

# Atmospheric CO<sub>2</sub> monitoring with single-cell NDIR-based analyzers

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- Introduction
- Methods
- Results
- Discussion and summary
- Inspiration



## Introduction

- Use of atmospheric CO<sub>2</sub> concentration measurements to estimate CO<sub>2</sub> fluxes has become finer scale in recent years.
- Current attempts to infer surface CO<sub>2</sub> fluxes from concentration measurements are limited by both errors in modeling atmospheric transport (*Lin et al., 2004*) and sparseness in the available data (*Gurney et al., 2002*).
- The history of atmospheric CO<sub>2</sub> measurements: flask-collection program — dual-cell NDIR-based analyzer — single-cell NDIR-based analyzer laser-based instrument



Reasons for select single-cell NDIR-based analyzer: data from these systems are sufficient; a number of these systems are still operating in the field and will continue to do so for years to come; low cost than laser-based instruments; many of the gas-handling, sample drying, calibration, and intercomparison issues are relevant to any atmospheric CO<sub>2</sub> measurement system regardless of sensor type.





- PSU measurement system description (PSU: Pennsylvania State University)
- Differences in AIRCOA system
  (AIRCOA: autonomous inexpensive, robust, CO<sub>2</sub> analyzer)
- Calibration using field standards
- Potential causes of measurement error and their solutions



#### • PSU measurement system description



Fig. 1. PSU system schematics of the single-cell NDIR-based CO<sub>2</sub> concentration measurement systems.



- ➤ The CO<sub>2</sub> levels are measured using a single-cell sensor employing NDIR absorption spectroscopy (*LI-COR, model LI-820*). The LI-820 actively and precisely controls the optical bench to 50°C and has good stability with respect to ambient temperature of around 0.1 ppm°C<sup>-1</sup>.
- The LI-820 also provides a measurement of cell pressure and applies its own internal concentration-dependent pressure correction.
- ➤ The enclosure is temperature controlled to 30°C, with a fan to minimize temperature gradients.
- Automated leak tests are performed following every calibration cycle.



#### • Differences in AIRCOA system



Fig. 2. AIRCOA system schematics of the single-cell NDIR-based CO<sub>2</sub> concentration measurement systems.



The AIRCOA data-processing software uses measured temperature variations and changes in pressure during leak checks to define monthly empirical temperature and concentration-dependent pressure effects on the LI-820 data.



### Calibration using field standards

- Even with internal or post-processing temperature and pressure compensation, the LI-820 CO<sub>2</sub> calibration typically drifts by 0.3 ppmday<sup>-1</sup> with fluctuations of similar magnitude possible over several hours.
- Four field standards, are measured every 4h by the systems for 2.5 min each. These four known values are used to develop a second-order linear regression between the LI-820 output and CO<sub>2</sub> concentration. Every 30 min the AIRCOA systems also analyze one of the four calibration gases to estimate short-term drift in the LI-820 zero offset.



In the 4th World Meteorological Organization round-robin reference gas intercomparison (WMO, 2009), PSU system and AIRCOA system performance is as follows.

system	differe from the NOAA-ESRL		
	test one	test two	test three
PSU	+0.05	-0.04	-0.05
AIRCOA	+0.04	0.00	0.01

Tab.1. PSU system and AIRCOA system performance in the 4th World Meteorological Organization round-robin reference gas intercomparison.



#### Potential causes of measurement error

- 1. Short-term LI-820 noise
- 2. Drift in LI-820 sensitivity
- 3. Drift in LI-820 pressure sensitivity
- 4. Drift in LI-820 temperature sensitivity
- 5. Leaks through fittings and valves
- 6. Incomplete drying of air
- 7. Incomplete flushing of cell or dead-volumes
- 8. Development of problems in the field





- Side-by-side system comparisons
- Known cylinder measurements
- Comparisons to co-located NOAA-ESRL measurements



Side-by-side system comparisons



Fig. 3. Results from side-by-side system comparisons for PSU systems.





Fig. 4. Results from side-by-side system comparisons for AIRCOA systems.



#### • Known cylinder measurements



Fig. 5. Results from field measurements of cylinders of known concentration for PSU systems.





Fig. 6. Results from field measurements of cylinders of known concentration for AIRCOA systems.



#### Comparisons to co-located NOAA-ESRL measurements



Fig. 7. Results from comparisons to co-located NOAA-ESRL measurements for PSU system.





Fig. 8. Results from comparisons to co-located NOAA-ESRL measurements for AIRCOA system.



## Discussion and summary

- In this paper authors describe relatively inexpensive singlecell NDIR-based systems for measuring CO<sub>2</sub> concentrations and evaluate their performance. Making accurate CO<sub>2</sub> measurements requires careful attention to gas handling, numerous automated quality control diagnostics, and a suite of reference cylinders closely linked to theWMO CO<sub>2</sub> mole-fraction scale.
- Once calibrations are performed, the performance of lessexpensive NDIR-based measurements is not dramatically disparate from that shown in field tests of laser-based instruments (*Richardson et al., 2011*), and this is likely because many of the potential causes of error in CO<sub>2</sub> systems relate to things other than sensor stability.



- It is worth noting that other longrunning intercomparison activities, typically see systematic biases on the order of 0.2 ppm(Masarie et al., 2001; WMO, 2009; Richardson et al., 2011). Thus, still have work to do in resolving and improving remaining compatibility issues.
- Suggestions: recommend introducing target or surveillance gases through the entire inlet system; the post-processing pressure, temperature, and flushing corrections can improve the quality of the final data; a program of multiple intercomparison activities.





> We can use several points calibrations on LI -840A .

> Consider the impact of temperature and pressure on LI -840A.

> Consider the impact of leaks on LI -840A.

> We can test the precision and accuracy of LI-840A.



Experimental design: Urban atmospheric CO<sub>2</sub> monitoring using mobile observation method

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Introduction

Method

Road selection



## Introduction

- Urban environments can modify the local climate and are net CO<sub>2</sub> emitters, both of which can affect the life of an increasing proportion of the world's population that lives in and around cities (Onil Bergeron, Ian B. Strachan, 2011).
- Among the largest carbon dioxide emitters in the world (IEA, 2009), China has been considered responsible for two thirds of the global increase in anthropogenic carbon dioxide emissions of 3.1% in 2007 (Yan andYang, 2010).
- CO<sub>2</sub> concentration measured with mobile observation method is very few in China (ZHAO De-Hua et al, 2009).
- Nanjing, as a developed city, we want to know its increase in CO<sub>2</sub> concentration caused by urbanization.





Fig. 9. Map of Nanjing City showing locations of the urban-forest gradient and measurement sites from S1 to S9 (ZHAO De-Hua et al, 2009).





> Instrument : LI -840A  $CO_2$  /H<sub>2</sub>O gas analyzer

- Time : daily observation at 05:00、08:00、14:00、18:00 (lasting for a week)
- > Experimental design :

at 05:00 and 14:00 each of the four transects will be simultaneously traversed by four separate automobile crews;

at 08:00 and 18:00 both on the Road 1 and Road 2, two automobile crews opposite driving and intersect in Xinjiekou.







Fig. 10. Select for Nanjing road





