Measurements of methyl chloride in air trapped in Antarctic ice cores

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Methyl chloride (CH3Cl), the most abundant atmospheric halocarbon, is emitted to the atmosphere from various natural sources and contributes to the stratospheric ozone depletion. Recently, polar firn air measurements have shown that the presence of CH3Cl through the twentieth century, although chlorofluorocarbons decreased rapidly with the firn depth. It is suggested that the contribution of CH3Cl to the ozone depletion was likely to have been relatively greater in pre-industrial times. Analysis of air extracted from polar ice cores is thought to be the most promising method to reconstruct variations of past atmospheric compounds. However, for CH3Cl, very few measurements in ice core are available. In this study a method is developed which allows the concentration measurements of CH3Cl in air extracted from ice core. Examples of the Antarctic ice core measurements are presented.

Analytical method is based on the combination of a sample preconcentration technique, and gas chromatographic separation on a capillary column, and determination of mixing ratios by mass spectrometer. Because the available size of ice samples is rather limited, sample air was preconcentrated by using vacuum line that consists of a glass beads trap, diaphragm valves, a 6-port valve and a vacuum pump to avoid loss of sample. Analytical precision using sample of 20 pg is found to be less than 3 %. For air extraction technique, it is found that air samples for CH3Cl measurements can be precisely extracted by crushing an ice under vacuum at low temperature.

By using these experimental techniques, Yamato core from Antarctica was analyzed. The results showed that the averaged CH3Cl concentration was 973 +/- 68 ppt, which higher by about 400 ppt than that in the present atmosphere. The CO2 concentrations from the core were obviously lower than the pre-industrial Holocene values, suggesting that this ice core was formed in the glacial period. The cause of such higher concentrations of CH3Cl in the glacial period might be attributed to 1) low OH radical concentrations in the glacial atmosphere, 2) slow biological uptake rate in the ocean, 3) increased oceanic emissions. However, a production of small amounts of trace gases by chemical reactions between impurities in the ice has been postulated. To discuss the artificial productions of CH3Cl in the ice, a shallow ice core collected at the YM85 site was analyzed. Average value of CH3Cl concentration is 555 +/- 48 ppt, which is similar to the present concentration in the remote atmosphere (ca. 550 ppt). It is likely that chemical artifacts in the ice are less significant for CH3Cl. Therefore the higher concentrations of CH3Cl in the Yamato core are suggested to be attribute to the atmospheric concentrations in the glacial time.