitude. Although being at high elevation,

Table 1 ^{10}Be and ^{10}Be/^{7}Be at WLG and at other sites

Location	Lat., Long., and altitude a.s.l.	^{10}Be (10^4 atoms m^{-3})	^{10}Be/^{7}Be
Jungfraujoch	46.533°N, 7.983°E, 3.58 km	5–12 [3]	2.0–3.0 [3]
Zugspitze	47.416°N, 10.983°E, 2.962 km	3–8 [3]	1.5–2.0 [3]
Alert	82.5°N, 62.3°W	0.5–8 [2]	1.8–3.4 [2]
Ljungbyhed	56.08°N, 13.23°E,	0.68–1.55 [3]	0.65–0.8 [3]
Visby	57.63°N, 18.32°E,	1.79–5.43 [20]	0.87–1.71 [21]
Kiruna	67.84°N, 20.34°E,	1.47–1.48 [20]	1.05–1.25 [21]
Antarctica	South Pole, 2.8 km	3.31–7.33 [1]	1.52–1.71 [1]
WLG (for all samples)	36.287°N, 100.89°E, 3.81km	7.53–25.4	0.61–1.75
WLG (Fall and Winter)	36.287°N, 100.89°E, 3.81km	7.53–12.3	0.97–1.11
PEM-B, Flight#17	39°–44°N, 136°–139°E, troposphere	0.9–3.6 [4]	0.97–3.82 [4]
SONEX, Flight#8	55°–68°N, 5.4°W–11.9°E, tropopshere	1.1–126 [4]	0.45–1.65 [4]
Northern Hemisphere	North to 50°N, West Pacific Ocean	N/A	1.24±0.27 [22]
Southern Hemisphere	South to 60°S, Pacific Ocean	N/A	1.92±0.44 [22]

the relatively lower ^{10}Be/^{7}Be (and the lower surface O_3 concentration) in winter indicates that impacts from STT on near-surface air masses is not obvious in the plateau region. This does not support the conclusions of certain models addressing the significance of STT on surface O_3 on the Tibetan Plateau [24]. The high winter concentrations of ^{7}Be and ^{10}Be at WLG are the result of continuous accumulation of aerosol particles at the residence altitudes of the surface boundary layer because of the little precipitation. In this study, the total precipitation from October 2005 to February 15, 2006 is no more than 10 mm, and only very weak wet scavenging was prevalent.

3 Discussion

Some transport processes at time scales of less than one week would be smoothed in the data because of the fixed weekly sampling for ^{10}Be/^{7}Be determination, especially in the case of deep STT that generally persists for just 1–2 d or less. For an individual sampling week with a lasting precipitation event, the correlations between surface O_3 and ^{10}Be/^{7}Be before, during or after the precipitation would be also filtered out by the averaging. Therefore, *in situ* aerosol sampling schedule based on synoptic changes is recommended. In addition, ^{10}Be/^{7}Be is considered to be little influenced by wet scavenging. However, because Be isotopes reside in aerosol particles, and the fact that behavior of aerosol particle differs from atmospheric trace gases such as O_3 may also influence the interpretation of ^{10}Be/^{7}Be. To utilize a tracer residing in the gaseous phase should better describe the contribution of STT to surface O_3, for example, ^{18}O in CO_2 [11], while ^{17}O in CO_2 which is entirely produced in the stratosphere deserves to be more considered [25,26].

4 Conclusion

Winter and spring concentrations of ^{10}Be and ^{7}Be at WLG are generally higher than those measured at other sites. However, in winter the relatively lower ^{10}Be/^{7}Be and surface O_3 concentration demonstrates the weakness of STT and its impact on surface O_3. From the end of winter to the middle of spring (from mid February to mid April), continuous elevations of ^{10}Be, ^{7}Be, and surface O_3 concentration and ^{10}Be/^{7}Be support the seasonal intensified STT and its positive contribution to the surface O_3 budget. At the end of spring (from the end of April to mid of May in this study), the reductions of ^{10}Be and ^{7}Be concentration and ^{10}Be/^{7}Be suggest weakening of the STT, while the continuous increase of surface O_3 at WLG is from the positive input of tropospheric photochemical reactions.

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