Global stable isotope composition of CO: comprehensive modelling with the ECHAM/MESSy Atmospheric Chemistry (EMAC) GCM

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We present a detailed modelling approach that is essential to the interpretation of atmospheric CO and its isotopic composition, applying an elaborate isotopic chemistry mechanism in the ECHAM/MESSy Atmospheric Chemistry (EMAC) general circulation model. The Modular Earth Submodel System (MESSy) framework incorporated in EMAC allows an explicit, more realistic treatment of the isotope effects, *i.e.* fractionation in chemical and physical processes. Conformably, we present the results of the global modelling of the stable carbon isotope composition of the bulk of tracers, with a focus on CO and the sensitivity of its isotopic composition to the key atmospheric processes. In particular, we estimate the tropospheric average value of the yield of produced CO from methane of λ_{CH4} = 0.94, which is a diagnosed variable in EMAC, rather than an assumed parameter. Furthermore, due to the preferential dry deposition of the lighter isotopologues of the intermediate species (*e.g.* formaldehyde and methanol), the photochemically produced CO becomes supplementary enriched in heavy ^{13}C by as large as 1-2‰.

Additionally, we revisit the parameterisation of the kinetic isotope effect (KIE) escorting the CO+OH sink. The complex rate coefficient parameterisation for this reaction suggests a slight ($\sim$0.5‰ per 10K) inverse temperature dependence of the ^{13}C KIE, owing to the change in partitioning between the different exit channels of this reaction. The missing larger fractionation during the CO sink at lower temperatures appears to be the plausible explanation for the larger underestimation of ^{13}CO at high latitudes (where the influence of the chemistry on the isotope composition of CO is greater), not conflicting with the high λ_{CH4} values. The comparison of the simulated CO composition with the UTLS observations available from the CARIBIC-1 project also supports this conclusion. Overall, the introduced refinements account for an additional global average enrichment of 2-3‰ in ^{13}CO content that may explain the consistent lacking of ^{13}C in atmospheric CO in the modelling studies, when compared to the observed isotope ratios.

Concurrently, we examine the global synthesis of the mass-independently fractionated (MIF) oxygen isotope composition of CO. The intrinsic MIF enrichment in CO induced by its oxidation by OH versus the ozone-impelled MIF source effect (due to reactions with unsaturated hydrocarbons) is assessed. The EMAC-simulated tropospheric Δ^{17}O(O$_3$) values are somewhat lower than customarily assumed in O$_3$ MIF source studies and are about +20‰. This is a result of the rapid isotope exchange between the mass-dependently fractionated air O$_2$ and O(^{3}P), with the latter participating in O$_3$ formation, thus reducing the ozone MIF. The O$_3$ source contribution is found to be less than +1‰ and +0.7‰ in Δ^{17}O(CO) in the NH and SH, respectively. Compared to the dominating OH effect of +4‰ to +6‰ in background air, this is a relatively minor enrichment. This renders a considerable importance of CO MIF for studying the atmospheric OH budget.