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Triple oxygen isotope composition of carbon dioxide from various anthropogenic sources and in urban air

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The triple oxygen isotope composition of CO_2 from different sources is gaining in importance as possible tracer of gross carbon exchanges between major reservoirs [1]. Anthropogenic CO_2 has little influence on the $\Delta^{17}O_{TFL}$ value of CO_2on global scale [1-3].However, regionally it may have a significant effect. In this study, we present the oxygen isotopic signatureof CO_2 with different anthropogenic provenance and we compare these values to the local atmospheric CO_2.

The CO_2 was isolated from non-condensable gases with a "Russian doll" cryogenic trap at -196 ˚C [4]. The $\delta^{13}C$ and $\delta^{18}O$ values of the CO_2 were determined (dual inlet - irmMS). The $\Delta^{17}O_{TFL}$ value of CO_2 was determined by equilibration with CeO_2 at 685˚C, and subsequent analysis of $\delta^{17}O$ and $\delta^{18}O$ of CeO_2 by means of IR laser fluorination GC-CF-irmMS [5]. All $\Delta^{17}O$ values were reported relative to the terrestrial fractionation line, with a slope (β) of 0.5251±0.0007 and an intercept (γ) of –0.014±0.008 ‰$\dot{C}O_2$ concentration in the ambient air was determined with a GC.

$CO_2$was collected from four different processes: (1) directly from high temperature combustion of fossil fuel (propane-butane and natural gas flame), (2) car exhaust, (3) combustion of wood chips, (4) human respiration.

These four processes were clearly distinguishable by the isotopic signature of CO_2. Combustion of propane-butane resulted in CO_2 with a $\Delta^{17}O_{TFL}$value of -0.378±0.009 ‰ (1σ, SE). For the CO_2 from natural gas burning a $\Delta^{17}O_{TFL}$ value of -0.364±0.014 ‰ (1σ, SE) was obtained. Our data show that CO_2 from high temperature combustion inherits the signature of tropospheric O_2 ($\Delta^{17}O_{TFL}$ = -0.370 ‰ [6]). Car exhaust CO_2 had a $\Delta^{17}O_{TFL}$ value of -0.418±0.013 ‰ (1σ, SE). This value was the result of high temperature combustion with a subsequent water equilibration in the exhaust line. Assuming that the CO_2 inherited oxygen isotope composition of tropospheric O_2 in the first step, the exponent β for CO_2-H_2O fractionation could be calculated to 0.521. This is in a good agreement with the exponent value of Hofmann et al. [7]. Burning of wood chips produced CO_2 with a $\Delta^{17}O_{TFL}$ value of -0.261±0.010 ‰ (1σ, SE). Kinetic fractionation of O_2 could be responsible for this value. The $\Delta^{17}O_{TFL}$ value of respiration CO_2 was -0.109±0.027 ‰ (1σ, SE). This value is due to the equilibration of CO_2 with body water, with a $\Delta^{17}O_{TFL}$ = 0.00 (ß$_{CO2-H2O}$ = 0.522 [7]).

Eleven atmospheric CO_2samples were collected in the campus of the University of Göttingen (NW Germany), throughout the last year. The $\Delta^{17}O_{TFL}$ values were between -0.150±0.04‰ and -0.037±0.04‰ with a mean of -0.087±0.013‰ (1σ, SE). Concentration of the CO_2 varied between 375±5 and 450±5 ppm. There was no correlation between CO_2 $\Delta^{17}O_{TFL}$ values and concentration. Assuming that enhanced CO_2 concentration was originated from anthropogenic sources, a shift of approx. 0.05‰ in the $\Delta^{17}O_{TFL}$ value should have been obtained. Further measurements should clarify, if the lack of correlation was the result of the measurements uncertainty, or CO_2 equilibration with different water reservoirs overwrites mixing effect even on the regional scale.

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