Field intercomparison of four methane gas analyzers suitable for eddy covariance flux measurements

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Outline

- 1 Background
- 2 Materials and methods
- 3 Results
- 4 Discussion and Summary

◆1 Background

- Development of gas analyzers based on laser absorption spectroscopy (LAS) has made sensitive and robust instruments commercially available.

- Accordingly, the number of gas analyzers applicable for EC measurements increased.

- The comparisons between the gas analyzer are necessary.

- This study is to compare and assess the performance of four CH_4 gas analyzer and corresponding CH_4 flux and it is done during April – October 2010 at fen.

◆The measurement system of this study

Three-axis sonic anemometer (USA-1, METEK, Germany)

(It is shared by the all gas analyzers in this study)

- LI-COR Prototype-7700 (LI-COR Bioscience, USA)
- Picarro G1301-f (Picarro Inc, USA)
- Los Gatos RMT-200 (Los Gatos Research, USA)
- Campbell TGA-100A (Campbell Scientific., USA)
- LI-7000 (LI-COR Bioscience, USA)

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◆LI-COR Prototype-7700

- Prototype-7700 is an early pre-production prototype of the open-path methane gas analyzer, tunable diode laser is utilized to create laser beams in the near-infrared region.
- Methane concentration is measured by using wavelength modulation spectroscopy (WMS) in order to reduce the effects of mirror contamination.

McDermitt, D et al (2010) A new low-power, open-path instrument for measuring methane flux by eddy covariance. Appl. Phys. B.

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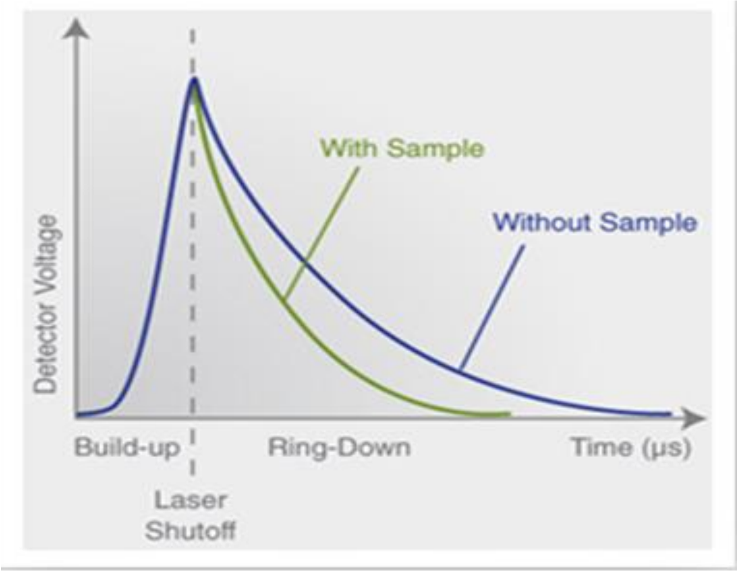
◆Picarro G1301-f

- G1301-f is based on wavelength-scanned cavity ring down spectroscopy (WS-CRDS).

- Picarro G1301-f is a closed-path gas analyzer, the analyzer was measuring water vapor and methane concentrations, and sampling line was heated.



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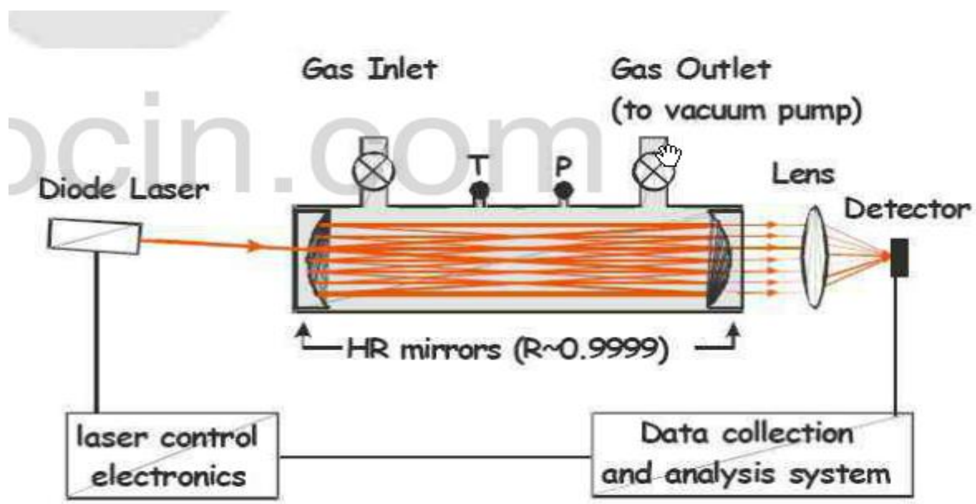
◆Los Gatos RMT-200

- RMT-200 is also a closed-path methane gas analyzer, it is based on the off-axis integrated cavity output spectroscopy (OA-ICOS).
- The tube that sample air to the gas analyzer was not heated but it was situated inside a protective cover.



◆Campbell TGA-100A

- Campbell TGA-100A closed-path gas analyzer is based on TDLAS measurement technique, and the laser was cooled using liquid nitrogen, tube was not heated but the air was dried with a diffusion drier.
- Dew point temperature remained at about -15 to -30 ℃, WPL terms or spectroscopic corrections were not needed.
- This instrument has been widely used in eddy covariance methane flux measurement studies , and is used in this study as a reference for the three new instruments.

Rinne, J et al (2007) Annual cycle of methane emission from a boreal fen measured by the eddy covariance technique. Tellus B.

Table.1 Characteristics of the four methane gas analyzers and their respective setups

	Prototype-7700	G1301-f	TGA-100A	RMT-200
Analyzer type	open-path analyzer enhanced with WMS	WS-CRDS	TDLAS	off-axis ICOS
Open/closed path	open	closed	closed	closed
Measured species	CH_4	CH_4, H_2O	CH_4	CH_4
Sampling height above the soil	2.3 m	2.5 m	2.5 m	2.5 m
Sampling height above significant structures	1.1 m	2.5 m	2.5 m	2.5 m
Horizontal sensor separation	10 cm	5 cm	5 cm	5 cm
Vertical sensor separation	45 cm	25 cm	30 cm	25 cm
Length of sampling line	–	16.8 m	13 m	15 m
Flow rate	wind speed	10 LPM	14 LPM	12 LPM
Sample cell volume	open	33 cm^3	480 cm^3	408 cm^3
Sample cell pressure	ambient pressure	187 hPa	60 hPa	189 hPa
Connected to dryer	No	No	Yes	No
System power demand	low (solar- and wind-powered)	high (grid powered)	high (grid powered)	high (grid powered)
Need of maintenance	low	low	high	low

- The height of sonic anemometer is 2.75m, and below 1.1m of Prototype-7700 is a wooded structure. The filters aperture of G1301-f、TGA-100A and RMT-200 are 1 um、 10um and 0.2um respectively.

◆ 2 Materials and methods

- 2.1 Site description

- 2.2 Eddy covariance method

- 2.3 Random error estimations method

- 2.4 Gap filling procedure

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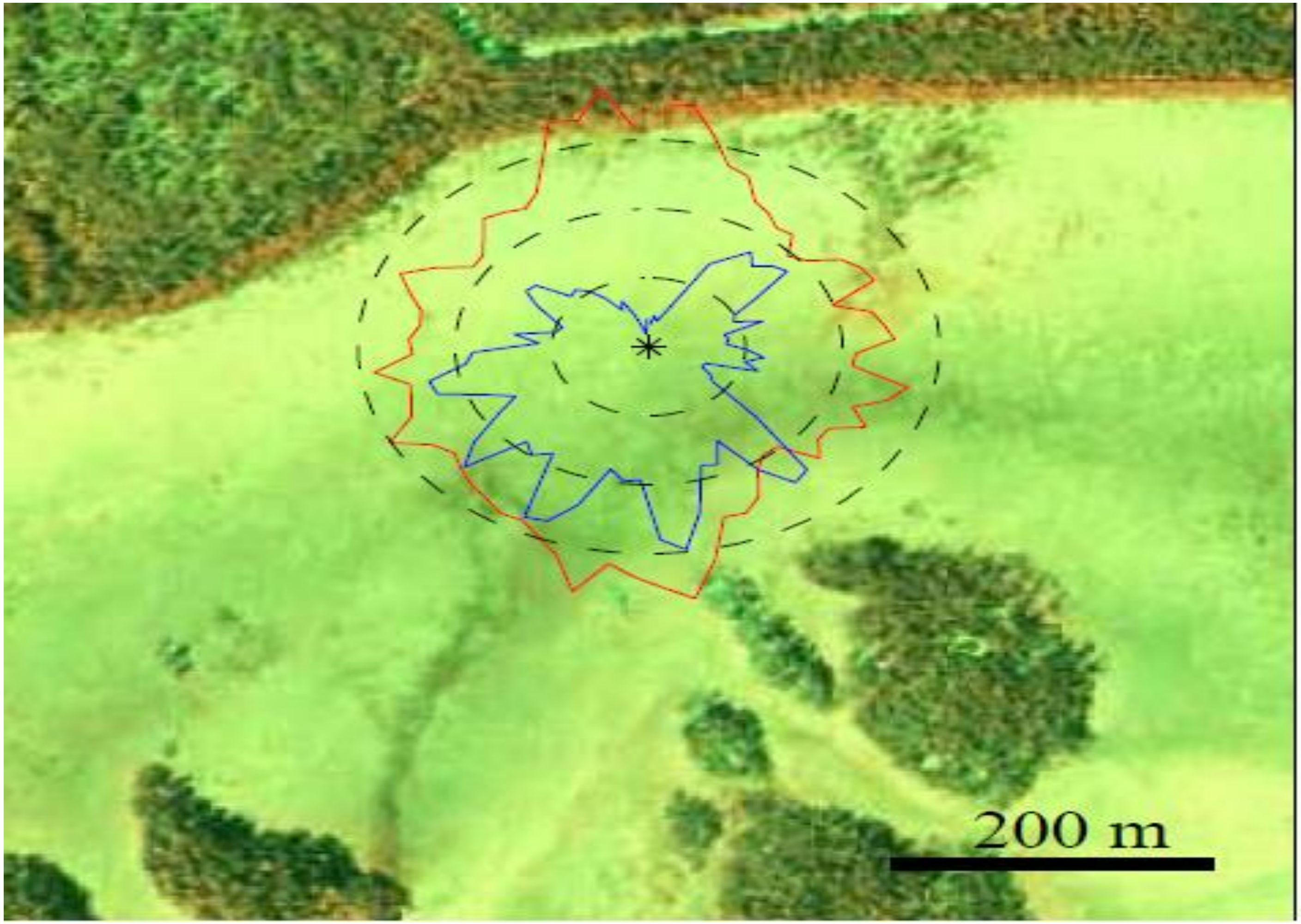

Fig.1 Aerial photograph of the measurement site. Star marks location of the measurements site, red line and blue lines show average methane flux and amount of obtained methane flux data as a function of wind direction. Dashed lines show where methane flux equals 1, 2 and 3 mg m^{-2} h^{-1} and amount of data equals 60, 120 and 180 points.

The gas analyzer intercomparison was carried out in Siikaneva fen, Southern Finland.

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2 Materials and methods

- 2.1 Site description
- 2.2 Eddy covariance method
- 2.3 Random error estimations method
- 2.4 Gap filling procedure

- Eddy covariance method was used in measuring the vertical turbulent fluxes of trace gases, sensible and latent heat.

$$H = \overline{\rho_a} c_p \overline{w'T'} \quad (1)$$

$$\mathrm{LE} = \mathrm{L}\overline{\rho_a}\overline{w'\chi_v'} \quad (2)$$

$$F_c = \overline{\rho_a}\overline{w'\chi_c'} \quad (3)$$

- Measurements were sampled at 10 Hz frequency, and 30-min averaging time was used in calculating the covariances. For the most part, data processing followed the methodology Described by Aubinet et al (2000).

Aubinet, M, et al (2000) Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology. Advances in ecological research.

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◆Data processing

- Step 1 The high frequency eddy covariance data were despiked by comparing two adjacent measurements
- Step 2 The coordinate rotation was applied
- Step 3 The mean values were removed from the time series using block-averaging method
- Step 4 Time lag between the concentration and wind measurements was corrected
- Step 5 Spectral corrections were applied
- Step 6 Humidity effect on temperature flux was accounted for
- Step 7 Webb-Pearman-Leuning (WPL) terms and spectroscopic corrections were applied

◆ 2.2.1 Spectral corrections

$$\mathrm{TF_{HF}} = \frac{1}{1 + (2\pi f \tau)^2} \qquad (4)$$

$$\mathrm{CF} = \frac{\int_0^\infty S_{wT}^{\mathrm{model}}(f)\,\mathrm{d}f}{\int_0^\infty \mathrm{TF_{HF}}(f)\,\mathrm{TF_{LF}}(f)\,S_{wT}^{\mathrm{model}}(f)\,\mathrm{d}f} \qquad (5)$$

- Magnitude of signal attenuation can be estimated with correction factor CF.

Aubinet, M, et al (2000) Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology. Advances in ecological research.

◆2.2.2 Effect of water vapor and temperature fluctuations

- Pressure, temperature and water vapor affect the shape and width of the absorption lines used to deduce gas concentration.

- Concentration measurements are affected by air density fluctuations.

- The effect of pressure fluctuations is small according to the test method proposed by Lee and Massam, so atmospheric pressure is assumed constant in this study.

Lee, X. and Massman, W. J (2011) A Perspective on Thirty Years of the Webb, Pearman and Leuning Density Corrections, Bound-Lay Meteorol.

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◆The correction of Prototype-7700 flux data

- The Prototype-7700 flux data was corrected for density fluctuations and spectroscopic effects at the same time

$$F_c^{\mathrm{corr}} = A\left\{\overline{w'\rho_{\mathrm{cm}}'} + B\mu\frac{\overline{\rho_{\mathrm{cm}}}}{\overline{\rho_{\mathrm{a}}}\mathrm{L}}\mathrm{LE} + C\frac{(1+\mu\sigma)\overline{\rho_{\mathrm{cm}}}}{\overline{\rho_{\mathrm{a}}}c_p\overline{T}}H\right\} \quad (6)$$

The coefficients A, B and C are obtained from look-up tables distributed with the instrument.

A: 0.94~ 0.99

B: 1.42~ 1.46

C: 1.21~1.34

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◆The correction of RMT-200 flux data

- In a closed-path gas analyzer temperature fluctuations in the sample gas are damped while the gas is transported in the long tube, the spectroscopic effects and density fluctuation caused by temperature fluctuations may be neglected.

- For RMT-200 the spectroscopic effects were corrected by adding water vapor flux multiplied with certain factor b_{ct} to the measured trace gas flux.

$$F_c^{\mathrm{SP}} = F_c^{\mathrm{meas}} + b_{\mathrm{ct}} \frac{M_c}{M_{\mathrm{v}}\mathrm{L}} \mathrm{LE} \qquad (10)$$

- The instrument specific coefficient b_{ct} was adopted from Tuzson with some modifications, LI-7000 H_2O measurements were used to correct RMT-200 CH_4 flux data.

Tuzson, B et al (2010) Field intercomparison of two optical analyzers for CH_4 eddy covariance flux measurements. Atmospheric Measurement Techniques.

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The correction of G1301-f and TGA-100A

- For G1301-f the corrections were performed using the method and coefficients presented in Chen et al. They use second order polynomial function which describes the effect of H_2O on methane concentration measurements.

- Closed-path gas analyzer TGA-100A was connected to dryer and therefore the CH_4 measurements were free of any interference from H_2O and these corrections were not needed.

Chen, H. et al (2010) High-accuracy continuous airborne measurements of greenhouse gases (CO_2 and CH_4) using the cavity ring-down spectroscopy (CRDS) technique. Atmospheric Measurement Techniques.

◆ 2 Materials and methods

- 2.1 Site description
- 2.2 Eddy covariance method
- 2.3 Random error estimations method
- 2.4 Gap filling procedure

The standard deviations of the covariances were calculated according to method proposed by Finkelstein and Sims

$$\sigma_F = \sqrt{\frac{1}{n_s}\left[\sum_{p=-m}^{m} \hat{\gamma}_{c,c}(p)\,\hat{\gamma}_{w,w}(p) + \sum_{p=-m}^{m} \hat{\gamma}_{w,c}(p)\,\hat{\gamma}_{c,w}(p)\right]} \quad (11)$$

Absolute value for fractional flux error describing the standard deviations as a fraction of the covariance calculated as:

$$\mathrm{AFFE} = \left|\frac{\sigma_F}{\overline{\overline{w'\chi_c{}'}}}\right| \quad (14)$$

Random uncertainty related to instrumental noise (inst) was estimated with a method proposed by Billesbach.

$$\sigma_{\mathrm{inst}} = \frac{1}{n_s}\sum_{i=1}^{n} w'(i)\,\chi_c{}'_{\mathrm{shuf}}(i) \quad (15)$$

Finkelstein, P et al (2001) Sampling error in eddy correlation flux measurements. J. Geophys. Res.-Atmos

Billesbach, D. et al (2011) Estimating uncertainties in individual eddy covariance flux measurements: A comparison of methods and a proposed new method. Agr. Forest Meteorol

◆ 2 Materials and methods

- 2.1 Site description
- 2.2 Eddy covariance method
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- In this study, methane flux was parameterized using peat temperature by assuming an exponential dependence.

$$F_{CH_4,\,daily} = ab^{(T_{p,\,daily}-10)/10} \qquad (16)$$

$F_{CH4,\,daily}$ is the average daily methane flux, mg m^{-2} h^{-1}

$T_{p,\,daily}$ is peat temperature (℃) at 35 cm depth

a = 1.88 ± 0.03

b = 5.34 ± 0.22

Conrad, R et al (1989) Control of Methane Production in Terrestrial Ecosystems. John Wiley & Sons Ltd, Chichester.

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◆3 Results

- 3.1 Data coverage
- 3.2 Spectral characteristics
- 3.3 Random error estimation
- 3.4 Systematic error estimation
- 3.5 Diurnal variation and CH_4 flux magnitude

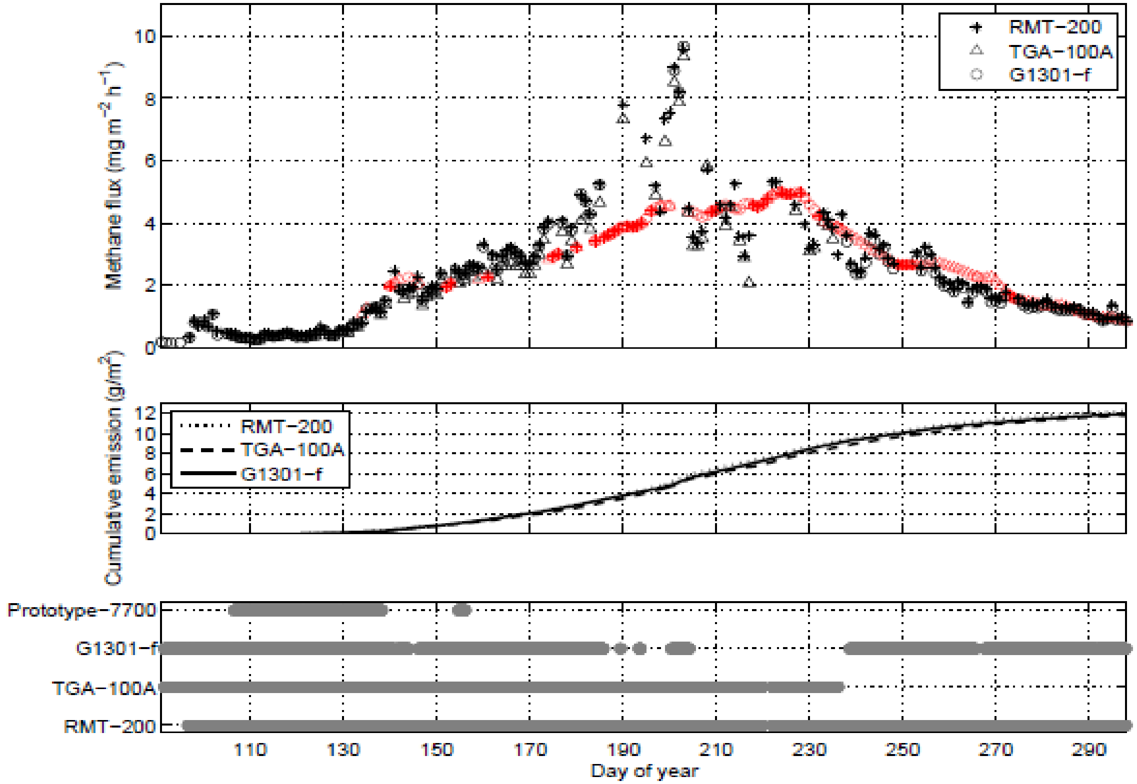

Fig.2 upper part: Gap filled daily averaged methane flux

- middle part: cumulative methane emission
- bottom part: the methane gas analyzers were working

- The parameterization is not able to capture the high flux periods, and around day 205 mean daily methane is sudden drop, and Rinne et al (2007) reported similar phenomenon in their study which was carried out at the same site. The CH_4 flux measured at MLW also has the phenomenon.

Riutta, T. et al (2007) Spatial variation in plant community functions regulates carbon gas dynamics in a boreal fen ecosystem. Tellus Series B.

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Table 2. Amount of data obtained between 17 April and 17 May

	RMT-200	G1301-f	TGA-100A	Prototype-7700
Data (points)	1178	1173	1141	1045
Data (%)	82	81	79	73
Flag 0 (%)	77	77	61	56
Flag 1 (%)	4	3	13	12
Flag 2 (%)	1	1	5	5

- Flags 0, 1 and 2 represent data with good, mediocre and bad quality according to criteria proposed by Foken and Wichura.

Foken, T. and Wichura, B (1996) Tools for quality assessment of surface based flux measurements. Agr. Forest Meteorol.

◆3.2 Spectral characteristics

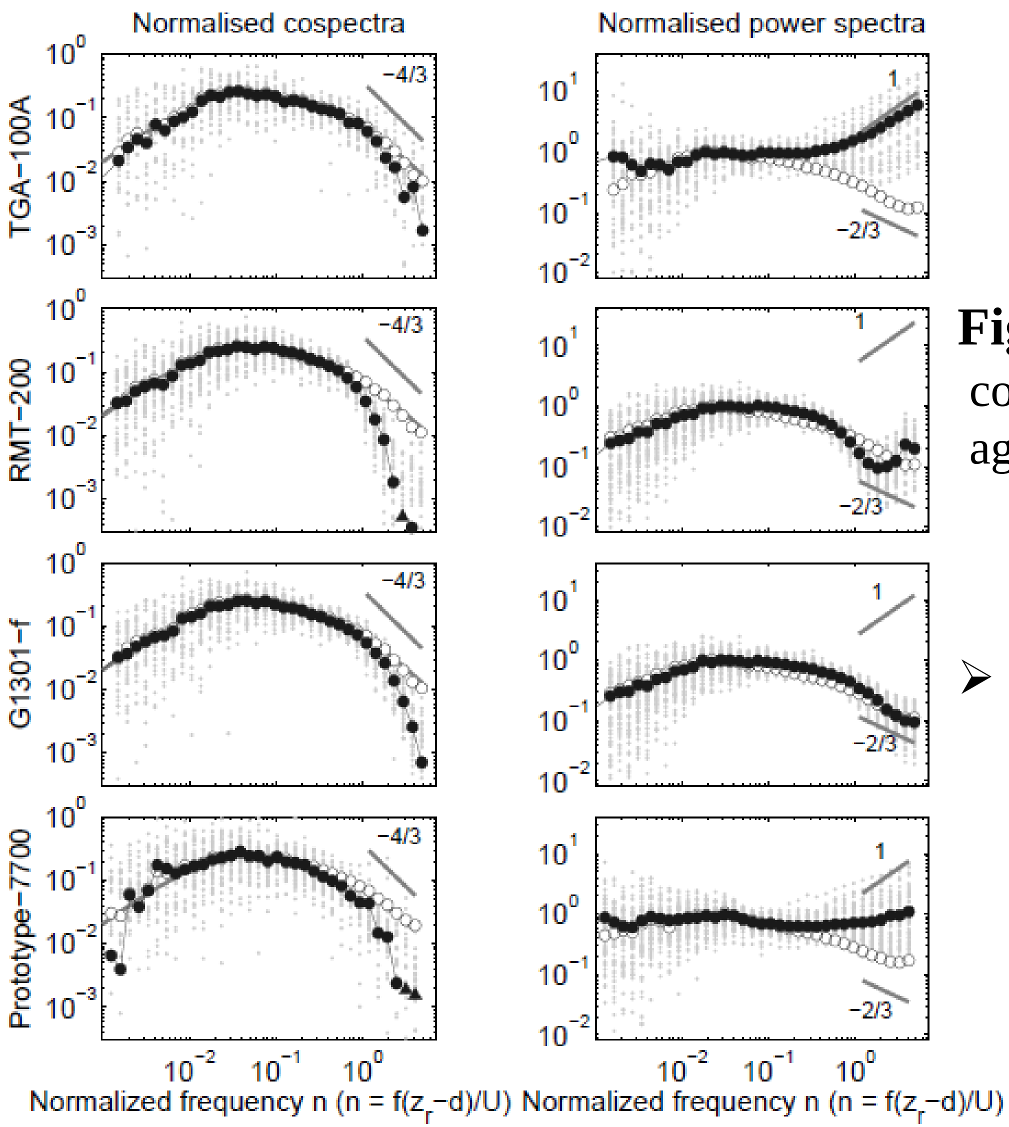

Fig. 3 Frequency weighted, normalized cospectra and power spectra plotted against normalized frequency n.

- The ensemble averaged methane and temperature cospectra and power spectra are shown with black and white dots, respectively.

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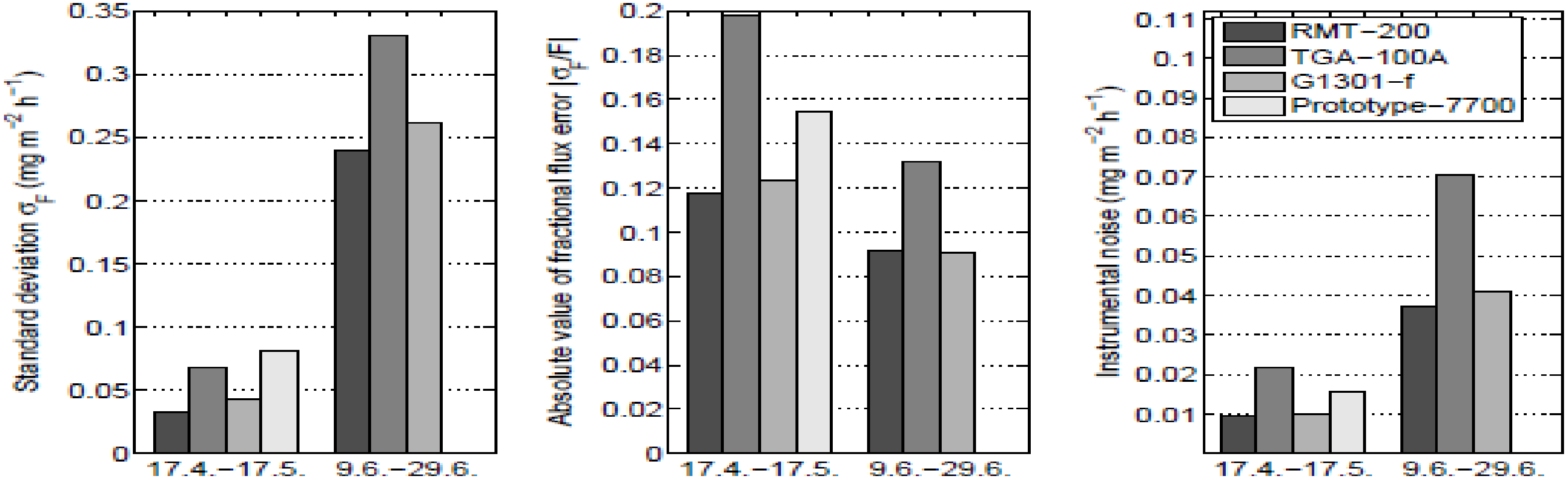
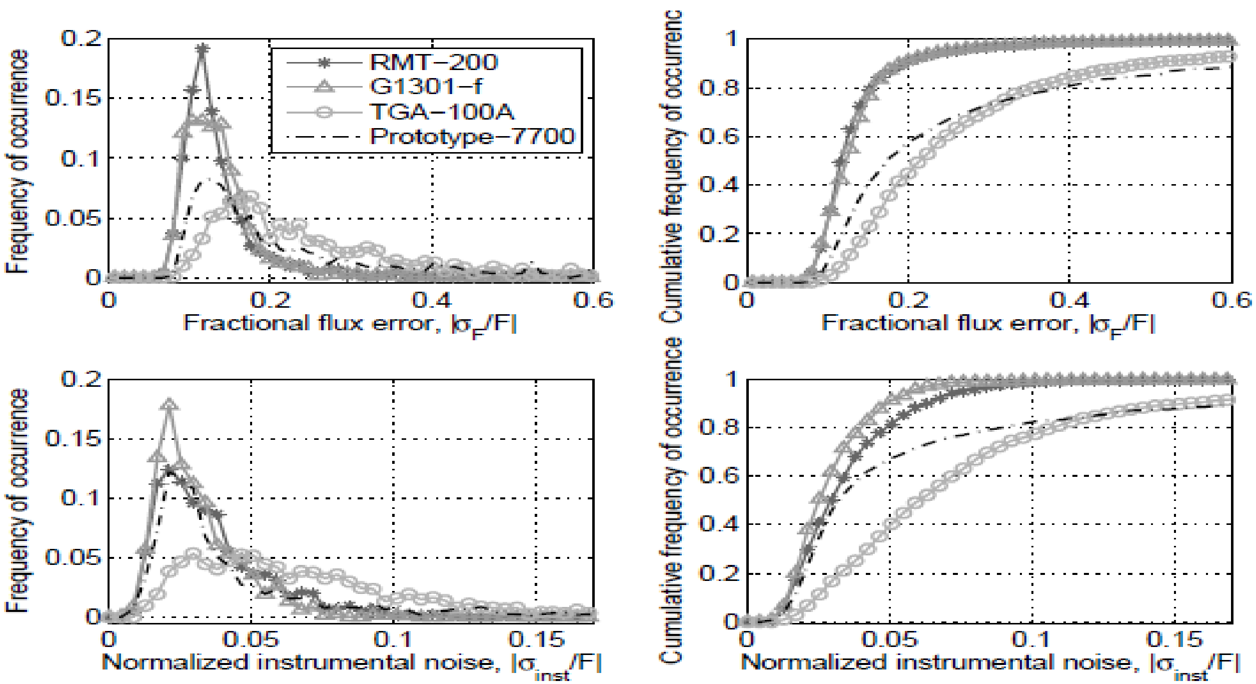

Standard deviation σ_F (mg m^{-2} h^{-1})
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
17.4.–17.5.
9.6.–29.6.
Absolute value of fractional flux error $|\sigma_F/F|$
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
17.4.–17.5.
9.6.–29.6.
Instrumental noise (mg m^{-2} h^{-1})
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
17.4.–17.5.
9.6.–29.6.
RMT–200
TGA–100A
G1301–f
Prototype–7700


Frequency of occurrence
0.2
0.15
0.1
0.05
0
RMT–200
G1301–f
TGA–100A
Prototype–7700
0
0.2
0.4
0.6
Fractional flux error, $|\sigma_F/F|$
Cumulative frequency of occurrenc
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
Fractional flux error, $|\sigma_F/F|$
Frequency of occurrence
0.2
0.15
0.1
0.05
0
0
0.05
0.1
0.15
Normalized instrumental noise, $|\sigma_{inst}/F|$
Cumulative frequency of occurrence
1
0.8
0.6
0.4
0.2
0
0
0.05
0.1
0.15
Normalized instrumental noise, $|\sigma_{inst}/F|$

◆3.4 Systematic error estimation

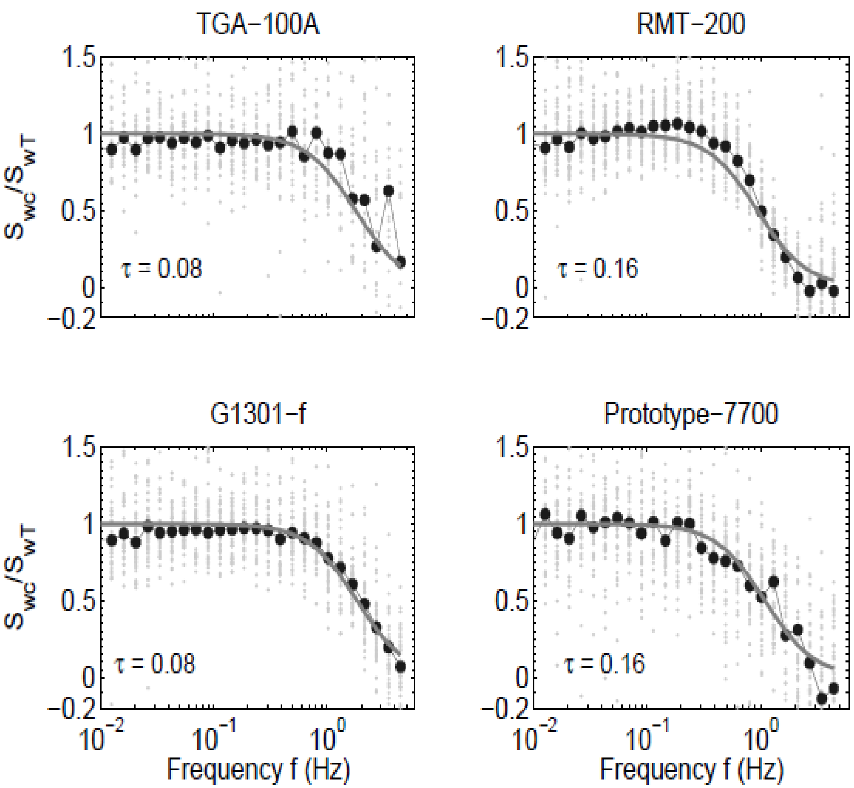


Fig. 6. Transfer function determined from measured cospectra

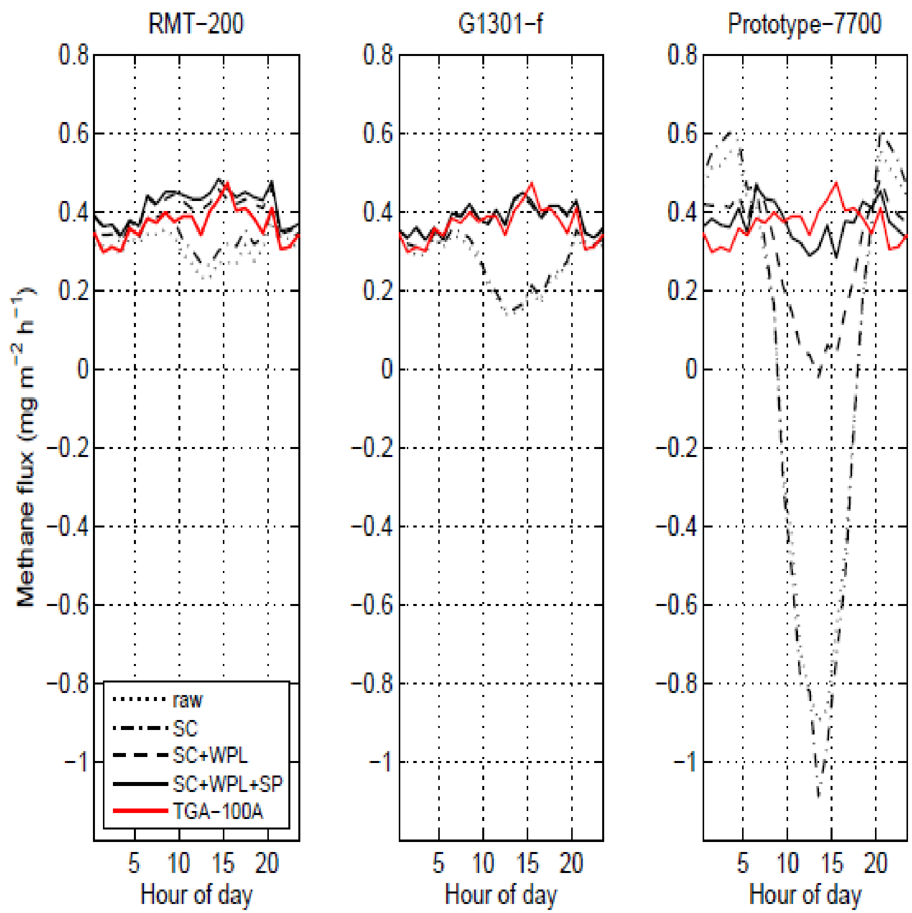


Fig. 7. Diurnal variations of gas analyzers

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Table 3. Magnitude of spectral corrections given as percentages of raw uncorrected covariance

	RMT-200	G1301-f	TGA-100A	Prototype-7700
All data (%)	11.1	5.1	5.4	3.5
Daytime (%)	12.1	5.8	6.2	−3.6
Night time (%)	9.1	4.0	4.1	7.3

Table 4. WPL terms and spectroscopic correction given as percentages of the uncorrected raw covariance

		RMT-200	G1301-f	Prototype-7700
All data	WPL terms (%)	15.3	21.1	80.1
	Spectroscopic correction (%)	3.2	0.9	23.6
Daytime	WPL terms (%)	23.9	38.4	105.1
	Spectroscopic correction (%)	5.0	1.2	31.8
Night time	WPL terms (%)	4.5	6.9	−27.9
	Spectroscopic correction (%)	0.9	0.6	−8.5

Table 5. Average difference between methane flux obtained from one instrument and mean flux obtained from the four instruments between 17 April and 17 May

(The mean value is 0.415mg m^{-2} h^{-1})

	RMT-200	G1301-f	TGA-100A	Prototype-7700
Flux ($mg\,m^{-2}\,h^{-1}$)	0.448	0.424	0.395	0.379
Difference ($mg\,m^{-2}\,h^{-1}$)	0.037	0.012	−0.017	−0.032
Relative difference (%)	8.2	2.9	−4.2	−8.6

Table 6. Average difference between methane flux obtained from one instrument and mean flux obtained from the four instruments between 9 June and 29 June

(The mean value is 3.007mg m^{-2} h^{-1})

	RMT-200	G1301-f	TGA-100A
Flux ($mg\,m^{-2}\,h^{-1}$)	3.159	3.104	2.759
Difference ($mg\,m^{-2}\,h^{-1}$)	0.151	0.097	−0.248
Relative difference (%)	4.8	3.1	−9.0

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◆3.5 Diurnal variation and CH_4 flux magnitude

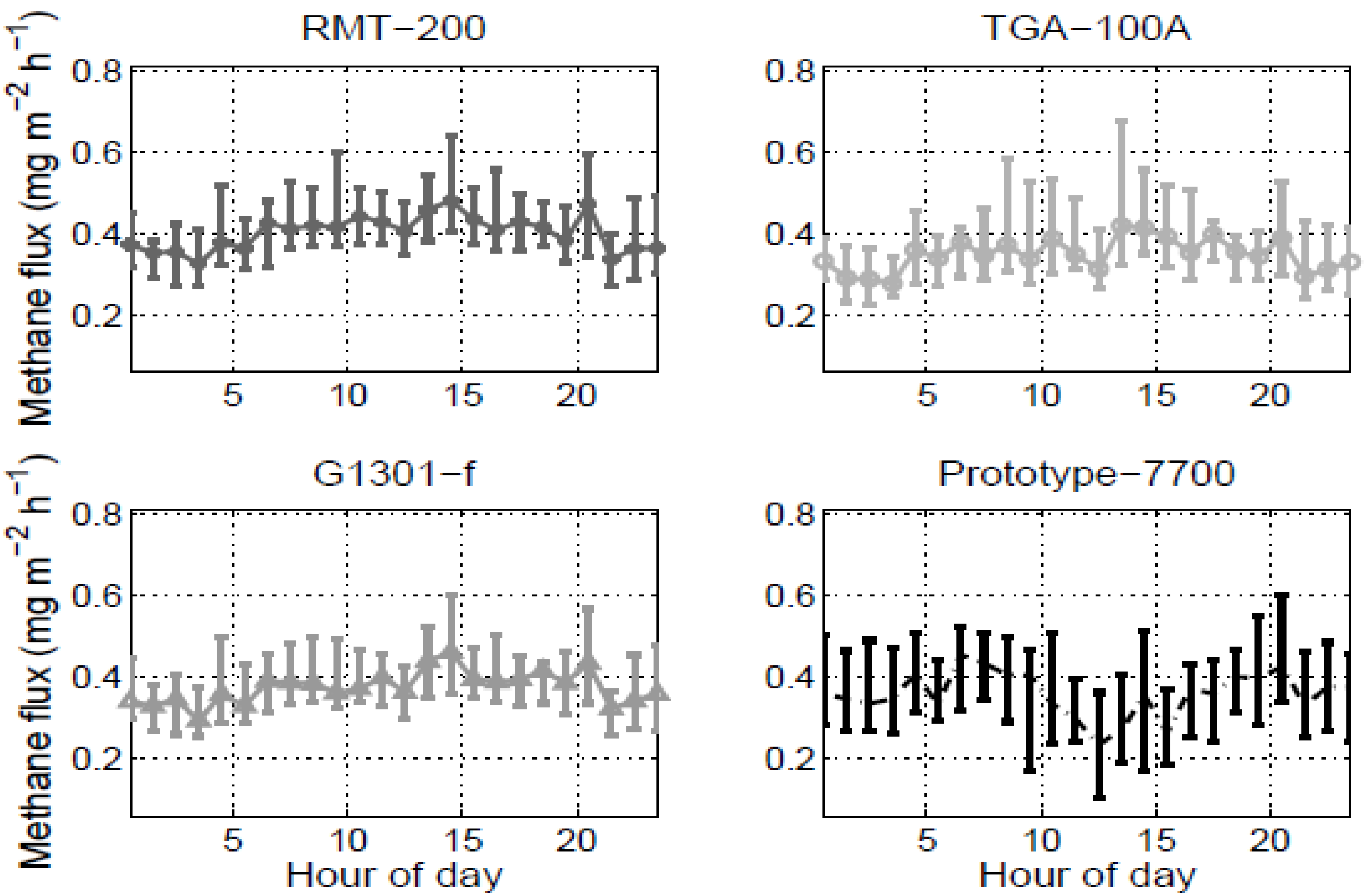

Fig. 8 Median diurnal variation of final fully corrected methane flux obtained from the four methane gas analyzers

◆4 Discussion and Summary

Discussion

- Concerning the random errors and instrument noise, the RMT-200 and G1301-f had on average the best performance

- Speaking of signal attenuation, the three closed-path instruments had the attenuation generally in the range that can be expected for closed-path design, however, The attenuation was larger from Prototype-7700.

- In terms of density and spectroscopic corrections, the open-path Prototype-7700 measurements had large WPL terms as expected for an open-path design.

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Summary

- All four gas analyzers performed quite well, and have proven suitable for eddy covariance measurements of methane flux at the study site.
- The observed differences were due to multiple factors, including instrument performance, instrument design, stage of instrument development, experimental setup, data processing, and available data coverage.
- Methane fluxes obtained with the four instruments were not significantly different from each other.
- In terms of field performance, the RMT-200 was the overall best performer, while the Prototype-7700 is a practical choice for measurement sites in remote locations.

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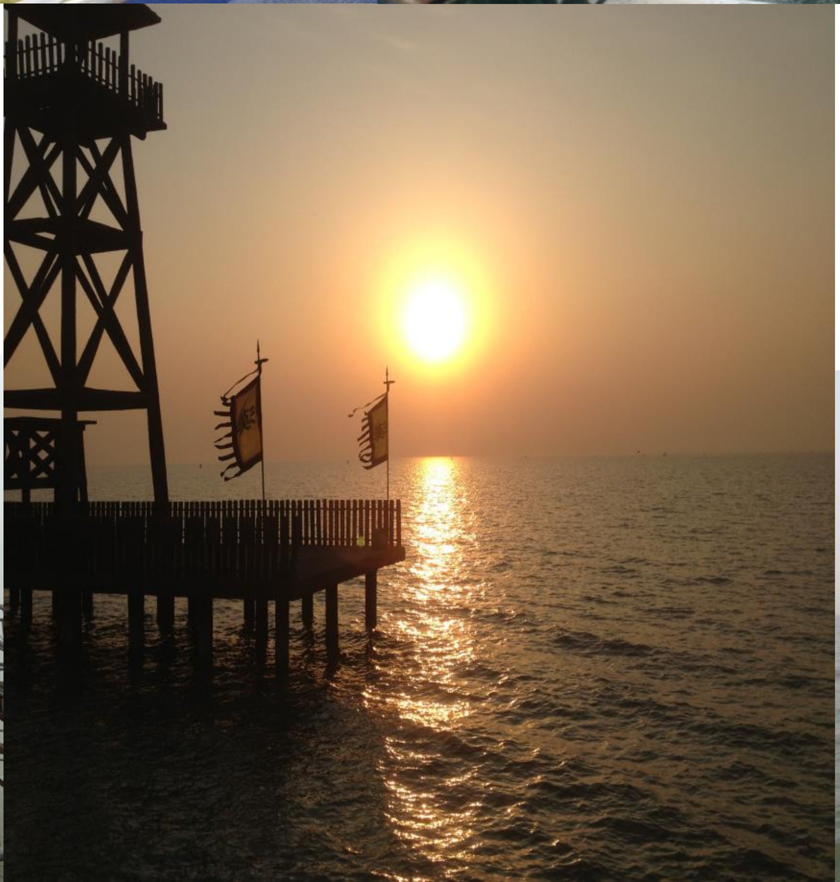
The end



Thank you