

An improved gas chromatography for rapid measurement of CO₂, CH₄ and N₂O

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Abstract: Combining improved injector, gas line and valve-driving modules, a GC equipped with FID and ECD, could simultaneously measure CH₄, CO₂ and N₂O in an air sample within 4 min. Test results showed that the system has high sensitivity, resolution and precision; the linear response range of the system meets the requirement of *in situ* flux measurements. Thus, the system is suitable for monitoring fluxes of main greenhouse gases in terrestrial ecosystem since it is easy to use, efficacious, stable and reliable to collect data.

Keywords: GC; valve; emission of greenhouse gases; ecosystem

Introduction

According to the IPCC 2001 report, the land-atmosphere carbon flux is -1.4 ± 0.7 PgC/a. Terrestrial ecosystems are currently acting as a global sink for carbon (IPCC, 2001). The land-atmosphere carbon flux estimated from atmospheric observation comprises the balance of net CO₂ release due to land-use changes and CO₂ uptake by terrestrial systems. But the uptake capacity of terrestrial ecosystem varies due to changes in climate and land-use, and the accuracy of the estimate is restricted due to the limited number of available *in situ* measurements.

CH₄ is the second important greenhouse gas after CO₂; it is also involved in tropospheric ozone chemistry. The atmospheric concentration of CH₄ has increased from about 1520 ppb in 1978 to 1745 ppb in 1998. Although the major sources of atmospheric methane have probably been identified, some of the sources such as natural wetlands and rice land are poorly constrained due to the difficulty in assessing the global emission rates of the biospheric sources. As for CO₂ also the biosphere atmosphere exchange of CH₄ needs more continuous and intensive observations to further reduce current uncertainties of the sink and source strength of terrestrial ecosystems for atmospheric CH₄.

N₂O is another important greenhouse gas in the earth atmosphere. Soil used for agriculture or forestry as well as grasslands are important sources for atmospheric N₂O. The emission strength of soils is highly influenced by anthropogenic activities, but this change is difficult to be assessed. In the past few decades many researchers carried out a wide variety of

measurements of *in situ* N₂O fluxes, but the comparability and assessment of results remained difficult due to the differences in applied methods.

Micrometeorological methods and chamber methods are common employed methods to measure greenhouse gas fluxes from terrestrial ecosystems. Methods based on micrometeorology include the eddy correlation and the flux gradient methods. These methods have in common that an unperturbed wind should under typical conditions pass over an uniform surface for a certain minimum distance (the fetch). The fetch required for such measurements is in the order of tens to hundred of meters. For eddy correlation methods, the variations in vertical wind and the trace gas-mixing ratio must be measured within 0.1—1.0 s, which place serious constraints on the trace gases measurement such as CH₄ and N₂O. For the flux gradient method, it requires very precise measurement of the small differences in mixing ratios in two or more heights (Galle *et al.*, 1994; Baldocchi *et al.*, 1996). Compared with micrometeorological methods, chamber methods disturbed the turbulent mixing of air at the soil surface so that the measured flux may not represent the natural situation. But it is the only feasible method for flux measurements, typically in forest floor and open areas with small-scale surface variability, and suitable for experiments with various treatments e.g. for research on processes and mechanisms. Of course, the price of chamber methods is another argument compared to expensive micrometeorological methods.

The measuring techniques for greenhouse gases are various. Conventional methods are including alkali absorption technique and infrared technique. Alkali

absorption technique is convenient and easy to use, but it can only measure CO₂ and the veracity and accuracy of this method has been questioned in the past (Jensen *et al.*, 1996; Myeong *et al.*, 2002). Measurements by infrared gas analysers is rapid and sensitive, especially the application of Fourier transform IR system (Galle *et al.*, 1994). But the equipment is expensive, difficult to use and not well suited for field studies or locations where necessary technique and maintenance support are not readily available. With the development of gas chromatographs (GC's), an effective tool for the analysis of greenhouse gas concentrations in air samples became available which is characterized by high sensitivity, stability and convenience to use. Many researchers have applied GC to analyse CO₂, CH₄ and N₂O (Clayton *et al.*, 1994; Khalil *et al.*, 1998; Zheng *et al.*, 1998, 2002). Combined with static chamber methods, GC has become one of the classical techniques to measure fluxes of greenhouse gases from terrestrial ecosystems. Commonly, most application where GC techniques are used concentrate on the measurement of one or two compounds, usually CH₄ and N₂O, or CO₂ and N₂O. Most GC systems are not effective enough to get all information of air samples, so that a lot of efforts needed for sampling is wasted. Loftfield had described a GC system that detected CH₄ with flame ionization detector(FID) and detected CO₂, N₂O with the same detector—an electron capture detector (ECD)(Loftfield *et al.*, 1994). But the sensitivity for CO₂ was not perfect and the disturbance of O₂ was still

a big problem. Here we describe an improved system with newly designed sampling and valve-driving modules for GC application, which allows the simultaneous detection of CH₄, CO₂ and N₂O in an air sample within 4 min using FID and ECD detectors. Test results presented here show that the system has high sensitivity, resolution and precision; the linear response range of the system meets the requirement of *in situ* flux measurement. Examples are provided in which the system was employed in different terrestrial ecosystems such as forest floor, grassland, wetland and cropland throughout China for measurements of the biosphere-atmosphere exchange of CH₄, CO₂ and N₂O.

1 Materials and methods

1.1 Gas chromatograph

A gas chromatograph (Agilent 4890D), equipped with flame ionization detector (FID) and electron capture detector (ECD), was linked to two 6-port, one 10-port and one 4-port pneumatically operated two-position valve(Valvo Instruments Co., USA). The two 6-port valves are used as sample injectors for CH₄ and CO₂, the 10-port valve incorporated with sample loop was used for the injection of N₂O and back flush, the 4-port valve was used to switch different gas lines to the ECD. All the valves are driven by two 4-way solenoid valves (120 VAC, Valvo Instruments Co. USA). Four packed columns are used; details are shown in Table 1. Other accessories such as mass flow controllers, press gauge and carrier gas filters are conventional market products(all made in China).

Table 1 GC parameters

Aimed compound	CH ₄	CO ₂	N ₂ O
Column	Col ₁ : SS-2 m×2 mm. packed with 13XMS (60/80 mesh) *	Col ₂ : SS-2 m×2 mm packed with porapak Q(60/80 mesh)	Col ₃ : SS-1 m×2 mm; packed with porapak Q(80/100) Col ₄ : SS-3 m×2 mm; packed with porapak Q(80/100 mesh)
Carrier gas/flow rate, cm ³ /min	N ₂ (99.999%)/30	N ₂ (99.999%)/25	N ₂ (99.999%)/25
Oven temp., °C	55	55	55
Converter/temp., °C	—	Nickel catalyst/375	—
Detector/temp., °C	FID/200	FID/200(H ₂ , 30 cm ³ /min; Air, 400 cm ³ /min)	ECD/330
Air and H ₂ flow rate, cm ³ /min	Air, 400 H ₂ , 30	Air, 400 H ₂ , 30	—
Retention time, min	1.75	1.4	3.5

Notes: *Material-length × inner diameter; packing material(mesh); SS: stainless steel

1.2 Structure and principle of analysis system

To measure CO₂, CH₄ and N₂O emissions simultaneously, the flow of carrier gases of a conventional GC must be modified. The auto-sampling assembled module, which have obtained

national patents (Patent NO. ZL92100938.0 and ZL96249356.2) was developed by the corresponding author in 1992 and 1996, respectively. The system's basic principle is that a computer program sends instructions to control electronic circuit, gas flow

direction and receive signals; solenoid valves select "normal open" or "normal close" to introduce the direction of compress air flow, so as to control the process of auto-sampling, analyzing and back-flushing. The system consists of a gas supply section I, auto-sampling section II, analyzing and detecting section III. Details of operating and program are as followed:

Section I include gas cylinders, air compressor and filters. Gas cylinders supply high purity(99.999%) nitrogen and hydrogen; air compressor supplies dry and pure air. After filtered by molecule sieve to eliminate trace moisture and hydrocarbons, high purity nitrogen is divided into 2 pathways, one is subdivided into 3 sub-pathways: these are carrier gases for CH₄ analysis (C₁), CO₂ analysis (C₂) and a back-flushing gas stream for the pre-column of N₂O analysis (C₃). The other pathway, in which trace oxygen is reduced to less than 1 μmol/mol through a deoxidizing filter (Chinese Dalian Guang Ming Chemical Factory), is subdivided into 2 sub-pathways, as purge gas for the ECD (C₄) and carrier gas for N₂O analysis (C₅). The compressed air, as produced by an

air generator, after excluded water by silica gel and purified by activated carbon (A₀), is divided into combustion-supporting air for FID (A₁) and air for driving sampling valves (A₂). Hydrogen purified by activated charcoal is supplied as reducer to a nickel catalytic converter, reducing CO₂ into CH₄. It also acts as combustion make-up gas for FID detector. The pressures of all gas supplies are 0.4 MPa.

Section II includes sampling valves, solenoid valves (omitted in Fig.1) and sample loops. Section III includes GC columns, switching valves, methane converter and detectors. CO₂, CH₄ and N₂O analysis is adopted with independent sampling and analysis columns, in which CO₂ and CH₄ analysis is adopted with single-valve-single-column gas line configuration and the use of a FID detector. N₂O analysis is adopted with two-valve-two-column and use ECD alone, 10-port injection and back-flush valve for sampling, and 4-port valve for vent oxygen which will damage ECD; a column 1 m in length for pre-separating and back-flushing, and another column 3 m in length for separating N₂O and O₂ absolutely.

CH₄ analysis: First, when valve 1 (V₁) at "A"

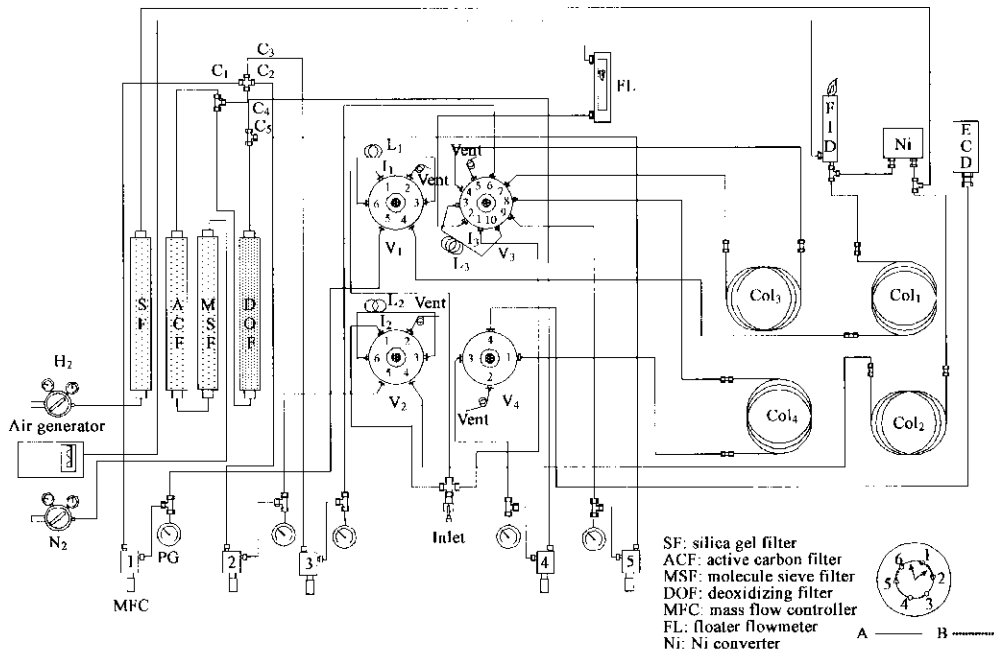


Fig 1 Schematic drawing of CO₂, CH₄ and N₂O analysis gas pathway

position, its ports 2→3, 4→5, 6→1 are interlinked, respectively. Gas samples are injected with a syringe into V₁ from the sample inlet (I₁), and go through ports 1→6 to fill the sample loop (L₁), then go through V₁ ports 3→2, eventually are vented by a float flowmeter (FL). When V₁ moves to "B" position, its ports 1→2, 3→4, 5→6 are interlinked, respectively. The carrier gas (C₁) goes from 5→6 through L₁ to 3→

4, and sweeps samples into GC column 1 (Col₁). The CH₄ in the gas sample detected by FID after it is separated from other components.

CO₂ analysis: The analysis process of CO₂ is similar to CH₄, except for that CO₂ must pass through the methane converter before detected by FID. The CO₂ analysis gas line system consists of I₂, V₂ and Col₂.

N₂O analysis: The analysis of N₂O is significantly different from CO₂ and CH₄ analysis. First, an ECD is chosen as detector for N₂O because an FID cannot detect N₂O. Secondly, since water vapor, CO₂ and CFCs in GC column can raise the base line of ECD, which may result in an instable and fluctuating peak area. Thirdly, abundant O₂ in air samples, which is eluting from the GC column before N₂O, not only oxidize the ECD, but can also reduce the lifetime of the detector. The using of back-flushing systems for N₂O detection was a widely applied technique. In this paper a gas line system named double-valve-double-column sampling, back-flushing, separating and venting is improved, which was developed by the authors in 1994 and 1997 (Wang *et al.*, 1994, 1997). The N₂O, CO₂ and CH₄ analysis gas line systems were integrated together so that one GC can analyze CO₂, CH₄ and N₂O simultaneously. The analytic process of N₂O is described as following: First, when 10-port valve(V₃) at "A" position, its ports 2→3, 4→5, 6→7, 8→9, 10→1 are interlinked, respectively. At same time, sample is loading in loop (L₃), carrier gas No.3 (C₃) is back-flushing the column No.3 (Col₃), and carrier gas No.4 (C₄) is purging the analysis column No.4 (Col₄). Gas samples are injected with a syringe from the inlet No.3 (I₃), go through V₃ ports 1→10 to fill the loop No.3 (L₃), and through ports 3→2, gases oversupplied are vented from a floater flow meter eventually. When V₃ in "B" position, its ports 1→2, 3→4, 5→6, 7→8, 9→10 are interlinked, respectively. The carrier gas No.5(C₅) goes from ports 9→10→L₃ to 3→4, sweeping samples into the column Col₃. O₂ and N₂O in gas samples, which separated from other components, are carried by C₅ into N₂O analysis column (Col₄) through 7→8 while the others (mainly water vapor, CO₂, CFCs etc. which disturbing N₂O detection) still remain in Col₃. Instantly V₃ switches to "A" position while carrier gas No.4(C₄, namely back-flushing gas) carries vapor, CO₂, CFCs etc. through V₃ ports 6→7→Col₃→4→5→vent. Flow direction of C₅ is opposite to C₄ in Col₃. In Col₄, N₂O and O₂ have been separated better. When O₂ flow out Col₄, switching-valve V₄ still in "A" position, its ports 1→2, 3→4 are interlinked, respectively. O₂ is separated from components and vented into ambience along V₄ ports 1→2. After that, V₄ moves back to "B", ports 1→4, 2→3 are interlinked, respectively. Through V₄ ports 2→3, N₂O is eluviated from Col₄, and detected by ECD.

Superiority of this analysis system is that it can separate and detect CH₄, CO₂, and N₂O simultaneously, accurately and quickly. And with a four

way connector, one injection of air sample can be subdivided into three and full three sample loops for CO₂, CH₄, and N₂O, separately. The analysis of the three gases will finish within 4 min. Fig.2 is a picture of the factual system.

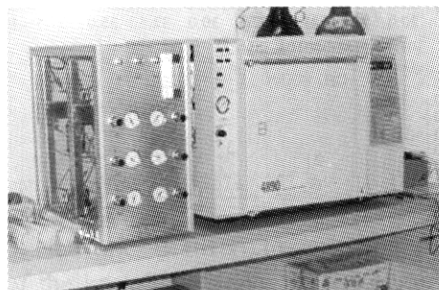


Fig.2 Picture of the improved GC system

2 Calibration and instrument testing

2.1 Chromatographic conditions

When setting analysis parameters, there are three principles which should be followed: (1) the aimed compound should be separated completely and detected exactly; (2) the parameters that analysis needed should be as far away from the terminal set points as possible; (3) the supply of consumable reagents and accessories should be considered. Listed in Table 1 are GC parameters that used in field laboratory.

Under these conditions, CO₂ and N₂O can be separated completely. Comparison of air samples with or without CO₂ absorber show that there is no significant difference of N₂O concentration (<1%). Fig.3 presents a gas graphic acquired under the conditions showed in Table 1.

2.2 Sensitivity and stability test

Under the conditions showed in Table 1, N₂O, CH₄ and CO₂ in gas samples can be separated from other components completely, with high sensitivity and stability. Generally, we use the minimum detection limit of a standard gas as criterion measure of the instrument sensitivity. It is difficult to determine the minimum absolute detection limit for a calibration standard, but it is easy to obtain response factors(RF) for certain compounds. Therefore in the actual tests, we always regard RF as the appraisalment index of instrument sensitivity. RF denotes that a peak area unit represents the concentration of object chemical compound. RF is smaller, instrument responds to chemical compound is more sensitive. Our method of determining RF is as following. First, calibration gases of certain concentration (provided by the National Research Center for CRMs of China) are diluted gradually with static method and are turned into

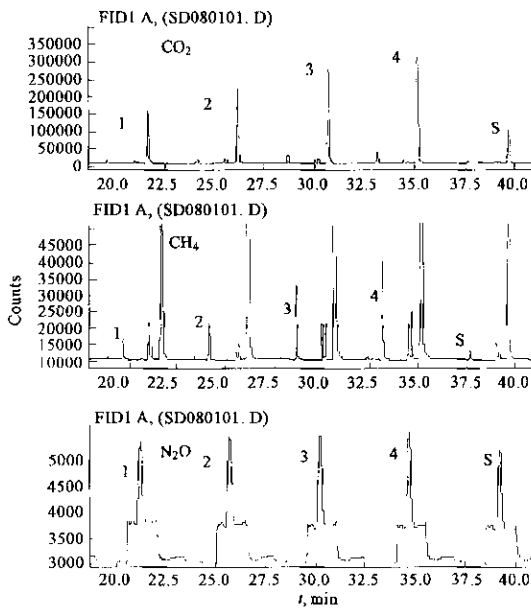


Fig.3 Chromatogram of the improved GC
1, 2, 3, 4: samples of time sequence; S: standard gas

standard sequence. According concentrations and peak areas of standard sequence, RF can be calculated. In identical conditions, synchronous test results show that RFs of CO₂ and CH₄ in Agilent 4890GC are 0.00047 and 0.00032, respectively; RFs of N₂O in low concentration (<3000 × 10⁻⁹ v/v) and high concentration (>3000 × 10⁻⁹ v/v) are 0.069 and 0.093, respectively. It indicates that the analysis system has enough sensitivity to determine CO₂, CH₄ and N₂O accurately, and the absolute sensitivity of ECD is 10 times as high as that of FID.

Stability is also an important index that may imply the property of a GC. CO₂, CH₄ and N₂O are measured by a GC in those conditions showed in Table 1. Results show average RF of CO₂ spanning (356 × 10⁻⁶—4020 × 10⁻⁶) v/v is 0.00047, and coefficient of variation (CV) is 0.07% to 0.20% (9 injections). RF of CH₄ spanning 2.02 × 10⁻⁶—60.6 × 10⁻⁶ v/v is 0.00032, and CV is 0.11% to 0.25%. RFs of N₂O in low concentration (333 × 10⁻⁹—2753 × 10⁻⁹ v/v) and high concentration (3362 × 10⁻⁹—9412 × 10⁻⁹ v/v) are 0.069 and 0.093, respectively, and CV in 3362 × 10⁻⁹—9412 × 10⁻⁹ v/v is 0.31% to 0.48%. Obviously, CVs of CO₂, CH₄ and N₂O are smaller than the level of 1% for our observation. The sensitivity and stability of the instrument completely satisfy the analysis of CO₂, CH₄ and N₂O emission *in situ* terrestrial ecosystem.

2.3 External calibration curve

When CO₂ and CH₄ concentrations in 356 × 10⁻⁶—4020 × 10⁻⁶ v/v and 2.02 × 10⁻⁶—60.6 × 10⁻⁶ v/v (normally, sample concentrations in terrestrial eco-

system will not exceed the upper limit), RFs of CO₂ and CH₄ nearly change less, and their average CVs are 3.01% and 3.16%, respectively. Figs. 4 and 5 indicate that concentration of samples is significantly linear with peak area. CO₂ and CH₄ concentrations of air samples in terrestrial ecosystem can be calculated by external calibration curve. As for N₂O, we can calculate its emission flux by using different kinds of external calibration curves in low concentration and high concentration, respectively (Fig.6).

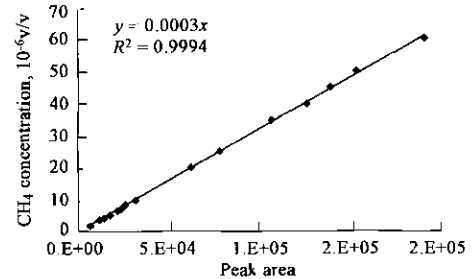


Fig.4 CH₄ standard curve

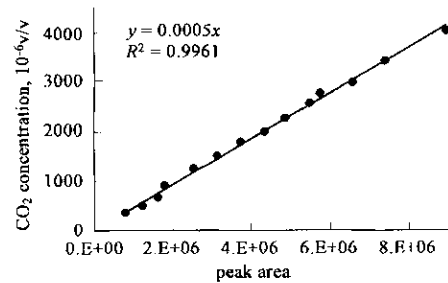


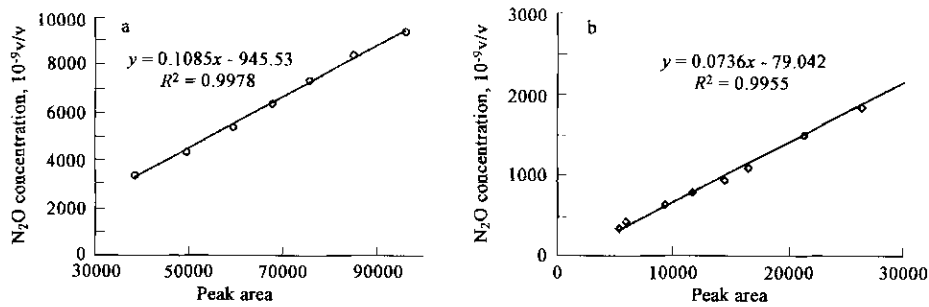
Fig.5 CO₂ standard curve

2.4 Detection limits of emission fluxes

The approach that measures the emission fluxes of GHGs in terrestrial ecosystem by static chamber/GC system is introduced as following. After the chamber is placed on the base that has been installed into the soil and never move during the whole observing season, samples are drawn about 100 ml at 0, 10, 20 and 30 min by labeled syringes. Then samples are collected and carried to the field laboratory, analyzed with the improved GC. Emission fluxes of GHGs are calculated with following equation:

$$F = \frac{M}{V_0} \frac{P}{P_0} \frac{T_0}{T} H \frac{dc}{dt} \quad (1)$$

Where, M is the molecular weight of compound; P_0 is the pressure of standard state, 1013.25 hPa; T_0 is the temperature of standard state, 273.16 K; V_0 is the molecular volume of objective gas in standard state, 22.41 L/mol; H is the height of sampling chamber; P is the actual air pressure while sampling; T is the actual air temperature while sampling; dc/dt is the rate of increase of gas concentration in chamber.

Fig.6 N₂O standard curve

a. high concentrations 3000×10^{-9} — 10000×10^{-9} v/v; b. low concentrations 333×10^{-9} — 2573×10^{-9} v/v

The chromatograms of four samples from the same chamber in time sequence are displayed in Fig.3. Concentrations can be computed by using an external calibration curve.

Analysis precisions of samples are: ± 1.29 $\mu\text{mol/mol}$ for CO₂, ± 32 nmol/mol for CH₄ and ± 5.0 nmol/mol for N₂O under 11 injections. Those concentrations are 524×10^{-6} v/v of CO₂, 2.02×10^{-6} v/v of CH₄ and 333×10^{-9} v/v of N₂O respectively. With precisions and Equation (1), detection limit of a gas flux can be confirmed. The limit is directly proportional to the height of sampling chamber, the atmosphere pressure of observing site; and inversely proportional to the enclosing time and the temperature (denoted by absolute temperature) in chamber. When atmosphere pressure is 1000 hPa and air temperature is 298 K, and chamber height is 50 cm or 100 cm (the two heights usually employed in practice), simultaneously the closing time is 30 min, the flux detection limit of CO₂, CH₄, N₂O are 1.2 or 0.6 mg/(m²·h), 0.004 or 0.002 mg/(m²·h), 0.002 or 0.001 mg/(m²·h), respectively. With this calculation, gas flux limit under other conditions also can be determined.

3 Field application

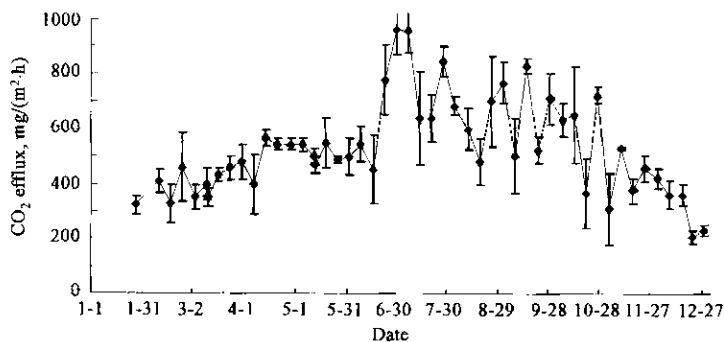
Combined with static chamber system, the GC system described in this paper were installed in 15 field experimental stations of Chinese Ecosystem

Research Network (CERN) to carry out the great project of the knowledge innovation program "Study on Carbon Budget in Terrestrial and Marginal Sea Ecosystems of China" of CAS. The analysis systems have run for more than one year in Inner Mongolia Grassland Ecosystem Research Station, Wuxi Agro-ecological Research Station, Nanjing Station of Jiangsu Province, and Sanjiang Wetland Research Station of Northeast China. In this part, we will show some observed results of different greenhouse gases as received for different terrestrial ecosystems.

From Figs.7 and 8, the magnitude of the CO₂ emissions obtained by this system is reasonable and comparable with results from other investigators (Davidson *et al.*, 1998; Longodz *et al.*, 2002; Myeong *et al.*, 2002). Fig.9 shows the CH₄ flux annual variation from Sanjiang Wetland and the highest value is 21.57 mg/(m²·h). The variation of N₂O emission from wheat field is extremely high from 0 to 1.66 mg/(m²·h)(Fig.10), which is consistent with results from Flessa *et al.*(1995).

4 Conclusions

The improved gas chromatographic system enables the rapid accurate measurement of three greenhouse gases CO₂, CH₄ and N₂O in 4 min with a single sample injection. Test results and *in situ* observations proved it is a useful and efficient tool for

Fig.7 CO₂ flux from tropic rain forest soil in Xishuangbanna(2003)

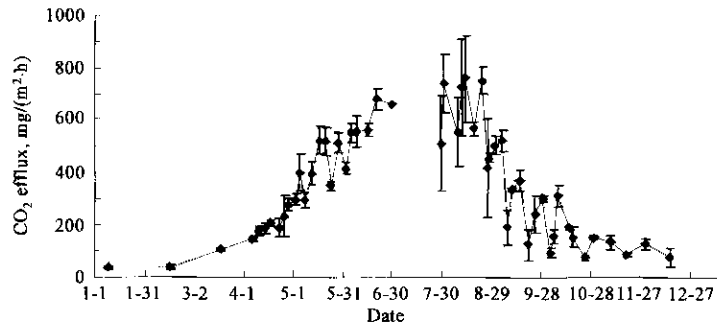


Fig.8 CO₂ flux from boreal temperate forest soil in Changbaishan(2003)

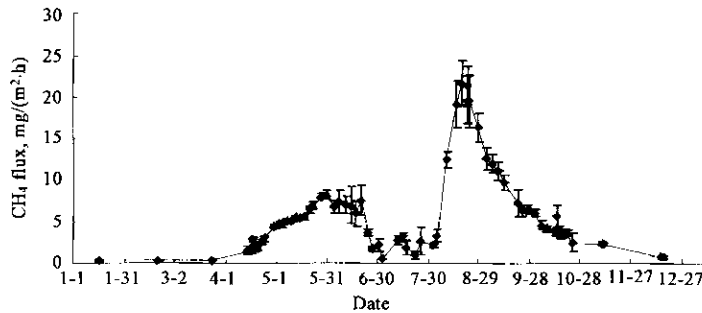


Fig.9 CH₄ flux from wetland in Sanjiang(2003)

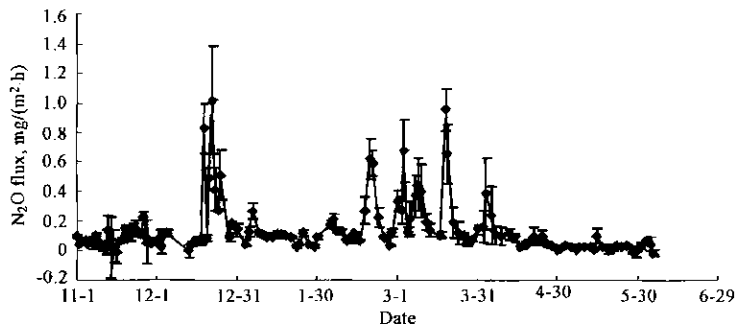


Fig.10 N₂O emissions from soil of wheat field in Wuxi (2002.12—2003.5)

long time observation and studies on greenhouse gases. Compared with other similar systems, the system characterized with higher sensitivity, lower detection limit, perfect stability, and easy operation.

Combined this system with static chamber method, we monitored about 16 sites, 5 kinds of terrestrial ecosystems in China, and the results have got are comparable with results from other investigators.

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