



## Development of a mobile and high-precision atmospheric CO<sub>2</sub> monitoring station

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Nowadays one of the most burning questions for the science is the rate and the reasons of the recent climate change. Greenhouse gases (GHG), mainly CO<sub>2</sub> and CH<sub>4</sub> in the atmosphere could affect the climate of our planet. However, the relation between the amount of atmospheric GHG and the climate is complex, full with interactions and feedbacks partly poorly known even by now. The only way to understand the processes, to trace the changes, to develop and validate mathematical models for forecasts is the extensive, high precision, continuous monitoring of the atmosphere.

Fossil fuel CO<sub>2</sub> emissions are a major component of the European carbon budget. Separation of the fossil fuel signal from the natural biogenic one in the atmosphere is, therefore, a crucial task for quantifying exchange flux of the continental biosphere through atmospheric observations and inverse modelling. An independent method to estimate trace gas emissions is the top-down approach, using atmospheric CO<sub>2</sub> concentration measurements combined with simultaneous radiocarbon (<sup>14</sup>C) observations. As adding fossil fuel CO<sub>2</sub> to the atmosphere, therefore, leads not only to an increase in the CO<sub>2</sub> content of the atmosphere but also to a decrease in the <sup>14</sup>C/<sup>12</sup>C ratio in atmospheric CO<sub>2</sub>.

The ATOMKI has more than two decade long experience in atmospheric <sup>14</sup>CO<sub>2</sub> monitoring. As a part of an ongoing research project being carried out in Hungary to investigate the amount and temporal and spatial variations of fossil fuel CO<sub>2</sub> in the near surface atmosphere we developed a mobile and high-precision atmospheric CO<sub>2</sub> monitoring station. We describe the layout and the operation of the measuring system which is designed for the continuous, unattended monitoring of CO<sub>2</sub> mixing ratio in the near surface atmosphere based on an Ultramat 6F (Siemens) infrared gas analyser. In the station one atmospheric <sup>14</sup>CO<sub>2</sub> sampling unit is also installed which is developed and widely used since more than one decade by ATOMKI.

Mixing ratio of CO<sub>2</sub> is measured at 2 m above the ground by the monitoring station. Air is pumped through a 9.5-mm-diameter plastic tube (PFA, Swagelok) to a CO<sub>2</sub> analyser located in a container box. Container box (Containex) is 1.5 m wide, 1.2 m deep and 2.2 m high, designed as a mobile measuring room which is field deployable, only electric power is required. A 15 micron pore size stainless steel Tee-Type (Swagelok) particle filter is located at the inlet of the sampler tube. Diaphragm pump (KNF) is used to draw air continuously through the sampling tube from monitoring level at flow rate of ~ 2 L/min. After leaving the pump, the air at 5 psig overpressure enters a glass trap for liquid water that 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 the trap. The air sample inlet tube and the standard gases (Linde Hungary) are connected to miniature solenoid valves (S Series, ASCO Numatics) in a manifold which are normally closed and controlled by the CO<sub>2</sub> analyser, 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 vapour interference and dilution effect are <0.1 ppm equivalent CO<sub>2</sub>. The Nafion drier is purged in a counter flow (300 cm<sup>3</sup>/min) arrangement using waste sample air that has been further dried by passage through anhydrous CaSO<sub>4</sub> (Drierite).

Analysis is carried out using an infrared gas analyser Ultramat 6F which is a specialised model for field applications by Siemens. A constant sample flow rate of

300 cm<sup>3</sup>/min is maintained by a mass flow controller (Aalborg). The reference cell of the CO<sub>2</sub> analyzer is continuously flushed with a compressed reference gas of 350 ppm CO<sub>2</sub> in synthetic air (Messer Hungarogáz). The basic calibration cycle is 2 hours, consisting of a zero-point calibration and a span calibration. Each calibration is consisting of 2 min flushing and 20 sec signal integration. The usual change of the response function is below

0.2 ppm after 2 hours following a previous calibration. The analyser measures the CO<sub>2</sub> mixing ratio in the sample gas in every 3 seconds. Output data are registered by a data logger developed for this application (Special Control Devices).

The overall uncertainty of our atmospheric CO<sub>2</sub> mixing ratio measurements is < 0.5 ppm (< 0,2 %). This level of error is acceptable for fossil fuel CO<sub>2</sub> calculations as the uncertainty of the other required parameter radiocarbon content of atmospheric CO<sub>2</sub> is usually 0.3-0.5%. Using the developed mobile and high-precision atmospheric CO<sub>2</sub> monitoring station we plan to determine the fossil fuel CO<sub>2</sub> amount in the air of different cities and other average industrial regions in Hungary.

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