

ATMOSPHERIC FOSSIL FUEL CO₂ MEASUREMENT USING A FIELD UNIT IN A CENTRAL EUROPEAN CITY DURING THE WINTER OF 2008/09

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ABSTRACT. A high-precision atmospheric CO₂ monitoring station was developed as a field unit. Within this, an integrating CO₂ sampling system was applied to collect samples for radiocarbon measurements. One sampler was installed in the second largest city of Hungary (Debrecen station) and 2 independent ¹⁴CO₂ sampling lines were installed ~300 km from Debrecen in a rural site at Hegyhátsál station as independent background references, where high-precision atmospheric CO₂ mixing ratios have been measured since 1994. Fossil fuel CO₂ content in the air of the large Hungarian city of Debrecen was determined during the winter of 2008 using both the measurements of CO₂ mixing ratio and ¹⁴C content of air. Fossil fuel CO₂ was significantly enhanced at Debrecen relative to the clean-air site at Hegyhátsál.

INTRODUCTION

Currently, one of the most heated questions in science is the rate and the reasons for recent climate change. Greenhouse gases (GHG), mainly CO₂ and CH₄, in the atmosphere could affect the climate of our planet. This recognition led to the formation of the Kyoto Protocol (1997) in which the developed countries committed themselves to limit their GHG emission. However, the relationship between the amount of atmospheric GHG and the climate is complex, filled with interactions and feedbacks partly poorly known even now (IPCC 2007). The only way to understand the processes, to trace the changes, and to develop and validate mathematical models for forecasts is the extensive, high-precision, continuous monitoring of atmospheric greenhouse gases (Nisbet 2007; Keeling 2008).

Fossil fuel CO₂ is the largest net annual input of CO₂ to the atmosphere, and these emissions are also a major component of the European carbon budget (Denning et al. 1995; Gurney et al. 2002). Therefore, we can assess the role of the continental biosphere as a net source or sink of carbon only if we are able to accurately separate fossil fuel CO₂ emissions from total CO₂ flux. As the biospheric CO₂ signal in the atmosphere is highly variable with diurnal and seasonal cycles caused by respective changes in the fluxes combined with changing atmospheric transport, the fossil fuel CO₂ signal also needs to be determined with high temporal resolution. This will provide a deeper understanding of global carbon cycle dynamics and allow the prediction of the future development of CO₂ in the atmosphere. Separating the fossil fuel from the natural biogenic signal in the atmosphere is thus a crucial task for quantifying exchange fluxes of the continental biosphere from atmospheric observations and inverse modeling.

In the Kyoto Protocol (1997), several countries committed themselves to reduce their greenhouse gas emissions, particularly CO₂, by ~5–10% relative to 1990. Classical emission estimates of CO₂ and other greenhouse gases are based on bottom-up statistics (estimating emissions using detailed process- or facility-specific data); however, the accuracy of these estimates is a matter of permanent debate, since current bottom-up inventory data are reported by governments, and have the potential to be biased, especially as emissions are regulated in the future. In the case of fossil fuel CO₂, stated errors range from ±2% to more than ±15%, exceeding the reduction target at the higher end (Mar-

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land and Rotty 1984). An independent method to estimate trace gas emissions is the top-down approach, using atmospheric measurements, but CO₂ concentration observations alone do not allow source apportionment.

Estimating fossil fuel CO₂ in the atmosphere is, in principle, possible via radiocarbon (¹⁴CO₂) measurements. CO₂ from burning of fossil fuels, due to their long storage time of several hundred million years, is essentially free of ¹⁴C. ¹⁴C observations in atmospheric CO₂ has been explored as an excellent tracer for recently added fossil fuel CO₂ in the atmosphere on the regional (Levin et al. 1980, 1989, 2003; Levin and Kromer 2004; Turnbull et al. 2006), the continental (Tans et al. 1979; de Jong and Mook 1982; Hsueh et al. 2007; Kuc et al. 2007), and also on the global scale (Stuiver and Quay 1981; Levin and Hesshaimer 2000). Adding fossil fuel CO₂ to the atmosphere, therefore, leads not only to an increase in the CO₂ content of the atmosphere, but also to a decrease in the ¹⁴C/¹²C ratio in atmospheric CO₂ (Suess 1955). From a ¹⁴CO₂ measurement at a polluted sampling site, for example, near the ground level on the continent, we can directly calculate the regional fossil fuel CO₂ surplus (recently added fossil fuel CO₂ amount in air) if the undisturbed background ¹⁴CO₂ level is known (Levin et al. 2003; Turnbull et al. 2006; Riley et al. 2008).

In the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), we have developed a mobile, field-deployable observation station for monitoring atmospheric fossil CO₂ in polluted areas, including continuous CO₂ mixing ratio measurement and integrated atmospheric CO₂ sampling for ¹⁴C analyses. For the first test run, the new field unit was installed in the backyard of ATOMKI in the summer of 2008 to start urban atmospheric fossil fuel CO₂ monitoring in the city of Debrecen (eastern Hungary). To have a solid base for regional atmospheric fossil fuel CO₂ concentration calculation in the second largest city in Hungary (Debrecen), we started synchronized ¹⁴CO₂ sampling and measurements in a rural site at Hegyhátsál station (western Hungary) as an independent background reference, where high-precision atmospheric CO₂ mixing ratio measurements have been ongoing since 1994 (Haszpra et al. 2005, 2008). These ¹⁴CO₂ measurements hopefully should help in validating fossil fuel CO₂ emissions in Hungary as described above.

MATERIALS AND METHODS

Monitoring Sites

The location selected for urban atmospheric CO₂ observations is the city of Debrecen (code hereafter: DEB) in eastern Hungary (47°32'10"N, 21°38'40"E). Its climate is characterized by dry summers and rather cold winters compared to other parts of the country. The area of the city covers 462 km² and it is only 85 m asl, which means that it is situated in a small basin. With its ~205,000 inhabitants, Debrecen is the second largest city and an industrial center in Hungary. A natural-gas-based power plant (95 MW) is located in the city. The ATOMKI, where the observation station is installed, is located close to the city center. Sample air intake is at 3 m above the ground level in the city center, ~200 m from the nearest road. This location should give an average picture regarding the air of Debrecen.

CO₂ sampling and ¹⁴C measurements in a rural site at Hegyhátsál (code hereafter: HUN) synchronized with the Debrecen city observations were begun to have a solid regional reference level for fossil fuel CO₂ calculations in the urban area. The measurements are carried out on a 117-m, free-standing TV and radio transmitter tower owned by Antenna Hungária Corp. The tower is located in a flat region of western Hungary (46°57'N, 16°39'E), at an altitude of 248 m asl. This observation station is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches.

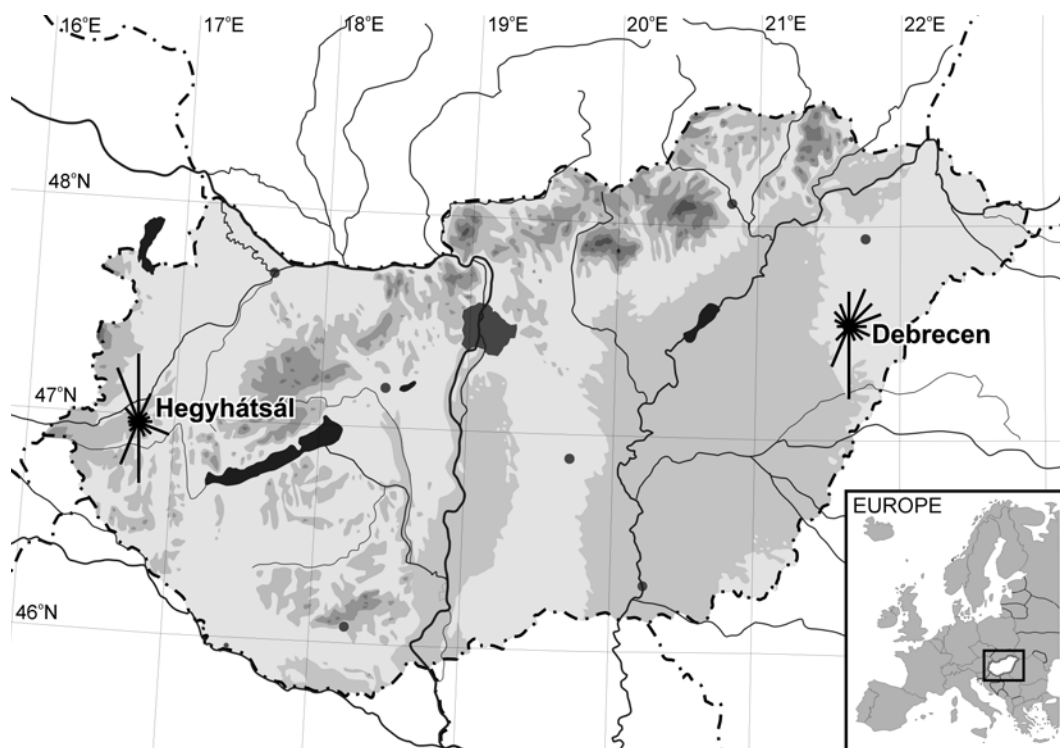


Figure 1 Shaded relief map showing the geographical location of the observation points Debrecen and Hegyhátsál inside Hungary, with the Hungarian capital (dark gray patch in the center) and larger cities (>100,000 people, dark gray dots) shown as well as the frequency distribution of the wind direction (proportional to the length of the lines) at Debrecen and Hegyhátsál.

Populated areas within 10 km of the HUN tower are only small villages (100–400 inhabitants). The nearest village is Hegyhátsál (170 inhabitants) about 1 km to the northwest. There is no notable industrial activity in this dominantly agricultural region. Local roads have mostly low levels of traffic. One of the few main roads of the region, which carries 3600 vehicles per day on average, passes ~400 m to the southwest of the tower. Sampling points on the tower are at 10 m and 115 m above the ground level.

Measurements of CO₂ mixing ratio profiles, temperature, humidity, and wind profiles began in September 1994 (Haszpra et al. 2001). Flux measurements began in April 1997. The tower is also a NOAA/ESRL Cooperative Air Sampling Network site (NOAA/ESRL site code: HUN; <http://www.esrl.noaa.gov/gmd/ccgg/flask.html>). The data set of the Hungarian station can also be found at the World Data Centre for Greenhouse Gases (WDCGG, <http://gaw.kishou.go.jp/wdcgg/>).

CO₂ Sampling and ¹⁴C Measurement

CO₂ samplers installed in Debrecen and Hegyhátsál were developed in the ATOMKI to obtain integrated samples for measuring ¹⁴C in the chemical form of CO₂. The sampler's inlet is connected to the exhaust line of a back-pressure regulator (BPR in Figure 2) built into the gas handling system of the CO₂ analyzer. This parallel connection between the CO₂ sampler and the analyzer ensures that the CO₂ analysis is not affected by the sample collecting process.

The CO₂ is trapped in bubblers filled with 500 mL of 3M NaOH solution. The flow rate is controlled by the sampling unit. Similar types of ATOMKI samplers have been routinely used in environmental ¹⁴CO₂ monitoring around a nuclear power plant in Hungary since 1991 (Veres et al. 1995; Molnár et al. 2007). The sampling period is 4 weeks and the flow rate of sampling is stabilized at 10.0 L/hr. The absorption yield of CO₂ in the 3M NaOH solution is 99.9% using a specially designed bubbler-type trap. A detailed description of the sampling devices is given by Uchirin and Hertelendi (1992).

We measured the ¹⁴C activity of the samples using the proportional counting method (Csongor and Hertelendi 1986; Hertelendi et al. 1989). To extract CO₂ from the samples, sulfuric acid was added to the NaOH solution. Prior to its measurement in the high-precision proportional system, the liberated CO₂ gas was purified over charcoal, then frozen into a CO₂ trap with liquid nitrogen at -196 °C, and the remaining non-condensable components were removed by a vacuum pump (Csongor et al. 1982). The standard deviation of a single Δ¹⁴C measurement applying this method was 4–5‰ after 1 week of measurement per sample according to the counting statistics (Hertelendi 1990). The reported Δ¹⁴C data were corrected for decay and δ¹³C as described by Stuiver and Polach (1977). δ¹³C corrections were measured using a stable isotope mass spectrometer developed in the ATOMKI (Hertelendi et al. 1987) until 2002, and by a ThermoFinnigan Delta^{Plus} XP mass spectrometer since 2002 (typical error ±0.2‰).

The Developed Field-Deployable CO₂ Measuring System

A mobile and high-precision atmospheric CO₂ monitoring station was developed in this project. The system is designed for the continuous, unattended monitoring of CO₂ mixing ratio in the near surface atmosphere based on an infrared gas analyzer (IRGA) with a setup that is very similar to that described by Zhao et al. (1997), and used for the measurements reported by Bakwin et al. (1995, 1998) and Haszpra et al. (2001, 2008) (Figure 2). At the station an ATOMKI type (described above) atmospheric CO₂ sampling unit was also installed.

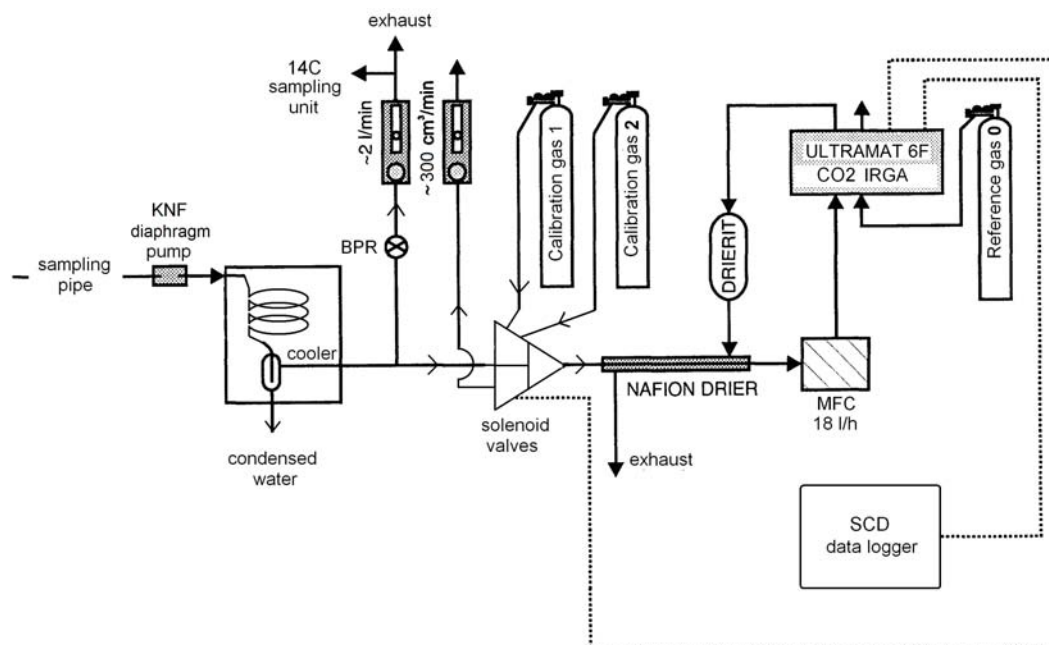


Figure 2 Layout of the gas handling line used in the field CO₂ monitoring system

The mixing ratio of CO₂ is measured at 3 m above ground at the monitoring station. Air is pumped through a 9.5-mm-diameter plastic tube (PFA, Swagelok) to a CO₂ analyzer located in a container box. The container box (Containex) is 1.5 m wide, 1.2 m deep, and 2.2 m high, and designed as a mobile measuring room that is field deployable; only electric power is required. A 15- μ m-pore size stainless steel Tee-Type (Swagelok) particle filter is located at the inlet of the sampler tube. A diaphragm pump (KNF) is used to draw air continuously through the sampling tube from the monitoring level at the flow rate of \sim 3 L/min.

The air at 1/3 bar overpressure enters a glass trap for water that is cooled in a regular household refrigerator (BPR), to dry the air to a dew point of 3–4 °C. The liquid is forced out through an orifice at the bottom of the trap. The air sample inlet tube and the standard gases (Linde Hungary) are connected to miniature solenoid valves in a manifold, which are normally closed and controlled by the CO₂ analyzer, which selects which gas is sampled. The air leaving the manifold through its common outlet is further dried to a dew point of about –25 °C by passage through a 360-cm-long Nafion drier (Permapure), so that the water vapor interference and dilution effect are <0.1 ppm equivalent CO₂.

Analysis is carried out using a non-dispersive infrared gas analyser (IRGA) Ultramat 6F, which is a specialized Siemens model for field applications. A constant sample flow rate of 300 cm³/min is maintained by a mass flow controller (MFC, Aalborg). The reference cell of the CO₂ analyzer is continuously flushed with a compressed reference gas of 350 ppm CO₂ in synthetic air (Messer Hungarogáz). The typically used calibration cycle is 2 hr, consisting of a zero-point calibration and a span calibration. Each calibration consists of 2-min flushing and 20-s signal integration. After 2 hr following a previous calibration, the usual change of the response function is below 0.2 ppm.

The analyzer measures the CO₂ mixing ratio in the sample gas every 3 s. Output data are registered by a data logger developed for this application (SCD data logger, Special Control Devices). The overall uncertainty of our atmospheric CO₂ mixing ratio measurements is <1 ppm (<0.3% of measured level). This level of error is acceptable for our fossil fuel CO₂ calculations as the uncertainty of the ¹⁴C content of atmospheric CO₂ is usually 3–5%. Figure 3 shows the developed field-deployable fossil fuel CO₂ monitoring station located in the backyard of ATOMKI.

RESULTS AND DISCUSSION

The CO₂ mixing ratio variation in Hegyhátsál (station HUN) and in the city of Debrecen (station DEB) are presented in Figure 4a. Three weeks of CO₂ data at the DEB station are missing in January 2009 due to an unexpected software error in the data logger, which was the only serious error during the whole run since the summer of 2008. For most of the period shown, the DEB CO₂ values are substantially (up to 30 ppm!) higher than the rural HUN site values, and there are also large differences between the 2 heights of the tower (10 and 115 m), although the phasing of the variability is mostly in agreement. On the other hand, despite the >300 km distance, sometimes for several periods (1 week in the middle of September, and 2 weeks in April) the daily averaged CO₂ mixing ratio results near the ground level (3 m in DEB and 10 m at HUN) are nearly the same at the 2 different locations (Figure 4a). According to the measured atmospheric CO₂ mole fraction data, these results could be interpreted as a well-mixed atmospheric CO₂ in the whole Carpathian Basin (including all of Hungary) during those periods.

The daily average outside air temperature and monthly wind direction distribution are also presented in Figure 4b and c, respectively. The conventional heating period started in the middle of October and finished at the end of March in Hungary during the 2008 winter. Mean wind conditions remained the same at the DEB station during the investigated period.



Figure 3 The developed field-deployable fossil fuel CO₂ monitoring station

There is a small seasonal variation in the background ¹⁴CO₂ observed at the HUN station (Figure 4d), which, to a large extent, is caused by the input from the stratosphere but also from a seasonal variation of the fossil fuel CO₂ component in background air at mid-northern latitudes (Hesshaimer 1997; Randerson et al. 2002). The extrapolated harmonic fit curve (Nakazawa et al. 1997) calculated from the Jungfraujoch long-term observations (hereafter JFJ, also in Figure 4d) can be assumed as the reference level over Europe (Levin et al. 2003, 2008). If we compare the JFJ data to our rural site observations, which can be stated as the regional reference in Hungary (HUN), it is clear that the ¹⁴CO₂ level at HUN remains very close to the extrapolated data at JFJ.

For the first month (September 2008) of the HUN observations, we ran the 2 independent lines of CO₂ samplers in parallel for sampling the same level at 10 m above the ground surface. The resulting ¹⁴CO₂ activity for the parallel samples showed that our sampling and ¹⁴C measurement technique provide a very good reproducibility (the observed ~2‰ difference between the 2 independent parallel Δ¹⁴C results: 46.0‰ and 44.3‰) was less than the measurement uncertainty. (See the two HUN_10m Δ¹⁴C points of September 2008 in Figure 4d.)

The similar monthly average ¹⁴CO₂ results at 10 m and 115 m in HUN suggest that this station was not be strongly affected by local ground-level anthropogenic fossil fuel sources. Small, but signifi-

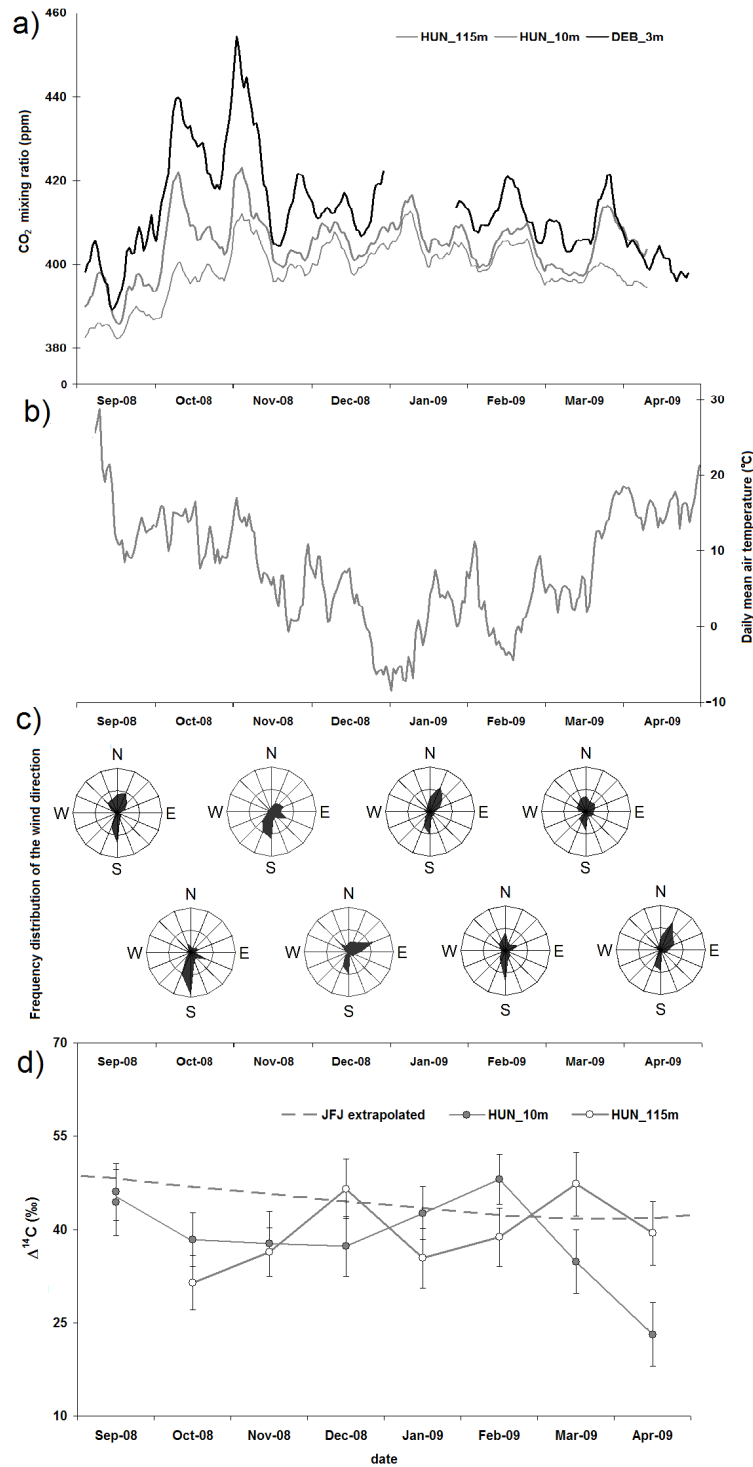


Figure 4 a) Daily average atmospheric CO₂ mixing ratio; b) daily average air temperature; c) monthly frequency distribution of wind direction at Debrecen; d) monthly average atmospheric $\Delta^{14}\text{C}$ variation at the Hungarian (Hegyhátsál as HUN) and European (Jungfraujoch station in the Swiss Alps as JFJ; Levin et al. 2008) background stations during the winter of 2008/09.

cant differences between 10 m and 115 m observations appeared only in the spring of 2009, but also at this time the extrapolated JFJ fit curve remained very close to the 115 m $\Delta^{14}\text{C}$ data from HUN. The JFJ extrapolation was given by I Levin (personal communication, 2009) according to a linear-trend fit curve on previous years of measured data.

Table 1 shows the monthly average atmospheric $^{14}\text{CO}_2$ and CO_2 mixing ratio results from Debrecen (DEB) and the reference $\Delta^{14}\text{CO}_2$ data measured at Hegyhátsál (HUN) during the winter of 2008.

Table 1 Atmospheric $^{14}\text{CO}_2$ and CO_2 mixing ratio results from Debrecen (DEB) and the reference $\Delta^{14}\text{CO}_2$ data measured at Hegyhátsál (HUN).

Month (mm/yyyy)	Debrecen_3m		HUN_10m $\Delta^{14}\text{C}$ (‰)	HUN_115m $\Delta^{14}\text{C}$ (‰)
	CO_2 (ppm) (± 1.0 ppm)	$\Delta^{14}\text{C}$ (‰)		
09/2008	400.9	39.1 ± 7.1	45.0 ± 4.0	n/a
10/2008	425.3	-4.5 ± 4.3	38.4 ± 4.6	31.4 ± 5.3
11/2008	426.5	21.5 ± 4.8	37.7 ± 4.3	36.4 ± 4.4
12/2008	414.6	21.4 ± 3.9	37.3 ± 5.2	46.5 ± 3.9
01/2009	415.6 ^a	10.9 ± 4.9	42.6 ± 4.8	35.4 ± 4.8
02/2009	412.9	17.8 ± 3.8	48.1 ± 4.3	38.8 ± 4.8
03/2009	408.2	25.4 ± 4.1	34.8 ± 4.0	47.3 ± 4.7
04/2009	408.4	34.2 ± 5.5	23.1 ± 5.1	39.4 ± 5.1

^aEstimated, interpolated data based on CO_2 mixing ratio trend at HUN reference station and its correlation to DEB_3m CO_2 data, due to 3 weeks of missing data caused by a data logger malfunction at DEB station.

To calculate the atmospheric fossil fuel CO_2 component ($\text{CO}_{2\text{fossil}}$) in Debrecen, we used the following formula suggested by Levin et al. (2003):

$$\text{CO}_{2\text{fossil}} = \text{CO}_{2\text{city}} \times \frac{\Delta^{14}\text{C}_{\text{refBG}} - \Delta^{14}\text{C}_{\text{city}}}{\Delta^{14}\text{C}_{\text{refBG}} + 1000}$$

where $\text{CO}_{2\text{city}}$, $\Delta^{14}\text{C}_{\text{city}}$, and $\Delta^{14}\text{C}_{\text{refBG}}$ are the CO_2 mixing ratio in the city and ^{14}C results from the city and the reference background observation station, respectively. There are more complex approaches described in the literature (Turnbull et al. 2006) where they do not neglect the $^{14}\text{C}/\text{C}$ ratio difference between regional biogenic CO_2 and the mean background CO_2 . However, due to the large heterogeneity of the biosphere, the mean $^{14}\text{C}/\text{C}$ ratio of the regional biogenic component is rather difficult to measure and reliable estimates for this required parameter were not available for the Debrecen region in the studied term.

Using the Hungarian background $^{14}\text{CO}_2$ observations from rural Hegyhátsál (HUN), we report atmospheric fossil fuel CO_2 component for Debrecen on a regional scale (Figure 5). This regional scale is likely close to the JFJ-based continental scale presented above. The Hegyhátsál station provided quite similar background results to the extrapolated $\Delta^{14}\text{C}$ data set of the high-altitude background data at Jungfraujoch in the Swiss Alps, located more than 3000 m asl.

The total CO_2 mixing ratio difference between the city (DEB) and the rural site (HUN) are reported in Figure 5 in ppm units. The observed well-expressed fossil fuel CO_2 peak with a maximum in the middle of winter (January) seems to be a realistic result as domestic heating is mainly based on fossil

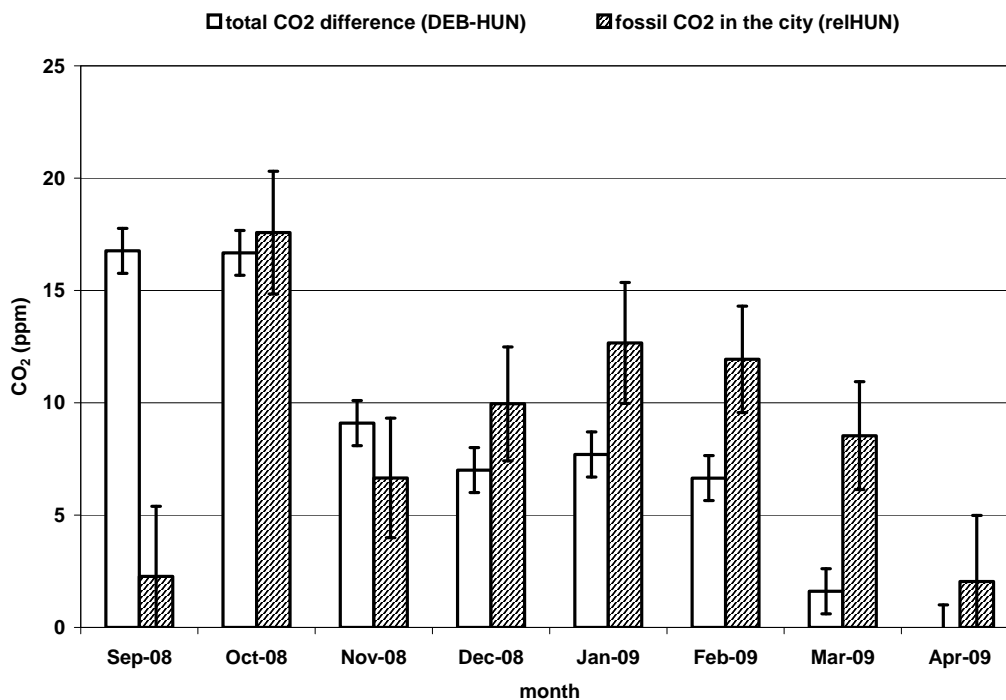


Figure 5 Total CO₂ surplus and fossil fuel CO₂ in Debrecen (DEB) vs. Hegyhátsál (HUN) during the winter of 2008

fuels in Hungary and the coldest temperature was also in the middle of the winter (first 2 weeks of January). This maximum in January was about 10–15 ppm fossil fuel CO₂ in the urban air, similar to the city of Heidelberg in Germany (15–20 ppm) reported by Levin et al. (2003) and also like that of Kraków (20 ppm) in Poland reported by K Rozanski (personal communication, 2009). Furthermore, we observed also a significant maximum (~20 ppm) in fossil fuel CO₂ during October 2008 in Debrecen. An accidental measurement error or sample contamination would be a realistic explanation for this strange behavior of ¹⁴C in the October sample of DEB_3m, but we also observed the lowest $\Delta^{14}\text{C}$ in the October sample of HUN_115m during the whole studied period (Figure 4d). The October fossil fuel CO₂ maximum result and/or possible source identification needs more study on meteorological conditions, including, for example, the monthly mean wind direction distribution in the city, which changed significantly from September to October (Figure 4c).

CONCLUSIONS

During the winter of 2008/2009, we measured the mixing ratio and ¹⁴C content of atmospheric CO₂ at Debrecen and a reference station simultaneously in Hungary. The Debrecen observation station is a novel ATOMKI-developed field-deployable unit that meets the requirements of fossil fuel monitoring in semi-polluted areas (typical CO₂ mixing ratio error is <0.3%; $\Delta^{14}\text{C}$ error <0.5%).

It was concluded that the CO₂ mixing ratio showed a similar temporal variation at the 3 different sampling elevations (at 3 m above ground in Debrecen, at 10 m and 115 m above ground in Hegyhátsál). Air quality in Debrecen during September 2008 seemed to be relatively clean from the point of view of its CO₂ content. When winter neared in October, with lower outside temperature and less sunshine hours, the CO₂ content of air increased in general at all 3 sampling points, but this effect was more intense closer to the ground surface.

According to our ^{14}C observations, there was not a significant amount of fossil fuel CO_2 in the air of Debrecen during September 2008. However, during the winter of 2008/09, the $\Delta^{14}\text{C}$ value of atmospheric CO_2 of Debrecen decreased more than 40‰ relative to September's results. According to our calculations, this decrease was caused by ~20 ppm fossil fuel CO_2 , which appeared as a surplus amount in the air above the September level.

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