DISMAL SWAMP NATIONAL WILDLIFE REFUGE
MANAGEMENT STUDY
TRANSMITTAL

Date: July 12, 1979

✓ Proposal
___ Amendment
___ Final Report
___ Progress Report - Time Period From Aug., 1979 To Sept., 1983

Permit # _____ (assigned by refuge)

Title of Study Biological Controls on Trace Gas Exchange with the Atmosphere in the Dismal Swamp

Project Supervisor Dr. Robert C. Harriss (Name) Senior Marine Scientist (Title)

M.S. 270, NASA Langley Research Center, Hampton, VA. 23665
Mailing Address Telephone - 804-827-3645

Person(s) Conducting Field Work On The Refuge:

Name	Title	Agency or Institution
Dr. Robert C. Harriss	Senior Scientist	NASA - Langley
Mr. Dan Sebacher	Environmental Chemist	NASA - Langley
Mr. Randy Cofer	Environmental Chemist	NASA - Langley

Cooperators (other agencies or individuals assisting in project)

Name	Title	Agency or Institution
Dr. Frank Day	Ecologist	O.D.U.

Signatures

Robert C. Harriss Submitted By	7/12/79 Date
Robert C. Harriss Project Supervisor	7/12/79 Date
Frank P. Day, Jr. Cooperator (other than Refuge)	8/3/79 Date

Approvals

Ralph M. Turgeon Refuge Manager	8/6/79 Date

Submit all transmittals and reports in duplicate.

All management study proposals must conform to the outline provided by the refuge office.

(OVER)

STUDY PLAN

1. Title of study:

"Biological Controls on Trace Gas Exchange with the Atmosphere in the Dismal Swamp"

2. Objectives.

A. This study will investigate temporal and spatial variations in the concentrations of methane, nitrous oxide, hydrocarbons, and sulfur compounds in the Dismal Swamp.

B. The proposed measurements will be made at sites being used by Old Dominion University scientists for ecological studies. The sources and sinks for atmospheric gases will be studied in relation to the ecology and nutrient cycling dynamics of specific plant communities.

C. The results of this investigation will be used in an assessment of the significance of biological controls on the chemical composition of the Earth's atmosphere.

3. Justification:

Most of the gases that presently cycle in the Earth's atmosphere are controlled, in part at least, by the biosphere. Changes in the input and removal of oxygen, carbon oxides, methane, nitrogen oxides, and certain other gaseous and particulates chemicals are related to the presence and quality of vegetation. Because these biogenic gases are important to understanding processes related to climate and air quality, it is critical to assess how anthropogenic and natural changes in regional and global ecosystems might impact the composition of the atmosphere. Wetland environments are particularly active sites of mineral cycling and gas exchange. Wetlands are also commonly subject to drainage and destruction by populations (e.g., Florida Everglades, Sudan swamps, etc.). The results of this investigation will contribute to a fuller understanding of the significance of freshwater wetlands to the maintenance of environmental quality.

This research area is identified as a top priority in a forthcoming report by the Committee on Planetary Biology and Chemical Evolution of the National Research Council.

4. Procedure:

A. Literature review (Please refer to Attachment A).

B. Data collecting

Quantitative measurements of atmospheric trace gases will be conducted using in situ gas filter correlation analysis (Sebacher, E. I., 1978, Rev. Sci. Instrum. 49: 1520-1525) and

grab samples for standard laboratory analysis by gas chromatography. Air samples will be collected at each of the field sites being studied by Dr. Frank Day. The NASA studies will not require any modification of the Refuge habitat. Measurements will be conducted monthly over a 3-year period to determine seasonal and annual variability in biogenic gas production and consumption.

5. Cooperators:

Old Dominion University
Department of Biological Sciences
Dr. Frank Day

6. Responsibility:

The study will be supervised by Dr. Robert C. Harriss, Senior Marine Scientist, NASA Langley Research Center, Hampton, Virginia 23665. Co-investigators will include Mr. D. I. Sebacher and Mr. W. R. Cofer, both members of the Environmental Chemistry Branch at the Langley Research Center. The NASA investigators will not require any special assistance from Refuge staff.

7. Costs:

This study will not involve any direct costs to the Bureau of Sport Fisheries and Wildlife. The estimated costs are:

F.Y. 1979 - 1.0 MY, $10,000 (R&D)
F.Y. 1980 - 1.5 MY, $20,000 (R&D)
F.Y. 1981 - 1.5 MY, $20,000 (R&D)
F.Y. 1982 - 0.5 MY, $ 5,000 (R&D)

8. Schedule:

Starting date - August 1979
Completion date - December 1982

9. Reports:

Annual progress reports will be prepared in June of each year. Information on the NASA research will be available to the Bureau of Sport Fisheries and Wildlife and Dismal Swamp National Wildlife Refuge staff at any time during the study.

10. Publications:

The results of the NASA research will be published in appropriate professional journals.

11. Submitted by: Robert C. Harriss
Dr. Robert C. Harriss
Principal Investigator

12. Approved by: _____

Date: _____

13. Cooperators Endorsements: Frank P. Day, Jr.

Date: 8/3/79

Attachment A

REFERENCES

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National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia
23665

NASA

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Reply to Attn of: 270

MAY 1 1980

Mr. Ralph M. Keel, Refuge Manager
Dismal Swamp National Wildlife Refuge
P.O. Box 349
Suffolk, VA 23434

Dear Mr. Keel:

This letter is to request renewal of our research permit for 1980. A completed Management Study Transmittal form and a Progress Report for 1979 research results are enclosed.

We appreciate the continued cooperation of the Dismal Swamp National Wildlife Refuge staff.

Sincerely,

Robert C. Harriss

Robert C. Harriss
Senior Marine Scientist
MATD

2 Enclosures

DISMAL SWAMP NATIONAL WILDLIFE REFUGE
MANAGEMENT STUDY
TRANSMITTAL

Date: April 22, 1980

___Proposal
___Amendment
___Final Report
✓Progress Report - Time Period From Aug., 1979 To March, 1980

Permit # _____ (assigned by refuge)

Title of Study Biological Controls on Trace Gas Exchange with the Atmosphere in the Dismal Swamp

Project Supervisor Dr. Robert C. Harriss (Name) Senior Marine Scientist (Title)

MS 270, NASA Langley Research Center, Hampton, VA. 23665
Mailing Address

Person(s) Conducting Field Work On The Refuge:

Name	Title	Agency or Institution
Dr. Robert C. Harriss	Senior Marine Scientist	NASA - Langley
Mr. Dan Sebacher	Environmental Chemist	NASA - Langley

Cooperators (other agencies or individuals assisting in project)

Name	Title	Agency or Institution
Dr. Frank Day	Ecologist	O.D.U.

Signatures

Robert C. Harriss (Submitted By)	4/22/80 (Date)
Robert C. Harriss (Project Supervisor)	4/22/80 (Date)
Cooperator (other than Refuge)	Date

Approvals

Refuge Manager	Date

Submit all transmittals and reports in duplicate.

All management study proposals must conform to the outline provided by the refuge office.

(OVER)

Permit Number: _____

Submitted By: _____

Date: _____
Mo. Day Year

NARRATIVE: (For proposal and final report, give brief abstract below and attach this transmittal form to full proposal or final report. For progress report and amendment, give brief statement below - no other report is needed.)

Quantitative techniques for the measurement of gaseous emissions from wetland soils have been developed in the Dismal Swamp. The emission measurement program will continue in the coming year.

TRIP REPORT SUMMARY: (To be completed with progress & final reports)

	Reporting Month	No. Trips To Refuge	Average No. Hrs. Per Trip	Average No. People	Purpose of Trips
	Jan.				
	Feb.				
	Mar.				
	Apr.				
	May				
	June				
	July				
36	Aug.	3	6	2	Measurement of gaseous emissions from soils.
36	Sept.	3	6	2	" " " " " "
20	Oct.	2	5	2	" " " " " "
20	Nov.	2	5	2	" " " " " "
8	Dec.	1	4	2	" " " " " "

120 = Total Activ. Hrs. //

PROGRESS REPORT

A CONTINUOUS SAMPLING AND ANALYSIS SYSTEM FOR MONITORING METHANE FLUXES FROM SOIL AND WATER SURFACES TO THE ATMOSPHERE

By

Daniel I. Sebacher and Robert C. Harriss
NASA Langley Research Center
Hampton, Virginia 23665

April 24, 1980

A Continuous Sampling and Analysis System for Monitoring Methane Fluxes from Soil and Water Surfaces to the Atmosphere

Daniel I. Sebacher and Robert C. Harriss
NASA Langley Research Center
Hampton, Virginia

INTRODUCTION

Measurements of mass-transfer rates at air-water and air-sediment interfaces are essential if we are to understand the critical problems of atmospheric chemistry, marine chemistry, and geochemical cycles. These fluxes are not measured directly, but are generally inferred from measurements of gas concentration increases with time in a chamber placed over the interface to trap emitted gases. A number of gas-transfer studies have been made using similar techniques for the nitrogen species,[1,2,3] methane[4,5] and various carbon species.[6,7,8] These studies have involved the use of chambers that either completely enclose a soil area (closed chambers) or chambers that are open to artificially induced air flow from outside (open chamber). After the chamber has set over the surface for some arbitrary time, an air sample is removed for analysis to determine the flux rate. For the open chamber, the gas flux calculation must include the effects of dilution by the air entering the chamber as well as the measured concentration change as a function of time within the chamber.

There are drawbacks associated with using any flux measurement systems, and some of the problems have been discussed in the literature. Criticisms of chamber techniques involve their influence on natural air turbulence and on natural soil and air temperatures.[9,10] These factors influence concentration gradient changes within the soil profile, and are often a function of the type and the size of the chamber.[1]

With these problems in mind, we have designed a system for measuring methane fluxes which: (1) is portable, (2) has sufficeint analytical sensitivity (0.01 ppm CH_4), (3) is a continuous monitoring system, and (4) has a fast time response (< 1 second). This system can use either an open or closed chamber which is integrated with a Gas-Filter-Correlation analyzer (GFC) so that the system can be evaluated for flux monitoring as a function of time. Natural methane fluxes have been measured in the Great Dismal Swamp and from salt water marshes in southeastern Virginia. These measurements show the effects of soil disturbances on methane flux measurements and illustrate the importance of continuous sampling for the design of flux monitoring techniques for natural gas emissions.

EXPERIMENTAL METHODS

Flux Measuring System

Continuous monitoring and analysis of methane fluxes from soil and water surfaces were achieved using the system illustrated schematically in figure 1. Concentration gradient changes within the soil profile were

minimized by using a relatively large ratio of chamber volume to the enclosed soil area.[1] Optional operation modes for the chamber consists of either the closed chamber mode (flowmeter valves closed) or open chamber mode (flowmeter valves open and pump on). Dilution of the chamber gases by outside air can be varied by controlling the valve downstream of the flowmeter. A circulation fan inside the chamber maintains uniform mixing of the soil/water flux gases and chamber air. Generally, the chamber air is not purged with hydrocarbon free air at the beginning of a test, therefore, the CH_4 concentration starts at ambient levels. Flexible hoses connect the chamber to the GFC sampling cell. A blower type pump circulates air from the chamber through a silica gel filter then through the GFC sampling cell and back to the chamber. The silica gel filter served to remove water vapor from the sampled gas since water vapor is an interfering gas for infrared absorption instruments like the GFC. Laboratory tests show no degradation of the methane signal when a silica gel filter is used and no significant changes occur in the chamber relative humidity. An electronic signal processor converts the GFC absorption signal to a d.c. voltage level calibrated as a methane concentration which is printed on a strip recorder as a function of time. Methane fluxes are calculated directly from this trace of methane concentration change with time since the volume of the chamber and the interface area are known.

Gas-Filter-Correlation Analytical System

A schematic of the methane detector is shown in figure 2. This Gas-Filter-Correlation analyzer (GFC) is a nondispersive infrared absorption instrument which uses a concentrated sample of gas to provide a selective filter for radiation absorbed in a gas mixture containing the specified gas. IR radiation from the source passes through the multipass sampling cell where it is spectrally absorbed by the gas specified (CH_4) and other absorbing gases in the sample. Upon leaving the sampling cell, the IR beam is focused by a lens onto a detector after being sent through a bandpass filter and alternately passed through the specifying cell and the reference cell and is chopped as the cell rotates. When the radiation passes through the reference cell, it is not attenuated further; but when it passes through the specifying cell (concentrated CH_4), it is strongly attentuated in the spectral interval of the absorbing CH_4 spectral lines. Therefore, a modulated chopped signal of three frequencies is generated by the detector as shown in figure 2. As the concentration of the gaseous CH_4 is increased in the sampling cell, the amplitude of the modulated signal (21 Hz) will change, and this change in magnitude is calibrated to the concentration change of CH_4 to be detected in the sampled air.

A narrow bandpass filter is selected which passes only a small portion of the absorption band of interest so that the detector views a very limited part of the wavelength being emitted by the source. In this manner, the effects of interfering gases and source variations with wavelength are minimized. The basic function of the signal processing circuit is to electronically lock in on the 21 Hz modulation signal containing the concentration data, divide this signal by the source level signal (420 Hz) to eliminate source variations, and process this ratio as a d.c. voltage output which follows the change in CH_4 concentration. Details on the design and operation of this instrument have been documented in reference 11. In

order to increase the sensitivity and decrease the weight of the instrument for field work, the optical system was redesigned to include a White-Cell[12] in place of the original multipass sampling cell. The new instrument provides up to 35 meters of sampling pathlength in a cell less than 1 meter long.

Instrument output for zero CH_4 concentration is obtained while flowing prepurified N_2 through the sampling cell. After the gain controls are set for the sensitivity range of interest, the calibration procedure is accomplished by recording the instrument output as the sampling cell is filled with measured concentrations of CH_4 diluted in N_2. Results of the calibration are shown in figure 3. The CH_4 detection limit is 25 ppbv at a time constant of 1 second and about 10 ppbv at a time constant of 3 seconds. Calibration procedures were carried out each day field data were gathered.

METHANE FLUX MEASUREMENTS

Site Selection

Preliminary measurements of methane flux were made in a saltwater marsh located on the inland side of the lower Chesapeake Bay and at two sites in the Great Dismal Swamp of southeastern Virginia. The two swamp sites were selected for their different physical characteristics. One was located in a relatively dry mixed-hardwood region and the other was located in a relatively wet maple-gum region. Methane flux measurements and relevant environmental data at the three sites are shown in table I. The mixed hardwood site is situated in a mesic area and is representative of vegetation found on remnant sand dunes located on the western edge of the Great Dismal Swamp.[13] Because of the well drained character of this part of the swamp and because it is underlain by sand and easily oxidized, little methane production was expected from this site. None was found. The salt water marsh produced a relatively low level CH_4 flux. As seen in table 1, the maple-gum site proved to be the most active methane production site of the three and was selected for system evaluation and more detailed study. The maple-gum site is dominated by water gum, red gum, and black gum; but was previously covered by cypress, gum, and maple, and was logged approximately 30 years ago.[13] Standing water is present during most of the year except for prolonged dry spells in which the soil remains very damp.

Typical measurements of chamber methane concentration with time are shown in figures 4, 5, and 6. Because ppmv concentration of CH_4 in air can be directly converted to g/m^3, and because the chamber volume is half a cubic meter with an open bottom of 1 m^2, the increase in concentration with time can readily be converted to flux units of g/m^2 day. To begin a sampling sequence, the chamber was first set up on its side with all systems connected and running. A measurement of the ambient CH_4 concentration was obtained in this position. The chamber was then gently rolled into the flux measuring position (see figure 1) and the bottom edges sealed with soil, if needed. When the instrument indicated that a sufficient rise in CH_4 concentration had occurred, the chamber was rolled back on its side and ventilated so that a second ambient CH_4 concentration check could be obtained.

An instrument calibration was conducted with each flux measurement using N_2 and CH_4 calibration gases.

Soil Disturbance Effects

It was obvious from the first attempt to obtain flux data with this system, that the increase in CH_4 concentration in our flux chamber was not linear with time at the beginning of the sampling sequence. The degree of non-linearity was also variable from sample to sample, but almost always became linear after a few minutes. A release of trapped CH_4 caused by a disturbance of the soil when the chamber was placed in position is an obvious source of the nonlinearity in concentration increase and was investigated as follows: The chamber was first rolled into position in a rough manner and soil was forced around the bottom edge with pressure, using the experimenter's foot. Abnormally high emissions of CH_4 from the soil resulted from this action as may be seen in the trace of CH_4 concentration with time presented in figure 4. After several minutes, the growth in CH_4 concentration settled down to a linear increase with time. The chamber was then ventilated and a second and third sample were taken with minimum disturbance. The second and third sample traces are also shown in figure 4, and indicate a lesser disturbance at the beginning of the sequence. All three traces give the same CH_4 flux when calculated from the linear slope of concentration versus time.

A second example of the soil disturbance effect is illustrated in figure 5. In this sequence, the chamber was placed over soil with standing water on the surface using minimum disturbance. Results of this procedure are labeled in figure 5. The chamber was then vented with ambient air and the procedure repeated with the exception that after 15 minutes of sampling the soil was disturbed around the outside edges of the chamber by walking around its periphery. An abnormal increase in CH_4 concentration of about 1 ppm resulted from this action. When the instrument again indicated a normal CH_4 flux rate, the soil disturbance was repeated with another resulting jump in CH_4 concentration of about 1/2 ppm. After the second jump, the rate of CH_4 concentration increase again settled down, but 20 minutes were required before the rate of CH_4 increase gave the same flux as calculated from the undisturbed sample.

It is obvious from figures 4 and 5 that great care must be exercised in making flux measurements. If continuous sampling is not possible, the soil should not be disturbed by forcing a chamber into soil. Since it is usually impossible not to cause some disturbance, the change in gas concentration with time should be measured only if disturbance effects can be accounted for.

Several observations were made during the course of these measurements concerning anomalous CH_4 emissions. First, the amount of CH_4 trapped in the soil and thereby released by a disturbance appears to be the greatest when the ground is completely saturated with water and when the ground temperature is low. Secondly, abrupt increases in CH_4 from the soil is accompanied by the release of gas bubbles. Since abnormal fluxes of CH_4 can be released from the soil by pressure disturbances, it should be expected that large pressure disturbances like earthquakes or even abrupt atmospheric pressure changes may liberate large quantities of natural gases into the atmosphere in marsh areas.

Open Chamber Measurements

Methane concentrations were continuously measured in an open chamber using the scheme described in figure 1. A flow rate of 6500 cc/minute of ambient air was pumped into the chamber and continuously mixed with the chamber air using a circulation fan. Results of this experiment are shown in figure 6 and are compared to a closed chamber trace of CH_4 concentration versus time measured under the same soil conditions. Both techniques gave the same CH_4 flux.

Systems Evaluation for Environmental Measurements

The continuous sampling and analysis system for measuring CH_4 fluxes described in this paper represents a significant advance in the state-of-the-art. The high sensitivity and fast response time for measuring CH_4 concentration changes enables a short term (< 20 minutes) closed-chamber flux measurement at rates as low as 1×10^{-4} g CH_4/m^2 day. With proper attention to shading from direct sunlight, the temperature and humidity in the flux chamber does not vary significantly from ambient conditions. The primary difficulty in the flux measurement process, as discussed above, is the problem of soil disturbance. The soil disturbance problem is most pronounced in saturated, organic-rich soils typical of swamp and marsh environments where CH_4 production is most active.

For short-term CH_4 flux measurements in an enclosed swamp or forrest canopy environment, our results indicate that open-chamber and closed-chamber measurements give identical results. In cases where CH_4 flux quantification is required for open field or water measurements where wind stress and boundary layer turbulence are potentially important in trace gas transfer processes,[14] open-chamber measurements with variable forced circulation will be of importance.

CONCLUSIONS

1. A continuous sampling and analysis system for in situ measurements of CH_4 flux from soil and water interfaces to the atmosphere has been successfully developed and tested at several marsh and swamp sites in southeastern Virginia. The system has high sensitivity (0.01 ppm CH_4) and fast response (1 second), enabling rapid (20 minutes or less) quantification of fluxes as low as 1×10^{-4} g/m^2 day.

2. With careful attention to minimizing soil disturbance and maintaining the flux collecting chamber at ambient temperature and humidity levels, the precision of measurements at a site is approximately ± 5 percent.

3. In the swamp environment, short-term CH_4 flux measurements with closed- and open-chamber collecting systems give identical results.

4. Methane fluxes of 1.9×10^{-4} g/m^2 day to 4.7×10^{-3} g/m^2 day were measured in wetland environments of southeastern Virginia.

ACKNOWLEDGEMENTS

This study was conducted with the assistance and cooperation of the staff of the Dismal Swamp National Wildlife Refuge. In addition, Dr. Frank P. Day, Jr., Department of Biological Sciences, Old Dominion University, provided advice and background data for site selection in the Dismal Swamp based on his research supported by the National Science Foundation.

REFERENCES

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Table 1. Methane flux measurements from various sites in southeastern Virginia.

Site	Soil Temperature c	pH	H_2O in soil %	CH_4 Flux g/m^2 day
1[a]	23	5.82	80	1.9×10^{-4}
2[b]	19	4.38	66	no flux after 7 days
3[c]	20	4.48	87	4.7×10^{-3}
3[c]	15	4.79	77	2.25×10^{-3}

[a]salt water marsh site
[b]mixed hardwood site in Dismal Swamp
[c]maple gum site in Dismal Swamp

CAPTIONS

Figure 1. Schematic of system used to measure methane fluxes.

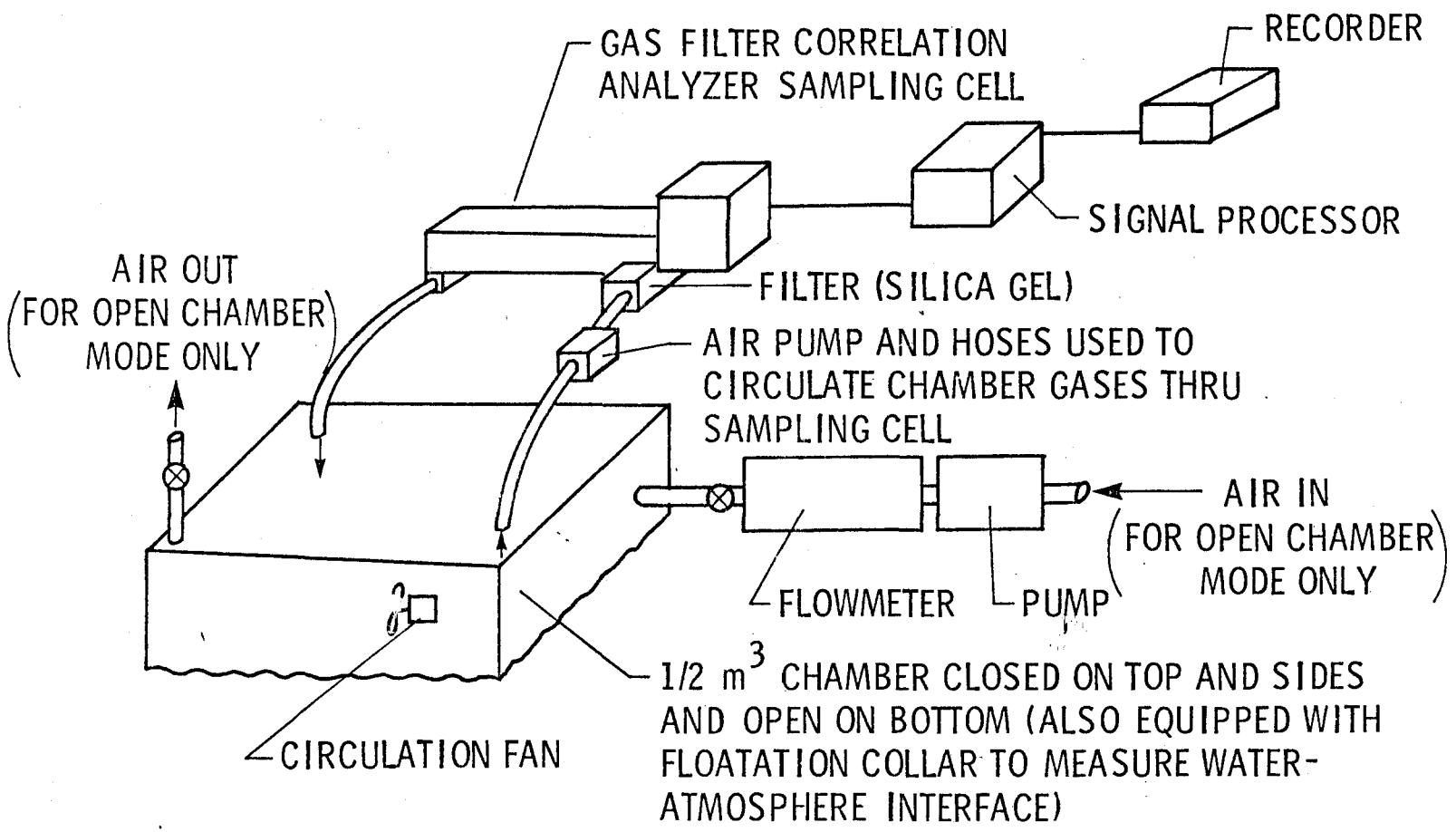
Figure 2. Schematic of methane Gas-Filter-Correlation analyzer.

Figure 3. Calibration for CH_4 detector.

Figure 4. Measured closed-chamber CH_4 concentration versus time after chamber has been set over soil surface. The first sample trace shows a typical transient increase of the CH_4 concentration due to the soil first being disturbed.

Figure 5. Measured closed-chamber CH_4 concentration versus time after chamber has been set over soil surface. The top trace shows transient increases in the CH_4 concentration when the soil was disturbed twice during the sampling.

Figure 6. Measured closed-chamber and open-chamber CH_4 concentrations versus time after chamber has been placed over the soil surface. 6500 cc/minute of ambient air was allowed to flow into the open chamber. Both samples indicated a flux of 1.9×10^{-3} g/m^2 day.



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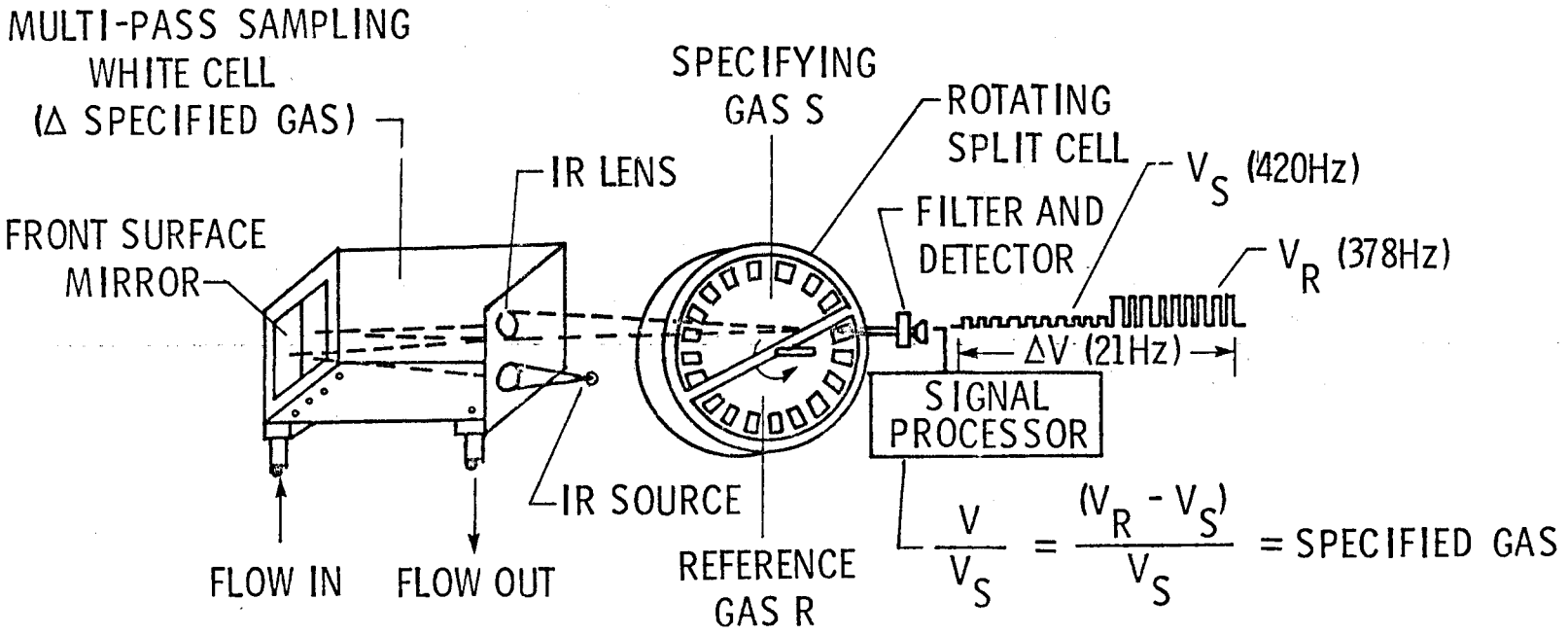
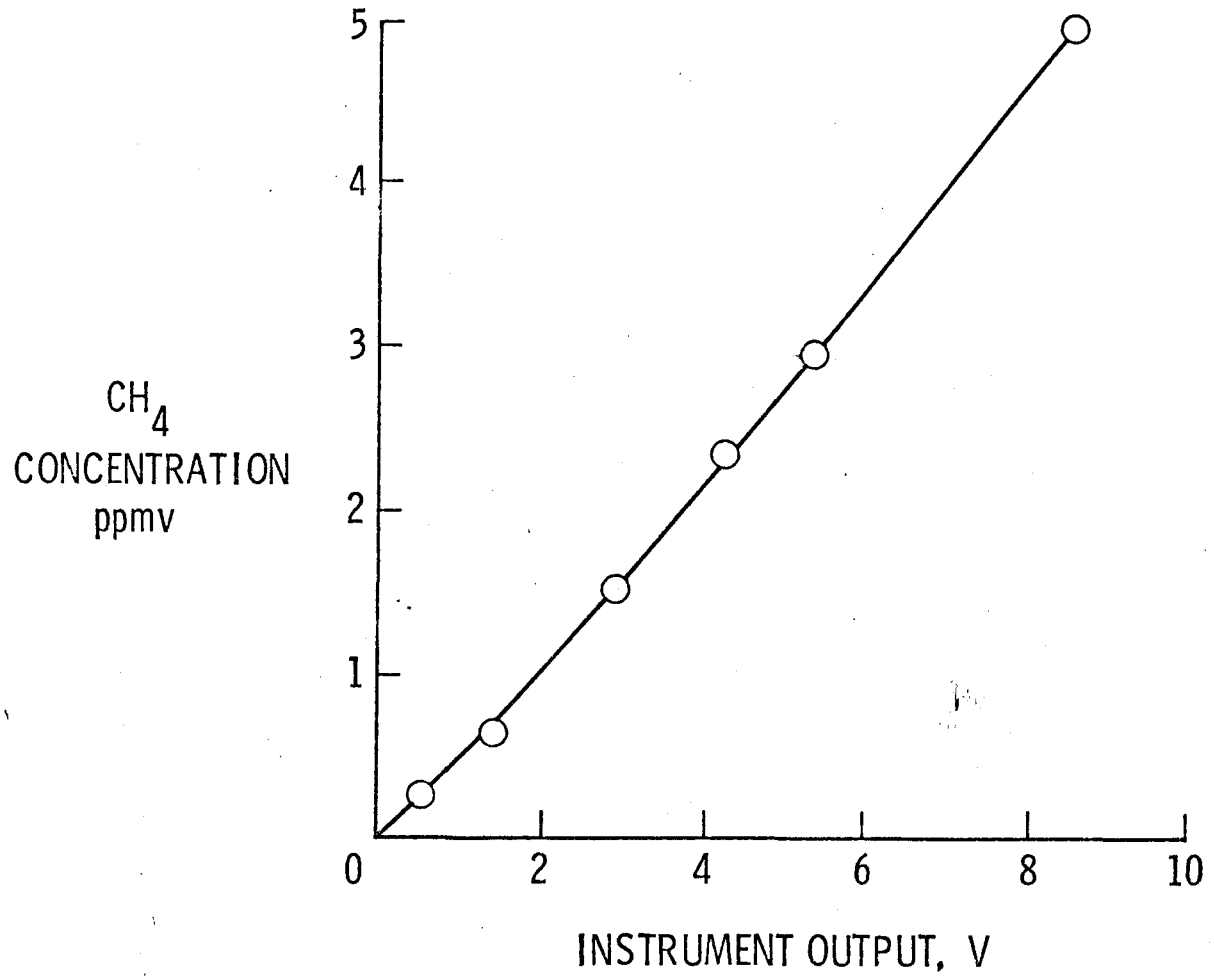


Figure 2. Schematic of methane Gas-Filter-Correlation analyzer.



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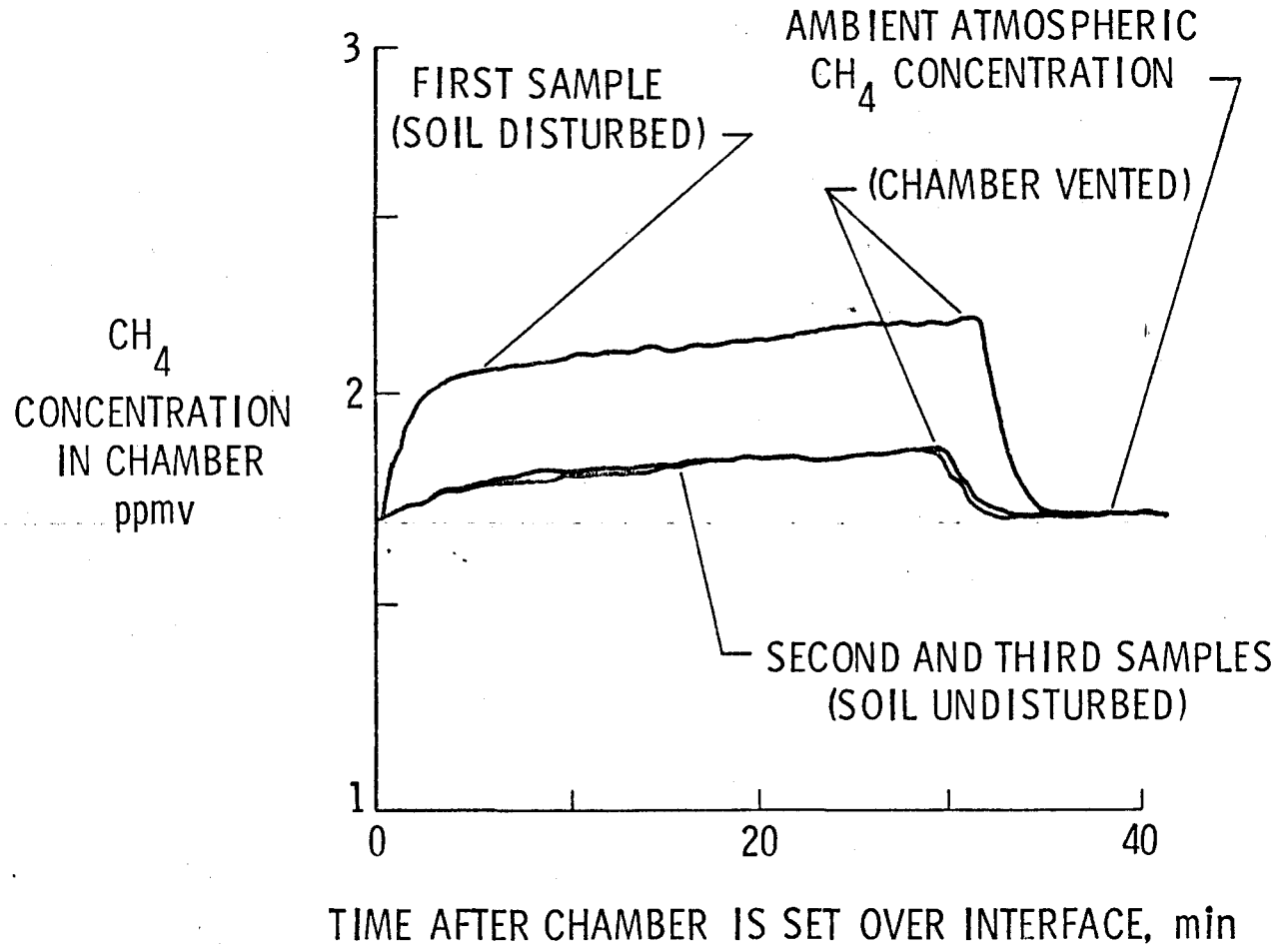

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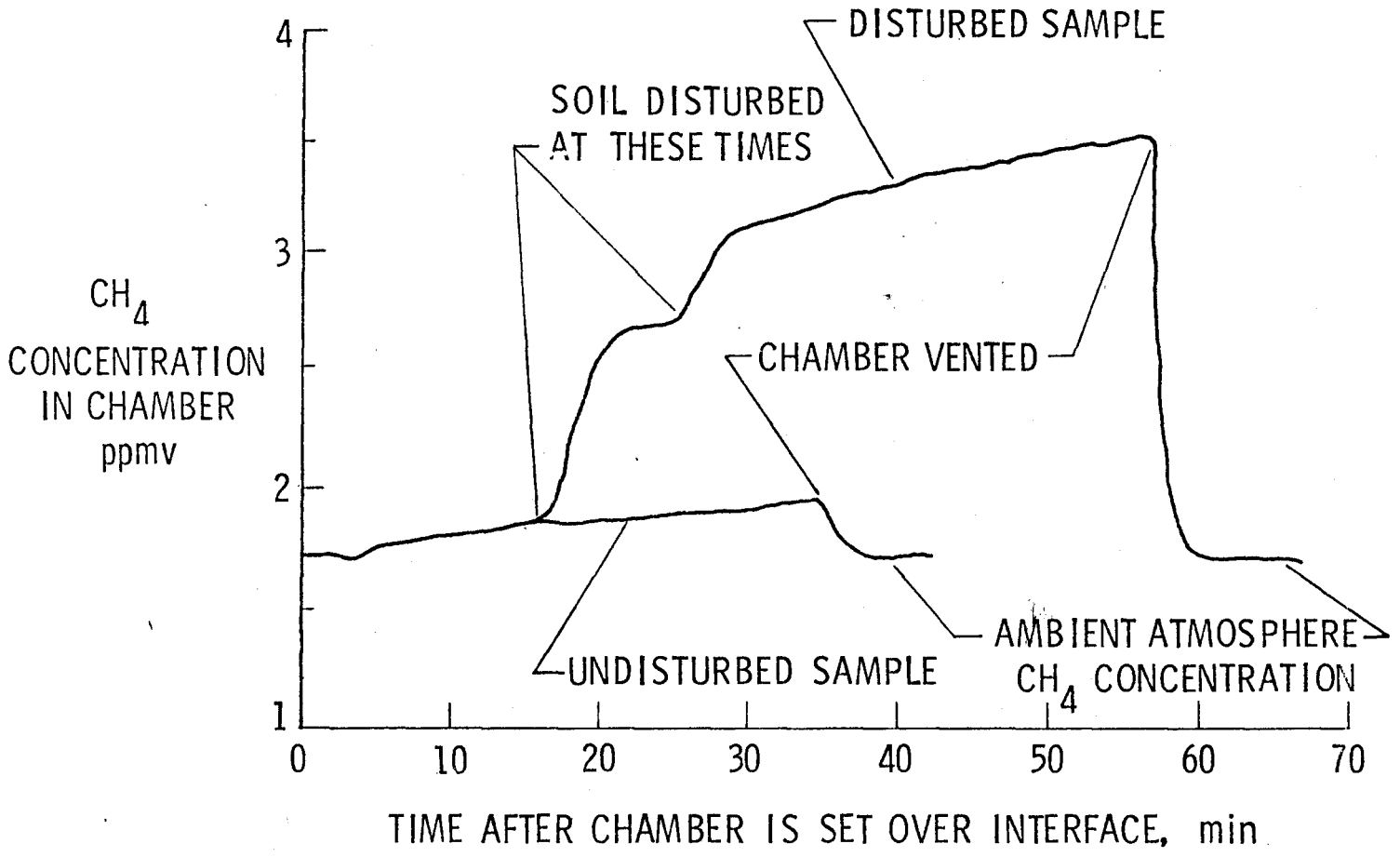

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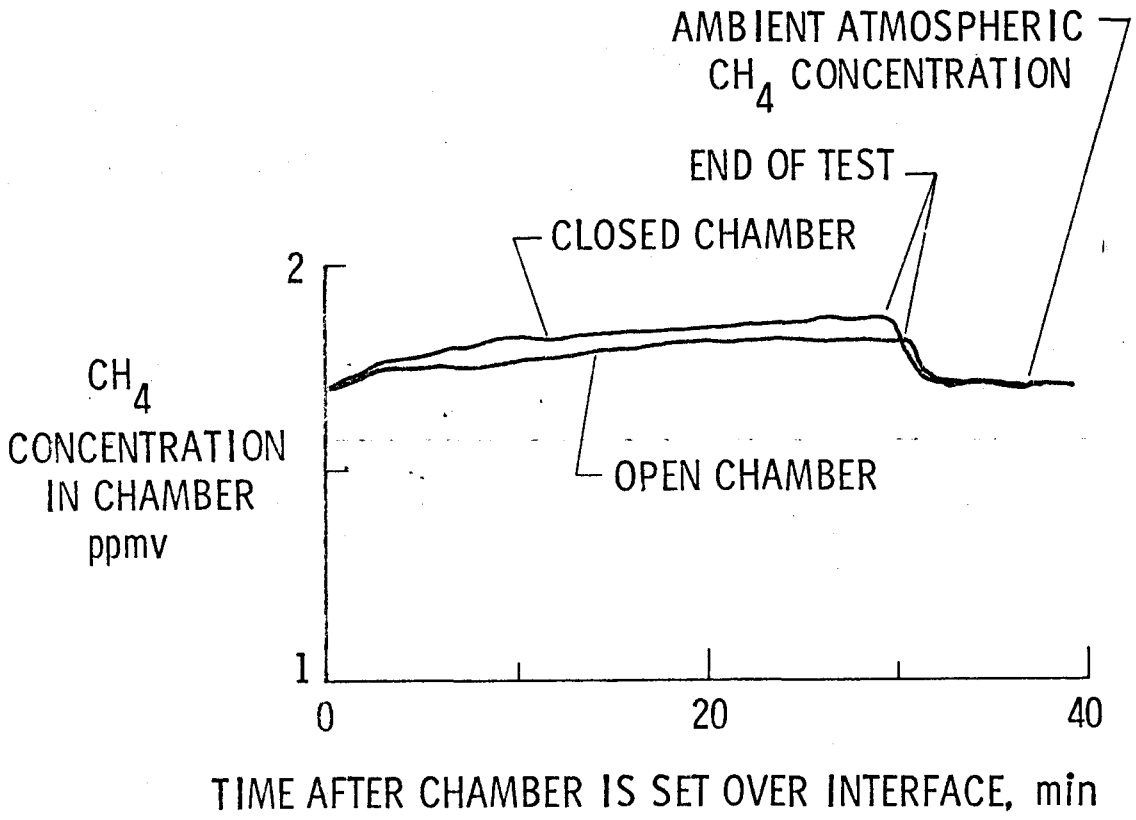

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