

## Long-term changes of CH<sub>4</sub> concentration and its carbon isotopic ratio in the lower stratosphere over Japan

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It is expected that  $\delta^{13}\text{C}$  of CH<sub>4</sub> provides us with useful information not only about CH<sub>4</sub> emissions from biogenic and abio-genic sources but also about its oxidation process in the atmosphere. Therefore, measurements of  $\delta^{13}\text{C}$  have been carried out for the major CH<sub>4</sub> sources as well as for the background atmosphere. However, the measurements are still insufficient for elucidating the CH<sub>4</sub> cycle on the earth's surface. In the stratosphere, CH<sub>4</sub> is destroyed by reactions with OH, O(1D) and Cl atom. These destruction processes play an important role in the stratospheric chemistry, but the respective contributions to the CH<sub>4</sub> loss and their temporal changes have not been yet well understood quantitatively. Measurements of the isotopic ratios of the stratospheric CH<sub>4</sub> are one of the most promising methods to detect possible change of the CH<sub>4</sub> destruction processes in the stratosphere on the basis of the different isotopic fractionations occurring in the different reactions. However, only a few measurements have been made so far, due mainly to difficulty of collecting air samples in the stratosphere. Systematic collections of stratospheric air samples have been carried out over Japan since 1985 using a balloon-borne cryogenic sampler. We analyzed the air samples collected in the period of 1994-2010 for concentrations of CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub> and SF<sub>6</sub>, and  $\delta^{13}\text{C}$  of CH<sub>4</sub>. In this study, we report the preliminary results of the long-term change of  $\delta^{13}\text{C}$  of CH<sub>4</sub> in the stratosphere. Almost linear and compact relationships between CH<sub>4</sub> and N<sub>2</sub>O concentrations were found for the all observations in the different years. CH<sub>4</sub> concentration and  $\delta^{13}\text{C}$  also showed compact relationships in the lower stratosphere, although those in the mid-stratosphere were less correlated. The tight correlations between CH<sub>4</sub> and N<sub>2</sub>O in spite of the different destruction processes suggest that the ratio of both destruction rates has been kept as almost constant during the transport process in the stratosphere. It is well known that tropospheric CH<sub>4</sub> and N<sub>2</sub>O have been secularly increasing in the recent decades. Such increasing trends should have been propagated into the stratosphere, and the compact relationships between the stratospheric CH<sub>4</sub> and N<sub>2</sub>O would change depending on their increase rates. To elucidate an inter-annual changes of the stratospheric CH<sub>4</sub> and its  $\delta^{13}\text{C}$ , we employed N<sub>2</sub>O-loss, instead of the N<sub>2</sub>O concentration, as an indicator of how the chemical reactions have proceeded during the stratospheric transport. The N<sub>2</sub>O-loss was calculated as a concentration difference between the tropical troposphere and the stratosphere by considering the mean age of air estimated from CO<sub>2</sub> and SF<sub>6</sub> concentrations. This procedure eliminates the effect of the secular N<sub>2</sub>O increase from the relationships between CH<sub>4</sub> and N<sub>2</sub>O, and enables us to detect possible change in the stratospheric CH<sub>4</sub>. As a result, we found that the CH<sub>4</sub> concentration increased at a rate of  $4.5 \pm 0.9$  ppbv/year in the lower stratosphere during 16 years. This increase rate is consistent with those observed in the troposphere. The same technique was applied to the correlations between CH<sub>4</sub> concentration and  $\delta^{13}\text{C}$ , and we found no significant changes of  $\delta^{13}\text{C}$  in the lower stratosphere. Considering the fact that  $\delta^{13}\text{C}$  in the troposphere also does not show a clear trend in a recent decade, our result implies that the relative contributions of the CH<sub>4</sub> destruction processes have been unchanged in the lower stratosphere over the observed period.

Keywords: stratospheric methane, carbon isotopic ratio