Radiocarbon, Vol 60, Nr 5, 2018, p 1285–1299 DOI:10.1017/RDC.2018.79
Selected Papers from the 2nd Radiocarbon in the Environment Conference, Debrecen, Hungary, 3–7 July 2017

TEMPORAL VARIATION OF ATMOSPHERIC FOSSIL AND MODERN CO_2 EXCESS AT A CENTRAL EUROPEAN RURAL TOWER STATION BETWEEN 2008 AND 2014

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ABSTRACT. In 2008, the atmospheric CO_2 measurements at the Hegyhátsál rural tower station were extended further by $^{14}CO_2$ air sampling from two elevations (115 and 10 m a.g.l.), in cooperation with HEKAL (ICER). Since then, a complete six-year-long (2008–2014) dataset of atmospheric CO_2, $\Delta^{14}C$, fossil, and modern CO_2 excess (relative to Jungfraujoch) has been assembled and evaluated. Based on our results, the annual mean CO_2 mole fraction rose at both elevations in this period. The annual mean $\Delta^{14}CO_2$ values decreased with a similar average annual decline. Based on our comparison, planetary boundary layer height obtained by modeling has a larger influence on the variation of mole fraction of CO_2 (relative to Jungfraujoch), than on its carbon isotopic composition, i.e. the boundary layer rather represents a physical constraint. Fossil fuel CO_2 excess at both elevations can rather be observed in wintertime and mainly due to the increased anthropogenic emission of nearby cities in the region. The mean modern CO_2 excess at both elevations was even larger in winter, but it drastically decreased at 115 m by summer, while it remained at the winter level at 10 m.

KEYWORDS: atmosphere, boundary layer, CO_2, fossil fuel, radiocarbon.

INTRODUCTION

CO_2 is one of the most important greenhouse gases in the atmosphere, and its concentration has been directly modified by humans due to the large amount of fossil fuel CO_2 emitted since the Industrial Revolution (Neftel et al. 1985; Tans 2009). To better understand the characteristics of the sources and the magnitude of CO_2 emissions, high-resolution CO_2 transport models require detailed information on both the spatial and temporal distribution of CO_2 in the atmosphere (Geels et al. 2007; Patra et al. 2011). The anthropogenic contribution is superimposed on relatively large and strongly variable natural fluxes of CO_2 between the atmosphere, the terrestrial biosphere, and the oceans (Bousquet et al. 2000; Rödenbeck et al. 2003; Geels et al. 2007). Hence, with a quantitative knowledge of the anthropogenic contribution, biogenic CO_2 sources and sinks can be more accurately estimated by inverse modeling.

Due to its considerable role in global climate change, the increase of atmospheric CO_2 was proposed to be mitigated by the reduction of anthropogenic emissions of the respective nations. In the Kyoto Protocol, Hungary declared it would reduce its greenhouse gas emissions by 6% by the period 2008–2012 (compared to the average of 1985–1987), which was successfully accomplished. The United Nations Framework Convention on Climate Change (UNFCCC) has obliged all participating countries, including Hungary, to regularly report their anthropogenic emissions by sources (and removal by sinks) of all greenhouse gases, in particular CO_2. In 2012, the total emissions of greenhouse gases in Hungary were 62 million tonnes CO_2 equivalents, which is the lowest value during the period of 1985–2012 and CO_2 accounted for 74.3% of the total greenhouse gas emissions (NIR 2014).

Due to similar requirements worldwide, there is an urgent need for reliable monitoring, regular assessment, and verification processes of greenhouse gas emissions. Conventional emission

estimations of CO_2 and other greenhouse gases are based on bottom-up statistics, which can be paired with uncertainties the same order of magnitude as the desired reductions themselves. Fossil fuel CO_2 now have a market value associated with these emissions, thus rigorous and verifiable quantification of emissions requiring multiple methodologies will be necessary in the future (Levin et al. 2011; Turnbull et al. 2015). Radiocarbon (^{14}C) plays a crucial role in global carbon cycle investigations and emission verification. Over the last century, the natural $^{14}C/C$ ratio of atmospheric CO_2 (expressed as $\Delta^{14}C$) has spectacularly been disturbed by human activities via nuclear bomb tests in the 1950s and 1960s and by the ongoing fossil fuel CO_2 input (Suess 1955). Over highly populated areas with large CO_2 emissions from fossil fuel burning, such as Central Europe, we are able to estimate the regional fossil fuel CO_2 burden from specific activity measurements of ^{14}C in atmospheric CO_2. Comparing the $\Delta^{14}C$ values of two sites of similar latitude, any depletion in the $^{14}C/C$ ratio of CO_2 at the polluted site relative to the background can then be directly translated into a regional fossil fuel CO_2 excess (Levin et al 1989, 2007, 2010; Meijer et al. 1996; Zondervan et al. 1996; Molnár et al. 2010a; Graven et al. 2012).

In this study, we aim to evaluate the temporal variation of the local CO_2 mole fraction and its $\Delta^{14}C$ values at two different elevations (115 and 10 m a.g.l.) at the Hegyhátsál rural tall tower station (Hungary). The measured results are then compared with modeled planetary boundary layer height data to reveal how this environmental factor can influence the mole fraction and carbon isotopic composition of atmospheric CO_2. In addition, we made some calculations for the contribution from fossil fuel and modern-derived CO_2 excess in this region, relative to the free tropospheric background station of Jungfraujoch (46°33'N, 7°59'E, 3450 m a.s.l., ~660 km west of Hegyhátsál), between 2008 and 2014, so we offer some details on this site as well. For this purpose, we obtained the CO_2 mole fraction and $\Delta^{14}C$ data measured continuously at Jungfraujoch from Markus Leuenberger (University of Bern, personal communication) and the ICOS – Central Radiocarbon Laboratory, respectively.

MATERIALS AND METHODS

Description of the Sampling Sites

A detailed description of the Hegyhátsál (HHS) tower measurement system in Hungary, as well as a characterization of the site, can be found in numerous previous publications (can be found as HUN in Haszpra et al. 2005, 2008, 2010, 2012). Briefly, the Hegyhátsál tall tower greenhouse gas monitoring station is located in western Hungary (46°57'N, 16°39'E, 248 m a.s.l.), in the Carpathian Basin, surrounded by agricultural fields (mostly crops and fodder of annually changing types), pastures and small areas of forest (Figure 1). The climate of the region is temperate continental and the soil type around the tower is dominated by "lessivated brown forest soil" (Alfisol, according to the USDA system). The industrial activity in the region is negligible and the local roads are free of heavy traffic. The nearest village is Hegyhátsál (~150 inhabitants) situated about 1 km to the northwest.

At the HHS station, the CO_2 mole fraction has been continuously monitored at four elevations (115, 82, 48 and 10 m above the ground) since September 1994. The basic instrument of the measuring system is a nondispersive infrared gas analyzer (Li-Cor Model LI-7000; Haszpra et al. 2008) and the overall uncertainty of the measurements is ±0.1 ppm. In 2008, these measurements were extended further by $^{14}CO_2$ air sampling from two elevations (115 and 10 m a.g.l.) on a monthly average basis, in cooperation with the Hertelendi Laboratory of Environmental Studies (HEKAL, a department of ICER). This site provides a rural regional background for the urban fossil fuel CO_2 excess studies of Debrecen city that is also situated in

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Figure 1 Locations of Hegyhátsál tower station and background site of Jungfraujoch. The atmospheric CO_2 mole fraction and $\Delta^{14}C$ data presented refer to the 115 and 10 m a.g.l. sampling elevation of the station.

Hungary, approximately 380 km east of Hegyhátsál. Hence, there is a rural and an urban site in the Carpathian Basin where the mole fraction of CO_2, fossil fuel and modern CO_2 excess relative to a free tropospheric reference as well as the influence of these factors can be investigated (Molnár et al. 2010b).

The CO_2 mole fraction data at the Jungfraujoch station has been continuously measured by the University of Bern since 2004, using a S710 UNOR type non-dispersive infrared gas analyzer. The overall uncertainty of the measurements is ±0.1 ppm (Sturm 2005).

CO_2 Sampling at Hegyhátsál and the ^{14}C Measurements

At the Hegyhátsál station, two ATOMKI-developed CO_2 samplers were installed for sampling of the respective elevations, to obtain monthly integrated samples for ^{14}C measurements (Molnár et al. 2010a, 2010b). The inlets of the samplers are connected to the exhaust lines of the CO_2 analyzer used, so the CO_2 monitoring is not affected by the sample collecting on process. CO_2 is trapped in bubblers filled with 500 mL of 3M NaOH solution. The flow rate of 10 Lhr^{-1} (STP) is stabilized by a dedicated control unit. The sampling is set for four- or five-week-long periods. A detailed description of the sampling device is given by Uchrin and Hertelendi (1992). ATOMKI samplers of similar type have routinely been used in the environmental $^{14}CO_2$ monitoring around the Paks nuclear power plant (NPP) in Hungary since 1991 (Molnár et al. 2007). In addition, this type of sampler is applied for atmospheric $^{14}CO_2$ sampling at the urban monitoring station in Debrecen.

To extract CO_2 from the alkaline samples, 40% sulphuric acid was added to the NaOH solution. The liberated CO_2 gas (typically 2.5 L STP) was purified over a charcoal column then frozen into a CO_2 trap using a dedicated vacuum system (Csongor et al. 1982). We measured the specific ^{14}C activity of the samples by a gas-proportional counting system designed and built at ATOMKI. According to counting statistics, the final uncertainty of the ^{14}C measurements (1σ) was around ±5‰ after a one-week-long measurement (Csongor and Hertelendi 1986; Hertelendi et al. 1989). The result of the samples regarding the respective months are reported in $\Delta^{14}C$ units (difference between Δ and $\Delta^{14}C$ is negligible in this case) corrected for decay and the fractionation of ^{13}C (Stuiver and Polach 1977). The $\delta^{13}C$ correction was measured on CO_2 gas

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originating from each processed sample by a ThermoFinnigan Delta Plus XP stable isotope mass spectrometer (overall uncertainty ±0.2‰) using the dual inlet method (Vető et al. 2004).

The High Alpine site Jungfraujoch in the Swiss Alps (Levin et al. 1989, 2008) provides a good background station for continental atmospheric comparison; hence we used the $\Delta^{14}C$ dataset of this site to evaluate the regional fossil fuel and modern CO_2 excess at Hegyhátsál (Hammer and Levin 2017). The $^{14}CO_2$ measurements at the JFJ station started in 1986 (Levin and Kromer 2004) and have been running continuously without interruption. As the station is located at an altitude of 3450 m a.s.l., generally free tropospheric air is sampled. Biweekly integrated CO_2 samples were collected by chemical absorption in basic solution (NaOH) (Levin et al. 1980) and analyzed for ^{14}C activity by conventional radioactive counting (Kromer and Münnich 1992). The 1σ uncertainty is generally ±2‰ for all samples analyzed during our period of interest.

Calculation of the Relative Fossil Fuel and Modern CO_2 Excess

By means of the combined measurement of the CO_2 mole fraction and its $^{14}C/C$ ratio at two different regions, the summed contribution from the respective fossil fuel CO_2 sources can be determined for the investigated site, relative to the reference site. Due to the long-term atmospheric $^{14}CO_2$ observations, the variation of fossil fuel CO_2 excess can be investigated as a function of time.

We used the atmospheric CO_2 mole fraction and $\Delta^{14}C$ data of the Hegyhátsál and the Jungfraujoch stations, with the latter as the background reference. In the case of the background site, as a free tropospheric atmospheric station in Europe, we had no exact information regarding the modern and fossil contributions to the atmospheric CO_2 but it was assumed to mostly be free of direct and heavy anthropogenic influences.

Based on a simple model suggested by Levin et al. (1989, 2003), the measured CO_2 mole fraction (c_{meas}) at a certain site consists of three different components: namely a continental background component (c_{bg}), a regional biospheric component (c_{bio}), and a fossil fuel component (c_{foss}). To estimate the fossil fuel CO_2 excess, we used the following mass balance Equation comprising the measured CO_2 mole fraction and $\Delta^{14}C$ values:

$$\begin{aligned} c_{meas} \cdot \left(\Delta^{14}C_{meas} + 1000\right) = {} & c_{bg} \cdot \left(\Delta^{14}C_{bg} + 1000\right) \\ & + c_{bio} \cdot \left(\Delta^{14}C_{bio} + 1000\right) \\ & + c_{foss} \cdot \left(\Delta^{14}C_{foss} + 1000\right) \end{aligned} \quad (1)$$

In this Equation, c_{meas} is the CO_2 mole fraction at the observed site, c_{bg} is the background mole fraction in the free troposphere, c_{bio} is the biogenic component, and c_{foss} is the fossil fuel component. The $\Delta^{14}C_{meas}$, $\Delta^{14}C_{bg}$, $\Delta^{14}C_{bio}$, and $\Delta^{14}C_{foss}$ are the deviation of the $^{14}C/C$ ratios from "modern," which is defined as 95% of the NBS oxalic acid (SRM4990B) standard activity corrected for fractionation and decay (Stuiver and Polach 1977). In the method used by Turnbull et al. (2006), the $\Delta^{14}C$ of the biospheric component can be slightly different from the atmospheric $^{14}CO_2$ background level but in the absence of corresponding data, we set $\Delta^{14}C_{bio}$ equal to $\Delta^{14}C_{bg}$. As background $\Delta^{14}C$ in our calculations, we used the measured values of the High Alpine Research Station Jungfraujoch. The fossil fuel term in Equation (1) is set to zero as $\Delta^{14}C_{foss} = -1000‰$ i.e. all the ^{14}C content of these materials has long decayed.

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In the comparison of measured CO_2 mole fractions at the 115 and 10 m elevations of the Hegyhátsál station relative to Jungfraujoch, the difference (δc) was calculated as follows:

$$\delta c = c_{meas} - c_{bg} \tag{2}$$

where c_{meas} and c_{bg} represent the CO_2 mole fractions at the respective elevations (115 or 10 m) of the Hegyhátsál and Jungfraujoch stations, respectively.

Rearranging the Equation (1), we get the following formula, which is suitable to calculate the fossil fuel component:

$$c_{foss} = c_{meas} \cdot \frac{\Delta^{14}C_{bg} - \Delta^{14}C_{meas}}{\Delta^{14}C_{bg} + 1000} \tag{3}$$

The mole fraction of modern CO_2 excess relative to the background (c_{mod}) was obtained as a residue of the difference of the CO_2 mole fractions (δc) subtracting the fossil fuel component calculated for the observation elevations:

$$c_{mod} = \delta c - c_{foss} \tag{4}$$

In the course of the relationship studies, data on the height of the planetary boundary layer (PBL) relating to Hegyhátsál were retrieved from the Meteorological Archive and Retrieval System (MARS) database of the European Centre for Medium-Range Weather Forecasts (ECMWF). PBL height data were calculated by the deterministic model in forecast time steps with a temporal resolution of 3 hr (Beljaars et al. 2001). For a better comparison with the investigated atmospheric components, one-month averages were generated from the 3-hr data, following the $^{14}CO_2$ sampling period at the Hegyhátsál station.

RESULTS AND DISCUSSION

Long-Term Seasonal Variation of the Atmospheric CO_2 Mole Fraction at Hegyhátsál

Figure 2(a) shows the calculated mean CO_2 mole fractions at the 115 and 10 m elevations of the Hegyhátsál tower from where air samples for $^{14}CO_2$ analysis were also collected. In the calculation of mean CO_2 concentrations, the start and end date of ^{14}C sampling periods were considered thus the CO_2 data differ from the ones that are published online in the database of the World Data Centre for Greenhouse Gases (WMO WDCGG – http://ds.data.jma.go.jp/gmd/wdcgg/). Additionally, the background CO_2 data at Jungfraujoch are also displayed. Figure 2(b) shows the linear detrended curves of the measured CO_2 values in the form of biases from the fitted line.

Particularly at Hegyhátsál but also at Jungfraujoch, a strong seasonal cycle in the CO_2 mole fraction can be observed with lower values in summer and higher ones in winter. During the measurement period of six years, the mean CO_2 mole fraction increased from 395 to 406 ppm and from 404 to 415 ppm at elevations of 115 and 10 m of the Hegyhátsál station, respectively. The increase rate was around 2 ppm yr^{-1} at both measuring levels, similarly to the growth rates observed at Jungfraujoch or other atmospheric background stations in the world (www.esrl.noaa.gov). As it can be seen in Figure 2(b), there is a significant variation in the seasonal fluctuation of the CO_2 at the two elevations of the Hungarian station and the Swiss free tropospheric site, moreover the phase of variations are also shifted slightly. The maximum and minimum values at Hegyhátsál were recorded mainly in November–January and June–August, respectively. In contrast, maxima and minima at Jungfraujoch can be observed between February and April as well as between August and September, respectively. The peak-to-peak

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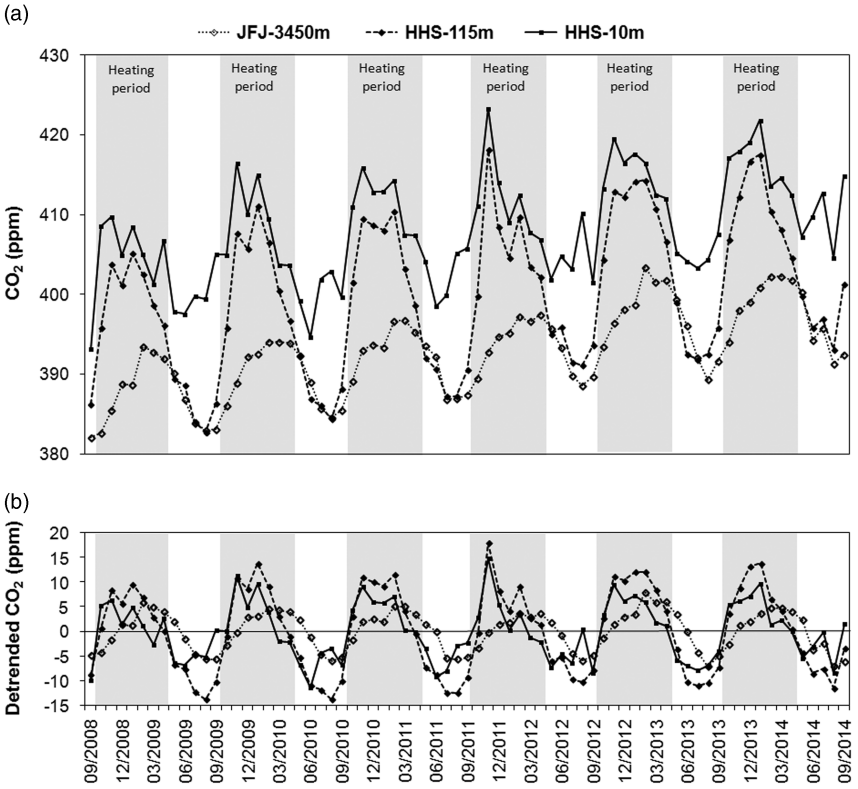

Figure 2 (a) Long-term seasonal variation of monthly mean CO_2 mole fraction at Hegyhátsál and Jungfraujoch between September 2008 and October 2014; (b) the biases of the linear detrended curves.

differences of the detrended data at Jungfraujoch varies from 10 to 15 ppm while it ranges from 21 to 30 ppm and from 15 to 24 ppm at the 115 and 10 m elevations of the Hegyhátsál station, respectively. Definite CO_2 peaks containing the maximum values were observed predominantly in winter periods associated with lack of CO_2 absorption by photosynthesis (i.e. the CO_2 source characteristic of autotrophic organisms becomes dominant), weak vertical mixing (thin planetary boundary layer), and enhanced anthropogenic emissions (residential heating) of the nearby large cities, which have an influence on this area on regional scale. Lower CO_2 mole fractions were recorded during summer when the vertical mixing of the atmosphere is strong (thick planetary boundary layer) and CO_2 uptake of the ambient natural and agricultural vegetation is significant. For example, CO_2 values at the 115 m and the free tropospheric background level at JFJ are very similar in summer due to the intensive daily mixing occuring in a thick boundary layer. However, we can observe characteristically much higher mole fractions at 10 m, which is the consequence of the nocturnal emissions of the vegetation and soil, accumulated in a much shallower nighttime surface layer [Figure 2(a)].

In order to better understand the influence of the height of the planetary boundary layer to the atmospheric CO_2 mole fraction at Hegyhátsál, the relationship between the CO_2 mole fractions of the Hegyhátsál and Jungfraujoch sites, and the maximum boundary layer heights obtained by modeling (by ECMWF) for the western Hungarian region were also studied. In these calculations, we determined the regression coefficient (R^2) of the best fit of a regression of

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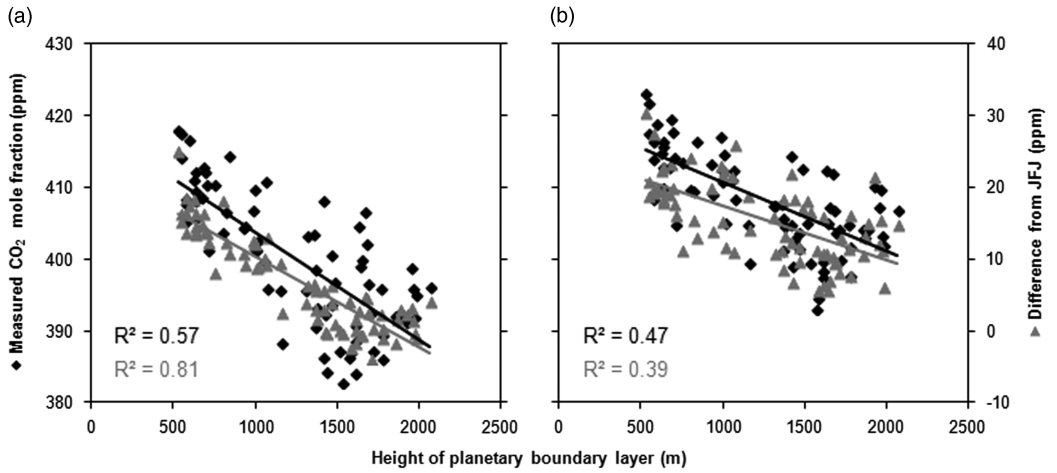

Figure 3 (a) The absolute CO_2 mole fraction (c_{meas}) and difference from the background (δc) at the 115 m level of Hegyhátsál as the function of the height of the planetary boundary layer; (b) the same quantities for the 10 m level are shown.

absolute CO_2 mole fractions (c_{meas}) or difference from the background (δc) and the height of the planetary boundary layer. The R^2 regarding the CO_2 mole fractions measured at Jungfraujoch and the boundary layer heights at Hegyhátsál is only 0.04. The highest boundary layer values of 2500–3000 m at Hegyhátsál are generally formed at around noon during the summer months, which are still lower than the 3450 m a.s.l. height of the Jungfraujoch station being constantly in the free tropospheric layer throughout the year. Consequently, this station represents an appropriate basic level from the perspective of variation of CO_2 mole fraction at Hegyhátsál.

Regarding the CO_2 concentration at the Hegyhátsál 115 m level, the R^2 is 0.57, which suggests a much larger effect of the boundary layer height to this elevation but other significant factors, such as CO_2 emission or absorption of the terrestrial biosphere also have to be considered [Figure 3(a)]. However, the maximum R^2 of 0.81 was achieved when the associated δc values (Jungfraujoch subtracted from Hegyhátsál 115 m) were considerred as a function of the boundary layer data. This is presumably explained by the fact that the boundary layer during the nighttime of summer can be as thin as some 10 m, i.e. the 115 m elevation is included at daytime while it is not at night. This suggests that the variation of the boundary layer height has a more considerable effect on the variation of δc at this elevation, over the formation of absolute CO_2 mole fraction. Regarding the 10 m elevation [Figure 3(b)], the R^2 for δc (Jungfraujoch subtracted from Hegyhátsál 10 m) and noon boundary layer height data is 0.39, which is lower than the R^2 for the absolute CO_2 mole fraction (0.47). This level is constantly situated in the surface layer of the lower atmosphere so the variation of boundary layer height has a less effect on it, which is confirmed by the weaker correlation, compared to the 115 m level.

LONG-TERM SEASONAL VARIATION OF THE ATMOSPHERIC $\Delta^{14}C$ IN CO_2 AT HEGYHÁTSÁL

For better visualization, three-month-centered moving average curves are fitted on the atmospheric $\Delta^{14}C$ results measured monthly, which are displayed in Figure 4(a). The average uncertainties of the measured values for Hegyhátsál and Jungfraujoch are ±5 and ±2‰, respectively. Figure 4(b) shows the biases of the linear detrended curves smoothed on the $\Delta^{14}C$ values.

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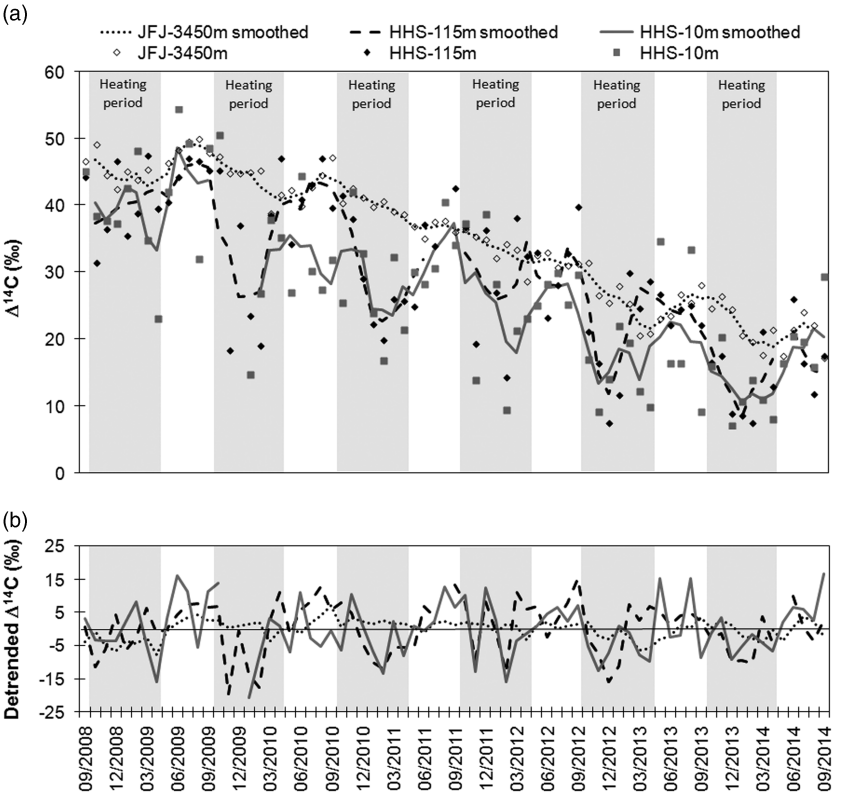

Figure 4 (a) Long-term seasonal variation of the $\Delta^{14}C$ at the Hegyhátsál and Jungfraujoch stations between September 2008 and October 2014, and the respective centered moving average curves fitted on the results. The biases of the linear detrended curves of smoothing are shown in part (b). Hegyhátsál data for November–December 2009 and for August 2011 are missing due to technical reasons, causing gaps in the dataset.

The $\Delta^{14}C$ values of atmospheric CO_2 are continuously decreasing at all sites, which is mainly explained by the ongoing worldwide input of fossil fuel CO_2 into the atmosphere (Levin et al. 2003; Kuc et al. 2007; Turnbull et al. 2015). During the observation period, the annual mean of $\Delta^{14}C$ values measured at the free tropospheric station Jungfraujoch decreased from 46 to 20‰ with an average decline of around 5.2‰ yr^{-1}.

During the same period, the annual mean $\Delta^{14}C$ values at the 115 m elevation decreased from 40 to 16‰ with an average decline of 5.0‰ yr^{-1}, following the approximate global trend of 5‰ yr^{-1} (Levin el al. 2008; Graven et al. 2013). The mean $\Delta^{14}C$ values calculated for the heating periods decreased from 39 to 13‰ while the summer mean values declined from 44 to 18‰. The minimum values can be observed in winter i.e. during the heating period (October–April) in each year, while the maxima characterize the summers [Figure 4(b)]. With moderate seasonal variations, the peak-to-peak amplitudes are between 19 and 32‰. It is worth noting that $\Delta^{14}CO_2$ at Hegyhátsál relative to Jungfraujoch is lower in winter, indicating that depletion of CO_2 is more emphasized in this period of the year. This can be due to the effect of residential heating and transportation using fossil fuel, which is enhanced further by the thinner planetary boundary layer formed in cold periods, therefore the emitted fossil fuel CO_2 accumulates in a shallower atmospheric layer,

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offering larger impacts. Consequently, the effect of the large elevation difference (a.s.l.) between the observation and background sites can be very considerable as it was already suggested in earlier studies (Turnbull et al. 2015). Studying the regression coefficient, the relation is weak ($R^2 = 0.12$) between the $\Delta^{14}C$ values at 115 m and the heights of the planetary boundary layer so this factor only slightly influence the specific ^{14}C activity of atmospheric CO_2. Higher $\Delta^{14}C$ values and boundary layer heights can be observed in summertime, which suggests that thicker boundary layer, nevertheless, enhances the downward transport and mixing of ^{14}C being produced in the upper layers. The rare positive deviations at Hegyhátsál relative to Jungfraujoch are well within the final uncertainty of the ^{14}C measurements.

The $\Delta^{14}C$ values of the monthly CO_2 samples collected at the 10 m level decreased from 43 to 16‰ with an average rate of –5.4‰ yr^{-1}. The maximum and minimum values, similarly to the 115 m level, can be observed in summer and winter, respectively. The peak-to-peak amplitudes vary in the range of 21 and 31‰. The mean value calculated for the winter periods decreased from 40 to 13‰. Although this sampling level is closer to the potential sources, the $\Delta^{14}C$ deviations compared to Jungfraujoch are similar to the ones observed at 115 m. The mean difference between Hegyhátsál 10 m and Jungfraujoch is about 10‰ in winter and 6‰ in summer. Comparing to the values at 115 m, the discrepancy is very similar in winter but it decreases only to 2‰ in summer, resulting a mean difference of < 4‰ through the observation period. The start of increase at Hegyhátsál occurs around January i.e. earlier than at Jungfraujoch, which can be explained by the gradual growth of the planetary boundary layer. The R^2 value of 0.02 indicates no significant relationship between the $\Delta^{14}C$ values at the 10 m level and the height of planetary boundary layer; nevertheless there has to be some relationship between these two factors. The annual mean values are very similar to those observed at 115 m, but the fluctuation of $\Delta^{14}C$ implies that the contribution of local CO_2 sources and sinks have a larger role here closer to the surface. Through nighttime periods, due to thermal stratification, the proximity of different sources can modify their shares in the final CO_2 contribution but in the sampling process with a resolution of one month, the daily and nocturnal differences get rectified and the differentiation is very difficult. Hence, the phase and amplitude of the variation at 10 m are very similar to the ones observed at the 115 m elevation. This suggests that the small elevation difference, in a small scale, is not an important factor in the case of the $\Delta^{14}CO_2$ values. In the successive summers, the local ^{14}C enrichment approximates the level of the free troposphere due to the intensive vertical mixing but a lower maximum value is achieved, relative to the previous summer. Consequently, the decreasing trend of the annual means along with similar summer values are mainly caused by the remarkably lower $\Delta^{14}C$ values occurring in winter periods. During the heating-free period in 2010, the $\Delta^{14}C$ is constantly lower at 10 m than at the 115 m elevation, which is still unexplained.

Zimnoch et al. (2012) presented that the $\Delta^{14}C$ values of atmospheric CO_2 at the rural station Kasprowy Wierch, High Tatra Mountains, Poland (49°14'N, 19°59'E, 1989 m a.s.l., 300 m above tree line) varied between ~55‰ and 30‰ in the period of September 2007 and December 2009. They also observed a seasonal variation with higher values in summer and lower ones in winter. In 2009, the $\Delta^{14}C$ values varied between 43 and 30‰, similarly to Hegyhátsál. In contrast, in the paper of Berhanu et al. (2017), isotopic analysis of the air samples collected in Beromünster (47° 11'N, 8°10'E, 797 m a.s.l., 217.5 m a.g.l.) between 2012 and 2015 yielded $\Delta^{14}C$ values between -12.3 and 22.8‰, with no clear seasonal trend. The absence of seasonal variation can be explained by the applied flask sampling method, providing only point samples throughout the year. Although this is a slightly later period, their results are more negative than ours due to the urban characteristic of that station, representing more ^{14}C-depleted CO_2 in the air.

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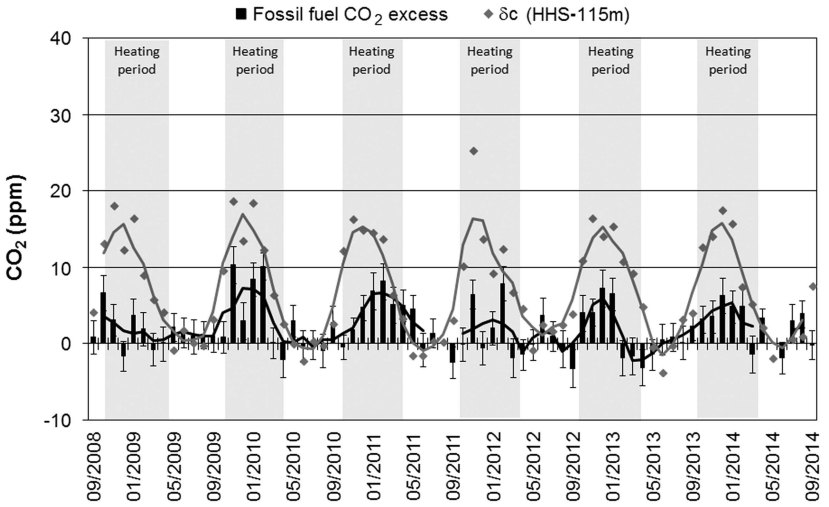

Figure 5 The calculated δc (CO_2 mole fraction difference) and fossil CO_2 excess (c_{foss}, black bars) values at the 115 m elevation of Hegyhátsál, relative to Jungfraujoch. The black and grey solid lines represent the three-month centered moving averages fitted on the respective datasets.

SEASONAL VARIATION OF ATMOSPHERIC FOSSIL AND MODERN CO_2 EXCESS AT HEGYHÁTSÁL, RELATIVE TO JUNGFRAUJOCH

In view of the absolute CO_2 mole fraction and $\Delta^{14}C$ data, we can calculate the fossil fuel CO_2 excess for the two elevations of the Hegyhátsál station, relative to Jungfraujoch. The Jungfraujoch station represents the free troposphere for the middle latitudes in the Northern Hemisphere, which should be free of direct anthropogenic contributions, but it is important to know that even this high altitude in the center of Europe, the site is also influenced slightly (mainly in summer) by the surrounding continental fossil sources (Levin et al. 2008). In addition, Turnbull et al. (2015) have shown that using a free tropospheric or a continental station as a background for the calculations, fossil fuel CO_2 excess effectively represents fossil CO_2 emitted not only from the observation area but also from the broader continental region, including other urban areas and regional emission sources. As Jungfraujoch is quantified as a continental station (whereas Hegyhátsál is a rural), this statement can be valid for our result as well. Nevertheless, this information has to be considered later for the fossil excess calculations regarding the urban site of Debrecen city.

The δc and the calculated fossil fuel CO_2 excess data for Hegyhátsál 115 m are displayed in Figure 5. A three-month centered moving average curve is also fitted on the data for better visualization. During the measuring period, a strong variability in CO_2 mole fractions can be observed at both sampling sites. The annual mean of δc is around 7 ppm constantly, while the peak-to-peak amplitude varies in the 17–27 ppm range. The annual maxima and minima of the differences range from 17 to 25 ppm and from –4 to –1 ppm, respectively. The maxima typically occur in winter while the minima are observed in summer, which is explained by the large elevation (a.s.l.) difference. In winter, an average 12–13 ppm CO_2 excess can be observed at Hegyhátsál relative to Jungfraujoch, but it decreases below 3 ppm by summer. As discussed above, the seasonality of CO_2 difference between the Hegyhátsál and Jungfraujoch elevations is highly influenced by the seasonal variation of the daily planetary boundary layer height.

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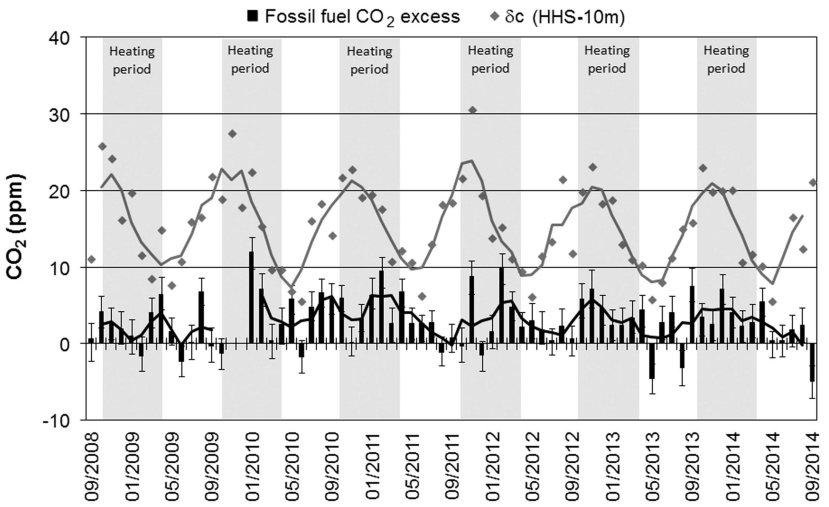

Figure 6 The calculated δc (absolute CO_2 difference) and fossil CO_2 surplus (c_{foss}, black bars) values at the 10 m elevation of Hegyhátsál, relative to Jungfraujoch. The black and grey solid lines represent the three-month centered moving averages fitted on the respective datasets.

The calculated annual mean of fossil fuel CO_2 excess is 2 ppm in the six years, varying from 1 to 3 ppm in different years. The annual maxima vary between 5 and 10 ppm and the minima from –3 and –1 ppm. The negative values are probably caused by the analytical uncertainty. A larger fossil fuel CO_2 excess at the level of 115 m characterizes the winters, varying between 2 and 6 ppm. In the summer i.e. heating-free periods, the mean value is around 1 ppm, which is well below the uncertainty of the calculations. During the measurement period, the fossil fuel CO_2 peaks coincide with the winter heating periods hence, according to our explanation, they are caused by the enhanced anthropogenic CO_2 emissions superimposed on the effect of the thin boundary layer where the vertical mixing is reasonably reduced. Due to the rural characteristics of the site, we suppose that this excess does not originate exclusively from local fossil sources such as residential heating or transportation but represents an averaged influence of a larger footprint region containing large cities like Budapest or Vienna. Performing the correlation calculations, we obtained a weak R^2 (0.28) between the fossil CO_2 values and the height of planetary boundary layer.

The mole fraction of modern CO_2 excess for the observation period was also estimated using Equation (4). At the 115 m elevation, the annual mean of the modern fraction is around 5 ppm. The peak-to-peak amplitude varies between 14 and 25 ppm. Interestingly, the larger modern fraction also appears in the winter period, with a mean of 9 ppm, while it almost disappears by summer giving a mean value of 1 ppm, relative to Jungfraujoch. Consequently, based on our data, the observed CO_2 excess at the 115 m elevation of the Hegyhátsál station relative to Jungfraujoch appears in the wintertime and largely derives from modern sources. Probably the large elevation difference of the stations also plays a significant role in the formation of the phenomenon. Unfortunately, using this method, CO_2 originating from anthropogenic wood burning cannot be distinguished from the natural emissions of terrestrial biosphere.

For the 10 m elevation of Hegyhátsál station, the annual mean of δc varies between 14 and 17 ppm in the measuring period, which is about a factor of two larger than the mean value for

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the 115 m elevation. The maximum differences of 23–31 ppm can be observed in winter whereas the minima of around 6 ppm appear mainly at the end of spring or beginning of summer (Figure 6). The annual peak-to-peak amplitude of 17–24 ppm is quite similar to that of the 115 m case. In winter and summer on average 16–19 and 11–13 ppm excess CO_2 can be observed at 10 m relative to Jungfraujoch, respectively. The difference from the respective result of the higher level is not so remarkable in winter but the discrepancy of 10 ppm in summer is significant. As we have seen earlier, the seasonal variation of the boundary layer is only partly responsible for the variation of CO_2 mole fraction at this level but the low boundary layer height represents a barrier for the CO_2 emitted by the vegetation and soil in the nighttime period even in summer (Haszpra et al. 2010).

Regarding the mole fraction of fossil fuel CO_2 excess at 10 m, the annual means are between 1 and 4 ppm, relative to Jungfraujoch, similar to the results of 115 m, giving a mean of 3 ppm for the observation period. The annual maxima and minima vary between 5 and 12 ppm, as well as –5 and 0 ppm, respectively. Mean fossil fuel values between 2 and 5 ppm characterize the winter periods. In summer, the fossil fraction being between 1 and 4 ppm is very close to the uncertainty of the measurements. Comparing the fossil values at the two measuring levels, there is no significant discrepancy in winter but in summer, systematically higher seasonal means were recorded at the lower elevation. This phenomenon, supposing a relatively homogeneous and thick daily mixing layer, could be caused by the local nocturnal fossil CO_2 emissions but due to the relatively high uncertainty of the calculations, the unpredictable variations and the lack of knowledge on transport processes, the exact reason still needs to be investigated. Since the sampling site is located far from direct fossil sources, the fossil contribution must be the mutual effect of local and regional sources, transported to this site by atmospheric circulations. In addition, the effect of the free tropospheric background, which was already been mentioned above, needs also to be taken into account at the station. Therefore, we are sure that the effective fossil fuel CO_2 emitted locally at Hegyhátsál is lower than that we determined by these calculations and it originates, at least partly, from regional sources. It is important to note that the fossil CO_2 contribution from transport and industrial sources can be significant even in summer but due to intensive vertical mixing, it cannot be detected in the high and relatively homogenous continental planetary boundary layer. Performing the correlation calculations, we obtained a weak R^2 (0.06) between the fossil CO_2 values and the height of planetary boundary layer.

For comparison, van der Laan et al. (2010) evaluated the seasonal variation of the mole fraction of fossil fuel CO_2 at the Lutjewad station in the Netherlands (6°21'E, 53°24'N, 1 m a.s.l., 60 m a.g.l.), relative to Jungfraujoch, and found that it varies from 2–3 ppm on average to its maximum of 20.6 ppm. The maximum fossil value of 12 ppm at our 10 m elevation is considerably below this value, reflecting the rural characteristic of the Hegyhátsál station. According to their study, seasonal amplitudes varied strongly between the years with a value of 4 ppm in 2006 and about 9 ppm in 2009 but our results did not show significant short-term variations. Higher fossil fuel CO_2 mole fractions, similar to our case, were generally observed in winter and lower values in the summer, influenced by atmospheric conditions (i.e. transport of air masses and height of the planetary boundary layer) as well as anthropogenic activity. Consequently, we conclude that the governing factors inducing or influencing the observed fossil CO_2 excess values at the Lutjewad and Hegyhátsál stations can be similar.

The modern contribution to the CO_2 difference at the Hegyhátsál 10 m elevation is around 12 ppm and this is more than twice as much as at the 115 m elevation. This suggests that the regional CO_2 enhancement includes a significant contribution from modern biological respiration as well. The peak-to-peak amplitudes are slightly higher than at the 115 m elevation. The difference

https://doi.org/10.1017/RDC.2018.79 Published online by Cambridge University Press

between the seasonal means is not so significant since it is around 12 ppm in winter and 10 ppm even in summer. Hence, we can conclude that the observed δc at 10 m mainly derives from modern sources such as respiration of the biosphere and soil. The CO_2 at the 10 m elevation is actively involved in the chemical and biological processes close to the surface thus, in winter, emissions from the vegetation, anthropogenic wood burning as well as the thin boundary layer together influence the fluctuation of the CO_2, resulting in higher mole fractions.

Turnbull et al. (2011) also observed a substantial contribution of biospheric CO_2 fluxes even during winter (20–30% from non-fossil sources including respiration) from samples in East Asia. According to Zimnoch et al. (2012), the modern biogenic fraction, even in an urban environment such as Krakow, reveals a distinct seasonality with maxima in summer and early autumn as well as with minima in winter and early spring. The reverse seasonality is interesting because this differs from the observations of our and other laboratories (Turnbull et al. 2015). However, they used only approximate CO_2 mole fraction values obtained from the GLOBALVIEW database, which could explain the differences.

CONCLUSIONS

In this study, we estimated the seasonal variation of atmospheric CO_2 mole fraction and $\Delta^{14}C$ at two elevations of the Hegyhátsál tall tower station. Using the measured results, we subsequently constructed respective fossil and modern CO_2 time series relative to Jungfraujoch for the period 2008–2014. The annual mean CO_2 mole fraction increased 11 ppm at both elevations of the Hegyhátsál station during the six years, following the global trend of CO_2 increase. The annual mean $\Delta^{14}CO_2$ values at the 115 and 10 m elevations decreased from around 40 to 16‰ with a similar mean annual decline (see supplementary Table S1). Based on a comparison of the mole fraction and $\Delta^{14}CO_2$ with the height of the boundary layer data, the latter has a larger influence on the CO_2 mole fraction differences (relative to the background) over the carbon isotopic composition. Consequently, the boundary layer likely represents a physical constraint to the sources and sinks. A pronounced seasonality in $\Delta^{14}C$ can be observed at Hegyhátsál with lower values in winter and higher values during summer. Deviations from Jungfraujoch are the largest in winter when anthropogenic emissions at the surface are at their maximum (e.g. residential heating, transportation) and atmospheric mixing, which would efficiently dilute these emissions, is largely suppressed for a thin planetary boundary layer. The mean fossil fuel CO_2 contribution relative to the free tropospheric reference site was larger in wintertime, whereas it decreased below the range of uncertainty of the calculations by summer. The mean mole fraction of modern CO_2 at the two elevations relative to Jungfraujoch was even larger in winter but this difference decreased by summer. Our fossil fuel and modern CO_2 data show a clear seasonality with peaks during winter associated with weak vertical mixing, while summer values are generally lower coinciding with intensive daily mixing in thicker planetary boundary layer and active photosynthesis of the vegetation. In the future, detailed analysis of more meteorological parameters and comparisons with $\Delta^{14}C$ values of other regions may also be useful to clarify better the sources and sinks as well as the amplitude of the seasonal variations. Additionally, calculations based on paired CO_2 and CO or other tracer measurements would be very useful to validate better the modern anthropogenic emission estimates, differentiating it from natural sources.

ACKNOWLEDGMENTS

The authors would like to thank Ingeborg Levin for maintaining the $\Delta^{14}CO_2$ sampling at Jungfraujoch for so many years and Markus Leuenberger for the CO_2 mole fraction data from the Jungfraujoch station. The research was supported by the European Union and the State of

Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2-15-2016-00009 "ICER." The authors would like to thank Marianna Kállai and Renáta Gönczi for the careful sample handling and preparation.

SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2018.79

REFERENCES

Beljaars A, Jakob C, Morcrette JJ. 2001. New physics parameters in the MARS archive. *ECMWF Newsletter* 90:17–21.

Berhanu TA, Szidat S, Brunner D, Satar E, Schanda R, Nyfeler P, Battaglia M, Steinbacher M, Hammer S, Leuenberger M. 2017. Estimation of the fossil fuel component in atmospheric CO_2 based on radiocarbon measurements at the Beromünster tall tower, Switzerland. *Atmospheric Chemistry and Physics* 17:10753–66. doi.org/10.5194/acp-17-10753-2017

Bousquet P, Peylin P, Ciais P, Le Quéré C, Friedlingstein P, Tans PP. 2000. Regional changes in carbon dioxide fluxes of land and oceans since 1980. *Science* 260:1342–6.

Csongor É, Szabó I, Hertelendi E. 1982. Preparation of counting gas of proportional counters for radiocarbon dating. *Radiochemical and Radioanalytical Letters* 55:303–7.

Csongor É, Hertelendi E. 1986. Low-level counting facility for ^{14}C dating. *Nuclear Instruments and Methods in Physics Research B* 17: 493–5.

Geels C, Gloor M, Ciais P, Bousquet P, Peylin P, Vermeulen AT, Dargaville R, Aalto T, Brandt J, Christensen JH, Frohn LM, Haszpra L, Karstens U, Rödenbeck C, Ramonet M, Carboni G, Santaguida R. 2007. Comparing atmospheric transport models for future regional inversions over Europe. Part 1: Mapping the CO_2 atmospheric signals over Europe. *Atmospheric Chemistry and Physics*. 7:3461–79. doi: 10.5194/acp-7-3461-2007

Graven HD, Guilderson TP, Keeling RF. 2012. Observations of radiocarbon in CO_2 at seven global sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles. *Journal of Geophysical Research: Atmospheres* 117 D02303. doi: 10.1029/2011JD016535

Graven HD, Xu X, Guilderson TP, Keeling RF, Trumbore SE, Tyler S. 2013. Comparison of independent $\Delta^{14}CO_2$ records at Point Barrow, Alaska. *Radiocarbon* 55(2-3):1541–5.

Hammer S, Levin I. 2017. Monthly mean atmospheric $\Delta^{14}CO_2$ at Jungfraujoch and Schauinsland from 1986 to 2016. doi: 10.11588/data/10100, heiDATA, V2.

Haszpra L, Barcza Z, Davis KJ, Tarczay K. 2005. Long-term tall tower carbon dioxide flux monitoring over an area of mixed vegetation. *Agricultural and Forest Meteorology* 13(1–2):58–77.

Haszpra L, Barcza Z, Hidy D, Szilágyi I, Dlugokencky E, Tans P. 2008. Trends and temporal variations of major greenhouse gases at a rural site in Central Europe. *Atmospheric Environment* 42 (38):8707–16.

Haszpra L, Barcza Z. 2010. Climate variability as reflected in a regional atmospheric CO_2 record. *Tellus B* 62:417–26. doi: 10.1111/j.1600-0889.2010.00505.x

Haszpra L, Ramonet M, Schmidt M, Barcza Z, Pátkai Zs, Tarczay K, Yver C, Tarniewicz J, Ciais P. 2012. Variation of CO_2 mole fraction in the lower free troposphere, in the boundary layer and at the surface. *Atmospheric Chemistry and Physics* 12:8865–75. doi: 10.5194/acp-12-8865-2012

Hertelendi E, Csongor É, Záborszky L, Molnár J, Gál J, Györffi M, Nagy S. 1989. A counter system for high-precision ^{14}C dating. *Radiocarbon* 31(3):399–406.

Kromer B, Münnich KO. 1992. CO_2 gas proportional counting in Radiocarbon dating—review and perspective. In: Taylor RE, Long A, Kra RS, editors. *Radiocarbon after Four Decades*. New York: Springer. p 184–97.

Kuc T, Rozanski K, Zimnoch M, Necki J, Chmura L, Jelen D. 2007. Two decades of regular observations of $^{14}CO_2$ and $^{13}CO_2$ content in atmospheric carbon dioxide in Central Europe: long-term changes of regional anthropogenic fossil CO_2 emissions. *Radiocarbon* 49:807–16.

Levin I, Münnich KO, Weiss W. 1980. The effect of anthropogenic CO_2 and ^{14}C sources on the distribution of $^{14}CO_2$ in the atmosphere. *Radiocarbon* 22:379–91.

Levin I, Schuchard J, Kromer B, Münnich KO. 1989. The continental European Suess effect. *Radiocarbon* 31:431–40.

Levin I, Kromer B, Schmidt M, Sartorius H. 2003. A novel approach for independent budgeting of fossil fuel CO_2 over Europe by $^{14}CO_2$ observations. *Geophysical Research Letters* 30(23) 2194. doi: 10.1029/2003GL018477

Levin I, Kromer B. 2004. The tropospheric $^{14}CO_2$ level in midlatitudes of the Northern Hemisphere (1959–2003). *Radiocarbon* 46:1261–72.

Levin I, Karstens U. 2007. Inferring high-resolution fossil CO_2 records at continental sites from combined $^{14}CO_2$ and CO observations. *Tellus B* 59 (2):245–50.

Levin I, Hammer S, Kromer B, Meinhardt F. 2008. Radiocarbon observations in atmospheric CO_2: determining fossil fuel CO_2 over Europe using Jungfraujoch observations as background. *Science of the Total Environment* 391:211–16. doi: 10.1016/j.scitotenv.2007.10.019

Levin I, Naegler T, Kromer B, Diehl M, Francey RJ, Gomez-Pelaez AJ, Steele LP, Wagenbach D, Weller R, Worthy DE. 2010. Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}CO_2$. *Tellus B* 62:26–46. doi: 10.1111/j.1600-0889.2009.00446.x

Levin I, Hammer S, Eichelmann E, Vogel F. 2011. Verification of greenhouse gas emission reductions: the prospect of atmospheric monitoring in polluted areas. *Philosophical Transactions of the Royale Society A* 369:1906–24.

Meijer HAJ, Smidt HM, Perez E, Keizer MG. 1996. Isotopic characterisation of anthropogenic CO_2 emissions using isotopic and radiocarbon analysis. *Physics and Chemistry of the Earth* 21(5–6):483–87.

Molnár M, Bujtás T, Svingor É, Futó I, Svetlik I. 2007. Monitoring of atmospheric excess ^{14}C around Paks Nuclear Power Plant, Hungary. *Radiocarbon* 49:1031–43.

Molnár M, Major I, Haszpra L, Svetlik I, Svingor É, Veres M. 2010a. Fossil fuel CO_2 estimation by atmospheric ^{14}C measurement and CO_2 mixing ratios in the city of Debrecen, Hungary. *Journal of Radioanalytical and Nuclear Chemistry* 286:471–6. doi: 10.1007/s10967-010-0791-2

Molnár M, Haszpra L, Svingor É, Major I, Svetlik I. 2010b. Atmospheric fossil fuel CO_2 measurement using a field unit in a Central European city during the winter of 2008/09. *Radiocarbon* 52 (2–3):835–45.

Neftel A, Moor E, Oeschger H, Stauffer B. 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature* 315:45–7.

NIR: National Inventory Report for 1985–2012. 2014. Hungarian Meteorological Service. Greenhouse Gas Inventory Division. Hungary, May 2014.

NOAA website: www.esrl.noaa.gov

Patra PK, Niwa Y, Schuck TJ, Brenninkmeijer CAM, Machida T, Matsueda H, Sawa Y. 2011. Carbon balance of South Asia constrained by passenger aircraft CO_2 measurements. *Atmospheric Chemistry and Physics*. 11: 4163–75. doi: 10.5194/acp-11-4163-2011 2011

Rödenbeck C, Houweling S, Gloor M, Heimann M. 2003. CO_2 flux history 1982–2001 inferred from atmospheric data using a global inversion of atmospheric transport. *Atmospheric Chemistry and Physics* 3:1919–64.

Stuiver M, Polach H. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Sturm P. 2005. Atmospheric oxygen and associated tracers from flask sampling and continuous measurements: tools for studying the global carbon cycle [PhD thesis]. University of Bern, Bern, Switzerland.

Suess HE. 1955. Radiocarbon concentration in modern wood. *Science* 122:415.

Tans P. 2009. An accounting of the observed increase in oceanic and atmospheric CO_2 and an outlook for the future. *Oceanography* 22(4):26–35.

Turnbull JC, Miller JB, Lehman SJ, Tans PP, Sparks RJ, Southon J. 2006. Comparison of $^{14}CO_2$, CO, and SF6 as tracers for recently added fossil fuel CO_2 in the atmosphere and implications for biological CO_2 exchange. *Geophysical Research Letters* 33 L01817. https://doi.org/10.1029/2005gl024213

Turnbull JC, Tans PP, Lehman SJ, Baker D, Conway TJ, Chung YS, Gregg J, Miller JB, Southon JR, Zhou LX. 2011. Atmospheric observations of carbon monoxide and fossil fuel CO2 emissions from East Asia. *Journal of Geophysical Research* 116 D24306. https://doi.org/10.1029/2011jd016691

Turnbull JC, Sweeney C, Karion A, Newberger T, Lehman SJ, Tans PP, Davis KJ, Lauvaux T, Miles NL, Richardson SJ, Cambaliza MO, Shepson PB, Gurney K, Patarasuk R, Razlivanov I. 2015. Toward quantification and source sector identification of fossil fuel CO2 emissions from an urban area: Results from the INFLUX experiment. *Journal of Geophysical Research* 120: 292–312. https://doi.org/10.1002/2014jd022555 2015

Uchrin G, Hertelendi E. 1992. Development of a reliable differential carbon-14 sampler for environmental air and NPP stack monitoring. Final Report of the OMFB contract No. 00193/1991. In Hungarian.

van der Laan S, Karstens U, Neubert REM, Van Der Laan-Luijkx IT, Meijer HAJ. 2010. Observation-based estimates of fossil fuel-derived CO_2 emissions in the Netherlands using $\Delta^{14}C$, CO and ^{222}Radon. *Tellus B* 62(5):389–402. doi: 10.1111/j.1600-0889.2010.00493.x

Vető I, Futó I, Horváth I, Szántó Z. 2004. Late and deep fermentative methanogenesis as reflected in the H-C-O-S isotopy of the methane-water system in deep aquifers of the Pannonian Basin (SE Hungary). *Organic Geochemistry* 35:713–23.

Zimnoch M, Jelen D, Galkowski M, Kuc T, Necki J, Chmura L, Gorczyca Z, Jasek A, Rozanski K. 2012. Partitioning of atmospheric carbon dioxide over Central Europe: insights from combined measurements of CO_2 mixing ratios and their carbon isotope composition. *Isotopes in Environmental and Health Studies* 48(3):421–33.

Zondervan A, Meijer HAJ. 1996. Isotopic characterisation of CO_2 sources during regional pollution events using isotopic and radiocarbon analysis. *Tellus B* 48:601–12.