Isotopic characteristics of molecular hydrogen from automobile exhaust.

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Molecular hydrogen is present in the troposphere at about 530ppb and the second most abundant reactive gas in the troposphere after methane. Main sources of H_2 to the troposphere are photochemical sources (the oxidation of methane and nonmethane hydrocarbons), fossil fuel combustion and biomass burning. The other small part is attributed to emissions from volcanoes, the oceans, and production during nitrogen fixation by legumes. On the other, sinks of H_2 are the reaction with OH radicals (about a quarter) and by deposition at the Earth's surface (about three quarter). The lifetime of atmospheric H_2 is about 2 years because of the annual H_2 flux of sources and sinks and abundant in the troposphere (Novelli *et al*., 1999, Rahn *et al*., 2003). If the concentration of atmospheric H_2 is increases, hole in the ozone layer will be deepening and expanding, and other trace gases that react with OH (like a methane) will be increased (Tromp *et al*., 2003). Hence, to understand the global budget and cycle of atmospheric H_2 is extremely important subject in order to identify what has caused the increase in H_2 in the future, and its effects on the atmospheric environment.

Until recently, knowledge of the isotopic terms in the global H_2 budget was sparse, but, the usefulness of isotopic constraints on the H_2 budget was clearly demonstrated in some researches. But there is a real need for baseline studies about each sources and sinks to set in the model analysis. The purpose of this study is to develop a rapid and simple isotope analysis of the deuterium/hydrogen ratio (dD) of molecular hydrogen in atmosphere at several hundreds ppm levels using a GC-IRMS (Gas Chromatograph - Isotope Ratio Mass Spectrometry), and apply this method to analysis of H_2 from automobile exhaust. First, measurement conditions were examined and precision and accuracy were evaluated. Next, measurement of automobile exhaust was carried out, and representative dD value for automobile exhaust gas were inferred. Since direct measurement of dD of H_2 from automobile exhaust has not been conducted, this study is expected to give a new indication of atmospheric H_2 budget.

The dD analyses of the automobile exhaust is ranging from -550 to -110 permil, and the concentration is 0 to 6000 ppm. Diesel automobile is not emit H_2 (1ppm under), and diesel need not to be taken account of H_2 budget. The representative dD of H_2 emitted from automobile exhaust was calculated to be -390 to -290 permil. On the basis of H_2/CO ratio evaluated in this study, the global emission of H_2 from automobile exhaust was calculated to be 4.4 - 21.8 Tg/yr in 1990', 7.2 - 36.4 Tg/yr in the present day. H_2 may be formed by action of imperfect combustion. Imperfect combustion could be dominating factor to dD of H_2 of exhaust. In the future, emission of H_2 from automobile exhaust would not be decrease, or rather, expected to increase gradually as an increasing number of cars at developing countries.