อัตราการปลดปล่อยของก๊าซ ไนตรัสออกไซด์ คาร์บอนไดออกไซด์ และไดเมธิลซัลไฟด์ ในพื้นที่ที่มีพืชพรรณต่าง ๆกัน

นาย คุณาวุฒิ บุญญานพคุณ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-1559-5

EMISSION FLUXES OF NITROUS OXIDE, CARBON DIOXIDE, AND DIMETHYL SULFIDE FROM VARIOUS VEGETATION AREAS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic year 2002
ISBN 974-17-1559-5

Thesis Title	EMISSION FLUXES OF NITROUS OXIDE, CARBON DIOXIDE, AND DIMETHYL SULFIDE FROM VARIOUS VEGETATION AREAS
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Field of Study	Chemical Engineering
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คุณาวุฒิ บุญญานพคุณ : อัตราการปลดปล่อยของก๊าซไนตรัสออกไซด์ คาร์บอนไดออกไซด์ และไดเมธิลซัลไฟด์ ในพื้นที่ที่มีพืชพรรณต่าง ๆกัน (EMISSION FLUXES OF NITROUS OXIDE, CARBON DIOXIDE, AND DIMETHYL SULFIDE FROM VARIOUS VEGETATION AREAS) **อาจารย์ที่ปรึกษาวิทยานิพนธ์: ผู้ช่วยศาสตราจารย์ ดร. ประเสริฐ ภวสันต์**, 128 หน้า. ISBN 974-17-1559-5

งานวิจัยนี้มีจุดมุ่งหมายในการศึกษาการวัดอัตราการปลดปล่อยของก๊าซมลพิษทางอากาศ 3 ชนิด ได้แก่ ก๊าซไนตรัสออกไซด์ คาร์บอนไดออกไซด์ และไดเมธิลซัลไฟด์ ณ ประเทศญี่ปุ่น โดยอาศัยหลักการของ chamber technique ซึ่งพื้นที่ที่ทำการศึกษาสามารถแบ่งได้เป็น พื้นที่เกษตรกรรม (ไร่ข้าวโพด ไร่ข้าวสาลี และไร่ถั่วเหลือง) และเขตพื้นที่ป่าสน จากผลการทดลองพบว่า อัตราการปลดปล่อยของก๊าซไนตรัสออกไซด์ และก๊าซคาร์บอนไดออกไซด์ในเขตพื้นที่เกษตรกรรมมีค่ามากกว่าพื้นที่ป่าไม้ ในขณะที่อัตราการปลดปล่อยของก๊าซไดเมธิลซัลไฟด์จากทั้งสองพื้นที่มีค่าใกล้เคียงกัน นอกจากนี้ผลการศึกษาแสดงให้เห็นชัดว่าอุณหภูมิมีผลกระทบต่ออัตราการปลดปล่อยก๊าซคาร์บอนไดออกไซด์และก๊าซไนตรัสออกไซด์ โดยอุณหภูมิที่สูงขึ้นมีผลให้อัตราการปลดปล่อยของก๊าซคาร์บอนไดออกไซด์ในทุกพื้นที่มากขึ้นตามไปด้วย ในส่วนของอัตราการปลดปล่อยของก๊าซไนตรัสออกไซด์ในป่าสน อุณหภูมิในช่วง 10-20°C เท่านั้นที่ส่งผลให้อัตราการปลดปล่อยมากขึ้น เมื่อพิจารณาผลกระทบของชนิดของปุ๋ยในเขตพื้นที่เกษตรกรรม พบว่า ปุ๋ยคอกมีผลช่วยเร่งอัตราการเกิดของก๊าซไนตรัสออกไซด์ และก๊าซคาร์บอนไดออกไซด์ สำหรับกรณีของการใช้ปุ๋ยเคมี ผลการทดลองพบว่าการใช้ปุ๋ยแอมโมเนียในปริมาณสูงจะทำให้กระบวนการผลิตก๊าซไนตรัสออกไซด์เกิดน้อยลง การพรวนดินเป็นอีกหนึ่งปัจจัยสำคัญที่ส่งผลกระทบต่ออัตราการปลดปล่อยก๊าซมลพิษ กล่าวคือ ก๊าซไนตรัสออกไซด์จะเกิดขึ้นมากในดินที่ไม่ผ่านการพรวน แต่สำหรับก๊าซคาร์บอนไดออกไซด์นั้น พื้นที่ที่ผ่านการพรวนจะปลดปล่อยก๊าซออกมาในปริมาณมากกว่าพื้นที่ที่ไม่มีการพรวน สำหรับปัจจัยที่ส่งผลกระทบต่อก๊าซไดเมธิลซัลไฟด์นั้นยังไม่สามารถสรุปได้จากงานวิจัยนี้ แต่ผลการทดลองแสดงให้เห็นถึงจุดที่น่าสนใจว่าความสัมพันธ์ระหว่างก๊าซไนตรัสออกไซด์และก๊าซไดเมธิลซัลไฟด์ มีลักษณะเป็นแบบเส้นตรงทั้งในไร่ข้าวสาลี และเขตพื้นที่ป่าสน

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา................................
ปีการศึกษา 2545

4270238921 :MAJOR CHEMICAL ENGINEERING
KEY WORD: EMISSION FLUX / NITROUS OXIDE / CARBON DIOXIDE / DIMETHYL SULFIDE / CHAMBER TECHNIQUE

KUNAWUT BOONYANOPAKUN: EMISSION FLUXES OF NITROUS OXIDE, CARBON DIOXIDE, AND DIMETHYL SULFIDE FROM VARIOUS VEGETATION AREAS. THESIS ADVISOR: ASSISTANT PROFESSOR PRASERT PAVASANT, Ph.D. 128 PP. ISBN 974-17-1559-5

The aim of this work was to measure the emission fluxes of three vital gaseous pollutants affecting the atmosphere, i.e. nitrous oxide (N_2O), cabon dioxide (CO_2), and dimethyl sulfide (DMS) by using the chamber technique. Both agricultural fields (corn, wheat, and soyabean) and pine forest in Japan were selected as a model study and the results showed that agricultural fields played a significant role as the emission sources of N_2O and CO_2. However, there was still not enough evidence at this point to conclude that turning the forest to agricultural field would affect the emission flux of DMS. In addition, it was found that there were some significant factors affecting the emission rates of the pollutants. Firstly, temperature was found to stimulate the mechanism of CO_2 production in all investigated vegetation areas. On the other hand, there was only a slight effect of temperature on N_2O where N_2O flux was observed to increase with temperature in the pine forest at low temperature range (10-20°C). Secondly, the application of manure in agricultural field intensified both N_2O and CO_2 emissions. Further investigation on the effect of high dose of chemical fertilizer applied in bared soil showed that ammonia could exhibit inhibition effect to the microbial activities of N_2O production. Tillage practice was also found to exert influential effect on N_2O and CO_2 fluxes. This work found that soil in the no-tillage plot was depleted in oxygen and led to a high emission of N_2O whereas the tilled soil resulted in the highest emission of CO_2 compared to other plots. Although all parameters investigated in this work seldom affected DMS emission, there seemed to be a relationship between the generation mechanisms of DMS and N_2O both in the wheat field and pine forest.

Department Chemical Engineering Student's signature........................

Field of study Chemical Engineering Advisor's signature........................

Academic year 2002

ACKNOWLEDGEMENTS

This thesis will never have been completed without the help and support of many people and organizers who are gratefully acknowledged here. Firstly, I would like to express my sincere gratitude to Assistant Professor Prasert Pavasant, my advisor, for his suggestions, guidance, warm encouragement and generous supervision throughout my master program. In addition, I would like to gratefully thank Professor Masatoshi Aoki for his valuable suggestions and knowledge during the research in Japan. I would also like to thank all of my thesis committees for their guidance and proof-read this manuscript.

Moreover, my work could not have been carried out without the help of all members in atmospheric environmental laboratory in Japan, i.e. Miss Yuko Kouda, Miss Sudsakhorn Pukngam, Miss Yukiko Okudera, Mr. Katsutoshi Horie, Mr. Keisuke Nonaka, Mr. Shang Xun Zhang, Mrs. Xuan Chen, Mr. Kazushi Hayashi, Mr. Kotaro Murotsu, Mr. Susumu Nozoe, and Mr. Daisuke Komori. I would like to express my deep appreciation to them and also to all of my Thai friends in Fuchu-city who encouraged me during my time in Japan. I cannot forget to express my thankfulness to my lovely friends, Mr. Sarit Chotchakornpant, Mr. Chaiyanun Tangtong, Miss Patchara Pupa, Miss Porntip Wongsuchoto, Miss Ratchat Chantawongvuti, Miss Narumon Charoentra, Miss Thanathorn Worapongsathorn, Mr. Sahat Chaiyo, Mr. Vichian Suksoir, Mr. Krit Lilittrakarnkul, Mr. Sontaya Krichnavaruk and Miss Siriwan Silapakul. Moreover, special thanks should be made for all members in the Environmental and Biochemical Engineering Laboratories for their pleasantness and encouragement.

Of course, I would like to express my sincere indebtedness to my family for their worthy supports throughout my Master course.

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CHAPTER 1

INTRODUCTION

1.1 Motivations

Air pollution problems contribute greatly to other environmental issues such as human health, soil acidification, eutrophication, and damages of natural ecosystems (EEA, 2000). A number of investigations have been conducted to study transport mechanisms of various gaseous pollutants. These transport mechanisms principally include the dispersion of the gaseous pollutants from any sources to the receptors, and their deposition from air to water or to the earth surface. An important issue regarding air pollution problems is to understand the generating kinetics of pollutants. To date, transportation and industrial activities are always considered as major sources of air pollutants. It is equally important to quantify the amount of pollutant emitted from each source so that abatement technologies can be consequently designed and developed. However, direct measurements of air pollutants are highly complex, and a number of assumptions still have to be made, and in many cases, they require complicated measurement methods. Rather, investigators have attempted to develop a “simpler” way of estimating the quantity of pollutants from various sources.

Estimation of pollutants, however, needs to be done based on a reasonable understanding of the mechanism that pollutants are generated. Recently researchers have shown that emission from agricultural activities might also be a major air pollutant source, and a number of investigations were carried out to develop a relationship between the terrain type and the rate of emission. It appears that agricultural emission depends markedly on a large number of parameters such as vegetation, temperature, primary production, soil nutrient status, livestock, water table, and hydrology (Workshop

Participants, 1996). It is therefore important to perform real measurement at various types of terrain with various kinds of vegetation in order to be able to develop a reasonable correlation that can be used to estimate the emission rate.

This work focuses on the emissions of N_2O, CO_2 and DMS (Dimethyl sulfide) from various terrain types, e.g. pine forests, and many kinds of croplands. The pollutants of interest are selected due to their indirect effects on terrestrial ecosystems as described in the next section.

1.2 Why are atmospheric N_2O, CO_2, and DMS selected?

Nitrous oxide (N_2O) is familiar to us as an anesthetic. It occurs naturally in the atmosphere at a very low concentration (about 0.3 part per million by volume, ppmv), but the concentration is now increasing at a rate of about 0.3% per year (Janzen et al., 2001). Much of this increase comes from agriculture, which accounts for up to 70% of the N_2O emissions from human activity. The increase poses two potential threats. Firstly, N_2O is a potent greenhouse gas with a long lifetime in the atmosphere (about 120 years). Its warming potential is about 310 times that of CO_2 over 100 years. Secondly, N_2O released is eventually converted in the upper atmosphere to nitric oxide (NO); a gas that breaks down ozone. Ozone in the upper atmosphere filters out UV radiation from the sun, so its depletion results in higher doses of harmful UV radiation reaching the earth's surface. Higher N_2O levels, therefore, not only contribute to the greenhouse effect but may also increase indirectly the intensity of UV radiation.

Carbon dioxide (CO_2) is a major greenhouse gas similar to nitrous oxide. Although its specific warming effect might not be as significant as N_2O, CO_2 affects our sea levels and our weather patterns, and could ironically introduce a new ice age prematurely (Logan, 1996). Hence, it is one of the serious global environmental problems. There are about 40,000 petagrams (1 Pg = 10^{15} grams) of carbon (C) in global circulation (Janzen et al., 2001). Most C is in the oceans but large pools also occur in soils, vegetation, and the atmosphere. Of these three pools, the atmosphere is the smallest but most active. The CO_2 in the air is continually being removed by plants through photosynthesis and being absorbed into the oceans. At the same time, however, CO_2 in the air is being replenished by releases from plants, soils, and oceans. Thus, because C is always cycled, the concentration of atmospheric CO_2 has remained constant from year to year. After the advent of the Industrial Revolution, the demand for energy has resulted in ever-increasing demands of fossil fuels that were finally converted to atmospheric CO_2. However, deforestation has resulted in vegetative C being converted to CO_2, and the cultivation of previously undistributed soils has resulted in soil C being converted to CO_2. Because of these processes, the emissions of CO_2 into the atmosphere now exceed the rate of withdrawal, resulting in a gradual buildup of CO_2.

Apart from the problems with N_2O and CO_2, organic sulfides in the atmosphere can pose a cloud formation problem which directly backscatters sunlight from the atmosphere (Quinn et al., 1993). This reflectance cloud often occurs from the dissolution of dimethyl sulfide (DMS) oxidation products in cloud droplets (Andrae et al., 1995). Eleven organic sulfides have been identified in the atmospheric emissions, and six of them are used particularly as odorant additives to natural gas. The other five are widely produced in nature such as microbial activities. Both oceanic and continental natural sources have been identified for the emission of dimethyl sulfide (DMS), which is probably the most common of the organic sulfur compounds in the atmosphere. Sources of DMS emission are: algae, animal waste, microbes, natural gas, petroleum manufacturing, plant volatile, sewage, starch manufacturing, trees, and wood pulping. Among these, microbes, animal waste, and natural gas are considered major sources of DMS emission (Graedel, 1978).

1.3 Objectives

This work aimed at the study of the emissions of N_2O, CO_2, and DMS from different vegetation areas. Several meteorological/soil parameters along with plantation practices i.e. fertilizing and tillage techniques, were included in the investigation. In addition, a relationship between the fluxes of various pollutants was examined.

1.4 Scopes of this work

1. The air pollutants of concerns were nitrous oxide, carbon dioxide, and dimethyl sulfide.
2. Samples were collected from different places, i.e. corn, wheat, and soyabean plantation, and pine forest; all are in Japan.
3. All measurements were based on the Chamber technique.

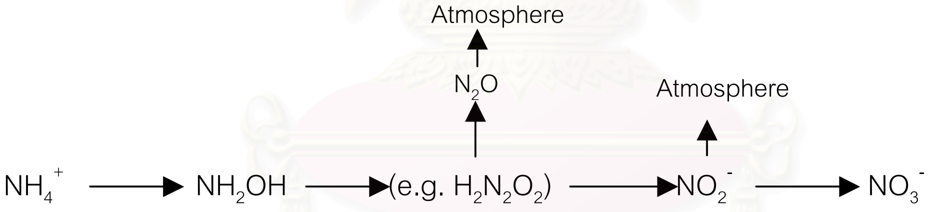
CHAPTER 2

BACKGROUNDS AND LITERATURE REVIEW

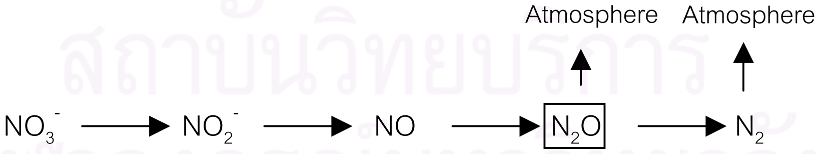
2.1 Nitrous oxide

2.1.1 N cycle and nitrous oxide emission

Most nitrous oxide is emitted into the atmosphere as a result of industrial, biomass burning, and biological processes in soils (Table 2.1) with the latter covers almost 90% of the total emissions (Freyney, 1997). The N cycle as illustrated in Fig.2.1 suggests that many sources of N disposed to agricultural land can be transferred back to the atmospheric in the form of N_2 and also N_2O by the biological processes. There are two main processes of N_2O formation, i.e. nitrification (Reaction 2.1) and denitrification (Reaction 2.2) (Aulakh et al., 1984), both of which are the activities carried out by bacteria living in soil according to the following stoichiometry.



$$NH_4^+ \longrightarrow NH_2OH \longrightarrow \overset{\overset{\overset{\text{Atmosphere}}{\uparrow}}{\overset{N_2O}{\uparrow}}}{(e.g.\ H_2N_2O_2)} \longrightarrow \overset{\overset{\text{Atmosphere}}{\uparrow}}{NO_2^-} \longrightarrow NO_3^- \qquad (2.1)$$



$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow \overset{\overset{\text{Atmosphere}}{\uparrow}}{\boxed{N_2O}} \longrightarrow \overset{\overset{\text{Atmosphere}}{\uparrow}}{N_2} \qquad (2.2)$$

Nitrification takes place in the upper soil surface, which can be regarded as an aerobic layer. Most N enters the soil either as NH_4^+ or in a form that converts to NH_4^+, such as urea. Hence, under conditions of good aeration and high NH_4^+ concentration, NH_4^+ is nitrified to NO_3^-, and a small portion of N may be emitted as N_2O. This results in a concentration gradient of NH_4^+ between the aerobic and anaerobic layers, which causes NH_4^+ in the anaerobic layer to diffuse into the aerobic layer where it is nitrified. When movement of oxygen into soil is restricted, nitrate (NO_3^-) can be converted into nitrogen gas (N_2) in the process called denitrification. The conversion of NO_3^- to N_2 in the denitrification process can lead to an emission of the intermediate N_2O. Similar to NH_4^+ diffusion, NO_3^- formed in upper soil surface can diffuse back into anaerobic layer where it is easily denitrified. Of the two processes, denitrification is probably a more important N_2O source than nitrification as emission of N_2O from denitrification may well be several times higher than that from nitrification (Janzen et al., 2001). There are three main factors that control the rate of denitrification, i.e. concentration of oxygen, concentration of NO_3^-, and the amount of available C used by bacteria as carbon and energy sources. High rates of denitrification occur with optimal environmental conditions: (i) low oxygen, (ii) high NO_3^-, and (iii) high available C. Evidence of this report includes the work of Janzen et al., 2001 who reported that the bursts of N_2O emission at snowmelt in Canada may have resulted from favorable conditions for denitrification and N_2O formation. This was because high moisture content led to oxygen deficiency condition, and if there existed adequate NO_3^-, and available C source with suitable temperature, N_2O could be emitted in large quantity. In addition, the N_2O flush may have been caused by the abrupt release of N_2O that was previously trapped underneath a layer of frozen soil or ice.

Nitrous oxide production is usually controlled by temperature, pH, water holding capacity of the soil, irrigation practices, fertilizer rate, tillage practice, soil type, oxygen concentration, availability of carbon, vegetation, land use practices, and uses of chemicals. Research has shown that nitrous oxide emission increased when tropical forests were converted to crop production and pasture (Freyney, 1997). Several investigations on N_2O emission from rice fields indicated that only less than 0.1% of the applied nitrogen was emitted as nitrous oxide if the soils were flooded for a number of days before being fertilized. However, if mineral nitrogen was presented in the soil before flooding it would serve as a source of nitrous oxide during wetting and drying cycles before permanent flooding. Thus flooded rice soils in the tropics could become an important source of nitrous oxide (Freyney et al., 1987; Moiser et al., 1989; Simpson et al., 1984). Moreover, tropical forests sometimes contributed a significant fraction of the global emission of atmospheric N_2O. Previous report showed that this fraction could be as large as 40% and could possibly be responsible for up to 75% of the pre-industrial total emission (Michael et al., 1986). This was because most of the N deposited from the atmosphere was retained in the forest, and only a small proportion seemed to be lost to ground and surface waters. Hence, this N retained in the forests could be escaped from ecosystems in forms of N_2O and N_2 (Abrahamsen and Stuanes, 1998).

There were also indirect contributions to N_2O emission through emissions of NO_x and volatilization of NH_3 into the atmosphere. The former when combined with clouds could form nitric acid, which comes back to the earth surface in a form of acid rain and retains in vegetation or soils. This N could finally be converted to N_2O by biological processes. The gaseous NH_3, on the other hand, had a short lifetime in the atmosphere, and could be re-deposited over the landscape through wet and dry depositions (Moiser et al., 1996). Then anhydrous ammonia becomes NH_4^+, and immediately reacts with water in the soil. As a result, most of NH_3 released from soil, floodwater, and irrigation water following fertilizer application to agricultural systems could become a secondary source of N_2O emission. Generally, NH_3 has ranged from negligible amounts to above 50% of the fertilizer N applied, depending upon fertilizer practice and environmental conditions (Bacon et al., 1986). Besides, as much as 50% of N excreted from livestock may be released into the atmosphere in a form of ammonia gas which could then be converted to N_2O according to the mechanism described above.

In conclusion, N_2O emission from soils depends not only on how fast it forms but also on how fast it diffuses or converts to other N forms (Janzen et al., 2001). Because of the sporadic and unpredictable pattern of N_2O releases, estimating amounts of emission is difficult. Hence, current estimation of N_2O emission are probably less reliable than those for other greenhouse gases.

2.1.2 Nitrous oxide emission from various sources

Examples of emission fluxes from various natural and agricultural sources are given in Table 2.2. It is interesting to notice that emission fluxes from each source can vary significantly. For instance, Situala et al., 1995 found that N_2O emission fluxes from temperate pine forest during summer in Norway could vary from 13.1 to 53.7 $\mu g\ m^{-2}\ h^{-1}$. Schmidt et al., 1998 measured N_2O fluxes from six different deciduous forest sites in Germany and reported that these fluxes varied between 9.17 to 34.0 $\mu g\ m^{-2}\ h^{-1}$ which was close to those obtained in Norway. However, Brumme and Beese, 1992 found that N_2O emission from a German beech forest could be as high as 196 $\mu g\ m^{-2}\ h^{-1}$. Moreover, the review of N_2O fluxes from deciduous and coniferous forests in the US showed that the emission rate varied from as low as 0.26 $\mu g\ m^{-2}\ h^{-1}$ in Massachusetts to as high as 115 $\mu g\ m^{-2}\ h^{-1}$ in Wisconsin (Bowden et al., 1990). The other coniferous forest in UK gave high variation of N_2O fluxes according with those obtained from the US. In addition, mean N_2O fluxes into the atmosphere from tropical forest soils in Brazil, Ecuador, and Puerto Rico were found to be in the same range of $44.7 \pm 5.1\ \mu g\ m^{-2}\ h^{-1}$ (Keller et al., 1986).

Agricultural soils often have higher rates of N_2O emission than comparable soils under natural vegetation because of high N inputs and disrupted N cycling. Several researchers have shown that N_2O emission increased when tropical forests were converted to crop production and pasture. For instance, fluxes from uncultivated land and natural ecosystems in temperate and tropical regions were found to be less than 35.9 and 71.5 $\mu g\ m^{-2}\ h^{-1}$, respectively, whilst those from fertilized lands both from temperate and tropical regions were greater than 108 $\mu g\ m^{-2}\ h^{-1}$ (Freyney, 1997). Moreover, the emission rates of N_2O from wheat and carrot cropping in Denmark and Potato field in Germany were reported to be as great as 509-4,170 $\mu g\ m^{-2}\ h^{-1}$ (Christensen et al., 1996; Flessa et al., 2002). More interestingly, N_2O emission from agricultural soil fertilized with liquid swine waste or constituents in the southeastern US was found to be as high as 160 times greater than that obtained from pre-fertilization soil (Whalen, 2000). Weitz et al., 2001 also found that fertilized soil in agricultural loam soil could cause 3-10 times N_2O emission more than unfertilized soil.

2.2 Carbon dioxide

2.2.1 C cycle and carbon dioxide emission

Although 70% of the emitted CO_2 is approximately from industrial activities, vegetation releases of CO_2 can be a serious contributor for the global greenhouse phenomenon. Naturally, plants, trees, and vegetation consume carbon dioxide by photosynthesis in much the same way as humans consume oxygen and there is a natural system that controls the level of CO_2 in the atmosphere (Janzen et al., 2001). Therefore, as the rain forests disappear, there is less vegetation to absorb CO_2 produced on earth. And since most of the forests are burnt, the resulting fires release large amounts of CO_2. Consequently, the balance of C cycle (Fig. 2.2) is destroyed, and the gradual buildup of CO_2 could be well observed. There are many parameters affecting the vegetation releases of CO_2, and these parameters can mainly be classified into (i) vegetation, (ii) seasonal changes, and (iii) agricultural ecosystems. These factors are usually inter-related. For instance, the net CO_2 flux in a forest depends on net photosynthesis and on soil respiration. These, in turn, depend, among others, on the length of the growing season and on the timing and amount of rain, snow, drought and cloud cover (Schloerer, 1996).

2.2.1.1 Vegetation

Types of vegetation significantly influence the release of soil CO_2 efflux. Investigations on this CO_2 emission were carried out in several terrain types such as, boreal aspen forest in Canada (Russell and Voroney, 1994) and Amazon rain forest in Rondonia (Grace et al.), and various relationships regarding fluxes of CO_2 emission were developed. For instance, Russell and Voroney, 1994 found that soil temperature was the single most effective variable used to predict soil CO_2 efflux rather than humus and volumetric moisture. However these parameters depended significantly on the type of vegetation in the forest. In addition, CO_2 flux over Amazon rain forest was reported to depend on natural ventilation of the canopy (Grace et al., 1995).

2.2.1.2 Seasonal change

The influence of seasonal change was reported by Miranda et al., 1993 in Brazil. In the wet season (from October to April), the Cerrado vegetation (*sensu stricto*) assimilated carbon dioxide from the atmosphere during the day. However, in the dry season (from June to October) the adsorption had gradually decreased. Finally, the Cerrado began to function as a carbon source in September. They also reported that annual net CO_2 exchange (source and sink) was likely to be dependent upon the length of the dry season.

Generally, fluxes of CO_2 emission are most highly correlated with deep soil temperature. However, if the soil is covered by snow for months in winter, the snow could act as an insulating layer and allowed the underlying soil to maintain temperature above $-6.5^{\circ}C$, which was thought to be the lowest temperature at which CO_2 production could occur by biological activities (Coxson and Parkinson, 1987). Richard et al., 1996 concluded that seasonal variability of CO_2 flux at alpine and subalpine sites could be characterized where CO_2 flux was found to be minimal in early winter and a 70% rise in CO_2 flux over the minimal values could be obtained within a period of one month. They also found that seasonal variability was not related to soil temperatures, which remained relatively constant under the snow layer. However, this result was contradicted to the finding of Mariko et al., 2000 who showed that the fluctuation of soil temperature between day and night in wintertime in Japan significantly influenced the CO_2 flux from soil.

2.2.1.3 Agricultural ecosystems

The production of CO_2 from cropped lands can easily be described using the C cycle. Firstly, CO_2 is absorbed from the atmosphere by plant leaves and is transformed, via photosynthesis into C-containing compounds such as sugars, carbohydrates, cellulose, and lignin. Then some of these materials are used by the plant for its own energy and are converted back to CO_2. The other remnants are removed during harvest and some is returned to the soil and decomposed by microorganisms in the soil, which finally releases CO_2 back into the atmosphere and closing the C cycle (Janzen et al., 2001). Hence, the quantity of released CO_2 depends on the amount of C stored in the system. This storage of C, in turn, depends on many factors, e.g. type of crops, tillage practices, fertilizer treatments, summer fallow, and other options. For instance, adding fertilizer to the soil increases crop yields, thereby increases the amounts of residues returned to the soil and so does the CO_2 flux. For soils under summer fallow, the practice of leaving land unplanted for a whole year usually leads to lower C content than those that are cropped annually. This is because fallow hastens decomposition of the soil C, so it reduces C input into soil during the year when there is no crop (Janzen et al., 2001).

2.2.2 Carbon dioxide emission from various sources

As shown in Table 2.3, CO_2 emission fluxes from tropical and temperate forest soils tend to be higher than those from colder environments such as tundra or arctic ecosystems. The reason might be that low temperature retards the rate of biological activity within the soil and suppresses CO_2 emission. Therefore, several researchers have concluded that soil temperature was the dominant factor for soil CO_2 emissions (Keller et al., 1986; Borken et al., 1999; Oechel et al., 1997; Sommerfeld et al., 1996).

The other important factor affected CO_2 emission flux is carbon source in soil. Gerlach et al., 2001 reported that CO_2 flux in Horseshoe Lake tree Kill, Mammoth mountain reached the highest of 871.25 mg dm^{-2} h^{-1}. This might be as a result from the composition of the extreme quantity of carbon source in those area. With respect to bare soil in Japan, which had lower carbon source, emission flux of CO_2 was as low as 3.074 mg dm^{-2} h^{-1}. Thus, the effect of carbon source in soil on CO_2 flux could not be neglected.

In addition, production and consumption of CO_2 can be influenced significantly by agricultural practices particularly the management of crop residues and soil organic matter. Turning the forests to agricultural fields, such as grassland, corn, barley, wheat, etc., can cause the rising in CO_2 emissions as illustrated in Table 2.3. This rise occurred because of tillage practices, fallowness, and fertilization. Reicosky, 1997 reported that for at least 19 days after tillage, moldboard plow, where reasonably good mixing of upper soil surface was achieved, caused 291.0 mg dm^{-2} h^{-1} of CO_2 to re-enter into the atmosphere. Moreover, Scala et al., 2001 also found that tillage practice in dark red latosol in Brazil had more CO_2 emission flux than those obtained from no tillage area. On the other hand, some investigations reported that CO_2 flux from soil with no-tillage was greater than the case of plow-tillage because as the soil was turned over in the tillage, substrates for micro-organisms disappeared from the top 5 cm resulting in a significant drop in soil respiration (Wagai et al., 1998; Maljanen et al., 2002; Aslam et al., 2000). With regard to fallow practice, Pomazkina et al., 1996 found that soil that was frequently under summer fallow had the lowest CO_2 flux (0.875 mg dm^{-2} h^{-1}) which was thought to be due to the lower C content than the areas that are continuously cropped (1.292 mg dm^{-2} h^{-1}).

2.3 Dimethyl sulfide

2.3.1 Dimethyl sulfide (DMS) cycle

DMS was recognized as an important component of the biogeochemical cycle of sulfurs (Figure 2.3). We know now that, after anthropogenic sulfur dioxide emissions from fossil fuel combustion, DMS is the second most important source of sulfur in the atmosphere. Once DMS is released to the atmosphere (10 to 20% of the total DMS is found in oceans) it is oxidized by OH and/or NO_3 radicals to a variety of acidic sulfur products which play an important role in the characterization of physicochemical properties of the atmosphere (DMS interactive). It has already been well established that the major biochemical precursor of DMS in seawater is dimethylsulfoniopropionate

(DMSP), a compound found in phytoplanktonic cells that are converted to DMS by the activity of some bacteria.

Figure 2.4 illustrates the summary of DMS transformation. In terrestrial regions, methionine and S-methylmethionine are probably the main precursor of DMS. Microorganisms produce DMS from DMSP and methionine under aerobic and anaerobic conditions. DMS is biochemically oxidized to dimethyl sulfoxide (DMSO) which may, in turn, be biologically reduced back to DMS. These interconversions occur in both oxic and anoxic habitats. Under anaerobic conditions where light is present, DMS may be oxidized to DMSO by phototrophic bacteria. DMSO is an electron acceptor which supports the anaerobic metabolism or growth of a variety of microorganisms, with DMS as the reduced endproduct. DMSO is also aerobically used as a carbon and energy source by some species of *Hyphomicrobium*. The biodegradation of DMS proceeds in oxic and anoxic environments. Aerobic metabolism supports the growth of obligate methylotrophs (*Hyphomicrobium* sp.) and obligate Calvin cycle autotrophs (*Thiobacillus* sp.). In anoxic sediments sulfates reducers and methanogens consume DMS. The decomposition of DMS was found to produce CO_2 and H_2S as end-products. Hence, microbial activities in soil could both generate and consume DMS (Taylor and Kiene, 1989).

2.3.2 Dimethyl sulfide emission from various sources

Table 2.4 shows the review of DMS fluxes emitted from the various sources. As for natural sources, the emission fluxes of DMS have been measured over a number of forests in Brazil, China and Japan. Watts, 2000 concluded that Brazillian tropical forest could act as a source of DMS with the emission rate of 1.91 to 2.87 nmol m^{-2} h^{-1}, and temperate forest in China and Japan yielded DMS emission fluxes of 3.31 to 5.14 nmol m^{-2} h^{-1}. The other vital natural source is peatland where anoxic condition always occur. This phenomenon leads to higher amount of DMS emitted to the atmosphere than forest ecosystems. The range of emission fluxes varied from 4.0 to 428.0 nmol m^{-2} h^{-1}. Moreover, Henk et al., 2000 hypothesized that DMS emission in sea grass sediment ecosystem occurred, with a relatively low net production during the day and a large net production during the night. This was because, at nighttime, sea or ocean had lower oxygen dissolved (as no photosynthetic activities), and this condition facilitated the growth of DMSP-cleaving organisms which then resulted in a higher level of DMS production. Moreover, initial DMS oxidation rates in sediment slurries, occurred by DMS-oxidizing microbes, appeared to be much higher under oxic/light (daytime) than under anoxic/dark (nighttime) condition. Hence, during the night, the DMS production rate exceeds the DMS oxidation rate resulting in a net DMS production.

Not only is DMS emitted from the surface layer of the ocean by marine algaes and plankton, but also DMS is emanated from flooded rice paddies and agricultural fields in terrestrial ecosystems. Nouchi et al., 1997 concluded that DMS emitted from rice paddies over the cultivation period was estimated to be approximately 5-6 mg/m^2. They also reported that DMS was emitted only from the floodwater during the first month after flooding and began to be emitted from rice plants during the middle of cultivation. DMS fluxes seemed to increase with the growth of rice plants and the highest flux, 243.08 nmol m^{-2} h^{-1}, was recorded before draining water from the field. For general paddy fields, the emission flux ranged from 11.0 to 27.0 nmol m^{-2} h^{-1} (Kanda and Minami, 1992; Kanda et al., 1992; Yang et al., 1998). Because DMS flux from the soil water was negligible during the entire cultivation period, these facts indicated that DMS emitted from rice paddies was produced by metabolic processes in rice plants. However, DMS emissions from rice paddies were reported to be negligible compared to those from marsh and the surface marine waters.

Emission rates of DMS from crops including corn, soyabeans, oats, and miscellaneous vegetables have been measured by Goldan et al., 1987. Fluxes from crops varied considerably from 24.97 to 973.89 nmol m^{-2} h^{-1} as some plants were reported to emit dimethyl sulfide.

It is also possible that plants emit volatile sulfur containing compounds which are not easily analyzed by current gas chromatographic methods. Thus, the use of other analytical methods may reveal compounds as yet unidentified which serve as a source of volatile biogenic sulfur compounds.

2.4 Air sampling techniques

Terrestrial gaseous fluxes are measured directly using either the Chamber or micrometerological techniques. Both techniques have their limitations. The more commonly used Chamber technique can disturb the natural habitat (e.g. damage roots or vegetation, increase the temperature in the chamber) and cause high and erratic gaseous fluxes (Austin et al., 1998). Because of this uncertainty, a new technique has been developed and known as the micrometerological technique where the average flux is obtained from a large number of measurements from several sampling points over a larger area of interest. This new technique was believed to be more accurate and subject to less uncertainty (Moiser et al., 1996). However, it requires a gaseous gradient in the atmosphere and eddy correlation measurements of some other parameters, generally water vapor, and it also requires a specific and sufficiently fast response detector to directly obtain gaseous fluxes. Hence, if appropriate equipment is not available, flux measurements are subject to extremely high uncertainty (Austin et al., 1998).

Matthias et al., 1980 summarized the advantages of the chamber technique used for the measurement of N_2O flux that (i) it had high sensitivity and allowed detection of very small emissions of N_2O from unfertilized soils; (ii) its use was not limited to sites where electricity or special equipment was available; (iii) the chamber used was inexpensive and easy to fabricate, transport, and use. For further details of the measurements of N_2O using these two techniques, the review of Moiser et al., 1996 should be consulted.

For CO_2 flux measurements, several techniques have been proposed. For instance, gas fluxes across the soil-air interface were determined by sampling air in the headspace of welded aluminum chambers (10x20x40 cm) placed 1-2 cm deep into the soil for short periods (20-40 min). Samples were analyzed using gas chromatography with ultrasonic shift detector (USD) for CO_2, and electron capture detection (ECD) for N_2O (Michael et al., 1986). CO_2 flux can also be estimated from the Fick's law. In this method, samples were drawn from the metal tubing above the snow surface at each location and were analyzed by gas chromatography. The diffusional flux could then be calculated from the Fick's law:

$$J = -\phi\tau D\left(\frac{dc}{dz}\right) \qquad (2.4.1)$$

where ϕ is the porosity of the layer, τ the tortuosity of the layer, D the diffusion coefficient for CO_2 in air, and dc/dz the concentration gradient across a uniform layer (Richard et al., 1996). In addition, the winter fluxes measurement in Japan was performed using the open-flow infrared gas analyzer (IRGA) method rather than with the more commonly used closed chamber technique (Mariko et al., 2000).

Similarly to both N_2O and CO_2, DMS sampling method can be done via several techniques. For instance, Henk et al., 2000 focused on the net production of DMS, and oxygen in marine ecosystems was employed as an environmental parameter. Hence, they sampled sea grass from different sites and DMS was determined by headspace gas chromatography after alkaline treatment with 5 N NaOH and incubated for 12 hours because DMSP could degrade to DMS under these procedures. Unlike oceanic fluxes, terrestrial biogenic emissions are extremely difficult to quantify because DMS can be dissociated in a number of sulfur compounds. A chamber technique is commonly used rather than micrometerological techniques since there are also no specific and fast response sulfur detectors to measure directly the sulfur fluxes (Bates et al., 1992).

Table 2.1: Global nitrous oxide quantity

Source	IPPC, 1992	IPPC, 1995a (Tg N yr^{-1})	IPPC, 1997
Natural			
- Ocean	1.4-2.6	3.0 (1-5)	3.0 (1-5)
- Tropical soils			
Wet forest	2.2-3.7	3.0 (2.2-3.7)	3.0 (2.2-3.7)
Dry savanas	0.5-2.0	1.0 (0.5-2.0)	1.0 (0.5-2.0)
- temperate soils			
Forests	0.5-2.0	1.0 (0.1-2.0)	1.0 (0.1-2.0)
Grasslands	?	1.0 (0.5-2.0)	1.0 (0.5-2.0)
Subtotal	4.6-8.3	9.0 (4.3-14.7)	9.0 (4.3-14.7)
Anthropogenic			
- agricultural soils	0.03-3.0	3.5 (1.8-5.3)	3.3 (0.6-14.8)
- biomass burning	0.2-2.1	0.5 (0.2-1.0)	0.5 (0.2-1.0)
- industrial sources	0.8-1.8	1.3 (0.7-1.8)	1.3 (0.7-1.8)
- cattle and feedlots	?	0.4 (0.2-0.5)	2.1 (0.6-3.1)
Subtotal	1.0-6.9	5.7 (3.7-7.7)	7.2 (2.1-19.7)
Total Sources	5.6-15.2	14.7 (8-22.4)	16.2 (6.4-34.4)
Sink			
- Atmospheric Increase	3.0-4.5	3.9 (3.1-4.7)	3.9 (3.1-4.7)
- Soils	?	?	?
- Stratospheric Sink	7.0-13.0	12.3 (9.0-16.0)	12.3 (9.0-16.0)

Source: Intergovernmental Panel on Climate Change (IPPC), Paris, France, 1997

(IPCC, 1997)

Table 2.2 N_2O fluxes from various sources.

Source	N_2O flux ($\mu g\ m^{-2}\ h^{-1}$)	Reference
- Tropical forest soils (Brazil, Ecuador, Puerto Rico)	44.7	Keller et al., 1986
- Temperate pine forest soil (Norway)	13.1 to 53.7	Situala et al., 1995
- German beech forests (Germany)	196	Brumme and Beese, 1992
- Deciduous forests (Germany)	9.17 to 34.0	Schmidt et al., 1988
- Deciduous forests (US) * from Massachusetts to Wisconsin	0.524 to 52.4	Bowden et al., 1990
- Coniferous forests (US) * from Massachusetts to Wisconsin	0.264 to 115.0	
- Coniferous forests (UK)	0.786 to 657.38	Carnol and Ineson, 1999
- Birch forests (Finland)	55.61	Prieme and Christensen, 2001
- Grassland (Germany)	179.39	Prieme and Christensen, 2001
- Grassland (Sweden)	16.14	
- Rye wheat (Germany)	261.90	
- Barley (Sweden)	102.25	
- Barley (Scotland)		Ball et al., 1999
* Spring season	64.20 to 245.10	
* Winter season	51.89 to 66.11	
- Silt loam soil (Germany)		Kaiser et al., 1998
* Winter wheat	37.58	
* Barley	37.06	
* Sugar beet	31.95	
* Rape	44.52	

Table 2.2 (Cont.)

Source	N_2O flux ($\mu g\ m^{-2}\ h^{-1}$)	Reference
- Wheat stubble (Denmark)	509 to 635	Christensen et al.,1996
- Carrot cropping (Denmark)	1,030 to 4,170	
- Potato field (Germany)	Less than 785.71	Flessa et al., 2002
- Organic boreal soil (Finland)		Maljanen et al., 2002
* Grassland	159	
* Barley	132	
* Bare cut soil	171	
* Bare tilled soil	62	
- Frozen soil (Germany)		Teepe et al., 2000
* Agricultural land	81.48	
* Fallow	37.83	
- Farm (New Zealand)		Choudhary et al., 2001
* Permanent pasture	116.29	
* Continuous grown maize for 17 year	122.57	
* Continuous grown maize for 34 year	84.86	
- Pasture (UK)		Williams et al., 1998
* Before application of urine	1,964.29	
* After application of urine	43,214.29	
- Temperate and tropical region		Freyney, 1997
* Uncultivated lands	Less than 35.9	
* Natural ecosystems	Less than 71.5	
* Fertilized lands	More than 108	
- Agricultural soil (US)		Whalen, 2000
* Pre-fertilization	31.4 to 78.6	
* After treatment with liquid swine waste	More than 12,600	

Table 2.2 (Cont.)

Source	N_2O flux ($\mu g\ m^{-2}\ h^{-1}$)	Reference
- Agricultural loam soil (Costa Rica)		
* Maize & Taro		
~ Unfertilized soil	32.68	
~ Fertilized soil	111.26	Weitz et al., 2001
* Papaya & Balsa		
~ Unfertilized soil	40.23	
~ Fertilized soil	391.29	

Table 2.3 CO_2 fluxes from various souces.

Source	CO_2 flux ($mg\ dm^{-2}\ h^{-1}$)	Reference
- Tropical forest soils (Brazil, Ecuador, Puerto Rico)	3.948	**Keller et al., 1986**
- Temperate pine forest soil (Norway)	2.015 to 2.718	Borken et al., 1999
- Boreal forests (Canada)	3.750	Rayment and Jarvis, 2000
- Birch forest (Finland)	5.7	Maljanen et al., 2002
- Alpine site (US)	0.397	Sommerfeld et al., 1996
- Subalpine site (US)	0.97	
- Arctic ecosystems (Siberia)	0.229	Zimov et al., 1993
- Tussock tundra ecosystems (US)	0.468	Oechel et al., 1997
- Wet sedge ecosystems (US)	0.105	
- Horseshoe Lake tree kill, Mammoth mountain (US)	129.17 to 871.25	Gerlach et al., 2001
- Bare soil (Japan)	0.907 to 3.074	Nakadai et al., 2002
- No-tilled silt loam soil, Central Ohio (US)	0.611 to 6.417	Duiker and Lal, 2000
- Grassland (Switzerland)	0.0090 to 0.013	Sowerby et al., 2000
- Grassland, California (US) * Serpentine plant communities * Sandstone plant communities	 0.419 to 0.527 0.439 to 0.490	Cardon et al., 2001
- Grassland (Germany)	4.353	Klemedtsson et al., 1999 cited on Prieme and Christensen, 2001
- Grassland (Sweden)	8.706	
- Grassland (Finland)	6.697	
- Tallgrass prairie, Texas (US)	4.186 to 8.790	Mielnick and Dugas, 2000

Table 2.3 (Cont.)

Source	CO_2 flux ($mg\ dm^{-2}\ h^{-1}$)	Reference
- Southern Wisconsin (US)		Wagai et al., 1998
* Prairie	3.010	
* Corn (Tilled)	2.126	
* Corn (No-tilled)	2.239	
- Rye wheat (Germany)	8.706	Klemedtsson et al., 1999 cited on Prieme and Christensen, 2001
- Barley (Sweden)	4.353	
- Organic boreal soil (Finland)		Maljanen et al., 2002
* Barley	14.9	
* Bare cut soil	10.6	
* Bare tilled soil	11.4	
- Gray forest soil (Russia)		Pomazkina et al., 1996
* fallow - wheat	1.208	
* fallow – fallow – wheat – wheat	1.125	
* fallow – fallow – wheat – wheat – wheat	1.292	
* resting fallow	0.875	
- Silt loam soil (New Zealand)		Aslam et al., 2000
* Maize cropping with plow tillage	5.496 to 12.37	
* Maize cropping with no tillage	6.565 to 13.89	
* Permanent pasture	8.397 to 20.15	

Table 2.3 (Cont.)

Source	CO_2 flux (mg dm^{-2} h^{-1})	Reference
- Clay loam (US)		Reicosky, 1997
* Mold board plow		
~ Initial	291.0	
~ After 55 minutes	20.0	
* No tillage		
~ Initial	7.0	
~ After 55 minutes	2.0	
* Mold board plow + Disk harrow twice		
~ Initial	70.0	
~ After 3 hours	20.0	
- Dark red latosol (Southern Brazil)		Scala Jr. et al., 2001
* No tillage	2.0	
* Tillage	3.2 to 4.8	

Table 2.4 DMS fluxes from various sources.

Source	DMS flux ($nmol\ m^{-2}\ h^{-1}$)	Reference
- Tropical forest (Brazil)	1.91 to 2.87	Andreae et al. 1990 cited on Watts, 2000
- Temperate forest (China and Japan)	3.31 to 5.14	Kanda et al., 1995 and Yang et al., 1996 cited on Watts, 2000
- Peatland (Canada)	4.0 to 428.0	Mello and Hines, 1994
- Sea grass sediment ecosystem (France)		Henk et al., 2000
* Anoxic condition	97.0	
* Dark condition	53.6	
- Paddy fields (Tsukuba, Japan)	14.63 to 26.04	Kanda and Minami, 1992
- Paddy fields (Tsukuba, Japan)		Nouchi et al., 1997
* Straw plot before heading	Less than 243.08	
- Paddy fields (Ibaraki, Japan)	16.05 to 24.61	Kanda et al., 1992
- Paddy fields (Nanjing, China)	11.06 to 23.19	Yang et al., 1998
- Maize and wheat field (Tsukuba, Japan)		Kanda et al., 1995
* Loam light color andosol		
~ +N plot	15.33	
~ - N plot	4.28	
* Clay loam soil		
~ +N plot	21.40	
~ - N plot	4.28	

Table 2.4 (Cont.)

Source	DMS flux (nmol m^{-2} h^{-1})	Reference
- Agricultural fields (US)		Goldan et al., 1987
* Soyabean	131.99	
* Oats	82.05	
* Orchard grass	28.54	
* Purple clover	24.97	
* Corn	973.89	

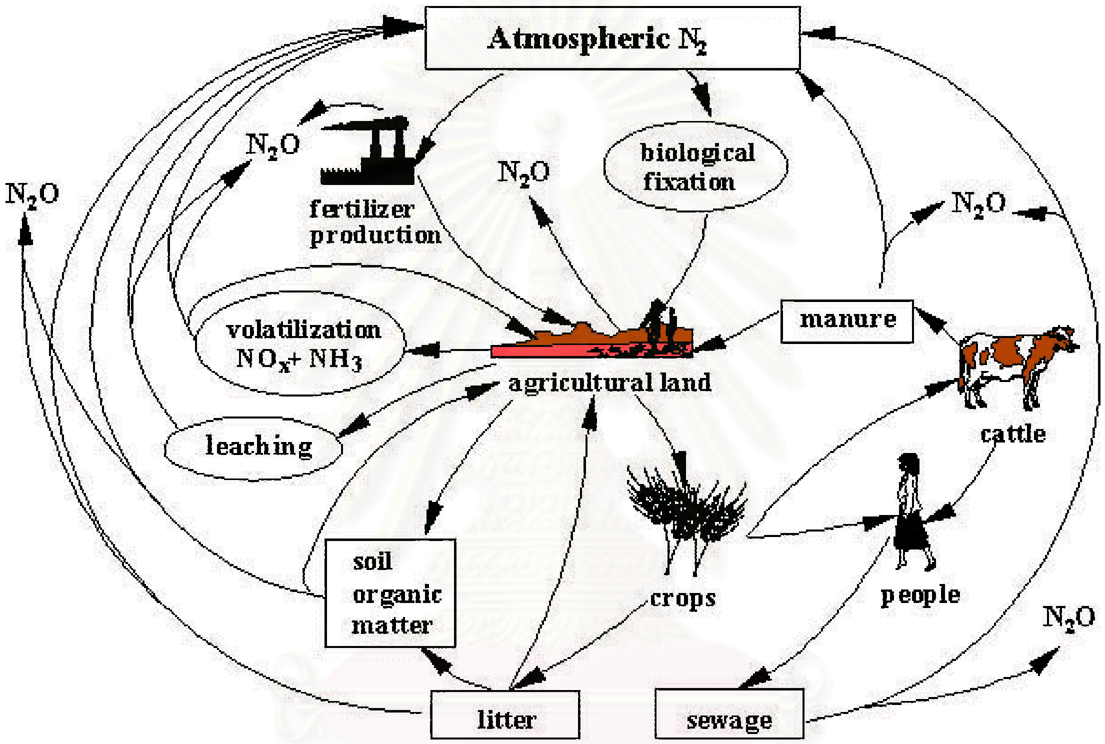


Figure 2.1 Diagram of agricultural soil N cycle and nitrous oxide production (Moiser and Kroeze, 1998).

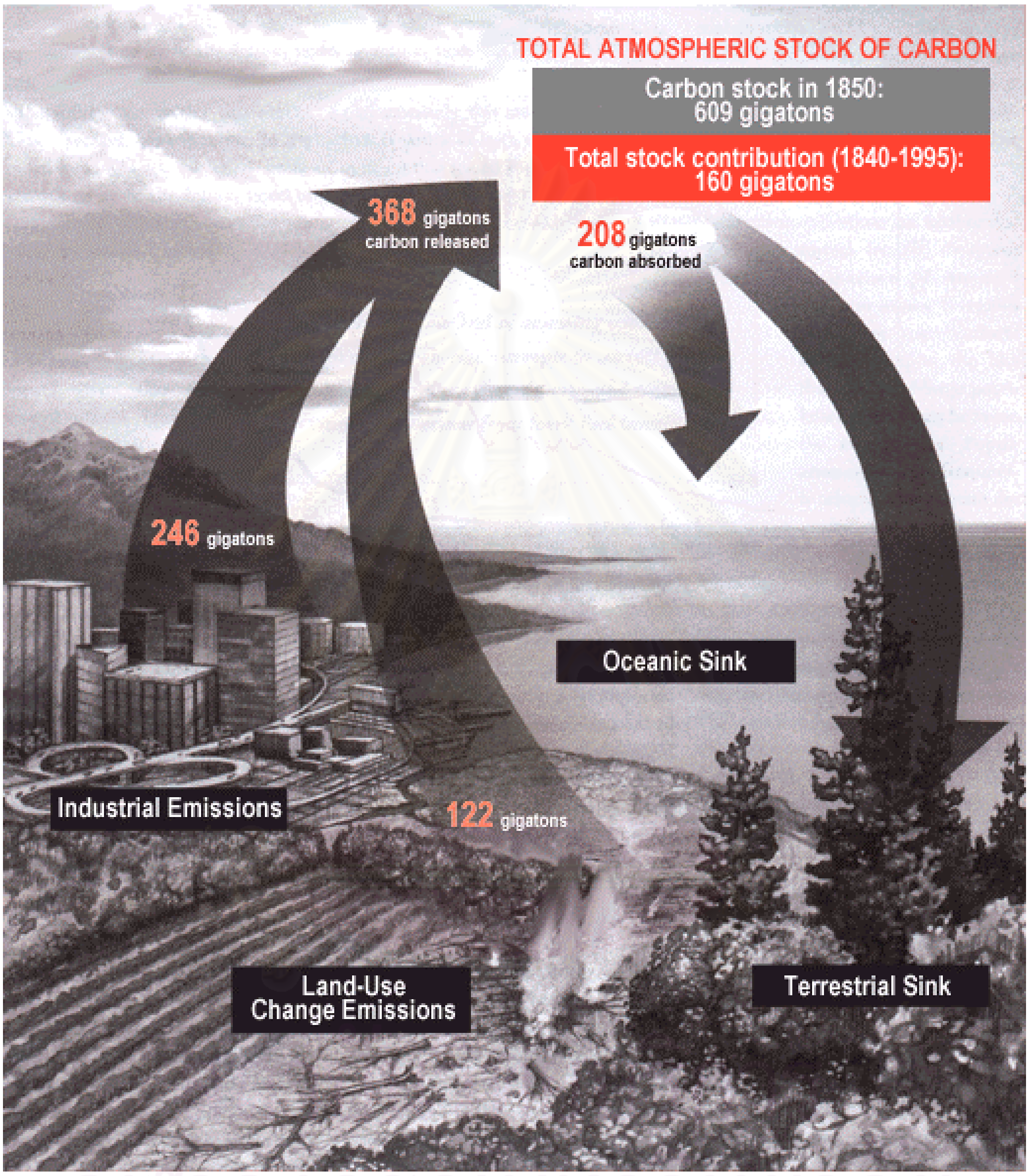


Figure 2.2 A simplified view of the global carbon cycle. (Austin et al., 1998)

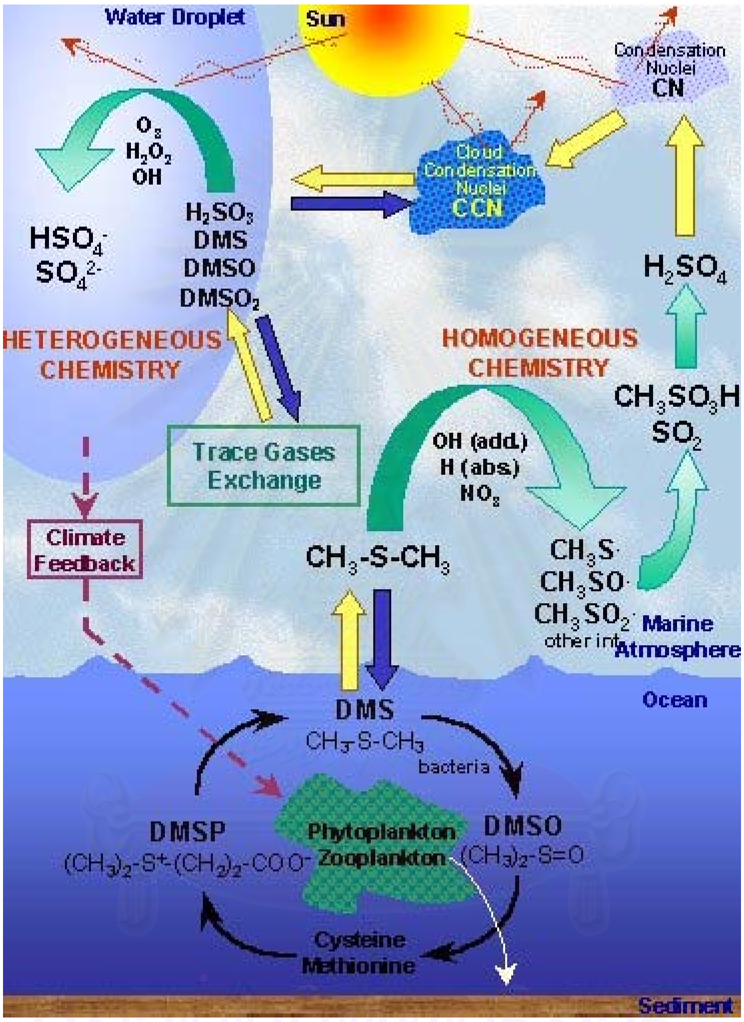


Figure 2.3 DMS cycle in global climate regulation (DMS interactive).

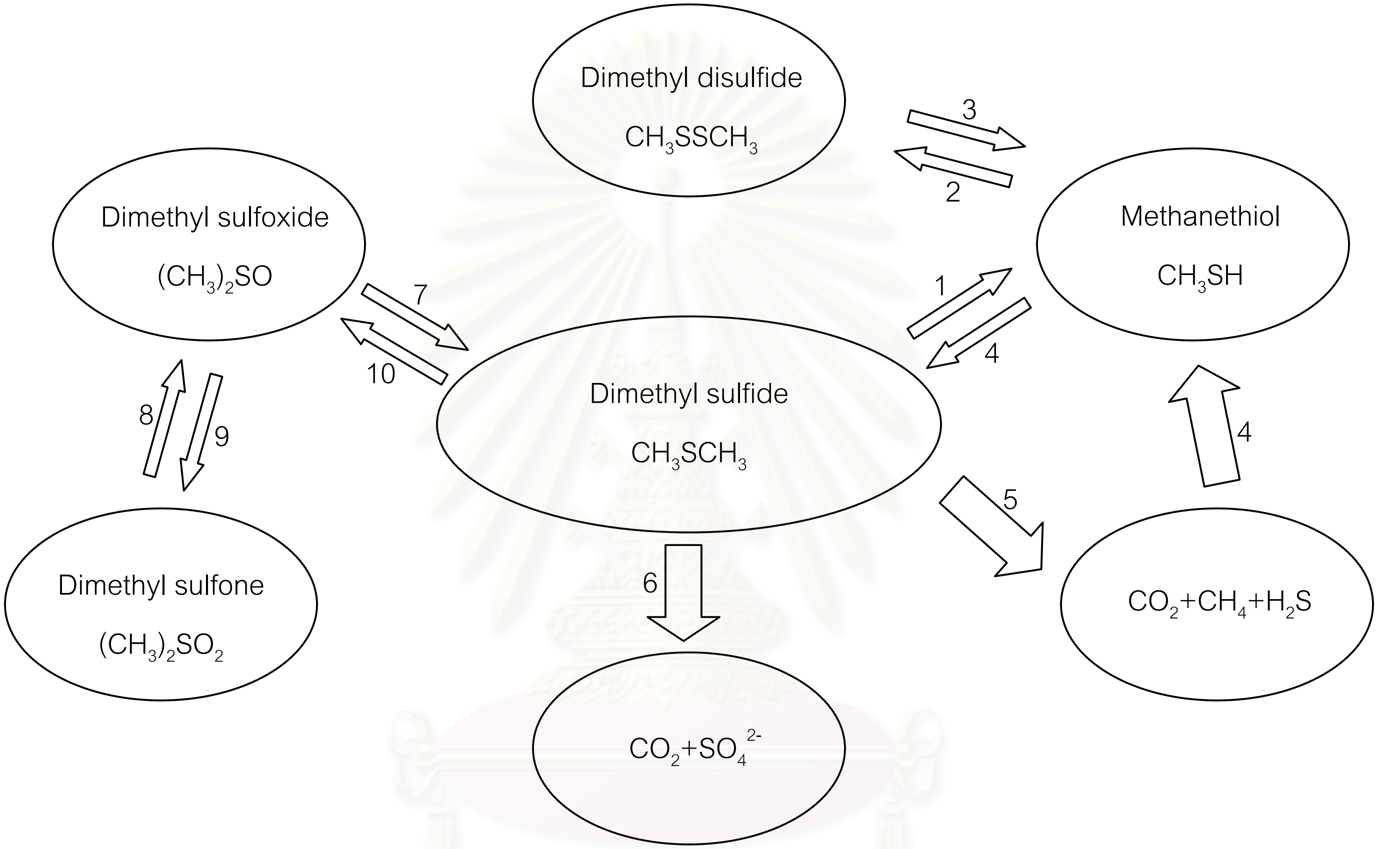


Figure 2.4 DMS cycle. 1) aerobic and anaerobic bacteria; 2) chemical and probably biochemical oxidation; 3) aerobic and anaerobic bacteria; 4) thiol S-methyltransferase; 5) sulfate reducers and methanogens; 6) aerobic bacteria (hyphomicrobia and thiobacilli); 7) chemical and biochemical (aerobic and anaerobic); 8) chloroperoxidase; 9) mechanism unknown; 10) aerobic and anaerobic bacteria

CHAPTER 3

METHODOLOGY

3.1 Site description

The sampling sites were located in agricultural field and forest, Japan, as described below.

3.1.1 Agricultural fields

The location of agricultural field was in Tokyo University of agricultural and technology, 35° 41’ N, 139° 29’ E, and 60 meter elevated from sea level. The vegetations were cropped in a total area of 100x150 m^2, and the schedule of the vegetation was:

- corn (*Zea mays L.)*: July – October 2001,
- wheat (*Triticum aestivum*): November 2001 – June 2002, and
- bean (soyabean, *Glycine max merrill*): July – October 2002.

Agricultural experiments were classified into different zones as illustrated in Figure 3.1. Symbols in this figure represent the characteristics of agricultural methods as illustrated below:

- +T tillage with rotary plow 25 cm. depth,
- -T no tillage,
- M application with manure, which composition is shown in Table 3.1,
- F application with chemical fertilizer, which composition is shown in Table 3.1,
- +P spray pesticide in field and
- -P no pesticide.

Four different plot areas (or will be, from this point onwards, called “plots” for simplicity) were selected to examine the effect of tillage and fertilizer on emission fluxes of pollutants, these included: +TF-P, -TF-P, +TM-P, and –TM-P. The effect of pesticide applied in field was ignored because chemicals in pesticide would have strongly affected activities of microorganisms and plants which were thought to be our main sources of pollutants. Hence, the effect of pesticide should be carried out as a separate investigation.

Table 3.1 shows the amounts of fertilizer and the date at which the fertilizer was applied to various vegetation fields. After the addition of fertilizer in each plot, soil in +T zone was tilled by rotary plow. In the case of wheat plantation, the application of total fertilizer was separated into two intervals due to the long cropping period. The first period started in November 2001 where a third-fourth of total weight of fertilizer was applied, and the rest was re-applied in February 2002.

3.1.2 Forests

Pine forest site was selected in Ohoshiba-Kougenn, Minami-Minowa Village, Kami-Ina Gun, Nagano Prefecture, Japan. The location is 35° 52’ N, 137° 58’ E, and the elevation is about 60 meter above sea level. The predominant plant species is red pine (*Pinus densiflora sieb. Etzucc.*) within this area of approximately 1600x1600 m^2.

Moreover, on April 27, 2002, emission fluxes were measured in Hakiuchi forest. One part of this forest is called “N-excess forest” where there was abundant of Oak tree, whereas the other part is called “Artificial forest” where Cedar was planted.

3.2 Air sampling

Because of the lack of specific detectors required for micrometeorological measurement, a simpler Chamber technique was employed for measuring the rate of emission of any pollutants from soil in this study . This could be separated into closed and opened chamber techniques. Both systems have individual advantages, and the selection among these two techniques depended on the kinds of pollutant and the location of the sampling site.

3.2.1 Nitrous oxide system

In Figure 3.2, N_2O chamber set onto soil was illustrated. The closed chamber was selected for the measurement of N_2O flux because the gas chromatography could not be operated in field, thus continuous system could not be applied to this experiment. Cylindrical chambers (17.4 cm inside diameter) were placed onto selected area, and air inside each chamber was then drawn using a 25 mL syringe at 10 or 15 minutes interval depending on temperature in that day, i.e. 10 minutes for warm days and 15 minutes for cold days. Air samples were injected into vacuum bottles before being transferred to the analyzer in the laboratory.

3.2.2 Carbon dioxide system

Figure 3.3 shows the diagram of the continuous opened chamber system set for CO_2 flux measurement. Firstly, air was pumped in the rate of 10 L/min into the chamber which had a fan inside in order to ensure perfect mixing. Then air inlet and outlet were drawn out by an air sampler at the rate of 0.5 L/min. After that, air samples were automatically transferred to the CO_2/H_2O analyzer model LI-6262 for CO_2 concentration measurement. Measurement data were collected in the data collector modeled ‘Solac III MP-090’. Buffer solution, dryer, and purge system were used to protect the analyzer should there be uncontrollable overflow of sample into analyzer. Each device was illustrated in Figures 3.4 to 3.7.

The setup of the closed chamber system was usually applied to cases where the setup of the opened chamber was difficult such as forests. Also this technique was preferable in the case where numerous data from different places were required as it was a more easily setting system. Figure 3.8 demonstrates the sampling technique from the chamber using a 5 mL of syringe. An air sample was drawn from the chamber at every 3 minute time interval, where the last sample was collected after closing chamber for 9 minutes. For this measurement, the inside diameter of cylindrical chamber was 17.4 cm., where the cover of chamber was equipped with a small fan to ensure perfect mixing.

3.2.3 Dimetyl sulfide system

Due to a rapid transformation of DMS in the air, a special technique is required for the flux measurement. The Tenax TA, a commercially porous polymer adsorbing agent, was selected to adsorb DMS from the field through the open chamber system. Firstly, Tenax tubes were prepared as shown in Figure 3.9. Before taking the air samples, Tenax tube should be purged by N_2 to ensure that no DMS was left in the tube. Figure 3.10 shows DMS system set on the measurement site while a schematic diagram of this system is illustrated in Figure 3.11. An ambient air was first freed of all sulfur compounds by adsorption using activated carbon. This S-free air was then pumped through a chamber at the rate of 1 L/min. The sample was drawn at the outlet of the chamber at the rate of 0.1 L/min and was adsorbed by Tenax tube. After taking samples for 15 minutes, Tenax tube should be kept in cool and dark place before being analyzed for DMS.

3.3 Analyses of N_2O, CO_2, and DMS

3.3.1 Nitrous oxide concentration

A gas sample collected in the collecting bottle was drawn by a pressure lock syringe and was injected into a gas chromatography (GC) equipped with electron capture detector (ECD). The air sample was mixed with the carrier gas in the GC column and passed through a pack column where a separation of various gaseous components took place before reaching the GC detector. The N_2O peak appeared in the sample chromatogram was thereafter converted to its associated concentration by comparing with the standard curve. The specifications of GC are listed below:

Specification of Gas cromatography (ECD)

Model	:	GC14B_ECD
Packing	:	63Ni
Column packing	:	Q50-80 mesh
Material and Size	:	Stainless comlumn 4mm x 3 mm x 2 m
Carrier gas	:	N_2 (99.9999%)
Flow rate	:	30 mL/min
Column temperature	:	60°C
Detector temperature	:	340°C
Recorder	:	GC6A shimatzu
Injector	:	A-2 Type Gas syringes 2.0 mL

3.3.2 Carbon dioxide concentration

Apart from CO_2/H_2O analyzer in the open chamber system, Infrared Gas Analyzer (IGA) was selected as an analyzer for the concentration of CO_2 from the closed chamber system. As illustrated in Figure 3.12, 0.3 L/min of ambient air was pumped through the analyzer as a carrier gas. Soda lime and magnesium perchlorate were used to remove CO_2 and H_2O, respectively, before reaching the analyzer. A standard curve was also made for the evaluation of CO_2 concentration in the gas sample. The specification of this system is:

Specification of analyzer system

- Infrared Gas Analyzer (Model ZRC)
- Recorder by Yokogawa 3056 Pen recorder (L-19)
- Range used is 0.25 mV/cm
- Standard gas (CO_2) 385 ppm is at 14.7 Mpa at 35 ^{o}C (Nippon Sanso)
- Standard gas (CO_2) 905 ppm is at 120 kg/cm^2 at 35 ^{o}C (K.K.)
- Standard gas (CO_2) 1880 ppm is at 150 kg/cm^2 at 35 ^{o}C (Juu Ten Gas)

3.3.3 Dimetyl sulfide concentration

Similar to the method of analyzing N_2O concentration, DMS concentration was also analyzed by using gas chromatography, but istead of ECD, GC was equipped with a flame photometric detector (FPD) (All devices were shown in Figure 3.13). However, the analysis for DMS was slightly more complicated than those of N_2O and CO_2. Firstly, standards were prepared at the concentrations of 100μM, 50μM, and 10μM by diluting the stock solution of DMS with a concentration of 13.433 M. The solvent for this dilution was ethanol because DMS is not soluble in water. Then all standards were filled in amber bottle glasses and were tightly sealed for oxidation protection, and then kept in a cool place. The standard was firstly injected into the Tenax tube together with a N_2 flow to ensure that all sulfur compounds were removed from the sample. This is illustrated in Figure 3.14. The final peak obtained from the GC for DMS came out at around 2.7 to 3.0 minute (with the setting of GC as shown below). The specification of GC is:

Specification of Gas chromatography (FPD)

Instrument : Shimazu Gas chromatograph GC-14B
Detector : Flame Photometric Detector
Column
    Material : glass
    Size : i.d.3mm; length,2m
    Packing : β, β'-oxydipropiontrile
    60-80 mesh chromosorb
Carrier gas : N_2
Injecter temperature : 130° C
Column temperature : 70° C
Detector temperature : 150° C
Flow rate of N_2 : 43ml/min.(100kPa)
Flow rate H_2 : 40ml/min.(60kPa)
Flow rate Air : 47ml/min.(60kPa)
Detector range : 10^1
Recorder : Shimazu Chromatopac C-R5A

3.4 Soil parameters collection

Because of the vital effect of soil parameters on pollutant fluxes, some soil parameters were measured simultaneously with the collection of air samples. Moreover, soil samples in the field were also collected and analyzed in the laboratory for some certain parameters as discussed below.

3.4.1 Soil temperature

Soil temperature in the continuous open chamber system was measured by using 10 sets of copper wires, where the precision of this system was as small as 0.0025°C. In addition, thermo recorders with 10 seconds interval detection were used for simultaneous measurements of both surface and subsurface (at 1 cm depth) soil temperatures.

3.4.2 Gas/liquid/solid fractions

Soil usually consists of three phases i.e. solid, liquid, and gas. The fraction of each phase was measured during the time of emission measurement. This parameter is also known simply as "three phase" parameter, and this name will be used throughout this text from this point onwards. Soil samples were collected by a three-phase collector (illustrated in Figure 3.15). These samples were analyzed by a three phase meter (Figure 3.16), where the percentage of all phases would be obtained.

3.5 Micrometorological parameters collection

Micrometeorological data were collected from the various devices installed on the meteorological tower settled near the measurement area, and the setting was as illustrated in Figure 3.17. Parameters of concerns include solar radiation, soil heat flux, net radiation, wind speed, and canopy temperature.

3.5.1 Energy associated parameters

Net radiometer (Eko Co. Ltd, model MS-40) is an instrument used to measure net all-wave heat flux from incoming (sun) and outgoing (ground) radiations. The receiving surface of a net radiometer was a black plate with temperature sensors attached both at upper and lower surfaces. This allowed the measurement of the temperature difference across the plate which was then translated into a voltage output. The net radiation readings from the net radiometer were the difference between the total incoming and outgoing radiation fluxes which were proportional to this voltage output from the temperature sensors. Close to the net radiometer, solarimeter was set on the same height to measure solar radiation from the sun. Under the soil near the tower, soil heat flux plates, circle in shape with a dimension of 7 cm (diameter) and 5 mm (thickness) were buried 1-2 cm below the ground level. The plates were attached with temperature sensors at the upper and lower surfaces. The soil heat flux was then calculated from difference between temperature at top and bottom surfaces multiplied by the conductance of metal. All device are illustrated in Figures 3.18 and 3.19.

3.5.2 Wind speed

An anemometor (R.M. Young company, Model 05103-16B) or wind vane is the wind monitor device installed at the top of the measuring tower (Figure 3.20). It was used to measure both wind speed and direction in horizontal plane (radian from north, clock-wise). The propeller and vertical shaft in the anemometer were made of stainless steel. The rotation of this propellor produced an AC wave signal, which was sent to the recorder at every ten seconds.

3.5.3 Canopy temperature

Canopy temperature was measured at 15 cm above canopy by two sets of dry-wet bulb thermometers (Figure 3.21) with a minimum detection limit of 0.01°C. The wet bulb thermometer was covered with moisturized cloth. The results were recorded every 10 seconds by the data logger device, Solac (Eko Co. Ltd).

3.6 Fluxes calculation

3.6.1 Closed chamber system

Regarding N_2O and CO_2 fluxes calculation in closed chamber system, the relation of concentration versus interval must be constructed to find the slope. Fluxes were then calculated from:

$$F = k\left(\frac{\Delta C}{\Delta t}\right)\left(\frac{273.15}{273.15+T}\right)\left(\frac{V}{A}\right) \qquad \text{(eq. 3.1)}$$

where F = the rate of emission [mass of pollutant area^{-1} time^{-1}];
k = a units conversion factor for calculation of emissions for each pollutants;
T = temperature of the air within the chamber [Kelvin];
V = the volume of the air within the chamber [Length^3];
A = the area of the soil within the chamber [Length^2];
$\frac{\Delta C}{\Delta t}$ = rate of change in the concentration of pollutants in the air within the chamber [Concentration time^{-1}].

3.6.2 Open chamber system

With respect to CO_2 fluxes and DMS fluxes from open flow chamber system, the difference in concentrations at outlet and inlet was used to calculated emission fluxes. In the case of DMS system, inlet concentration was zero as sulfur compounds in air sample was removed through the activated carbon adsorption, whereas inlet concentration of CO_2 was measured from ambient air nearby the chamber.

Fluxes were calculated from:

$$F = k\left(\frac{V}{A}\right)\left(C_{outlet} - C_{inlet}\right) \qquad \text{(eq. 3.2)}$$

where F = the rate of emission [mass of pollutant area^{-1} time^{-1}];

k = a units conversion factor for calculation of emissions for each pollutants;

V = volumetric flow rate [Length^{3} time^{-1}];

A = the area of the soil within the chamber [Length^{2}];

C_{outlet} = outlet concentration [mass of pollutant Length^{-3}];

C_{inlet} = intlet concentration [mass of pollutant Length^{-3}].

<u>Corn field</u> (Applying on July 5, 2001)

Plot	Mineral contents (%)				Total amount (kg/100 m^2)	Amount (kg/100m^2)		
	H_2O	N	P_2O_5	K_2O		N	P_2O_5	K_2O
Chemical fertilizer								
- *14-14-14*		14	14	14	143	20.0	20.0	20.0
Summary						20.0	20.0	20.0
Manure plot								
- *14-14-14*		14	14	14	36	5.0	5.0	5.0
- *Cattle dung*	64	0.68	0.15	0.70	2,200	15.0	3.3	15.4
Summary						20.0	8.3	20.4

<u>Wheat field</u> (Applying on November, 2001 & February, 2002)

Plot	Mineral contents (%)				Total amount (kg/100 m^2)	Amount (kg/100m^2)		
	H_2O	N	P_2O_5	K_2O		N	P_2O_5	K_2O
Chemical fertilizer plot								
- *14-14-14*		14	14	14	128	17.9	17.9	17.9
Summary						17.9	17.9	17.9
Manure plot								
- *Cattle dung*	64	0.68	0.15	0.70	2,650	18	4.0	18.6
Summary						18	4.0	18.6

<u>Soyabean field</u> (Applying on June 4, 2002)

Plot	Mineral contents (%)				Total amount (kg/100 m^2)	Amount (kg/100m^2)		
	H_2O	N	P_2O_5	K_2O		N	P_2O_5	K_2O
Chemical fertilizer plot								
- *3-10-10*		3	10	10	150	4.5	15.0	15.0
Summary						4.5	15.0	15.0
Manure plot								
- *Cattle dung*	64	0.68	0.15	0.70	2,150	14.6	3.2	15.1
- *0-17-0*		0	17	0	70	0.0	11.9	0.0
Summary						14.6	15.1	15.1

<u>Table 3.1</u> Amount of fertilizer applied in agricultural field.

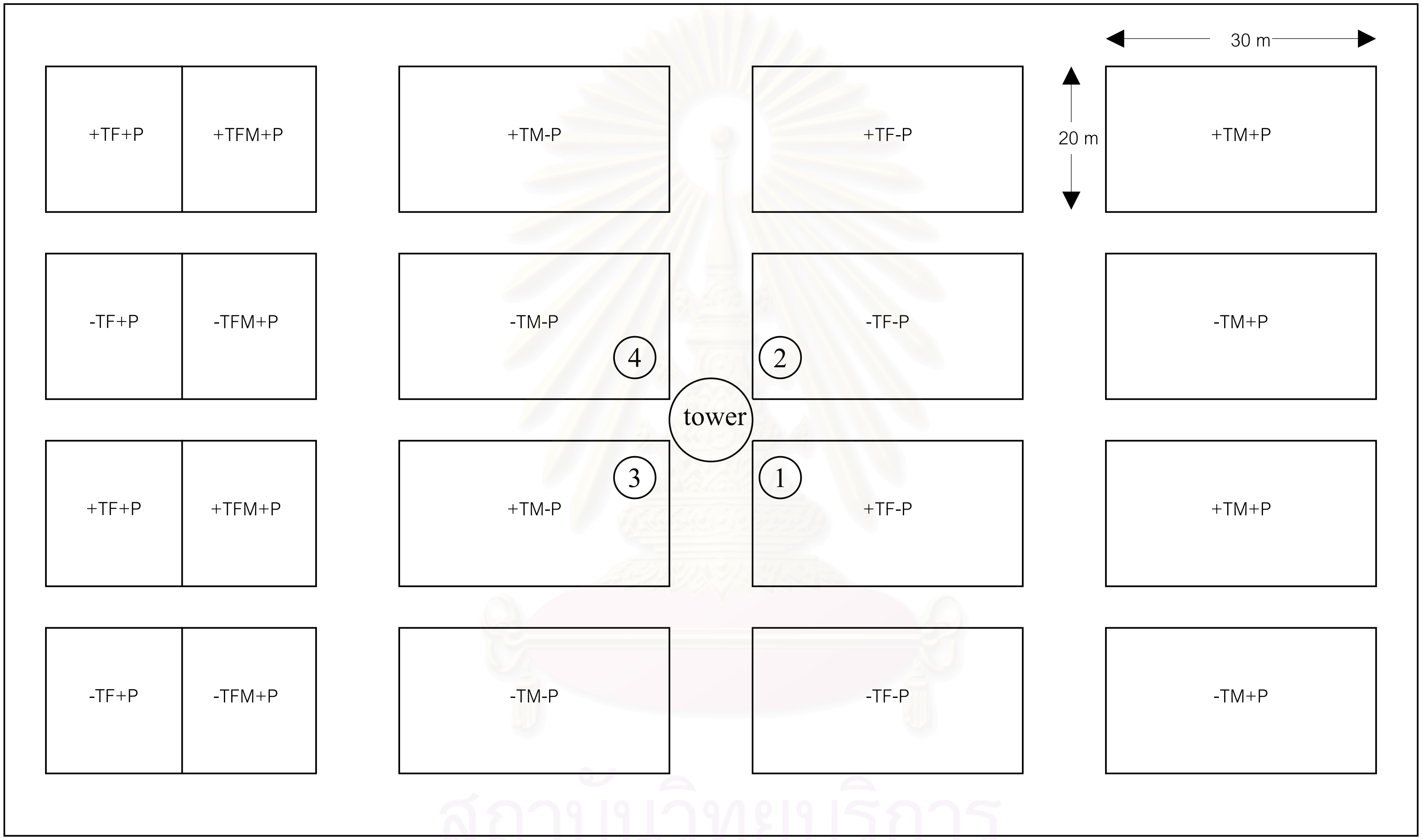
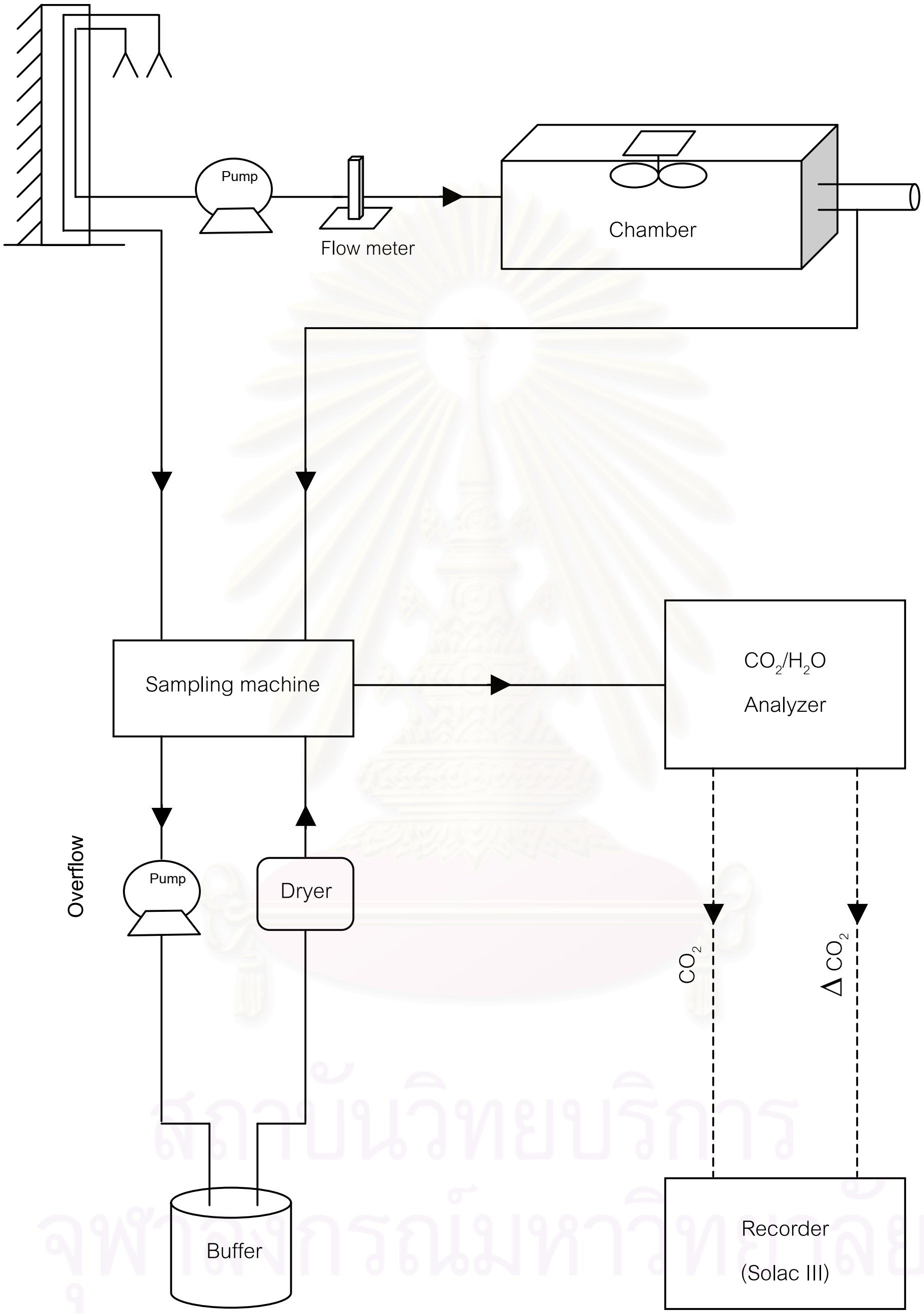


Figure 3.1 Different plots in agricultural field located at Tokyo University of Agricultural and Technology, Japan

Figure 3.2 N_2O chamber



<u>Figure 3.3</u> Schematic diagram of CO_2 open chamber system.

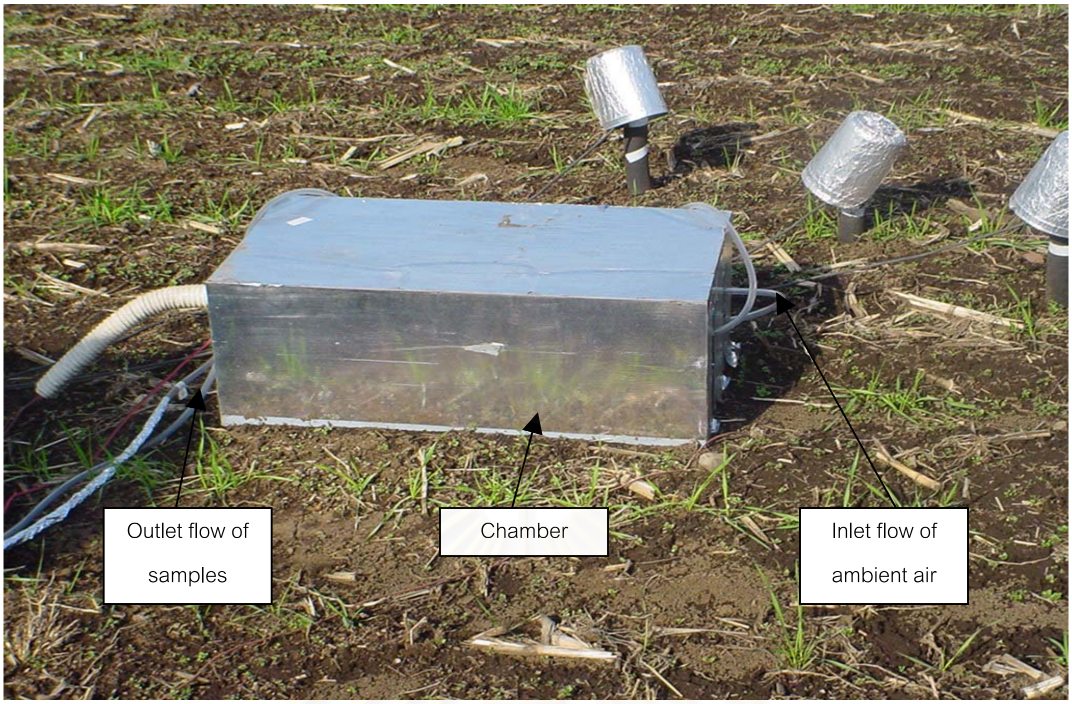


Figure 3.4 CO_2 chamber

Figure 3.5 CO_2/H_2O analyzer

Figure 3.6 CO_2 sampling machine

Figure 3.7 Data collector (SOLAC III)

Figure 3.8 Demonstration of sampling technique from closed chamber.

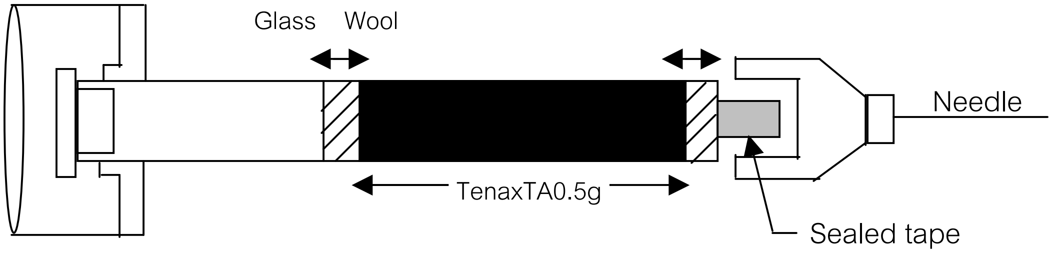


Figure 3.9 Tenax TA tube

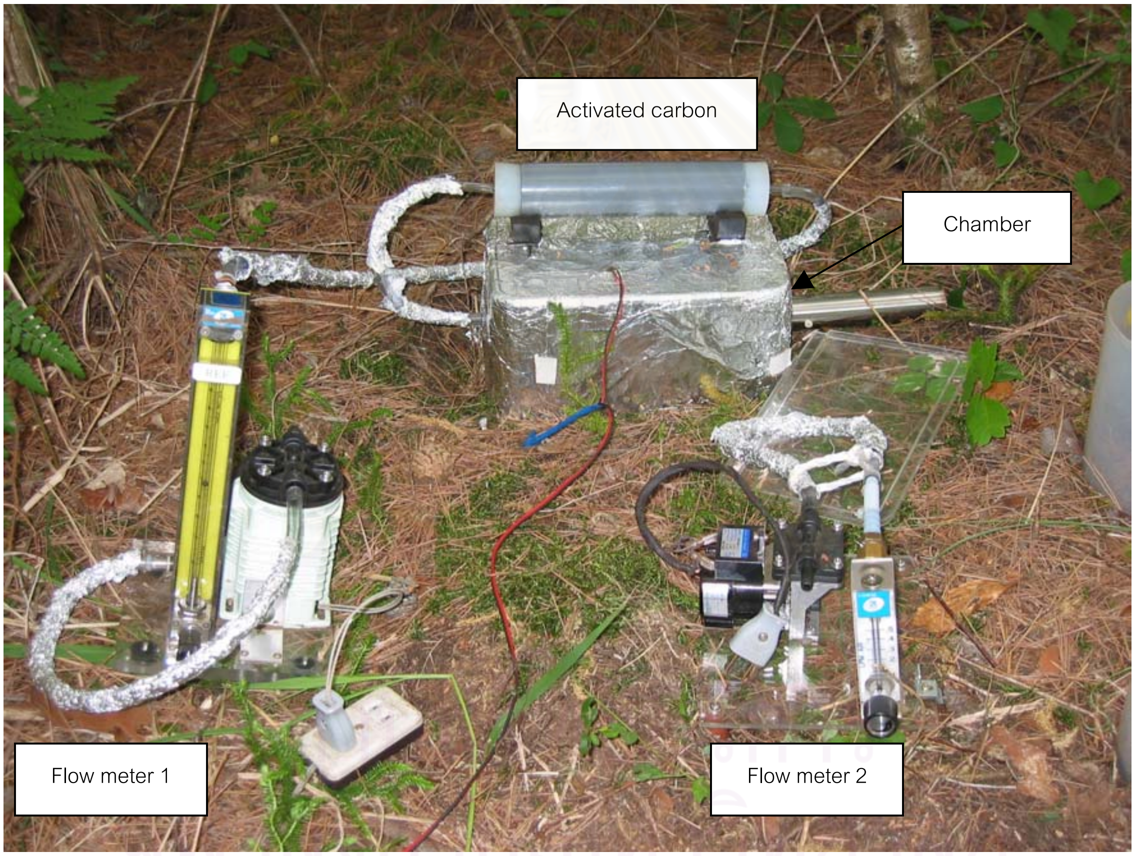


Figure 3.10 DMS system set on measurement site.

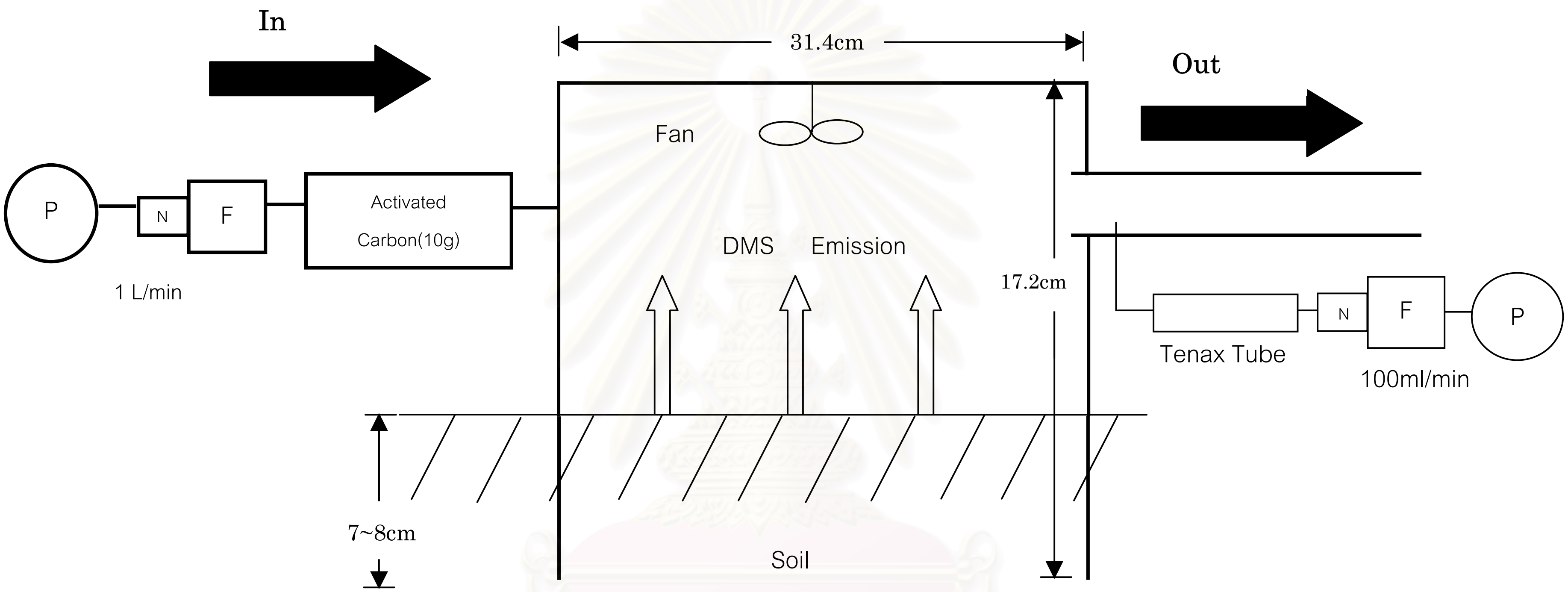


Figure 3.11 Schematic diagram of DMS gas collecting system

F : Flow meter N : Needle Valve P : Air Pump

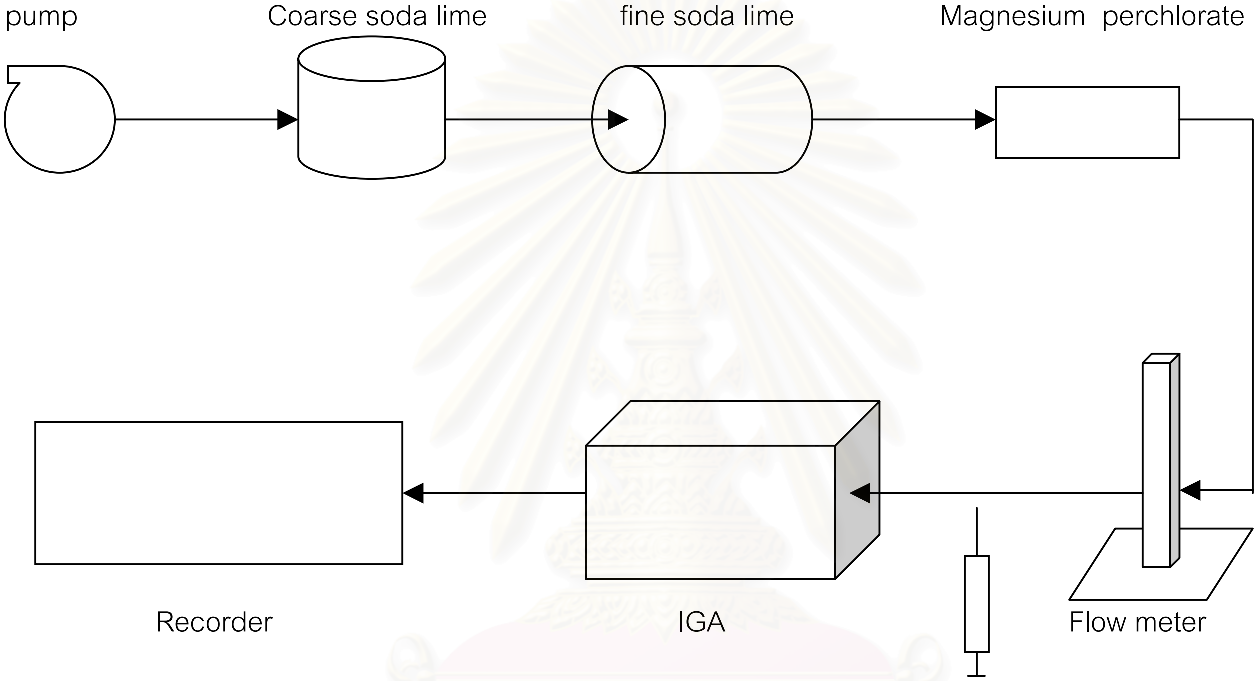


Figure 3.12 Schematic diagram of CO_2 concentration analyzer by Infrared Gas Analyzer (IGA).

Figure 3.13 Gas chromatography equipped with flame photometric detector.

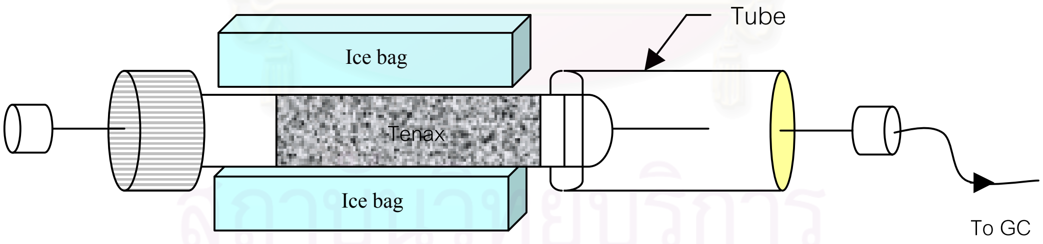


Figure 3.14 DMS Standard preparing system before flowing through GC.

Figure 3.15 Three phases sample collector.

Figure 3.16 Three phase meter (Model DIK-1121).

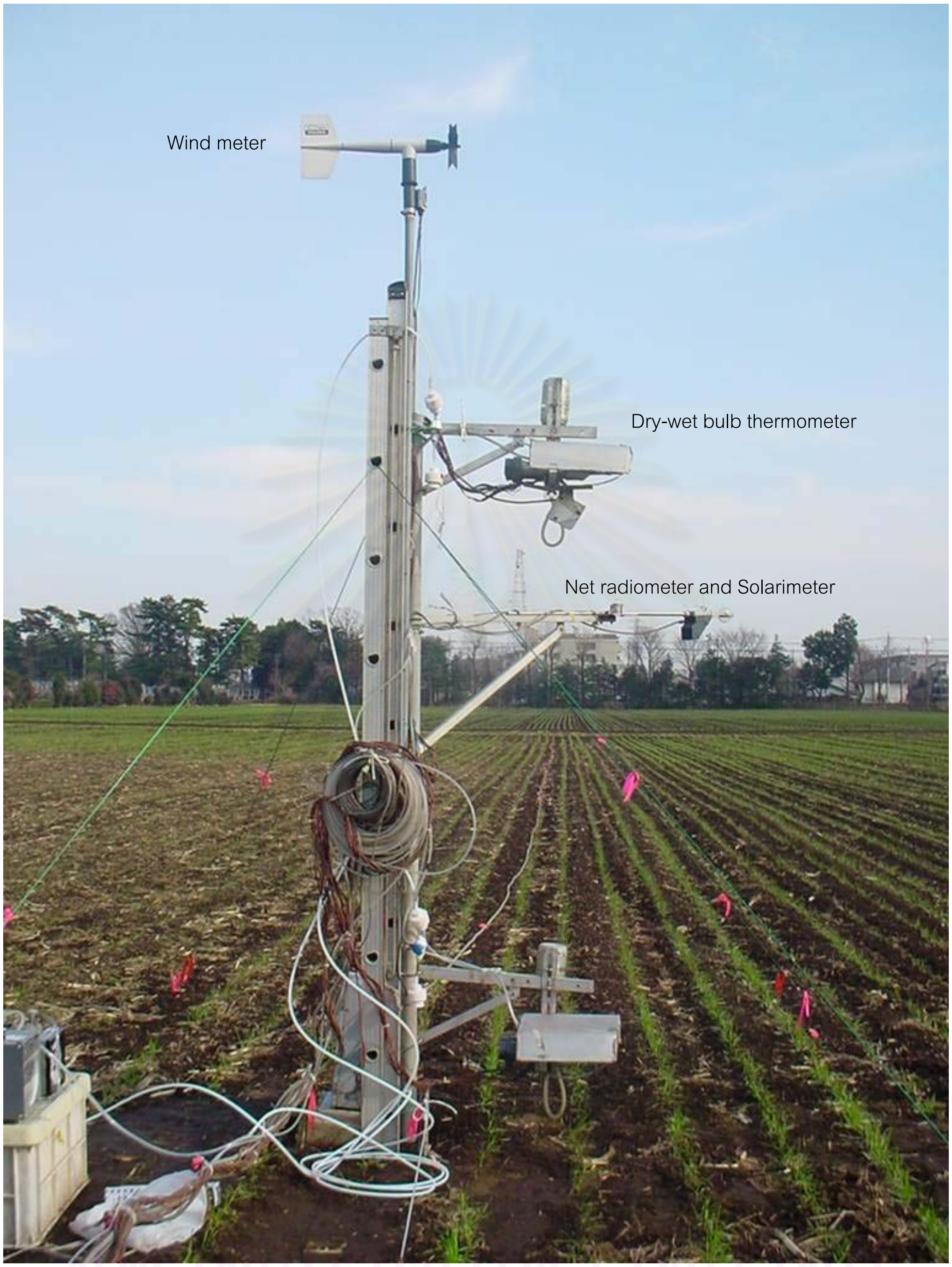


Figure 3.17 The tower setting in the field.

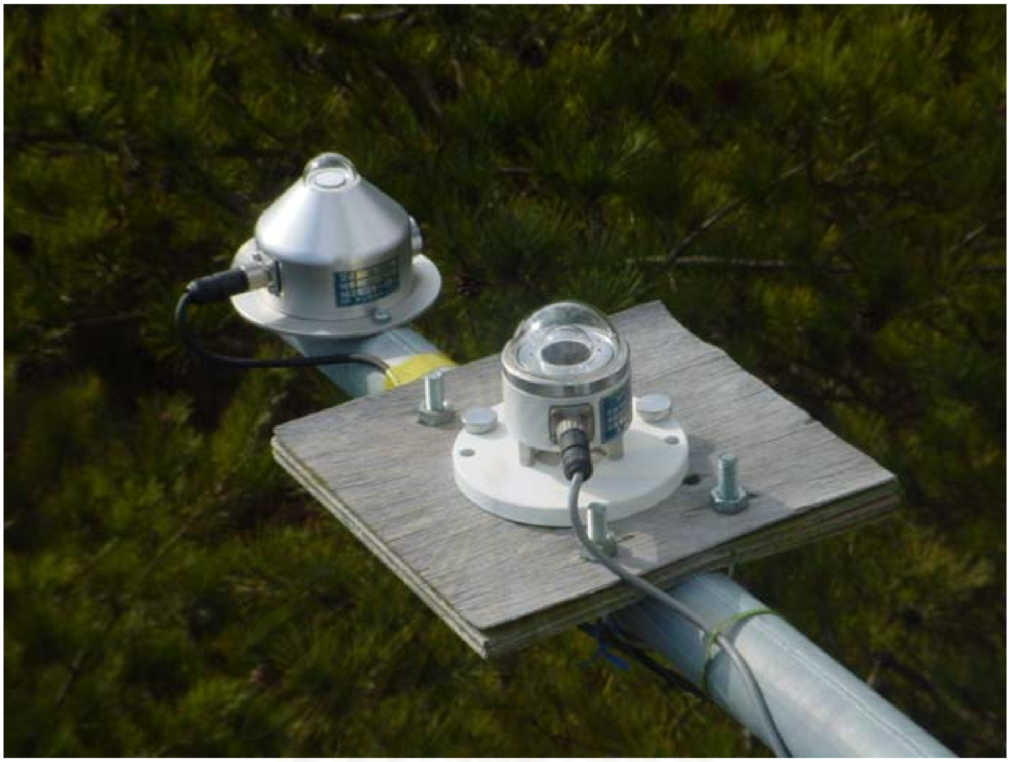


Figure 3.18 Net radiometer and Solarimeter.

Figure 3.19 Soil heat flux plate.

Figure 3.20 Anemometer at the top of tower.

Figure 3.21 Dry-wet bulb thermometers.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Emission fluxes of nitrous oxide, carbon dioxide, and dimethyl sulfide from various areas

4.1.1 Nitrous oxide fluxes

Due to the time constraint, N_2O emission fluxes in the corn field could only be measured on the 24th of August, 2001 (summer season) and the results are illustrated in Figure 4.1.1. Emission fluxes were found to be rather high with a value in a range of 650 to 1,100 ng dm $^{-2}$ h^{-1}. This was apparently greater than emission fluxes in the wheat field measured during March to June, 2002 (Figure 4.1.2). It is worth noting that wheat was annually cropped from winter to spring seasons. The maximum rates of N_2O emission in the wheat field were not over 350 ng dm $^{-2}$ h^{-1}, with the average of less than 200 ng dm $^{-2}$ h^{-1} (the average N_2O emission flux was 111 ng dm $^{-2}$h^{-1} and the standard deviation was 70 ng dm $^{-2}$ h^{-1}). Soyabean was cropped during July to August 2002, which was in the same area soon after the harvesting of wheat. The N_2O emission fluxes from the soyabean field were reported in Figure 4.1.3. Interestingly, fluxes reached the high value of 1,500 ng dm $^{-2}$ h^{-1} during the early period of soyabean plantation in the -TF plot afterwhich the fluxes gradually decreased to a low range of less than 300 ng dm $^{-2}$ h^{-1}. The average N_2O emission fluxes in the soyabean field was 393 ng dm $^{-2}$ h^{-1} with a high standard deviation of 349 ng dm $^{-2}$ h^{-1}.

The probable explanation of high fluxes obtained from the corn and soyabean fields was that both corn and soyabean were cropped during the summer time, and the high temperature might accelerate the production rate of N_2O. The effect of temperature will be discussed later. In addition, the comparison of N_2O emission rates from the various types of vegetation cropped in the same season, i.e. between corn and soyabean, demonstrated that soil in the corn field could emit more N_2O than that from the soyabean field. Although a high level of N_2O was observed in the early period of soyabean plantation, the emission rate had decreased as much as 5 times within only 3 weeks of seeding. This might potentially be because nitrogen content in soil was being fixed by bacteria living in the soyabean roots after seeding which left less N available for the N_2O production mechanism by other microorganisms in the soil.

Turning to N_2O fluxes in the pine forest at Nagano from April to August, Figure 4.1.4 illustrates that the average N_2O flux was found to be around 65 ng dm $^{-2}$ h^{-1}. This was considerably less than those obtained from agricultural areas. The highest flux obtained from the pine forest was less than 250 ng dm $^{-2}$ h^{-1} whereas the lowest became negative at night. This means that the pine forest could actually absorb N_2O from the atmosphere at the night time. However, N_2O flux measured at the Oak and Cedar forest in Hakiuchi was as high as 128.32 ± 74.80 ng dm^{-2} h^{-1}, which was close to the emission rate from the wheat field. The unreported measurement from our laboratory (in the department of agriculture, Tokyo University of Agriculture and Technology) indicated that the soil in this Hakiuchi forest was quite rich in nitrate and was known as the "N-excess forest" and this nitrate could potentially become a significant source of N_2O emission. Hence, N_2O emission in this natural area was found to be as high as that found in the agricultural area.

4.1.2 Carbon dioxide fluxes

Figure 4.1.5 shows average daily CO_2 fluxes measured by the continuous open chamber system in the corn field (-TM plot) in 2001. It could be noticed that CO_2 emission fluxes gradually decreased from August to September (from summer to autumn) and the standard deviation of each day was not over 2.0 mg dm^{-2} h^{-1}. Interestingly, Figure 4.1.6 also indicates that the temperature also gradually decreased from summer to autumn seasons.

Average daily CO_2 fluxes were also measured by the continuous open chamber system in the wheat field in 2002 as illustrated in Figure 4.1.7. Mostly, daily fluxes were not greater than 7.5 mg dm^{-2} h^{-1} with low variation. However, during the change of season from March to April (from Winter to Spring), CO_2 fluxes reached 20.0 mg dm^{-2} h^{-1}, and varied significantly with a high standard deviation of 5 mg dm^{-2} h^{-1}. To ensure the accuracy of the measurement in this period, the closed chamber experiment was carried out in this area, and the results were shown in Figure 4.1.9. With regard to CO_2 flux on the 28th of March, 2002, diurnal flux from the closed chamber, which was in the same area as the open chamber, could reach 10 mg dm^{-2} h^{-1}. This meant that the emission rates obtained from the continuous system during March to April were quite accurate and reliable. The cause of this deviation was still uncertain as it could be either the error of measurement system, or the effect of seasonal change in this period. Considering the trend of CO_2 fluxes and temperature in the wheat field shown in Figure 4.1.8, except the seasonal change duration in March and April as discussed above, the time profile of CO_2 fluxes closely followed the time profile of temperature. This results suggested that there could be a relation between CO_2 emission flux and temperature, this aspect will be discussed in more detail later on.

As said earlier, after the harvest of wheat in July 2002, soyabean was cropped in the same agricultural field. Figure 4.1.10 shows the CO_2 emission fluxes in the soyabean field, where the average of CO_2 fluxes was 10.95±6.75 mg dm^{-2} h^{-1}. The emission rate of CO_2 in +TM plot was some time as high as 30 mg dm^{-2} h^{-1}.

In the pine forest in Nagano (Figure 4.1.11), the average emission rate of CO_2 in summer season was 6.04±3.14 mg dm^{-2} h^{-1} which was less than the fluxes found in the soyabean field cropped in the same season. Moreover, the maximum flux in the pine forest was observed to occur during the daytime of mid-July when the temperature reached maximum in the summer season. Compared to all sources of CO_2 emission flux, the Oak and Cedar forest in Hakiuchi emitted the lowest rate of CO_2.

In conclusion, the variation in CO_2 fluxes obtained from the various vegetation areas might be affected by many parameters such as temperature, fertilizer, tillage, etc. The discussion of the effects of these parameters will be provided in Section 4.2. At this point, it is quite obvious that temperature might be the major influencing parameter on the CO_2 emission flux in each vegetation site as observed from Figures 4.1.6 (Corn field), 4.1.8 and 4.1.9 (Wheat field), and 4.1.11 (Pine forest).

4.1.3 Dimethyl sulfide fluxes

DMS fluxes in the wheat field were measured during March and May 2002 by the open chamber system. Figure 4.1.12 shows that the average flux was 26.41 ± 16.74 nmol m^{-2} h^{-1}. Although temperature in May (spring season) was higher than in March (Winter), trend of DMS emission fluxes in May was found to be much lower (twice as low) than those obtained from March. On the other hand, with respect to DMS fluxes on each sampling day, the emission rate reached the maximum around noon in which temperature was highest.

The measurement in the soyabean field (Figure 4.1.13) could be performed for only two days in summer i.e. 23 July and 15 August 2002 (due mainly to time and equipment limitations). The average flux was 15.52 ± 6.68 nmol m^{-2} h^{-1} which was less than that obtained in the wheat plantation area. However, there are still not enough experimental data to conclude on the effect of vegetation types on DMS fluxes as our data were obtained from the two types of vegetation that were planted in different seasons. It could well be that the type of vegetation affected the emission rate of DMS as Goldan et al., 1987 reported that both wheat and soyabean could emit DMS , but further quantitative analysis is still needed to be carried out.

Turning to the pine forest at Nagano, DMS emission fluxes were measured in April, June, and August. Mostly, DMS fluxes were less than 40 nmol m^{-2} h^{-1} and the average emission rate was 21.20±14.77 nmol m^{-2} h^{-1}. Figure 4.1.14 suggests that DMS fluxes in the pine forest could vary from spring to summer seasons, where the fluxes from this forest were in the same range as those obtained from agricultural areas such as wheat and soyabean fields. At this point, hence, DMS flux was not found to be influenced by the transformation of the forest to agricultural field.

4.1.4 Concluding remarks

The summary of all pollutants fluxes measured in this study was tabulated as follows:

Sources	N_2O flux (ng dm^{-2} h^{-1})	CO_2 flux (mg dm^{-2} h^{-1})	DMS flux (nmol m^{-2} h^{-1})
Corn field (Open chamber)	-	4.80 ± 1.23	-
Corn field (Closed chamber)	911.37 ± 213.37	-	-
Wheat field (Open chamber)	-	5.41 ± 3.44	26.41 ± 16.74
Wheat field (Closed chamber)	111.46 ± 70.31	6.84 ± 2.12	-
Soyabean field	393.36 ± 348.99	10.95 ± 6.75	15.52 ± 6.68
Pine forest	64.86 ± 46.63	6.04 ± 3.14	21.20 ± 14.77
Oak and Cedar forest	128.32 ± 74.80	3.43 ± 1.98	22.16*

* The emission flux was collected only one time in a day.

4.2 Effect of parameters on emission fluxes

4.2.1 Effect of soil parameters

Temperature

Soil temperature was measured in this experiment along with the soil surface temperature which was the temperature at the top of the soil inside the chamber. Since the chamber is quite small, the soil surface temperature was assumed to be equal to the air temperature inside the chamber, and this temperature will, thereafter in this report, be called "air temperature".

The measurement suggests that there was only slight effect of soil and air temperatures on the N_2O emission rate. The explanation follows. Firstly, it should be noted that the results from the corn field were not included in this discussion as the number of data points were too few and did not support reliable discussion. Figures 4.2.1 and 4.2.2 illustrate that N_2O emission rate in the wheat and soyabean fields were rather independent of the temperature. For instance, emission fluxes in the wheat field during May 8th increased with temperature, however, opposite results were obtained on May 22th. Note that the measurement was performed in the area with the highest emission flux, i.e. plot —TM. A possible explanation for this result is that, although rate of denitrification which is thought to be the significant mechanism for N_2O production increases with temperature (from 25 upto 60°C) (Alexander, 1977 cited in Bouwman, 1990), the quantity of N_2O was not accordingly elevated. N_2O is an intermediate, and not the end product, in the denitrification process (see Eq. 2.2) and its emission is a result of N_2O being escaped from the soil before being reduced to nitrogen gas. Hence, the concentration of N_2O might not have rightly reflected the reaction rate, and consequently the effect of temperature on N_2O emission was not apparent. In addition, there might be other parameters affecting N_2O fluxes such as fertilizer application and tillage practices. Similarly, N_2O fluxes in the pine forest at Nagano was found not to be affected by temperature, except at a low range of temperature (10-20 °C) where an increase in temperature seemed to increase N_2O flux (see Figure 4.2.3). The reason for this temperature dependency was still unclear at the time of this experiment.

In the case of CO_2 fluxes, air temperature, soil temperature at 1 cm depth, and soil temperature at 15 cm depth were plotted versus the emission rate in Figure 4.2.4 a, b, and c, respectively, and a strong effect of temperature on CO_2 emission rate in the corn field could be observed. Fluxes seemed to increase linearly with soil and air temperatures. For the wheat field (Figure 4.2.5), except CO_2 fluxes during March to April, the correlation between emission rate and temperature was also found to be linear. Duration between March and April indicates that there existed a period where the fluxes of CO_2 emission from the agricultural area were abnormally high (20 mg dm^{-2} h^{-1}). The exact reason for this peak is still unknown but it is possible that this was a transition period between winter and spring where a major change in soil/air temperature took place. This outbreak in temperature might have caused the microorganism in soil to generate more CO_2. It should also be noted that there existed a lot of rainfall during this change of season which might also have affected the CO_2 flux. In this period, however, the relation between CO_2 fluxes and temperature could still be represented by a linear equation. This meant that temperature was the major factor that influenced CO_2 fluxes. These results were confirmed with the experiment in the close chamber as illustrated in Figure 4.2.6. This finding was attributed to the simple relation between temperature and reaction rate, e.g. Arrhenius law. As the temperature increased, the decomposition rate of organic constituents in soil took place at a higher rate resulting in a higher emission rate of CO_2 which is one of the end products from the decomposition process.

To clearly describe the effect of temperature on CO_2 fluxes in the wheat field, hourly fluxes of CO_2 were plotted with temperature and the results are shown in Figure 4.2.7. From the trend of emission rate shown in this figure, CO_2 fluxes had gradually decreased in the first period of the day before sunrise. After sunrise, fluxes increased to the maximum point around noon and then decreased towards the nighttime. With respect to air temperature, before sunrise, the effect of radiation cooling that caused heat loss from terrestrial to the atmosphere led to a gradual decrease in temperature. As sun rose, temperature began to increase due to solar radiation. The maximum temperature occurred 1-2 hours after the time of highest solar radiation and then gradually decreased towards the nighttime. The maximum soil temperature of any depth occurred later than that at the surface. This time lag in soil temperature was due to the time needed for the heat transfer mechanisms in the soil. Figure 4.2.7 shows that a lag time of more than 1 hour was not unusual. In addition, the difference between highest and lowest temperature of soil at all depth was also less than the surface due to energy dissipation. The comparison between the trends of CO_2 fluxes and temperature in Figure 4.2.7a and 4.2.7b clearly emphasized the effect of temperature on CO_2 flux as the hourly CO_2 fluxes followed the temperature profile reasonably closely.

In regard to the effect of temperature on CO_2 fluxes in the pine forest at Nagano, Figure 4.2.8 shows that high CO_2 fluxes were often obtained in the very same days as those with high soil and air temperatures. Moreover, the relation of CO_2 flux versus soil and air temperatures seemed to be linear.

Turning now to the effect of temperature on DMS fluxes, Figure 4.2.9 shows that DMS fluxes in the wheat field decreased from winter (March) to spring (April). However, daily fluxes suggested that DMS fluxes especially in winter increased with temperature whereas no relation between DMS fluxes and temperature in spring was apparent. Hence, it is difficult at this point to give a solid conclusion on the effect of temperature on DMS flux, unless more experimental evidence is available. Concerning DMS fluxes in the pine forest at Nagano, Figure 4.2.10 does not show any relation between DMS fluxes and temperature.

4.2.2 Effect of micrometeorological data

The mechanisms of pollutants generated from soil activities might be affected either directly or indirectly by micrometeorological parameters such as canopy temperature, solar radiation, wind speed, etc. This section provides experimental findings that might lead to some substantial conclusion.

Canopy temperature

Canopy temperature was the temperature measured above the top layer of vegetation. Figure 4.2.11 (m and n) shows clearly a relation between fluxes of N_2O and CO_2 with canopy temperature (T_c) in the pine forest. Normally, canopy temperature had the same time-profile as the soil temperature. Hence, the influence of canopy temperature on pollutant fluxes was identical to that of soil temperature and this was explained earlier in Section 4.2.1.

Energy associated parameters

The energy associated parameters in this report mean the parameters involved with the transfer of energy between the atmospheric layer and soil, i.e., net radiation, soil heat flux, and solar radiation. Figure 4.2.12 demonstrates that there was no influence of these parameters and the emission fluxes of each pollutant of concern. However, it is interesting to note that the trend of DMS/N_2O fluxes versus energy associated parameters seemed to show similar trajectories. This might reflect the fact that the generation mechanisms of these two pollutants were closely related, and this point will be discussed in detail later on in this discussion section. Similarly, Figure 4.2.11 illustrates that no conclusion could be drawn regarding the effect of energy associated parameters on emission fluxes in the pine forest at Nagano.

__Wind speed__

The relation between wind speed and emission fluxes was demonstrated in Figures 4.2.11 and 4.2.12. It can be observed that wind speed seemed not to affect the pollutants fluxes both in the wheat field and pine forest. This was because mechanism of pollutants production in the chamber was not directly affected by the wind flowing outside the chamber, particularly the closed chamber system. Hence, large scatters of fluxes of pollutants were observed and a clear conclusion on the effect of wind speed on emission rate of N_2O, CO_2, and DMS could not be drawn.

4.2.3 Effect of tillage and fertilizer

To examine the influence of tillage on N_2O fluxes, Figures 4.1.2-4.1.3 should be brought back to attention once again. However, the initial date of gaseous sampling from the wheat field started as late as 4 months after the tillage practice. Therefore soil in the tillage plots at the time of sampling was not much different from soil in the no-tillage plot in terms of soil looseness. Data in Figure 4.1.2 which is the emission rates from the wheat field cannot be used to examine the effect of tillage.

In the case of soyabean field (Figure 4.1.3), N_2O flux from the no-tillage plots was greater than that from tillage plots after applied with chemical fertilizer. This was because soil in the no-tillage zone had lower oxygen content than the tillage zone. Figure 4.2.13 confirmed that the volume ratio of gas in soyabean soil of the tillage zone (+TF), which allowed an easier access of oxygen from the atmosphere into soil, was greater than the no-tillage zone (-TF). Hence, soil in the no-tillage plot was depleted in oxygen which facilitated the denitrification process and led to a high generation/emission of N_2O. In addition, Figure 4.1.3 also illustrates that soil with the application of manure fertilizer could stimulate more N_2O flux than soil with chemical fertilizer in tillage plot. Generally, anaerobic nitrifying bacteria need an organic-carbon source in the denitrification reaction, whilst aerobic nitrifying bacteria can derive carbon from the carbonate compounds. This means that after the addition of manure in the field, soil became enriched in carbon source and denitrification was encouraged. This also explains why N_2O flux in the soil with chemical fertilizer was not as great as that from soil with manure addition. Although chemical fertilizer has high NH_4^+ content which could well be reduced to NO_3^- and also N_2O as a by-product in nitrification mechanism, the soil lacked organic carbon source and denitrification seldom took place. And if the soil was tilled, a high level of oxygen content would be obtained, and there would hardly be any denitrification taking place in the soil.

For a clear understanding of the effect of fertilizer, additional experiment was performed to investigate the effect of intense fertilizer on N_2O fluxes in bared soil. Firstly, N_2O flux in bared soil was measured (Experiment was started on November 5) after which this area was divided into 2 plots (1 x 1.3 m^2). 500 gram of NH_4^+ fertilizer was added into one plot and the N_2O fluxes from these two plots were monitored as shown in Figure 4.2.14. It was anticipated that soil with more Nitrogen content (the fertilized soil in this case) would yield more N_2O flux as there was more raw material for the nitrification/denitrification reactions. Unexpectedly, the results showed quite clearly that unfertilized soil had a higher initial N_2O flux than fertilized soil before they came down to the same level on the third day after the application of fertilizer (Nov 8). This experiment was repeated with the soil from the first experiment. The soils from the two plots were mixed and separated again into 2 plots. 600 grams of fertilizer was re-added into one of the plots (on Nov 28) and N_2O fluxes were monitored as illustrated in Figure 4.2.15. Again, N_2O flux in the fertilized soil was found to be lower than unfertilized soil, this time in a much greater extent.

A probable explanation of the results found in Figures 4.2.14 and 4.2.15 was that high level of N-compound intermediate from the nitrification/denitrification processes could exhibit inhibition effect to the microbial activities. In addition, Bouwman, 1990 reported that after NH_3 or NH_4^+ type of fertilizers were applied at higher doses, ammonia might inhibit the further reduction of nitrite to N_2 or N_2O. This was because ammonia was presumed to be toxic to *Nitrobacter* in denitrification mechanism.

With respect to CO_2 flux, the effect of fertilizer and tillage in the soyabean field was clearly observed in Figure 4.1.10. The tilled soil with the application of manure resulted in the highest emission of CO_2 compared to other plots. This was because tillage could mix residue of wheat straw left before the soyabean plantation (as they were planted in the same area) into the soil, which enhanced the organic carbon source in the soil. Moreover, more carbon source was also obtained from the manure that was applied to the field. Hence, this carbon source could be decomposed by bacteria and the CO_2 as a product from the decomposition was then emitted into the atmosphere.

4.3 Correlation of emission flux

In order to examine the relation between each pollutant flux, simultaneous samplings for the various gases were performed in the same vegetation field. Then the emission fluxes of two pollutants were plotted. The following sections describe the relations between DMS and N_2O fluxes, DMS and CO_2 fluxes, and N_2O and CO_2 fluxes. The objective of this part of the work is to investigate whether there exists a relation between various pollutant emissions which would be useful in the estimation of the emission rate of one pollutant when others' are known without the need to carry out tedious measurement. This will be particularly useful for the gas that requires complicated measurement system such as DMS.

4.3.1 Dimethyl sulfide flux vs Nitrous oxide flux

As discussed in Section 4.2.2; Figure 4.2.12, DMS and N_2O fluxes versus all micrometeorological parameters in the wheat field were having similar trends. To investigate the relation between DMS and N_2O fluxes in the wheat field and Hakiuchi forest, both fluxes were plotted in Figure 4.3.1. As expected, a linear relation was clearly observed where N_2O flux increased with DMS flux or vice versa. Moreover, the same relation was also detected in the pine forest at Nagano as illustrated in Figure 4.3.2. This was because one of the DMS generation pathways involved the production of NH_3 as a by-product. An example of this pathway is the decomposition of methionine ($CH_3SCH_2CH_2CH(NH_2)COOH$) which is one of the reactants for DMS. Equation 4.1 shows that the decomposition of methionine results in 2-ketobutyrate ($CH_3CH_2COCOOH$), methanethiol (CH_3SH) and ammonia (NH_3) where CH_3SH is subsequently undergone methylation and formed DMS $(CH_3)_2S$ (See Eq. 4.2) (Taylor and Kiene, 1989).

$$CH_3SCH_2CH_2CH(NH_2)COOH + H_2O \longrightarrow CH_3SH + CH_3CH_2COCOOH + NH_3 \qquad (4.1)$$

$$CH_3SH + \text{S-adenosylmethionine} \longrightarrow (CH_3)_2S + \text{S-adenosylhomocysteine} \qquad (4.2)$$

NH_3 from Equation 4.1 can therefore enter the nitrification/denitrification mechanisms which leads to the production/emission of N_2O. Hence, it might be possible that both DMS and NH_3, which was thought to subsequently evolve N_2O, in the areas investigated in this experiment were generated in the above pathway.

4.3.2 Dimethyl sulfide flux vs Carbon dioxide flux

High scattering relation between DMS and CO_2 fluxes was observed in the results from the wheat field and Hakiuchi forest as demonstrated in Figure 4.3.3. More specifically, there were times where DMS fluxes increased with CO_2 fluxes such as fluxes in May, and on the other hand, there were also times that the emission rate of DMS decreased with CO_2 fluxes such as that in March. Therefore it is concluded here that there was no relation between DMS and CO_2 fluxes in the vegetation areas investigated in this work.

Turning to the relation in the pine forest at Nagano illustrated in Figure 4.3.4, if the high fluxes of DMS (3 points which had the value more than 30 nmol m^{-2} h^{-1}) were ignored, the trend of relation between DMS and CO_2 fluxes could be assumed to be linear. This meant that when CO_2 flux increased, DMS flux increased accordingly. This might be because the existence of the sediment in the forest. This sediment could undergo microbial metabolisms and yield both CO_2 (decomposition) and DMS (methylation). Some part of this DMS was released to the atmosphere and some was consumed by the sulfate-reducing bacteria, which converted this DMS to CO_2 (Taylor and Kiene, 1989). Therefore, it was then possible that both DMS and CO_2 fluxes were found to increase especially in the area with high amount of residue such as pine forest.

4.3.3 Nitrous oxide flux vs Carbon dioxide flux

The denitrification process involves the consumption of organic carbon source which results in a generation of CO_2 together with N_2O, and there was evidence regarding the relation between the N_2O and CO_2 productions from this process (Robinson and Conroy, 1999). However, the results in Figure 4.3.5 could not express any relation between N_2O and CO_2 fluxes in the wheat field during both winter and spring seasons. The same result was also observed in the pine forest at Nagano as shown in Figure 4.3.6. It should be mentioned that organic carbon could also pass through other microbial pathway apart from the anaerobic denitrification mechanism. In other metabolisms, organic carbon could be decomposed and resulted in the generation of CO_2, and in this case, there would not be a relation between CO_2 and N_2O fluxes. Hence, the amounts of CO_2 and N_2O emitted from the soil depend remarkably on the extent of the independent decomposition and denitrification processes. This explains why no relation between the two fluxes could not be seen from Figures 4.3.5-4.3.6.

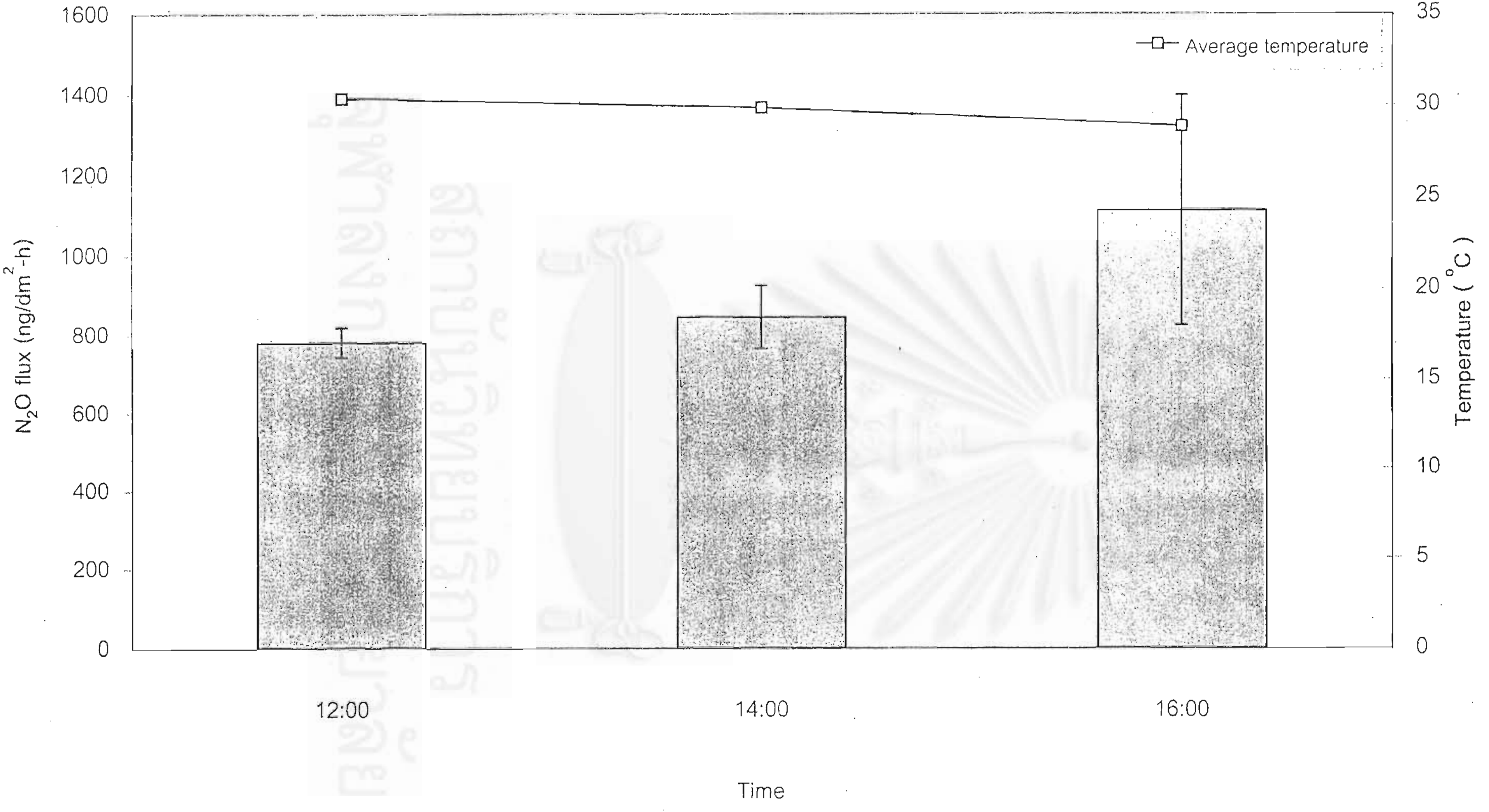


Figure 4.1.1 N_2O flux in corn field on 24/08/2001

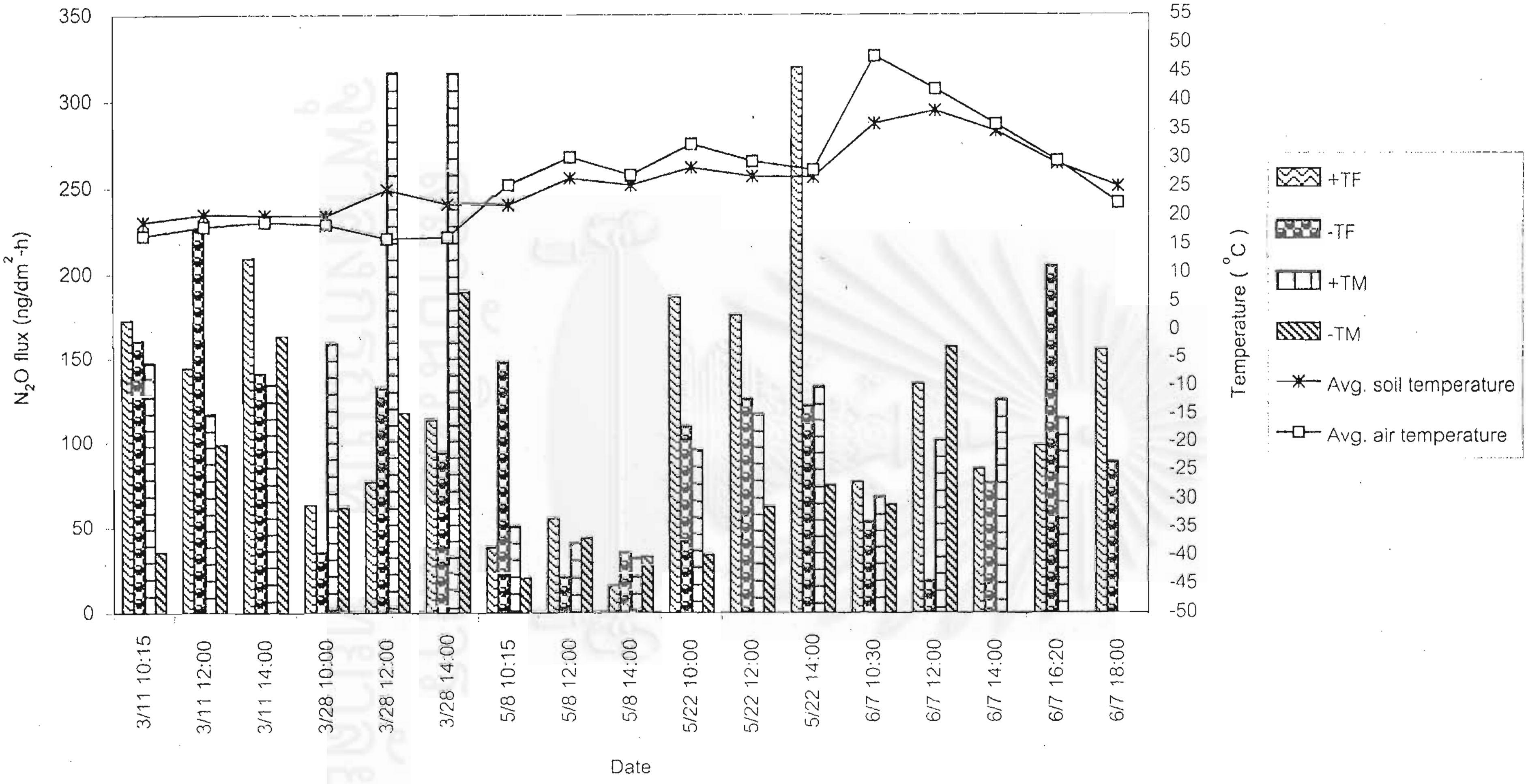


Figure 4.1.2 N$_2$O flux on sampling date in wheat field

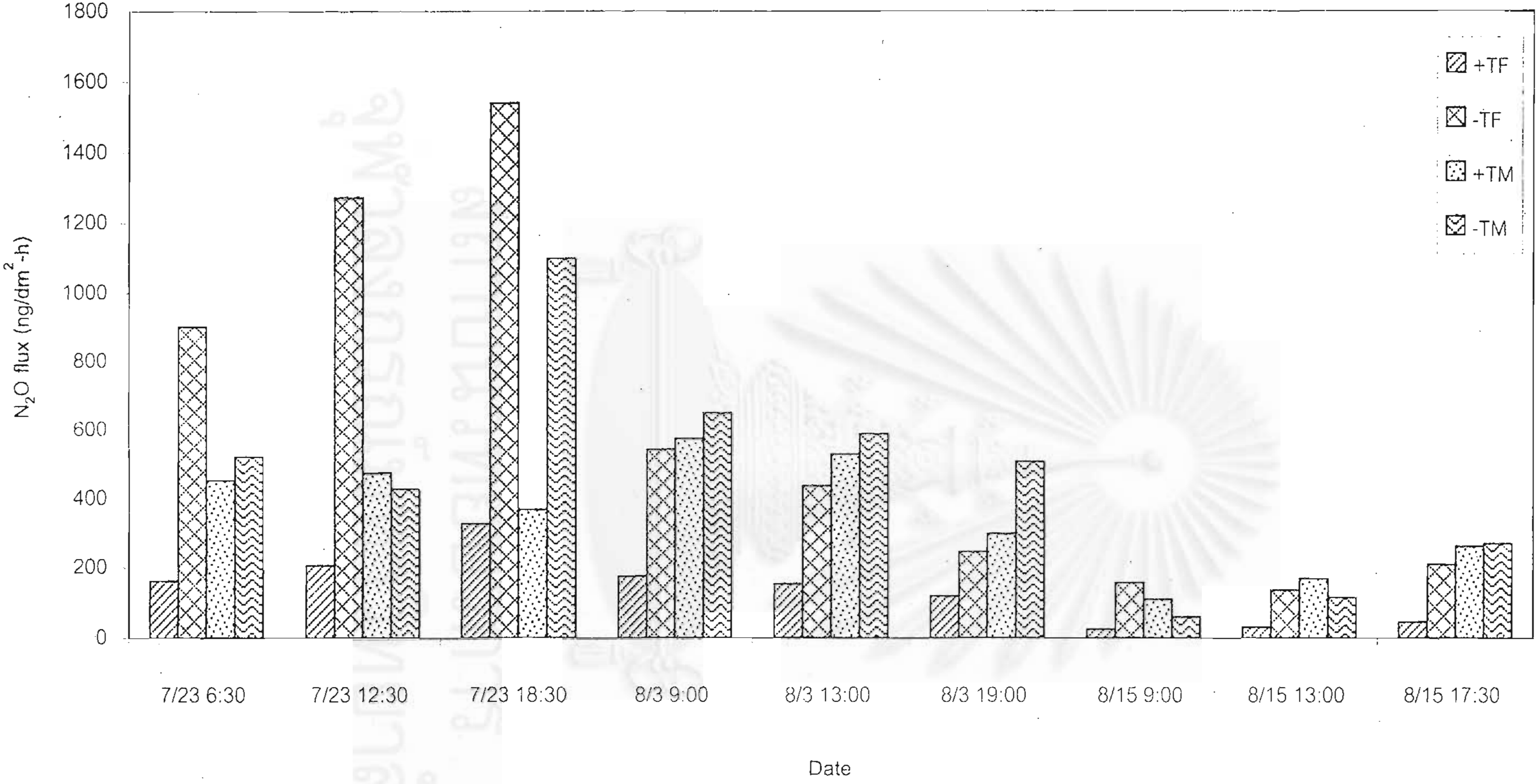


Figure 4.1.3 N_2O fluxes on sampling date in Soyabean field with different treatments

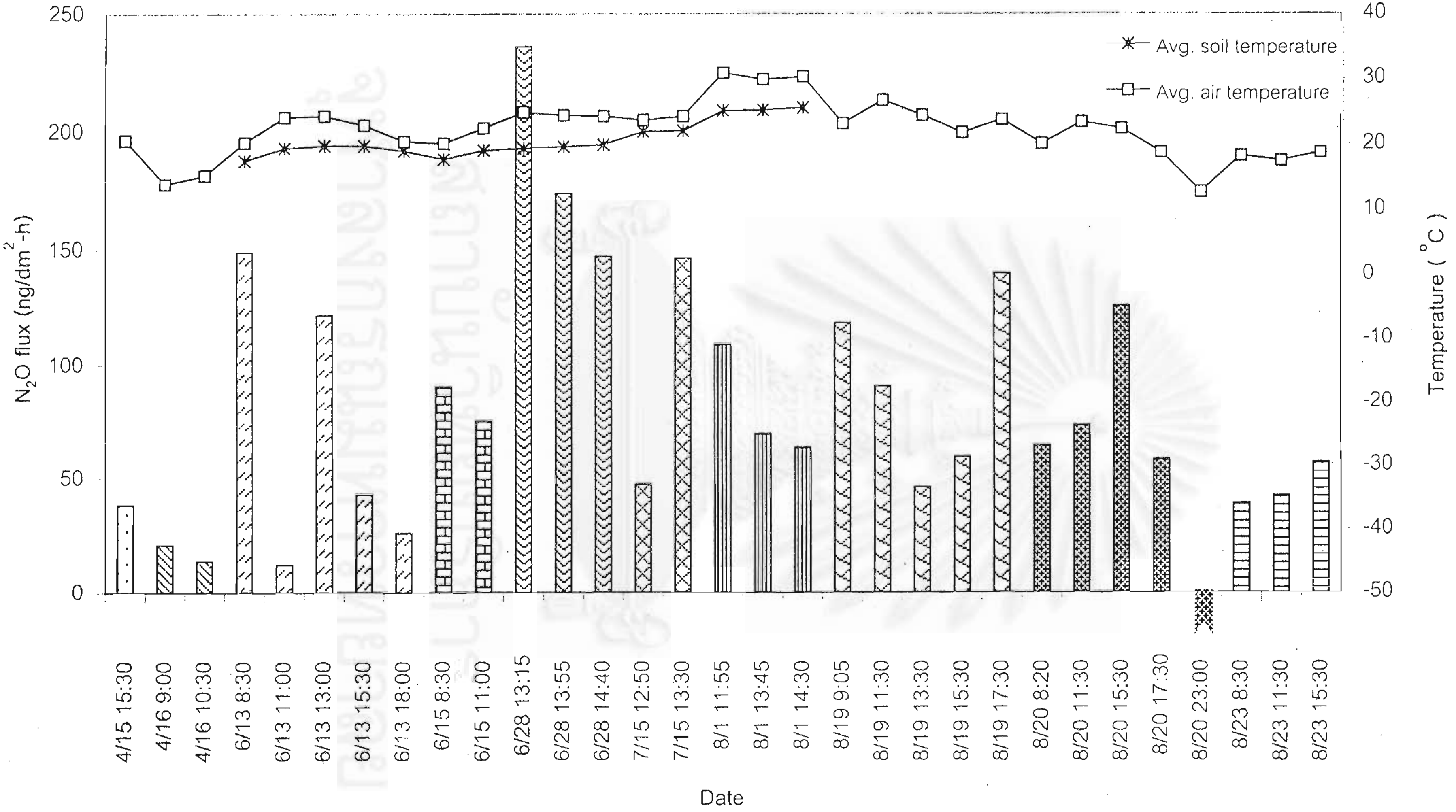
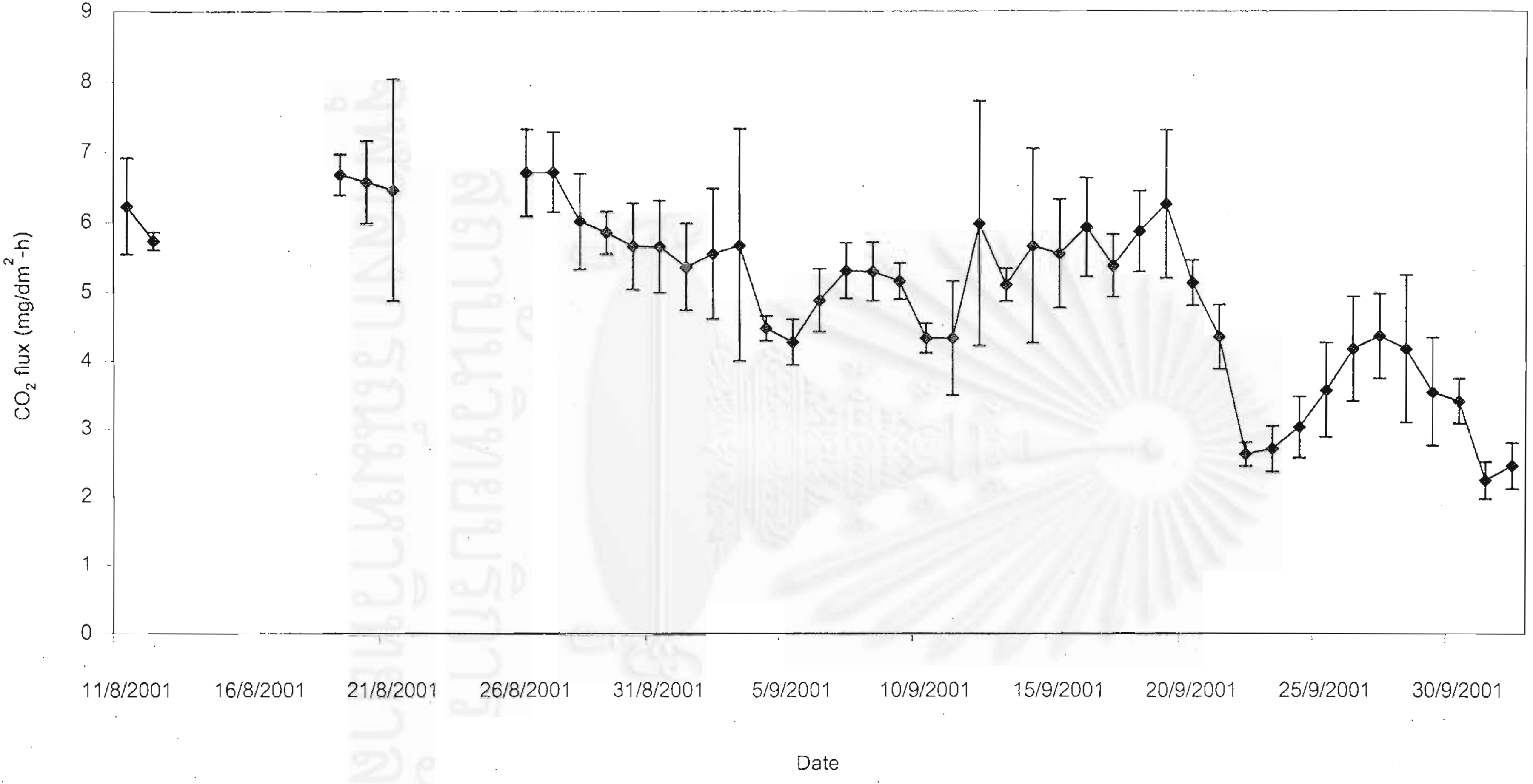


Figure 4.1.4 N_2O flux on sampling date in pine forest (Nagano)



<u>Figure 4.1.5</u> Daily CO_2 flux in corn field, 2001 (Open chamber)

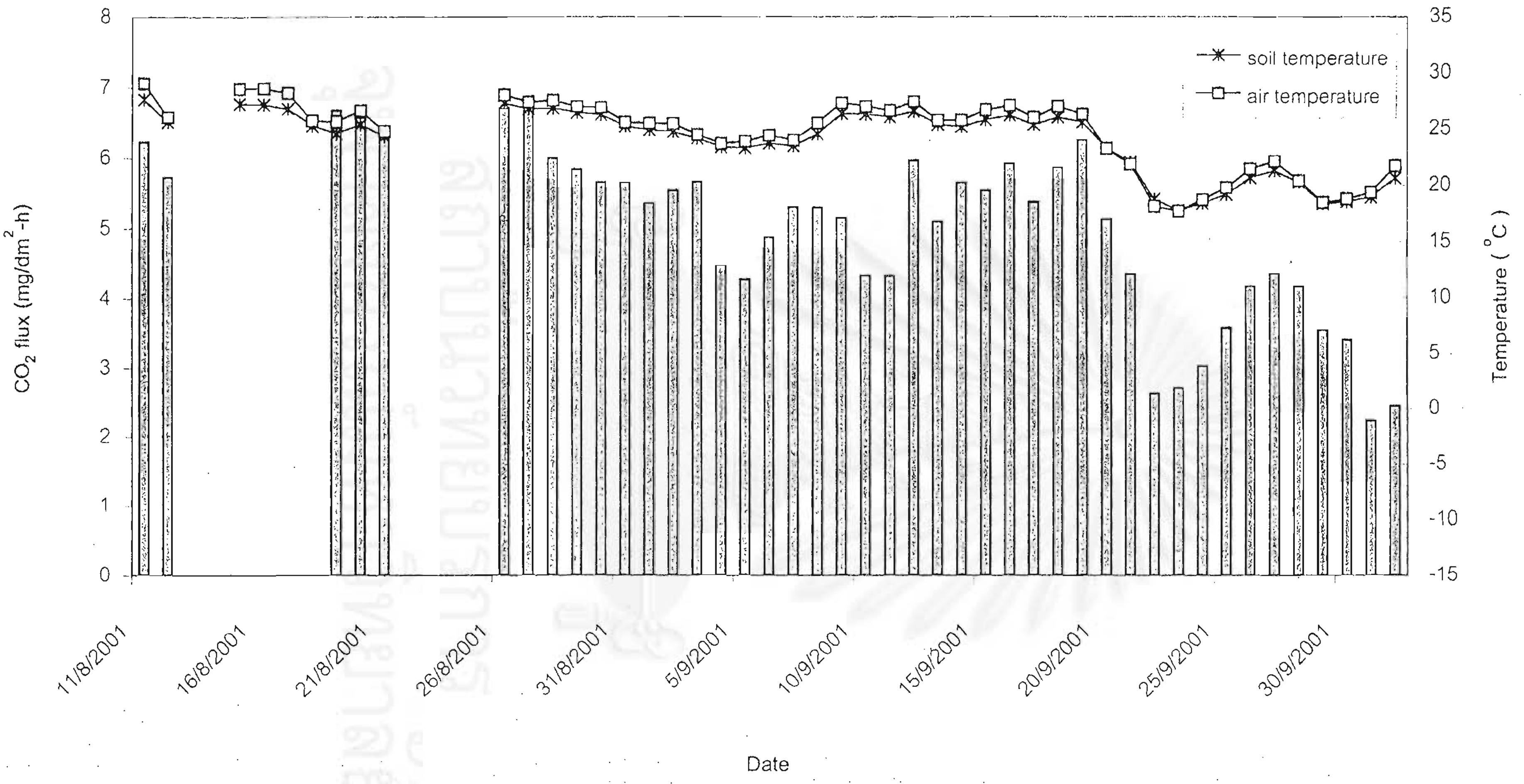


Figure 4.1.6 Daily CO_2 flux and temperature in corn field, 2001 (Open chamber)

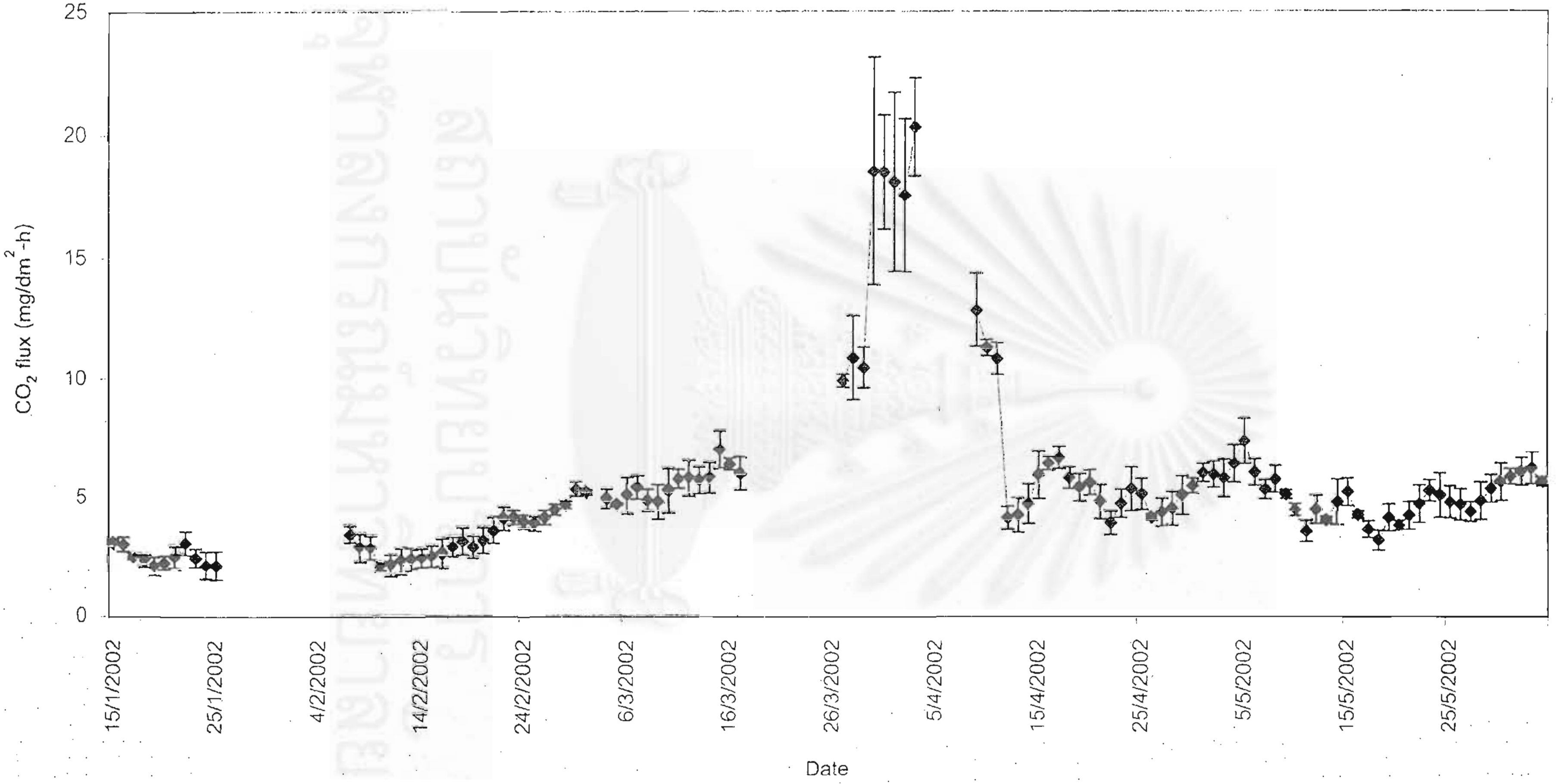


Figure 4.1.7 Daily CO_2 flux in wheat field, 2002 (Open chamber)

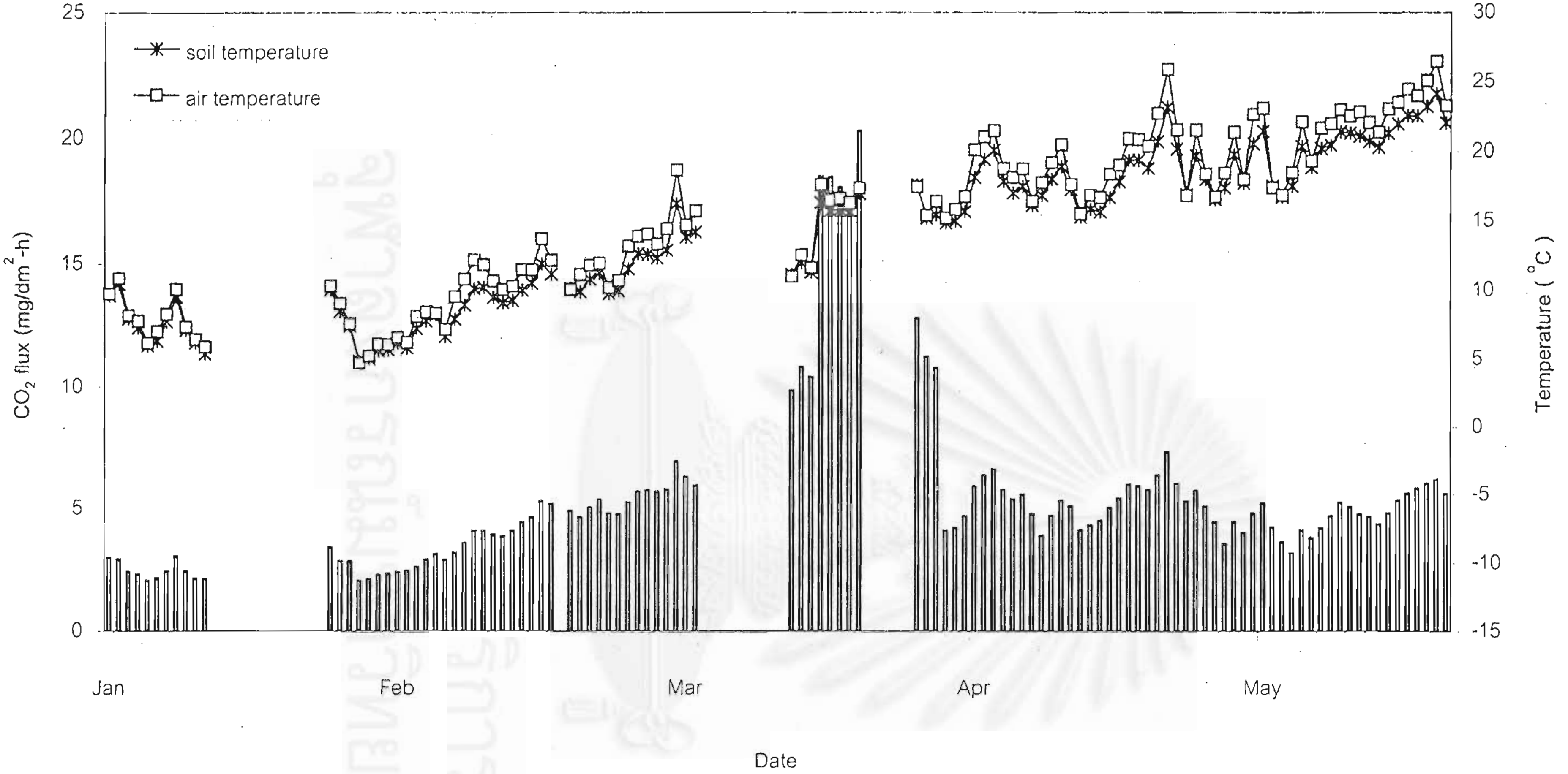


Figure 4.1.8 Daily flux of CO$_2$ and temperature in wheat field, 2002 (Open chamber)

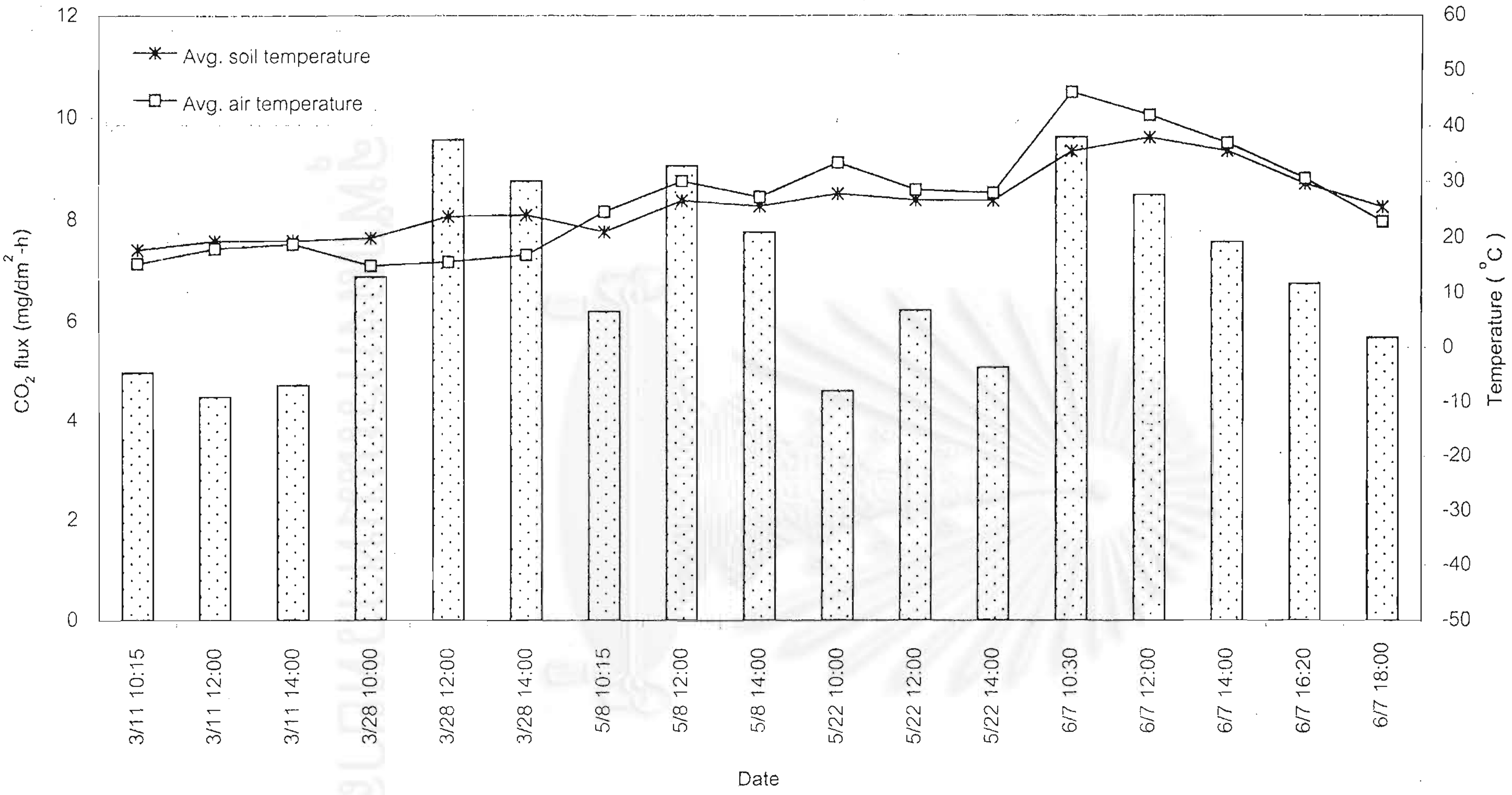


Figure 4.1.9 CO$_2$ flux on sampling date in Wheat field (Closed chamber)

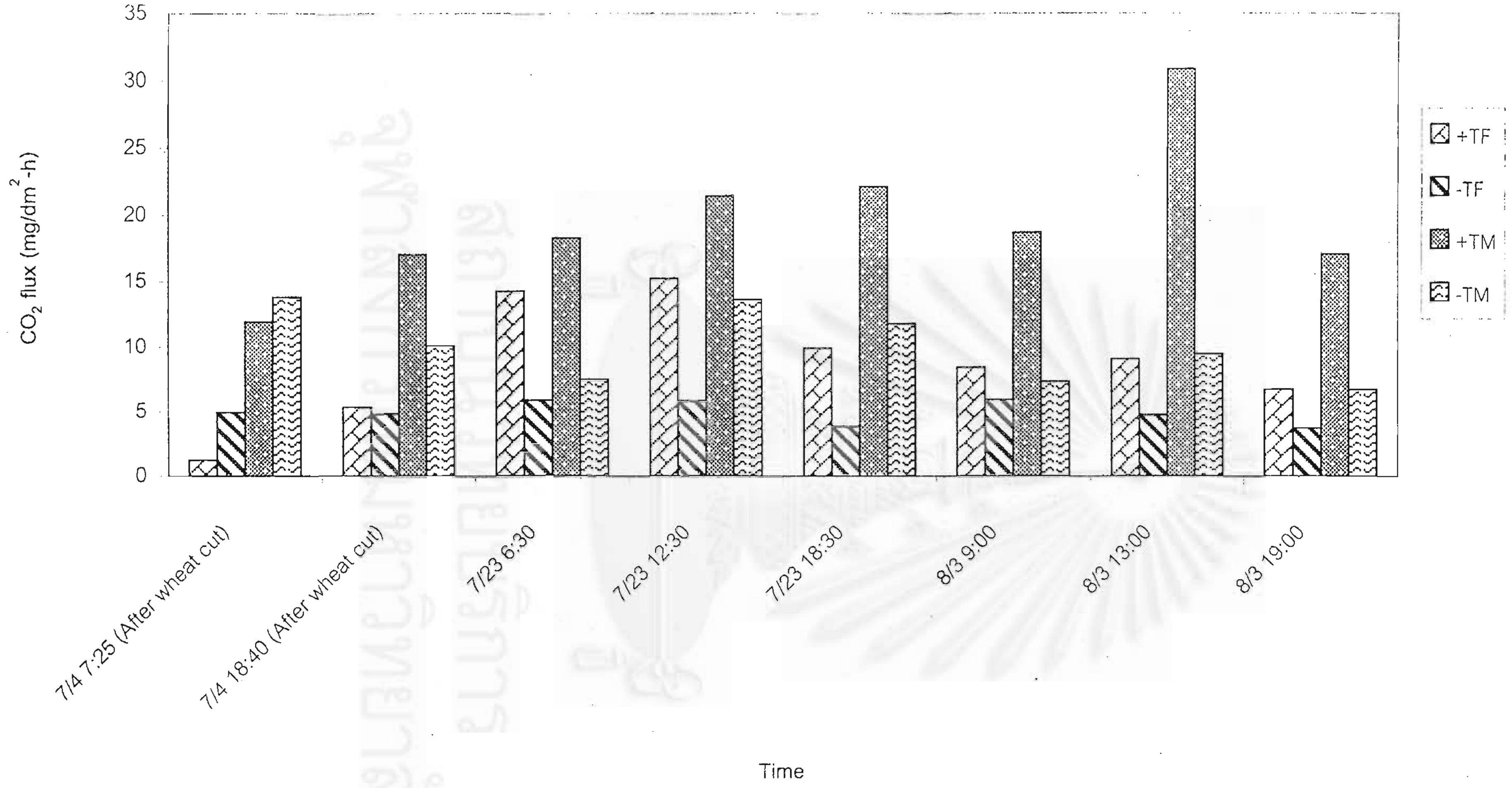


Figure 4.1.10 CO_2 flux on sampling date in Soyabean field with different treatments

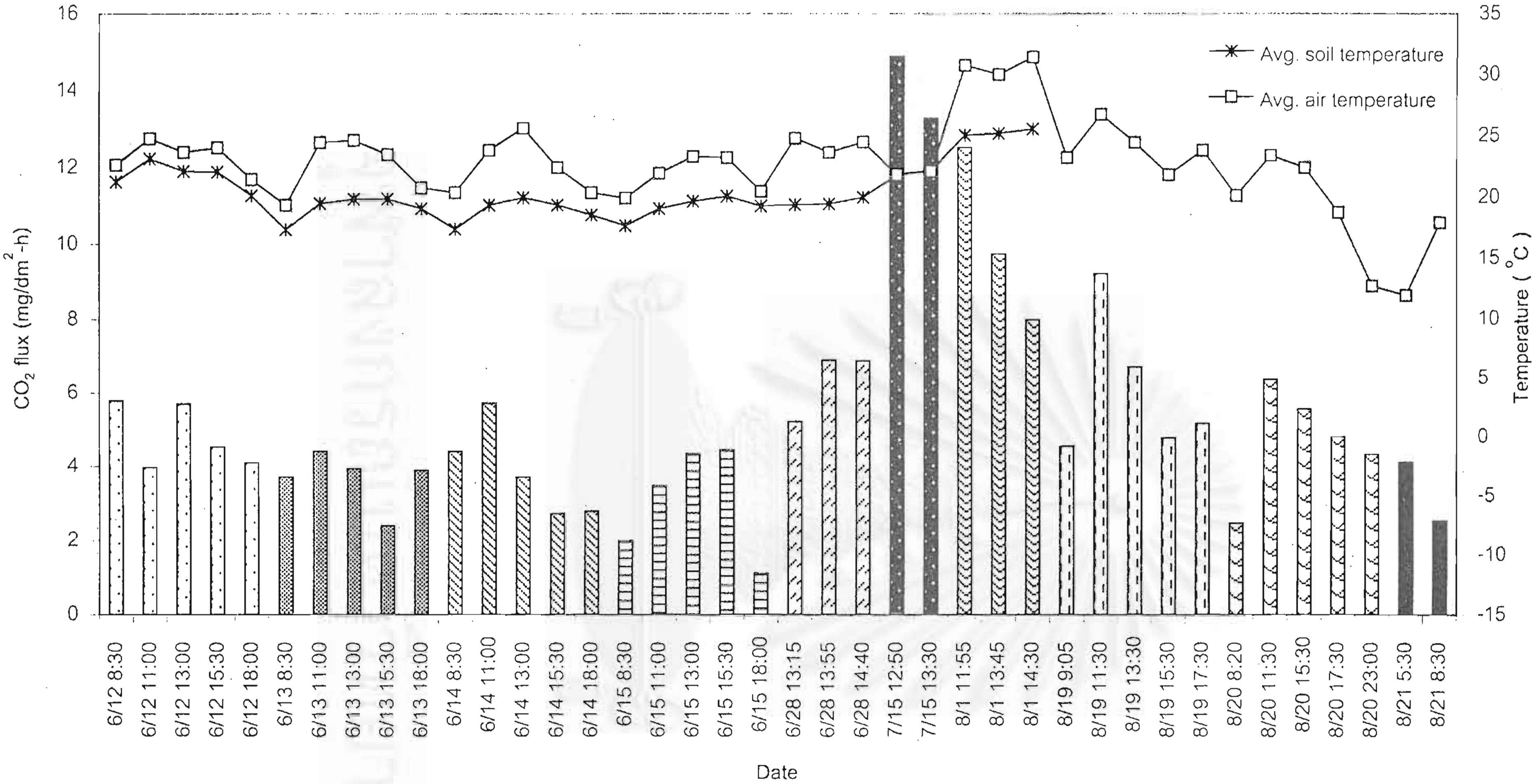


Figure 4.1.11 CO_2 flux on sampling date in pine forest (Nagano)

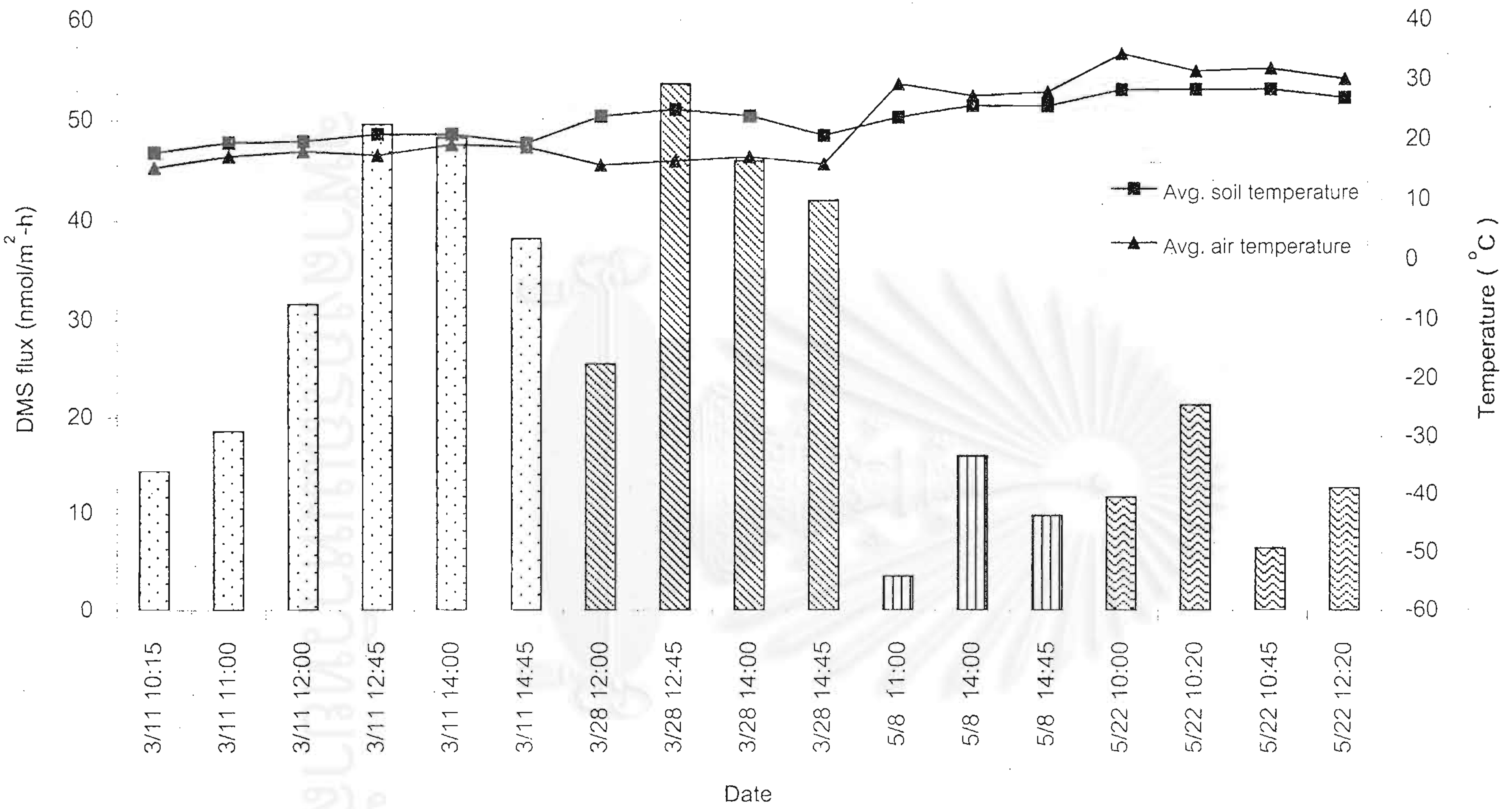
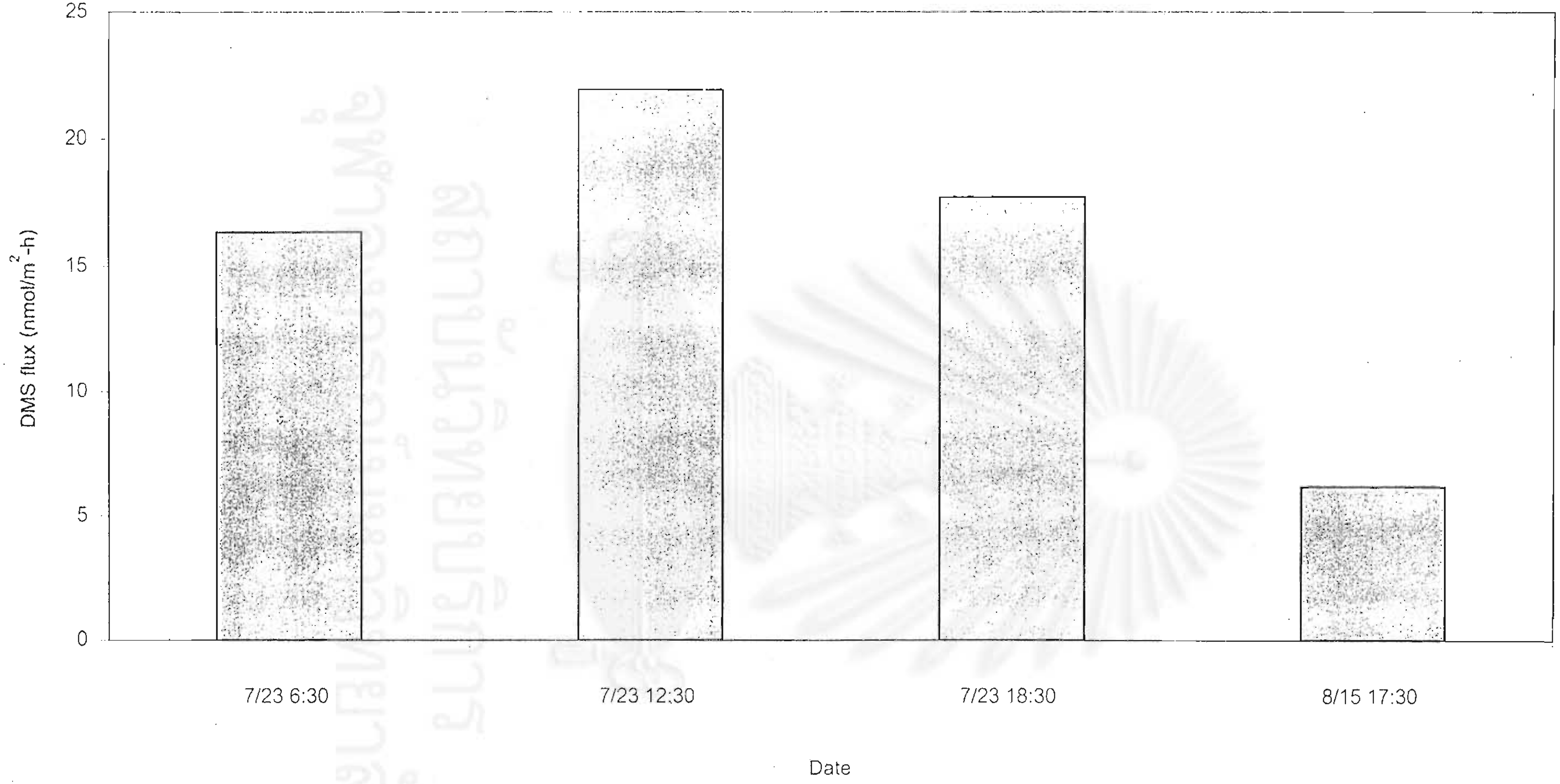


Figure 4.1.12 DMS flux and temperature on sampling date in Wheat field



<u>Figure 4.1.13</u> DMS flux on sampling date in Soyabean field

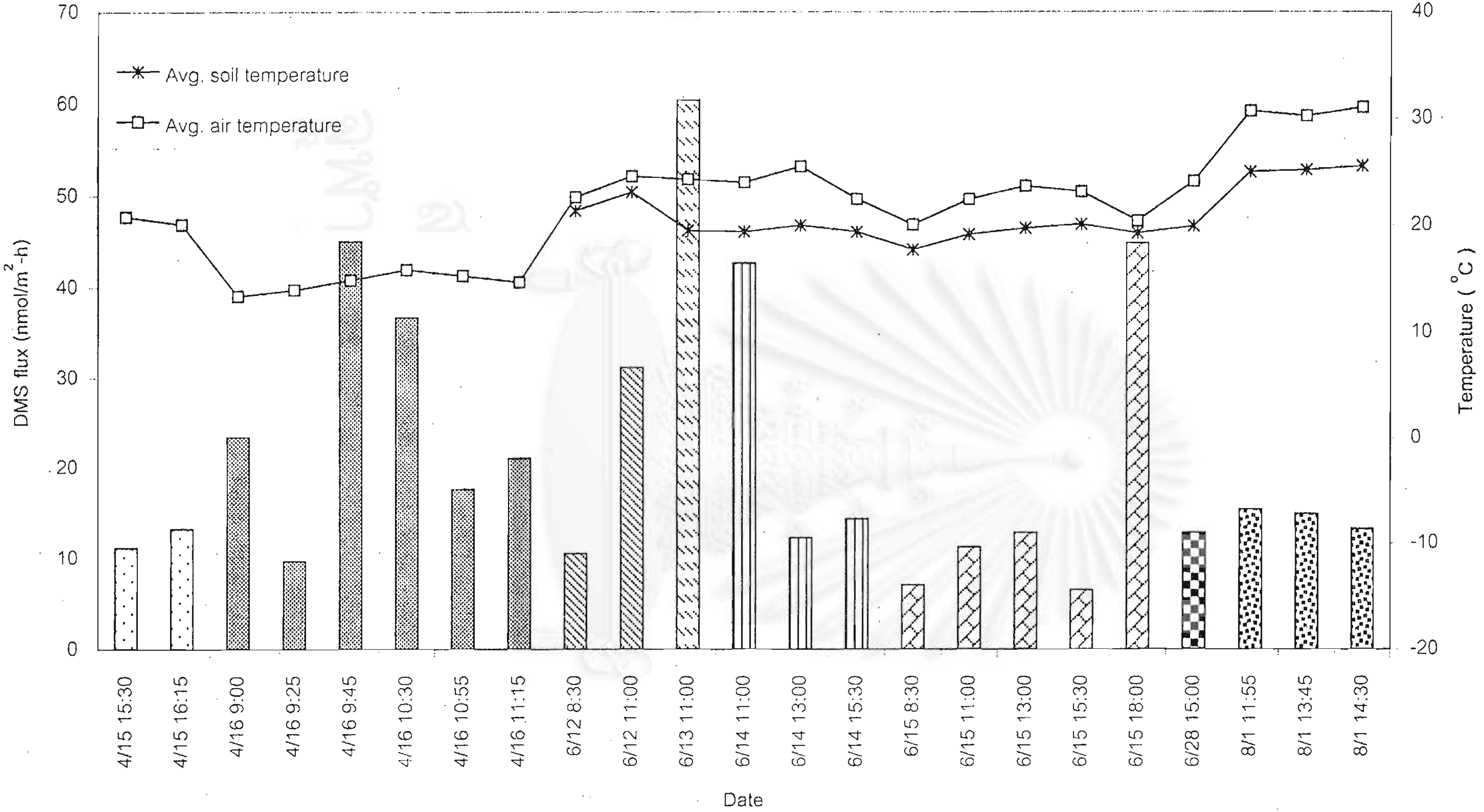
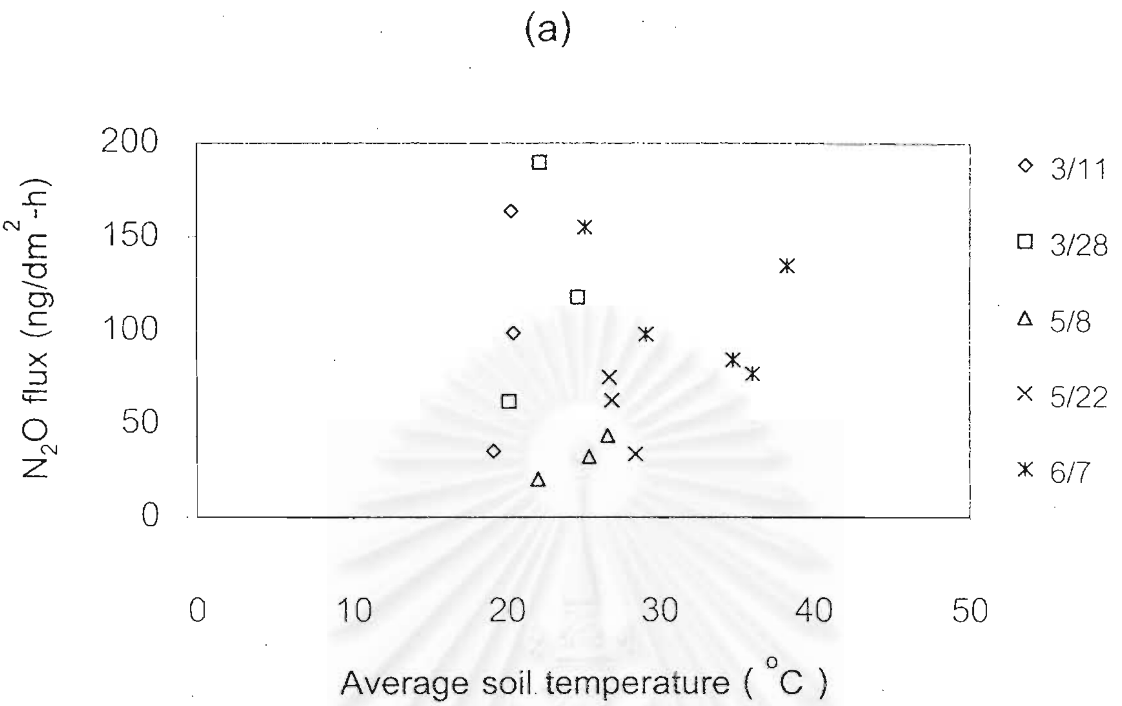


Figure 4.1.14 DMS flux and temperature on sampling date in pine forest (Nagano)



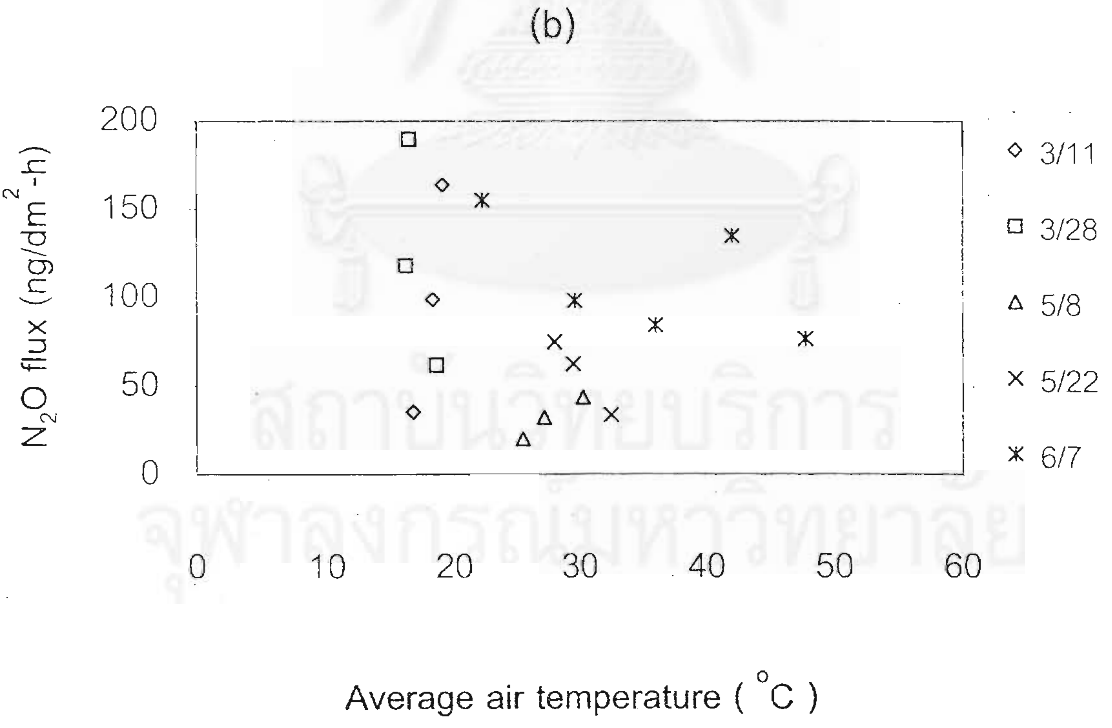


Figure 4.2.1 Effect of (a) soil temperature, and (b) air temperature on N_2O flux in wheat field

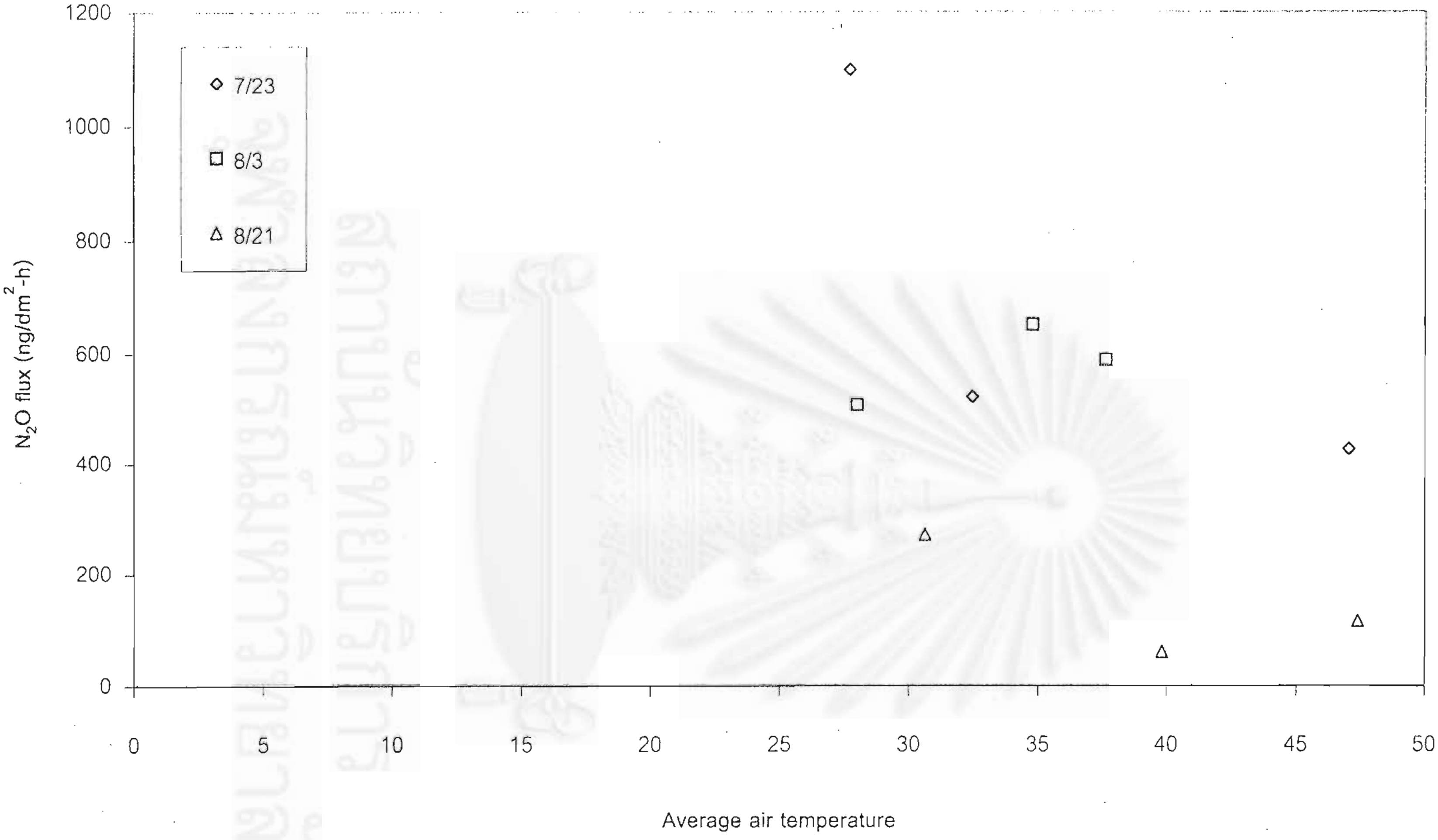


Figure 4.2.2 Effect of air temperature on N_2O flux in soyabean field

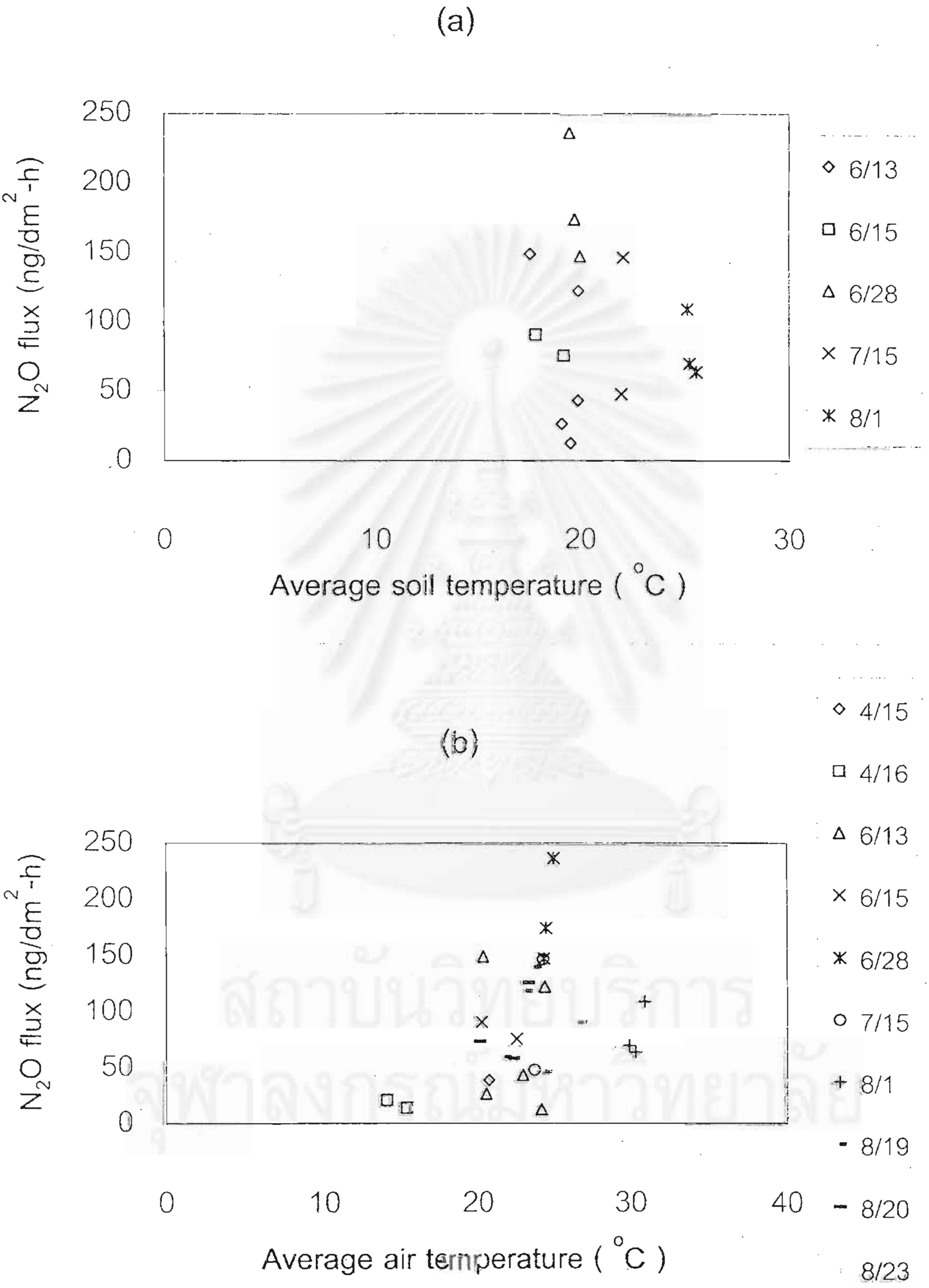


Figure 4.2.3 Effect of (a) soil temperature, and (b) air temperature on N_2O flux in pine forest

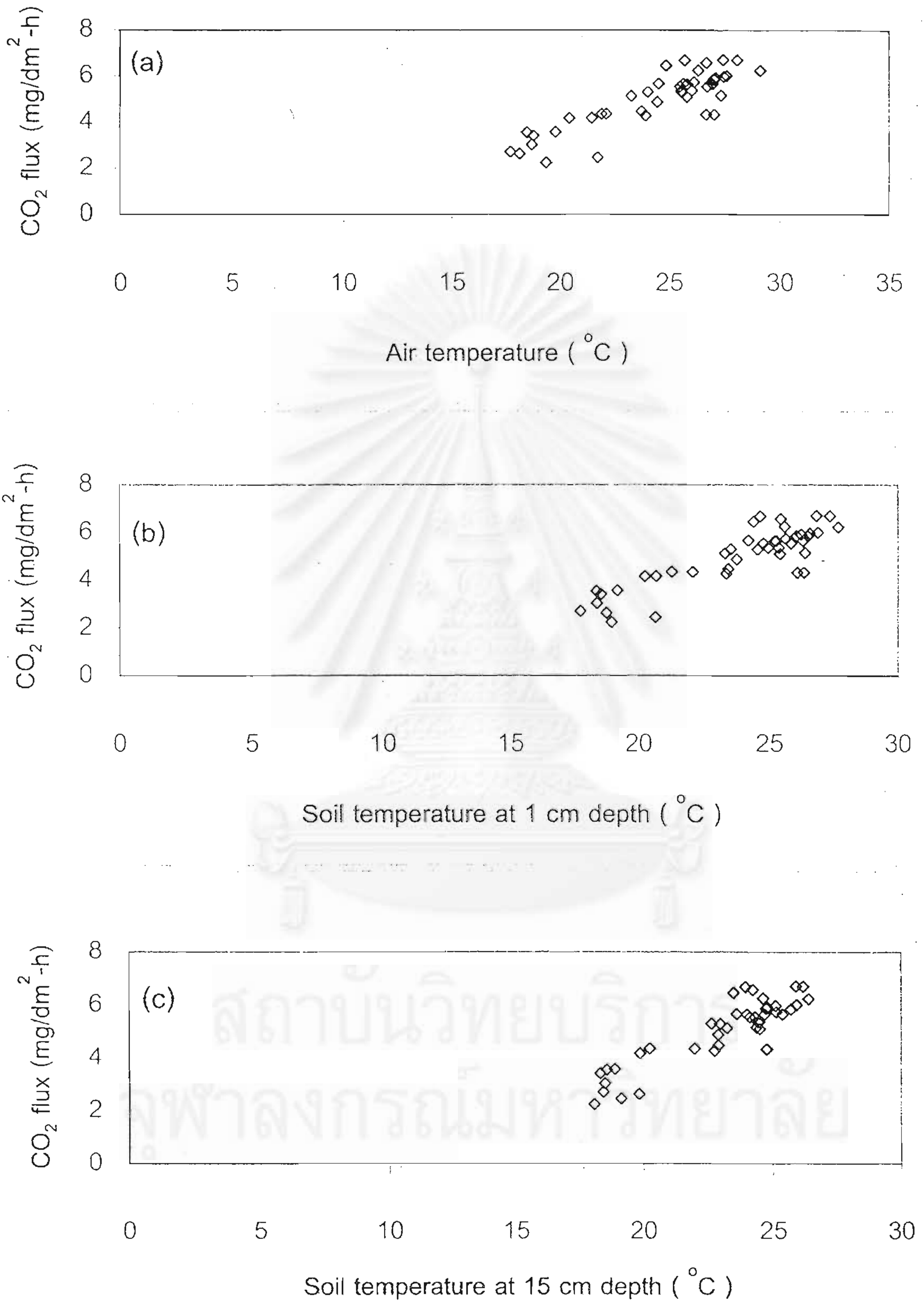


Figure 4.2.4 Effect of temperature on CO$_2$ flux in corn field

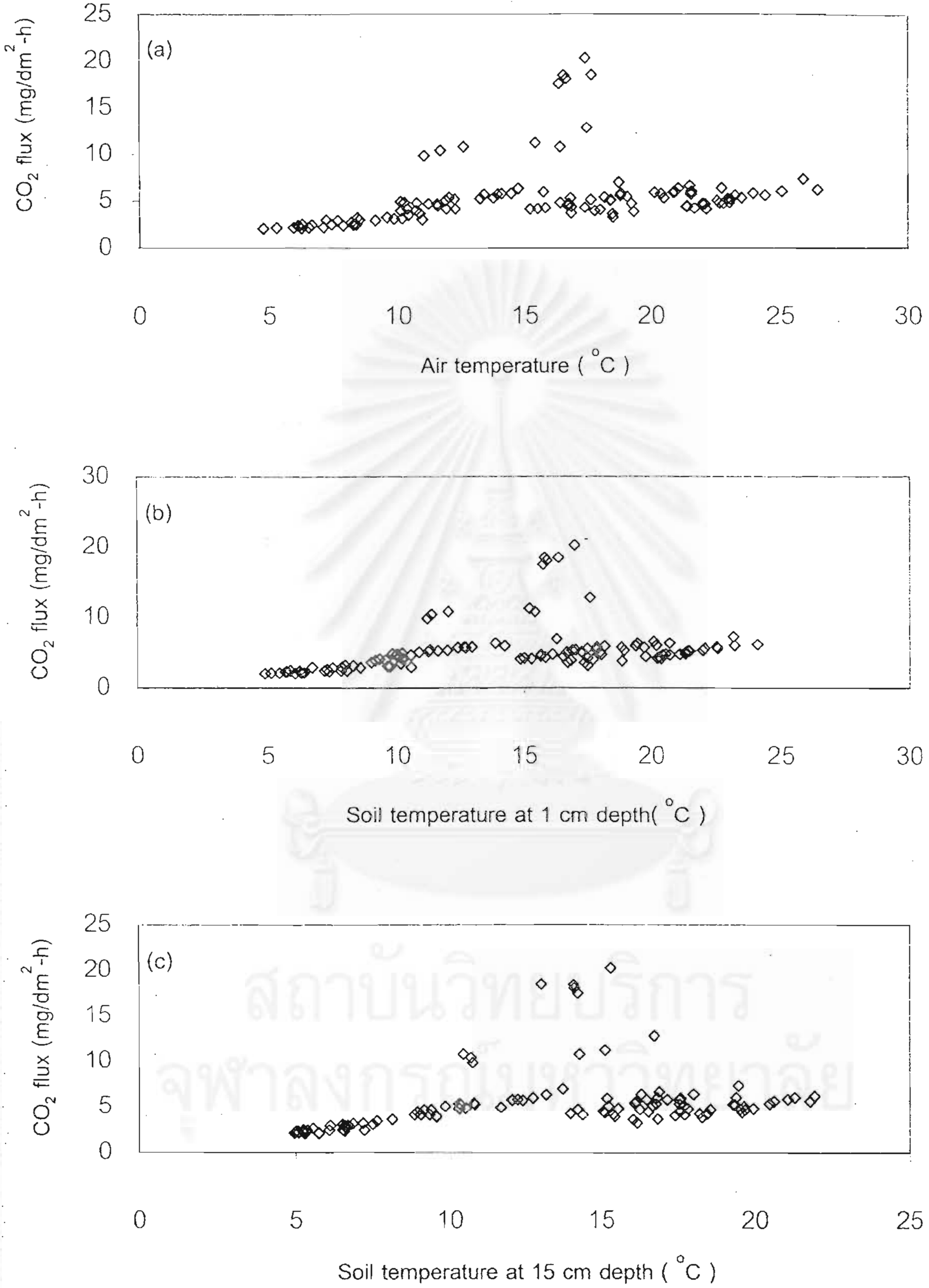
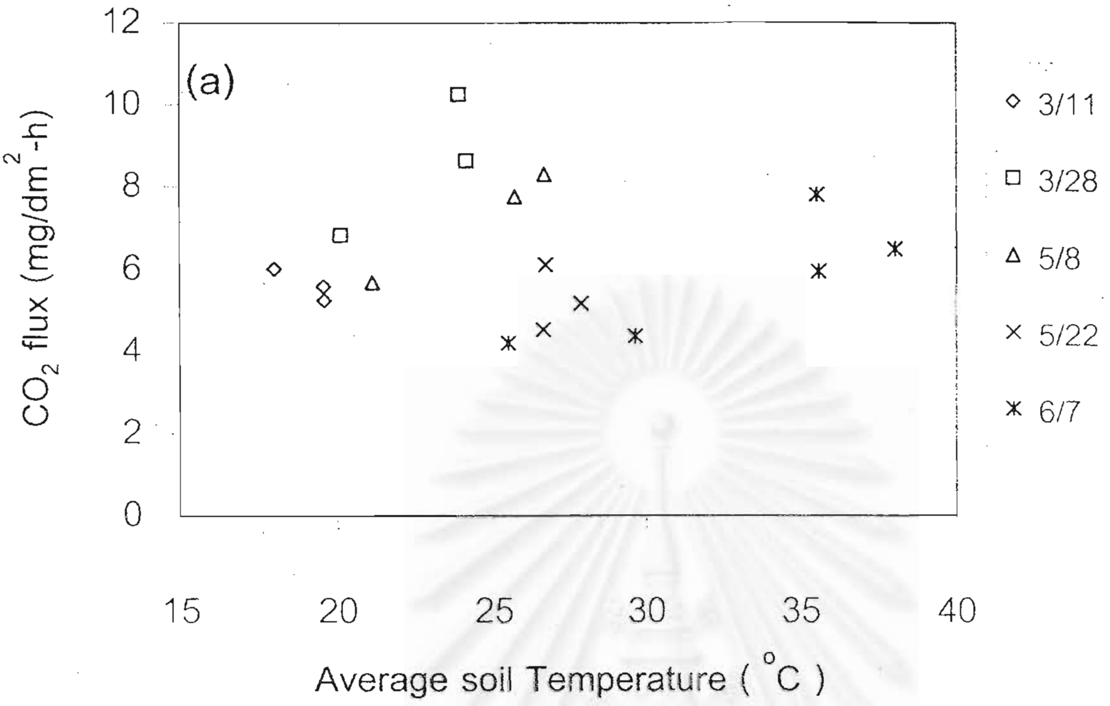


Figure 4.2.5 Effect of temperature on CO_2 flux in wheat field



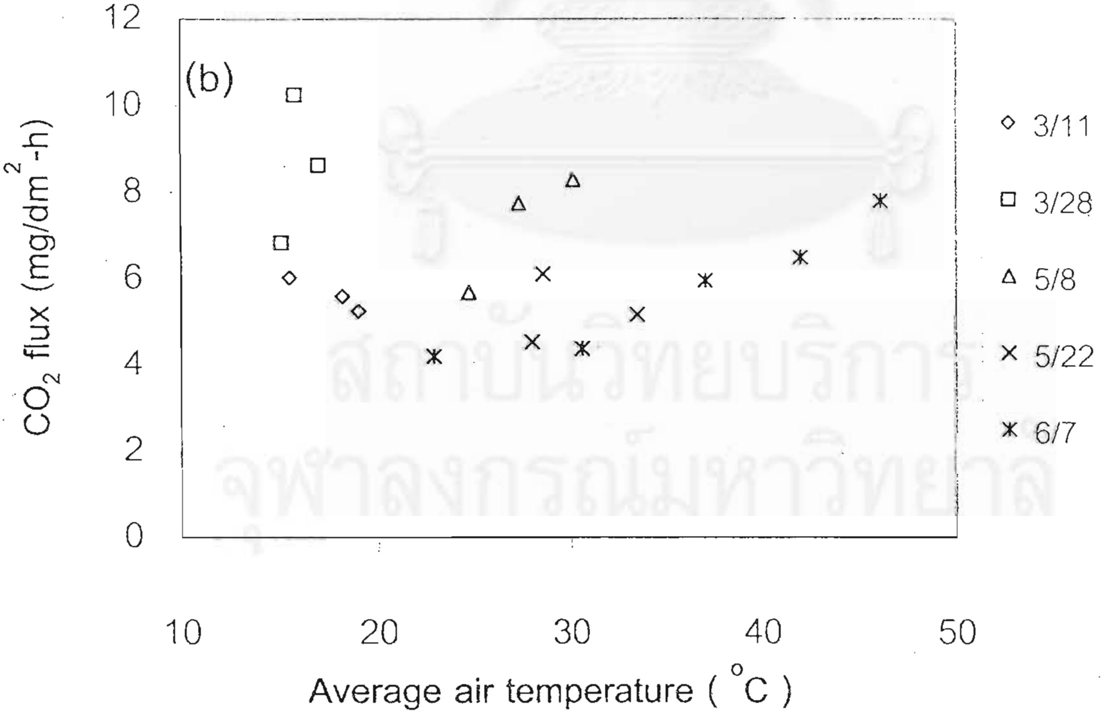
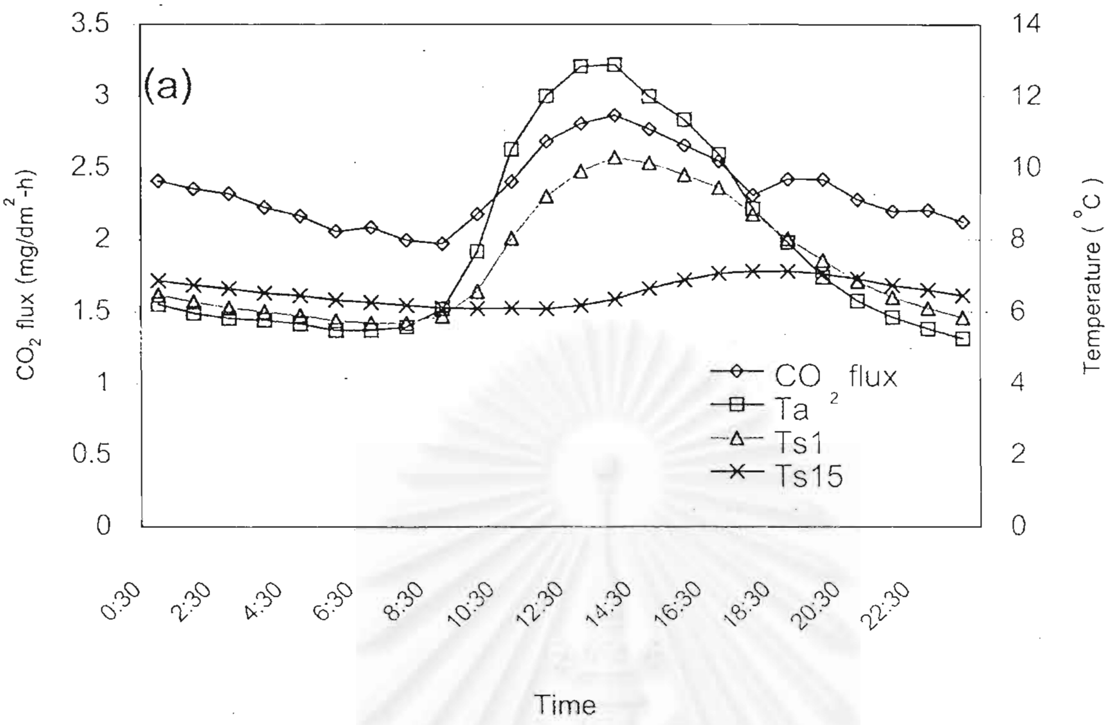


Figure 4.2.6 Effect of temperature on CO_2 flux (closed chamber) in wheat field



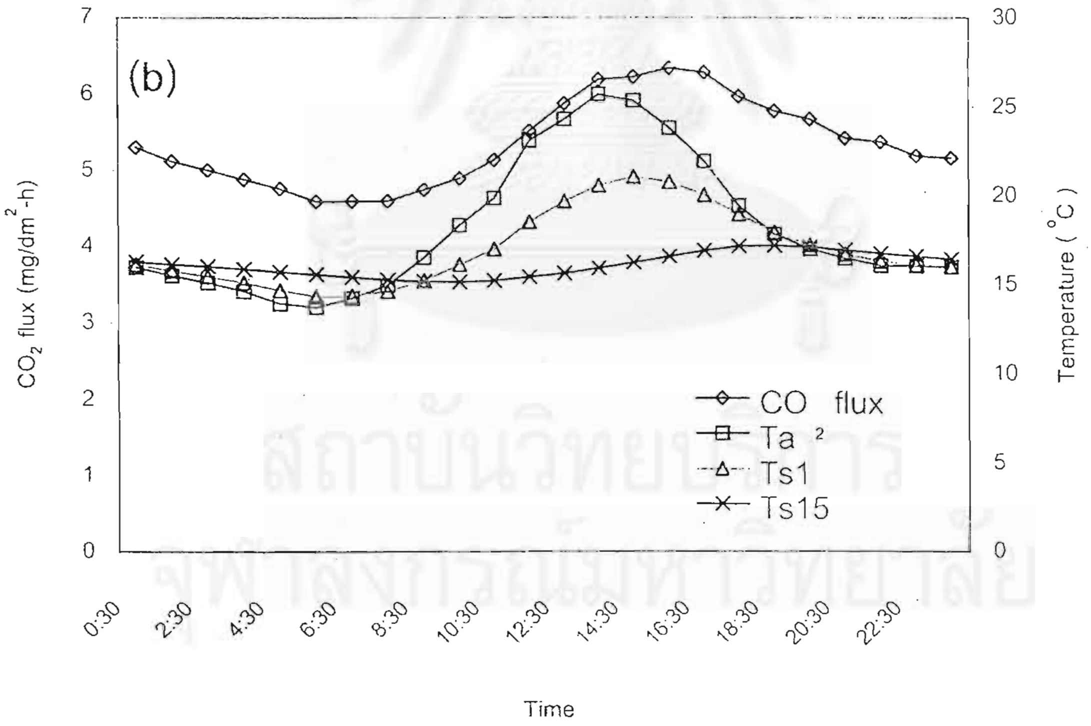
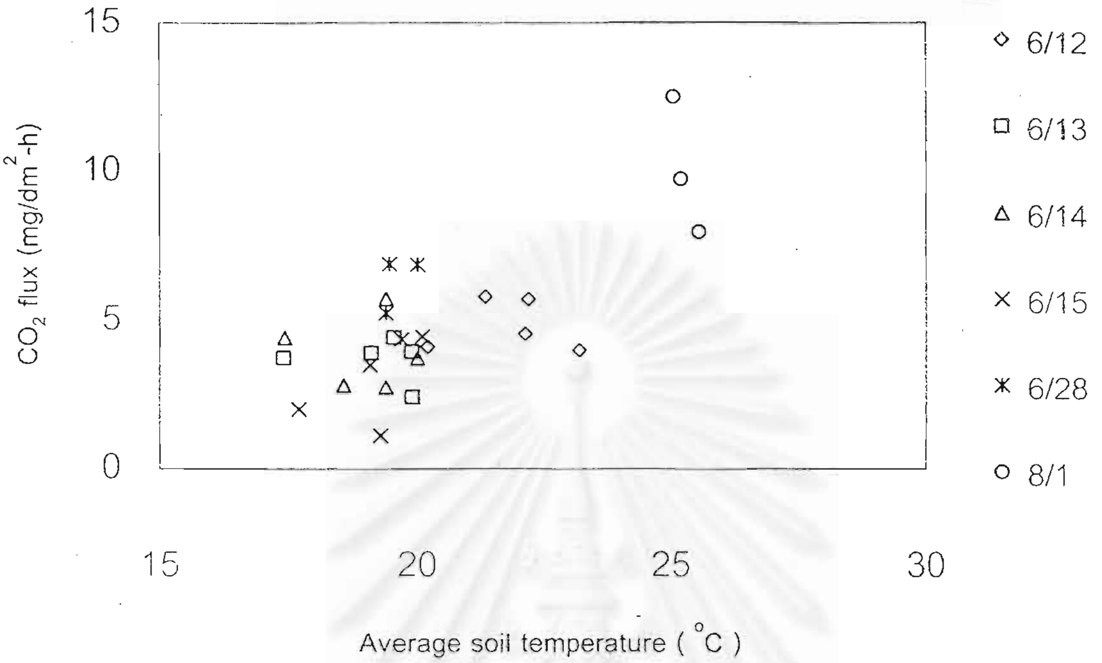


Figure 4.2.7 Hourly flux of CO_2 and temperature in wheat field on (a) 2002/01/18, and (b) 2002/04/19 (Ta = air temperature, Ts1 = soil temperature at 1 cm depth, Ts15 = soil temperature at 15 cm depth)

(a)



(b)

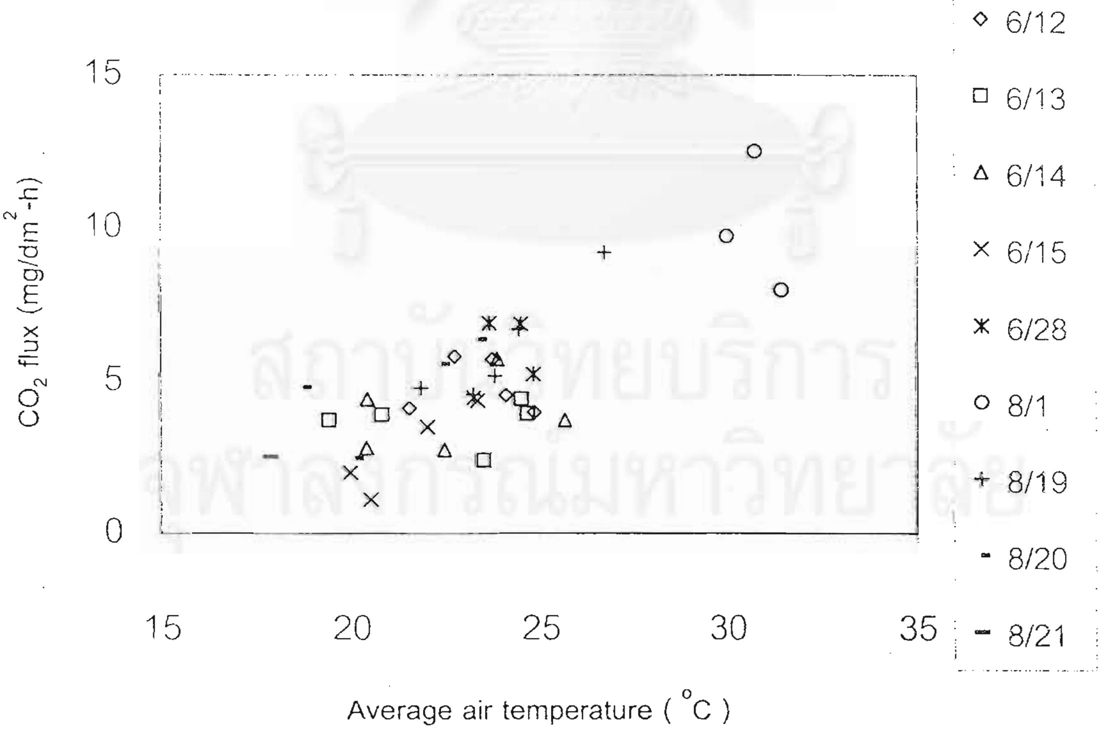
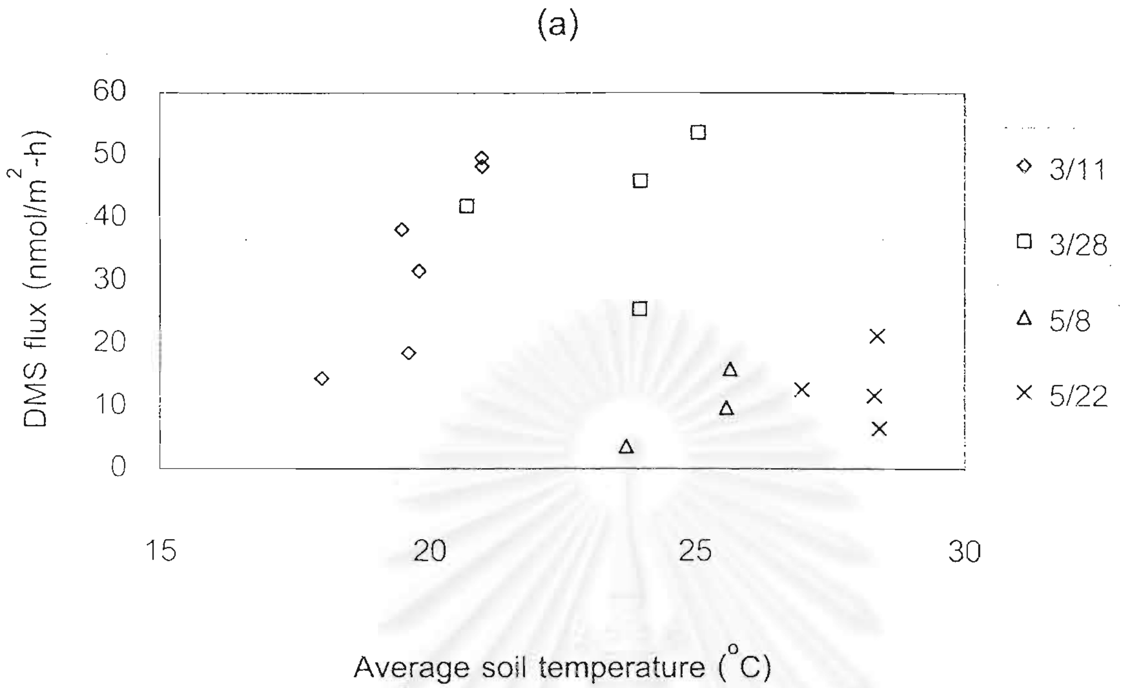


Figure 4.2.8 Effect of temperature on CO_2 flux in pine forest at Nagano



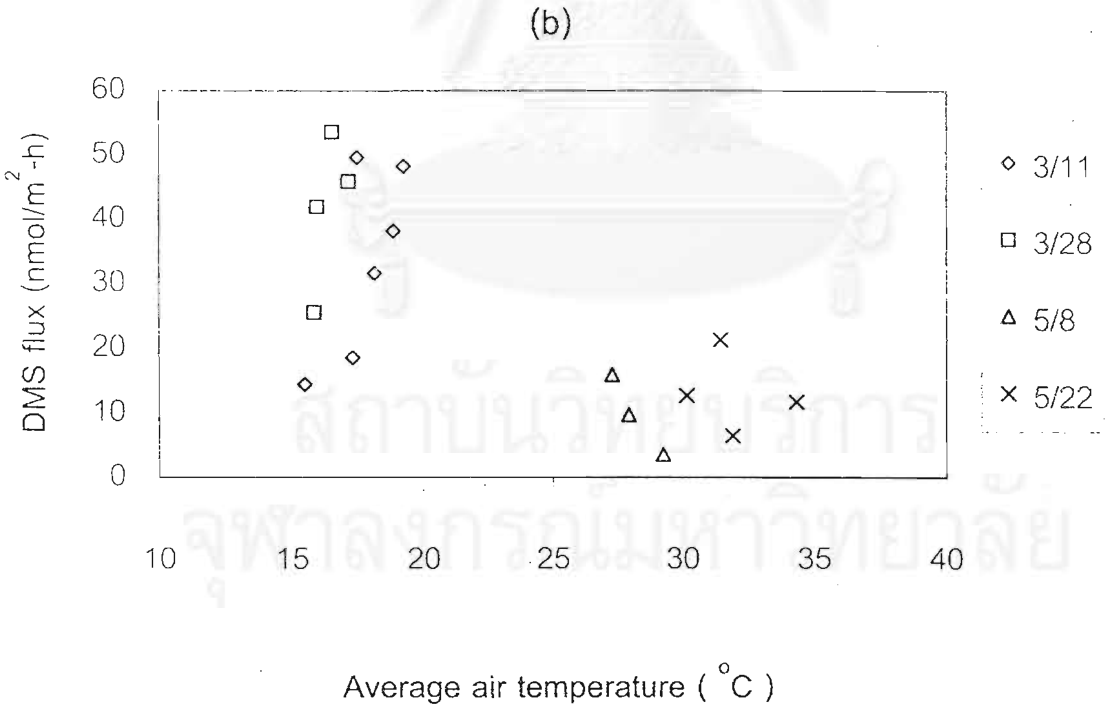
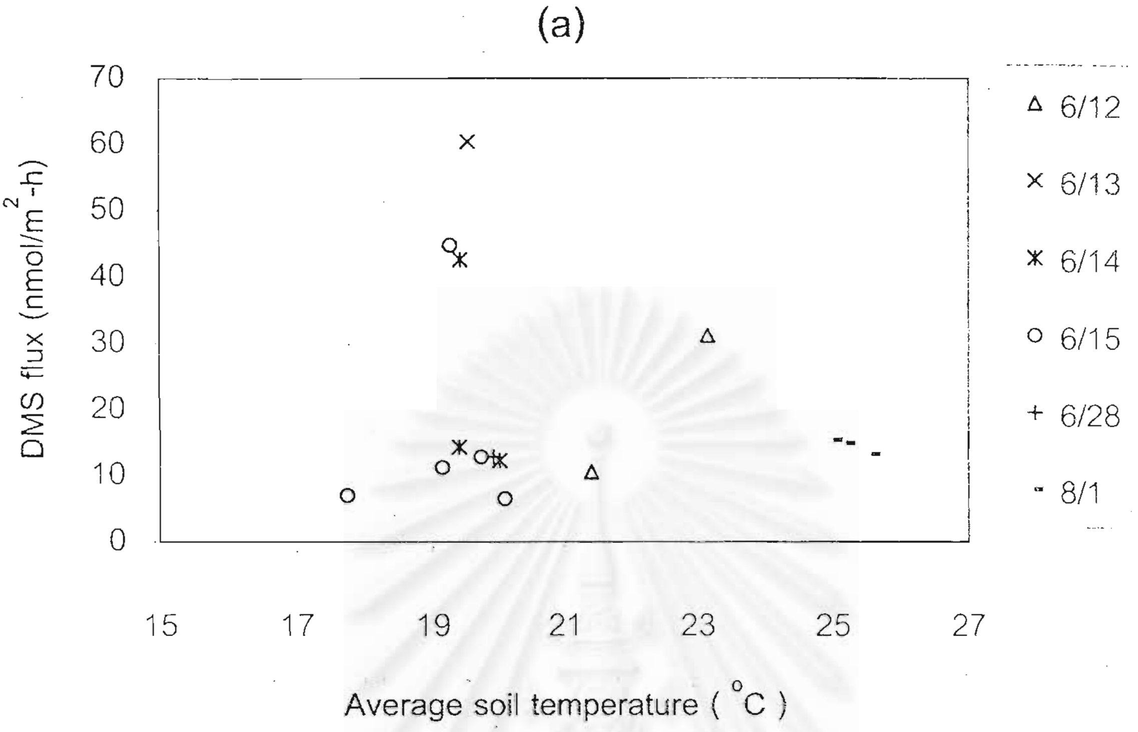


Figure 4.2.9 Effect of temperature on DMS fluxes in wheat field



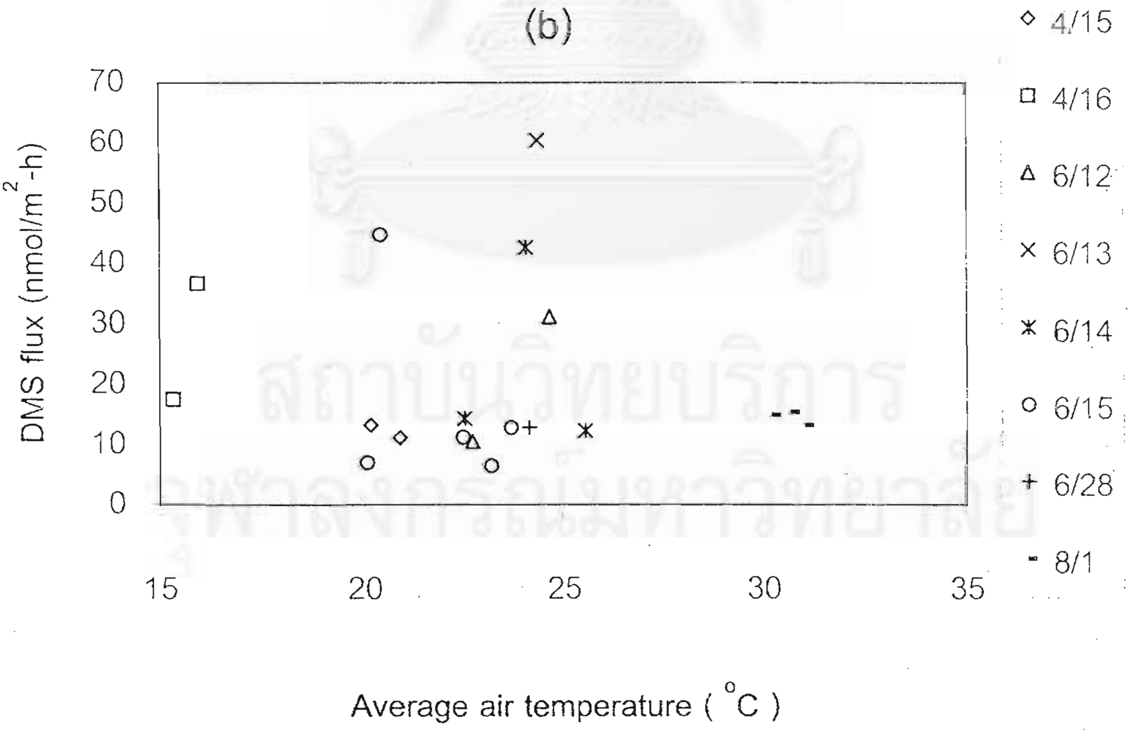


Figure 4.2.10 Effect of temperature on DMS fluxes in pine forest at Nagano

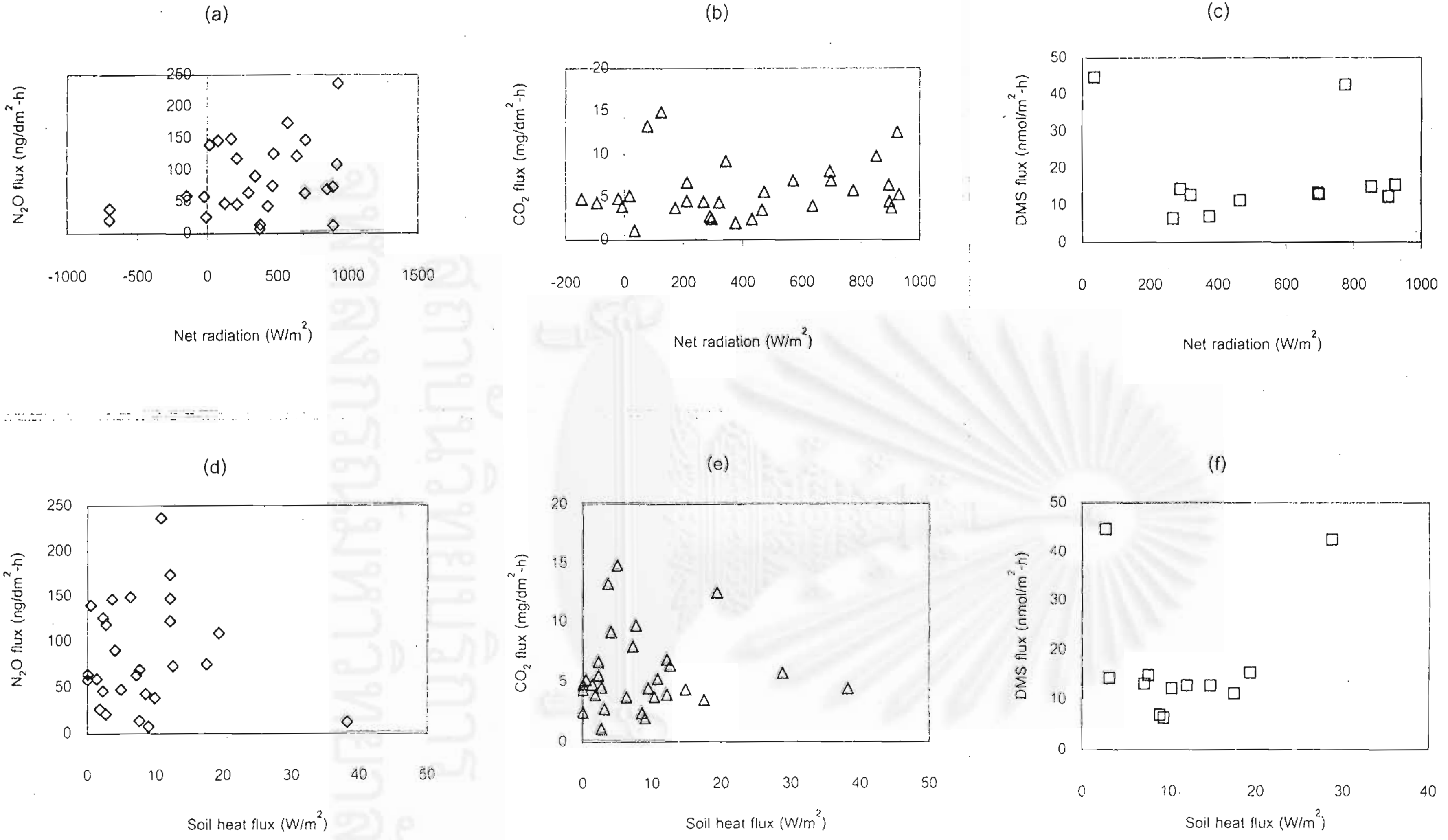


Figure 4.2.11 Effect of energy associated parameters on emission fluxes in pine forest at Nagano

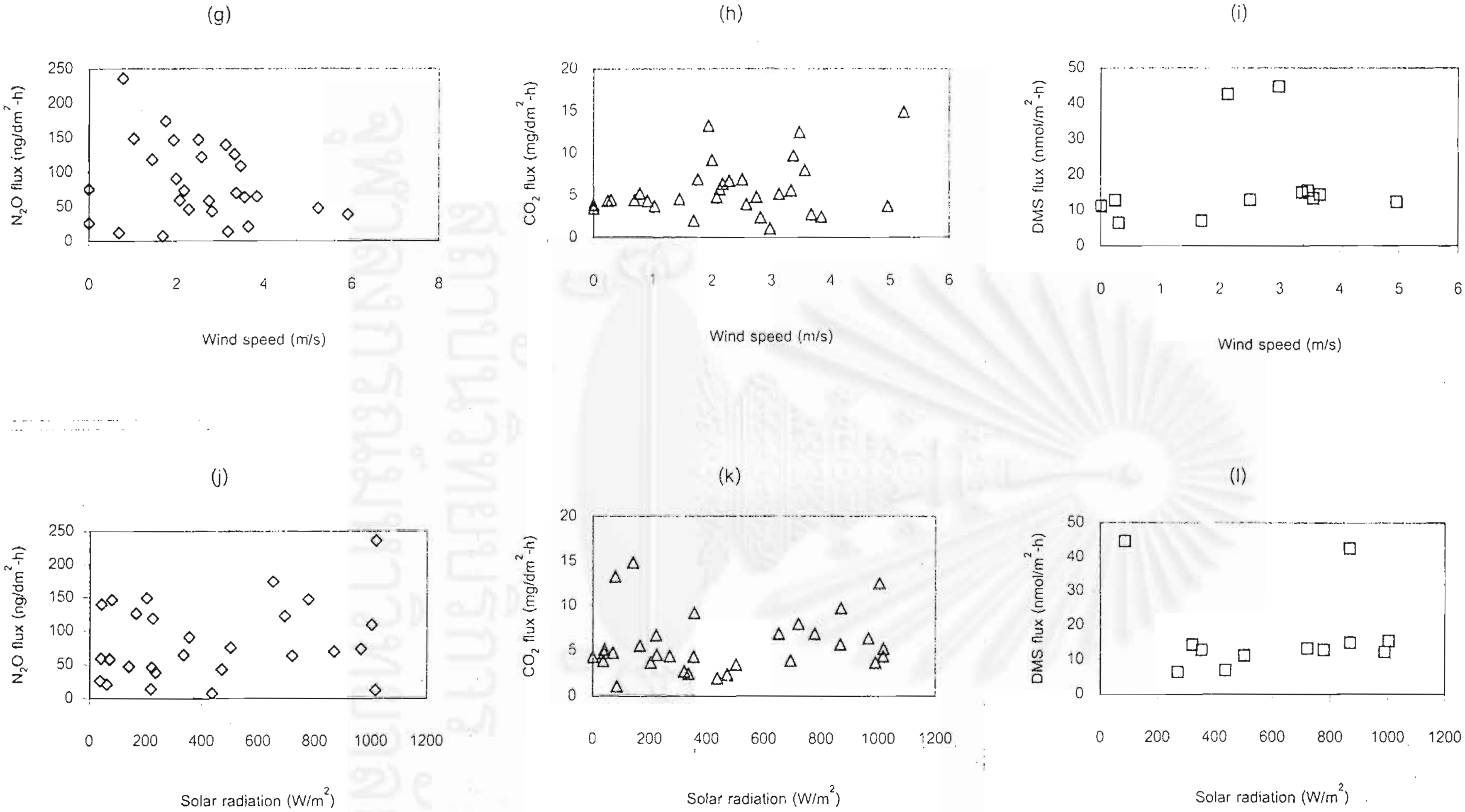


Figure 4.2.11 (Cont.)

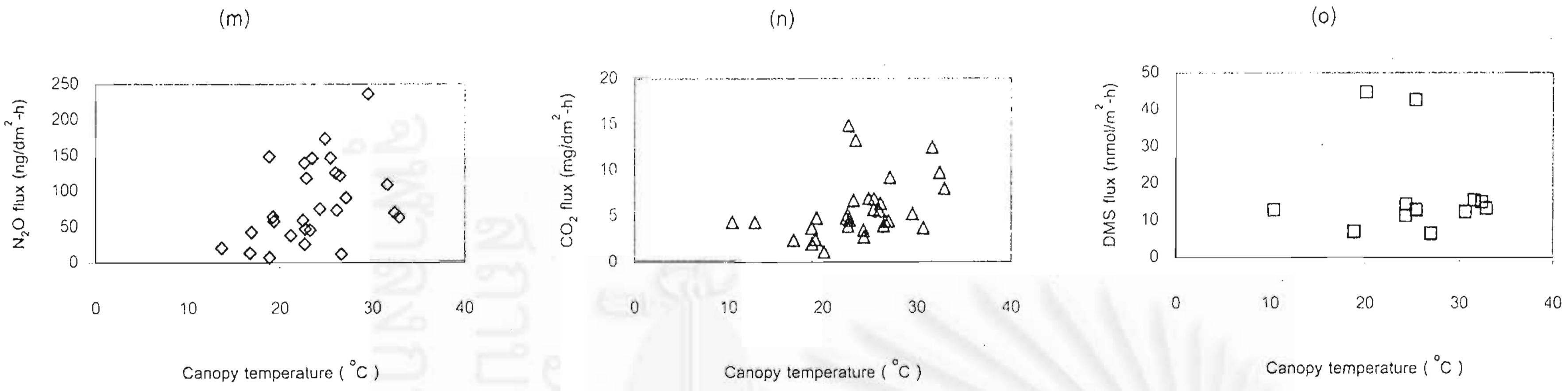


Figure 4.2.11 (Cont.)

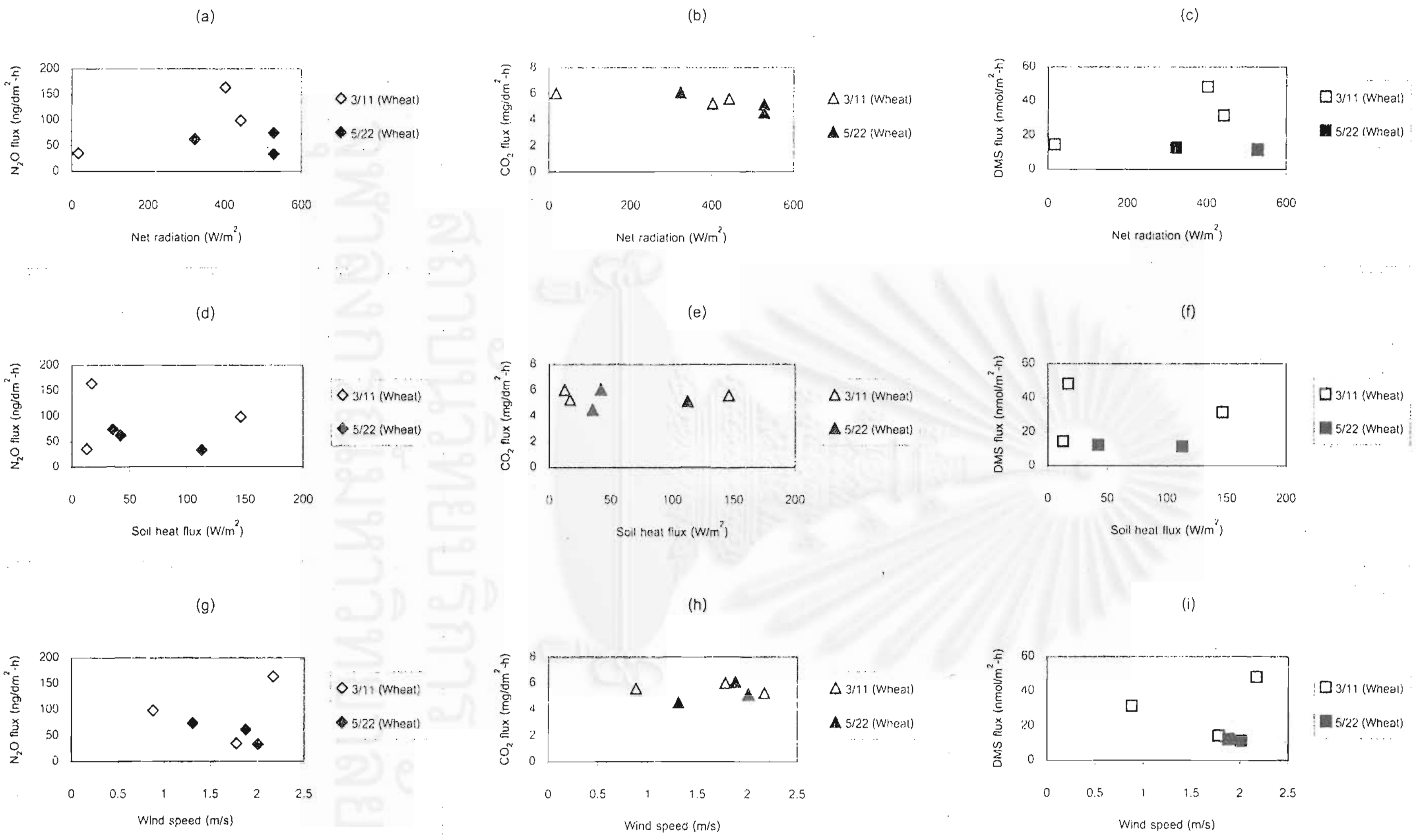


Figure 4.2.12 Effect of energy associated parameters on emission fluxes in wheat field

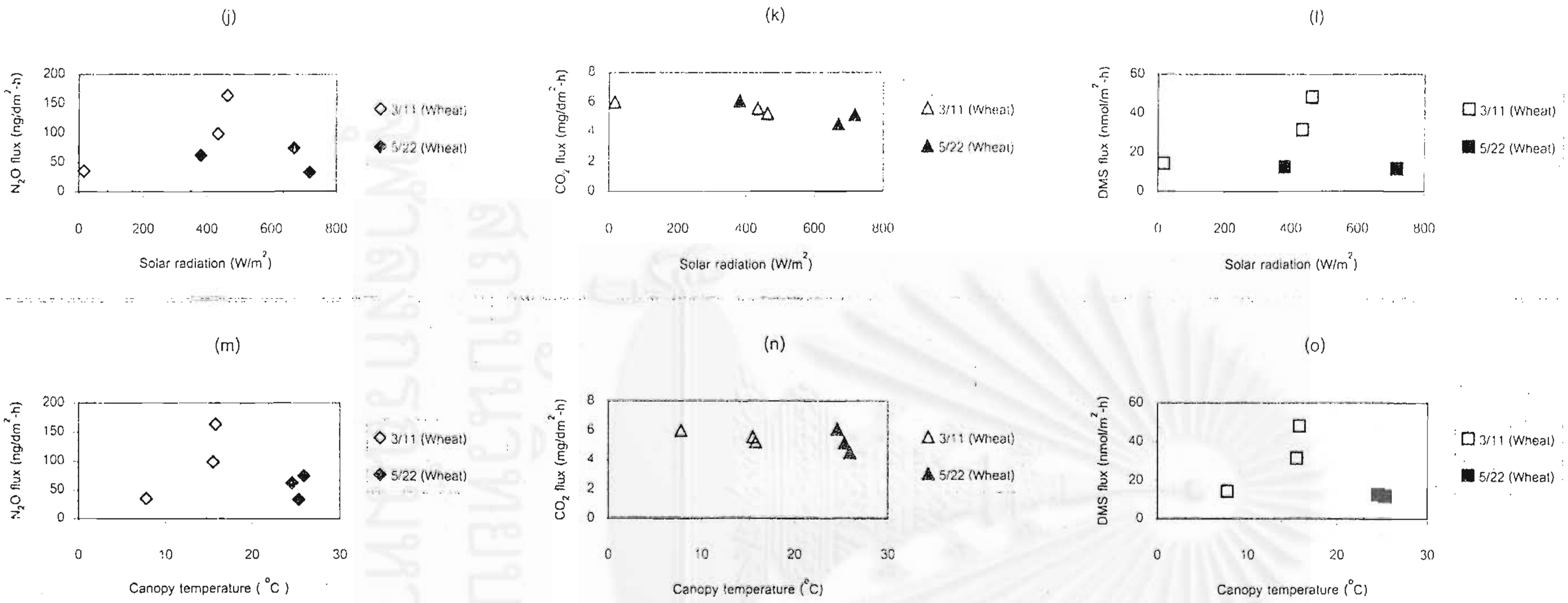


Figure 4.2.12 (Cont.)

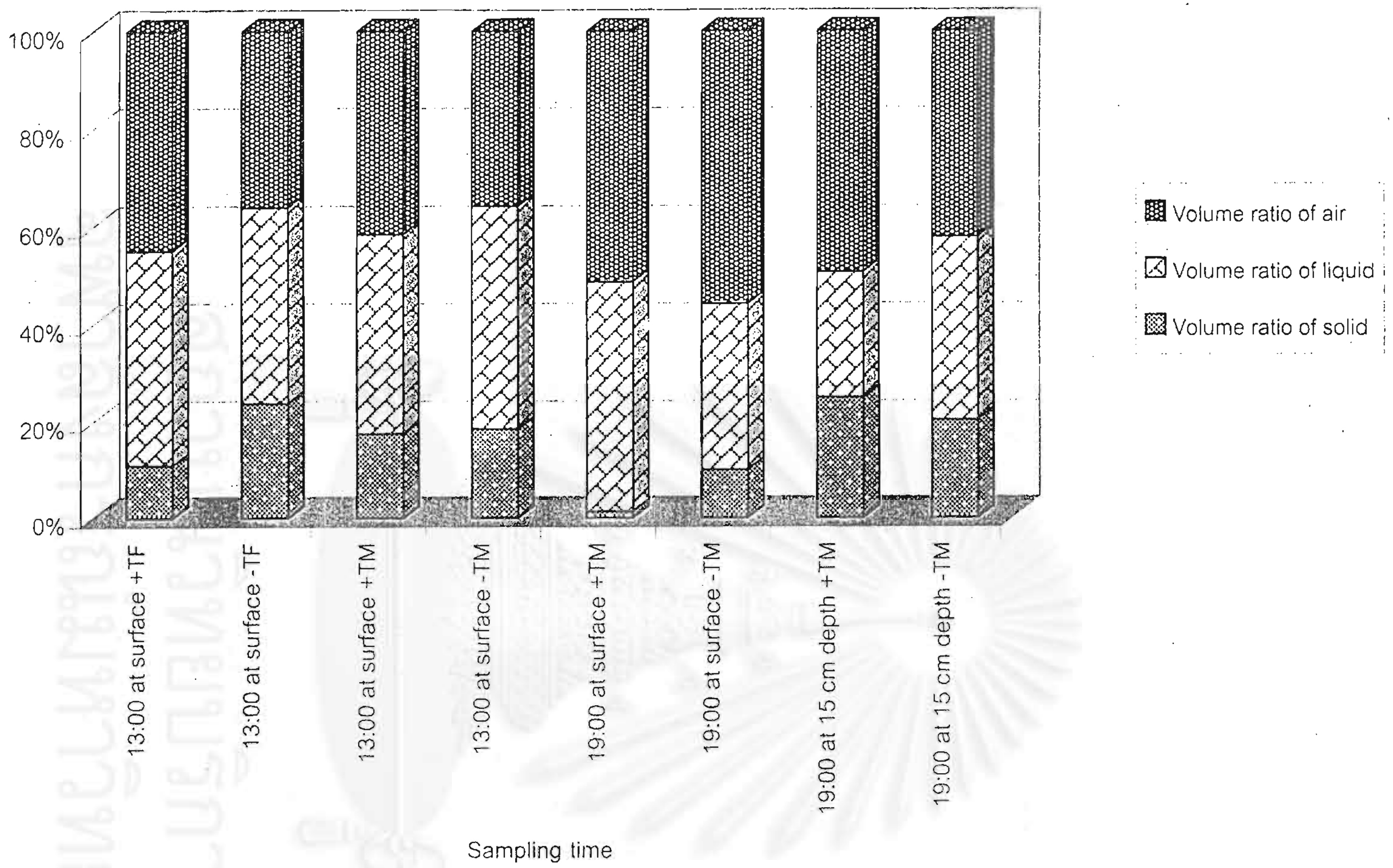


Figure 4.2.13 Volume ratio of three phases in soil at Soyabean field on 23/7/2002

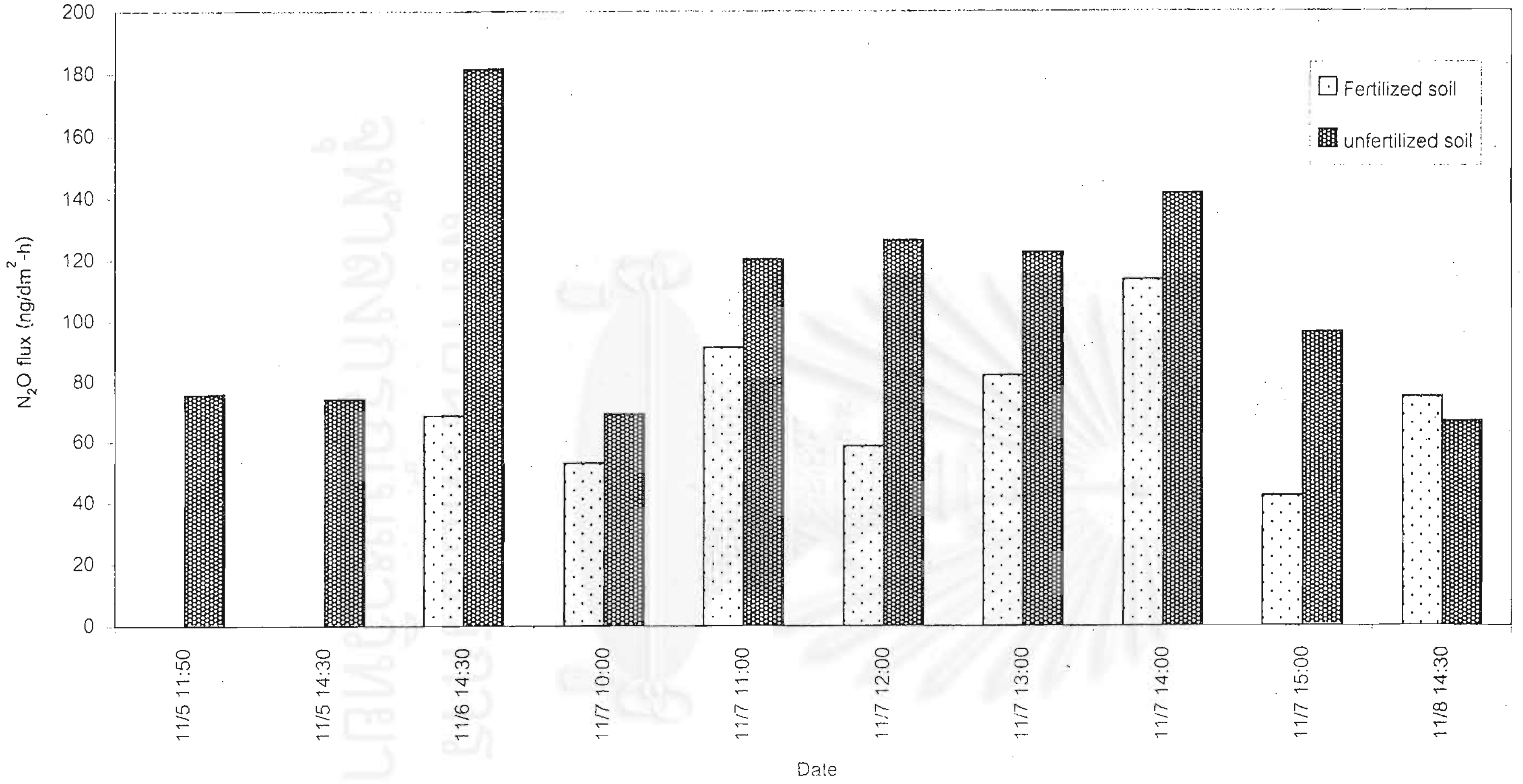


Figure 4.2.14 Comparison of N_2O flux between fertilized and unfertilized zone in bared soil (From November 5-8, 2001)

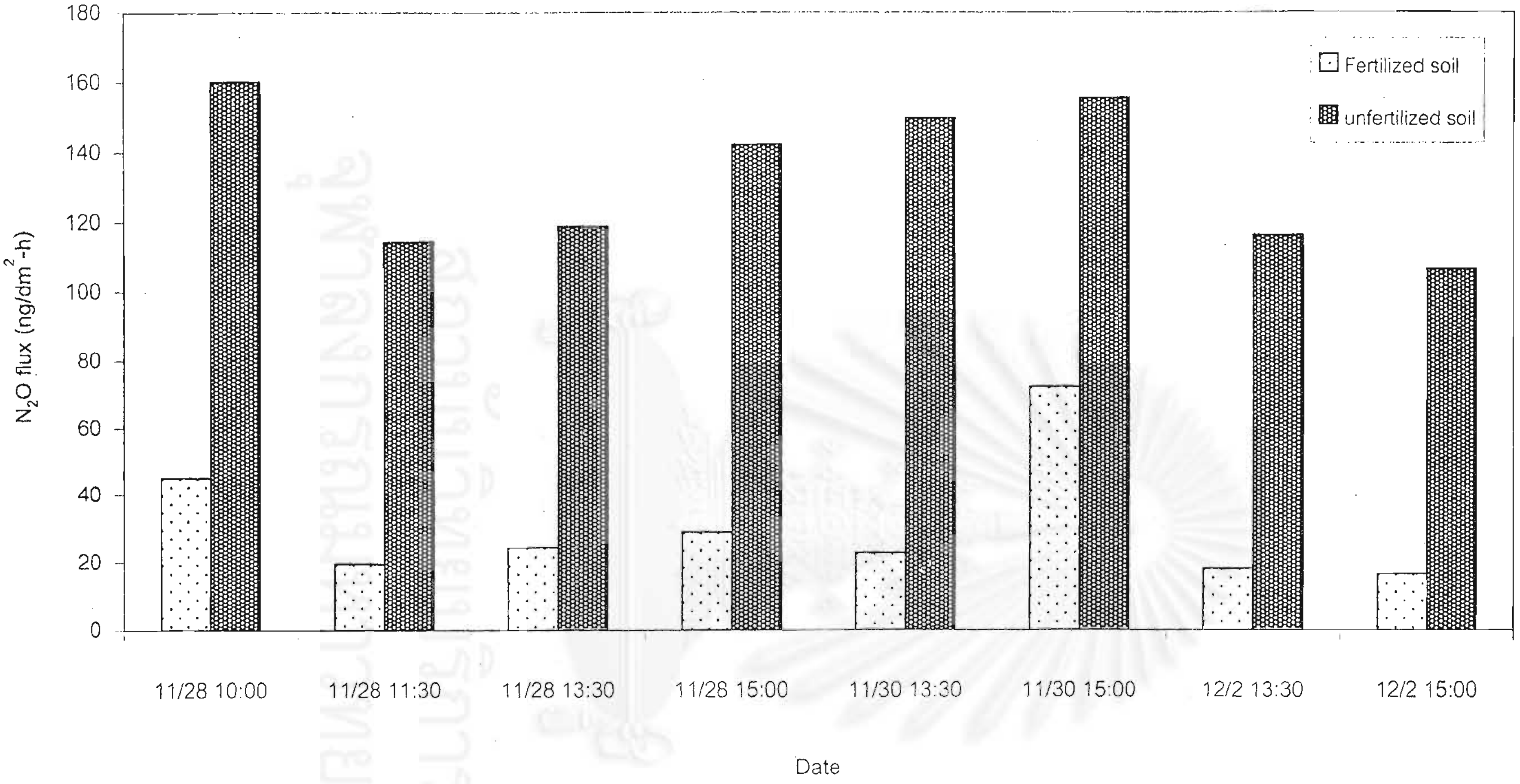
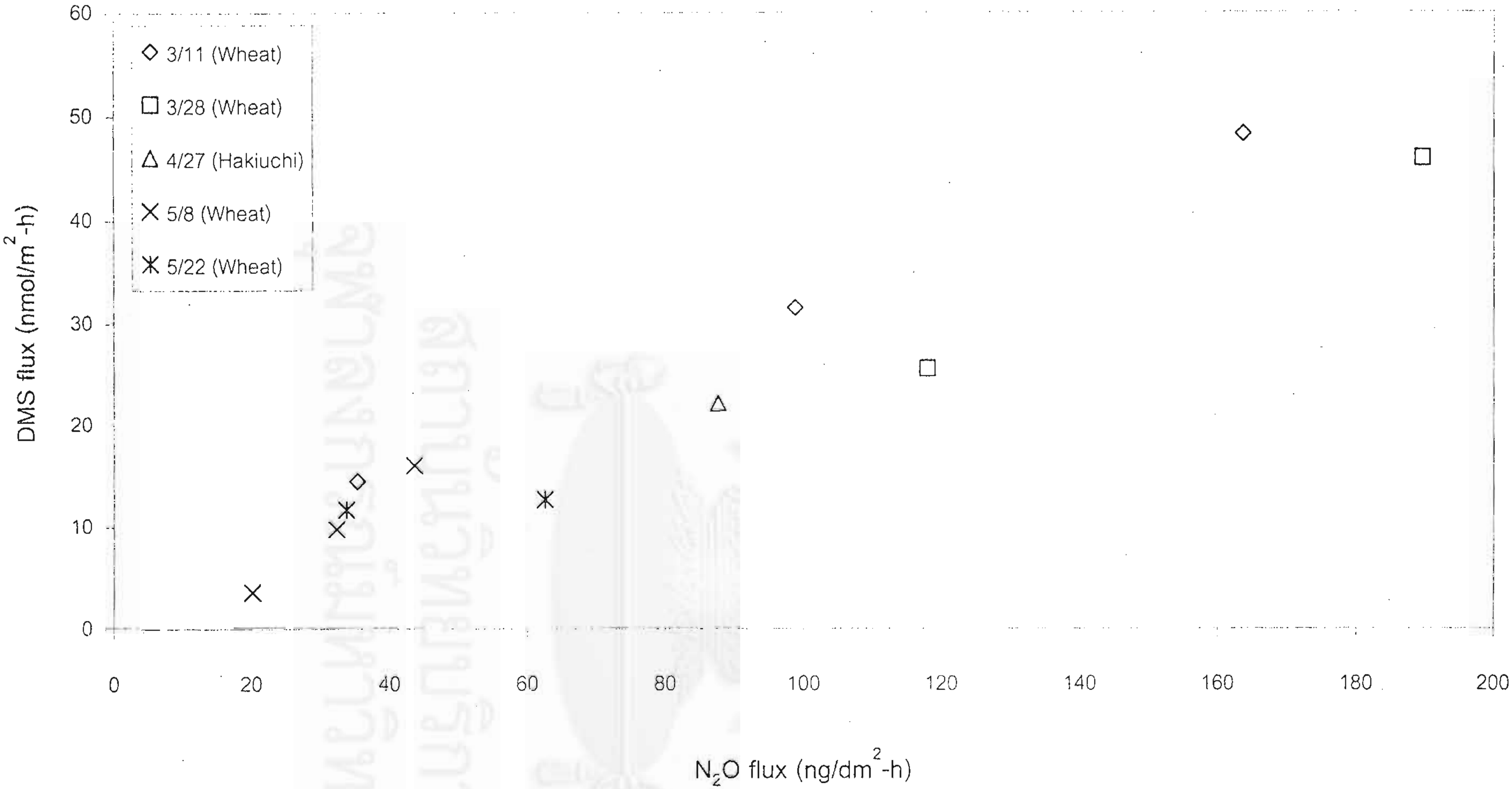


Figure 4.2.15 Comparison of N_2O flux between fertilized and unfertilized zone in bared soil

(From November 28 to December 2, 2001)



<u>Figure 4.3.1</u> Correlation of DMS flux and N$_2$O flux in Wheat field and Hakiuchi forest

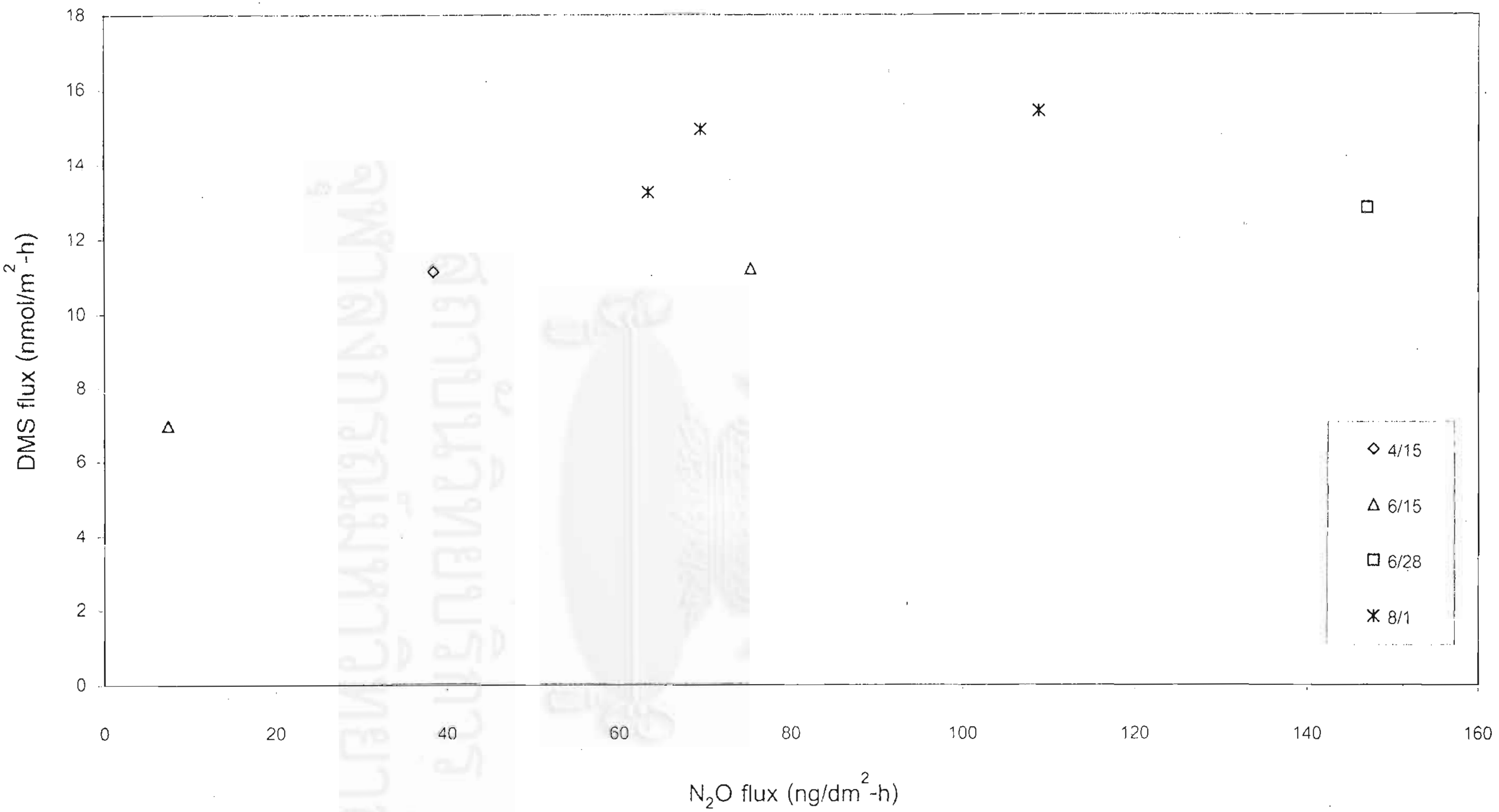


Figure 4.3.2 Correlation of DMS flux and N_2O flux in pine forest at Nagano

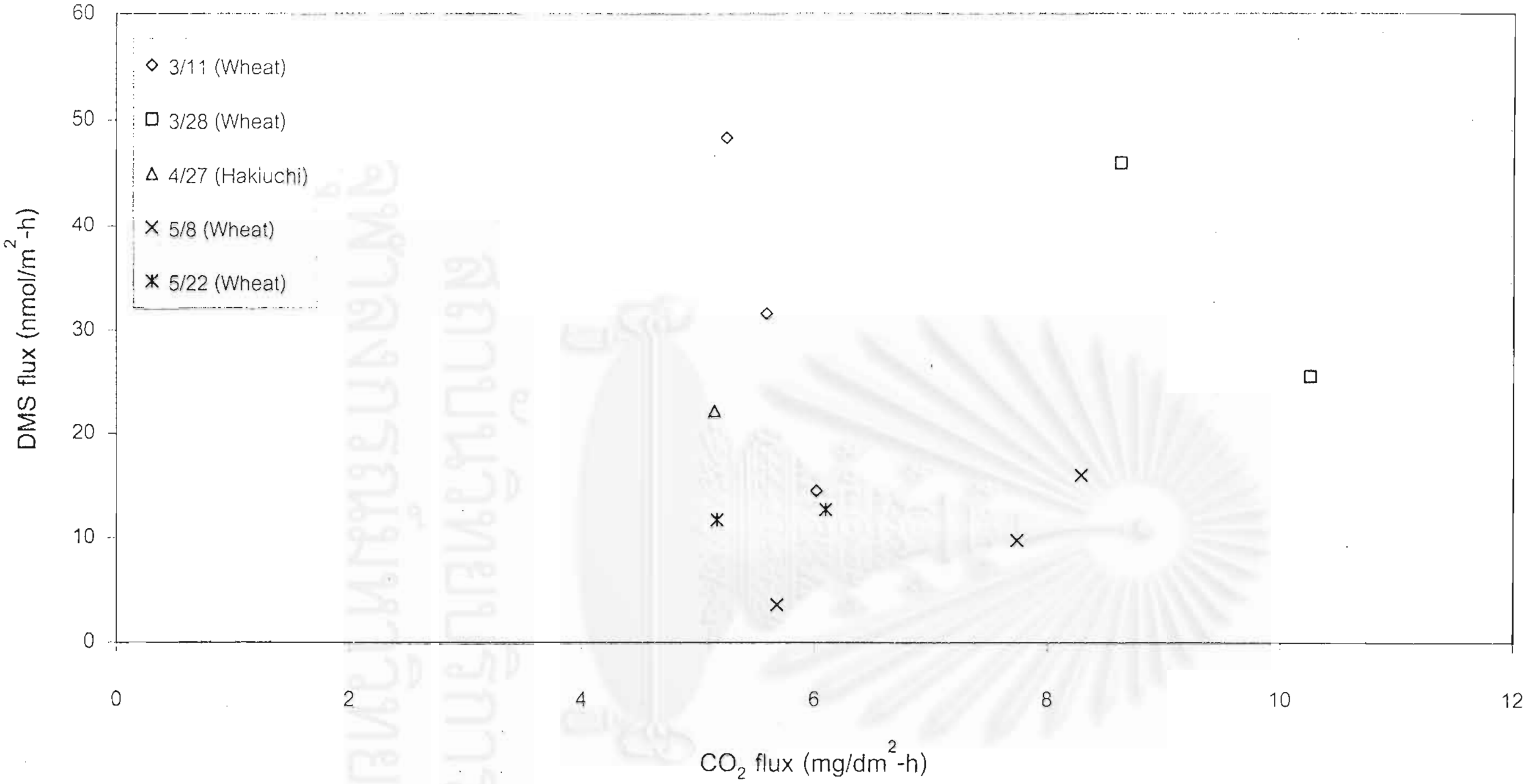


Figure 4.3.3 Correlation of DMS flux and CO$_2$ flux in Wheat field and Hakiuchi forest

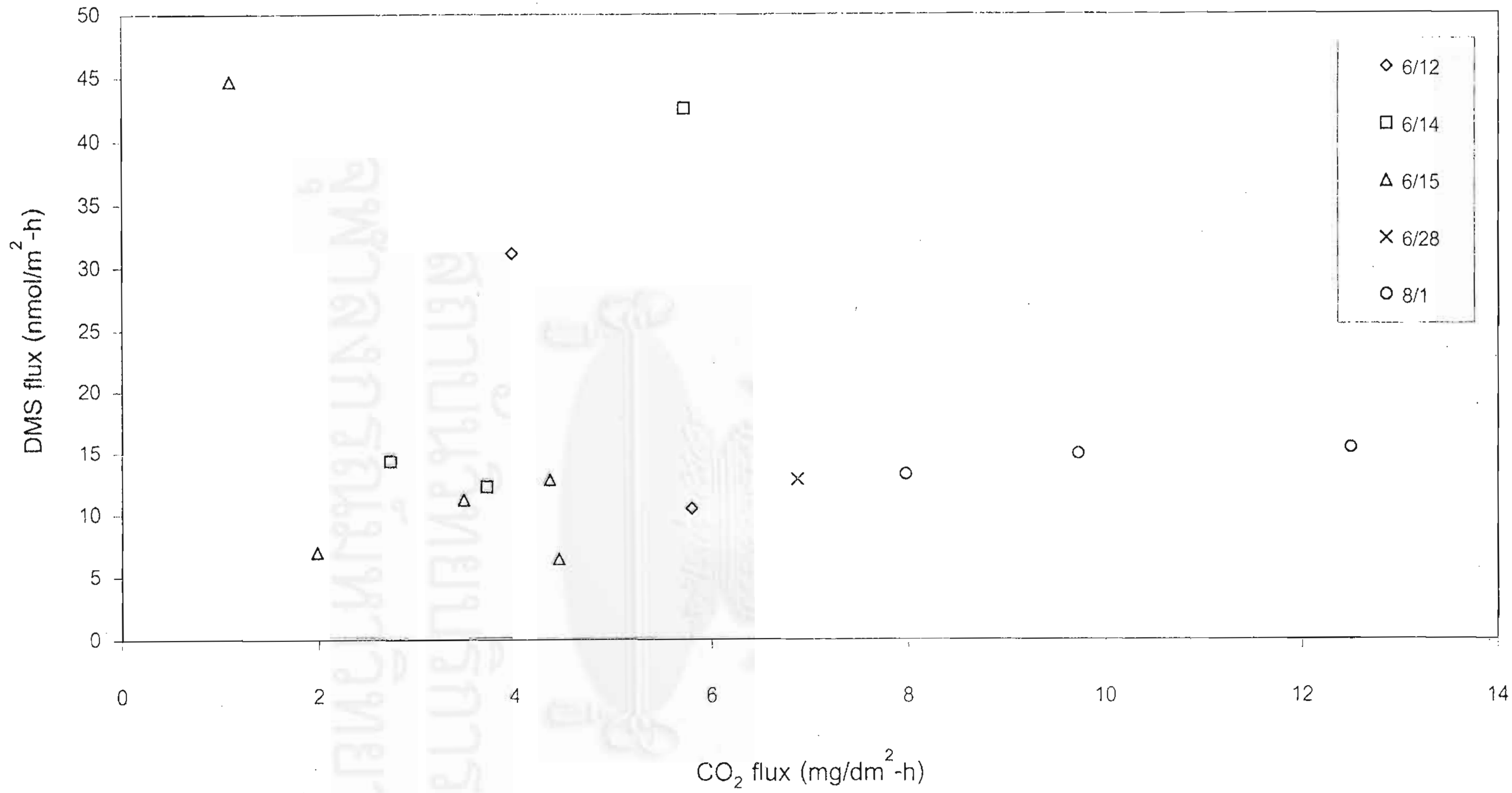


Figure 4.3.4 Correlation of DMS flux and CO$_2$ flux in pine forest at Nagano

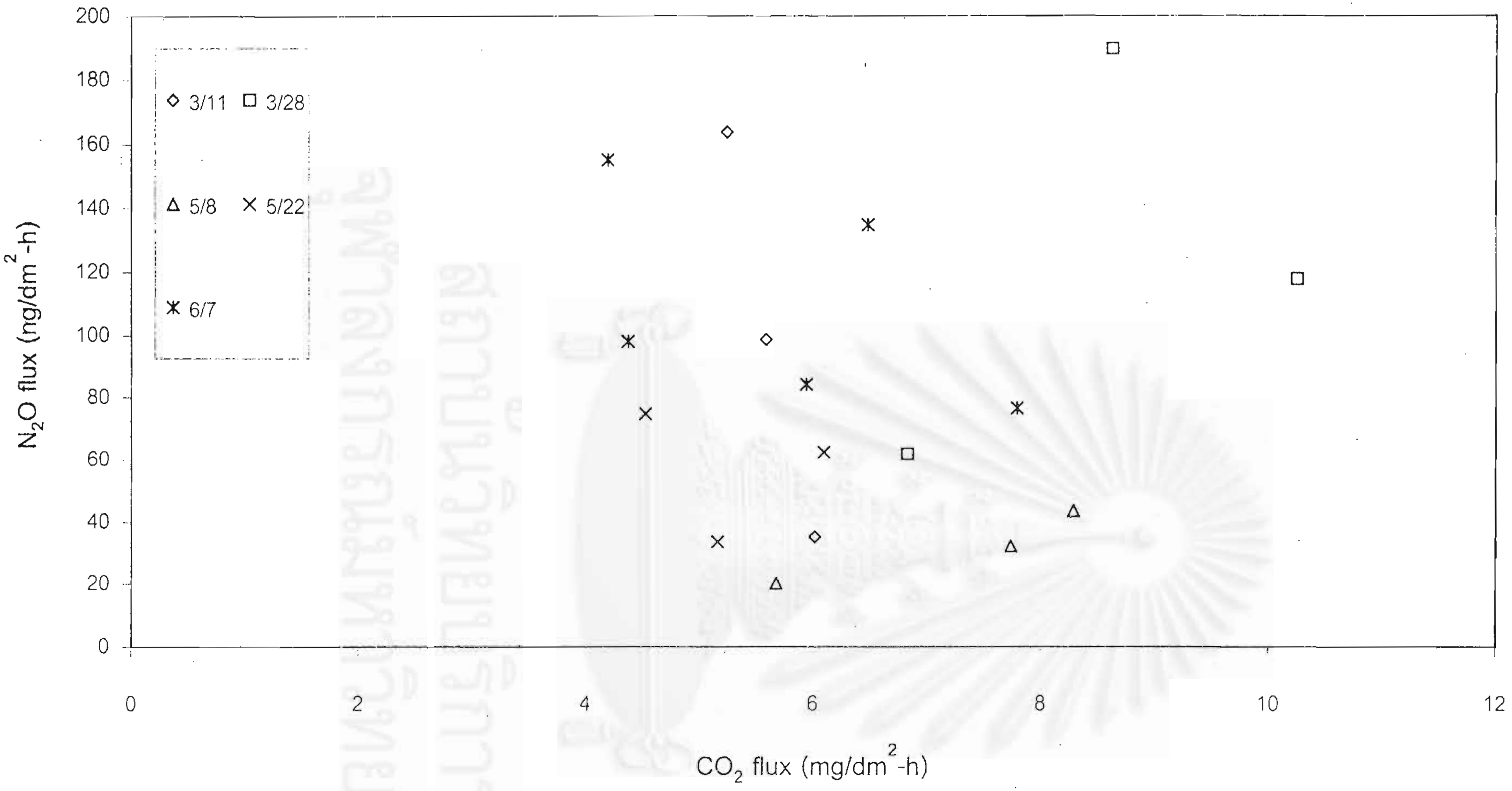


Figure 4.3.5 Correlation of N_2O flux and CO_2 flux in wheat field

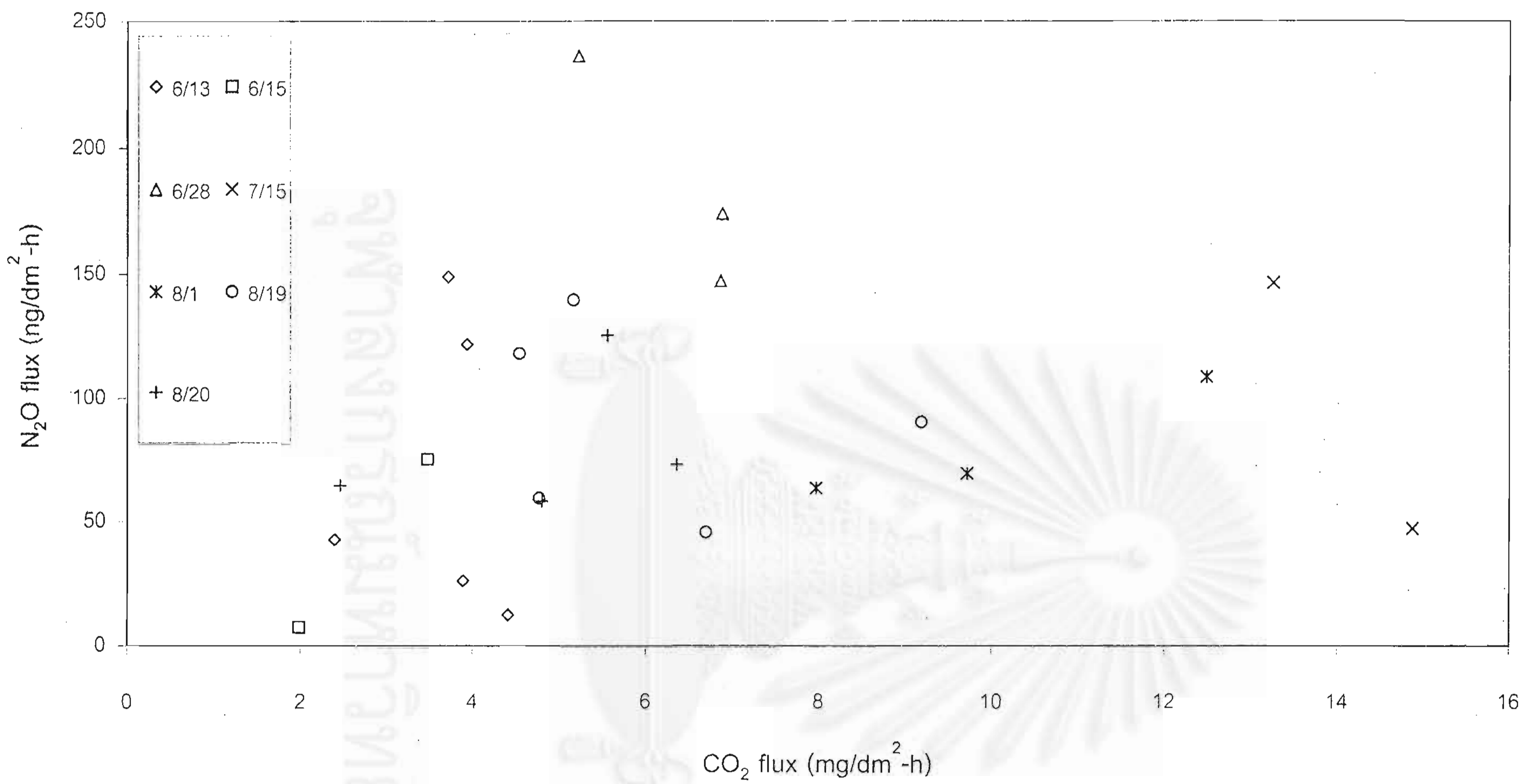


Figure 4.3.6 Correlation of N_2O flux and CO_2 flux in pine forest at Nagano

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The investigation in this work leads to the following conclusions:

1. The comparison of all emission fluxes measured in this work shows that CO_2 from all areas was emitted in a greater quantity than N_2O and DMS. It was found that agricultural fields could emit N_2O and CO_2 into the atmosphere more than the pine forest. However, DMS emitted from all vegetation areas seems to have a similar rate.

2. Soil temperature, air temperature, and canopy temperature were thought to be a major effect on CO_2 emission fluxes.

3. High emission fluxes of N_2O and CO_2 were observed in the soil with the following characteristics:
    - Soil applied with manure (for both N_2O and CO_2)
    - Soil without tillage practice (for N_2O)
    - Soil with tillage practice (for CO_2)

4. Improper ratio of chemical fertilizer application added in bared soil could result in inhibition effect on microbial actiivities of N_2O production.

5. A linear relation was clearly observed between the emission of N_2O and DMS where N_2O flux increased with DMS flux both in the wheat field and pine forest.

5.2 Contributions

Agriculture has long been ignored in the environmental impact evaluation. It is, however, clear from this work that various gaseous pollutants could in fact be generated in a significant quantity when the forest was converted to agricultural area. Hence, the results from this work contribute greatly to an appraisal of global environmental aspects such as global warming potential, acidification, backscatter of sunlight, etc.

This work reveals that the emission rates of pollutants from vegetation areas were dependent on several factors such as temperature and tillage/fertilizing practices. This knowledge is important in the future planning of agricultural strategy as there is a potential that these emissions could be controlled through the adjustment of plantation techniques.

In addition, experimental data from this work will be useful as an extension to the existing database on the emission fluxes of gaseous pollutants from agricultural areas. The completion of this kind of database is vital for the development of a reliable mathematical model in the field of air pollution control where the deposition and emission of pollutants are required to estimate the exact amount of pollutants in the atmosphere.

5.3 Recommendations / Future works

The acquisition of experimental data in this work was subject to many constraints particularly the limitations of measurement duration, equipments, and techniques. It is recommended that the followings be carried out to overcome these constraints:

1. The period of measurement should include the whole cropping period to allow a complete measurement from a single type of vegetation.

2. The number of measuring devices should be adequate for a simultaneous measurement of each pollutant from several locations within one cropping area to ensure high accuracy of measuring data.
3. A better measuring technique for DMS should be developed to eliminate the loss of data due to the unavoidable error from measurement.

There is still a need for a further collection of data on the emission fluxes of pollutants from other vegetation areas to complete the dataset regarding the contribution of agriculture to the global environmental problems. Various other types of pollutants such as methane, volatile sulfur compounds, etc. should be taken into consideration along with the various types of vegetation. This opens up a wide area of research for the future. In addition, it will also be useful to extend this investigation to the cropping in Thailand particularly the emission from rice field or other major vegetation types.

References

Abrahamsen G., and Stuanes O. 1998. Retention and leaching of N in Norwegian Coniferous forests. *Nutr. Cycl. in Agroeco.* 52, 171-178.

Andreae M.O., Elbert W. and de Mora S.J. 1995. Biogenic sulfur emissions and aerosols over the tropical South Atlantic, 3. Atmospheric dimethylsulfide, aerosols and cloud condensation nuclei. *J. Geophys. Res.* 100, 11335-11356.

Aslam T., Choudhary M.A., and Saggar S. 2000. Influence of land-use management on CO_2 emissions from a silt loam soil in New Zealand. *Agr. Ecosys. & Env.* 77, 257-262.

Aulakh M.S., Rennic D.A., and Paul E.A. 1984. Acetylene and N-serve effects upon N_2O emissions from NH_4^+ and NO_3^- treated soils under aerobic and anaerobic conditions. *Soil Biol. Biochem.* 16, 351-356.

Austin D., Goldemberg J., and Parker G. 1998. Contributions to climate change: Are conventional metrics misleading the debate? [Online]. Available from: http://www.wri.org/cpi/notes/metrics2.html [2000, January 20]

Bacon P.E., Hoult E.H., and Mcgarity J.W. 1986. Ammonia volatillizzation from fertilizers applied to irrigated wheat soils. *Fert. Res.* 10, 27-42.

Ball B.C., Parker J.P., and Scott A. 1999. Soil and residue management effects on cropping conditions and nitrous oxide fluxes under controlled traffic in Scotland. 2. Nitrous oxide, soil N status and weather. *Soil & Till. Res.* 52, 191-201.

Bates T.S., Lamb B.K., Guenther A., Dignon J., and Stoiber R.E. 1992. Sulfur emissions to the atmosphere from natural sources. *J. of atmos. Chem.* 14, 315-337[Online].

Available from: http://www.pmel.noaa.gov/pubs/outstand/bate1229/estimate.shtml [2000, January 11]

Borken W., Xu Y.J., Brumme R., and Lamersdorf N. 1999. A climate change scenario for carbon dioxide and dissolved organic carbon fluxes from a temperate forest soil: drought and rewetting effect. *Soil Sci. Soc. Am. J.* 63, 1848-1855.

Bouwman A.F. 1990. *Soils and the greenhouse effect.* John Wiley and Sons, England.

Bowden R.D., Steudler P.A., Melillo J.M., and Aber J.D. 1990. Annual nitrous oxide fluxes from temperate forest soils in the northeastern United states. *J. Geophys. Res.* 95, 13997-14005.

Brumme R. and Beese F. 1992. Effects of liming and nitrogen fertilization on emissions of CO_2 and N_2O from temperate forest. *J. Geophys. Res.* 97, 12851-12858.

Cardon Z.G., Hungate B.A., Cambardella C.A., Chapin III F.S., Field C.B., Holland E.A., and Mooney H.A. 2001. Contrasting effects of elevated CO_2 on old and new soil carbon pools. *Soil. Biol. Biochem.* 33, 365-373.

Carnol M. and Ineson P. 1999. Environmental factors controlling NO_3^- leaching, N_2O emissions and numbers of NH_4^+ oxidisers in a coniferous forest soil. *Soil. Biol. Biochem.* 31, 979-990.

Choudhary M.A., Ahramkhanov A., and Saggar S. 2001. Nitrous oxide emissions in soils cropped with maize under long-term tillage and under permanent. *Soil & Till. Res.* 62, 61-71.

Christensen S., Ambus P., Arah J.R.M., Clayton H., Galle B., Griffith D.W.T., Hargreaves K.J., Klemedtsson L., Lind A.M., Maag M., Scott A., Skiba U., Smith K.A., Welling M., and Weinhold F.G. 1996. Nitrous oxide emission from an agricultural field:

comparison between measurements by flux chamber and micrometerological techniques. *Atmos. Env.* 30, 4183-4190.

Coxson D.S. and Parkinson D. 1987. Winter respiratory activity in aspen woodland forest floor litter and soils. *Soil. Biol. Biochem.* 19, 49-59.

DMS interactive, An interactive presentation of Dimethyl sulfide chemistry[Online]. Available from: http://ecpl.chemistry.uch.gr/~baboukas/Java/3Dmol/DMS_multim.html [2000, January 14]

Duiker S.W. and Lal R. 2000. Carbon budget study using CO_2 flux measurements from a no till system in central Ohio. *Soil & Till. Res.* 54, 21-30.

European Environment Agency (EEA) 2000. *Emissions of Atmospheric Pollutants in Europe, 1980-1996.* Belgium.

Flessa H., Ruser R., Schilling R., Loftfield N., Munch J.C., Kaiser E.A., and Beese F. 2002. N_2O and CH_4 fluxes in potato fields: automated measurement, management effects and temporal variation. *Geoderma.* 105, 307-325.

Freyney J.R. 1997. Emission of nitrous oxide from soils used for agriculture. *Nutr. Cycl. in Agroeco.* 46, 1-6.

Freyney J.R., Denmead O.T., Watanabe I., and Craswell E.T. 1981. Ammonia and nitrous oxide losses following applications of ammonium sulfate to flooded rice. *Aust. J. Agri. Res.* 32, 37-45.

Gerlach T.M., Doukas M.P., McGee K.A., and Kessler R. 2001. Soil efflux and total emission rates of magmatic CO_2 at the Horseshoe Lake tree Kill, Mammoth mountain, California, 1995-1999. *Chem. Geo.* 177, 101-116.

Goldan P.D., Kuster W.C., Albritton D.L., and Fehsenfeld F.C. 1987. The measurement of natural sulfur emissions from soils and vegetation – 3 sites in the eastern United States revisited. *J. Atmos. Chem.* 5, 439-467.

Grace J., Lloyd J., McIntyre J., Miranda A.C., Meir P., Miranda H.S., Moncrieff J., Massheder J., Wright I.R., and Gash J.H.C. 1995. Fluxes of carbon dioxide and water vapour over an undisturbed tropical rain forest in south-west Amazonia. *Glob. Clim. Change*. 1, 1-12 [Online]. Available from: http://www.cptec.inpe.br/abracos/cabf.html [2000, January 10]

Graedel T.E. 1978. *Chemical Compounds in the Atmosphere.* London. Academic Press, INC.

Henk M., Stef A., and Hans G. 2000. Microbial production and consumption of dimethyl sulfide (DMS) in a sea grass (Zostera noltii)-dominated marine intertidal sediment ecosystem. *Microbiol. Ecol.* 31, 163-172.

IPCC, *Intergovernmental Panel on Climate Change Guidelines for National Greenhouse Gas Inventories, Chapter 4. Agriculture: Nitrous oxide from agricultural soils and manure management*, OECD, Paris, France, 1997.

Janzen H.H. et al. 2001. Estimates of Emissions[Online]. Available from: http://res2.agr.ca/research-researche/science/Healthy_Air/toc.html [2000, January 20]

Kaiser E.A., Kohrs K., Kucke M., Schnug E., Heinemeyer O., and Munch J.C. 1998. Nitrous oxide release from aerable soil: importance of N-fertilization, crops and temporal variation. *Soil. Biol. Biochem.* 30, 1553-1563.

Kanda K. and Minami K. 1992. Measurement of dimethyl sulfide emission from lysimeter paddy fields. *Ecolo. Bull.* 42, 195-198.

Kanda K., Tsuruta H., and Minami K. 1992. Emission of dimethyl sulfide, carbonyl sulfide, and carbon disulfide from paddy fields. *Soil Sci. Plant Nutr.* 38, 709-716.

Kanda K., Tsuruta H., and Minami K. 1995. Emissions of biogenic sulfur gases from maize and wheat fields. *Soil Sci. Plant Nutr.* 41, 1-8.

Keller M., Warren A., Kaplan and Steven C. 1986. Emission of N_2O, CH_4 and CO_2 from tropical forest soils. *J. Geophys. Res.* 91, 11791-11802.

Logan R.H. 1996. Why should we be concerned about Carbon Dioxide in the atmosphere?[Online]. Available from: http://edie.cprost.sfu.ca/~rhlogan/co2.html [2000, January 12]

Maljanen M., Martikainen P.J., Aaltonen H., and Silvola J. 2002. Short-term variation in fluxes of carbon dioxide, nitrous oxide and methane in cultivated and forested organic boreal soils. *Soil. Biol. Biochem.* 34, 577-584.

Mariko S., Nishimura N., Mo W.H., Matsui Y., Kibe T., and Koizumi H. 2000. Winter CO_2 flux from soil and snow surfaces in a cool-temperate deciduous. *Ecol. Res.* 15, 363-372.

Matthias A.D., Blackmer A.M., and Bremner J.M. 1980. A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *J. environ. Qual.* 9, 251-256.

Mello W.Z. and Hines M.E. 1994. Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in *Sphagnum* peatlands: Implication for the magnitude and direction of flux. *J. Geophys. Res.* 99, 14601-14607.

Michael K., Warren A., Kaplan and Steven C. 1986. Emissions of N_2O, CH_4 and CO_2 from tropical forest soils. *J. of Geophys. Res.* 91, 11791-11802.

Mielnick P.C. and Dugas W.A. 2000. Soil CO_2 in a tallgrass prairie. *Soil. Biol. Biochem.* 32, 221-228.

Miranda A.C. et al. 1993. Fluxes of CO_2 over a Cerrado sensu stricto in Central Brazil., Brazil[Online]. Available from: http://www.cptec.inpe.br/abracos/cabf.html [2000, January 20]

Moiser A., Kroeze C. 1998. A new approach to estimate emissions of nitrous oxide from agriculture and its implications to the global nitrous oxide budget[Online]. Available from: http://web.mit.edu/afs/athena.mit.edu/org/i/igac/www/newsletter/highlights/n2o.html [2000, January 22]

Moiser A.R., Chapman S.L., and Freyney J.R. 1989. Determination of dinitrogen emission and retention in floodwater and porewater of a lowland rice field fertilized with ^{15}N-urea. *Fert. Res.* 19, 127-136.

Moiser A.R., Duxbury J.M., Freyney J.R., Heinemeyer O., and Minami K. 1996. Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation. *Plant and Soil* 181, 95-108.

Nakadai T., Yokozawa M., Ikeda H., and Koizumi H. 2002. Diurnal changes of carbon dioxide flux from bare soil in agricultural field in Japan. *Appl. Soil Eco.* 19, 161-171.

Nouchi I., Hosono T., and Sasaki K. 1997. Seasonal changes in fluxes of methane and volatile sulfur components from rice paddies and their concentrations in soil water. *Plant and Soil* 195, 233-245.

Oechel W.C., Vourlitis G.L., and Hastings S.J. 1997. Cold season CO_2 emission from arctic soils. *Glob. Biogeo. Cycl.* 11, 163-172.

Pomazkina L.V., Lubnina E.V., Zorina S.Y., Kotova L.G., and Khortolomei I.V. 1996. Dynamics of CO_2 emission from the gray forest soil in the Forest-Steppe of the Cisbaikal region. *Eura. Soil Sci.* 29, 1355-1359.

Prieme A. and Christensen S. 2001. Natural perturbations, drying-wetting and freezing-thwaing cycles, and the emission of nitrous oxide, carbon dioxide and methane from farmed organic soils. *Soil. Biol. Biochem.* 33, 2083-2091.

Quinn P.K., Covert D.S., Bates T.S., Kapustin V.N., Ramsey-Bell D.C., and McInnes L.M. 1993. Dimetylsulfide/cloud condensation nuclei/climate system: Relevant sizeresolved measurements of the chemical and physical properties of atmospheric aerosol particles. *J. Geophys. Res.* 98, 10411-10427.

Rayment M.B. and Jarvis P.G. 2000. Temporal and spatial variation of soil CO_2 efflux in a Canadian boreal forest. *Soil. Biol. Biochem.* 32, 35-45.

Reicosky D.C. 1997. Tillage-induced CO_2 emission from soil. *Nutr. Cycl. in Agroeco.* 49, 273-285.

Richard A., William J., and Robert C. 1996. Diffusional flux of CO_2 through snow: Spatial and temporal variability among alpine-subalpine sites. *Glob. Biogeochem. Cycl.* 10, 473-482.

Robinson D. and Conroy J.P. 1999. A possible plant-mediated feedback between elevated CO_2, denitrification and the enhanced greenhouse effect. *Soil. Biol. Biochem.* 31, 43-53.

Russel C.A. and Voroney R.P. 1994. Carbon dioxide efflux from the floor of boreal aspen forests. I. Relationship to environmental variables and estimates of C respired, Canada[Online]. Available from: http://www.nrc.ca/aic-journals/may98ab.html [2000, January 14]

Scala Jr. N.L., Lopes A., Marques Jr. J., and Pereira G.T. 2001. Carbon dioxide emissions after application of tillage systems for a dark red latosol in southern Brazil. *Soil & Till. Res.* 62, 163-166.

Schloerer J. 1996. Why does atmospheric CO_2 rise?, Germany[Online]. Available from: http://www.radix.net/~bobg/faqs/scq.co2rise.html [2000, January 27]

Schmidt J., Seiler W., and Conrad R. 1988. Emission of nitrous oxide from temperate forest soils into the atmosphere. *J. Atmos. Chem.* 1, 95-115.

Simpson J.R., Freyney J.R., Wetse laar R., Muirhead W.A., Leuning R., and Denmead O.T. 1984. Transformations and losses of urea nitrogen after application to flooded rice. Aust. *J. Agri. Res.* 35, 189-200.

Situala B.K., Bakken L.R., and Abrahamsen G. 1995. N-fertiliztion and soil acidification effects on N_2O and CO_2 emission from temperate pine forest soil. *Soil. Biol. Biochem.* 27, 1401-1408.

Sommerfeld R.A., Massman W.J., and Musselman R.C. 1996. Diffusional flux of CO_2 through snow: spatial and temporal variability among alpine-subalpine sites. *Glob. Biogeo. Cycl.* 10, 473-482.

Sowerby A., Blum H., Gray T.R.G., and Ball A.S. 2000. The decomposition of Lolium perenne in soils exposed to elevated CO_2: comparisons of mass loss of litter with soil respiration and soil microbial biomass. *Soil. Biol. Biochem.* 32, 1359-1366.

Taylor B.F. and Kiene R.P. 1989. *Microbial metabolism of dimethyl sulfide.* American Chemical Society, Washington, DC.

Teepe R., Brumme R., and Beese F. 2000. Nitrous oxide emissions from frozen soils under agricultural, fallow and forest land. *Soil. Biol. Biochem.* 32, 1807-1810.

Wagai R., Brye K.R., Gower S.T., Norman J.M., and Bundy L.G. 1998. Land use environmental factors influencing soil surface CO_2 flux and microbial biomass in natural and manged ecosystems in Southern Wisconsin. *Soil. Biol. Biochem.* 30, 1501-1509.

Watts S.F. 2000. The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide. *Atmos. Env.* 34, 761-779.

Weitz A.M., Linder E., Frolking S., Crill P.M., and Keller M. 2001. N_2O emission from humid tropical agricultural soils: effects of soil moisture, texture and nitrogen availability. *Soil. Biol. Biochem.* 33, 1077-1093.

Whalen S.C. 2000. Nitrous oxide emission from an agricultural soil fertilized with liquid swine waste or constituents. *Soil Sci. Soc. Am. J.* 64, 781-789.

Williams P.H., Jarvis S.C., and Dixon E. 1998. Emission of nitric oxide and nitrous oxide from soil under field and laboratory conditions. *Soil. Biol. Biochem.* 30, 1885-1893.

Workshop Participants, 1996. Global Wetland Distribution and Functional Characterization: Trace Gas and the Hydrology Cycle[Online]. Available from: http://gaim.unh.edu/Products/Reports/Report_2/ [2000, January 13]

Yang Z., Kong L., Zhang J., Wang L., and Xi S. 1998. Emission of biogenic sulfur gases from Chinese rice paddies. *The Sci. of the Tot. Env.* 224, 1-8.

Zimov S.A., Zimova G.M., Davidov Z.V., Prosiannikov S.F., Prosiannikova O.V., Semiletova I.V., and Semiletov I.P. 1993. Winter biotic activity and production of CO_2 in Siberian soils: a factor in a greenhouse effect. *J. Geophys. Res.* 98, 5017-5023.

APPENDIX

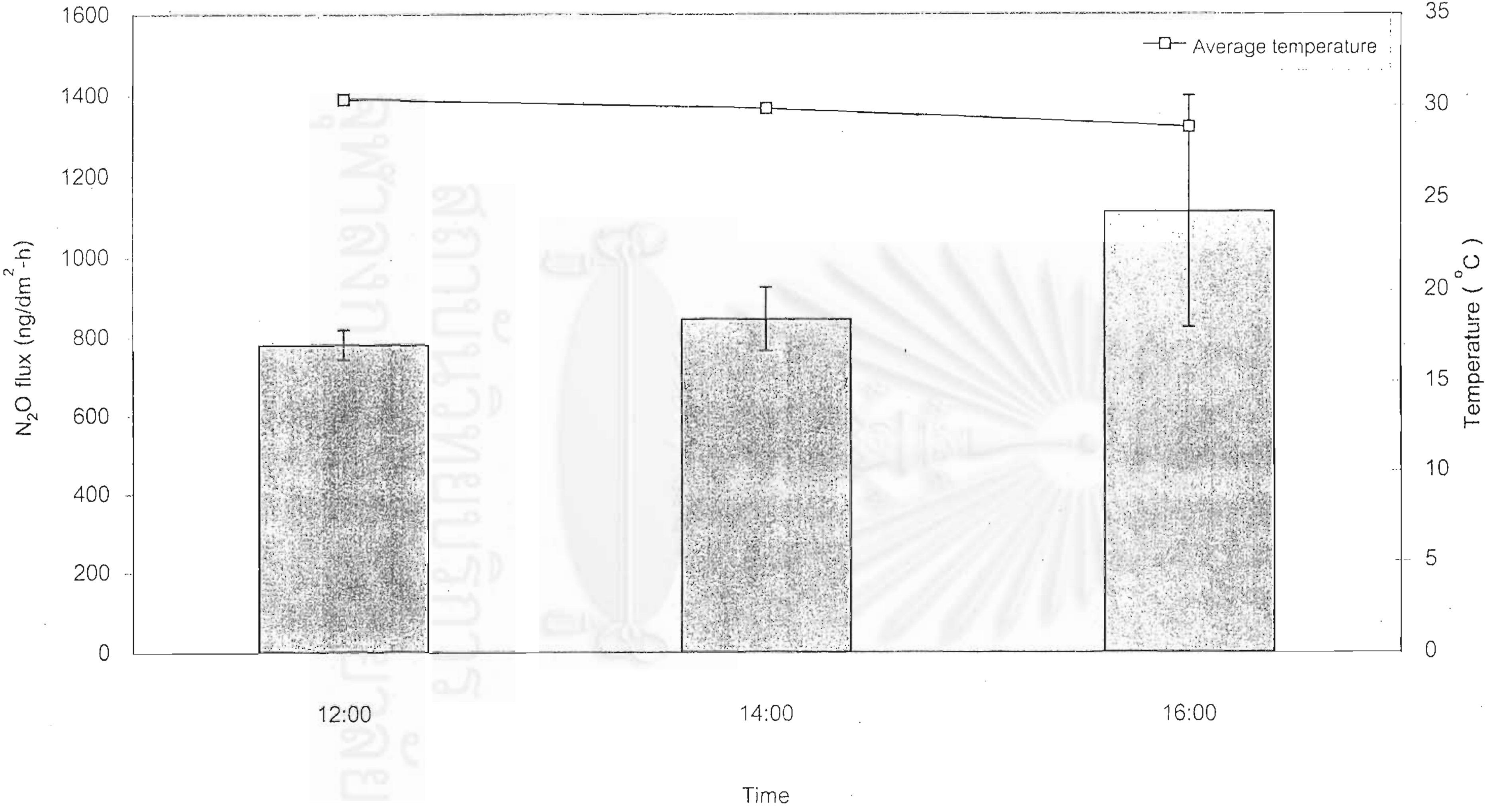


Figure 4.1.1 N_2O flux in corn field on 24/08/2001

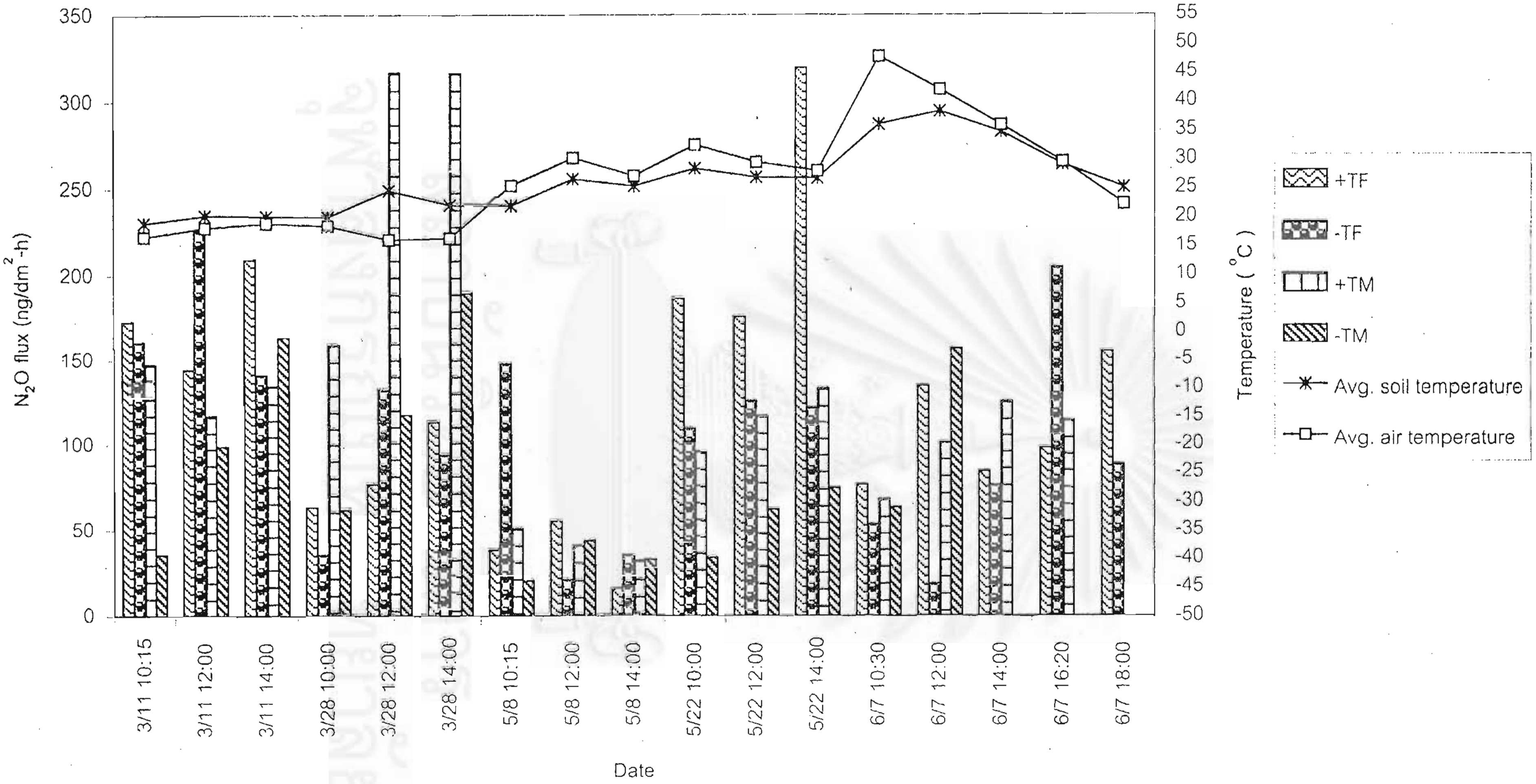


Figure 4.1.2 N_2O flux on sampling date in wheat field

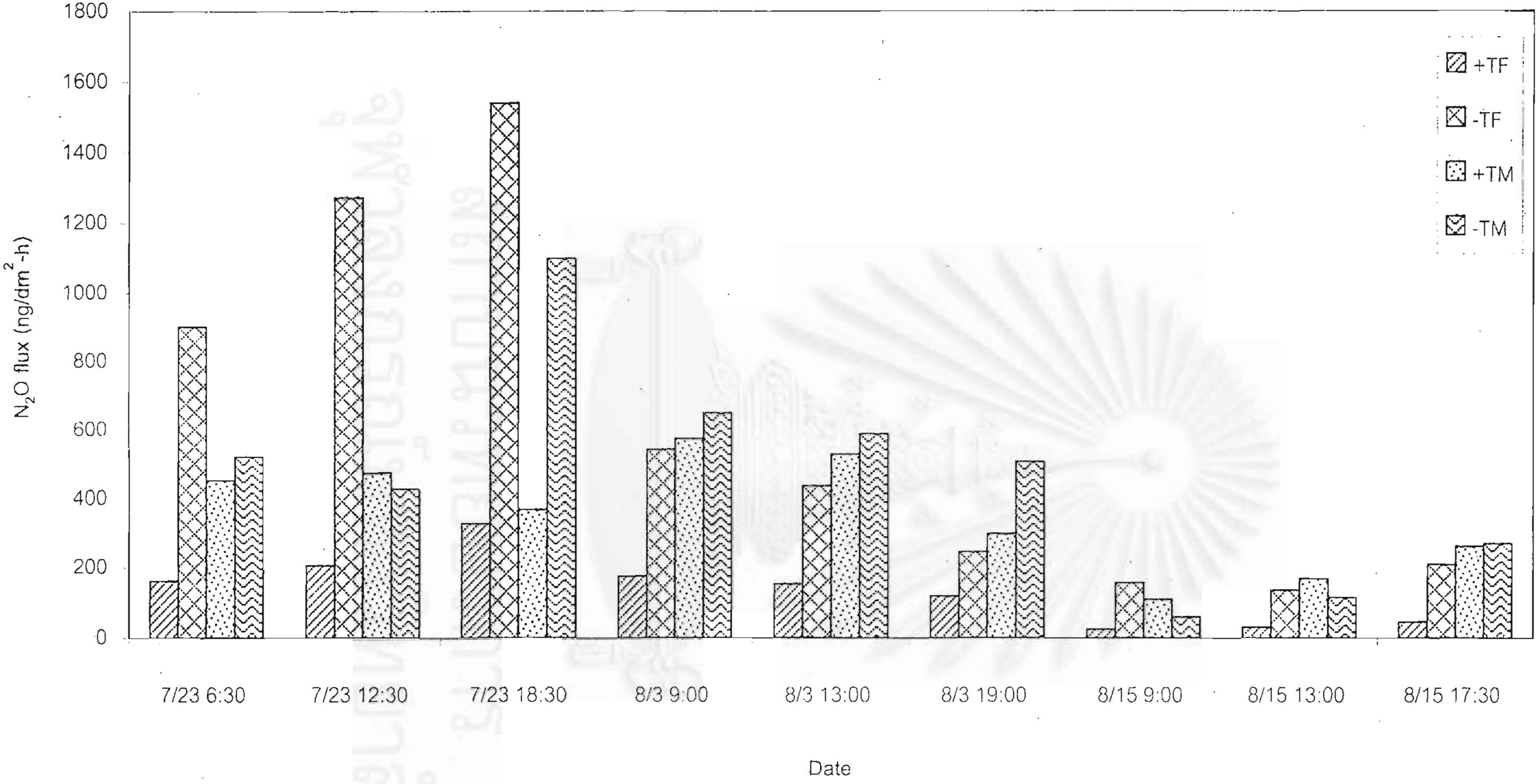


Figure 4.1.3 N_2O fluxes on sampling date in Soyabean field with different treatments

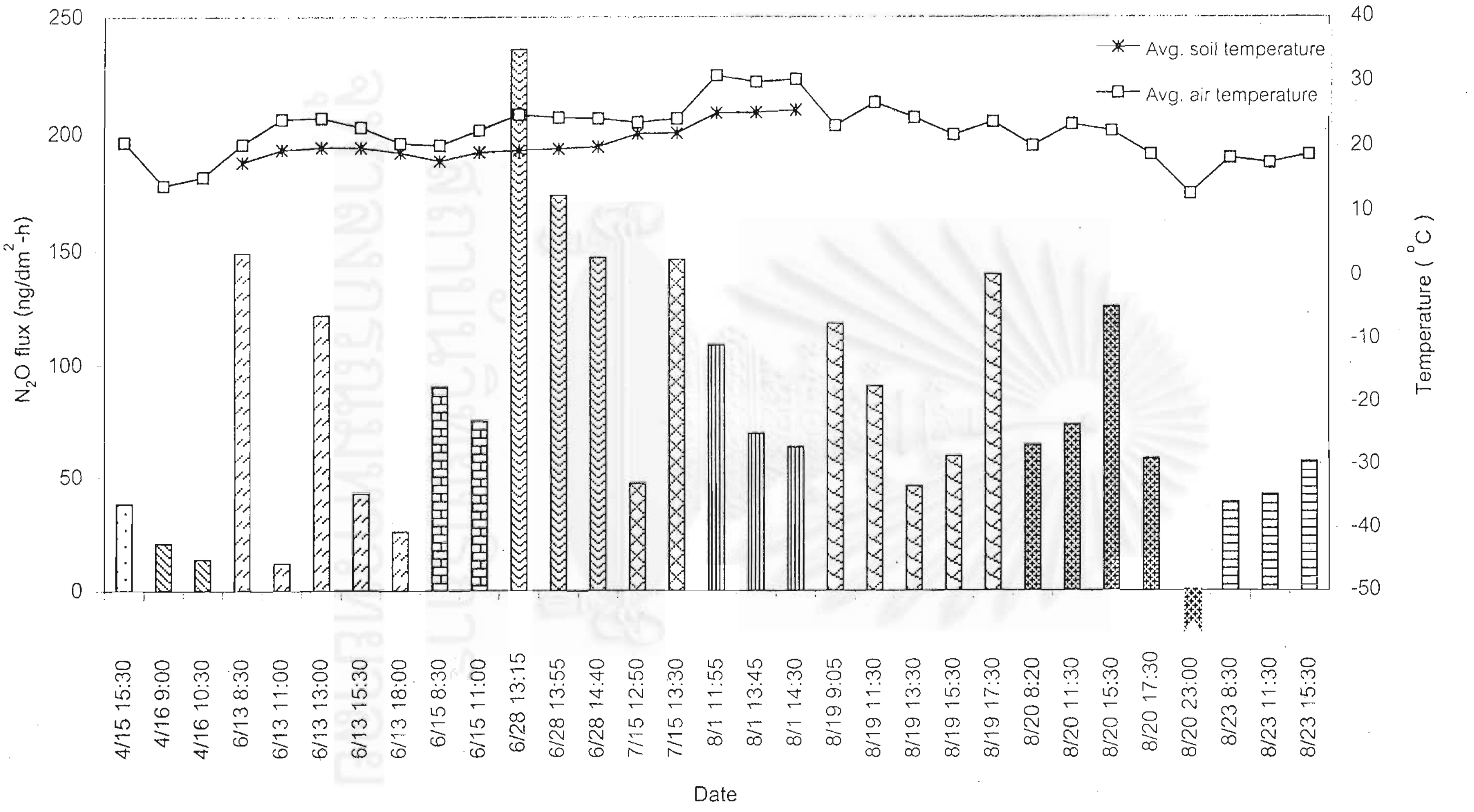


Figure 4.1.4 N$_2$O flux on sampling date in pine forest (Nagano)

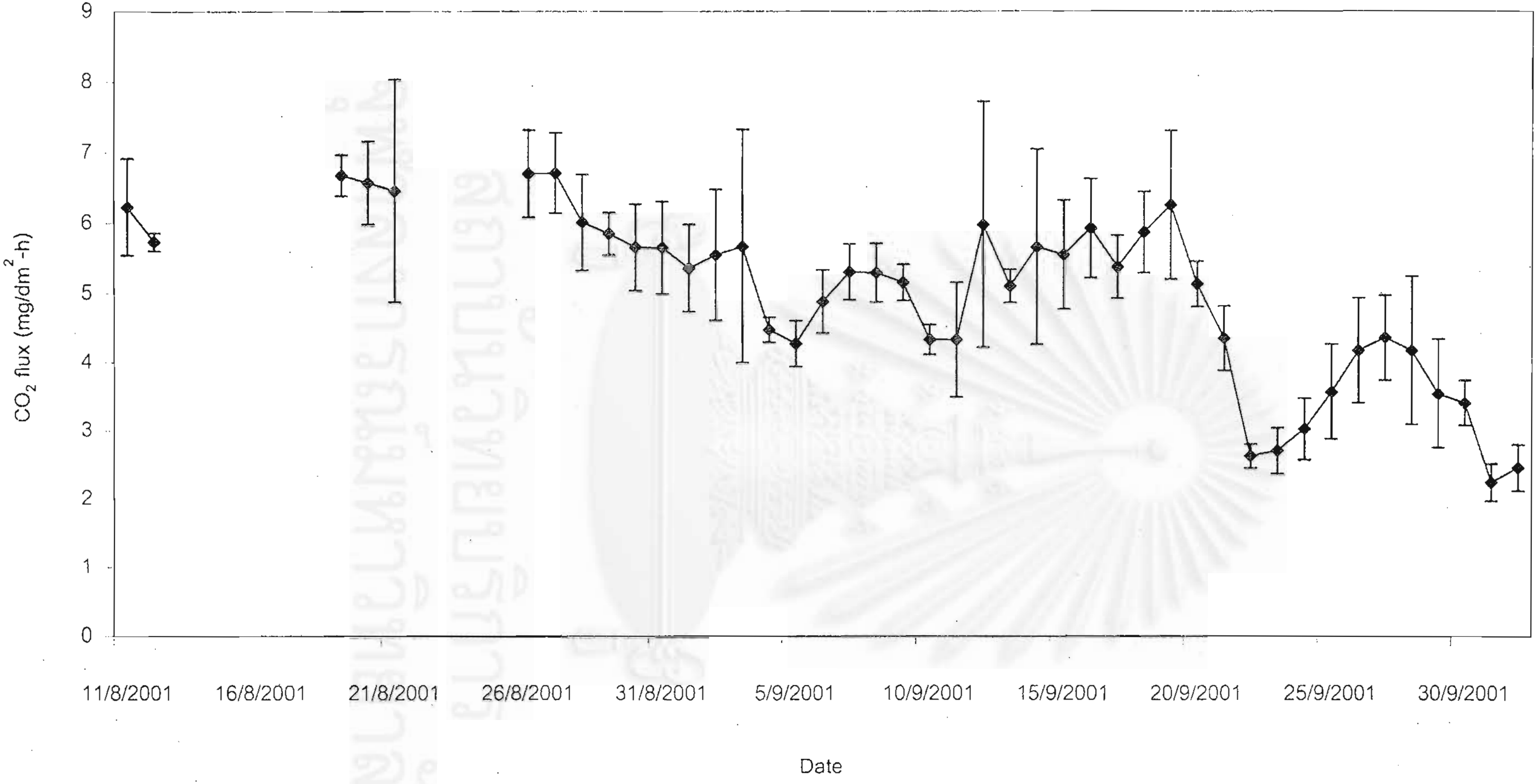


Figure 4.1.5 Daily CO_2 flux in corn field, 2001 (Open chamber)

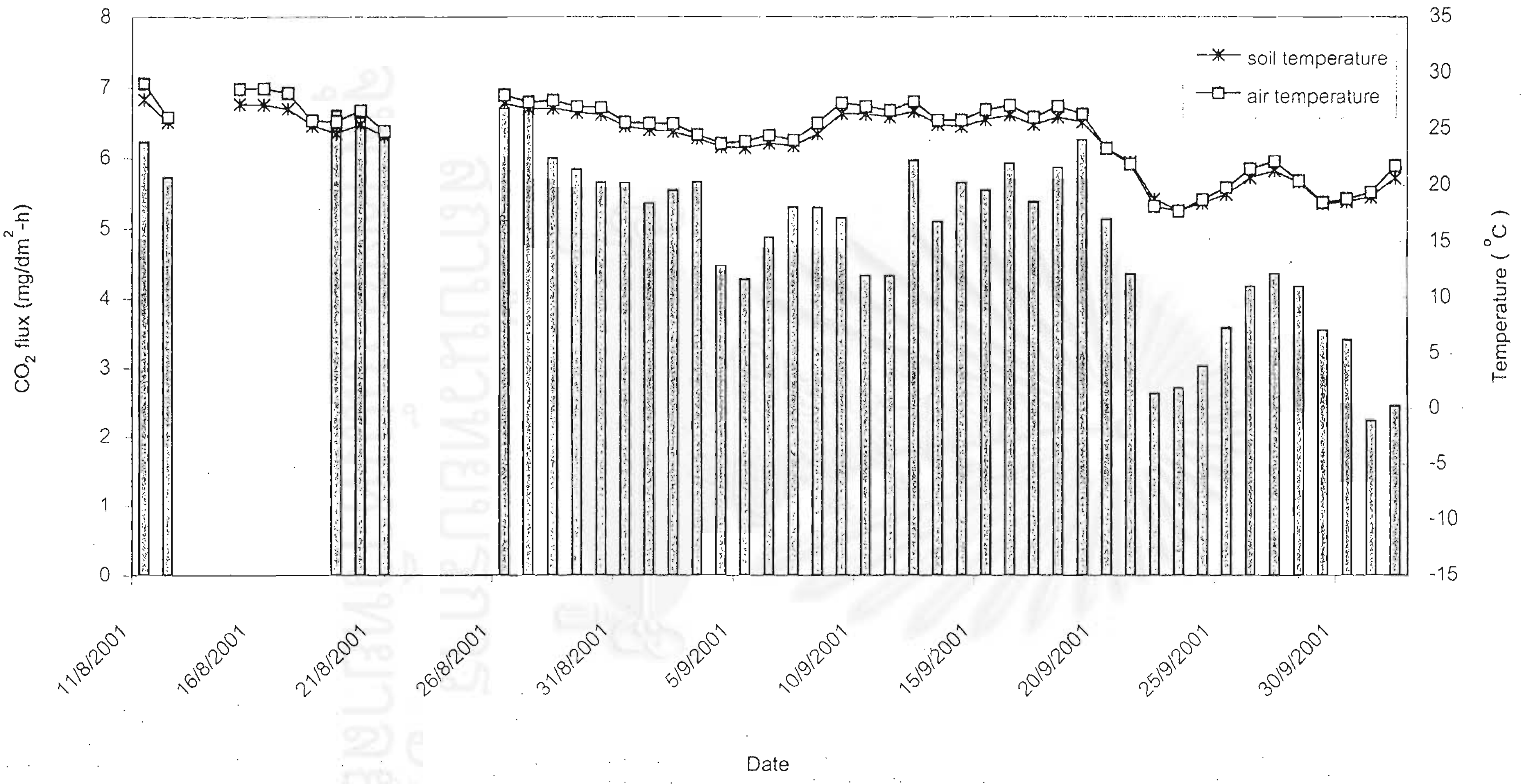


Figure 4.1.6 Daily CO_2 flux and temperature in corn field, 2001 (Open chamber)

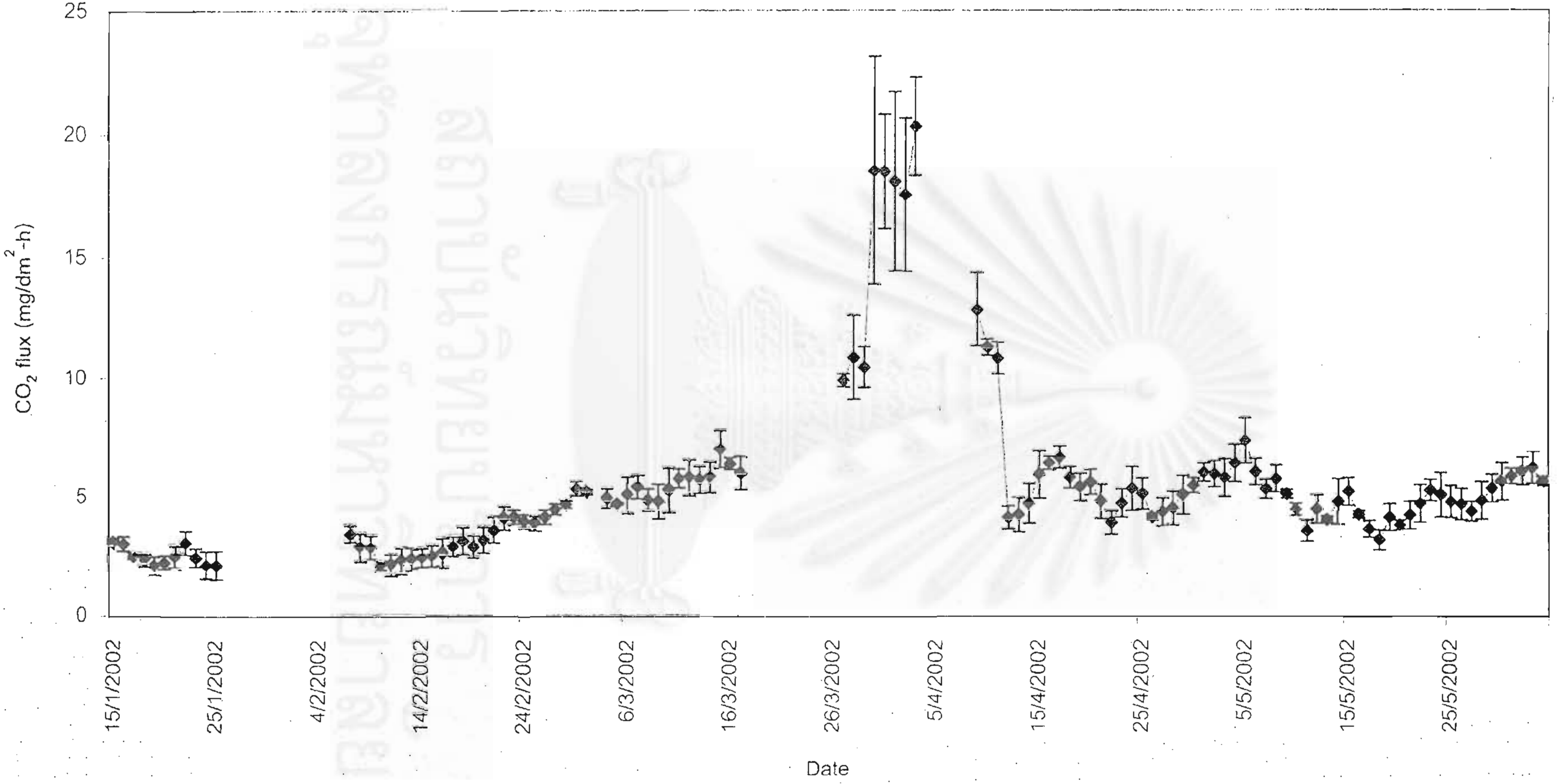


Figure 4.1.7 Daily CO$_2$ flux in wheat field, 2002 (Open chamber)

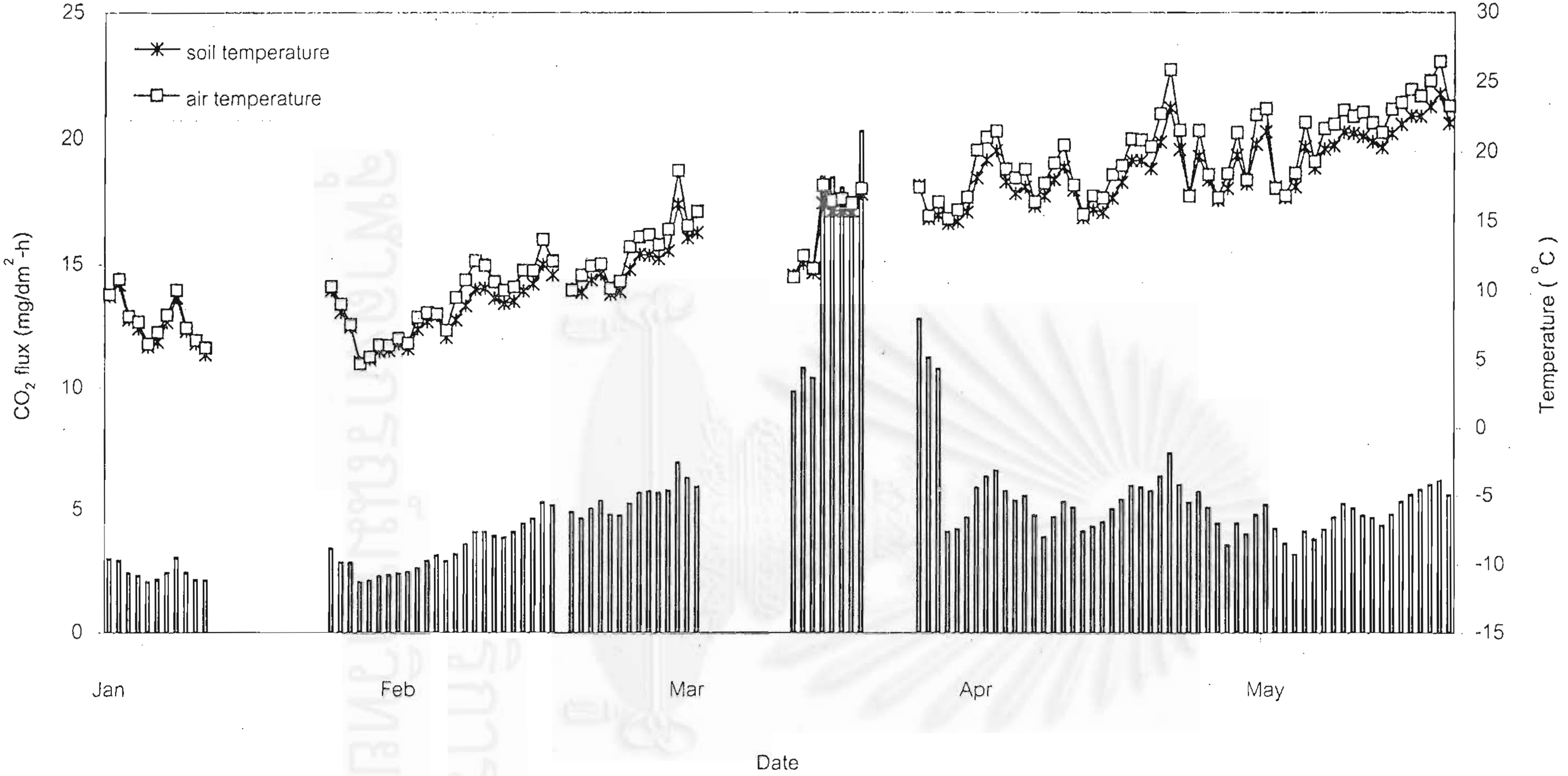


Figure 4.1.8 Daily flux of CO$_2$ and temperature in wheat field, 2002 (Open chamber)

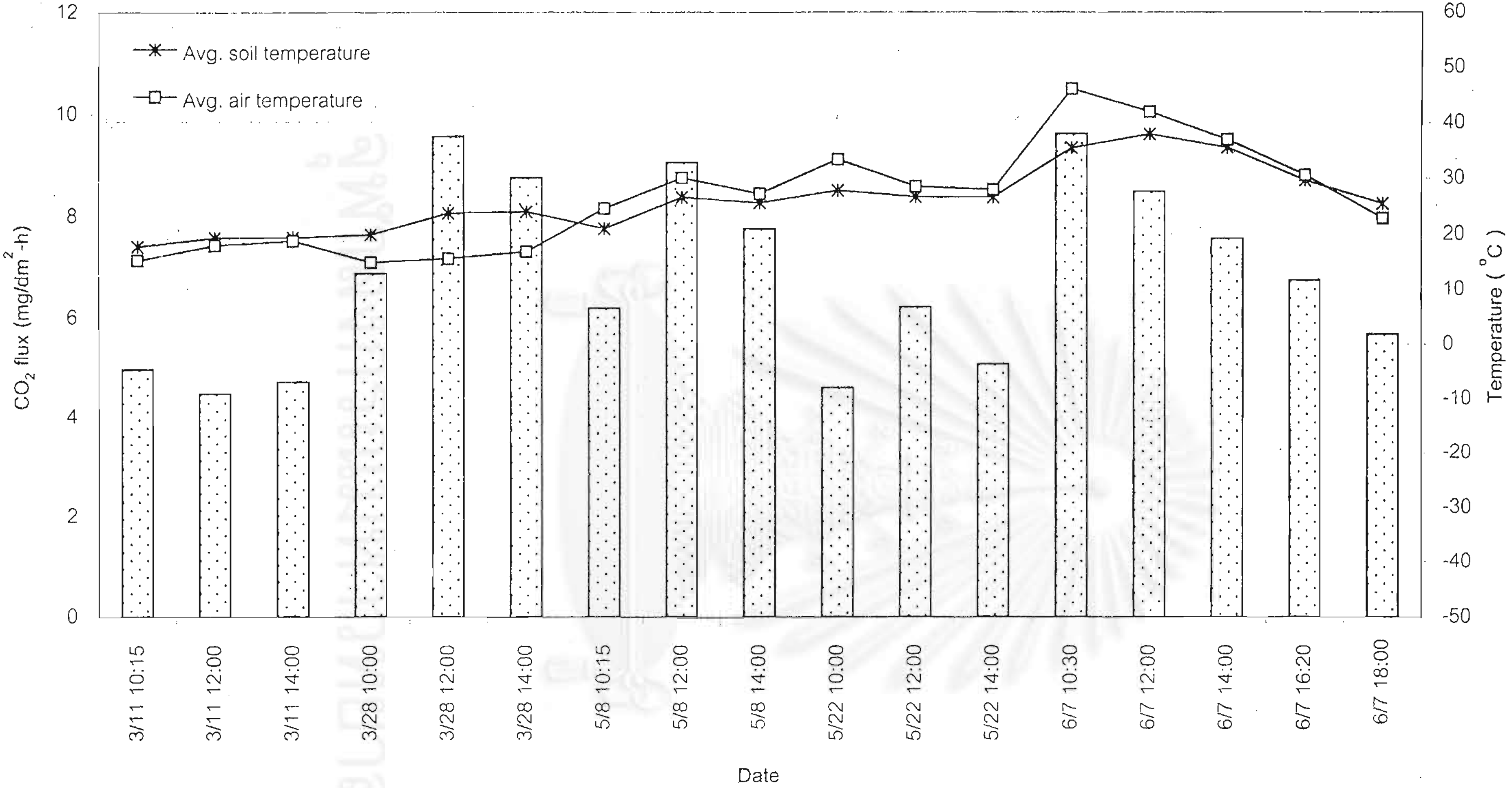


Figure 4.1.9 CO$_2$ flux on sampling date in Wheat field (Closed chamber)

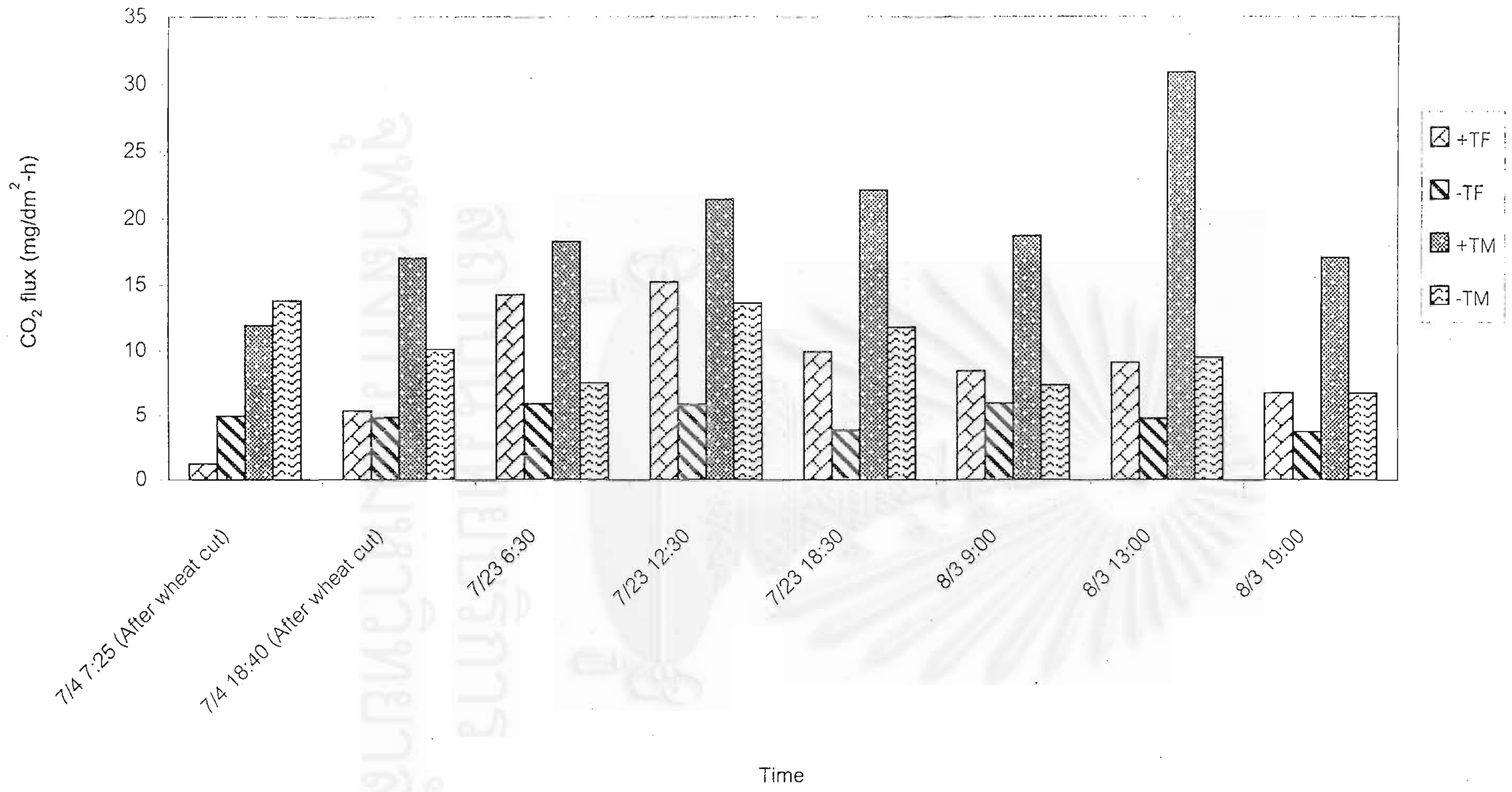


Figure 4.1.10 CO$_2$ flux on sampling date in Soyabean field with different treatments

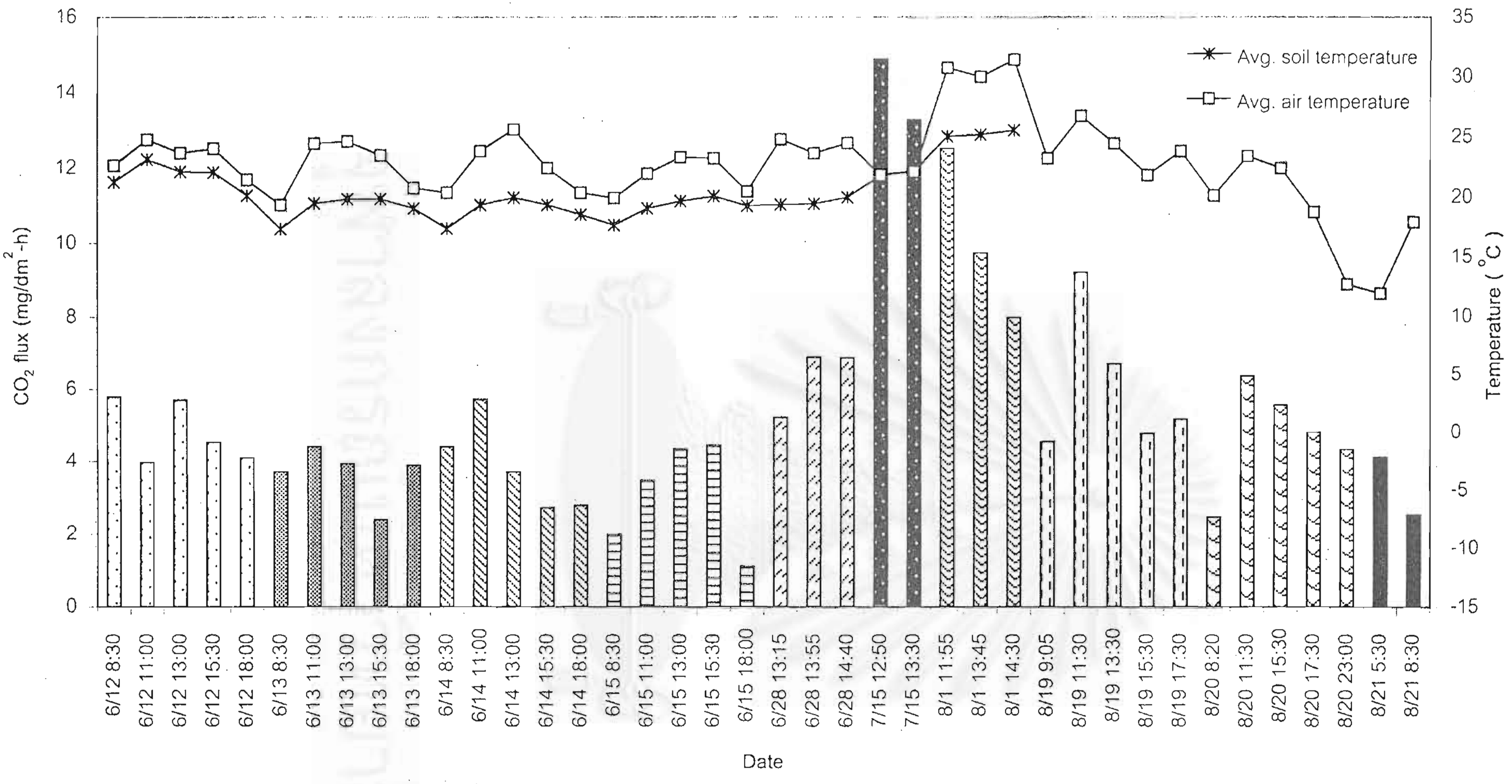


Figure 4.1.11 CO$_2$ flux on sampling date in pine forest (Nagano)

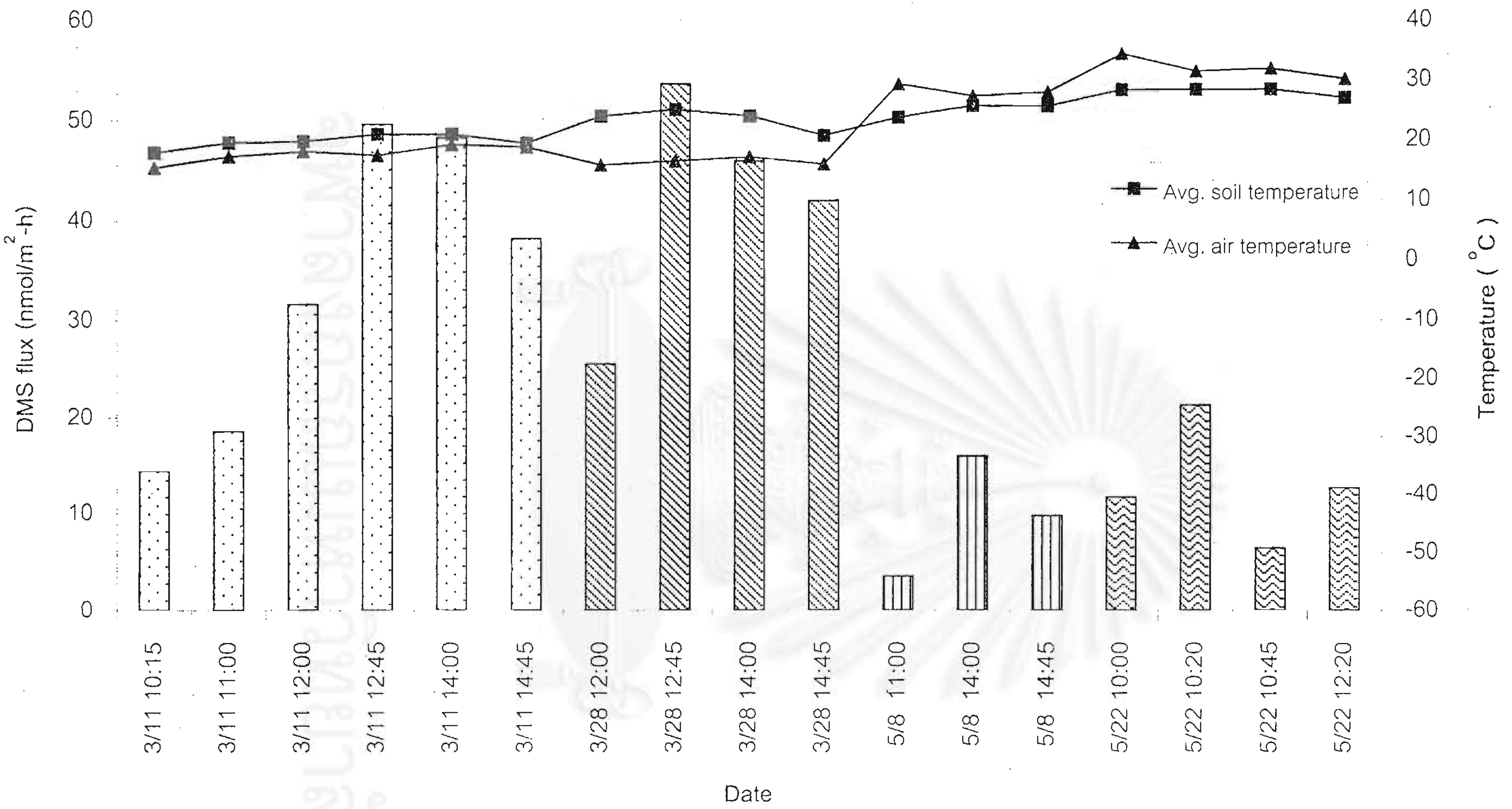
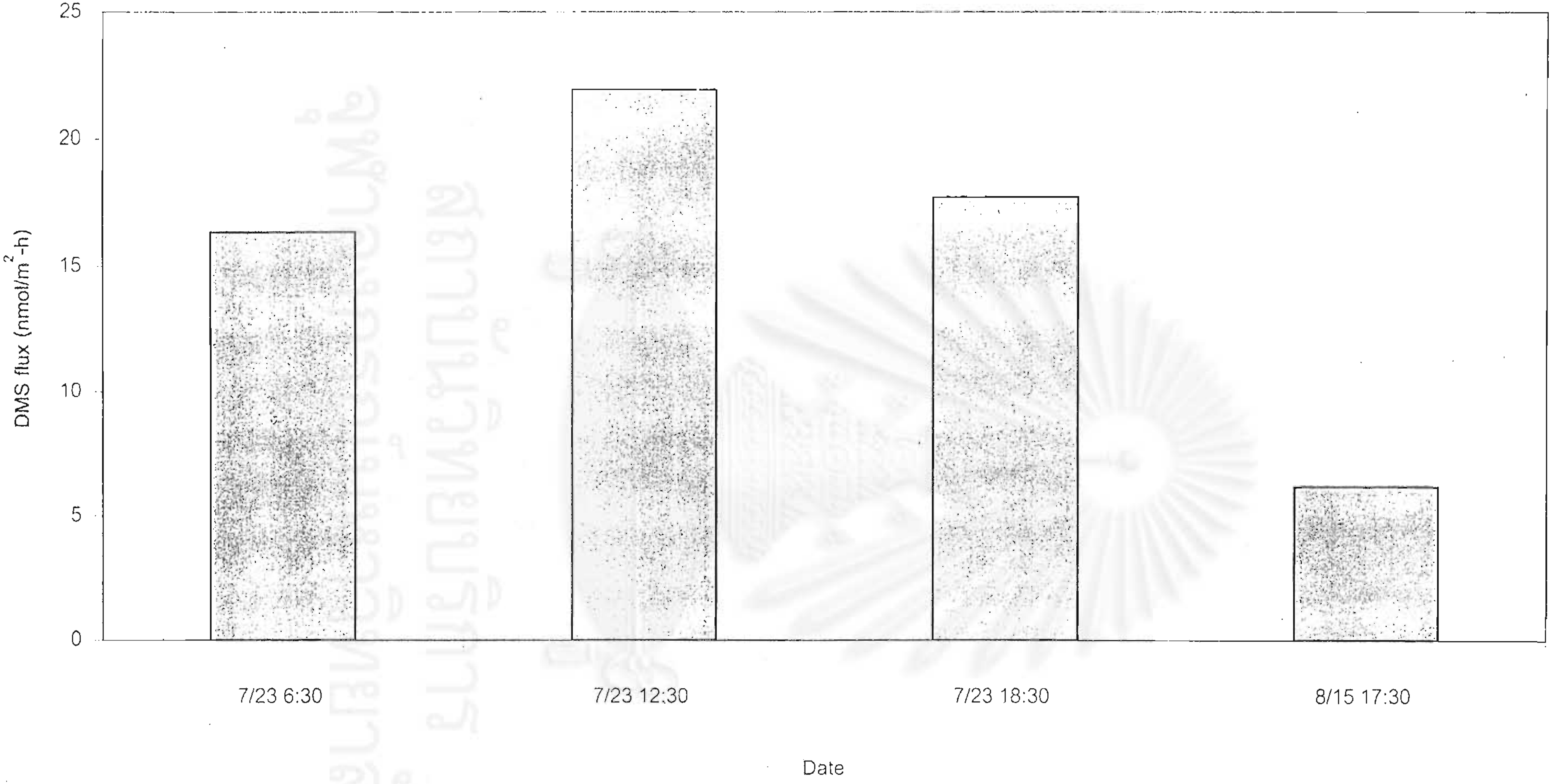


Figure 4.1.12 DMS flux and temperature on sampling date in Wheat field



<u>Figure 4.1.13</u> DMS flux on sampling date in Soyabean field

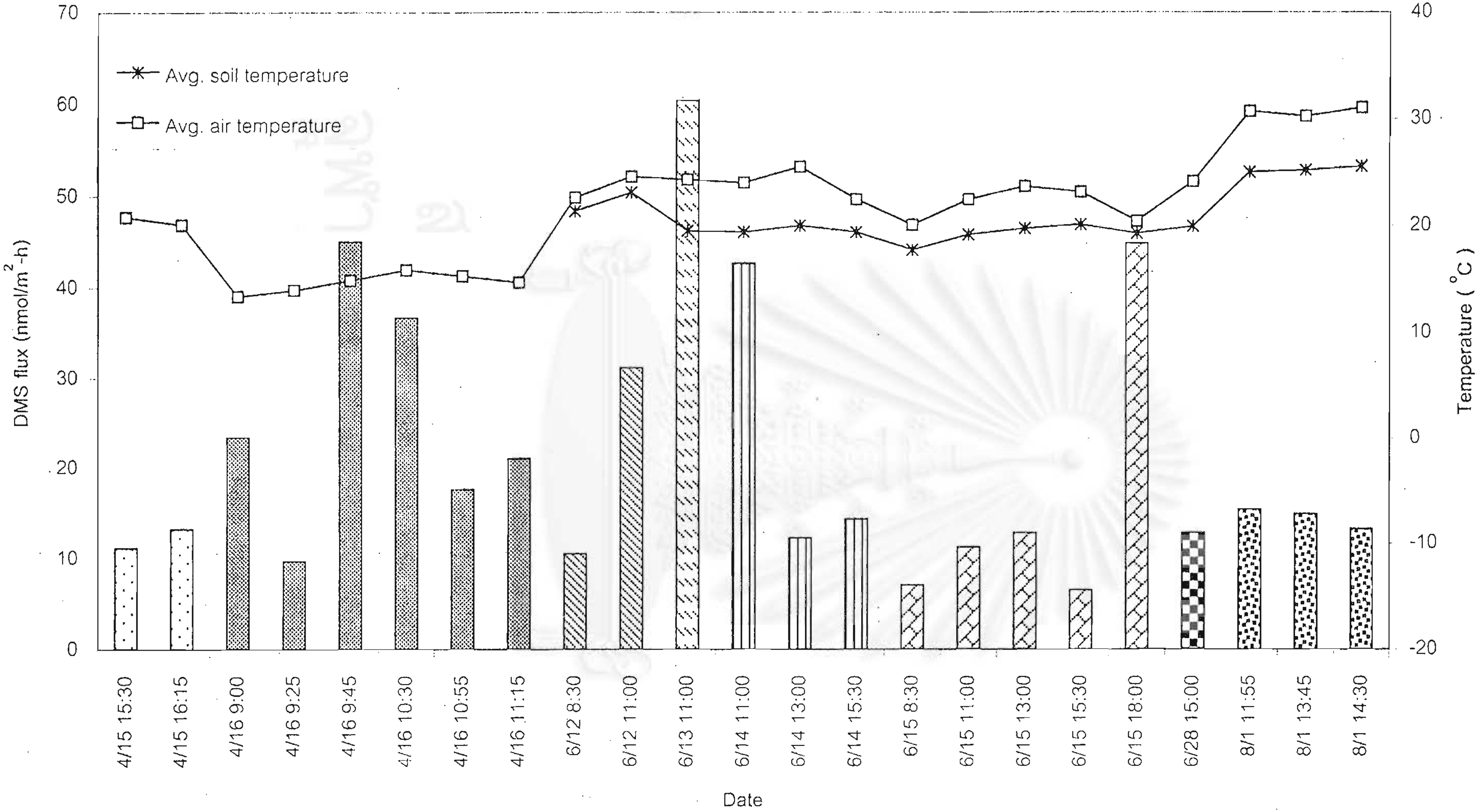
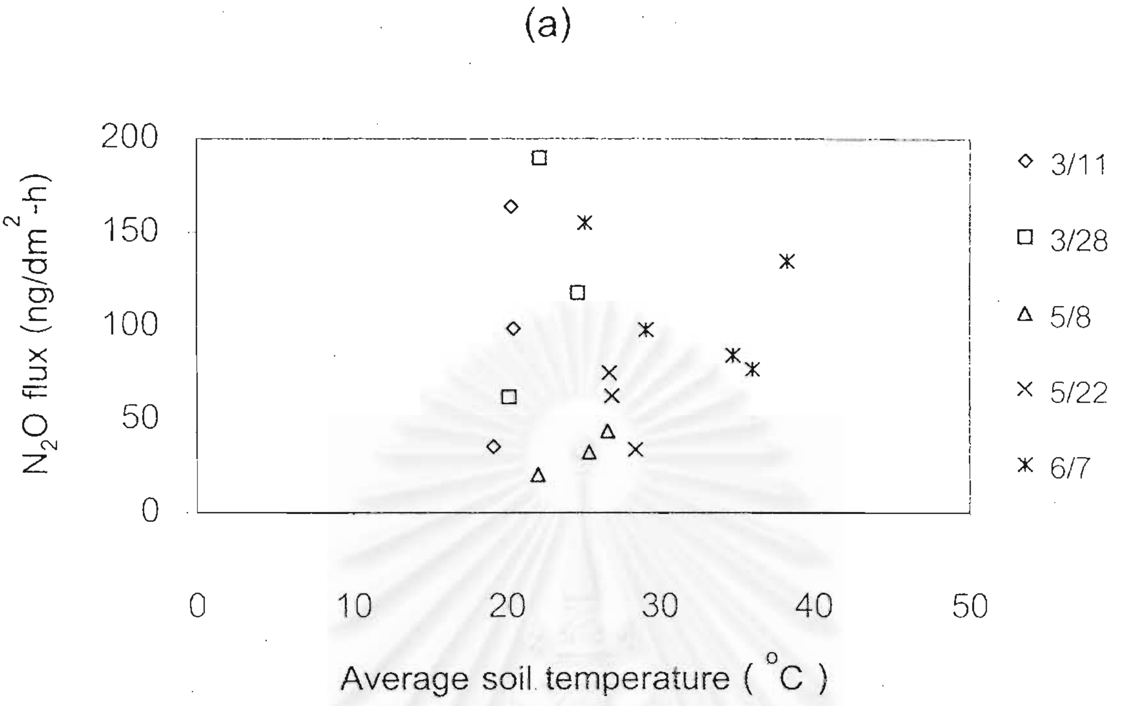


Figure 4.1.14 DMS flux and temperature on sampling date in pine forest (Nagano)



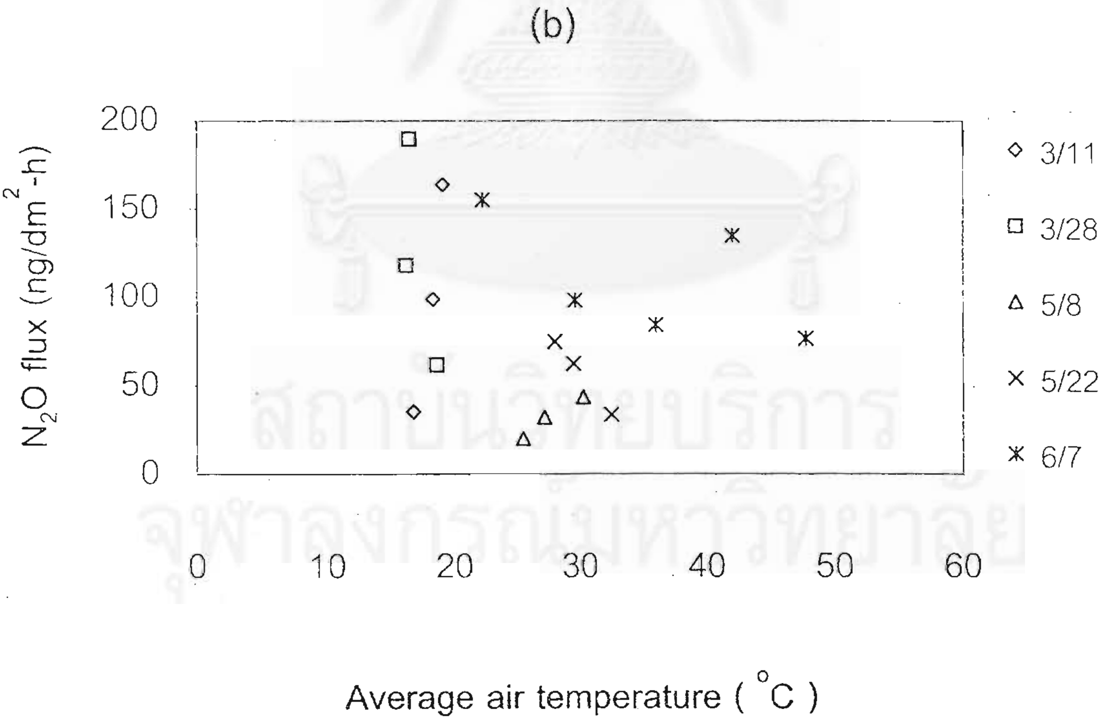


Figure 4.2.1 Effect of (a) soil temperature, and (b) air temperature on N_2O flux in wheat field

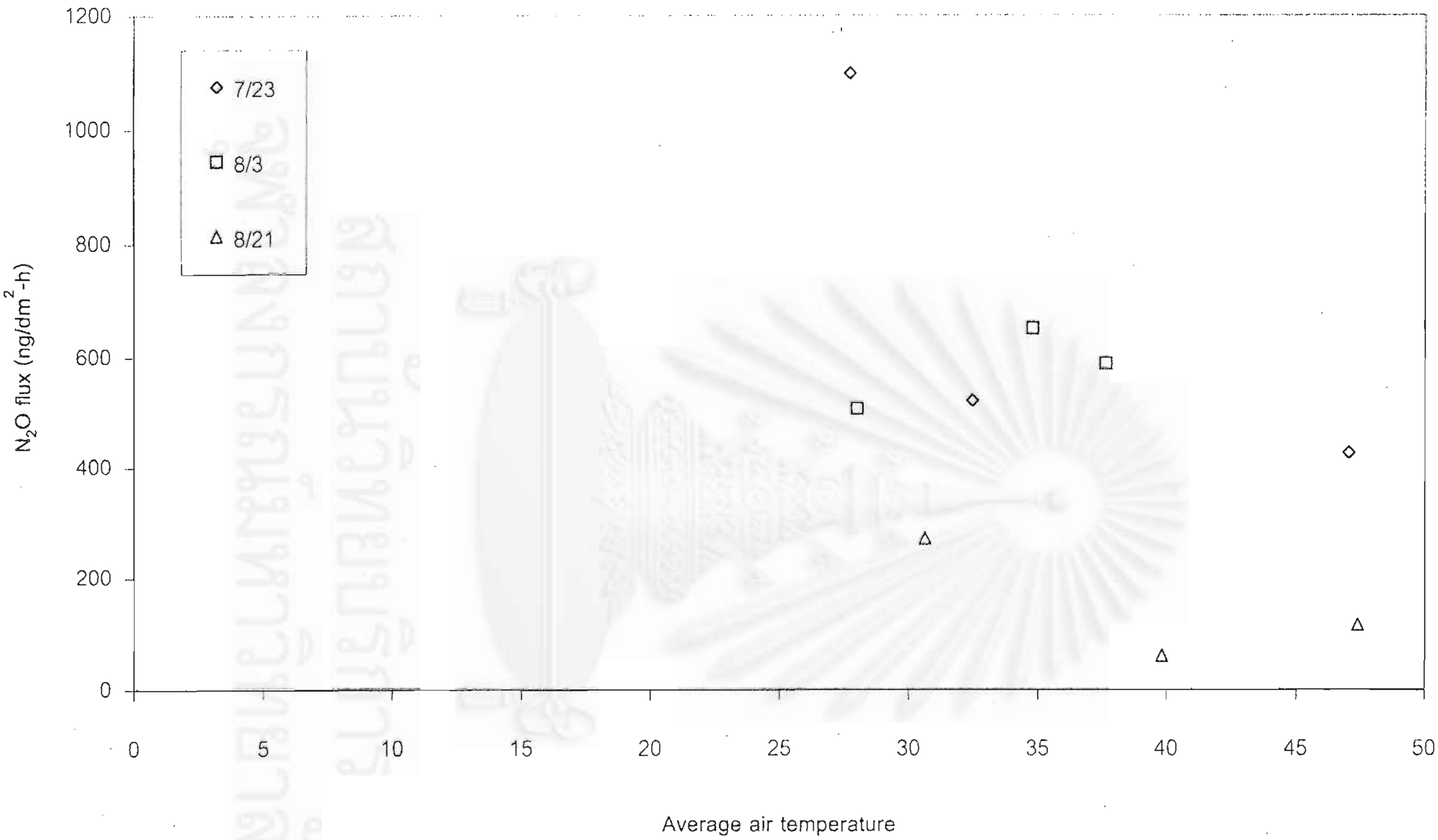
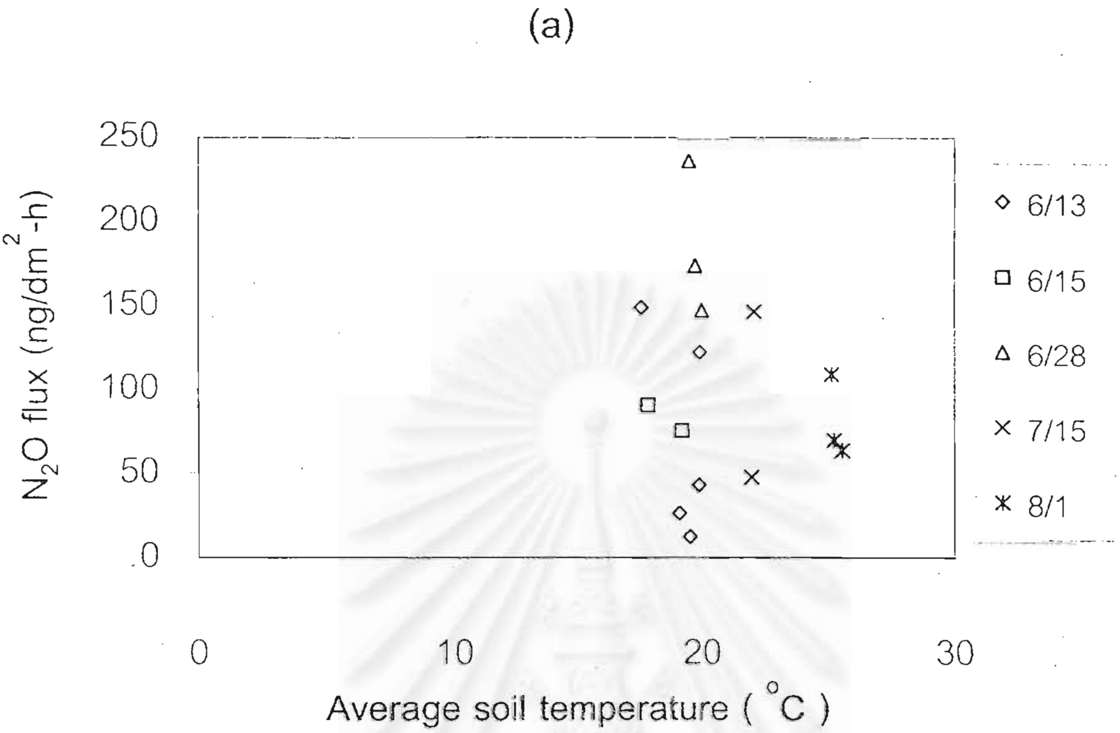


Figure 4.2.2 Effect of air temperature on N_2O flux in soyabean field



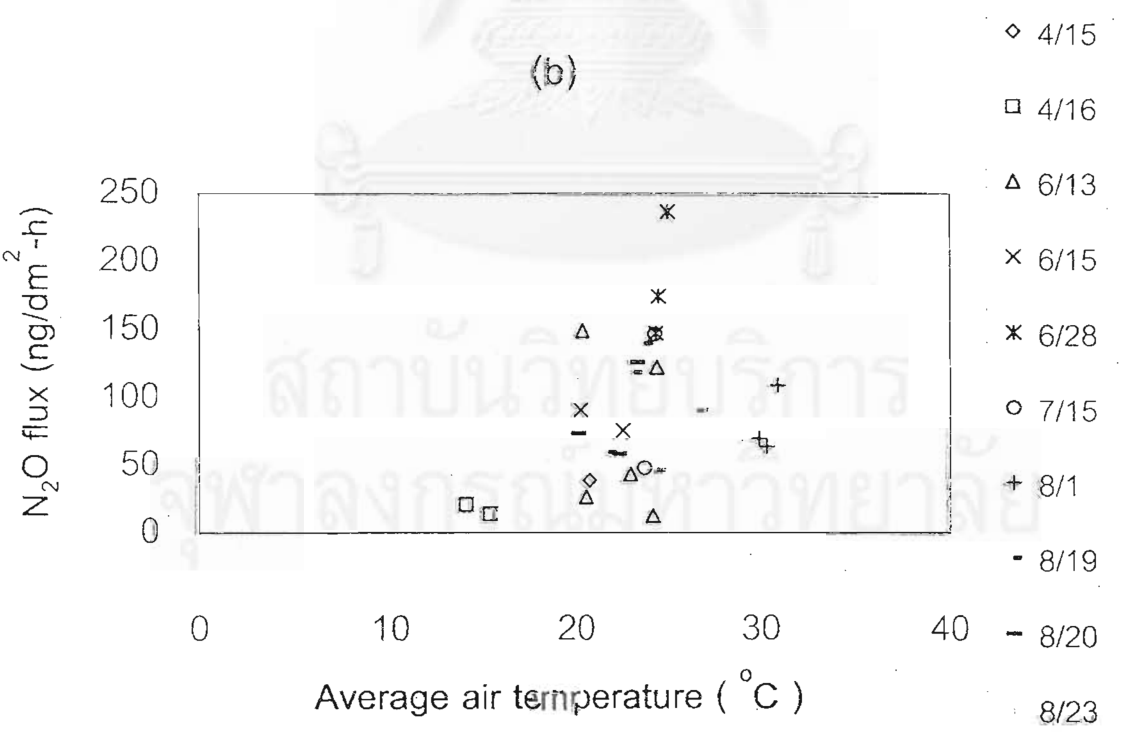


Figure 4.2.3 Effect of (a) soil temperature, and (b) air temperature on N_2O flux in pine forest

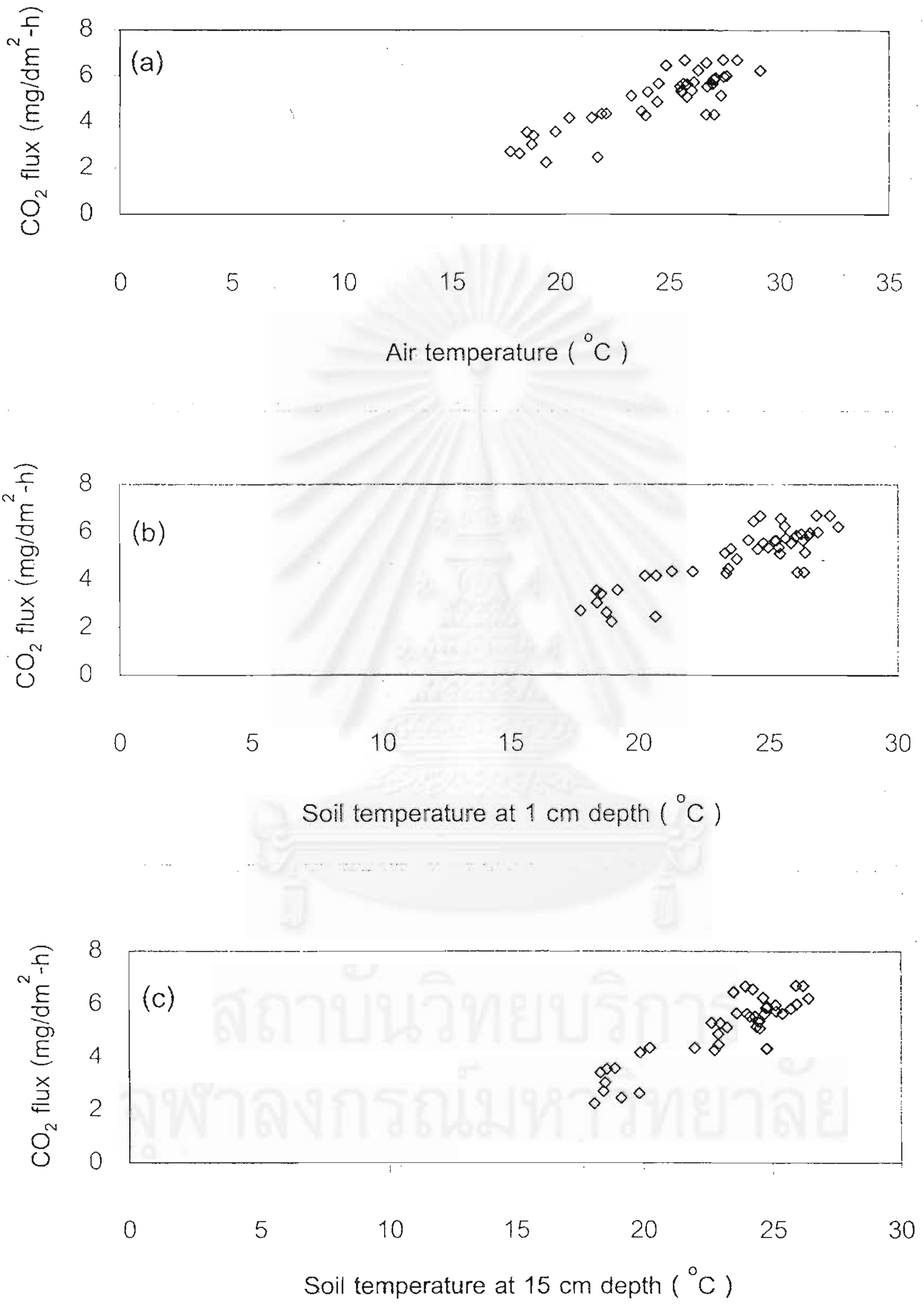


Figure 4.2.4 Effect of temperature on CO_2 flux in corn field

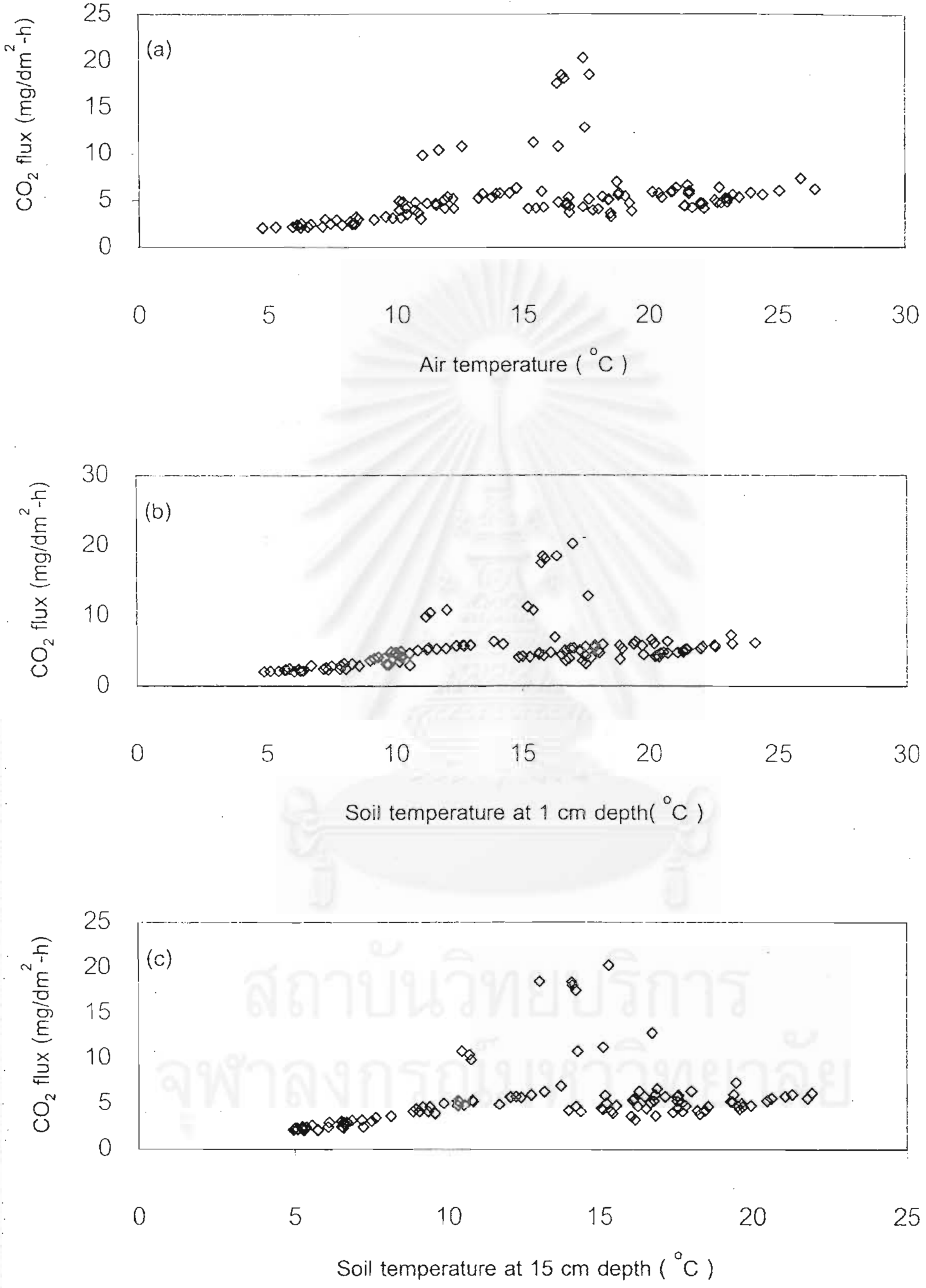
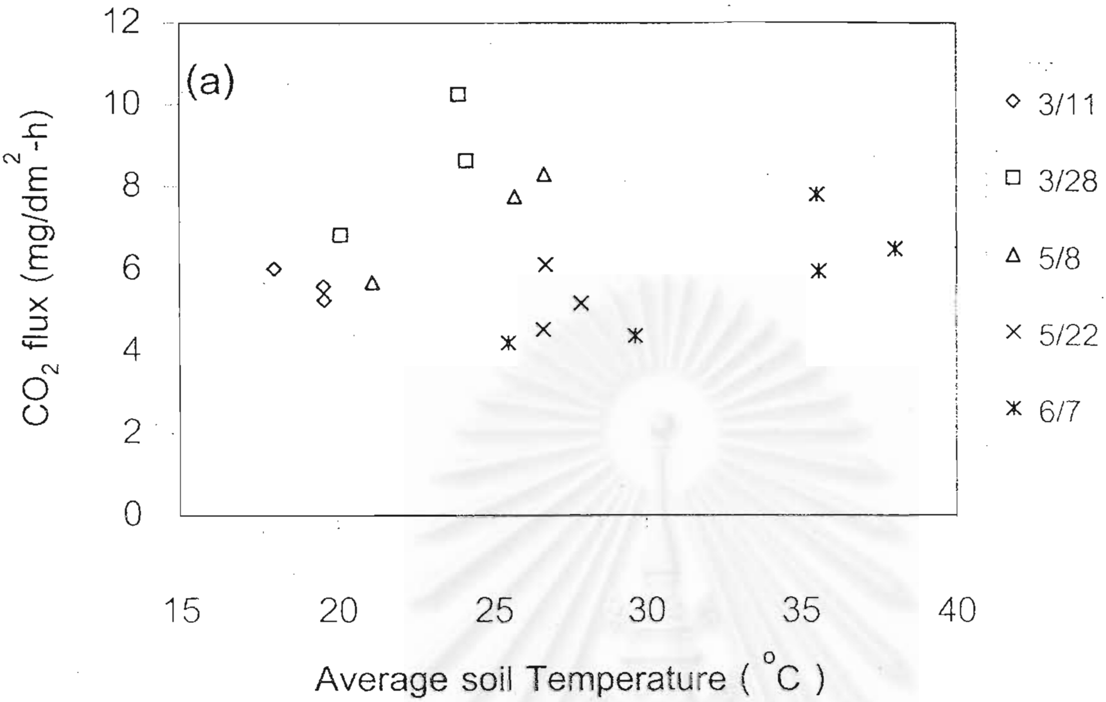


Figure 4.2.5 Effect of temperature on CO_2 flux in wheat field



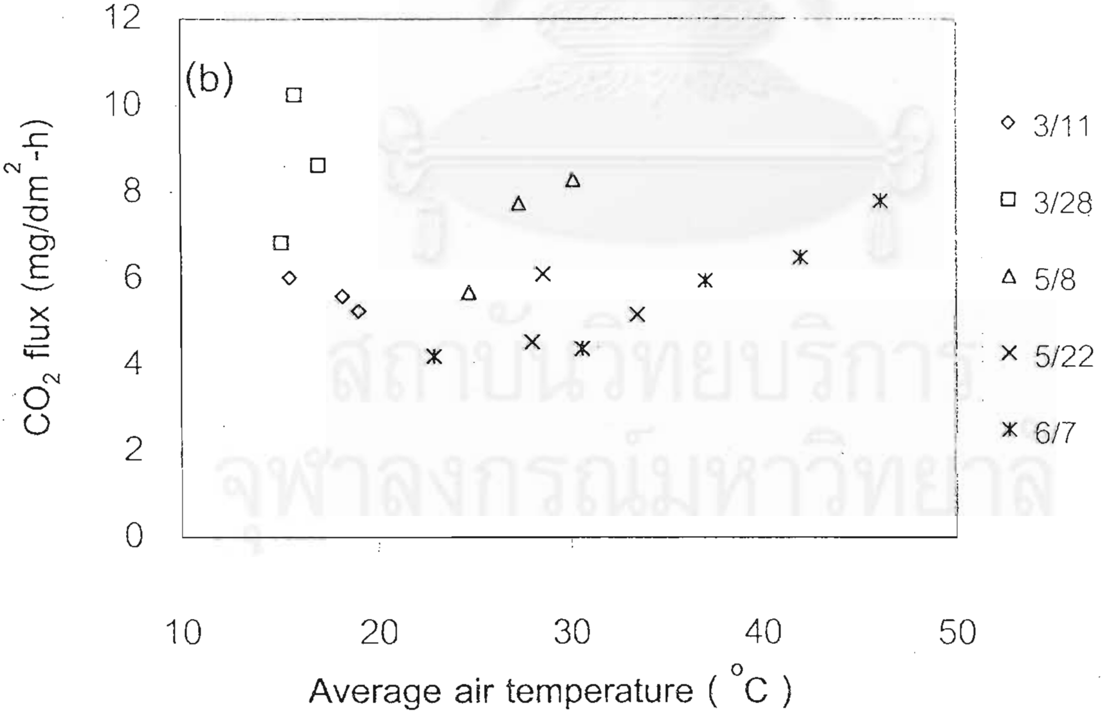
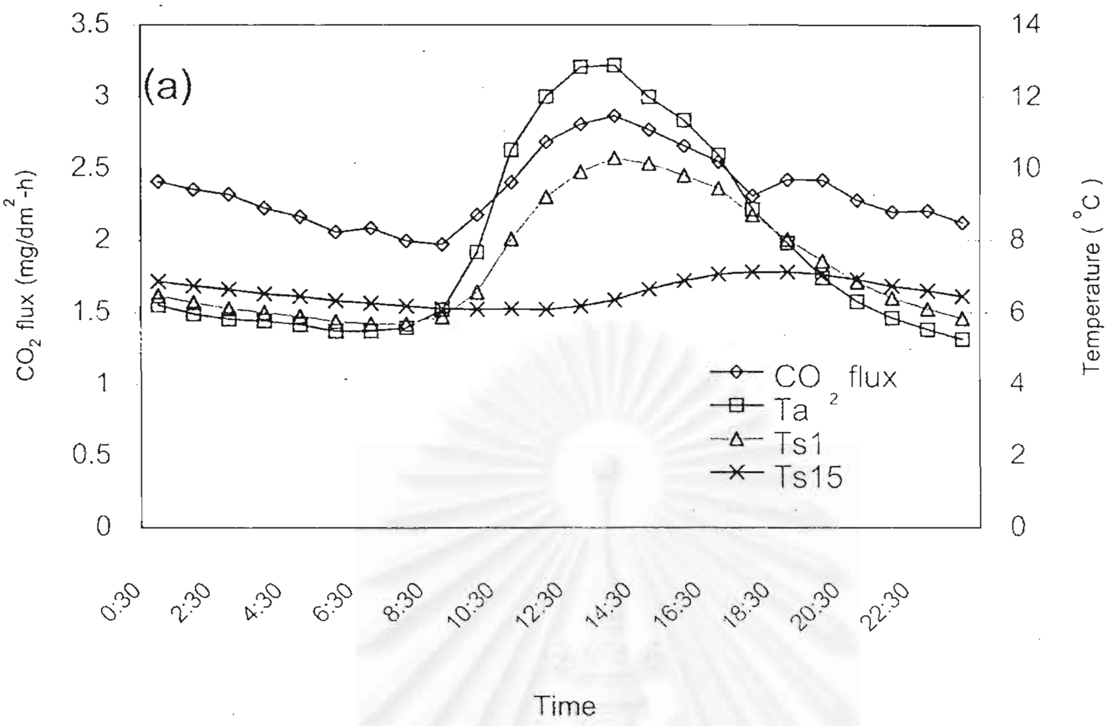


Figure 4.2.6 Effect of temperature on CO_2 flux (closed chamber) in wheat field



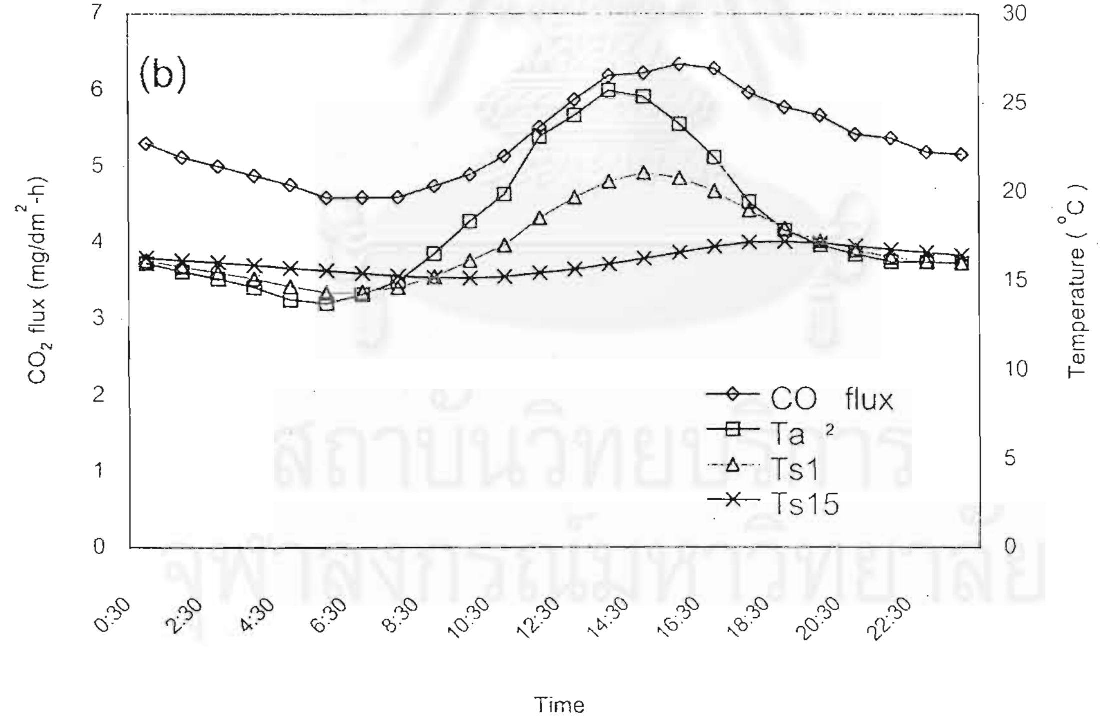
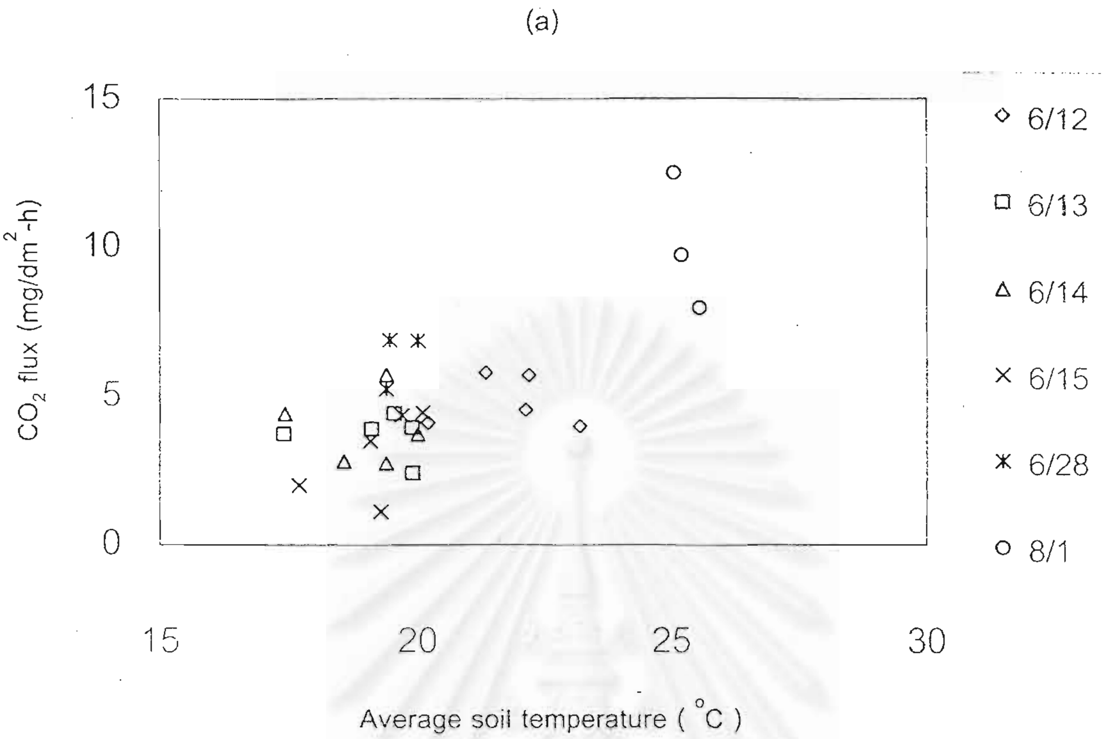


Figure 4.2.7 Hourly flux of CO_2 and temperature in wheat field on (a) 2002/01/18, and (b) 2002/04/19 (Ta = air temperature, Ts1 = soil temperature at 1 cm depth, Ts15 = soil temperature at 15 cm depth)



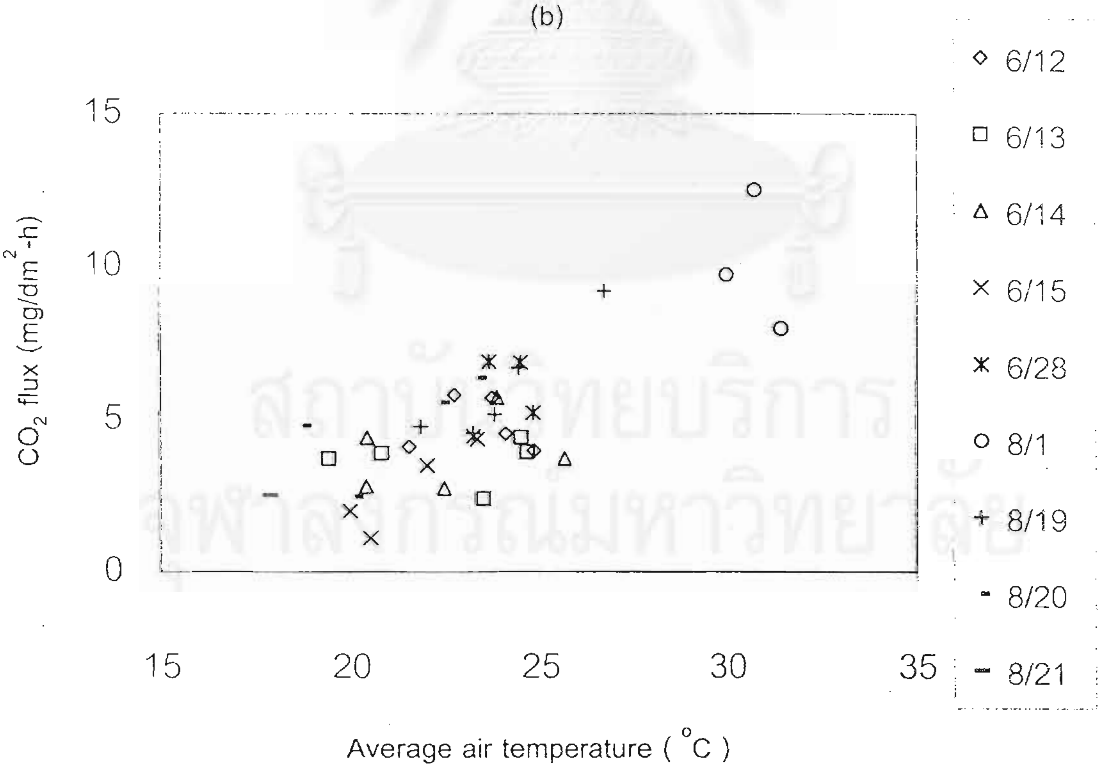
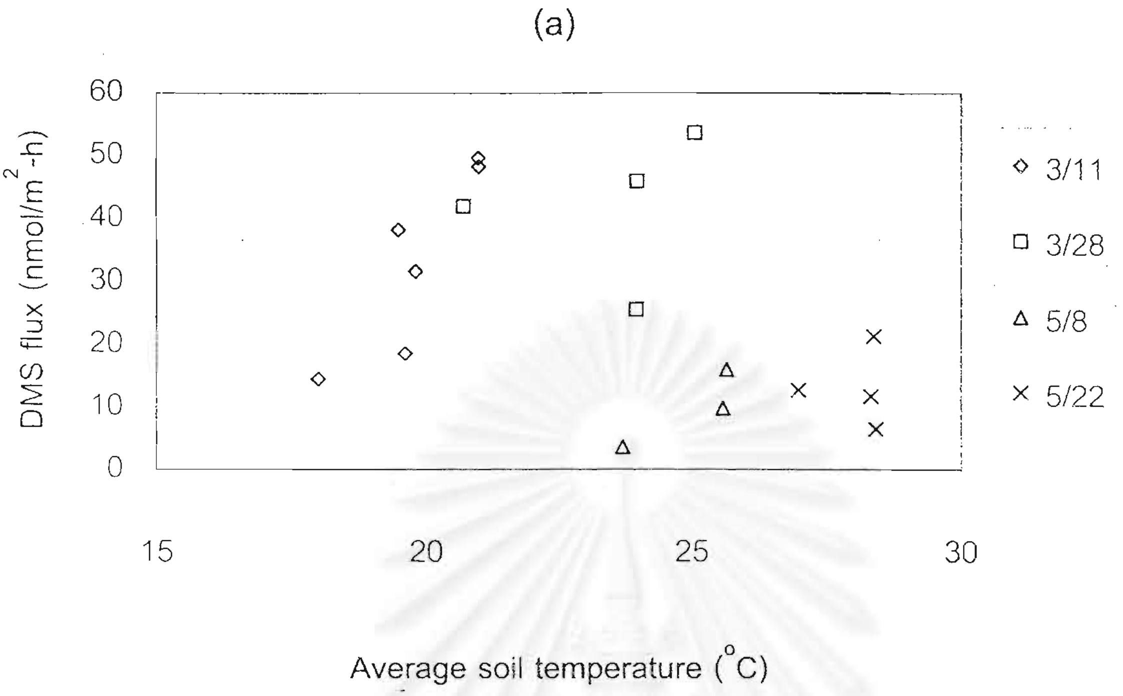


Figure 4.2.8 Effect of temperature on CO$_2$ flux in pine forest at Nagano



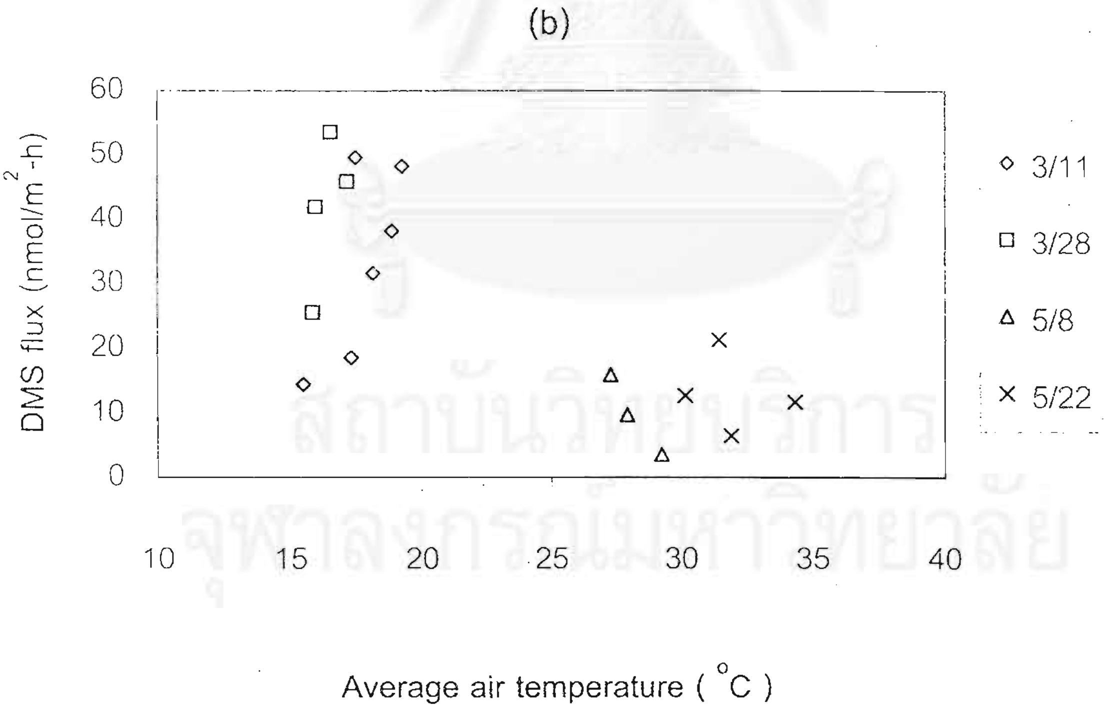
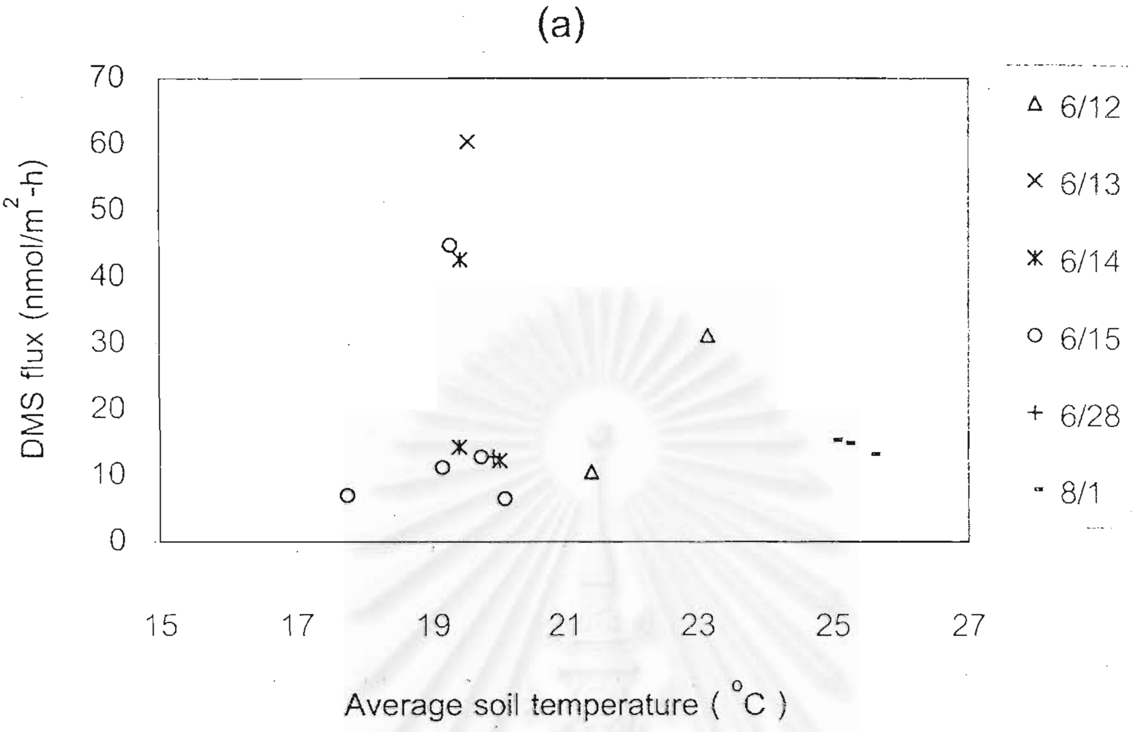


Figure 4.2.9 Effect of temperature on DMS fluxes in wheat field



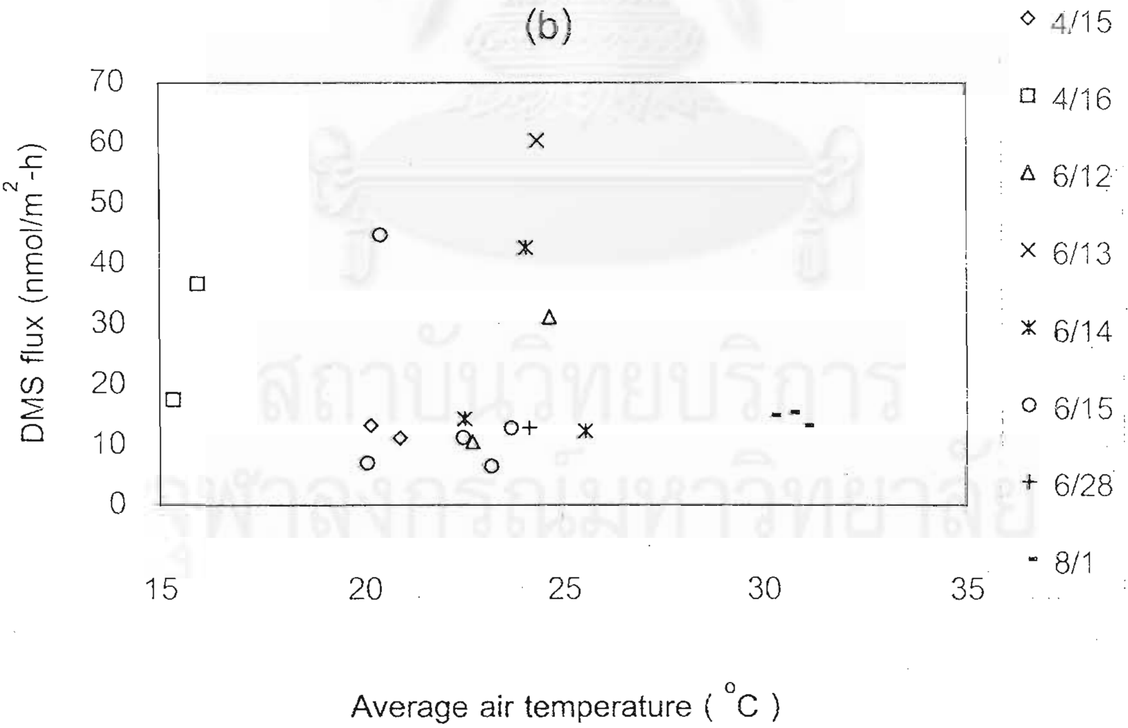


Figure 4.2.10 Effect of temperature on DMS fluxes in pine forest at Nagano

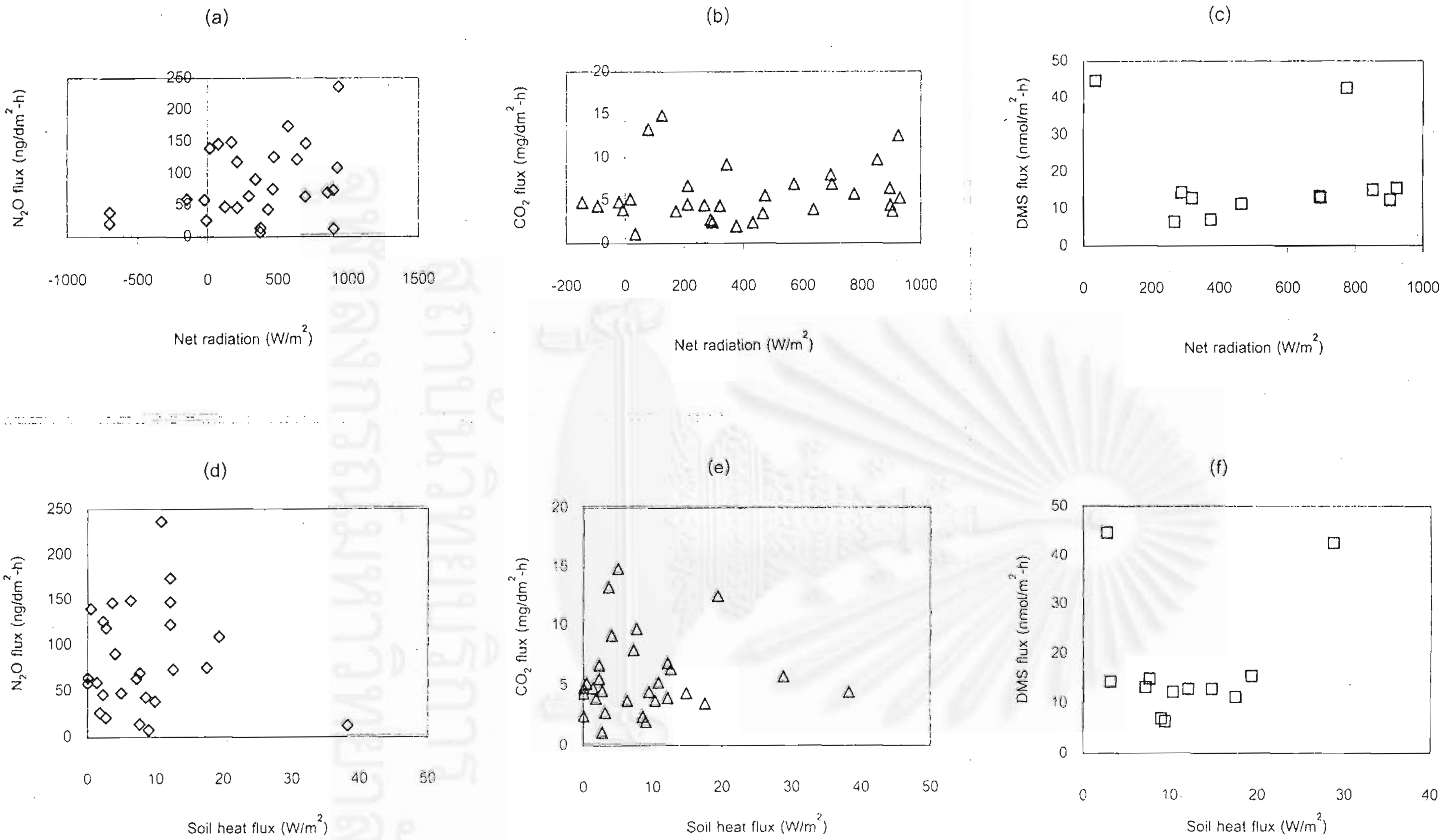


Figure 4.2.11 Effect of energy associated parameters on emission fluxes in pine forest at Nagano

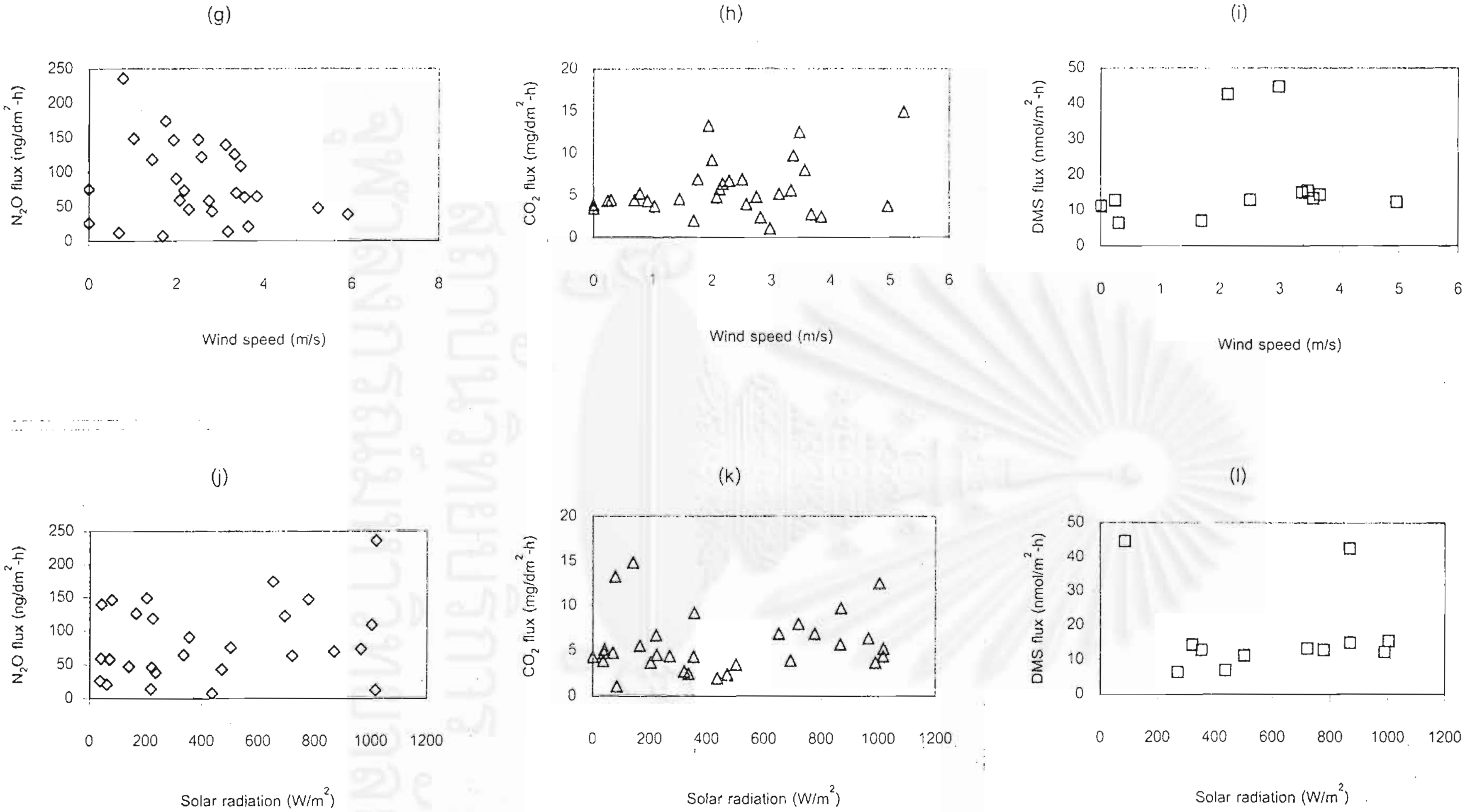
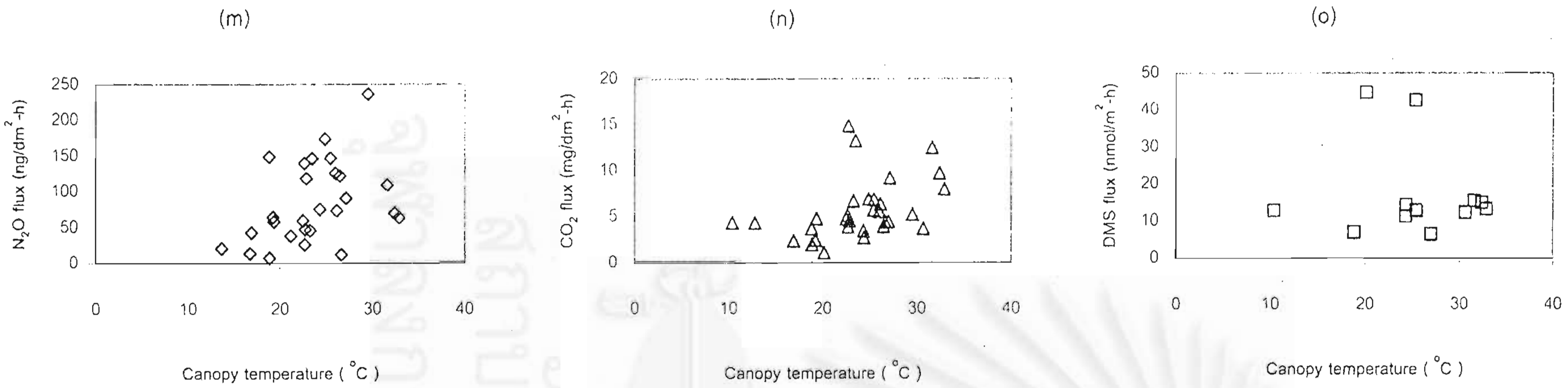


Figure 4.2.11 (Cont.)



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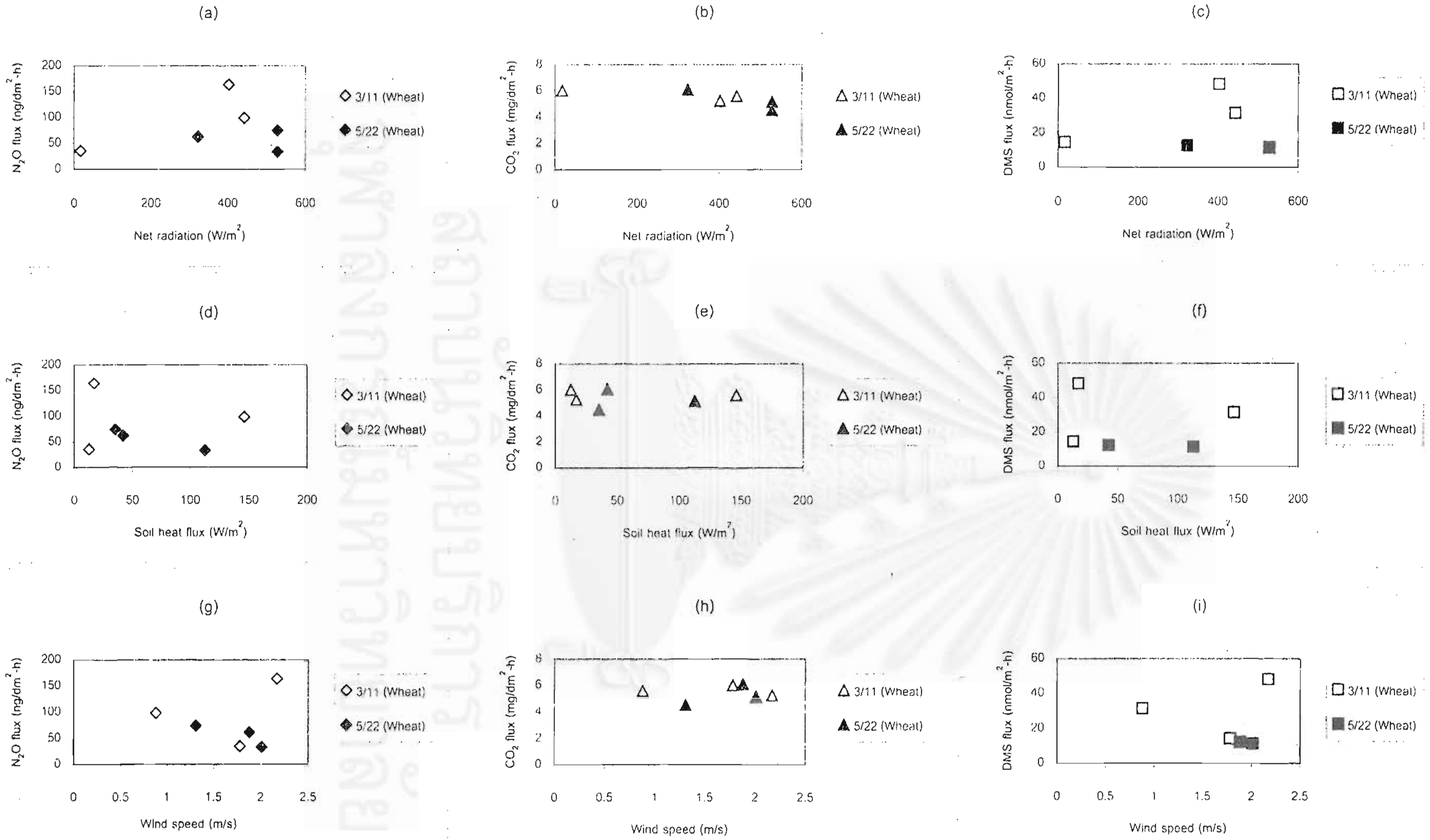
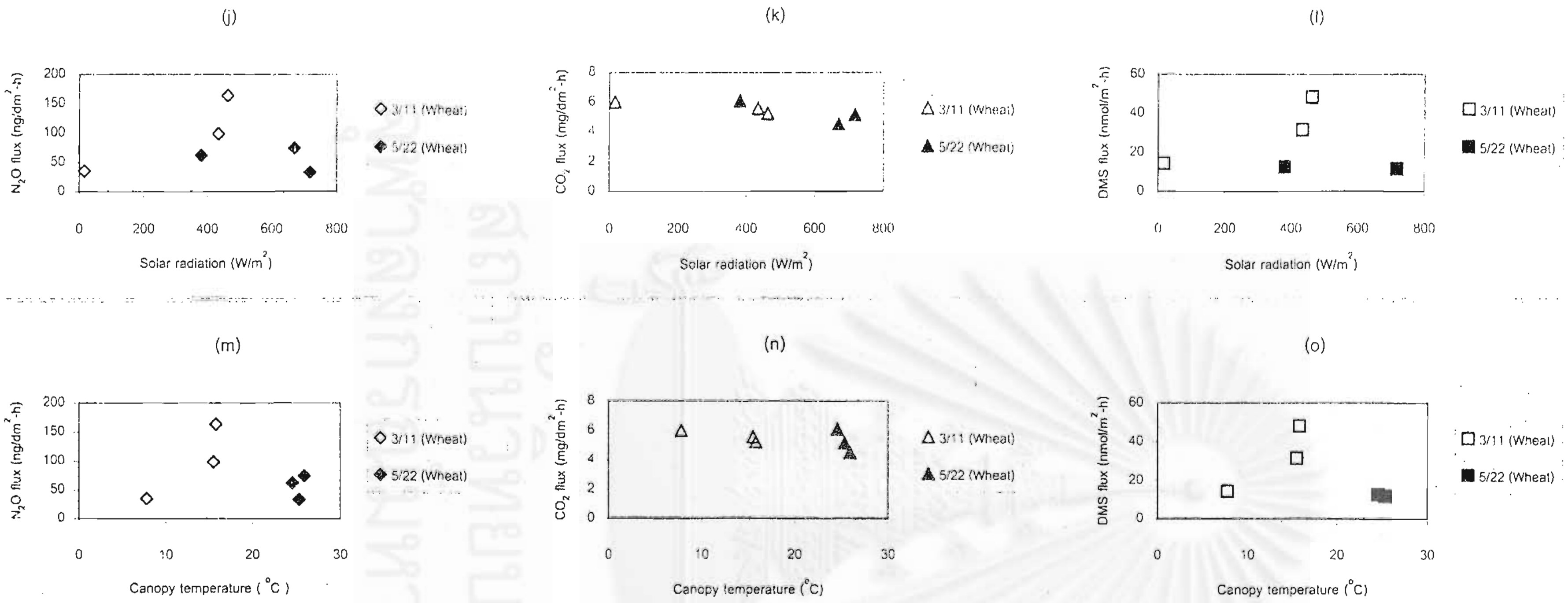


Figure 4.2.12 Effect of energy associated parameters on emission fluxes in wheat field



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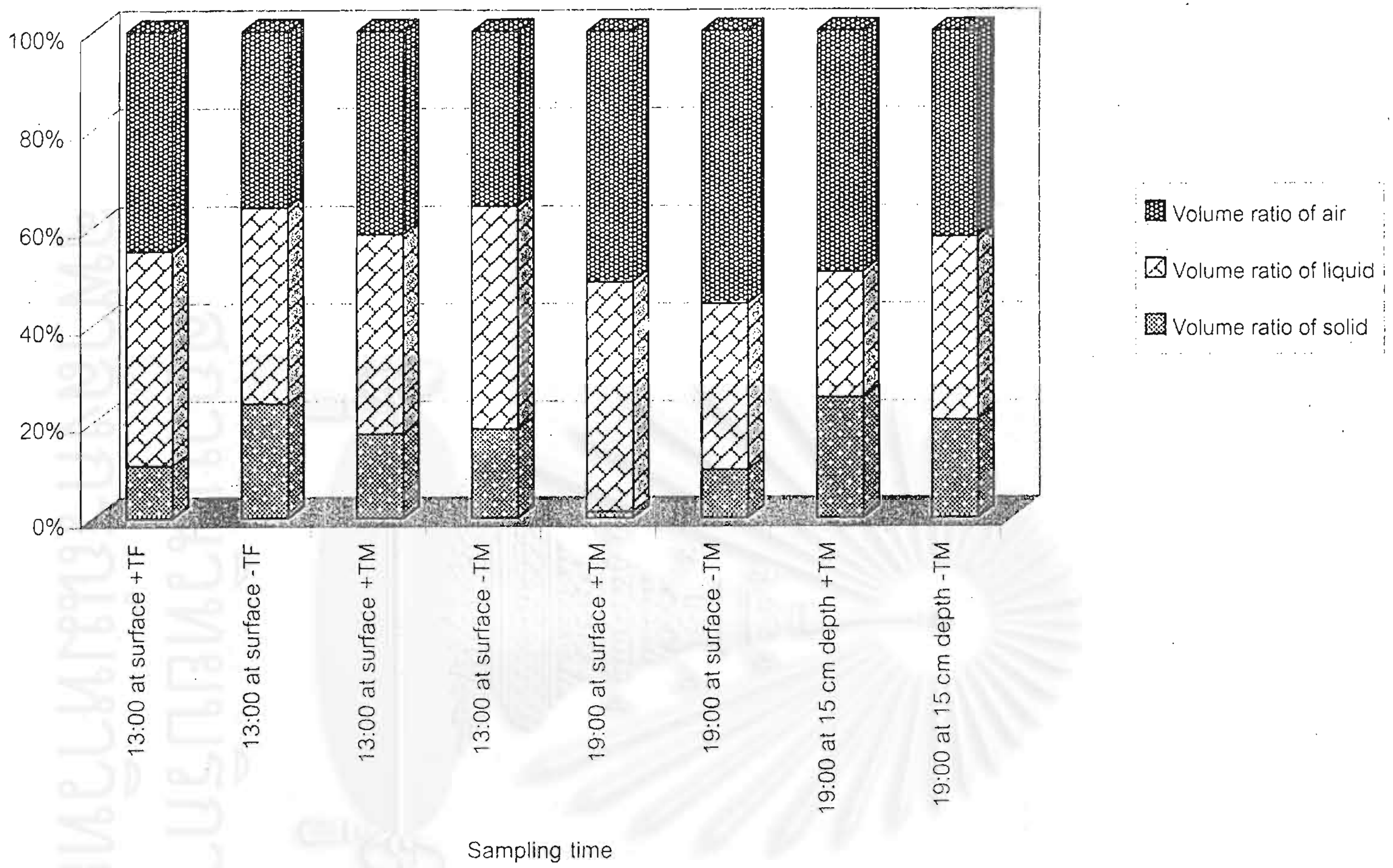

Figure 4.2.13 Volume ratio of three phases in soil at Soyabean field on 23/7/2002

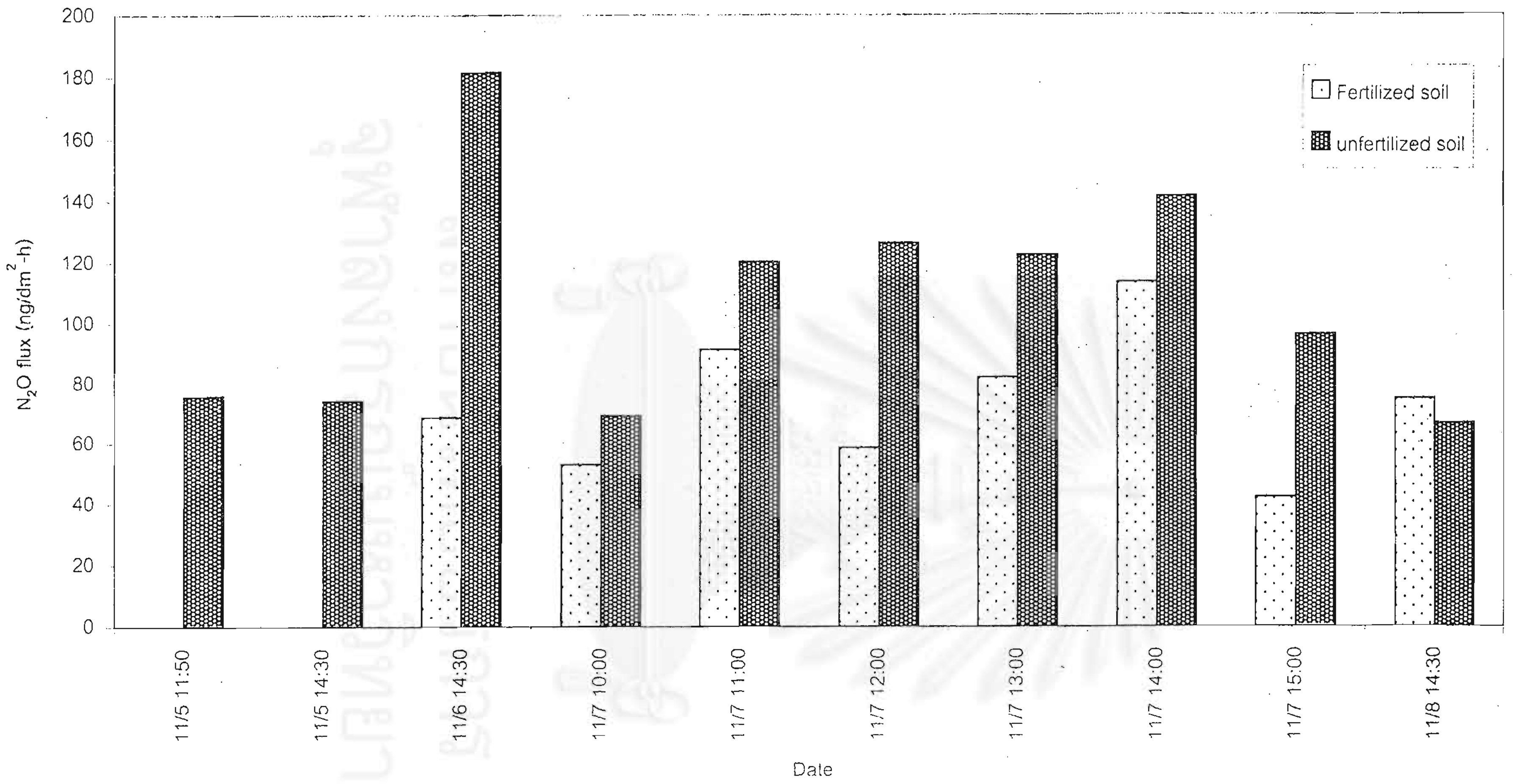

Figure 4.2.14 Comparison of N_2O flux between fertilized and unfertilized zone in bared soil (From November 5-8, 2001)

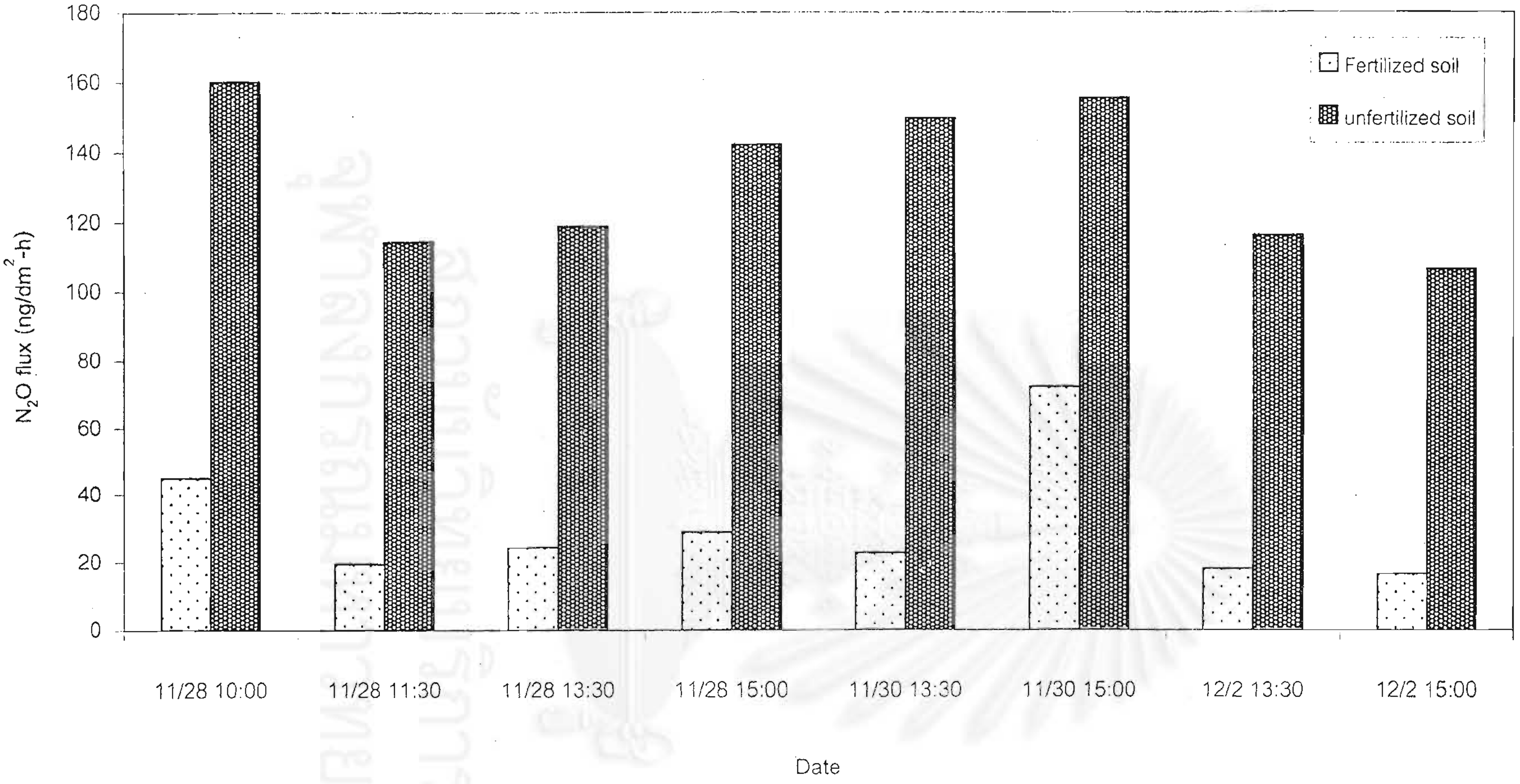

Figure 4.2.15 Comparison of N_2O flux between fertilized and unfertilized zone in bared soil

(From November 28 to December 2, 2001)

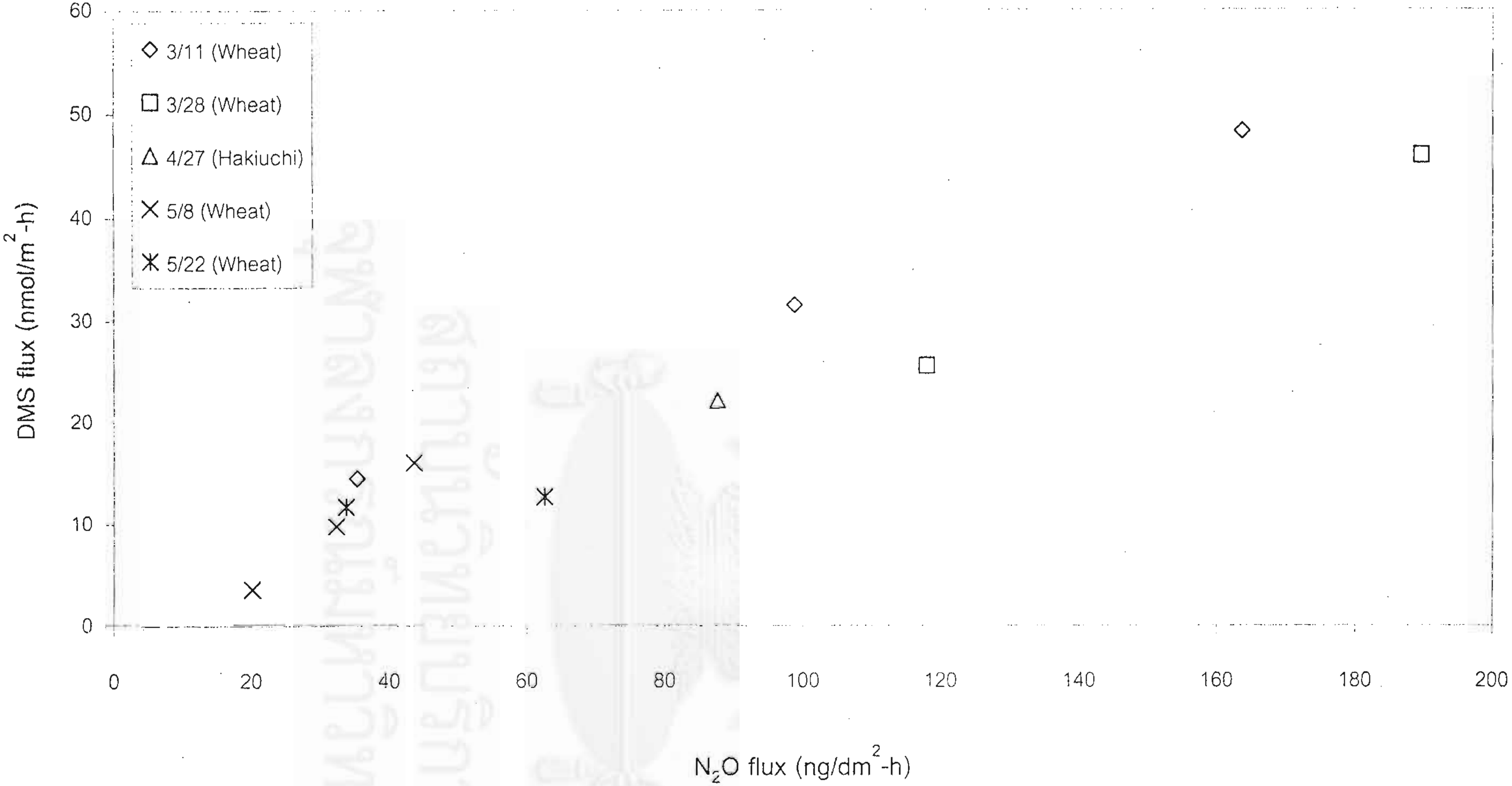

Figure 4.3.1 Correlation of DMS flux and N_2O flux in Wheat field and Hakiuchi forest

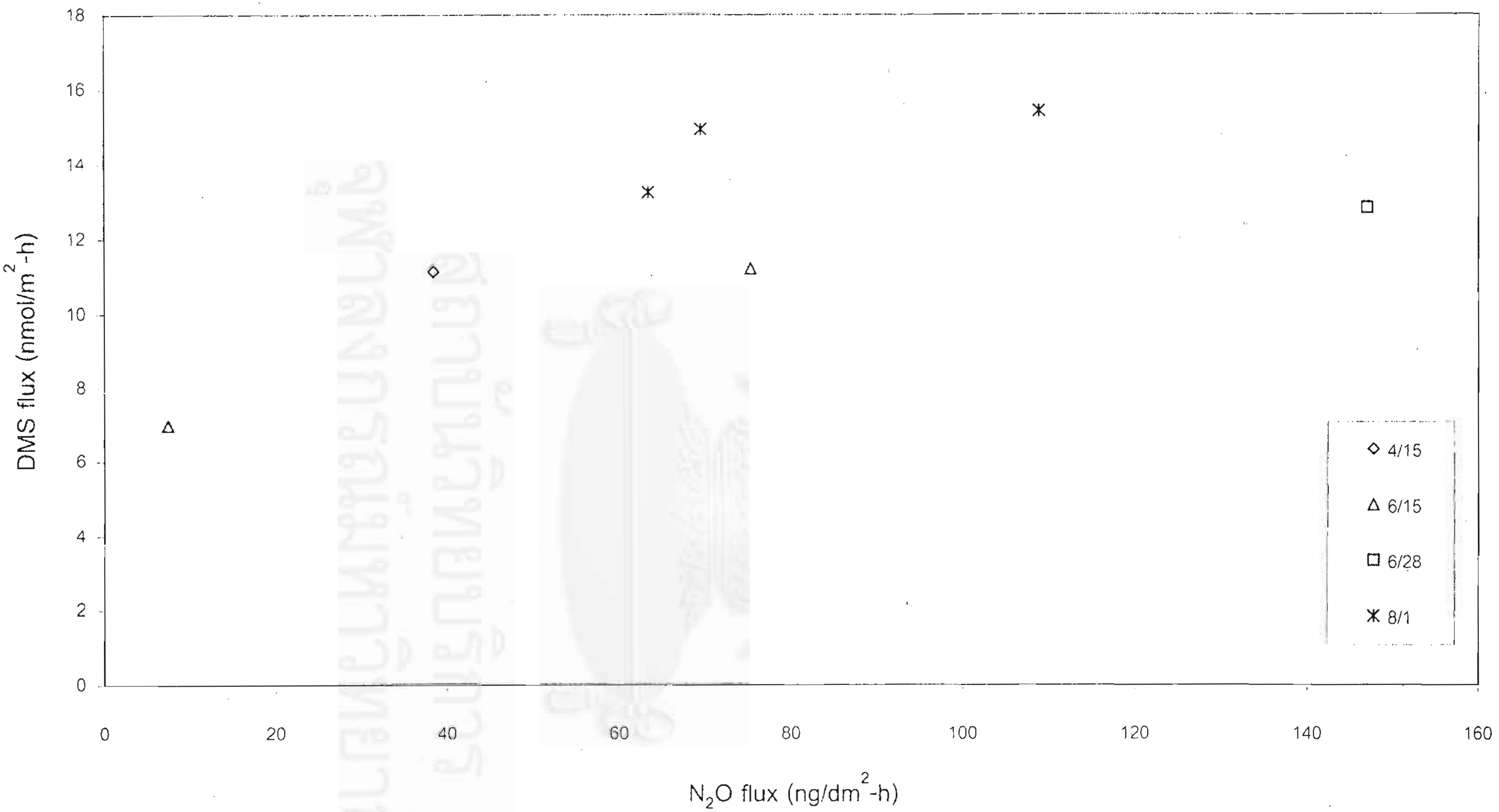

Figure 4.3.2 Correlation of DMS flux and N_2O flux in pine forest at Nagano

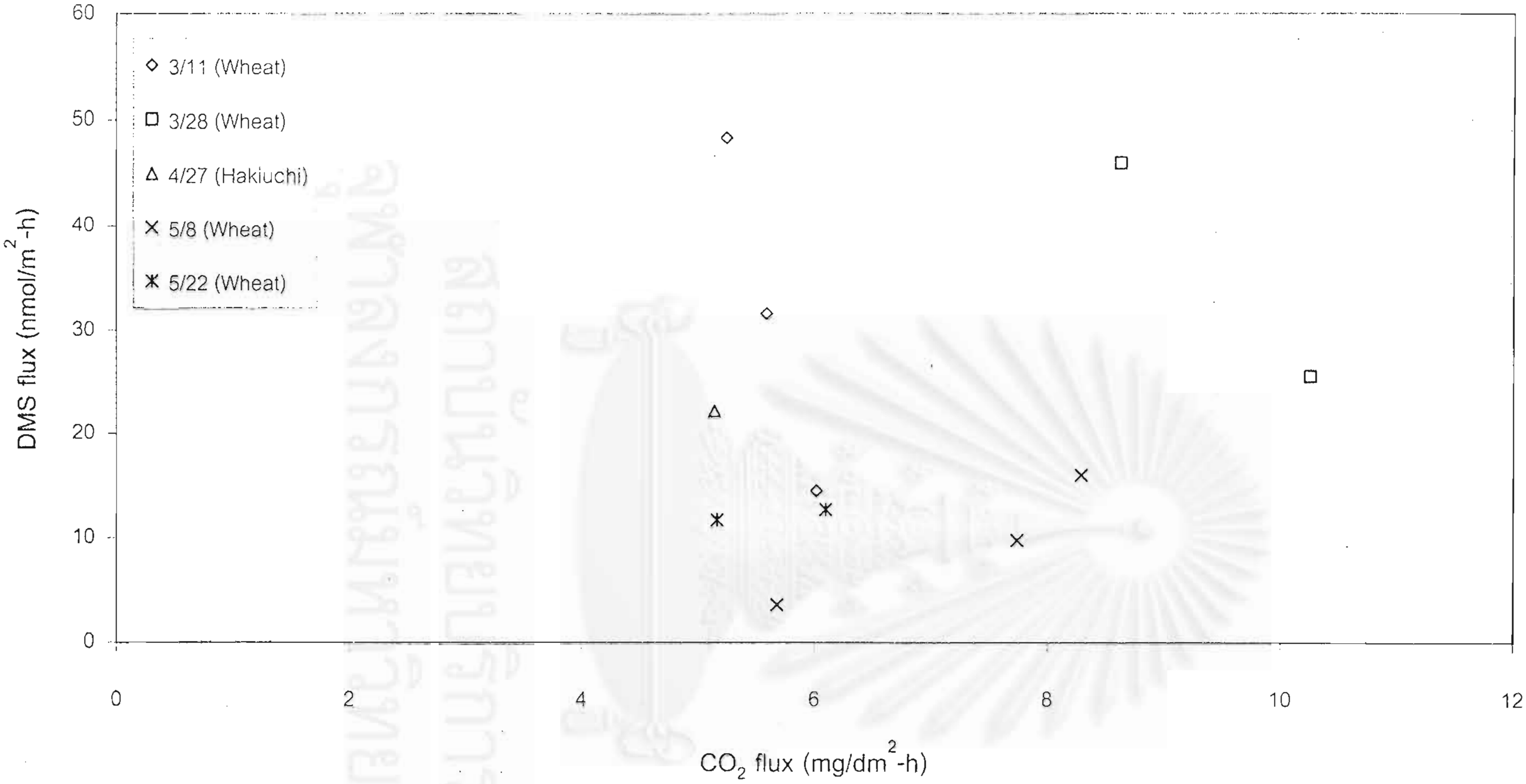

Figure 4.3.3 Correlation of DMS flux and CO_2 flux in Wheat field and Hakiuchi forest

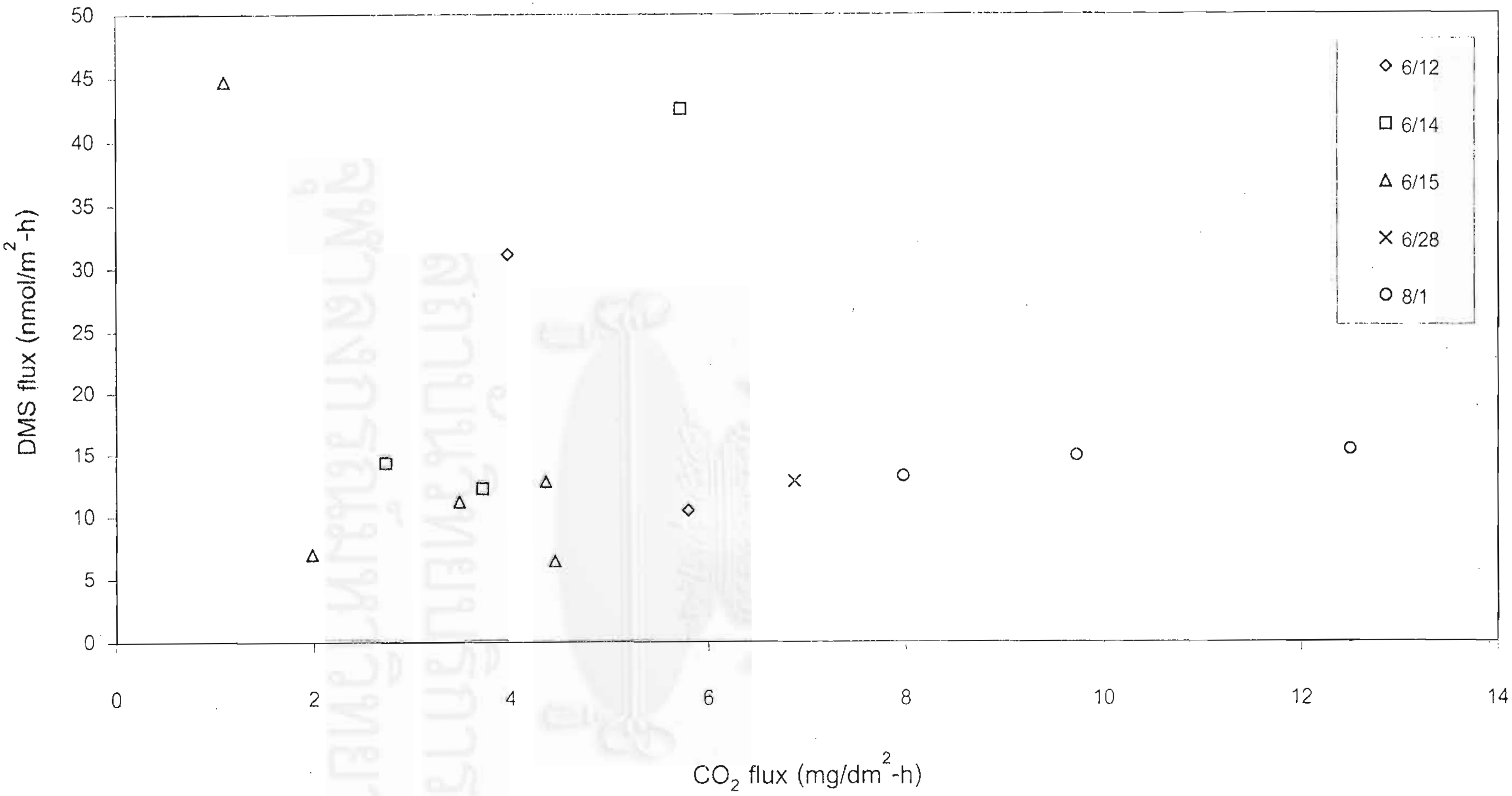

Figure 4.3.4 Correlation of DMS flux and CO_2 flux in pine forest at Nagano

Journal of The Institution of Engineers, Singapore
Vol. 42, No. 2 2002

Comparative Evaluation of Industrial and Agricultural Emissions of CO_2 and N_2O

Kunawut Boonyanopakun[1] **and Prasert Pavasant**[2]

ABSTRACT

This paper emphasizes the significance of greenhouse gas emissions, i.e. nitrous oxide (N_2O) and carbon dioxide (CO_2), from agricultural areas. Emission fluxes of N_2O and CO_2 from various sources were reviewed and it was shown that agricultural activities were significant sources for N_2O emission. A 100MW coal fired power plant was employed as a modeled industrial system to illustrate the magnitude of emission from agriculture. The evaluation indicated that an area of only 400 km² used for cropping of carrot could emit the same level of N_2O emission as the power plant. CO_2 emission from vegetation, on the other hand, was still lower than that emitted from industry and a maize cropping area of as large as 58,000 km² would be needed to emit the same amount of CO_2 as the 100MW power plant. However, a rapid increase in deforestation and other land applications have continually augmented the CO_2 and other greenhouse gas emissions, and it was expected that CO_2 and other greenhouse gas emissions from agriculture would surpass that of industry within 50 years.

INTRODUCTION

The N cycle and nitrous oxide emission

Nitrous oxide (N_2O) is well known as a greenhouse gas. The level of N_2O is controlled naturally from the N cycle (Fig. 1) where microbial mechanisms such as degradation of nitro-organic compounds end up with the emission of N_2O which is the intermediate in the denitrification process. This gas is slowly decomposed into N_2 and O_2. In fact, the natural level of N_2O is, at present, as low as 0.3 part per million by volume (ppmv) which is not considered dangerous for ecosystems (permission exposure limit in air is regulated at 25 ppm [Sittig, 1985]). However, changes in human activities have disturbed the N-cycle and it was found that the atmospheric concentrations of N_2O have risen by about 15% since the beginning of the industrial revolution (about 0.3% increase per year) [USEPA, 2001]. However, industry might not be the only factor responsible for this rise in atmospheric N_2O concentration. Literature showed that 70% of the total N_2O emission was derived from agricultural activity [Janzen, 2001]. The increase in N_2O on a global scale poses two potential threats to mankind: global warming and stratospheric ozone depletion. N_2O is a potent greenhouse gas with a long lifetime in the atmosphere (about 120 years). Its warming potential over 100 years is about 310 times that of CO_2. Increase in N_2O, hence, could potentially result in more heat absorbed in the earth's atmosphere leading to a problem of global warming. In addition, part of N_2O is eventually converted in the upper atmosphere to nitric oxide (NO): a gas that breaks down ozone. Since ozone in the upper atmosphere filters out UV radiation from the sun, its depletion means that there will be higher doses of harmful UV radiation reaching the earth's surface.

The N cycle in Fig.1 illustrates how N_2O is generated from various natural sources. The two main activities that account for most of N_2O emission are biological nitrification and denitrification. These processes are carried out by bacteria living in soil according to the following pathways [Aulakh et al., 1984].

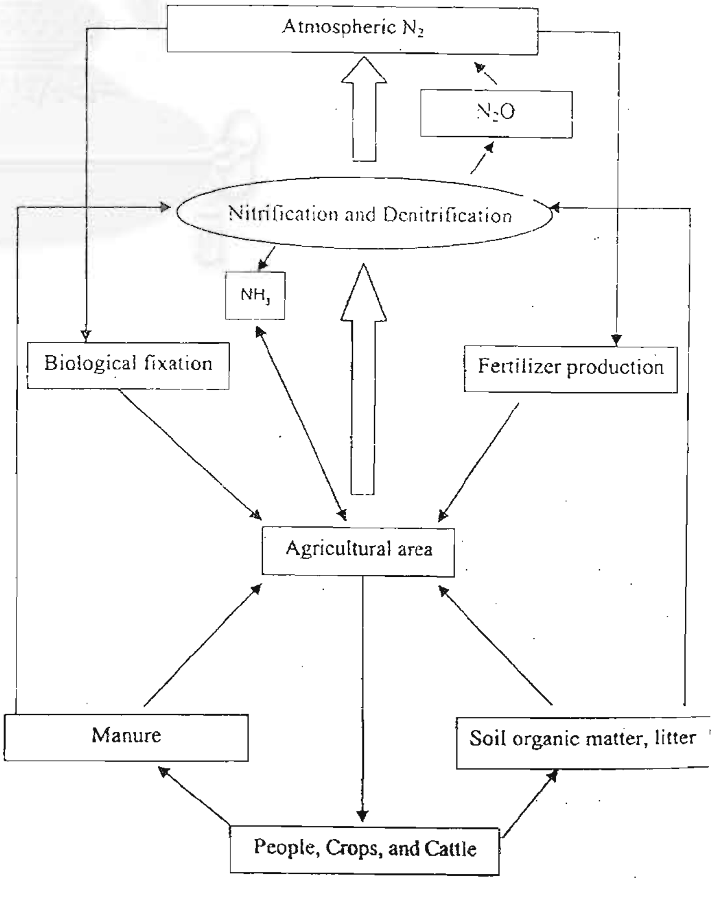

Figure 1: Diagram of the simplified N cycle and nitrous oxide production

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$$\begin{tikzcd} & & \boxed{N_2O(g)} & & \\ NH_4^+(l) \arrow[r, Rightarrow] & NH_2OH(l) \arrow[r, Rightarrow] & (e.g.\ H_2N_2O_2) \arrow[u, Rightarrow] \arrow[r, Rightarrow] & NO_2^-(g) \arrow[r, Rightarrow] & NO_3^-(g) \quad (1) \end{tikzcd}$$

$$NO_3^-(l) \Rightarrow NO_2(l) \Rightarrow NO(g) \Rightarrow \boxed{N_2O(g)} \Rightarrow N_2(g) \qquad (2)$$

Nitrification takes place in the upper soil surface, which can be regarded as an aerobic layer. Most N enters the soil either as NH_4^+ or in a form that can readily be converted to NH_4^+ such as urea. Hence, under conditions of good aeration and high NH_4^+ level, NH_4^+ is nitrified to NO_3^-, and a small portion of N may be emitted as N_2O (Eq.1). This results in a concentration gradient of NH_4^+ between aerobic and anaerobic soil layers, and causes NH_4^+ in the anaerobic layer to diffuse into the aerobic layer where it is nitrified. When movement of oxygen into soil is restricted, nitrate (NO_3^-) can be converted into nitrogen gas (N_2) in the denitrification process (Eq.2) from which the intermediate N_2O can escape to the environment. Similar to NH_4^+, NO_3^- formed in upper soil surface can diffuse back into the anaerobic layer where it is denitrified. Of the two processes, denitrification is probably a more important N_2O source than nitrification because emission of N_2O from denitrification may well be several times higher than that from nitrification [Rong, 1994]. There are three main factors that control the rate of denitrification, i.e. concentration of oxygen, concentration of NO_3^-, and the amount of available C used by bacteria as carbon and energy sources. High rates of denitrification occur with optimal environmental conditions, i.e. (i) low oxygen, (ii) high NO_3^-, and (iii) high available C. For instance, the conditions at snowmelt in Canada were reported to release large quantity of N_2O because high moisture content led to oxygen deficiency in the soil. In addition, the N_2O flush may have been caused by the abrupt release of N_2O that was previously trapped underneath a layer of frozen soil or ice. A comprehensive detail of these processes can be found in Janzen (2001) and Alleman (1997).

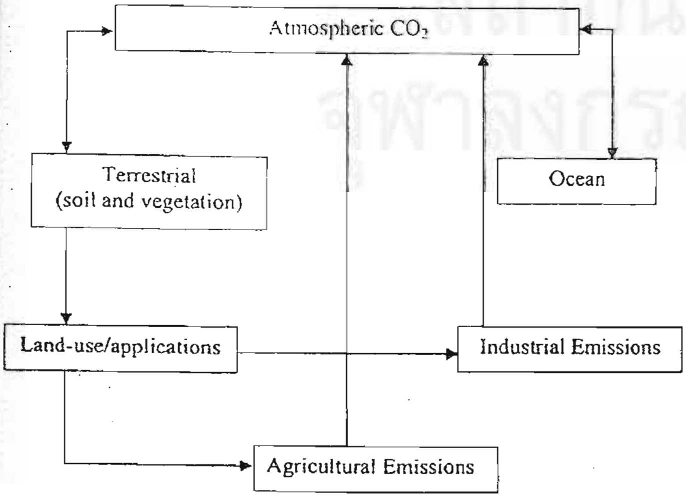

Figure 2: A simplified view of the global C cycle

The C cycle and carbon dioxide emission

Although the specific warming effect of carbon dioxide (CO_2) is not as significant as that of N_2O, CO_2 is considered a major greenhouse gas as it is usually present in large quantity. CO_2 was reported to drastically affect sea levels and weather patterns due to its global warming potential [Logan, 1996]. It might not be fallacious, hence, to treat CO_2 as one of the serious global environmental problems. Similar to the N cycle, the nature has a way to control quantities of various carbon compounds in the C cycle (Fig. 2). Total carbon in global circulation is about 40.000 petagrams (1 Pg = 10 grams) where most of this is in the oceans [Janzen, 2001]. Large carbon pools can also be found in soils, vegetation, and the atmosphere, and out of these three pools, the atmosphere is the smallest in size, yet most active. CO_2 in the air is continually being removed by plants through photosynthesis and by being absorbed into the oceans. At the same time, however, CO_2 is being replenished by release from plants, soils, and oceans. After the advent of the industrial era, the demand for energy resulted in ever-increasing demands of fossil fuels that were finally converted to atmospheric CO_2. This accounted for as large as 70% of total CO_2 emission. Other activities have also favoured increases in atmospheric CO_2: deforestation resulted in large quantity of biomass C being converted to CO_2, and the cultivation of previously undistributed soils resulted in soil C being converted to CO_2. Because of these processes, the emissions of CO_2 into the atmosphere have exceeded the rate of withdrawal, resulting in a gradual buildup of CO_2.

From an environmental point of view, one usually pays more attention to environmental impacts from industry. However, this paper thus far indicated that even agriculture can contribute, to some significant extent, to the global environmental problems. This investigation focuses on the effect of vegetation on the emission rate of N_2O and CO_2.

COMPARISON OF THE MAGNITUDE OF EMISSIONS OF N_2O AND CO_2 FROM VARIOUS NATURAL/AGRICULTURAL SOURCES

Nitrous oxide emissions

Previous reports showed that large amount of N_2O in the forest could be emitted into the atmosphere. Examples of emission fluxes from various natural and agricultural sources are given in Table 1. It is interesting to notice that emission fluxes from each source can vary significantly. For instance, Situala et al. (1995) found that N_2O emission fluxes from temperate pine forest during summer in Norway could vary from 13.1 to 53.7 $\mu g\ N_2O\ m^{-2}\ h^{-1}$. Schmidt *et al.* (1988) measured N_2O fluxes from six different deciduous forest sites in Germany and reported that these fluxes varied between 9.17 to 34.0 $\mu g\ N_2O\ m^{-2}\ h^{-1}$ which was close to those obtained in Norway. However, Brumme and Beese (1992) found that N_2O emission from a German Beech forest could be as high as 196 $\mu g\ N_2O\ m^{-2}\ h^{-1}$. Moreover, the review of N_2O fluxes from deciduous and coniferous forests in the US showed that the emission rate varied from as low as 0.26 µg N_2O m^{-2} h^{-1} in Massachusetts to as high as 115 µg N_2O m^{-2} h^{-1} in Wisconsin [Bowden *et al.*. 1990]. In addition. mean N_2O fluxes into the atmosphere from tropical forest soils in Brazil. Ecuador, and Puerto Rico were found to be in the same rage of 44.7 ± 5.1 µg N_2O m^{-2} h^{-1} [Keller *et al.*. 1986].

Generally, N_2O fluxes depend significantly on the interactions between chemical. physical. and biological parameters. Acidity of rain is one of the main parameters that affects the rate of N_2O release, and it was found that rain with high acidity (pH 2.5-3) could suppress microbial activities in soil leading to a marked decrease in N_2O fluxes [Situala *et al.*. 1995]. The examination of the statistical distributions in N_2O fluxes in the dwarf forest in South America revealed that dry soils produced more N_2O than wetter soils. This was because slow diffusion characteristics of wet soil would lower the net release of N_2O allowing more time for the reduction of N_2O to N_2 [Keller et al., 1986]. In addition, types of vegetation in the forest could significantly influence the rate of N_2O emission. Vegetation with a high capacity of retaining N usually causes more N to undergo microbial metabolisms and to escape from ecosystems in forms of N_2O and N_2 [Abrahamsen and Stuanes. 1998].

Agricultural soils often have higher rates of N_2O emission than comparable soils under natural vegetation because of high N inputs and disrupted N cycling. Several researchers have shown that nitrous oxide emission increased when tropical forests were converted to crop production and pasture. For instance. fluxes from uncultivated land and natural ecosystems in temperate and tropical regions were found to be less than 35.9 and 71.5 µg N_2O m^{-2} h^{-1}. respectively. whilst those from fertilized lands both from temperate and tropical regions were greater than 108 µg N_2O m^{-2} h^{-1} [Freyney, 1997]. Moreover. the emission rates of N_2O from wheat and carrot cropping in Denmark were reported to be as great as 509-4.170 µg N_2O m^{-2} h^{-1} [Christensen *et al.*. 1996]. More interestingly. N_2O emission from an agricultural soil fertilized with liquid swine waste or constituents in the southeastern US was found to be as high as 160 times greater than that obtained from pre-fertilization soil [Whalen, 2000]. This was because as much as 50% of applied N (in fertilizer) was released into the atmosphere as ammonia (NH_3). This NH_3 was eventually deposited onto soil or water. where it was converted to NH_4^+ and finally N_2O. Hence. manure practices often led to a much higher rate of N_2O emission to the environment [Janzen, 2001].

Table 1. N_2O emission from various areas

Source	Flux(µg/m^2-h)
- Tropical forest soils (Brazil, Ecuador, Puerto Rico), [Keller et al., 1986]	44.7
- Temperate pine forest soil (Norway), [Situala *et al.*, 1995]	13.1 to 53.7
- German beech forests (German), [Brumme and Beese, 1992]	196
- Deciduous forests (Germany), [Schmidt *et al.*, 1988]	9.17 to 34.0
- Deciduous forests (US), [Bowden *et al.*, 1990] * from Massachusetts to Wisconsin	0.524 to 52.4
- Coniferous forests (US), [Bowden et al., 1990] * from Massachusetts to Wisconsin	0.264 to 115.0
- Hudson river (US), [Cole and Caraco, 2001]	10.1
- Temperate and tropical region, [Freyney, 1997]	
* uncultivated lands	Less than 35.9
* natural ecosystems	Less than 71.5
* fertilized lands	More than 108
- Agricultural soil fertilized with liquid swine waste or constituents (US), [Whalen, 2000]	
* pre-fertilization	31.4 to 78.6
* after treatment with N-fertilized	More than 12,600
- Wheat stubble (Denmark), [Christensen *et al.*, 1996]	509 to 635
- Carrot cropping (Denmark), [Christensen *et al.*, 1996]	1,030 to 4,170
- Pre-burned sites, [Freyney, 1997]	Less than 22.6
- Burned and wetted sites, [Freyney, 1997]	102 to 249

Apart from emission from biological processes in soils. N_2O could also be emitted during combustion of biomass. The nitrogen in biomass fuel either as in end groups, open chains and heterocyclic rings can also be converted into gaseous forms during their decomposition. and its form is changed to combustion products such as ammonia, nitric oxide. dinitrogen and hydrogen cyanide. Most of the biomass burning takes place in the tropics from forest clearing. savanna and sugar cane fires. and burning of agricultural waste [Freyney, 1997]. As shown in Table 1. emissions from the pre-burned sites were less than 22.6 µg N_2O m^{-2} h^{-1} compared with emissions of 1.020-2.490 µg N_2O m^{-2} h^{-1} from burned sites.

Carbon dioxide emissions

The intensity of the emission of carbon dioxide from the soil surface is a result of metabolic processes of plants. animals. and microorganisms and is related to physicochemical processes in soils. These parameters are dynamic, therefore, emission fluxes from agroecosystems of different natural zones vary accordingly with regional characteristics [Pomazkina, 1996]. As shown in Table 2, CO_2 emission fluxes from temperate and tropical forest soils tend to be higher than those from colder environments such as tundra or arctic ecosystems. The reason might be that low temperature (below -6.5°C) retards the rate of biological activity within the soil and suppresses CO_2 emission. Therefore, several researchers have concluded that soil temperature was the dominant factor for soil CO_2 emissions [Keller *et al.*, 1986; Borken *et al.*, 1999; Oechel *et al.*, 1997; Sommerfeld *et al.*, 1996].

In addition, production and consumption of CO_2 can be influenced significantly by agricultural practices particularly the management of crop residues and soil organic matter. This includes tillage practices, fallowness, and fertilization. Tillage is one of the main tools available to farmers for controlling weeds and preparing land for seeding, and there

Table 2. CO_2 emission from various areas

Source	Flux(g/m^2-h)
- Tropical forest soils (Brazil, Ecuador,Puerto Rico), Puerto Rico), [Keller *et al.*, 1986]	0.3948
- Temperate forest soil (Norway), [Borken *et al.*, 1999]	0.2015 to 0.2718
- Alpine site (US), [Sommerfeld *et al.*, 1996]	0.0397
- Subalpine site (US), [Sommerfeld *et al.*, 1996]	0.097
- Artic ecosystems (Siberia), [Zimov *et al.*, 1993]	0.0229
- Tussock tundra ecosystems (US), [Oechel *et al.*, 1997]	0.0468
- Wet sedge ecosystems (US), [Oechel *et al.*, 1997]	0.0105
- Gray forest soil (Russia), [Pomazkina *et al.*, 1996]	
• fallow - wheat	0.1208
• fallow - fallow - wheat - wheat	0.1125
• fallow - fallow - wheat - wheat - wheat	0.1292
• resting fallow	0.0875
- Silt loam soil (New Zealand), [Aslam *et al.*, 2000]	
• maize cropping with plow tillage	0.5496 to 1.237
• maize cropping with no tillage	0.6565 to 1.389
• Permanent pasture	0.8397 to 2.015
- Clay loam (US), [Reicosky, 1997]	Initial after 55 min
• Mold board plow	29.1 to 2
• No tillage	0.7 to 0.2
	Initial after 3 h
• Mold board plow + Disk harrow twice	7 to 2

is still contradiction over the influence of tillage on CO_2 evolution. Reicoskey (1997) reported that for at least 19 days after tillage, moldboard plow, where reasonably good mixing of upper soil surface was achieved, caused more CO_2 to re-enter into the atmosphere compared to other treatments. On the other hand, Aslam *et al.* (2000) found that CO_2 efflux from soil with no-tillage was greater than from plow-tillage because as the soil was turned over in the tillage, substrates for micro-organisms disappeared from the top 5 cm resulting in a significant drop in soil respiration. With regard to fallow practice, the practice of leaving land unplanted for a whole year could replenish soil moisture and increased available nutrients in the soil. This may potentially increase the rate of carbon decomposition, which leads to higher CO_2 production rate. However, soil that is frequently under summer fallow often has far lower C content than the areas that are continuously cropped. This limitation in available C reduces the total rate of CO_2 generation. In the areas with continual cropping, although the rate of C decomposition might not be as fast, they contain high C level which leads to a higher emission rate of CO_2 [Pomazkina, 1996]. Within each crop rotation, soil that receives fertilizer has higher gains of C than unfertilized soil due primarily to higher residue inputs with fertilization. Manure application increases soil C to a much greater extent than using other types of fertilizer. This is because manure not only increases crop yield, but also provides direct input of C [Janzen, 2001]. All of these factors lead to a higher rate of CO_2 emission to the atmosphere.

EMISSION OF NITROUS OXIDE AND CARBON DIOXIDE: INDUSTRY VS AGRICULTURAL

Transportation and industry have always beer recognized for their high contribution to the globa greenhouse effect. From the discussion above, it becomes obvious that agriculture can also be another substantia source and should, indeed, be taken into consideration along with other environmental issues. There are direct an indirect contributions to the emission of greenhouse gase from agriculture. Direct mechanism occurs from th activities of microorganisms as stated earlier, whilst th latter occurs mostly from volatilization of ammonia (NH_3) from manure as an example. This NH_3 could be re-deposite over the landscape through wet and dry depositions [Moise *et al.*, 1996], where anhydrous ammonia becomes NH_4^+, an immediately reacts with water in soil. N_2O can, again, b generated from mechanism in Eq.1. As a result, most of NH released from soil, floodwater, and irrigation water followin fertilizer application to agricultural systems will b converted to N_2O, and it was reported that this secondar source was responsible for the largest fraction of overal emission from agricultural area [EEA, 2000].

It is rather cumbersome to compare emission rates c greenhouse gases from agriculture with industry becaus they are usually present in different dimensions (or units) For instance, emissions from agriculture are often reporte based on area (e.g. g-N_2O m^{-2} h^{-1}), whereas emissions fron industry are commonly based on the quantity of produc generation or main raw material consumption (g-N_2O g-Coa $^{-1}$). Hence, some assumptions or simplifications have to b made in order to illustrate the magnitude of greenhouse ga emissions from agriculture. In this work, emission from coal fired power plant with a capacity of 100MW is used a a basis for calculation. Figs. 3 and 4 summarize area required by various terrain types to produce the sam quantity of greenhouse gases as the power plant (reported a equivalent agricultural area). Note that the calculation for th modeled power plant is based on the following assumption (i) the main raw material to the power plant is har anthracite coal with a maximum heating value of 26.5 MJ/kg, and (ii) the efficiency of the power plant i approximately 35%.

In reading these figures, it is reminded that an item wit small equivalent area indicates that the correspondin source only needs small area to produce the same amount c greenhouse gas with the 100 MW coal fired power plan Fig. 3 reveals that, most forests produced N_2O with a mor or less the same rate as that of pre-fertilized land. For N_2 emission from the forests, the land with a size of 10,000 kn to 50,000 km^2 would be needed to produce N_2O in the sam magnitude as the power plant. However, in an agricultur area where the soil was fertilized with liquid swine wast only as small as 132 km^2 was required to produce the sam quantity of N_2O with the power plant. This figure might n have much meaning if it was not mentioned that the sam

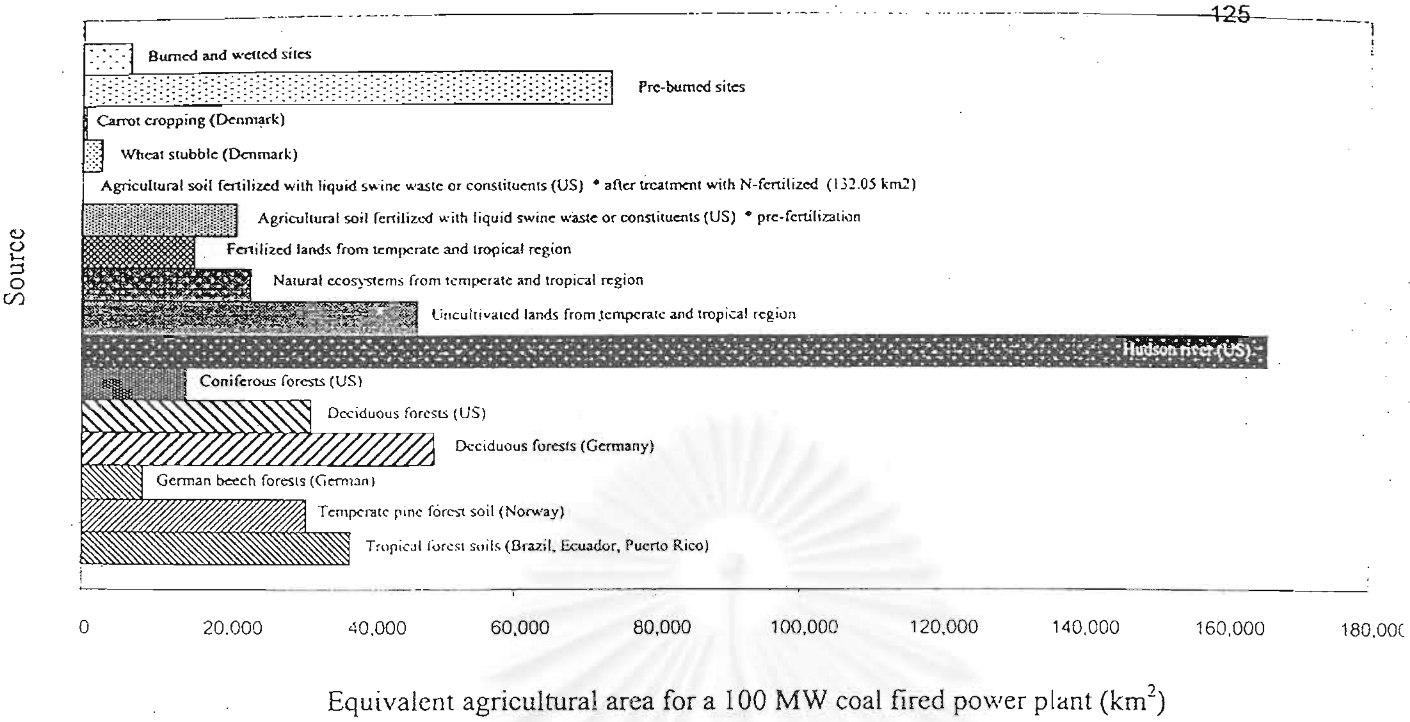

Figure 3: N_2O emission from various natural/agricultural areas

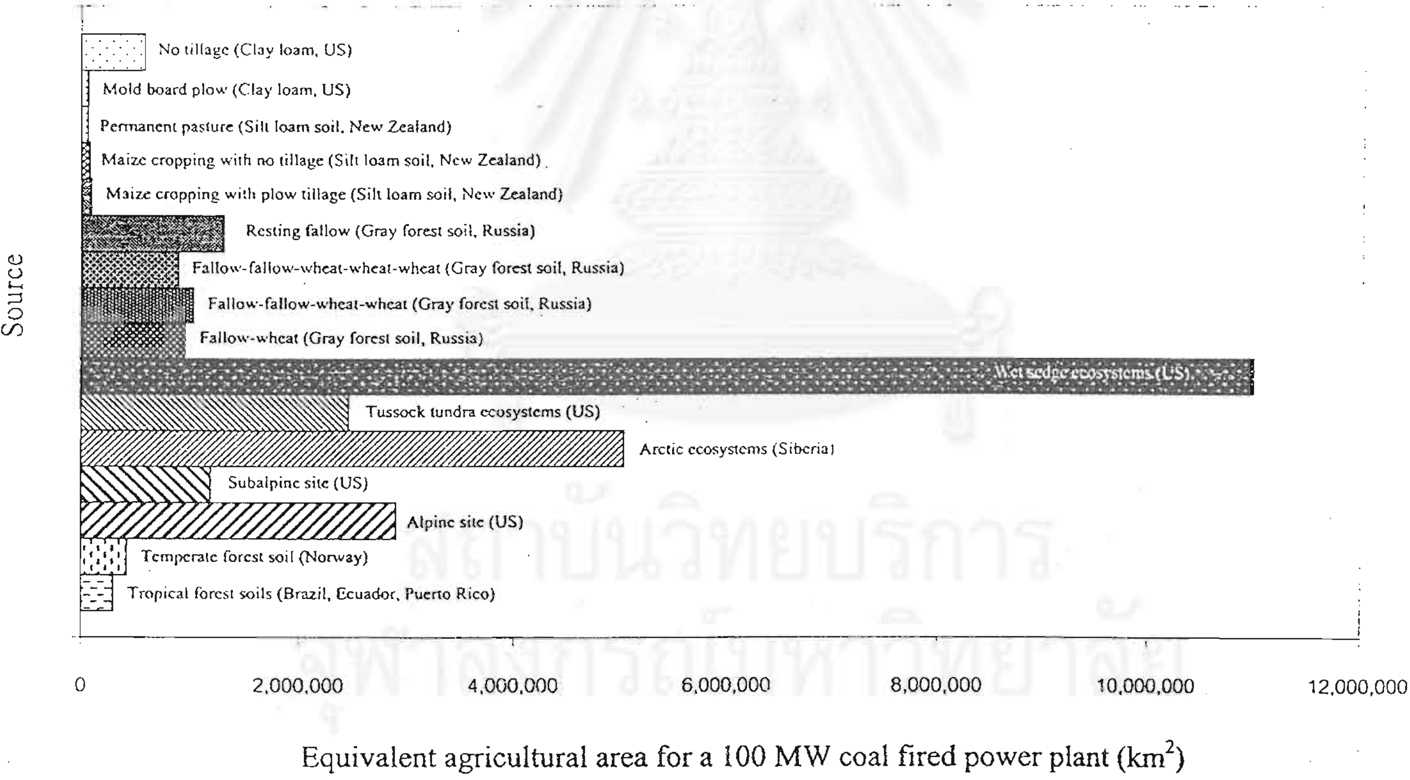

Figure 4: CO_2 emission from various natural/agricultural areas

area without fertilization (pre-fertilized soil) would produce much less N_2O emission and as large as 21,200 km^2 would have been needed to match the power plant. This means that once a farmer fertilized their land with liquid swine waste, he already increased the N_2O emission rate by approximately 160 times. In actual fertilizing practice (without usage of swine waste), nevertheless, carrot and wheat plantations required approximately 400 km^2 and 2,600 km^2, respectively, to be equivalent with the power plant in terms of N_2O emission. According to CIA (2000: data as in 1996), Thailand spent approximately 30,706 km^2 in cropping, and if all crops produced similar range of N_2O, the quantity of N_2O emitted from agriculture in Thailand could be as much as 77% of N_2O from country's total electricity production (approximately 85x10^6 MW-h in 1996).

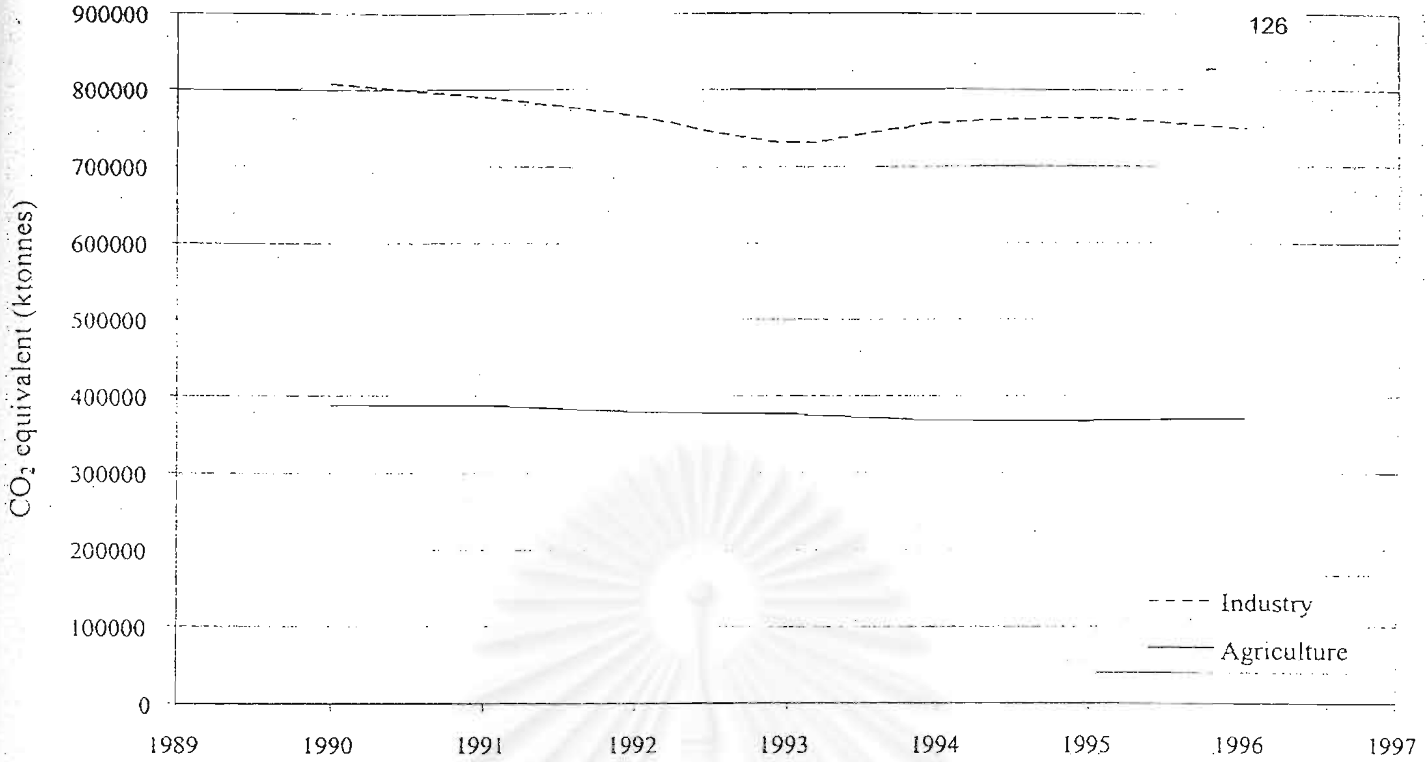

Figure 5: Estimation of greenhouse gas emissions from industry and agriculture

Fig. 3 also demonstrates that N_2O emission was found to be minimum at the river. This was due primarily to a low N input in the natural water courses. Nevertheless, river may become an important source for the production of N_2O in cases where there was high usage of N-containing fertilizers. This was because 20% of N compounds in the fertilizer could escape to the rivers promoting both nitrification and denitrification processes [Cole and Caraco, 2001].

Fig. 4 shows that natural systems only contributed very little to the overall CO_2 flux. It can be seen that the summation of emission rates from Tussock Tundra, arctic, wet sedge ecosystems and alpine site, areas covering almost about 9% of the global land area, was merely 12% of the total CO_2 emission from fossil fuel used [Oechel and Vourlitis, 1994]. Temperate and tropical forests that covered 13% of the global land area, however, emitted a larger quantity of CO_2 due to a higher temperature, which enhanced the rate of biological activities in soil. The same reason could also apply to explain why the emission from sub-alpine site was higher than that from the cooler alpine site. Turning the forests into cropped or pasture areas increased the CO_2 emission considerably. For instance, Fig. 4 indicated that maize cropping in New Zealand emitted a one order of magnitude higher CO_2 than the similar climate boreal forests. Besides, the management in agricultural area such as tillage, fallow, or fertilization usually led to stimulation of the CO_2 emission [Pomazkina *et al.*, 1996; Reicosky, 1997; Aslam *et al.*, 2000]. For instance, the moldboard plow that turned over the soil surface led to a much larger initial CO_2 emission. As illustrated in Fig. 4, the agricultural area that was tilled with moldboard would emit as much as 10 times CO_2 over that without tillage soil.

In most cases, large vegetation areas (50,000-100,000 km^2) were needed in order to have equivalent CO_2 emission with the power plant. Indeed, this indicates the superiority of the power plant in converting the organic carbon into CO_2 over the vegetation activity, i.e. 2,835 kg-CO_2 will be generated per ton of coal utilized in the power plant, whilst only 0.036 kg-N_2O is produced from the same amount of coal [USEPA, 1995]. However, this fact might not remain the same as the trend for CO_2 emission from industry was found to move downwards while that of agriculture was not. Fig. 5 illustrates that, within 50 years from now if the agricultural practice remained unaltered, the degree of greenhouse gas emissions from agricultural areas could probably match or even exceed that from the industrial sector whose trend was reported to reduce approximately 8% from 1990 to 1996 (and if this trend was assumed not to change) [EEA, 2000]. This is because there has always been improvement in technologies. The increasing efficiency in power generation strategies, such as switching from the carbon rich fuels of coal and oil to renewable or natural gas, has resulted in a great reduction in CO_2 and other greenhouse gas emissions. This conclusion might imply that the plan of global pollution control should focus more at the management in plantation, for instance, the control of the uses of fertilizers, the development of efficient land treatment, soil fertilizing techniques, etc.

CONCLUSION

This article emphasizes the significance of agricultural activities on the global environmental problems. Both N_2O

and CO2 emissions from agricultural areas should certainly be taken more seriously as one of the main causes for the global climate change particularly the rise in the temperature. Although greenhouse gas emissions per unit area might not be of eminent environmental concern, it should be mentioned that agricultural area covers as much as 10% of the overall area on earth (not including the water surface) and the overall emission rate is highly significant. Moreover, there is a high possibility that this problem will not be solved as more forests are still being converted into various land applications.

REFERENCES

Abrahamsen G., and Stuanes O. (1998). Retention and leaching of N in Norwegian Coniferous forests. Nutr. Cycl. In Agroeco. 52, 171-178.

Alleman J.E. (1997). Nitrification & Denitrification process and treatment literature search.

Aslam T., Choudhary M.A., Saggar S. (2000). Influence of land-use management on CO2 emissions from a silt loam soil in New Zealand. Agr. Ecosys. and Env. 77, 257-262.

Aulakh M.S., Rennic D.A., and Paul E.A. (1984). Acetylene and N-serve effects upon N_2O emissions from NH_4^+ and NO_4^- treated soils under aerobic and anaerobic conditions. Soil Biol. Biochem. 16, 351-356.

Austin D., Goldemberg. J., and Parker G. (1998). Contributions to climate change: Are conventional metrics misleading the debate?

Borken W., Xu Y.-J., Brumme R., and Lamersdorf N. (1999). A climate change scenario for Carbon Dioxide and dissolved organic Carbon fluxes from a temperate forest soil: Drought and Rewetting effect. Soil Sci. Soc. Am. J. 63, 1848-1855.

Bowden R.D., Steudler P.A., Melillo J.M., and Aber J.D. (1990). Annual nitrous oxide fluxes from temperate forest soils in the northeastern United states. J. Geophys. Res. 95, 13997-14005.

Brumme R. and Beese F. (1992). Effects of liming and nitrogen fertilization on emissions of CO_2 and N_2O from temperate forest. J. Geophys. Res. 97, 12851-12858.

Central Intelligence Agency (CIA) (2000). The world factbook.

Christensen S., Ambus P., Arah J.R.M., Clayton H., Galle B., Griffith D.W.T., Hargreaves K.J., Klemedtsson L., Lind A.-M., Maag M., Scott A., Skiba U., Smith K.A., Welling M., and Wienhold F.G. (1996). Nitrous oxide emission from an agricultural field: comparison between measurements by flux chamber and micrometerological techniques. Atmos. Env. 30, 4183-4190.

Cole J.J. and Caraco N.F. (2001). Emissions of nitrous oxide (N_2O) from a tidal, freshwater river, the Hudson River, New York. Env. Sci. & tech. 35, 991-996.

European Environment Agency (EEA) (2000). Emissions of Atmospheric Pollutants in Europe, 1980-1996. Belgium.

Freyney J.R. (1997). Emission of nitrous oxide from soils used for agriculture. Nutr. Cycl. Agroeco. 49, 1-6.

Janzen H.H. (2001). Estimates of Emissions. 127

Keller M., Warren A., Kaplan and Steven C. (1986). Emissions of N_2O, CH_4 and CO_2 from tropical forest soils. J. Geophys. Res. 91, 11791-11802.

Logan R.H. (1996). Why should we be concerned about Carbon Dioxide in the atmosphere?

Moiser A.R., Duxbury J.M., Freyney J.R., Heinemeyer O., and Minami K. (1996). Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation. Plant and Soil 181, 95-108.

Moiser A.R., and Kroeze C. (1998). A new approach to estimate emissions of nitrous oxide from agriculture and its implications to the global nitrous oxide budget.

Oechel W.C. and Vourlitis G.L. (1994). The effect of climate change on Arctic tundra ecosystems. Trends in Eco. and Evol. 9, 324-329.

Oechel W.C., Vourlitis G.L., and Hastings S.J. (1997). Cold season CO_2 emission from arctic soils. Glob. Biogeo. Cycl. 11, 163-172.

Pomazkina L.V., Lubnina E.V., Zorina S. Yu., Kotova L.G., and Khortolomei I.V. (1996). Dynamics of CO_2 emission from the gray forest soil in the Forest-Steppe of the Cisbaikal region. Eura. Soil. Sci. 29, 1355-1359.

Reicoskey D.C. (1997). Tillage-induced CO_2 emission from soil. Nutr. Cycl. In Agroeco. 49, 273-285.

Rong X. (1994). Estimation of methane and nitrous oxide emissions from rice fields in Thailand. M.Sc. thesis, Asian Institute of Technology, Thailand.

Schmidt J., Seiler W., and Conrad R. (1988). Emission of nitrous oxide from temperate forest soils into the atmosphere. J. Atmos. Chem. 1, 95-115.

Sittig M. (1985). Handbook of toxic and hazardous chemicals and carcinogens (2nd edition), Noyes Publication, USA.

Situala B.K., Bakken L.R., and Abrahamsen G. (1995). N-fertilization and soil acidification effects on N_2O and CO_2 emission from temperate pine forest soil. Soil. Biol. Biochem. 27, 1401-1408.

Sommerfeld R.A., Massman W.J., and Musselman R.C. (1996). Diffusional flux of CO_2 through snow: Spatial and temporal variability among alpine-subalpine sites. Glob. Biogeo. Cycl. 10, 473-482.

United State Environmental Protection Agency (EPA) (1995). Compilation of air pollutant emission factors: stationary point and area sources. Volume I, 5th edition, AP42.

United State Environmental Protection Agency (EPA) (2001). Global warming.

Whalen S.C. (2000). Nitrous oxide emission from an agricultural soil fertilized with liquid swine waste or constituents. Soil Sci. Soc. Am. J. 64, 781-789.

Zimov S.A., Zimova G.M., Davidov S.P., Davidova A.I., Voropaev Y.V., Boropaeva Z.V., prosiannikov S.F., Prosiannikova O.V., Semiletova I.V., and Semiletov I.P. (1993). Winter biotic activity and production of CO_2 in Siberian soils: A factor in the greenhouse effect. J. Geophys. Res. 98, 5017-5023.

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