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Atmospheric concentrations of carbon dioxide and its isotopic composition in southern Poland: comparison of high-altitude mountain site and a near-by urban environment.

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Transition to market economy in east European countries is associated with major changes of industrial technologies and resulting shifts in the structure of total energy consumption (gradual shift from coal to oil and natural gas). These changes have significant impact on strength and distribution of major sources of greenhouse gas emissions into the atmosphere in this part of Europe. In particular, large urban and industrial centres are affected by these emissions and the extent of these change need to be quantified.

Regular observations of atmospheric mixing ratios of CO_2 and its isotopic composition ($\delta^{13}C$, $\Delta^{14}C$, $\delta^{18}O$) are performed since 1994 at two contrasting sites in southern Poland: the high-altitude mountain station Kasprowy Wierch located in the Tatra Mountains (1987 m.a.s.l., 300 m above the tree line) and the city of Krakow located ca. 80 km north of the Kasprowy station, in the valley of the Vistula river. While the Kasprowy Wierch site is mostly free of local anthropogenic influences, the Krakow sampling site represents typical urban environment, with high density of local CO_2 emissions and significant impact of large industrial centre (Upper Silesia) located approximately 100 km west of Krakow.

Comparison of CO_2 mixing ratios recorded at both sites reveals significant differences in the amplitude of diurnal cycle. Mean amplitude of carbon dioxide concentration at Kasprowy station is very small (1.5 to 5 ppm for winter and summer period, respectively) when compared to Krakow, where the amplitude of diurnal CO_2 changes reaches 100 to 150 ppm. Also the shape of diurnal variations is different. In Krakow, nocturnal maxima in CO_2 concentrations are observed throughout the whole year due to building up the inversion layer. At Kasprowy site, assimilation process reduces the amount of CO_2 in the atmosphere during the day in summer season, while during winter period, a day time elevated concentrations are observed due to influence of local emissions.

Amplitude of diurnal variations of δ^{13} CO₂ at Kasprowy Wierch varies between 0.5 and 2 per mille, depending on local meteorological conditions. During the period 1994 - 2004 the average δ^{13} CO₂ was decreasing by approximately 0.05 per mille/y with mean amplitude of seasonal variations equal around 1 per mille. Similar measurements performed at Krakow indicate higher diurnal variation of δ^{13} CO₂ (4-5 per mille) reaching the minimal values of -12 per mille. In case of δ C¹⁸O₂ no significant long term trend was observed. The amplitude of diurnal variations of δ^{C18} O₂measured at Kasprowy Wierch varies between 0.5 and 1.5 per mille, while at Krakow it reaches up to 4 per mille for same period. The mean seasonal amplitude of δ C¹⁸O₂ measured in Krakow equals 2 per mille.

Comparison of Δ^{14} C records shows distinct differences in yearly-mean values and seasonal fluctuations which amplitude is modulated by anthropogenic emissions and biological sources and sinks. The multi-year decreasing trend has the similar slope for the both sites equal approximately 2.5 per mille/y. The observed seasonal fluctuations are regular at Krakow sampling site, with the peak-to-peak amplitude reaching 45 per mille, while at Kasprowy Wierch the shape as well as the amplitude reveal distinct irregularities and recorded changes are below 25 per mille. The available Δ^{14} C records are used to derive the contribution of fossil carbon to the local level of atmospheric CO₂ at both sampling sites.

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