

Vertical profiles of halocarbons in the stratosphere over Japan in 2020 and implications for the “mean age” of the stratospheric air

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In this study, we developed analysis methods to quantify the mixing ratios of halocarbons with a reduced amount of air sample ($\sim 0.5 L_{STP}$) at first, and analyzed the air samples collected in the stratosphere over Japan in July, 2020.

A Gas Chromatograph/Mass Spectrometer system (6890/5973N) with a pre-concentration unit was used for the analysis of long-lived halocarbons, and sample air was injected into the pre-concentration unit by Helium gas flow through a sample flask. By determining the optimum conditions for the pre-concentration experimentally, the analytical precisions were the same level as conventional measurement systems. The stratospheric air samples were collected at altitudes of 15 - 35 km over Japan by a cryogenic air sampler launched by a plastic balloon with a volume of 100,000 m³ when fully inflated. Our analyses showed clear vertical variations of HFCs, PFCs, CFCs, HCFCs and SF₆. The mixing ratios of CFC-11 and CFC-12 in the stratosphere, thus obtained, were compared with those observed in 1995 and 1999. The mixing ratio of CFC-11 increased from 1995 to 1999, and then decreased from 1995 to 2020 at all altitudes, reflecting the temporal variations of CFC-11 in the troposphere. On the other hand, the average CFC-12 mixing ratio increased at all altitudes between 1995 and 1999, but increased or decreased depending on the altitudes between 1999 and 2020.

The mean ages of the stratospheric air (the elapsed time since the air masses entered the stratosphere from the tropical troposphere) over Japan were calculated from the mixing ratios of selected long-lived halocarbons (HFC-23, HFC-134a, HFC-227ea, PFC-218, and PFC-318) in the stratospheric air samples. Of these compounds, PFC-218 was not considered to provide a precise mean age estimate because the mixing ratio was less than 1 ppt in the stratosphere and the analytical precision was not sufficient. It became also clear that HFC-134a was not appropriate to use for mean age estimation because of ineligible photodissociation effect in the stratosphere.

The most probable mean age ("halocarbon age") was calculated from the mean age estimates obtained by the mixing ratios of HFC-23, HFC-227ea and PFC-318 in the stratosphere and compared with the mean age estimates using the mixing ratios of stratospheric CO₂ observed in 2015 and SF₆ observed in 2015 and 2020. As a result, the halocarbon ages were in good agreement with the CO₂ and SF₆ ages below 25 km and the CO₂ ages above 25 km. On the other hand, the halocarbon ages were systematically smaller than the SF₆ ages above 25 km. This result is consistent with previous studies suggesting that the SF₆ age is overestimated in the middle and upper stratosphere.