

Chapter 2

History and Sites of Atmospheric Greenhouse Gas Monitoring in Hungary*

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Abstract This chapter introduces the Hungarian atmospheric greenhouse gas monitoring stations, their environment, monitoring program, and instrumentation. Quality of the measurements is discussed using the results of interlaboratory comparisons and independent parallel measurements. Study on the spatial representativeness of the measurements leads to the revelation that only the early afternoon measurements can be used for studies other than investigation of diurnal variations. The early afternoon carbon dioxide data may be representative for 200,000–300,000 km², and they can characterize the average boundary layer mixing ratio with a reasonable accuracy. Finally, the chapter lists the major international projects, in which the Hungarian monitoring sites participate, the databases, where their data are accessible, and the projects, which support or supported the monitoring activity.

Keywords Hegyhátsál • Interlaboratory comparison • K-pusztá • Monitoring system • Quality control • Representativeness

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2.1 Introduction

Keeling's measurements performed at South Pole and Hawaii made the accumulation of anthropogenic carbon dioxide (CO_2) in the atmosphere evident (Brown and Keeling 1965; Pales and Keeling 1965). The recognition of the potential social, economical, and overall environmental risks of an anthropogenically induced global climate change resulted by the strengthening atmospheric greenhouse effect stimulated the World Meteorological Organization (WMO) to initiate the monitoring of atmospheric CO_2 on global level. WMO was organizing its Background Air Pollution Monitoring Network (BAPMoN) in the late 1960s, and CO_2 concentration measurement was also included in the monitoring program of the BAPMoN stations (WMO 1974). This measurement was primarily expected from the so-called baseline stations located at very remote places, far away from any local anthropogenic source and extended vegetated area (source and sink for CO_2). WMO contracted the Hungarian Meteorological Service (HMS) to host training courses for the staff of BAPMoN (from 1989: Global Atmosphere Watch, GAW) stations between 1978 and 1992 (Mészáros 1978). For these courses, demonstration instruments were also provided by WMO. For the training on atmospheric CO_2 measurements, a Siemens Ultramat 3 nondispersive infrared (NDIR) gas analyzer was donated to HMS. This instrument was deployed at the newly established regional background air pollution monitoring station of HMS (K-pusztá) in 1981 to demonstrate this measurement to the participants of the training courses in real-world environment rather than in a classroom. The operative use of the instrument at a regular monitoring station also gave an insight into the variation of atmospheric CO_2 concentration in a region where it had never been studied before, although the location of the station (middle of a highly industrialized, densely populated continent, surrounding vegetation) did not comply with the siting criteria prescribed by WMO.

The measurements performed at K-pusztá attracted little scientific attention because of the improper location. The situation changed significantly at the end of 1980s when the model calculations revealed that the northern hemispheric continental biosphere played a crucial role in the global carbon budget. Any data from this previously avoided region became valuable. It was the first time when the Hungarian atmospheric CO_2 measurements could be published in the international scientific literature (Haszpra 1995).

The change in the focus of the global carbon budget research required the expansion of the monitoring networks to the continents, vegetated regions. Tans (1991) suggested the use of tall towers in the monitoring to increase the spatial representativeness of the measurements in the regions where the local biosphere generates a significant “noise” in the CO_2 signal. In 1992, the US–Hungarian Scientific and Technological Joint Fund offered a unique opportunity to both the Hungarian scientists, who wanted to develop the measurements and integrate them into the international efforts, and National Oceanic and Atmospheric Administration (NOAA), U.S.A., who was seeking for new monitoring sites in the critical continental regions. In the framework of this cooperation, building

on the available Hungarian measurement tradition and on NOAA's experience with the first tall tower monitoring site in North Carolina, U.S.A. (Bakwin et al. 1995), one of the first European tall tower monitoring sites dedicated to greenhouse gas measurements was put into operation at Hegyhátsál, Hungary, 220 km to the west from K-pusztá, where no tall tower was available. It was not scientifically reasonable and economically feasible to operate two CO₂ monitoring sites so close to each other; therefore, the outdated, worn-out system at K-pusztá was switched off in 1999.

The state-of-the-art tall tower monitoring site attracted further international projects since the late 1990s that allowed the development and expansion of the monitoring program. After the signature of the Kyoto Protocol, the European Commission supported several greenhouse gas oriented research projects in the framework of its R&D Framework Programmes. Hegyhátsál station, and the scientists working there, joined AEROCARB, CHIOTTO, CarboEurope-IP, IMECC, GEOMON, etc., projects (also involving Hungarian financial support), which allowed the introduction of non-CO₂ greenhouse gas measurements, vertical CO₂ flux measurements, aircraft measurements, carbon and oxygen isotope measurements, as well as the installation of a state-of-the-art, remotely controllable data acquisition and real-time data reporting system.

2.2 K-pusztá

2.2.1 Location and Environment

K-pusztá, the regional background air pollution monitoring station of the HMS, the member of the WMO GAW and the European EMEP¹ networks, is located at 46°58'N, 19°33'E, 125 m above the sea level, on the Hungarian Great Plain, in the middle of the Carpathian Basin (Fig. 1.1). The station is located in a large forest clearing, where the immediate surroundings of the station are kept undisturbed. The dominant tree species in the region are Scots Pine and Black Pine with acacia patches. The organic layer of the sandy soil is thin. The nearest public road carried approximately 700–800 vehicles per day during the time of CO₂ measurements (1981–1999), and there is a small settlement (370 inhabitants in 2001) about 3 km to the east/southeast off the station. The nearest big city is the dominantly agricultural Kecskemét (85,000 inhabitants in 2001). It is located approximately 20 km to the southeast, opposite to the prevailing wind direction. In the direction of the prevailing north-westerly wind, the nearest remarkable anthropogenic source is Budapest (1.9 million inhabitants in 2001) located about 80 km off the station. In general, K-pusztá is as free from direct anthropogenic pollution as it is possible in this geographical region.

¹Co-operative Programme for Monitoring and Evaluation of the Long-range Transmissions of Air Pollutants in Europe (European Monitoring and Evaluation Programme – EMEP).

2.2.2 Carbon Dioxide Monitoring System

At K-pusztá, the HMS was operating a Siemens Ultramat 3 CO₂ NDIR analyzer between July 1981, and June 1999. The air inlet of the instrument was mounted at 10 m above the grass-covered sandy ground. The data acquisition system recorded the 30-min average mixing ratio. For the calibration, three CO₂-in-nitrogen standards prepared by the Scripps Institution of Oceanography, La Jolla, California, U.S.A., were used until 1992, when they were replaced by four CO₂-in-air standards prepared and certified by NOAA Climate Monitoring and Diagnostics Laboratory (CMDL), Boulder, Colorado, U.S.A. The pre-1992 mixing ratio data have been corrected for the pressure broadening effect, and they are expressed on the WMO X2007 scale in this book and in the WMO World Data Centre for Greenhouse Gases (<http://gaw.kishou.go.jp/wdcgg/>) at the time of writing.

In the case of the Siemens Ultramat 3 CO₂ analyzer, the water vapor content of air to be analyzed influences the output CO₂ signal. Usually, water vapor is removed by a freezer to avoid this interference, but this method requires a powerful gas cooler taking into account the flow rate of 1 L min⁻¹. At K-pusztá, Köhler's method (Köhler 1974) was applied to handle the water vapor interference: both air to be analyzed and standard gases were saturated with water vapor at room temperature, then cooled down to +4°C on the way to the analyzer (Fig. 2.1). In this way the water vapor content of the gases to be analyzed was kept approximately constant (saturated at +4°C), and the variable water vapor content of atmospheric air did not influence the CO₂ measurements any more. Köhler's method is not perfect, among others, because of the low frequency noise of relatively large amplitude caused by

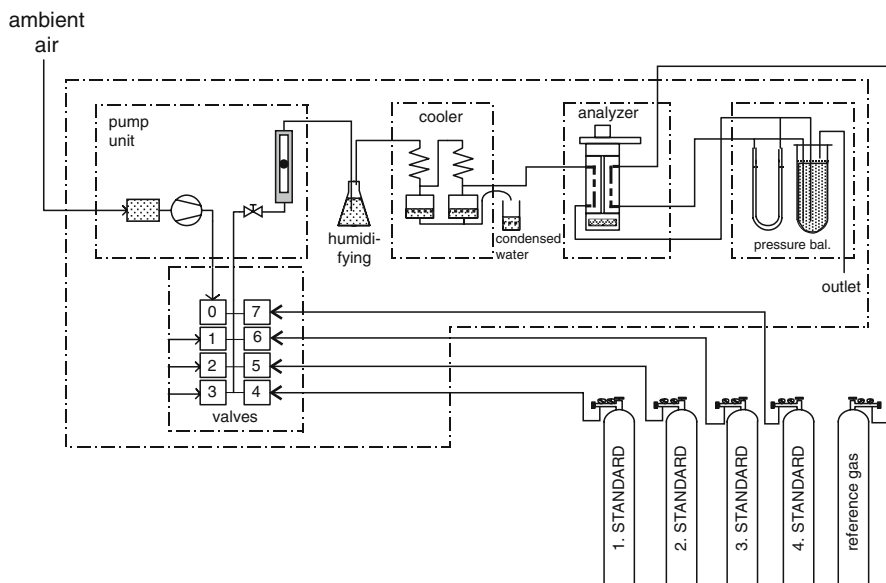


Fig. 2.1 Schematic of the CO₂ monitoring system used at K-pusztá between 1981 and 1999

the switch on/off hysteresis of the gas cooler, but it was used at a few sites until the 1990s (e.g. Hensen et al. 1997). However, it should be mentioned that the low frequency noise caused by the improper removal of water vapor is largely eliminated by the longer time averaging, and thus the hourly and longer term averages may be fairly accurate. The outline of the measuring system can be seen in Fig. 2.1.

2.3 Hegyhátsál

2.3.1 Location and Environment

At Hegyhátsál, a 117 m tall, free-standing TV/radio transmitter tower owned by Antenna Hungária Corp. is equipped with intake tubes, meteorological sensors, and other instrumentation. The lower 56 m of the tower is a 7.8-m diameter cylinder made of reinforced concrete, while the upper 61 m is a steel cylinder of 1.8 m diameter. The tower is located in a fairly flat region of western Hungary (46°57'N, 16°39'E), at an altitude of 248 m above the sea level (Fig. 1.1). The tower is surrounded by agricultural fields (mostly crops and fodder of annually changing types) and forest patches. The distribution of vegetation types (53% arable land, 35.5% forest, 11.5% other [vineyard, settlements, etc.]) within 10 km of the tower is not greatly different from the average for the Western Hungarian Landscape Unit (7,300 km²) or the whole country (93,030 km²) (48.4% arable land, 19.7% is forest, 11% grassland, 17.7% other; see Chapter 13). The soil type in the region of the tower is lessivated brown forest soil (Alfisol, according to USDA system). These soils have clay migration and moderate acidity as well as the more widespread humification, leaching, and clay formation (Stefanovits 1971). The upper layer is generally 10–20 cm thick, and its organic matter content is 5–8%.

Human habitations within 10 km of the tower are only small villages (100–400 inhabitants). The nearest village is Hegyhátsál (170 inhabitants) about 1 km to the northwest. The nearest city is Körmend (13,000 inhabitants), 9 km to the northwest of the station. 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 approximately 3,600 vehicles per day on average, passes approximately 400 m to the southwest of the tower. The monitoring site is fairly free from direct anthropogenic pollution as it is shown by sulfur hexafluoride measurements (see Chapter 3).

Further details can be found on the website of the monitoring station: <http://nimbus.elte.hu/hhs/>.

2.3.2 Monitoring of Atmospheric Carbon Dioxide Mixing Ratio

At Hegyhátsál tall tower site, CO₂ mixing ratio has been continuously monitored at four elevation levels along the tower (10, 48, 82, and 115 m above the ground) since

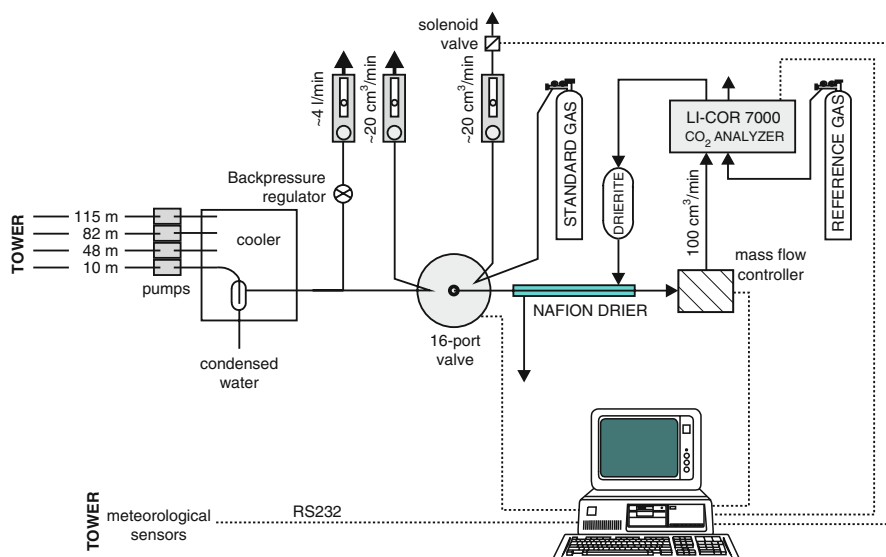


Fig. 2.2 Schematic of the CO₂ monitoring system used at Hegyhátsál tall tower site. For clarity, only one standard gas and one sampling line are presented

September 1994. The schematic diagram of the CO₂ mixing ratio profile monitoring system is shown in Fig. 2.2.

Air is pumped through 9.5 mm diameter tubes (Dekoron Type 1300) from the intake levels on the tower to the CO₂ analyzer located on the ground floor of the transmitter building. 47 mm diameter (Whatman EPM) particle filters are applied in each intake tube to prevent the pumps, valves, and the analyzer from dust. The setup for CO₂ analysis is very similar to that described by Zhao et al. (1997). Diaphragm pumps (1994–2005: KNF Neuberger type UN73MVP; from 2005: KNF Neuberger type N 811 KN.18) are used to draw air continuously through each of the tubes from the four monitoring levels at a flow rate of about 2 L min⁻¹ (4 L min⁻¹ since 2005). After the pump, the air at 40 kPa overpressure enters a glass trap for liquid water, which is cooled in a regular household refrigerator to dry the air to a dew point of 3–4°C. Liquid water is forced out through an orifice at the bottom of each trap.

The four inlet tubes and the standard gases are connected to a computer-controlled 16-position valve (VICI AG, Valco Europe) that selects which monitoring level or standard gas is sampled by the analyzer. The valve head is protected by 7 µm in-line filters. Ambient air flows continuously through the multiport valve so that the system is constantly flushed. The (expensive) standard gases are shut off when they are not in use by means of computer-controlled solenoid valves. The air leaving the multiport valve through its common outlet is further dried to a dew point below –25°C by passage through a 182 cm long Nafion drier (Permapure, type MD-110-72P), so that the water vapor interference and dilution effect are less than 0.1 µmol mol⁻¹ equivalent CO₂ (Zhao et al. 1997). The Nafion drier is purged in a counterflow (100 cm³

min⁻¹) arrangement using the waste sample air that has been further dried by passage through anhydrous CaSO₄ (W.A. Hammond Drierite Co. Ltd.).

CO₂ analysis is carried out using an infrared gas analyzer (1994–2007: Li-Cor Inc. model LI-6251; from 2007: Li-Cor Inc. model LI-7000). A constant sample flow rate of 100 cm³ min⁻¹ is maintained by a mass flow controller (Tylan, model FC-260). The reference cell of the CO₂ analyzer is continuously flushed at a flow rate of 5–10 cm³ min⁻¹ with a compressed reference gas of 330–350 μmol mol⁻¹ CO₂ in synthetic air (Messer Hungarogáz). Calibration of the analyzer is carried out using four standards spanning 330–440 μmol mol⁻¹ CO₂ prepared by NOAA CMDL (from 2007: NOAA Earth Systems Research Laboratory, ESRL) (Kitzis et al. 1999). Both the CO₂ mixing ratio in the reference gas and the calibration range have been slightly shifted upward since the beginning of the measurements to follow the changes in the atmosphere.

The basic measuring cycle is 2 min, consisting of 1 min flushing and 1 min signal integration. (Note, as the intake tubes are permanently flushed, only the analyzer and the short 1/8 in. ID tube from the selector valve to the analyzer have to be flushed during this relatively short time.) Each 1-min average and standard deviation is based on 6–7 individual measurements. The multiport valve steps through the four monitoring levels in 8 min. Every 32 min, after four 8-min measuring cycles, the standard gas with the lowest CO₂ mixing ratio is selected and analyzed, and this measurement is termed “zero.” After every sixth cycle (every 202 min), a full four-point calibration is carried out. The reference and sample cells of the CO₂ analyzer are not pressure or temperature controlled. The “zero” measurements are used to account for any short-term drift of the analyzer due to changes in ambient pressure or temperature. A quadratic response function is fit to each set of calibration gas measurements. The “zero” offsets and response functions are linearly interpolated in time to obtain values appropriate to calculate CO₂ mixing ratio from the instrument response.

2.3.3 *Monitoring of the Atmospheric Mixing Ratio of non-CO₂ Greenhouse Gases*

At Hegyhátsál tall tower site, methane (CH₄), nitrous oxide (N₂O), and sulfur hexafluoride (SF₆) mixing ratios have been monitored since January 2006. The sampling elevation is at 96 m above the ground. For the monitoring of the mixing ratios, a measuring system built on an Agilent 6890N gas chromatograph is used. Its design is similar to those at other present European sites (Thompson et al. 2009; van der Laan et al. 2009). The schematic diagram of the system is shown in Fig. 2.3.

The gas chromatograph is equipped with two analysis lines. One of them is used for methane and carbon monoxide (CO – not discussed here) measurements. It consists of a 4 ft Unibeads 1S precolumn followed by a 6 ft Molecular Sieve 5A analytical column and a flame ionization detector (FID). The other line consists of a 4-ft Hayesep Q precolumn followed by a 6-ft Hayesep Q analytical column and

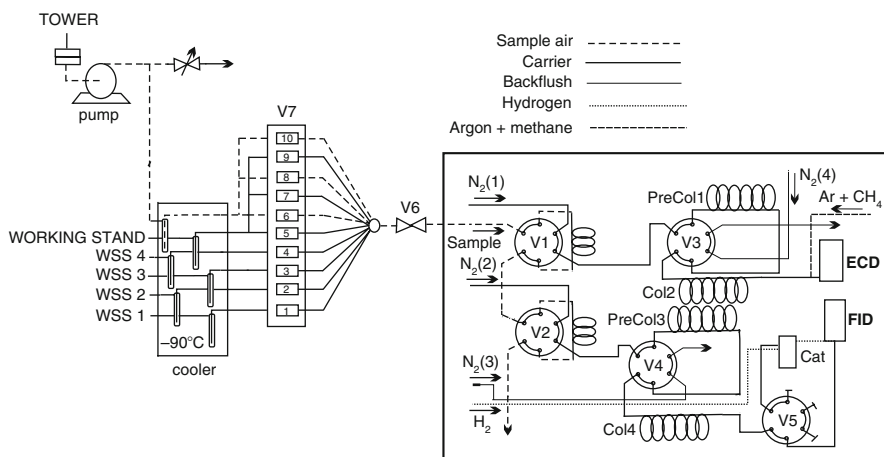


Fig. 2.3 Schematic of the gas chromatographic system used at Hegyhátsál tall tower site for the monitoring of non- CO_2 greenhouse gases

an electron capture detector (ECD), and it is capable to measure the nitrous oxide and sulfur hexafluoride mixing ratios. Nitrogen with 5.0 purity (Linde Gáz, Hungary), further purified by a Supelco 23801 high-capacity gas purifier, is used as carrier gas for both lines. Hydrogen for FID and methanizer nickel catalyst (for CO analysis only) is produced by a Parker–Balston hydrogen generator (model H2PEM-100), while air is supplied by a Jun-Air oil-less compressor (model OF-302) through a Parker Zero Air Generator. For the ECD, 5% methane/95% argon make-up gas is used.

Air to be analyzed is continuously pumped by a diaphragm pump (KNF Neuberger Type N86) through a 9.5 mm diameter tube (Dekoron Type 1300) from the intake level on the tower, at 96 m above the ground, at a rate of about 6 L min^{-1} to the measuring system located on the ground floor of the transmitter building. A 47 mm diameter (Whatman EPM) particle filter is applied to prevent the system from dust. The inlet tube, the four standard gases used for the calibration of the system, and a so-called working standard with approximately ambient mixing ratios used to check the stability of the system are connected to a computer-controlled, 10-position valve (VICI AG, Model: DCSD10MWE) through separated glass water vapor traps held at -90°C in a freezer (FTS System, Model VT490). The 10-position valve selects a standard, the working standard or the ambient air to be analyzed to forward it to the gas chromatograph.

At the beginning of an analysis the gas, selected by the 10-position valve (V7 in Fig. 2.3), flows through the loops of the two gas sampling valves (Valco, DC6UWE, V1 and V2 in Fig. 2.3). After 40 s flushing time, the on/off valves (Numatics S series, V6 in Fig. 2.3) between the 10-position valve and the gas sampling valves closes, and the pressure in the loops equilibrate to atmosphere pressure. The two sampling valves simultaneously inject the sample to the precolumns. For the separation of methane and carbon monoxide, a $0.9 \text{ m} \times 1/8 \text{ in.}$ Unibeads S1 (Alltech)

precolum and a 1.2 m \times 1/8 in. Molecular Sieve 5A (Alltech) separating column (PreCol3 and Col4, respectively, in Fig. 2.3) are used. When the air, methane, and carbon monoxide have left the precolum and entered the main column, the backflush valve (Valco DC6WE, V4 in Fig. 2.3) changes the direction of flow in the precolum, eliminating the heavier compounds to enter the Molecular Sieve column. When air/oxygen has left the main column, valve 5 (V5 in Fig. 2.3) switches and directs the separated CH₄ and CO to the nickel catalyst converting carbon monoxide to methane. Methane sweeps through the catalyst unchanged. The analyses are executed at 60°C isothermally. The FID is held at 250°C.

The separation of nitrous oxide and sulfur hexafluoride is executed on a Hayesep Q (Alltech) columns of 1/8 in. diameter. The 1.2 m precolum (PreCol1 in Fig. 2.3) separates the heavier substances from the two compounds to be measured, and it is backflushed (V3 in Fig. 2.3). N₂O and SF₆ are separated on a 1.8 m long main separating column (Col2). ECD is held at 370°C.

We use a 12-h long analysis program started at midnight and noon. Each 12-h long sequence begins with the calibration of the system using the four standard gases (WSS1-WSS4) prepared by Max-Planck-Institute for Biogeochemistry (Jena, Germany) in the framework of the European Commission funded CHIOTTO project (<http://www.chiOTTO.org>). The scales are traceable to the WMO GAW Central Calibration Laboratory for these gases operated by NOAA. During this initial calibration the mixing ratios in the working standard (WS) are also determined. Later in the sequence the ambient air and the WS are analyzed alternately (WS-air-WS-air-WS-air-...) to monitor and correct the potential drift in the scale. An analysis takes 10 min; thus ambient air data is available in every 20th minute.

2.3.4 Ancillary Measurements

For the interpretation of the mixing ratio data, meteorological and other measurements are indispensable. The basic meteorological measurements (wind speed, wind direction, air temperature, relative humidity) are available from the same elevation levels (10, 48, 82, 115 m) as the CO₂ mixing ratio data. The distance of the sensors from the tower is 4.4 m at 82 and 115 m elevations, 2.5 m at 48 m elevation, while the sensors of 10 m are mounted on the top of a freestanding mast. The flow distortion caused by the tower influences the measured wind speed at 48, 82, and 115 m. We correct the measured wind speeds based on a theoretical laminar flow pattern around a cylindrical body using wind direction information (Barcza 2001). Especially in sunny summer days, when the temperature sensors are on the lee side of the tower, the warmed body of the tower may influence the temperature measurements. This effect is also checked and corrected (Haszpra et al. 2001). The station is also equipped with several other sensors (global solar radiation sensor, radiation balance sensor, photosynthetically active radiation sensor, soil temperature, soil moisture, and soil heat flux sensors), which are primarily used in the surface-atmosphere gas exchange studies (see Chapters 6 and 8).

The biosphere plays a crucial role in the formation of the atmospheric concentrations. To have a better insight into the processes and to help in the interpretation of the mixing ratio measurements, two independent vertical CO₂ flux measuring systems based on eddy covariance technique are in operation at Hegyhátsál. One of them is mounted on the tall tower at 82 m above the ground. Its large footprint covers the neighboring agricultural fields and it gives information about the CO₂ exchange of the typical Hungarian agricultural lands in general. Further details on this measuring system can be found in Chapter 8. The other eddy covariance system is mounted at 3 m elevation and it monitors the CO₂ flux between a seminatural grassland and the atmosphere. This monitoring system and its measurements are discussed in Chapter 6.

Hegyhátsál tall tower site has been a member of NOAA global cooperative air sampling network for greenhouse gases (station code: HUN) since March 1993. Every week, two flasks (2.5 L each) have been flushed and pressurized in series with air in the early afternoon hours, when the vertical mixing of the atmosphere is the most vigorous. The sampling height is 96 m above the ground. The samples are analyzed by NOAA ESRL Carbon Cycle Greenhouse Gases group (Boulder, Colorado, U.S.A.) for greenhouse gases and by the Institute for Arctic and Alpine Research (University of Colorado, Boulder, Colorado, U.S.A.) for carbon and oxygen stable isotope composition of CO₂. Carbon dioxide content of the samples is measured by means of an NDIR analyzer, while for CH₄, N₂O, and SF₆, a gas chromatograph equipped with FID and ECD is used. For details, see <http://www.esrl.noaa.gov/gmd/ccgg/flask.html>. The parallel in situ and flask measurements offer a unique opportunity to monitor the quality of the measurements regularly.

In the framework of the European Commission supported AEROCARB project and CarboEurope Integrated Project (IP) regular aircraft measurements of greenhouse gases were also performed over the tower between 2001 and 2008. Flask air samples were taken between 200 and 3000 m elevation above the ground 8–16 times a year. The samples were analyzed by Laboratoire des Sciences du Climat et l'Environnement, Gif-sur-Yvette, France.

2.4 Quality Assurance and Quality Control of the Measurements

Comparability of the measurements made at different monitoring sites or by different laboratories is a basic requirement in any scientifically sound study. One of the prerequisites to the acceptable comparability is the use of standards traceable to the same etalon. Since 1992, both K-pusztá and Hegyhátsál have been using CO₂ standards prepared and certified by the Central Calibration Laboratory (CCL) of the World Meteorological Organization (NOAA ESRL, Boulder, Colorado, U.S.A.). The N₂O, CH₄, and SF₆ standards are also traceable to the WMO standards maintained by the CCLs of these gases, also operated by NOAA ESRL.

The monitoring sites should regularly participate in interlaboratory comparisons when air samples of unknown composition are distributed among the participating

laboratories to control their scales. WMO requests the interlaboratory comparability in case of CO_2 , CH_4 , N_2O , and SF_6 within $\pm 0.1 \mu\text{mol mol}^{-1}$, $\pm 2 \text{ nmol mol}^{-1}$, $\pm 0.1 \text{ nmol mol}^{-1}$, and $\pm 0.02 \text{ pmol mol}^{-1}$, respectively (WMO 2009). WMO organizes an interlaboratory comparison approximately in every fourth year. In the framework of the European Commission supported CarboEurope-IP, a more frequent interlaboratory comparison exercise was initiated in Europe, which has been continued after the end of CarboEurope-IP at the end of 2008 (<http://www.cucumbers.uea.ac.uk/>).

In the first two WMO interlaboratory comparisons (1992 and 1996) the measuring system at K-pusztá was used. In 1992, CO_2 -in-nitrogen was used as standards yet, so the average $-2.47 \mu\text{mol mol}^{-1}$ offset (<http://gaw.kishou.go.jp/wcc/co2/co2comparison.html>) was quite understandable. In 1996, the average offset was $-1.02 \mu\text{mol mol}^{-1}$ indicating that the Köhler's method for the removal of water vapor interference (Köhler 1974) could not provide the requested accuracy. The Köhler's method caused at least $\pm 0.5 \mu\text{mol mol}^{-1}$ low-frequency noise that strongly influenced the momentary measurements, like the measurement of a sample of unknown mixing ratio from WMO, while this noise was largely smoothed out from the longer term averages. Consequently, the accuracy of the longer term averages (hourly, daily, monthly, etc.) used in different studies was significantly higher. Nevertheless, the potential inaccuracy of the values in a few tenth of $\mu\text{mol mol}^{-1}$ range should be considered in the evaluations.

In the next three WMO interlaboratory CO_2 comparisons (1999, 2003, 2005) already the measuring system at Hegyhátsál participated. The more developed system provided significantly better results (0.06 , 0.07 , and $-0.38 \mu\text{mol mol}^{-1}$, respectively – unpublished results). In the CarboEurope-IP interlaboratory CO_2 comparisons (2008–2009) the new LI-7000 analyzer was already used, the stability of which exceeded that of the previous model. The results of the interlaboratory comparison were within the required range in all five exercises performed so far (overall mean offset: $0.06 \mu\text{mol mol}^{-1}$, stability of offset: $\pm 0.03 \mu\text{mol mol}^{-1}$ – Manning et al. (2009) and results unpublished yet).

As the monitoring system for methane, nitrous oxide, and sulfur hexafluoride was installed in the beginning of 2006, we could not participate in WMO interlaboratory comparison yet. However, the interlaboratory comparisons organized by CarboEurope-IP indicate that the accuracy of the methane measurements satisfies the WMO requirement (overall mean offset: $1.3 \text{ nmol mol}^{-1}$, stability of offset: $\pm 0.9 \text{ nmol mol}^{-1}$, unpublished project results). The bias of the SF_6 measurements ranges from 0.09 to $0.14 \text{ pmol mol}^{-1}$, which is out of the range requested by WMO. SF_6 measurements are not easy as it is indicated by the fact that meeting the accuracy requirement causes problems even to some of the regional reference laboratories (Manning et al. 2009). There are more serious problems with the nitrous oxide measurements. The scale at Hegyhátsál is biased from the reference scale by 0.8 – $1.1 \text{ nmol mol}^{-1}$ without obvious reason. That is why, these data are used only for the characterization of the local daily variation.

Interlaboratory comparisons by means of circulation of air samples of unknown composition offer only rare, occasional possibility to check the performance of the monitoring systems, and they cannot simulate the normal atmospheric sampling. The parallel, independent measurements give a more rigorous control on data quality.

As it was mentioned in the previous section, Hegyhátsál tall tower site is a member of NOAA global cooperative air sampling network for greenhouse gases, where every week two flasks (2.5 L each) are filled with ambient air. The samples are analyzed by NOAA ESRL Carbon Cycle Greenhouse Gases group (Boulder, Colorado, U.S.A.) for all those greenhouse gases that are also measured in situ at the station. In the case of methane, nitrous oxide, and sulfur hexafluoride, the sampling elevation of the flasks and the in situ measurements coincides (96 m above the ground); however, CO₂ mixing ratio is measured at 82 and 115 m by the in situ system. While the flasks contain momentary air samples, in situ non-CO₂ measurements are available only in every 20th minute, and in situ CO₂ measurements are usually performed only in every 8th minute at a given sampling elevation. The dislocation of the intakes of the NOAA sampler unit and that of the in situ CO₂ analyzer, the time synchronization problem, the different residence time of air in the sampling systems cause methodological problems in the comparison.

For the comparison, in the case of CO₂ measurements, the arithmetic mean of the consecutive in situ measurements carried out at 115 and 82 m are calculated. For the comparison, those in situ measurements are taken into account, and averaged, which fall in a ± 10 min time-window around the recorded NOAA sampling time. Usually, three in situ measurement pairs (82 and 115 m) can be used to calculate a data to compare with the flask measurements. In the case of unfortunate timing, zeroing or calibration in the time-window, there might be only two or one in situ data pairs for the comparison. In the case of the other greenhouse gases, in situ data from a ± 20 min time-window around the recorded NOAA sampling time are used. In most cases, the time-window includes two in situ measurements. The temporal and spatial dislocations of the samples in the comparison cause significant scatter in the flask–in situ deviation, especially if significant short-term fluctuation can be observed in the atmospheric mixing ratios. These periods and a few extreme outliers (potential sampling or instrument errors) are rejected from the data series.

After data filtering mentioned above, the atmospheric CO₂ mixing ratios measured from the flask samples and by the in situ analyzer deviate by $-0.03 \mu\text{mol mol}^{-1}$ on average (standard deviation is $1.50 \mu\text{mol mol}^{-1}$, correlation coefficient is 0.99 – based on 407 flask–in situ data pairs), which is much better than expected taking into account the absolute independence of the methods and the methodological difficulties. The flask–in situ difference does not show any recognizable temporal variation or tendency (Fig. 2.4).

For methane, nitrous oxide, and sulfur hexafluoride, shorter data series are available (63–71 valid data pairs). The atmospheric mixing ratios measured from the flask samples and by the in situ gas chromatograph deviate by $-4.71 \text{ nmol mol}^{-1}$, $-0.79 \text{ nmol mol}^{-1}$, and $-0.02 \text{ pmol mol}^{-1}$ for CH₄, N₂O, and SF₆, respectively (standard deviations are $9.35 \text{ nmol mol}^{-1}$, $0.77 \text{ nmol mol}^{-1}$, and $0.10 \text{ pmol mol}^{-1}$, respectively, while the correlation coefficients are 0.98, 0.74, and 0.93). Temporal variations in the biases do not show any trend or regular variation (Fig. 2.4). In the case of methane, the bias indicated by this comparison is somewhat higher than it could be expected from the results of the interlaboratory comparisons (1.3 and $4.71 \text{ nmol mol}^{-1}$), while the present comparison confirms that the SF₆ measurements are reasonably

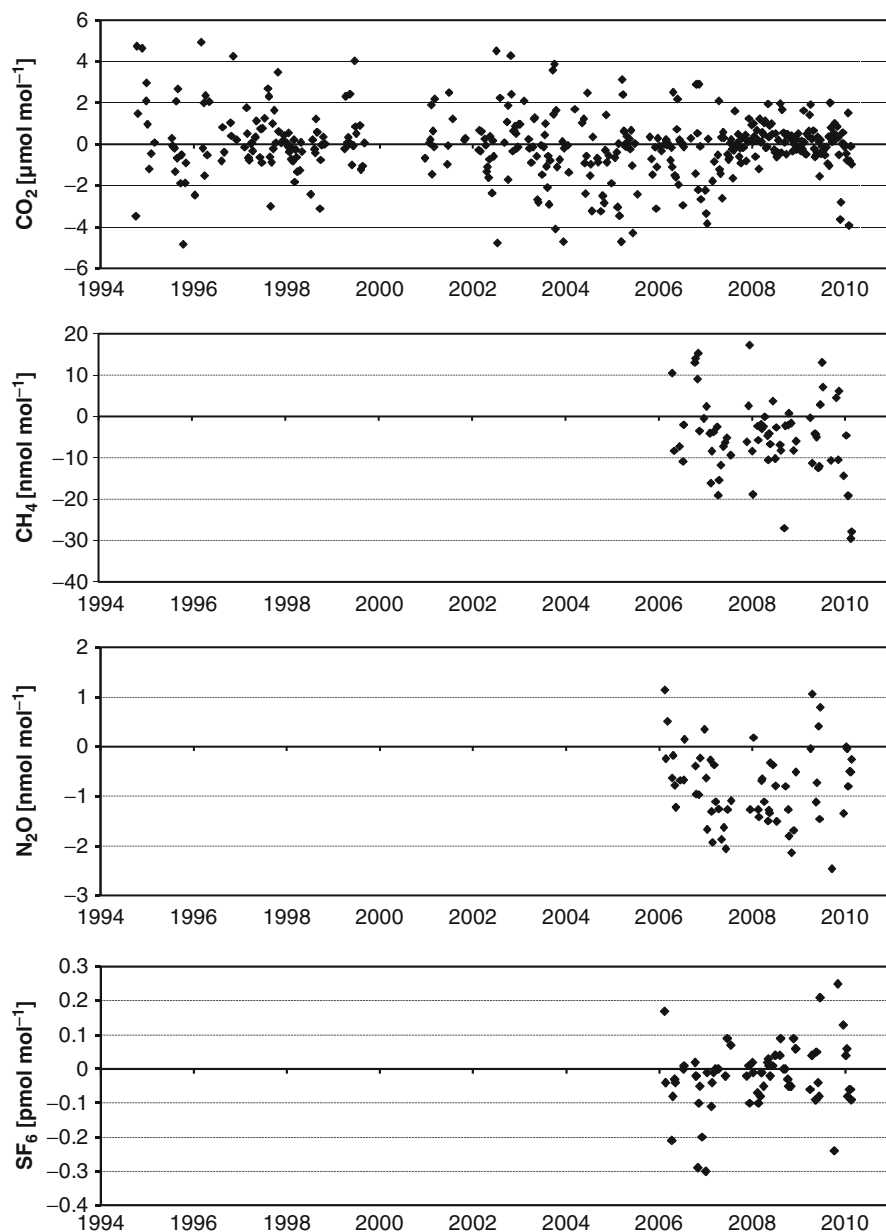


Fig. 2.4 Temporal variations of flask – in situ difference (flask minus in situ mixing ratio) for the different greenhouse gases measured at Hegyhátsál

accurate, although their accuracy does not satisfy the WMO requirement yet. The flask–in situ difference in the nitrous oxide measurements call the attention again to a possible scale problem, to the overestimation of the actual mixing ratio by the in situ system.

At several monitoring sites a clean air sector is defined. Data measured in the air masses arriving from the complement sector are rejected because of the potential contamination from anthropogenic sources. In the case of the Hungarian monitoring stations no clean air sector can be defined because the stations are located in the middle of a highly industrialized, densely populated continent where the natural and anthropogenic sources (and natural sinks in the case of CO_2) are distributed more or less evenly around them. The topography of the Carpathian Basin also helps the mixing of air masses arriving from different directions. The sectoral distribution of the atmospheric CO_2 mixing ratio does not show any characteristic feature at either monitoring sites (Haszpra 1999b). At several monitoring stations, minimum wind speed criteria are applied to avoid the dominance of local sources. Both Hungarian measuring sites are located in climatologically calm regions, where the annual average wind speeds are 3.5 m s^{-1} (Hegyhátsál) and 1.7 m s^{-1} (K-pusztá), respectively. Therefore, a data selection based on wind speed is not introduced either. Under the given environmental conditions, any algorithmic data selection procedure might lead to some sort of bias. Therefore, the data measured are manually checked using data visualization software, and only the technically false data are removed from the data series.

2.5 Representativeness of the Monitoring Sites

Representativeness is the extent to which a set of measurements taken in a space-time domain reflects the actual conditions in the same or different space-time domain taken on a scale appropriate for a specific application (Nappo et al. 1982). Knowledge of the representativeness of the measurements is essential in the interpretation of the data. The parallel CO_2 concentration measurements performed at Hegyhátsál and K-pusztá between 1994 and 1999 offered a possibility to get an insight into the horizontal representativeness of these measurements.

For the estimation of the horizontal representativeness of the measurements and its temporal variation, the average differences between the mixing ratios measured at the two stations were calculated for every hour for summer (June–August) and winter (December–February) separately (Fig. 2.5). In summer daytime hours (12–16 h local standard time, LST), the difference between the two stations is negligible ($0.06 \mu\text{mol mol}^{-1}$). In winter and in the transition seasons (not presented in Fig. 2.5), the mixing ratio at Hegyhátsál is higher by 1.84 and $1.55 \mu\text{mol mol}^{-1}$, respectively, on average. It is suspected to be the consequence of the higher anthropogenic source density in Western Europe closer to Hegyhátsál than to K-pusztá in the prevailing wind direction and the more limited atmospheric mixing in the Carpathian Basin, especially in winter.

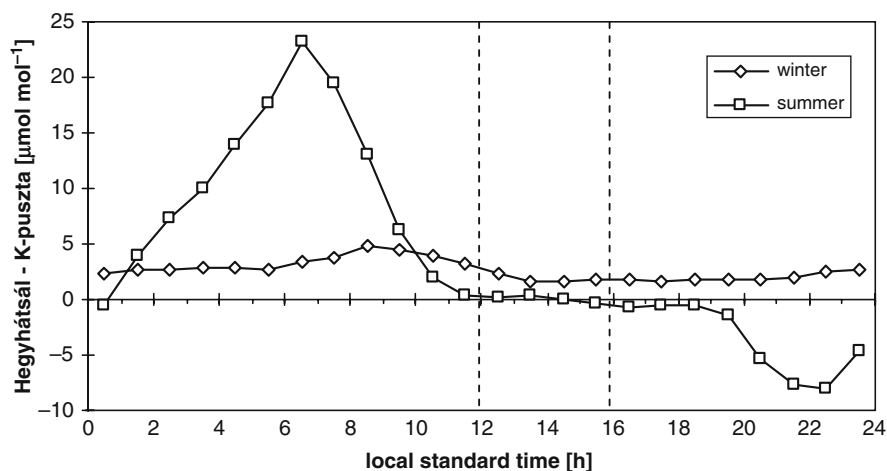


Fig.2.5 Daily variations of the average differences between the mixing ratios measured at K-pusztá and Hegyhátsál at 10 m elevation above the ground in winter and summer

During summer nights, the difference between the two monitoring sites is remarkable; it is above $20 \mu\text{mol mol}^{-1}$ in the early morning hours. In the evening, the mixing ratio is higher at K-pusztá. This region is climatologically calmer than the other, and a stable boundary layer may form here earlier in the evening in which CO_2 starts to accumulate. Later, the intensity of the soil/vegetation respiration takes over the control on the CO_2 content of the boundary layer. The respiration at Hegyhátsál is more intensive than at the sandy K-pusztá. As a consequence of this process, the mixing ratio becomes higher at Hegyhátsál, and the difference is the most remarkable in summer. The smallest and almost constant difference between the two sites can be observed in the early afternoon hours.

Figure 2.6 shows the average vertical CO_2 mixing ratio profiles measured at the Hegyhátsál tall tower site for different seasons and for different periods of the day. In Fig. 2.7, the daily variation of the correlation between the mixing ratios measured at 10 and 115 m is presented. Both figures suggest that the representativeness of the early afternoon measurements is high enough to allow the use of the data in regional scale studies. Therefore, in all studies, except for those focusing on the diurnal variation, the data measured between 12 and 16 o'clock LST are used, and this period is defined as “early afternoon” in our studies.

Gloor et al. (2001) developed a simple method for the estimation of the horizontal representativeness of CO_2 concentration measurements based on the tall tower measurements in Wisconsin, U.S.A. Supposing that the parameters estimated for that region are also valid for our region, the area from where the signal contribution to the measured mixing ratio is greater than 2.5% is 200,000–300,000 km^2 depending on the season. The influencing area is not concentric around the station. Due to the prevailing northwesterly wind direction, it is somewhat more extended to the northwest.

Figure 2.6 shows that due to the intensive vertical mixing of the atmosphere in summer, the mixing ratio at 115 m above the ground is almost the same as at 10 m.

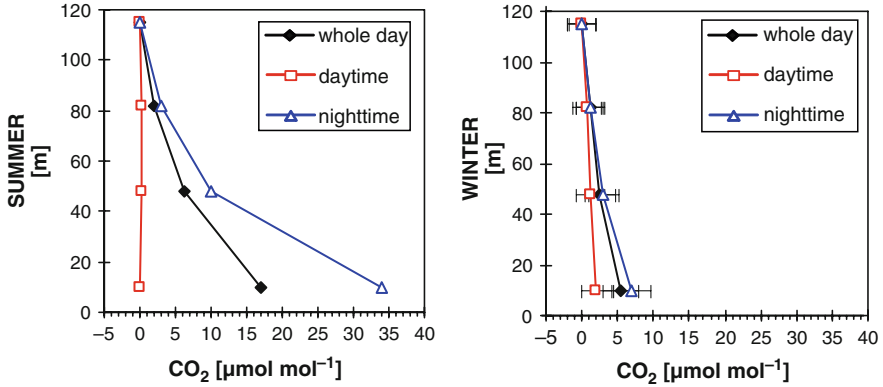


Fig. 2.6 Mean vertical CO_2 mixing ratio profiles in different seasons and in different periods of the day at Hegyhátsál, relative to the values measured at 115 m

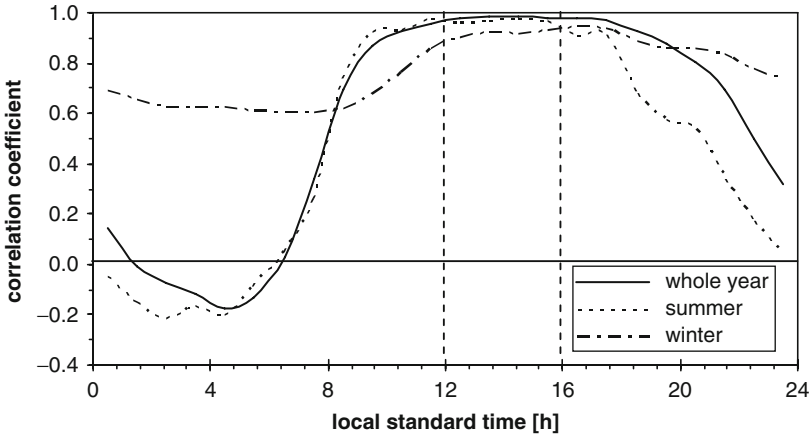


Fig. 2.7 Daily variations of the correlation coefficient between the mixing ratios measured at 10 and 115 m

The measurements presented by Bakwin et al. (1995) suggest that the mixing ratio measured at about 100 m above the ground may not differ from the characteristic value of the planetary boundary layer (PBL) by more than a few tenths of $\mu\text{mol mol}^{-1}$. Therefore, it can also be assumed that during summer, the measurements carried out at 10 m elevation do not underestimate the regional CO_2 mixing ratio of the boundary layer by much more. Following the same reasoning, it can also be assumed that in winter time, the measurements close to the surface (10 m) in a low-elevation temperate continental region do not overestimate the mixing ratio of the PBL by more than 2–3 $\mu\text{mol mol}^{-1}$. Combining the CO_2 mixing ratio data from air samples taken on board of a small aircraft over the tower and those measured in situ on the tower, as well as knowing the height of the PBL (MARS archive,

European Centre for Medium-Range Weather Forecasts), the average mixing ratio of the PBL can be calculated. In the summer half year (April–September), this value is underestimated by the measurements at 115 m above the ground on the tower by $0.84 \mu\text{mol mol}^{-1}$ (standard deviation: $1.79 \mu\text{mol mol}^{-1}$), indicating the intensive CO_2 uptake at the surface by the vegetation. In the winter half year (October–March), the top monitoring level on the tower overestimates the PBL average by $1.51 \mu\text{mol mol}^{-1}$ (standard deviation: $3.68 \mu\text{mol mol}^{-1}$) on average. This average deviation would be reduced to $0.61 \mu\text{mol mol}^{-1}$ if we rejected those three profiles from the available 38 where the deviation is bigger than $+10 \mu\text{mol mol}^{-1}$. These profiles indicate either internal stratification in the PBL or problems in the determination of the PBL height. (It should be noted that some sort of “fair weather bias” cannot be excluded in the case of the above data because air samples could only be taken when the weather was suitable for flying).

The time scale is a critical issue in the evaluation of the representativeness. The longer the averaging period the more extended the represented area. As we will see in Chapter 3, the annual growth rate of the CO_2 mixing ratio calculated from the measurements performed at K-pusztá/Hegyhátsál correlates well with the global growth rate calculated from the data of the most remote monitoring sites. In this sense, the CO_2 data of the Hungarian monitoring sites are globally representative.

The data series are too short yet to estimate the representativeness of the non- CO_2 measurements directly. Taking into account the long atmospheric residence time of those gases and the less intensive interaction with the surface, we can suppose that the discussion above is also more or less valid for those measurements.

2.6 Summary

Monitoring of atmospheric greenhouse gases was started in Hungary as early as 1981 with the measurements of CO_2 at K-pusztá. During the past almost 3 decades, several publications presented the data to the scientific community (e.g. Haszpra 1995, 1999a, b; Haszpra et al. 2008), and they have infiltrated into regional and global studies (e.g. Bakwin et al. 2004; Geels et al. 2007; Ramonet et al. 2010). K-pusztá and Hegyhátál are regional GAW stations. The results of the atmospheric CO_2 measurements are publicly available at the World Data Centre for Greenhouse Gases of WMO (WMO WDCGG – <http://gaw.kishou.go.jp/wdcgg/>). The data from Hegyhátál are also used for the preparation of NOAA’s GLOBALVIEW- CO_2 data product (<http://www.esrl.noaa.gov/gmd/ccgg/globalview/>). In addition to WMO WDCGG, the monthly mean CO_2 mixing ratios are reported to the Carbon Dioxide Information Analysis Center, Oak Ridge, U.S.A. (<http://cdiac.esd.ornl.gov/>). The data measured by NOAA from the air samples taken at Hegyhátál are publicly available from NOAA (<http://www.esrl.noaa.gov/gmd/ccgg/iadv/>) and WMO WDCGG. Hegyhátál also reports its measurements to the CarboEurope database (http://ce-atmosphere.lsce.ipsl.fr/database/index_database.html). In situ non- CO_2 greenhouse gas data are available only there yet. Hegyhátál has its own website

(<http://nimbus.elte.hu/hhs/>) where, in addition to other information, quasi-real-time data are also accessible.

Hegyhátsál tall tower site participated and participates in several international research projects. Since 2000, it has been a permanent participant (full-right partner or subcontractor) in several European projects in the field of greenhouse gas research (AEROCARB – <http://aerocarb.lsce.ipsl.fr/>, CHIOTTO – <http://www.chiotto.org/>, CarboEurope-IP – <http://www.carboeurope.org/>, IMECC – <http://imecc.ipsl.jussieu.fr/>, GEOMON – <http://geomon.ipsl.jussieu.fr/>, etc.).

In addition to the continuous work for WMO and NOAA, Hegyhátsál is also a potential node for the forming unified European greenhouse gas observation system, ICOS (<http://www.icos-infrastructure.eu/>).

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