धाान-मृदा से ओजोन मधयस्तित मीथेन एवं नाइट्रस आक्शाइड का उत्सर्जन

OZONE MEDIATED CHANGES IN METHANE AND NITROUS OXIDE EMISSIONS FROM RICE SOIL

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NEW DELHI, INDIA - 110 012
2008

OZONE MEDIATED CHANGES IN METHANE AND NITROUS OXIDE EMISSIONS FROM RICE SOIL

By

AYAN GHOSH

A thesis
Submitted to the Faculty of Post-Graduate School,
Indian Agricultural Research Institute, New Delhi,
in partial fulfillment of the requirements
for the award of the degree of

MASTER OF SCIENCE
IN
ENVIRONMENTAL SCIENCES
2008

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CERTIFICATE

This is to certify that the thesis entitled **"Ozone mediated changes in methane and nitrous oxide emissions from rice soil"** submitted to the Faculty of the Post-Graduate School, Indian Agricultural Research Institute, New Delhi, in partial fulfillment of the requirements for the award of the degree of **Master of Science** in **Environmental Sciences** is a faithful record of *bona fide* research work carried by **Mr. Ayan Ghosh** under my guidance and supervision and that no part of the thesis has been submitted for any other degree or diploma.

It is further certified that the assistance and help received during the course of the investigation has been duly acknowledgement by him.

Date: June 23,2008
Place: New Delhi

Dr. Arti Bhatia
Chair-person,
Advisory Committee

DEDICATED TO MY CHAIRPERSON

ACKNOWLEDGEMENT

Euripides (484 BC – 406 BC) once told that, "The best and safest thing to keep a balance in your life, acknowledge the great powers around us and in us. If you can do that, and live that way, you are really a wise man." So it is essential that I acknowledge the great powers, who paved the way on which I have walked so far. As a prelude to my thanksgiving, at first I wish to thank the almighty for giving my powers to complete my entire course…after all He is the "greatest".

My diction is too poor to translate my esteemed and profound sense of gratitude into words for the judicious and precious advice, constructive criticism, constant encouragement, concrete suggestion and painstaking supervision throughout the course of investigation and preparation of manuscript extended by Dr. (Mrs.) Arti Bhatia, the chairperson of my advisory committee, Senior Scientist, Division of Environmental Sciences, IARI, New Delhi.

I am equally indebted to my Co-chairperson Dr. S. D. Singh, Principal Scientist, Division of Environmental Sciences, IARI, New Delhi for his inspiring guidance, generous advice, cooperating attitude and scientific discussion throughout the investigation.

I am grateful to Dr. Himanshu Pathak. His sagacious guidance, persistent involvement, scholarly suggestions, prudent admonitions, constant and ungrudging help and affectionate behaviour has been a fountain of great inspiration to me.

I express my sincere gratitude to the members of my Advisory Committee, Dr. H.C.Joshi, Proffesor, Environmental Sciences, Dr. Bidisha Banerjee, Scientist, Environmental Sciences for their sincere advice, help, constructive, and valuable suggestions at various stages of this investigation.

I avail myself of this opportunity to convey my heartfelt thanks to the Dr. R.K. Chowdhary, Head of the Division, Environmental Sciences, for providing necessary facilities and valuable suggestions throughout this study.

I implore my feeling of profound gratitude to Dr. H. C. Joshi, Professor, Environmental Sciences for his friendly behaviour and steadfast help during this investigation.

This is my proud privilege to express my deepest sense of gratitude to Dr. Lata, Principal Scientist, Division of Microbiology, IARI, New Delhi for his always- ready- to- help attitude throughout this study.

I also express my heartfelt thankfulness to the respected scientists of the Division of Environmental Sciences, Dr. Niveta Jain, Dr. Shivprasad, Dr. Ravinder Kaur, Dr. Anita Choudhary, for their priceless co-operation and stimulating encouragement.

I do also wish to express my cordial thanks to Ms. Usha Rani, P.A of professor, Division of Environmental Sciences, for scholarly advice and extending helping hands during the course of investigation.

It gives me great pleasure to express my heartfelt gratitude to Binodji, Ritu mam for their constant help, enthusiasm and friendship.

I will be failing in my duties if I do not thank Manojji, Joginderji, Jagpalji and Bansalji,Amar Singhji for their constant help and co-operation.

Many thanks to all staffs and students of the Division of Environmental Sciences for making it a great place to learn and a memorable one.

I am equally thankful to all my juniors, seniors and my friends in IARI. In particular wish to thank Satyaban, Rosin, Dhania Di, Bhaskar, Rakesh, Ajoy, Arnab, Sudip, Somenda, Manjudidi, for their encouragement and ready gesture to help through out the research work. I am very much thankful to my friend Sujata Bhattacharjee for her continuous support, endless care and love.

No words of mine would be adequate to express my indebtedness to my beloved parents for their painstaking and untiring efforts to educate me to this and make me what I am today.

A Special word of thanks goes to my brother and sister in law for their endless care and love and constant inspiration, which kept me enthusiastic throughout my educational career.

The junior research fellowship awarded by Indian Council of Agricultural Research, during the course of my study is gratefully acknowledged.

There are many others who have helped me in various ways and supported me. I sincerely thank all of them and request their forgiveness for not mentioning them here by name.

Place: New Delhi

Date: *Ayan Ghosh*

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1. INTRODUCTION

The Indian sub-continent has seen a rapid increase in population and urbanisation in recent years. This has resulted in a growth in motor vehicle numbers and decline in air quality with an increase in concentrations of ozone, nitrogen dioxide and other oxidants. Ozone (O_3) is a phytotoxic air pollutant produced in the troposphere where sunlight reacts with VOC's or oxides of nitrogen emitted by vehicles and industry. Since the industrial revolution anthropogenic activity has increased the tropospheric concentrations of ozone (Vingarzan, 2004). Generation of ozone is based on solar energy and higher concentrations occur from May to September in the afternoon (Stockwell *et al.*, 1997). Tropospheric ozone (O_3) is a greenhouse gas and its concentrations are increasing annually by 0.5±2%. Nearly one-quarter of the Earth's surface is currently at risk from mean tropospheric ozone in excess of 60 ppbV during midsummer with even greater local concentrations occurring (Morgan *et al.*, 2006). The phytotoxic effects of ozone are of particular concern as background tropospheric concentrations are already close to potentially damaging levels.

Ozone is a major air pollutant and causes more damage to plants than all other air pollutants combined. There are reports that there may be tremendous losses of crop yields in India in the near future due to projected increase in O_3 concentrations during the kharif season (Marshall *et al.*, 1997). Large variations are obtained between cultivars in sensitivity to different ozone levels because of varied physiological responses. Physiological changes in roots in response to elevated ozone can lead to altered below-ground processes and changes in soil organic carbon. Long-term environmental change in the biosphere is occurring from greater photochemical synthesis of tropospheric O_3.

Elevated surface ozone is known as bad ozone due to its detrimental effect on crop productivity from agricultural point of view. Ozone pollution is known to have a substantial effect on agricultural production in North America, Western Europe and many other countries of the world and have increased considerably during the last century throughout Europe and is expected to rise further in the future (Ashmore *et al.*, 2004). Elevated ozone is known to decrease net photosynthesis via oxidative damage to cell membranes, especially to chloroplasts (Karberg *et al.*,

2005) and consequently to reduce dry matter production. Elevated ozone may lead to significant alterations in plant residue decomposition (both litter quality and quantity), nutrient cycling and microbial activities (Fig. 1).

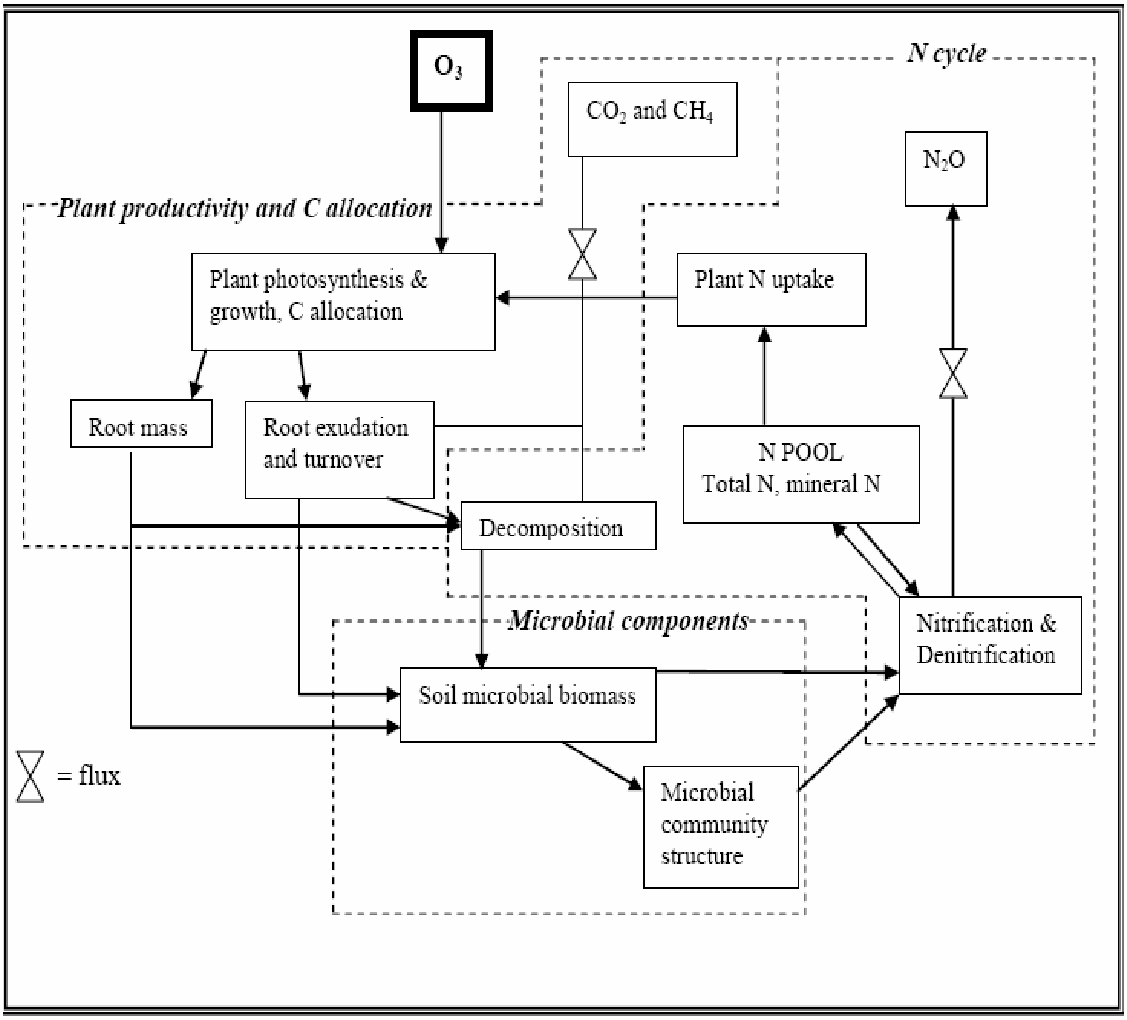

Fig.1. - Conceptual model of plant and soil interdependencies on responses to elevated O_3.

Tropospheric ozone may affect N cycling by altering plant litter production and available substrates for microbial metabolism. Ozone is known to impair plant metabolism leading to yield reduction in agricultural crops. Cereals are highly sensitive to O_3 and have shown decreased yields with increasing O_3 levels (Heagle, 1989).

India has to produce 380 million tonnes against the present production of 206 million tonnes of food grain per annum in order to feed a population of 1.4

billion by 2025. Rice-wheat is one of the major cropping system in India. Recent reports have indicated decline in rice-wheat yields over the past few years (Pathak *et al.,* 2003). There may be several reasons for stagnating/declining yields. One of the main reasons is the degradation of the natural resource base. Another major reason given for declining yields is the potential of ground level ozone to cause yield loss in sensitive crops. Ozone affects plant productivity and chemistry, which might change rates of organic C turnover and affect the global C cycle (Andersen, 2003; Islam *et al.,* 2000; Larson *et al.,* 2002). Thus, it may be assumed that soil N_2O and CH_4 fluxes will also be altered. However, so far studies on GHG fluxes have only been conducted with forests (Edwards, 1991; McGrady and Andersen, 2000; Loya *et al.,* 2003), peatland (Niemi *et al.,* 2002; Rinnan *et al.,* 2003) or meadows (Kanerva, 2005) which are highly different ecosystems than cropped soils. There is still no knowledge on the effect of surface ozone levels on underground soil processes especially the emission of greenhouse gases from rice soil.

Methane and nitrous oxide are two important greenhouse gases contributing approximately 19% and 5% respectively to enhanced greenhouse effects (IPCC, 2007). Rice fields are considered to be one of the major sources of methane and nitrous oxide emission from soils. Thus the impact of surface ozone on the emission of methane and nitrous oxide from soil needs to be quantified. The proposed research work will be carried out with the following objectives:

a) To assess the impact of surface ozone concentrations on methane and nitrous oxide emissions from rice soil.

b) To quantify the effect of increased surface ozone on growth and yield of rice.

2. REVIEW OF LITERATURE

2.1. Introduction

Ozone is a special form of oxygen where three oxygen atoms form one molecule of ozone (O_3) and is a highly reactive oxidant. It reacts readily with any chemical compound, both organic and inorganic, that is present in a reduced state. Ozone can be either “good or bad” depending upon where it is in the atmosphere. Approximately 90 per cent of the atmospheric ozone layer is located in the stratosphere (which represents the atmospheric layer between 10 and 100 km height above the earth surface). This ozone layer formed in the stratosphere is a very efficient UV scavenger. Without the protective action of stratospheric ozone against ultraviolet radiation, which prevents high UV levels at the surface, no terrestrial life on earth would be possible since ultraviolet radiation breaks the double-strands of the DNA, which contains the genetic information of any living being. While at present a reduction of the ozone layer in the stratosphere is being observed, the opposite happens in the atmospheric boundary layer of our planet, the troposphere. Tropospheric ozone contributes only 10 per cent to the total ozone column, but its concentrations have been steadily rising during the past one hundred years**.**

In the troposphere, ozone is a major secondary air pollutant, produced by a complex series of photochemical reactions from primary precursor emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs). High concentrations of ozone are associated with hot sunny weather and occur over wide areas. The adverse effects of ozone on plants were first identified in the 1950s, and it is now recognized as the most important rural air pollutant, affecting human health and materials, as well as vegetation. Ozone (O_3) is part and parcel of global climatic change. Although ozone at the ground level is also a greenhouse gas as it absorbs outgoing long wave radiation and plays a role in regulating our air temperature contributing to about 7 per cent to the total warming effect (Kurpa, S.V., 1997)**.** It also absorbs solar radiation, in particular the UV-B radiation.

2.2. Chemistry of Tropospheric O_3 Formation

Ozone is a pollutant that is formed in the troposphere from a complex series of sunlight driven reactions between nitrogen oxides ($NOx=NO+NO_2$), carbon monoxide (CO), and hydrocarbons, and it is also transported into the troposphere from the stratosphere. The primary source of NOx to the troposphere is fossil-fuel combustion. Secondary sources of NOx include biomass burning, lightning, and soils. Hydrocarbons are emitted from a range of human activities, including fossil fuel combustion, direct evaporation of fuel, solvent use and chemical manufacturing. Terrestrial vegetation also provides a large natural source of hydrocarbons. O_3 production occurs via the catalytic reactions of NOx with CO and hydrocarbons in the presence of sunlight. O_3 production is favoured during periods of high temperature and insolation, which typically occur under stagnant high-pressure systems in summer. Stagnant air masses, varying in duration from one to several days, will result in high surface O_3 concentrations (e.g. >80 nl l^{-1}), with other periods of relatively low concentrations (e.g. <40 nl l^{-1}). The average lifetime of O_3 is about 16 hours, and once produced can be transported long distances to rural agricultural and forested area. Thus, surface level O_3 is an inter regional even a continental scale problem.

2.3. Current and background Ozone concentrations

A wide range of O_3 concentration, from tenths to hundreds of ppb, exists simultaneously in the troposphere at any given time. The highest concentrations are usually associated with emission of precursors (NOx, VOC) from urban areas and are often found downwind of these locations. More remote areas can show elevated concentrations during spring and summer. At any certain location O_3 displays daily and annual concentration pattern that reflects the presence and changes in the precursors and scavengers (Monks, 2000). The daily pattern shows an early morning minimum and early afternoon maximum. The concentration varies seasonally, thus it is smaller during winter when the production capacity is lower.

Seasonal variations in ozone concentration show pronounced maxima in summer and autumn seasons and minima in monsoon and winter seasons. Monthly average maximum concentrations in summer ranged from 62 to 95 ppb and 50-82 ppb in autumn during October and November in New Delhi, India (Jain, *et al.*, 2005). On large number of days the surface ozone values at Delhi exceeded the WHO ambient air quality standards (hourly average of 80 ppb) for ozone. Average background O_3 concentration is roughly 20 to 30 nl l^{-1} (ppb) (Finlayson-Pitts, B.J., and Pitts, J.N., 1999). Annual average concentrations of 27 ppb ozone have been reported for the year 1991-92 for Pune, India (Khemani *et al.,* 1995). Studies of background ozone concentrations in the mid-latitude northern hemisphere suggest an increase of 0.5–2% per year (Vingarzan, 2004), which modeling studies suggest is primarily due to rising NOx emissions, augmented by intercontinental transport. Volz and Kley (1998) have reported that background ozone concentration have been increasing from 10-20 ppb at beginning of 20th century to 20-40 ppb in recent years. Tropospheric O_3 is currently viewed as a widespread and growing problem that suppresses crop productivity on a large scale (EPA 1996; Mauzerall and Wang, 2001; Fuhrer and Booker, 2003). The problem was originally perceived to be limited in nature, confined to urban centres, proximity to power plants, and areas downwind or nearby these sources. However, the scale of the problem has increased in scope in the last 25 years as a result of increasing population densities, industrialization and transportation-related activities in large parts of the world, particularly in the less developed countries. In addition there is increased recognition of transboundary transport of O_3 precursors in the troposphere.

Current worldwide average tropospheric O_3 levels were approximately 50 ppb in the year 2000, already 25% above the threshold established for damage to sensitive plants (Fuhrer, *et al.,* 1997). While global mean values have increased from an estimated pre-industrial level of 38 ppb [25–45 ppb, 8-h summer seasonal average (EPA,1996)] to about 50 ppb in 2000, the most pessimistic projections suggest a further increase to 80 ppb by 2100. Most of this increase would be driven by a nearly three-fold increase in NO_X and CH_4 emissions (Prather *et al.,* 2001). It is critical to understand that these global means are comprised of local means, many of which are already substantially above the projections and typically occur sometime during the cropping season.

2.4. Impact on plants

Plant response to O_3 varies with the genus, species, cultivars or variety and genotype. Ozone is deposited from the atmosphere on to plant canopies by diffusion and enters the leaf through stomata. Both acute and chronic O_3 exposures can result in symptoms of foliar injury on sensitive plants. Environmental, biological and cultural (e.g., irrigation) factors that promote stomata opening increase the risk of O_3

injury to plants (Krupa *et al.*, 1998). Ozone causes negative effects on a number of plant processes, including photosynthesis, water use efficiency, rate of senescence, dry matter production, flowering, pollen tube extension and yield (Kurpa, 1997). Fiscus *et al.*, (2005) reported that the inhibitory effects of tropospheric O_3 on crop photosynthesis, growth and yield have been documented in numerous studies over the past 35 years.

Plants can be subjected to acute and chronic exposures of ground-level O_3. An acute exposure consists of relatively high O_3 concentrations (e.g. >80 nl l^{-1}) from a few consecutive hours to days. In comparison, a chronic exposure consists of relatively low O_3 concentrations (e.g. <40 nl l^{-1}) for the entire life of plant, with periodic intermittent or random episodes of high concentrations. Both acute and chronic O_3 exposures can result in symptoms of foliar injury on sensitive plants. Although O_3 is known to cause stomatal closure, that effect appears to be secondary, since electrophysiological studies have demonstrated that O_3 affects stomatal opening only indirectly perhaps by influencing CO_2 fixation or altering hormone level. The amount of active carboxylating (acceptance of CO_2) enzyme, RUBISCO (ribulose biphosphate carboxylase), can be reduced by O_3 (Enyedi *et al.*, 1992). In addition to its effect on shoots, O_3 is known to adversely affect carbon flow to the roots and consequently their biology and biomass. Acute symptoms of ozone damage are necrosis, chlorosis and so-called watermarks. Both acute and chronic O_3 exposures can result in symptoms of foliar injury on sensitive plants.

2.4.1. Effect of ozone on germination

Stewart (1998) found that germination was promoted in seed harvested from *Brassica compestris* in plants in which the terminal raceme was exposed to 100 nl l^{-1} ozone (6 h d^{-1}) on single or multiple occasions during flowering. This response was apparent for all positions on the raceme, suggesting a general effect on seed development. By contrast, in seed from plants in which the vegetative and reproductive structures were both exposed to 70 nl l^{-1} ozone for 10 days before first flowering, although the final germination percentage was unaffected, it delayed germination. Moreover, Stewart (1998) reported that exposure of the flowering spikes of four populations of *Plantago major* to 120 nl l^{-1} ozone for 9 days during flowering (7 h d^{-1}) invoked differing effect on seed germination. Thus, exposure had no effect on the rate or extent of germination in Sibton, even though mean seed weight was significantly increased, but reduced both parameters at all positions on the exposed spike in Lullington. Exposure to 70 nl l^{-1} ozone for 7 days also reduced the germination rate and percentage germination for seed from capsules on the terminal third of the spike, but not for seed from the basal capsules.

Stewart (1998) also noted that some seeds germinated precociously within the pods of *Brassica compestris* following exposure to ozone, particularly in the older, more mature pods. Precocious germination has also been recorded for *Brassica campestris* cv. Macro and *Brassica napus* cv. Lair (Brown and Dyer, 1991) following ozone treatment. Johnson-Flanagan and Spencer (1994), Petruzzeli *et al.,* (1994), Ward *et al.,* (1995) and Parcy *et al.,* (1997) noticed that ABA and ethylene are both known to have a regulatory role in seed maturation and germination although the mechanisms responsible have still to be identified as exposure to ozone has also been shown to promote ethylene production (Mehlhorn and Wellburn, 1987), suggesting a possible causal link.

2.4.2. Effect of ozone on plant growth

High concentration ozone in the atmosphere can also affect plant growth and reproduction. It is capable of inhibiting photosynthesis, carbohydrate production and altering carbon allocation to roots and stems and reducing carbohydrate formation of mycorrhizae (a symbiotic fungus/root relationship), uptake of important minerals, e.g., nitrogen, phosphorus, potassium and sulphur, and root and stem growth. Sensitivity to ozone is defined as the relative change induced by ozone on plant growth, morphology or yield and depends on plant species, cultivar, developmental stage and experimental conditions. Karberg *et al.,* (2005) reported that the elevated O_3 is known to decrease net photosynthesis via oxidative damage to cell membranes, especially chloroplasts. In the leaves of crop species exposed long term, the onset of senescence is advanced and accelerated catalysis leads to the rapid loss of protein and chlorophyll (Grandjean and Fuhrer, 1989). Chlorotic mottle of leaves, early leaf senescence and possibly increased susceptibility to diseases are problems incurred by cucurbit species in Southern Ontario each year due to ozone exposure (Ormrod, 1980). Amundson *et al.,* (1987) found that exposure of winter wheat before anthesis reduced grain number. Decreased rate of photosynthesis during ozone exposure in *Brassica campestris* might have been sufficient to affect carbohydrate accumulation (Stewart, 1998). As carbohydrate provide the metabolic substrates required as an energy source in germinating pollen, any reduction in carbohydrate content might adversely affect the success of germination (Stanley, 1971). Reich (1987) demonstrated that readily transpiring plants grown under moist soil conditions are more susceptible to ozone than plants grown under a slight drought stress. Ozone induces premature senescence in *Achillea ptarmica*, *E. cannabinum* and *Plantago lanceolata* (Franzaring, *et al.*, 2000). O_3 reduces root growth more than shoot growth in a wide range of plant species (Cooley and Manning, 1987). Most of the work to date has concentrated on crop plants from temperate regions, whereas little has been done on tropical plants.

2.4.3. Effect of ozone on reproduction

Most studies of the effect of ozone on the performance of agricultural and native species have involved exposure of both vegetative and reproductive structures, making it impossible to distinguish direct effects on the reproductive structures from indirect effects mediated via injury to the vegetative organs or alterations in the production and partitioning of assimilates. Study on petunia (*Petunia* x *hybrida*) showed that ozone might alter the topography of stigmatal surface (Feder and Shrier, 1990), suggesting a direct effect on the maternal structures. Studies of oilseed rape *Brassica napus*' (Bosac, 1992; Bosac *et al.*, 1998), Wisconsin Fast Plants (*Brassica compestris*, Stewart *et al.*, 1996; Stewart,1998) and *Plantago major* (Stewart,1998) provide evidence that exposure to realistic ozone episodes at critical developmental stages can influence the reproductive structures directly, promoting significant effect on floral development, seed yield and quality and seedling vigour.

2.4.3.1. Effect of ozone on pollen germination and pollen tube growth

The availability of viable pollen and sufficient number of germinating pollen grains, and the successful growth of the pollen tube to the ovule, are of fundamental importance for sexual reproduction. Few studies have examined the effect of ozone, most have shown that exposure of pollen either *in vivo* on the anthers (Feder and Campbell, 1968) or *in vitro* (Feder and Campbell, 1968; Masaru *et al.*, 1976; Hormaza *et al.*, 1996) reduces germination and / or tube growth in various species. Pollen from tomato (*Lycopersicon esculentum*) and petunia (*Petunia* x *hybrida)* (Krause *et al.*, 1975), lily (*Lilium longiflorum*', Masaru *et al.*,1976) and oil seed rape (*Brassica napus* cv Libravo, Bosac *et al.*,1993) has been reported to be insensitive even to relatively high concentrations of ozone under some exposure conditions. Stewart (1998) showed that in populations of *Plantago major* vegetative growth was most affected in the absence of visible injury (Sibton and Lullington) also exhibited the greatest effects on germination. Exposure concentration and conditions are also important in determining the sensitivity of pollen. For example, Hormaza *et al.,* (1996) reported that reductions in pollen germination and tube growth, induced when the pollen of various fruit and nut tree species- apricot (*Prunus armeniaca*), apple (*Malus domestica*), nectarine and peach (*Prunus persica*), pear (*Pyrus communis*) and almond (*Prunus dulcis*) was exposed *in vitro* to 20, 40 or 60 nl l^{-1} ozone for 4 hrs were directly related to exposure concentration in most species.

Stewart (1998) reported that exposure of *Brassica compestris* pollen to 120 nl 1^{-1} ozone for 6 hrs had significant effects on suggesting the existence of a threshold concentration for damage.

2.4.3.2. Effect of ozone on floral initiation and development

Exposure to ozone has been reported to delay flowering in various species, including soybean (*Glycine max*, Amundson *et al.*, 1986), cotton (*Gossypium hirsutum*, Oshima *et al.*, 1979), duckweed (*Lemna perpusilla*, Feder and Sullivan, 1969; Feder, 1970), geranium (*Pelargoniu horturum*, Feder, 1970), carnation (*Dianthus caryophyllus*, Feder and Campbell, 1968; Feder, 1970) and buddleia (*Buddleia davidii;* Findley *et al.*, 1997).

Exposure of individual flowers or inflorescences to ozone can affect various reproductive structures and processes and hence reproductive performance, in a range of species. Studies of two oilseed rape cultivars, cv. Tapidor and cv. Libravo, demonstrated that a single 6 hrs exposure of the inflorescences to 100 nl l^{-1} ozone or to a mixture of 100 nl l^{-1} ozone and 30 nl l^{-1} sulphur dioxide, when the flowers were fully open, was sufficient to affect various aspects of reproductive development (Bosac, 1992; Bosac *et al.,* 1993, 1994, 1998).). Similarly, direct exposure of inflorescence to ozone had no significant effect on the timing of bud and flower opening in *B. napus* (Bosac *et al.,* 1994) and *B. campestris* (Stewart, 1998).The impact of ozone on timing of flowering therefore varies markedly between species. Fernandez-Bayon *et al.,* (1993) reported that flower production was significantly reduced in two cultivars of watermelon (*Citrullus lanatus* cvs Suger Baby and De La Reina) and muskmelon *(Cucumis melo* cvs Verde Tendral Tardio and Amarillo Temprano) following 21 days exposure to 70 $nl1^{-1}$ ozone for 6h d^{-1}. Certain species are particularly susceptible to ozone-induced abortion of floral sites; for instance, Bosac *et al.,* (1994) reported that a single 6 h exposure of the inflorescences of *B. napus* cvs Tapidor and Libravo to 100 nl l^{-1} ozone was sufficient to increase flower bud abortion 5 days after exposure.

2.4.4. Effect of ozone on plant biochemical processes

In higher plants ozone treatment causes inhibition of photosynthesis (Bennet and Hill, 1974). Photosynthesis is disturbed in several ways, like decrease of stomatal conductance (Farage *et al.,* 1991) and inhibition of CO_2 assimilation (Doming and Heath, 1985). The latter occurs due to oxidation of the –SH groups of Rubisco (Pell *et al.,* 1997). Ozone causes decreases in both the light and dark reactions of photosynthesis.

Ozone after passing through the stomatal pore reacts with organic molecules (e.g. ethylene, isoprene) in the intercellular air space or with components of the extra cellular fluid. In both cases, secondary oxidants (e.g. primary ozonides, hydroxyhydroperoxides) may be formed, which in turn could react with the protein component of the cell membrane (Banerjee *et al.,* 1992). This reaction is prevented to some extent by the presence of radical scavengers, such as ascorbic acid and polyamines (Runeckles *et al.,* 1992). Formaldehyde, formate and acetate accumulate in damaged tissue, possibly as a result of the reaction between ozone and ethylene or between ozone and the phenylpropanoid residues of lignin (Wellburn *et al.,* 1994). There is evidence that ethylene formation determines the sensitivity of plants to ozone (Wenzel *et al.,* 1995). High levels of ozone cause target cells to collapse, leading to local visible tissue destruction. The effect on the plasma membrane can cause changes in membrane functions that may affect the internal concentrations of ions (e.g. Ca^{2+}) (Heath *et al.,* 1988). This changes the osmotic potential of the cytoplasm, which in turn can reduce photosynthetic processes in the chloroplasts.

Reduction in carbon dioxide fixation by the enzyme ribulosebisphosphate carboxylase is a typical symptom found in leaves exposed to ozone over longer periods of time (Lehnherr, *et al.,* 1988). Further inhibition of carbon dioxide assimilation results from direct or indirect inhibition of stomatal opening that reduces uptake (Saurer *et al.*, 1991). Stimulated dark respiration often occurs together with reduced photosynthesis, probably due to increased respiration associated with maintenance and repair (Amthor *et al.*, 1988). The combined effects of reduced assimilation and increased respiratory loss of carbon dioxide consist of an overall reduction of assimilate production and export from the source leaves.

The nitrogen metabolic cycle of the plants is mainly affected by ozone through changes in the amino acid and protein contents (Rowland *et al.*, 1988). Ting and Mukerji (1971) observed an increased quantity of amino acids in pine needles (*Pinus taeda* and *Pinus strobus*) after fumigation with ozone and also an increase in proteins. Ozone was also found to distort nitrite and nitrate reductase, and impairs nitrogen metabolism (Tingey *et al.*, 1973; Leffler and Cherry, 1974). Soluble protein contents decreased with increasing ozone concentration, but ozone can decrease Rubisco contents and increase the antioxidant enzymes at the same time.

Ozone exposed pollen maize on biochemical analysis showed increase in free amino acids and decrease in reducing and neutral sugar contents (Mumford *et al.*, 1972). Seed protein content increases with ozone concentration in soybean (Kress and Miller, 1983; Mulchi *et al.*, 1988) and wheat (Kress and Miller, 1983; Mulchi *et al.*, 1986; Pleijel *et al.*, 1989; Fuhrer *et al.*, 1990; Finnan *et al.*, 1996; Rudorff *et al.*, 1996; Pleijel *et al.*, 1997), but is decreased in oilseed rape (Bosac *et al.*, 1998; Ollerenshaw *et al.*, 1999). Decrease in soluble carbohydrate or solids have been noted for both grain (oilseed rape, Bosac *et al.*, 1998) and fruit crops (watermelon, Gimeno *et al.*, 1999). In Lima bean (*Phaseolus lunatus*), exposure to ozone increased the concentrations of nitrogen and several essential amino acids in the seed (Meredith *et al.*, 1986), while the calcium, magnesium, potassium and phosphorus content of the grain was increased in spring wheat (Fuhrer *et al.*, 1990).

2.4.5. Effect of ozone on seed, fruit yield and other yield components

Numerous studies have shown that seed and fruit yield are commonly reduced in wide range of agricultural and native species, not only when the ozone levels are experimentally increased, but also by the prevailing ozone climate in many parts of the world (Pearson *et al.*, 1996, Mulholland *et al.*, 1998; Bergweiler and Manning, 1999; Ollerenshaw and Lyons, 1999; Ollerenshaw *et al.*, 1999, Takemoto *et al.*, 1988, Reiling and Davison, 1992). These yield losses often been attributed to reductions in photosynthetic activity and assimilate supplies to support reproductive development and seed or fruit growth (Zelitch, 1982; Heagle, 1989; Krupa and Kickert, 1989; Balaguer *et al.,* 1995; Pleijel *et al.,* 1998). However, long-term exposure to low ozone concentrations has been reported to increase seed yield in wheat (Finnan *et al.,* 1996) and soybean (Endress and Grunwald, 1985), and pod number per plant and seed yield in french bean (Sanders *et al.,* 1992). Oshima *et al.,* (1975) reported that the weight of fruit was decreased on exposure to elevated ozone. Oshima *et al.,* (1979) reported that exposure to ozone decreased boll production in cotton, although boll size and the proportions of boll components were unaffected. Similarly, the adverse effect of ozone on floral initiation reported for muskmelon and watermelon by Fernandez-Bayon *et al.,* (1993) reduced fruit numbers and yield (Gimeno *et al.,* 1999).

Finnan *et al.,* (1996) reported that exposure to ozone decreased yield in spring wheat cv. Promessa by reducing both grain weight and the number of grains per ear. Amundson *et al.,* (1987) reported that exposure of wheat commencing at anthesis reduced yield by decreasing only grain weight, suggesting that the timing of exposure might be important in determining the response of individual yield components. Season-long exposure of spring wheat cv. Minaret in open-top chambers to a seasonal mean of 60 nl l^{-1} ozone (7 h d^{-1}) had no significant effect on grain yield (Mulholland *et al.,* 1997). However, when the seasonal mean was increased to 84 nl l^{-1}, yield was reduced by 30% relative to ambient-air control plants as a result of a combination of decreases in the number of ears, grains per ear and per spikelet, and individual grain weight (Mulholland *et al.,* 1998)

Several species have been reported to tolerate substantial foliar injury and or reductions in biomass in the absence of significant yield losses (e.g. potato, *Solanum tuberosum,* Clark *et al.,* 1978; cotton, Oshima *et al.,* 1977; wheat, Mulholland *et al.,* 1997). Wahid *et al.,* (1995) reported reductions of 42% and 37% in the grain yield of two cultivars of rice (*Oryza sativa* L.). This yield reduction was primarily due to the reduction in mean panicle number per plant. Xiaoping Wang (2004) have reported that due to O_3 concentrations in 1990, China, Japan and South Korea lost 1–9% of their yield of wheat, rice and corn and 23–27% of their yield of soybeans and in 2020, assuming no change in agricultural production practices grain loss due to increased levels of O_3 pollution has been projected to increase to 2–16% for wheat, rice and corn and 28–35% for soybeans respectively.

Thus the impact of ozone on specific yield components appears to vary depending on factors including ozone concentration, exposure conditions and the timing of exposure.

2.4.6. Impact of ozone on carbon allocation to different plant parts

Cooley and Manning, (1987) and Spence *et al.,* (1990) reported that elevated O_3 reduce dry matter production. Andersen, (2003), Bortier *et al.,* (2000) and Coleman *et al.,*(1995) proposed that many O_3 induced reactions, such as repair processes and production of secondary compounds in leaves, cause an increase in C demand, and thus a reduction in C allocation below-ground. While Andersen and Rygiewicz (1991), Cooley and Manning (1987), Edwards (1991), Kasurinen *et al.,* (2005), King *et al.,* (2001), Rennenberg *et al.,* (1996) and Spence *et al.,* (1990) stated that this C limitation decreases root biomass and growth as well as root carbohydrate concentrations, effects that have been reported in several species. In addition to reducing root growth, exposure to elevated O_3 can also decrease the amount of root exudates (Edwards *et al.,* 1990; McCool and Menge, 1983). Decomposition of biotic residues is a process by which much organic C is mineralized and returned to the atmosphere as CO_2. Andersen *et al.*, (2001), Boerner and Rebbeck (1995), Scherzer *et al.*, (1998) and Reid *et al.*, (1998) reported that O_3 reduce leaf N content and thus affect quality of needle and leaf litter. However, all knowledge of O_3 related changes in litter quality is related to either forest trees or grasslands. A three year study of Scots pine seedlings led to the conclusion that in a relatively O_3 tolerant species, the chronic effects of O_3 exposure include growth reduction, increased needle abscission and changes in C allocation that are influenced by plant N availability (Utriainen and Holopainen, 2001). Response to ozone in ponderosa pine was greatest when there was low nutrients supplied (Scagel and Andersen, 1997). Significant effects on below-grown respiratory activity were apparent before any reduction of total plant growth was found.

2.4.7. Impact of ozone on the N cycle

Along with changes in biomass production, allocation and rhizodeposition, elevated O_3 may lead to significant alterations in plant residue decomposition (both litter quality and quantity), nutrient cycling and microbial activities. Leaf litter is a major nutrient supply, since plant residues are degraded in the soil by microorganisms and nutrients once bound to the plant material are hence mineralized (Paul and Clark, 1996). In addition to changes in litter quality, elevated O_3 may affect decomposition processes by reducing residue mass input, i.e. litter quantity. This effect has been reported in several species, such as soybean and blackberry (Booker *et al.,* 2005; Kim *et al.,* 1998). Such changes in litter quantity may cause modifications in mineralization of organic N and other nutrients. If, then, soil mineral nutrients such as N are reduced, the whole N cycling process is affected (Booker *et al.,* 2005; Holmes *et al.,* 2003).

Soil microbial activities, i.e. nitrification and denitrification, are of vital importance to N cycling, since nitrification converts ammonium to plant-available nitrate while denitrification reduces nitrate through intermediates to gaseous NO, N_2O and N_2, which are the lost to the atmosphere (Paul and Clark, 1996). O_3-induced changes in N cycling and available C would be expected to slow potential nitrification and denitrification, although there is considerable uncertainty regarding how these changes in microbial activity are modified. A previous study with forest trees only reports no changes (Holmes *et al.,* 2003) in potential microbial activities and the actual processes are yet unstudied. As soil nitrification and denitrification are related to N_2O emissions (Muller *et al.,* 2004), decreases in substrate availability (i.e. changes in quantity and quality of leaf litter, and root exudates) for nitrifying and denitrifying bacteria may also decrease N_2O emissions.

2.4.8. Impact of ozone on microbial content

Soil microbial biomass is linked to plant roots and decomposition of plant residue, as the microbes feed on the roots, root exudates or litter (Paul and Clark, 1996). Microbial growth and activity are commonly constrained by the availability of organic C; therefore, a decline in C inputs combined with reduction in the soil N through altered decomposition could lead to shifts in the size and composition of soil microbial biomass and affects the metabolic activities of microbes (Andersen, 2003; Holmes *et al.,* 2003; Islam *et al.,* 2000; Mulchi *et al.,* 1992). The assumed decrease in soil microbial population size may also cause changes in the structure of microbial communities, and this, in turn, may have significant effects on the functioning (including emissions of GHGs and nutrient cycling) of the microbial community and its interaction with the plant community (Andersen, 2003; Yoshida *et al.,* 2001). In addition, alteration of the abundance of certain soil organisms, such as mycorrhizal fungi, may have a greater impact on ecosystem productivity than others (van der Heijden *et al.*, 1998). However, predicting these ecosystem-level changes is extremely difficult, since there are not at all-inclusive studies on the effects of O_3 on the structural or functional components of soil microbial communities. In previous studies, O_3 has led to changes (Phillips *et al.,* 2002; Yoshida *et al.,* 2001) or no changes (Dohrman and Tebbe, 2005; Kasurinen *et al.,* 2005) in soil microbial community structure. All in all, the impact of elevated O_3 on the complicated interactions found in the N cycle and its microbial activities are poorly understood (Andersen, 2003; Bender *et al.*, 2002). These processes are, however, probably significant in determining the magnitude of plant response to O_3. Ozone seems to have very little effect on soil nematodes. It seems to have more of an effect on soil bacteria than soil fungi. Treatment of strawberry fields with high rates of ozone improved colonization of *Trichoderma* when this microbial was used subsequently as an inoculants, so there must have been either an initial knock back of competing microbial or releases of nutrients favorable for *Trichoderma* sp. growth (Pryor, 2001).

2.5. Soil GHG emissions

2.5.1. Methane

Methane (CH_4) with its current concentration of 1774 ppbv is an important greenhouse gas accounting for approximately 19% of the total greenhouse effect atmospheric concentration of CH_4 is increasing at a rate of 0.3% per year against 1.2% in the late 1970s (Prinn, 1995). Rice fields represent globally one of the main sources of CH_4. Rice is generally grown in waterlogged condition, which create an anoxic environment and is conducive for CH_4 production by the anaerobic methanogenic bacteria. Paddy fields have been considered to be one of the most important sources of CH_4. At present, the CH_4 source strength of wetland rice fields is estimated at 60 Tg yr^{-1}, with a range of 20 – 100 Tg yr^{-1} (IPCC, 1996). However, this estimate is still highly tentative.

2.5.1.1. Methanogenesis

Methanogenesis, the biological formation of CH_4, is geo-chemically important process that occurs in all-anaerobic environments in which organic matter undergoes decomposition. The biogenic CH_4 results from the metabolic activity of a small and highly specific bacterial group, which are terminal members of the food chain in their environment and called methanogens. Methane is produced by the reduction of soil organic carbon by methanogens under anaerobic conditions and redox potential of less than –150 mV (Wang *et al.,* 1993). When soil is under oxidized environment, aerobic decomposition occurs with the consequent release of carbon dioxide. Anaerobic conditions occur in wetland rice fields as a result of soil submergence. Water saturation of soil highly limits the transport of O_2 into the soil and within a few hours after submergence, microbial activity renders water-saturated soil practically devoid of O_2. Under this anaerobic condition microorganisms start using alternative electron acceptors in their respiration causing further soil reduction.

The processes regulating transfer of methane to the atmosphere are ebullition, diffusion and vascular transport. Of which the most important is vascular transport followed by ebullition and diffusion.

2.5.1.2. Factors affecting methane emission

Methane production and consumption are biologically mediated processes. Methane emissions from rice fields are affected by weather, water regime, soil properties and various cultural practices like irrigation and drainage, organic amendments, fertilization and rice cultivars. Temperature plays an important role in the rate of activity of soil microorganisms including those involved in methane production and consumption and temperature influences the three phases i.e. anaerobic C-mineralisation, amount of available alternative electron acceptors and methanogenic activity of CH_4 production. Most of the methanogens are neutrophilic, hence CH_4 production is most efficient in a pH range between 6.4 and 7.8 (Jenkins, 1963) and the optimal pH is about 7 (Alexander, 1977; Oremland, 1988). Methanogenesis can only occur in a strictly anaerobic condition redox potential should be between -150 to -230 mv. Availibility of soil organic matter is another important factor influencing the methanogenesis process in soil. Application of organic matter such as manure and crop residues enhances methanogenesis (Chidthaisong *et al.,* 1999). The amount of CH_4 formed in paddy soils is positively correlated with soil organic-C and water-soluble organic-C (Inubushi *et al.,* 1990; Kimura, 1992). For methanogenesis to take place, it is of primary importance that the soils should have enough moisture to create an anoxic condition. Soil texture and mineralogy through their effect on puddling can affect percolation rate and thereby net emission of CH_4 in waterlogged paddy soils (Neue *et al.,* 1990). Clay soils upon drying form crack and thus facilitate the entrapped CH_4 to go into the atmosphere.

2.5.2. Nitrous oxide

Nitrous oxide (N_2O) with its current concentration of 319 ppbv is an important greenhouse gas accounting for approximately 5% of the total greenhouse effect. It is also responsible for the destruction of stratospheric ozone. The concern due to the presence of N_2O in atmosphere becomes greater due to the fact that N_2O has a lifetime of 166 ± 16 years in the atmosphere. Agricultural soils contribute 65% of anthropogenic N_2O emission (Mosier *et al.,* 1998).

Biological processes (denitrification, nitrification, dissimilatory nitrate reduction and assimilatory nitrate reduction) as well as abiological reactions (chemodenitrification) are the possible mechanisms of N_2O emissions from soil. However, it has been established that denitrification and nitrification are the most important mechanisms (Sharawat and Keeney, 1986) others contributing very little to this pool (Webster and Hopkins, 1996).

2.5.2.1. Factors affecting the emissions of nitrous oxide

A range of soil, climate and management factors affect the emissions of N_2O from soils (Sharawat and Keeney, 1986; Webster and Hopkins, 1996; Duxbury *et al.,* 1982). Some of the important findings are presented here. Moisture regime is one of the important factors. The primary effect of water on N_2O production in aerobic and partially aerobic soils is to restrict O_2 levels by reducing the air-water interfacial area within air-filled pores thus producing the anaerobic condition (Davidson, 1992). Oxygen is considered to be inhibitory for denitrifying enzymes (Knowels, 1982) although the critical limit of O_2 varied among different species of denitrifying bacteria. The optimum pH for N_2O emissions via denitrification varies with species and age of organisms and NO_3 concentration but most denitrifiers have optimum pH for growth between 6 and 8. The effect of soil texture on N_2O emissions likely results from physical variations in air and water proportions. Temperature plays a significant role in the process of N_2O emissions. The N_2O emissions increased with increase in soil temperature from up to 40^oC (Blackmer *et al.*, 1980). Denitrifiers use organic C compounds as electron donors for energy and synthesis of cellular constituents. Plant residues, greenmanure and farm yard manure have been reported to increase rates of denitrification (Aulakh, 1988). Plants affect the emissions of N_2O by influencing nitrate and carbon content of soil and partial pressure of oxygen. Plants can directly influence nitrate availability through uptake and assimilation making it unavailable to denitrification.

Since ozone causes reduction in carbon allocation and root exudates, which serves as substrates for GHG emissions, and it also has an impact on soil microbial content, and N cycling, thus there must be some effect on the methane and nitrous oxide emissions from soil.

3. MATERIALS AND METHODS

3.1. Study Area

To meet the above said objectives a field experiment was conducted in the research farm of Indian Agricultural Research Institute (IARI), New Delhi in rice in Kharif 2007, situated at 28°40’ N and 77°12’ E, at an altitude of 228 m above mean sea level. The climate of Delhi is continental type. Average rainfall of this area is 75 cm annually, approximately 80% of which occurs during southwest monsoon. The mean annual maximum and minimum atmospheric temperatures are 35 and 18 ^{o}C, respectively. The soils are well drained with the groundwater table at 6.6 and 10 m deep during the rainy and summer seasons, respectively. The soil of experimental site was alluvial with pH 8.8 and sandy loam in texture (Table 1).

3.2. Experimental setup

3.2.1. Field operation

A field experiment growing rice in open-top chambers was carried out for studying the impact of different ozone concentrations on methane and nitrous oxide emissions from rice soil and also for quantifying the effect on growth and yield of rice in the farms of Indian Agricultural Research Institute (IARI), New Delhi in Kharif 2007. The experiment was carried out in rice (June-November) in open top chambers of 3 meter diameter and 2.5 meter height. Transplanting of PS-5 seedlings was carried out in open-top chambers in crates (size 0.224 m^2). Farmyard manure consisting of well-rotten cattle and buffalo dung and cattle-shed wastes were incorporated into the moist soil 4 week before planting of rice. Urea was added to rice @120 kg ha^{-1} in three splits of 60, 30 and 30 kg ha^{-1} at 0, 30 and 60 DAT. Phosphorus (26.2 kg P ha^{-1}) and potassium (50 kg K ha^{-1}) were applied at the time of transplanting using single super phosphate and muriate of potash, respectively in all treatments (Table 2). $ZnSO_4$ (60 kg ha^{-1}) was applied to all treatments in rice. Irrigation was provided on every alternate day in all treatments to keep soil in saturated condition. Weeds, pests and diseases were controlled as required.

Table 1. Physico-chemical properties of the experimental soil

Parameters	**Values**
Sand (%)	46
Silt (%)	33
Clay (%)	21
Texture class	Sandy loam
Bulk density (g cm^{-3})	1.38
Hydraulic conductivity (cm day^{-1})	3.53
Percolation rate (cm day^{-1})	2.85
pH (1:2::Soil:Water)	8.8
Electrical conductivity (dS m^{-1})	0.437
CEC [C mol (p^{+}) kg^{-1}]	7.3
Organic carbon (%)	0.349
Dissolve organic carbon (%)	0.01873
Total N (kg ha^{-1})	234.27
Ammonical N (kg ha^{-1})	27.77
Nitrate N (kg ha^{-1})	9.62
Available P (kg ha^{-1})	17
Available K (kg ha^{-1})	335

Table 2. Dates of various agronomic operations in the field experiment

Operation	**Date**
Initial Soil sampling	18.07.07
Transplanting of rice	18.07.07
Application of P and K	18.07.07
Application of 1st dose of N fertilizer	18.07.07
Application of 2nd dose of N fertilizer	17.08.07
Second Soil sampling	24.08.07
Application of 3rd dose of N fertilizer	16.09.07
Third Soil sampling	27.09.07
Fourth Soil sampling	08.10.07
Final soil sampling	09.11.07
Harvesting	09.11.07

3.3. Treatments

The experiment was carried out with four treatments arranged in randomized block design with five replications. The treatments were: charcoal filtered air (CF), elevated ozone (EO) and non-filtered control (NF) and chamber less ambient control (Table 3). Charcoal filters were used to adsorb ozone from ambient air blown inside the CF treatment. In NF treatment only air was blown in the open top chambers. The NF treatment was the open top chamber control and the control plot outside the open top chambers was the chamber less ambient control. In EO treatment 25 to 35 ppb of ozone generated using ozone generators were blown into the open top chambers along with the ambient air. Ozone concentrations in OTC were controlled using a flow device to achieve required ozone levels.

Table 3 – Treatments

S. No.	**Treatment**	**Ozone concentration (ppb)**
1.	Chamber less ambient control	Ambient
2.	Non-filtered (NF) control	15-20 % less than ambient
3.	charcoal-filtered (CF**)**	60-70% less than ambient
4.	Elevated Ozone (EO)	Ambient +25-35 ppb

The weekly average ozone concentrations were measured during the experiment period i.e. from the month of July to November. The peak average concentration was observed from 28th August to 18th October (Fig. 2).

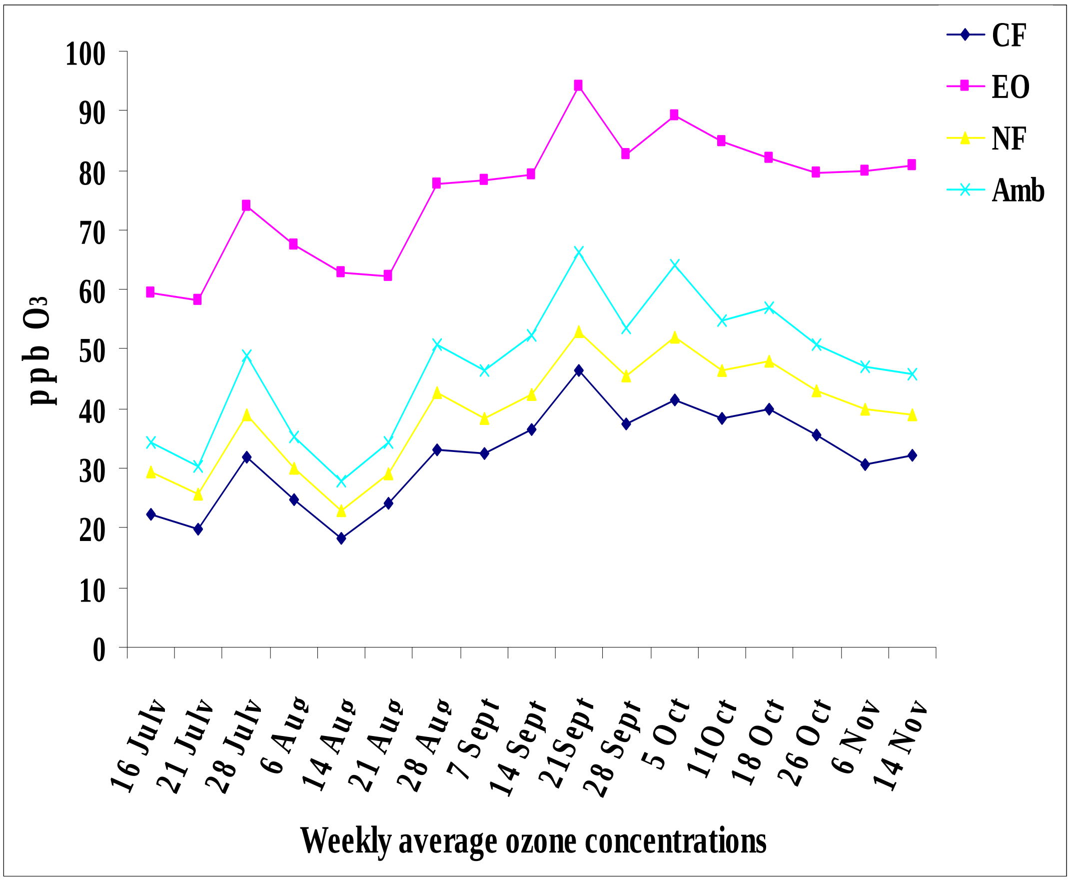

Fig. 2. – Weekly average ozone concentrations (ppb) in different treatments during experimental period.

3.4. Collection of gas samples

3.4.1. Methane

Collection of gas samples were carried out by closed chamber technique as described by Hutchinson and Mosier (1981). Gas samples were collected on 1, 3, 7, 10, 15, 17, 24, 27, 29, 33, 36, 43, 50, 52, 62, 64, 78, 84, 92 and 99 DAT for analysis of methane emissions from different treatments. Chambers of 50 cm × 30 cm × 100 cm made of 6 mm acrylic sheets were used. Aluminium channels placed in the field were used with each chamber. The aluminium channels were inserted 10 cm inside the soil and the channels were filled with water to make the system air tight. A battery operated fan was fixed inside the chamber to homogenize the inside air. A thermometer was also inserted inside to monitor the inside temperature. One 3-way stopcock (Eastern Medikit Ltd. India) was fitted at the top of chamber to collect gas samples. The chamber was thoroughly flushed several times with a 50 ml syringe. Gas samples were drawn with the help of hypodermic needle (24 gauge). After drawing the sample, syringes were made air tight with a three-way stopcock. Gas samples from four replicates of each treatment were taken and their average was taken as representative value for the treatment. Head space volume inside the box was recorded, which was used to calculate flux of CH_4. Gas samples at 0, 30 minute and 1 hr were collected from the chamber.

3.4.1.1. Gas analysis

Methane concentration in the gas samples collected from the field was estimated by Gas Chromatograph (Hewlett Packard 5890 Series II) fitted with a flame ionization detector (FID) and 6’ x 1/8” stainless steel column packed with (Porapak N). Column, injector and detector temperatures were 60°C, 120°C and 120°C, respectively. The carrier gas was N_2 with a flow rate of 14 ml min^{-1}. A GC-computer interface was used to plot and measure the peak area. Methane standard of 5 ppmV was used.

3.4.1.2. Calculation of CH_4 flux

Cross sectional area of the chamber = $A\ m^2$

Headspace = $H\ m$

Volume of headspace = $AHm^3 = 1000 \times AH\ L$

CH_4 concentration at 0 time = Co

CH_4 concentration after time t = C_t

Change in concentration in time t = $(C_t - C_o)$ ppmV

= $(C_t - C_o)\ \mu l\ l^{-1}$

Volume of CH_4 evolved in time t = $(C_t - C_o)\ \mu l\ l^{-1} \times 1000\ AH\ L$

= $(C_t - C_o) \times AH$ ml

When t is in hours, then flux = $[(C_t - C_o) \times AH)/ (A \times t)$ ml $m^{-2}\ h^{-1}$

Now 22.4ml of CH_4 is 16 mg at STP

Hence, Flux = $[(Ct - Co)/t] \times H \times 16/22.4 \times 10000 \times 24$ mg $ha^{-1}\ d^{-1}$

3.4.2. Nitrous oxide

Collection of gas samples were carried out for analysis of nitrous oxide emissions by closed chamber technique as described by Hutchinson and Mosier (1981) and as earlier used in this laboratory (Bhatia *et al.,*2005). Chambers of 50 cm × 30 cm × 100 cm were made of 6 mm acrylic sheets. Aluminium channels placed in the field were used with each chamber. The channels were inserted 10 cm inside the soil and were filled with water to make the system air-tight. One 3-way stopcock (Eastern Medikit Ltd. India) was fitted at the top of chamber to collect gas samples. The chamber was thoroughly flushed several times with a 50 ml syringe to homogenize the inside air. Gas samples were drawn into a 50 ml syringe with the help of hypodermic needle (24 gauge). After drawing the sample, chambers were made air tight with a three-way stopcock. Gas samples from four replicates of each treatment were taken and their average was taken as representative value for the treatment. Head space volume inside the box was recorded, which was used to calculate flux of nitrous oxide. Gas samples at 0, 30 minute and 1 hr were collected from the chamber.

3.4.2.1. Gas sample analysis

Nitrous oxide concentration in the gas samples collected from the fields was estimated by Gas Chromatograph (Hewlett Packard 5890 Series II) fitted with an electron capture detector (ECD) and 6’ x 1/8” stainless steel column packed with (Porapak N). Column, injector, and detector temperatures were 50°C, 120°C and 350°C, respectively. The carrier gas was N_2 with a flow rate of 14 ml min^{-1}. Hewlett Packard integrator was used to plot and measure the peak area. A N_2O standard (500 ppbv) was obtained from National Physical Laboratory, New Delhi. A compressed air cylinder was then calibrated against this standard. The concentration of this gas was recorded as 313 ppbV, which was used as secondary standard.

3.4.2.2. Calculation of N_2O flux

Cross sectional area of the chamber = A m^2
Headspace = H m
Volume of headspace = AHm^3 = 1000 x AH L
N_2O concentration at 0 time = Co
N_2O concentration after time t = Ct
Change in concentration in time t = $(C_t - C_o)$ ppbv
= $(C_t - C_o)$ nl l^{-1}
Volume of N_2O evolved in time t = $(C_t - C_o)$ nl l^{-1} x 1000 AH L
= $(C_t - C_o)$ x AH µl

When t is in hours, then flux is

$$F = [(C_t - C_o) \times AH)/(A \times t)\ \mu l m^{-2}\ h^{-1}$$

$$= Y\ \mu l\ m^{-2}\ h^{-1}$$

Now 22.4µl of N_2O is 44 µg at STP
So, Y µl of N_2O is (44xY/22.4) µg at STP
Therefore, Flux = Y x 44/22.4 µg $m^{-2}h^{-1}$
Hence, Flux = $[(C_t - C_o)/t]$ x H x 44/22.4 µg $m^{-2}h^{-1}$
So, for one hectare /day N_2O

$$\text{Flux} = \frac{[(Ct - Co)/t] \times H \times 44/22.4 \times 10000 \times 24\ \text{mg}}{1000}$$

$$N_2O\text{-}N \text{ flux mg ha}^{-1}\text{ d}^{-1} = \frac{[(Ct - Co)/t] \times H \times 44 \times 240 \times 28 \text{ mg ha}^{-1}\text{ d}^{-1}}{22.4 \times 44}$$

$$= [(Ct - Co)/t] \times 300 \text{ mg ha}^{-1}\text{ d}^{-1}$$

3.5. Soil Sample analysis

Soil samples from 0-15 cm soil layer at 3 locations in each treatment were collected using a core sampler of 8 cm diameter on 0, 36, 69, 80 and 111 DAT and analyzed for soil available N, total N and moisture content. The entire volume of soil was weighed and mixed thoroughly and a sub-sample was taken to determine dry weight. The fresh soil was air-dried for 7 days, sieved through a 2-mm screen, mixed and stored in sealed plastic jars for analysis. Representative sub-samples were drawn and then analyzed for different soil parameters using standard procedures (Table 4). Initial soil samples were analyzed to determine the physico-chemical properties. Soil samples collected at the time of harvest were also analyzed for pH and electrical conductivity (EC). Changes in soil fertility was assessed in terms of changes in soil C dynamics. Soil samples collected at 0, 36, 69, 80 and 111 DAT were analyzed for soil organic carbon and dissolved organic carbon.

3.6. Plant sample collection

Plant samples representative for growth parameters such as root length, shoot length, root dry weight and shoot dry weight were collected at 99 DAT and the crop was harvested at 111 DAT. Yield related parameters such as number of tillers, number of panicles per hill, number of filled grains per panicle, grain yield, straw yield and harvest index were recorded after the final harvest.

3.7. Global warming potential and carbon efficiency ratio

Global warming potential is an index defined as the cumulative radiative forcing between the present and some chosen later time '*horizon*' caused by a unit mass of gas emitted now. It is used to compare the effectiveness of each greenhouse gas to trap heat in the atmosphere relative to some standard gas, by convention CO_2. The GWP for N_2O is 310 and GWP for CH_4 is 21 when GWP value for CO_2 is taken as 1. The GWP of different treatments were calculated using the following equation (Watson *et al.,* 1996).

$$GWP = N_2O * 310 + CH_4 * 21$$

Table 4. Methods of soil analysis

Parameters	***Method***	***Reference***
Mechanical analysis	Bouyoucos hydrometer	Piper (1966)
Soil Moisture content	Gravimetric	Piper (1966)
Hydraulic conductivity	Constant head method	Klute and Dirksen (1986)
pH (1:2 :: Soil: Water)	Potentiometric	Jackson (1967)
Electrical conductivity (1:2 :: Soil: Water)	Conductimetric	Jackson (1967)
Cation exchange capacity (CEC)	$BaCl_2$	Jackson (1967)
Organic carbon	Walkley and Black	Jackson (1967)
Dissolve organic carbon	Hot water extractable	Ghani *et al.*(2003)
Total Nitrogen	Kjeldahl method	Page *et al.* (1982)
Ammoniacal Nitrogen	KCl extraction and steam distillation method	(Keeney and Nelson 1982)
Nitrate Nitrogen	KCl extraction and steam distillation method	(Keeney and Nelson 1982)
Available P	Olsen method	Olsen *et al.* (1954)
Available K	NH_4 OAC (pH 7.0)	Jackson (1967)

The carbon equivalent emissions (CEE) and carbon efficiency ratio (CER) of the treatments were calculated using the following equations.

$$\text{CEE} = \text{GWP}*12/44$$

$$\text{CER} = \text{Grain yield (in terms of C) of the rice} / \text{CEE}.$$

3.8. Data Analysis

Statistical analysis of the data were done using MSTATC statistical package. Analysis of variance was done to test whether the differences were statistically significant. Unless indicated otherwise, differences were considered only when significant at $P<0.05$.

4. RESULT AND DISCUSSION

4.1. Methane emission from rice soil under different ozone levels

The flux of CH_4 fluctuated between - 30.76 mg m^{-2} d^{-1} to 168.79 mg $m^{-2}d^{-1}$ during the total crop growing period (Fig.3). Lower emissions of methane were observed during the initial crop growth period and the methane flux was almost same in all the treatments till 24 DAT. Subsequently some difference in the methane flux was observed and the maximum emission of methane occurred between 43 to 50 DAT in all the treatments. The peak emission of 168.8 mg $m^{-2}d^{-1}$ was obtained on 43 DAT in the charcoal filtered treatment and this coincided with the maximum tillering stage in rice. The use of charcoal filters which lowered the ozone concentrations by around 65% led to an average increase in daily methane emission by 17% over the non filtered control, whereas the presence of elevated ozone decreased the average daily methane emission by 32% over the non filtered control. There was found to be low dissolved organic carbon availability (Fig.8) under the elevated ozone treatment, probably because of lowered carbon allocation to the roots which resulted in lower root weight and lesser amount of root exudates. Therefore, in this experiment the flux of CH_4 was dictated by the availability of carbon substrate. So it can be inferred that elevated ozone might have a negative impact on methane emission.

With every dose of N application there was a small peak of methane flux observed in all the treatments. The additional amount of N provided might have increased the activity of the microorganisms, involved in the production of methane (Jain *et al.*, 2000) resulting in higher emission. Negative flux of methane emission was also observed during the later stage of crop growth. The aerobic conditions prevailing in soil after 84 DAT might have led to favaourable conditions for the growth of methanotrophs resulting in an uptake of CH_4 and thus negative flux of methane were observed on 99 DAT in charcoal filtered, non filtered and ambient controlled treatment and from 84 DAT onwards in case of elevated ozone treatment.

The amount of CH_4 formed in paddy soils was positively correlated with several soil parameters such as the content of organic-C and mineralizable-N (Inubushi *et al.*, 1990; Kimura, 1992). Better crop growth in the charcoal filtered

Fig 3CH4 graph.

Cumulative figure4,5

treatment resulted in higher amount of root exudates providing substrates for methanogenesis.

The cumulative seasonal methane emission was significantly effected by different ozone concentrations in our experiment. The cumulative seasonal methane emission was observed to be the highest in charcoal - filtered treatment at 5.31 g m^{-2} and the lowest cumulative methane emission was observed in the elevated - ozone treatment at 3.07 g m^{-2} (Fig.4). Under elevated ozone treatment, cumulative methane emission was 29% less than non - filtered control treatment while in charcoal filtered treatment the methane emission was found to be higher by 21% over the non filtered control. In the non - filtered treatment there was a 10 to 20% reduction in the ozone concentrations over the ambient chamber less control, a 12 % increase in methane emissions over the chamber - less ambient control treatment were obtained.

4.2. Nitrous oxide emission from rice soil under different ozone levels

Significant impact of ozone filtration was obtained on the emission of nitrous oxide from soil. The cumulative emissions were also significantly reduced under the elevated ozone treatment. The nitrous oxide emission ranged from 94.27 µg m^{-2} d^{-1} to 1678 µg m^{-2} d^{-1} during the crop growth period (Fig. 6). The N_2O-N flux during initial crop growth period was dictated by fertilizer application. First peak flux of nitrous oxide emission on 3 DAT varied from 1522 to1678 µg m^{-2} d^{-1} under different ozone treatments. This coincided with the first dose of fertilizer application. Subsequently there was a lowering of the emission till the next date of fertilizer application. Similar peaks of N_2O-N flux were observed after every dose of N application, which supplied the substrate for nitrification (NH_4^+-N) and subsequently for denitrification (NO_3^--N). In the soil both the above processes might have occurred simultaneously. The temperature during the summer grown rice remained congenial for denitrification. With irrigation applied on alternate days there was increased production and emission of N_2O-N by nitrification of NH_4^+ nitrogen. The aerobic–anaerobic cycles present due to alternate wetting and drying triggered inter changeable nitrification and denitrification enhancing the N_2O-N emissions (Suratno *et al.,* 1998). Average daily emissions of N_2O-N during the rice crop ranged from 575 µg m^{-2} d^{-1} in elevated ozone to 661 µg m^{-2} d^{-1} in the charcoal

Fig6 n2o

filter treatment. Greater root biomass and C allocation to the soil in the charcoal filter treatment (CF) provided more energy for denitrification under suitable anaerobic conditions, thus resulting in increased N_2O emissions. There was no statistical difference in the average daily emissions in the non filtered control (NF) and ambient chamber less treatments (Amb), implying no significant impact of the open top chambers on the soil nitrogen.

Cumulative seasonal emission of N_2O-N ranged from 47.8 mg m^{-2} in the elevated ozone treatment to 54.6 mg m^{-2} under the charcoal filtered treatment (Fig.5). The cumulative emission of N_2O-N in the charcoal filtered treatment was 5% higher than the non filtered control and it was 9% lower in the elevated ozone treatment as compared to the non-filtered control. In the charcoal filter treatment, there was higher availability of organic carbon and greater microbial activity as compared to elevated ozone, which enhanced nitrification and denitrification (in micro-sites) resulting in higher emission of N_2O-N. Lowering in above ground and below ground biomass quantity in the elevated ozone treatment may have caused modifications in mineralization of organic N and other nutrients, thereby reducing the availability of soil N and affecting the whole N cycling process (Booker *et al.,* 2005; Holmes *et al.,* 2003).

4.3. Effect of ozone on growth and yield parameters

4.3.1. Grain yield

The different ozone levels affected the yield parameters significantly. The average number of panicles/hill was the lowest in elevated ozone treatment and highest in charcoal filtered treatment (Table 5). In charcoal filtered treatment, number of panicles/ hill was increased by 9.65% over the non - filtered control and in elevated ozone treatment it decreased by 18.57% over the non filtered control treatment. From the Table 5. it could be observed that the average no. of filled grains/panicle was lowest in elevated ozone treatment and it decreased by 10.14% over the non filtered control. In the charcoal filtered treatment the filled grains/ panicle increased by 10.14% over the non filtered control treatment. This was due to the fact that higher translocation of carbohydrates to sink and thus leading to higher grain filling (Reddy and Reddy, 1989). The data presented in Table 6. clearly indicates that ozone filtration had a significant influence in increasing the grain yield of rice. The

Table 567

grain yield ranged between 116 g m^{-2} to 152 g m^{-2} under different levels of ozone. Grain yield was the highest in the charcoal filtered treatment. In charcoal filtered treatment, grain yield was increased by 16.81% over the non - filtered control. In elevated ozone treatment grain yield decreased by 11.31% over the non filtered control, while in non filtered treatment grain yield increased by 3.15% over the chamber less ambient control treatment. Ozone concentration was always higher in the elevated ozone treatment over the non filtered control. So, it could be inferred that higher levels of ozone had a negative impact on grain yield. Wahid *et al.*, (1995) reported reductions of 42% and 37% in the grain yield of two cultivars of rice (*Oryza sativa* L.). This yield reduction was primarily due to the reduction in mean panicle number per plant. It can be observed that the number of tillers per hill was the lowest in case of elevated ozone and highest in case of charcoal filtered treatment (Table 7.). In charcoal filtered treatment, number of tillers was increased by 22.51% and in elevated ozone treatment decreased by 11.91% over the non filtered control treatment. However, there was statistically significant impact of only elevated ozone treatment on the 1000 grain weight of the rice (Table 7.). Finnan *et al.*, (1996) also reported that exposure to ozone decreased yield in spring wheat by reducing both grain weight and the number of grains per ear.

It could thus be concluded that all grain yield related parameters were significantly affected by elevated levels of ozone. The removal of ozone from ambient air also significantly increased the productivity as could be seen in all the parameters related to the charcoal filter treatment.

4.3.2. Straw Yield

The straw yield was also significantly impacted under different ozone concentrations. It was the highest in charcoal filtered treatment at 199.3 g m^{-2}. In elevated ozone treatment straw yield was the lowest and decreased by 6.29% than non filtered control treatment. From the Table 6. it could be observed that there was significant difference between treatments. There was however no effect of the open top chamber on the straw yield as no significant difference was observed between the ambient chamber less control and the non filtered treatment. Higher straw yield in charcoal filtered was due to higher availability of NH_4^+-N in this treatment. Increased C input in the charcoal filter treatment could have increased the N availability by enhancing N mineralization (Hungate *et al.*, 1996). Also higher tiller production due to favorable condition at the different growth stages increased the photosynthetic assimilation resulting in enhanced dry matter. In the leaves of rice plants exposed to elevated ozone, the onset of senescence was advanced as compared to the non - filtered control and charcoal filtered treatment.

4.3.3. Harvest Index

From the above section it was seen that grain yield and straw yield were lowest in elevated ozone treatment. Similarly both parameters were highest in charcoal filtered treatment. As harvest index is dependent on these two parameters, same trend could be seen in this case also. Harvest index ranged from 0.39 to 0.43 in the different treatments (Table 6).

4.3.4. Root Length and Shoot Length

Root length ranged from 25.42 to 34.48 cm in the given treatments (Table 8). Root length in charcoal filtered treatment increased by 10.51% and in elevated ozone treatment it decreased by 18.52% over the non filtered control treatment. Root length was smaller in elevated ozone treatment and this inhibited the roots to uptake nutrients from soil which resulted in reduced grain yield and straw yield and vice versa in charcoal filtered treatment. Shoot length also showed a similar trend (Table 8).

4.3.5. Root Dry Weight and Shoot Dry Weight

Root dry weight and shoot dry weight was similarly highest in charcoal filtered treatment and lowest in elevated ozone treatment (Table 9). As discussed in the section 4.3.4., it was obvious that elevated ozone had negative impact on shoot length and root length which ultimately led to a decrease in the root and shoot biomass. Ozone is capable of inhibiting photosynthesis, sugar production and altering carbon allocation to roots and stems. Root dry weight and shoot dry weight ranged from 0.56 to 0.76 g per plant and 3.08 to 4.14 g per plant respectively (Table9). Injury due to ozone to the lower leaves of the plant, which act as the main source of photosynthates for root growth, might explain decreases in root and shoot dry mass (Cooley and Manning 1987; Andersen 2003) under elevated ozone treatment.

Table 8 and 9

4.4. Effect of ozone on soil carbon and nitrogen

4.4.1. Organic Carbon

No significant impact on soil organic C was observed under different ozone levels in rice. Organic C content ranged from 0.346% to 0.364% during the crop growth period (Fig 7). Under charcoal filtered treatment, organic C content was highest at 0.364% on 80 DAT. In all other treatments no significant change in organic C could be seen on different days of sampling. Under elevated ozone treatment, the value of organic C was the lowest among all treatments on most of the sampling days. Soil organic carbon is a very stable parameter and is not impacted by short term carbon changes in soil (Banerjee *et al.,* 2006).

4.4.2. Dissolved Organic Carbon (DOC)

Dissolved organic carbon is a labile form of carbon and any short term changes in the carbon dynamics are very rapidly reflected in this parameter. DOC ranged from 0.013% to 0.023% under different treatment and the minimum was observed under elevated ozone treatment (Fig.8). The reduced ozone concentration in the charcoal filtered treatment led to a statistically significant increase in the dissolved organic carbon in soil, probably because of increased root exudation due to higher root carbon allocation as compared to non filtered control treatment. Similarly there was a decline in the DOC parameter under the elevated ozone treatment due to lower root weights in this treatment. In addition to reducing root growth, exposure to elevated O_3 can also decrease the amount of root exudates (Edwards *et al.,* 1990; McCool and Menge, 1983) and the labile C pool.

4.4.3. NH_4^+ - N Concentration in soil

The soil NH_4^+–N concentration varied between 18.91 kg ha^{-1} to 37.72 kg ha^{-1} under the different ozone treatments (Fig.9). A peak of NH_4^+- N concentration was observed on 36 DAT in all the treatments. This increase in concentration was due to the fertilizer applied on 30 DAT which increased the availability of NH_4^+-N in soil. Subsequently the NH_4^+ -N in soil decreased till 69 DAT, probably due to because of plant uptake and also its conversion to NO_3^-– N during the drying phase of soil. At harvest on 111 DAT, low NH_4^+- N concentrations were observed in all treatments. Minimum value was observed in elevated ozone treatment on 111 DAT

Fig oc and doc

In charcoal - filtered treatment, NH_4^+-N concentration on 111 DAT was increased by 20.93% than non - filtered control. Since maximum decrease in value was observed under elevated ozone treatment it could be inferred that elevated ozone had negative impact on NH_4^+- N concentration. O_3-induced changes in N cycling and available C would be expected to slow potential nitrification and denitrification, although there is considerable uncertainty regarding how these changes in microbial activity are modified.

4.4.4. NO_3^-- N concentration in soil

The initial soil NO_3^-– N concentration varied between 9.24 kg ha^{-1} to 10.16 kg ha^{-1} (Fig. 10). No significant impact of ozone filtration was observed on soil NO_3-N concentration during the crop growth period. On 36 DAT in charcoal filtered, NO_3^- –N was increased by 4.08% than non filtered control while in elevated ozone value was lowered by 8.75%. On 111 DAT, NO_3^- – N concentrations were slightly lower than initial concentrations and ranged from 8.55 kg ha^{-1} to 10.42 kg ha^{-1}. Highest concentration of 11.02 kg NO_3^-- N ha^{-1} was observed on 80 DAT in charcoal filtered treatment. Lowest concentration of 8.36 kg NO_3^--N ha^{-1} was observed in elevated ozone treatment at harvest of the crop. In charcoal - filtered treatment on 111 DAT, NO_3^--N was increased by 13.5% than non filtered control. Low nitrate concentrations under elevated ozone treatment were also probably responsible for lower nitrous oxide emission by the denitrification pathway.

4.4.5. Total N

There was no significant impact of ozone filtration on the soil total N concentrations (Fig.11). Elevated ozone levels though had a significant impact on soil N levels. The total N concentration decreased significantly at harvest under the elevated ozone concentration. The concentration ranged from 241 kg ha^{-1} to 196 kg ha^{-1} in the elevated ozone treatment. The decrease in soil total N under elevated ozone treatment was due to reduced carbon allocation to the below ground biomass, which effected the soil carbon and nitrogen mineralization processes, and ultimately affected the N cycling in soil.

Fig nh4,no3 and tort

GWP

4.5. Carbon Equivalent Emissions and Carbon Efficiency Ratio (CER)

Due to higher methane and nitrous oxide emissions under the charcoal – filtered treatment, the carbon equivalent emissions also were higher under the charcoal filtered treatment and were the lowest in elevated ozone treatment. In charcoal filtered treatment GWP was higher by 38.27% than elevated ozone treatment due to higher nitrous oxide and methane emissions (Fig.12). Carbon equivalent emissions ranged from 21.62 g m^{-2} to 35.03 g m^{-2} under four different treatments (Table 10).

The Carbon Efficiency Ratio, (CER) i.e. carbon fixed/ carbon emitted from soil in a fertilizer treatment, is an index of the efficiency of the particular treatment. It was found to be lowest in charcoal - filtered treatment at 2.09 and highest in elevated ozone treatment at 2.57 (Table 10). It could be seen from the table that in charcoal filtered treatment carbon fixed was higher by 24.05% than elevated ozone treatment and simultaneously the carbon emitted was also higher by 38.27% and thus the CER was found to be lower in charcoal filter treatment as compared to elevated ozone. Thus we can conclude that as yields increase on ozone filtration, the carbon emissions may also increase and thereby lowering the efficiency of the treatment.

6. SUMMARY AND CONCLUSION

Ozone (O_3) is a phytotoxic air pollutant produced in the troposphere when the VOC's and oxides of nitrogen emitted by vehicles and industry react in the presence of sunlight. Generation of ozone is based on solar energy, annual patterns may cause higher concentrations during the growing season from May to September in the afternoon. Tropospheric ozone (O_3) is also a greenhouse gas and its concentrations are increasing annually by 0.5±2%. Average background O_3 concentration is roughly 20 to 30 ppb. Nearly one-quarter of the Earth's surface is currently at risk from mean tropospheric ozone in excess of 60 ppbV during midsummer with even greater local concentrations occurring. Elevated surface ozone is known as bad ozone due to its detrimental effect on crop productivity from agricultural point of view. Tropospheric O_3 is currently viewed as a widespread and growing problem that suppresses crop productivity on a large scale. Ozone is known to decrease net photosynthesis via oxidative damage to cell membranes, especially to chloroplasts and consequently to reduce dry matter production. Many ozone induced reactions such as repair processes and production of secondary compounds in leaves, cause an increase in C- demand and thus reduction in C-allocation above and belowground. In addition to reducing root growth, exposure to elevated ozone can also reduce the amount of root exudates, and may affect decomposition processes by reducing residue mass input and may affect N cycling. Ozone affects plant productivity and chemistry, which might change rates of organic C turnover and affect the C cycle. Thus, it may be assumed that soil N_2O and CH_4 fluxes will also be altered. Methane and nitrous oxide are two important greenhouse gases contributing approximately 19% and 5% respectively to enhanced greenhouse effects (IPCC, 2007). Few studies on GHG fluxes under the impact of elevated ozone have only been conducted in forests, peatland and meadows which are highly different ecosystems than cropped soils. Thus, a need was felt to quantify the impact of surface ozone on methane and nitrous oxide emissions from rice soil. Therefore the present investigation was conducted 1) to assess the impact of surface ozone concentrations on methane and nitrous oxide emissions from rice soil and 2) to quantify the effect of increased surface ozone on growth and yield of rice.

To meet the above said objectives a field experiment was conducted in the research farm of Indian Agricultural Research Institute (IARI), New Delhi, in rice (June- November) on alluvial sandy loamy textured soil. The experiment was carried in open top chambers by transplanting PS 5 rice cultivar in crates of size 0.224 m^2 with four treatments arranged in a randomized block design with five replications. Fertilizers were applied according to recommended doses and irrigation was given on alternate days.

Gas samples were collected from the treatments by closed chamber technique on different days. The analysis was carried out by Gas Chromatography using ECD detector for N_2O and using FID detector for CH_4. Soils from different treatments were sampled at regular intervals for analysis of soil physico-chemical properties. Yield and growth parameters were recorded after harvest of crop.

The salient findings emerged out of this investigation are listed below:

1) The temporal as well as cumulative methane emissions were highest in charcoal filtered treatment and lowest in elevated ozone treatment. In charcoal filtered treatment, there was an average increase in daily methane emission by 17% over the non filtered control, whereas the presence of elevated ozone decreased the average daily methane emission by 32% over the non filtered control. The cumulative emissions from charcoal filtered treatment were 21% higher than non filtered treatment and elevated ozone treatment was lowered by 29% over the non filtered treatment and there was significant difference between charcoal filtered, elevated ozone and non filtered treatment.
2) The flux of CH_4 fluctuated between – 30.76 mg m^{-2} d^{-1} to 168.79 mg $m^{-2}d^{-1}$ during the total crop growing period.
3) Average daily emissions of N_2O-N were lowest at 575 µg m^{-2} d^{-1} in elevated ozone and highest at 661 µg m^{-2} d^{-1} in the charcoal filter treatment.
4) Cumulative seasonal emission of N_2O-N in charcoal filter treatment was significantly different from non filtered control treatment. There was no significant difference in non filtered and ambient chamber less control.

5) Significant difference in grain yield was observed within the treatments. The grain yield was lowest in elevated ozone treatment at 116 g m^{-2} and highest in charcoal filtered treatment at 152 g m^{-2} under different levels of ozone.

6) In charcoal filtered treatment, no. of tillers was increased by 22.51% and in elevated ozone treatment decreased by 11.91% over the non filtered control treatment.
7) No. of panicles/ hill in charcoal filtered treatment was increased by 9.65% over the non filtered control and in elevated ozone treatment it decreased by 18.57% over the non filtered control treatment.
8) In elevated ozone treatment average no. of filled grains/panicle was decreased by 10.14% over the non filtered control while in the charcoal filtered treatment the average no. of filled grains/ panicle increased by 10.14% over the non filtered control treatment.
9) Significant impact of elevated ozone treatment on the 1000 grain weight of the crop was observed.
10) Elevated ozone treatment had negative impact on all growth and yield related parameters and therefore a decline in grain and straw yield was observed.
11) Straw yield was highest in charcoal filtered treatment and was significantly different from elevated ozone and non filtered treatment.
12) Harvest index was observed to be highest in charcoal filtered treatment and lowest in elevated ozone treatment.
13) Shoot length and root length were reduced in elevated ozone treatment and increased in the charcoal filtered treatment. Hence, root and shoot dry weight also increased in the charcoal filtered treatment by 5.13% and 12.80% over non filtered control treatment respectively. In elevated ozone treatment root and shoot dry weight decreased by 22.65% and 16.07% over non filtered control treatment respectively.
14) Organic C was highest at 0.364% in charcoal filtered treatment on 80 DAT. No significant change was observed in organic C in the treatments on all sampling days.
15) Significant difference was observed in DOC between charcoal filtered treatment and non filtered control treatment. Dissolved organic carbon was lowest in elevated ozone treatment.
16) NH_4^+ -N and NO_3^- -N was observed to be lowest in elevated ozone treatment and highest in charcoal filtered treatment.

17) Lowest total N concentration was observed in elevated ozone treatment but no significant impact of ozone filtration was observed on the soil total N concentrations.
18) In charcoal filtered treatment GWP was higher by 38.27% than elevated ozone treatment due to higher nitrous oxide and methane emissions. Carbon efficiency ratio was the highest in elevated ozone treatment and lowest in charcoal filtered treatment.

OZONE MEDIATED CHANGES IN METHANE AND NITROUS OXIDE EMISSIONS FROM RICE SOIL

ABSTRACT

Ozone (O_3) is a phytotoxic air pollutant produced in the troposphere where sunlight reacts with VOC's or oxides of nitrogen emitted by vehicles and industry. Since the industrial revolution anthropogenic activity has increased the tropospheric concentrations of ozone. Tropospheric ozone (O_3) is a greenhouse gas and its concentrations are increasing annually by 0.5±2%. Seasonal variations in ozone concentration ranged from 35 ppb-65 ppb during July to October at IARI, New Delhi. Surface ozone is known as bad ozone because of its detrimental effect on crop productivity by decreasing net photosynthesis via oxidative damage to cell membranes, especially to chloroplasts and consequently reducing dry matter production. Ozone affects plant productivity and chemistry, which might change rates of organic C turnover and affect the soil C cycle and N cycle. Thus, it may be assumed that soil N_2O and CH_4 fluxes will also be altered. Methane and nitrous oxide are two important greenhouse gases contributing approximately 19% and 5% respectively to enhanced greenhouse effects. Therefore the present investigation was conducted to assess the impact of surface ozone concentrations on methane and nitrous oxide emissions from rice soil and to quantify the effect of increased surface ozone on growth and yield of rice.

CH_4 and N_2O emissions were highest in charcoal filtered treatment and lowest in elevated ozone filtered treatment. Under elevated ozone treatment, cumulative seasonal CH_4 emissions were reduced by 29% over the non filtered control treatment while the emissions increased by 21% in the charcoal filtered treatment over the non filtered control. The cumulative seasonal N_2O emissions in the charcoal filtered treatment were 5% higher than the non filtered control and were 9% lower in the elevated ozone treatment as compared to the non-filtered control. Soil organic C did not change under different treatments whereas dissolved organic C was the lowest under elevated ozone. Grain yield was significantly impacted by different levels of ozone. It reduced by 11.31% under elevated ozone concentration. Filtration of ozone, which led to sub ambient ozone concentration significantly $_{(P=0.05)}$ increased the grain yield and other growth parameters as compared to the non filtered control. The Carbon Efficiency Ratio (CER) was found to be lowest in charcoal filtered treatment and highest in elevated ozone treatment.

धान-मृदा से ओजोन मध्यस्तित मीथेन एवं नाइट्रस आक्शाइड का उत्सर्जन

सारांश

ओजोन एक पादपविष के रूप में वायु प्रदूषक गैस है जो वाहनों द्वारा उत्सर्जित गैसों नत्रजन आक्शाइडस एवं वाष्पन योग्य जैविक यौगिकों (Volatile organic compounds), एचसी द्वारा सूर्य के प्रकाश की उपस्थिति में रासायनिक अभिक्रिया द्वारा धरातल में निर्मित होती है। औद्यौगिक क्रान्ति व मानवीय स्रोतों से धरातलीय ओजोन के सांद्रण में वृद्धि हुई है। ओजोन एक हरित-गृह गैस है। जिसका सांद्रण 0.5±2.0% की वार्षिक दर से बढ रहा है। भारतीय कृषि अनुसंधान संस्थान, नई दिल्ली में जुलाई से अक्टूबर के मध्य ओजोन का मौसमी वितरण 35-65 पीपीबी के बीच रहा। स्थलीय सतही ओजोन की बढ़ी मात्रा का पौधों पर भी बुरा प्रभाव पाया गया है। जिससे उनमें प्रकाश-संश्लेषण कम होने के कारण कोषिका झिल्ली तथा हरितलवक में क्षति के कारण शुष्क पदार्थ निर्माण में कमी हो जाती है। ओजोन पादप उत्पादकता व उनके रसायन को प्रभावित कर मृदा जैविक कार्बन, कार्बन एवं नत्रजन चक्र को प्रभावित कर सकता है। इस प्रकार धरातल में ओजोन मीथेन एवं नाइट्रस आक्शाइड का उत्सर्जन में परिवर्तन कर सकती है। मीथेन एवं नाइट्रस आक्शाइड दो प्रमुख हरित-गृह गैस है जिनका हरित-गृह गैस क्रमश: 19 एवं 5 % योगदान होता है। सतही ओजोन की बढ़ती मात्रा का प्रभाव, धान-मृदा से ओजोन मध्यस्तित मीथेन एवं नाइट्रस आक्शाइड का उत्सर्जन और धान की वृद्धि तथा उत्पादकता को ध्यान में रखते हुये यह अध्ययन किया गया।

मीथेन एवं नाइट्रस आक्शाइड का उत्सर्जन चारकोल क्षनित उपचार में अधिकतम तथा क्षनित आजोन वाले उपचार में न्यूनतम पाया गया। इलेवेटेड आजोन वाले उपचार में संचयित मीथेन उत्सर्जन क्षनित कन्ट्रोल की तुलना में 29% कम पाया गया। जबकि चारकोल क्षनित उपचार में क्षनित कन्ट्रोल की तुलना में 21% की वृद्धि पायी गयी। संचयित नाइट्रस आक्शाइड का उत्सर्जन चारकोल क्षनित उपचार में कन्ट्रोल की तुलना में 5% अधिक तथा इलेवेटेड आजोन वाले उपचार में 9% की कमी पायी गयी। मृदा जैव-कार्बनिक पदार्थ में विभिन्न उपचारों में कोई अन्तर नहीं, जब कि जैविक-कार्बन इलेवेटेड आजोन वाले उपचार में न्यूनतम पाया गया। दानों की उत्पादकता विभिन्न आजोन वाले उपचारों में निश्चित रूप से प्रभावी रही। दानों की उत्पादकता में कमी इलेवेटेड आजोन वाले उपचार में 11.13% पायी गयी। कार्बन क्षमता अनुपात (सीईआर) चारकोल क्षनित उपचार में अधिकतम तथा क्षनित आजोन वाले उपचार में न्यूनतम पाया गया।

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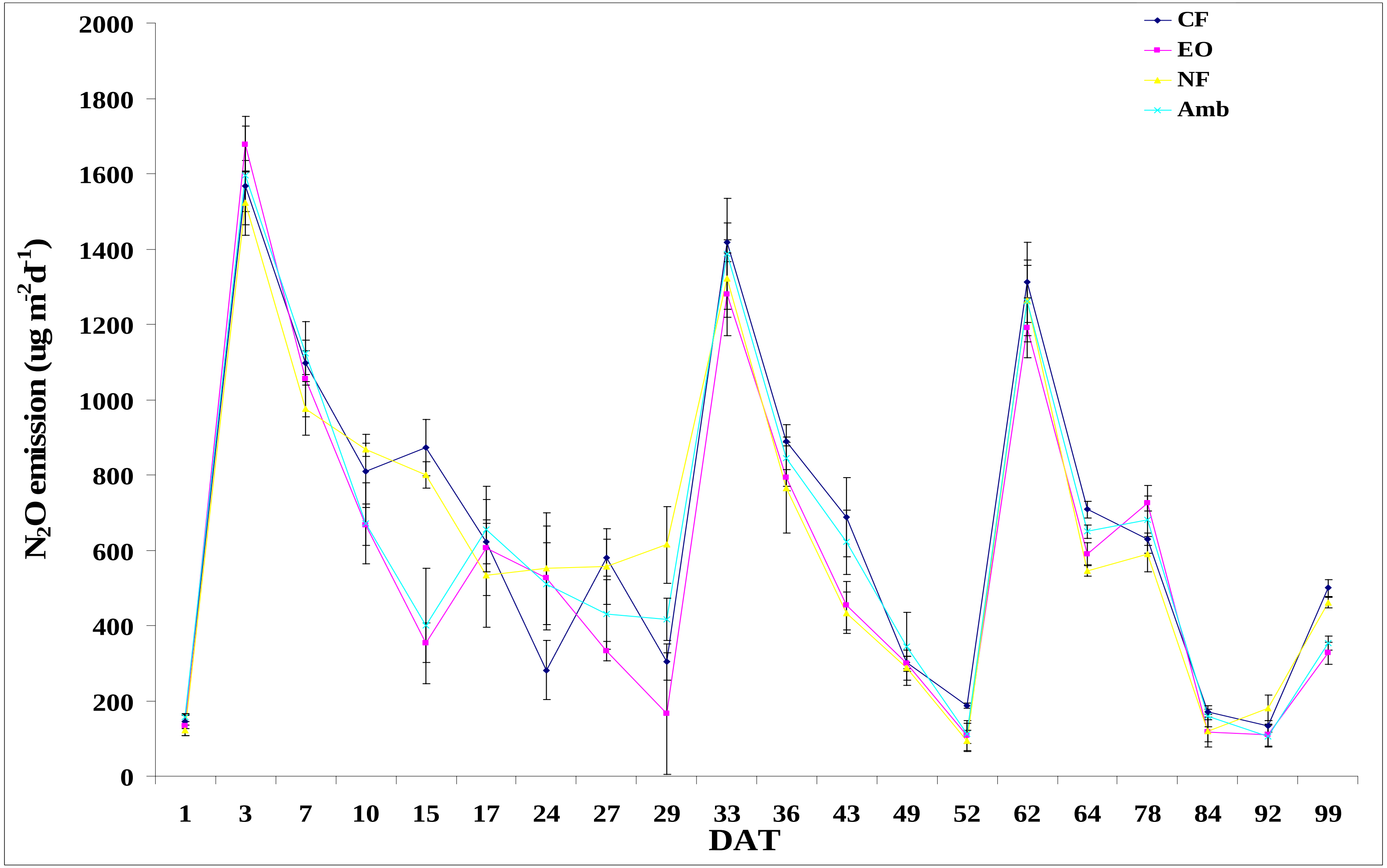

Fig. 6. Emission of N_2O-N from rice soil under different ozone treatments.

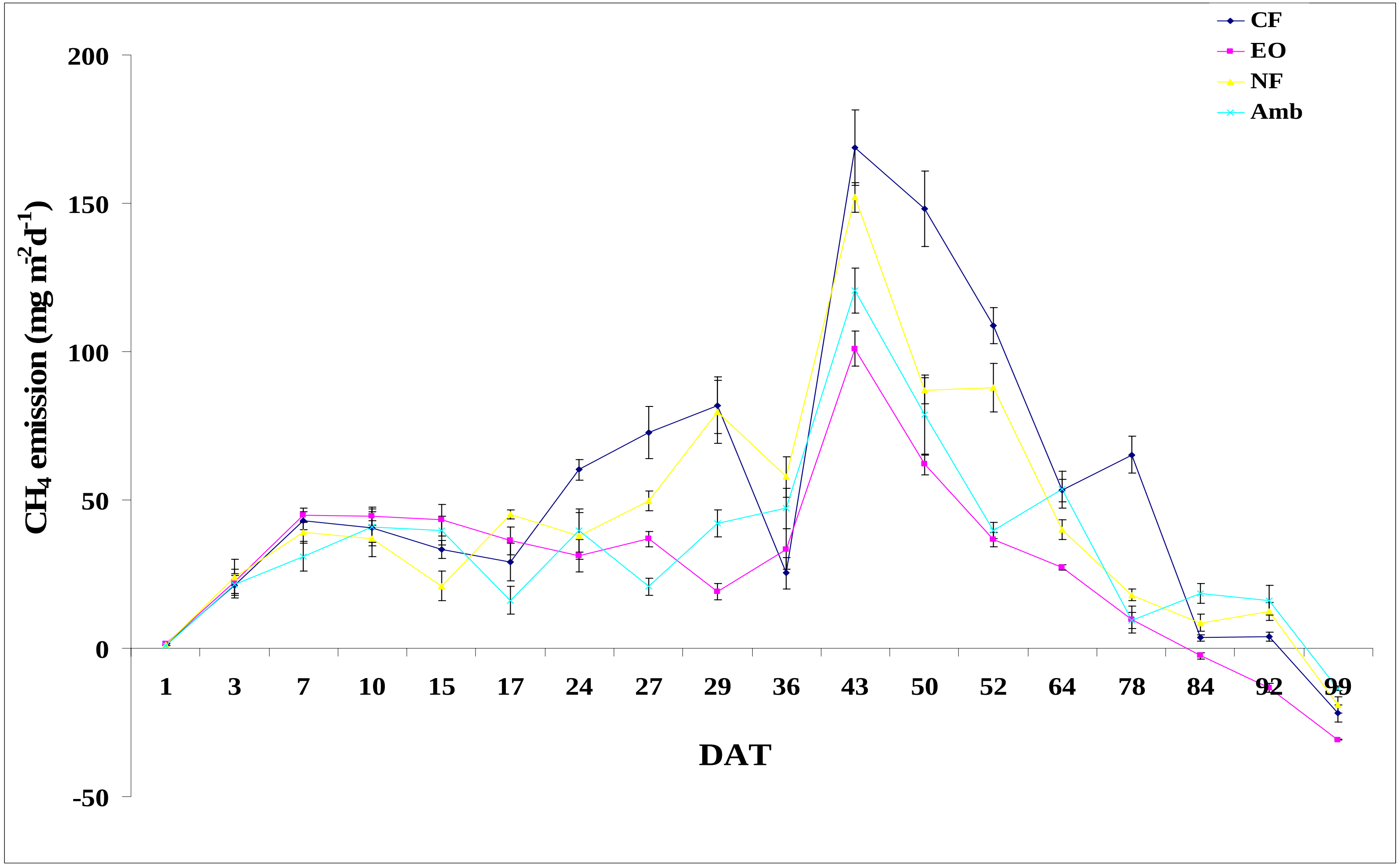

Fig. 3. Emission of CH_4 from rice soil under different ozone treatments.

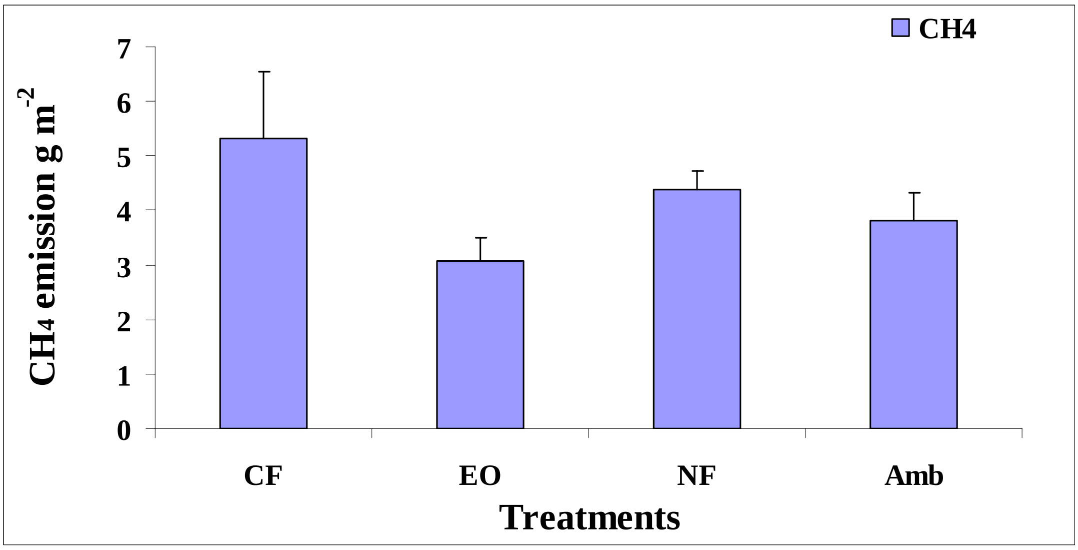

Fig. 4. Cumulative seasonal CH_4 emission from rice soil under different ozone treatments.

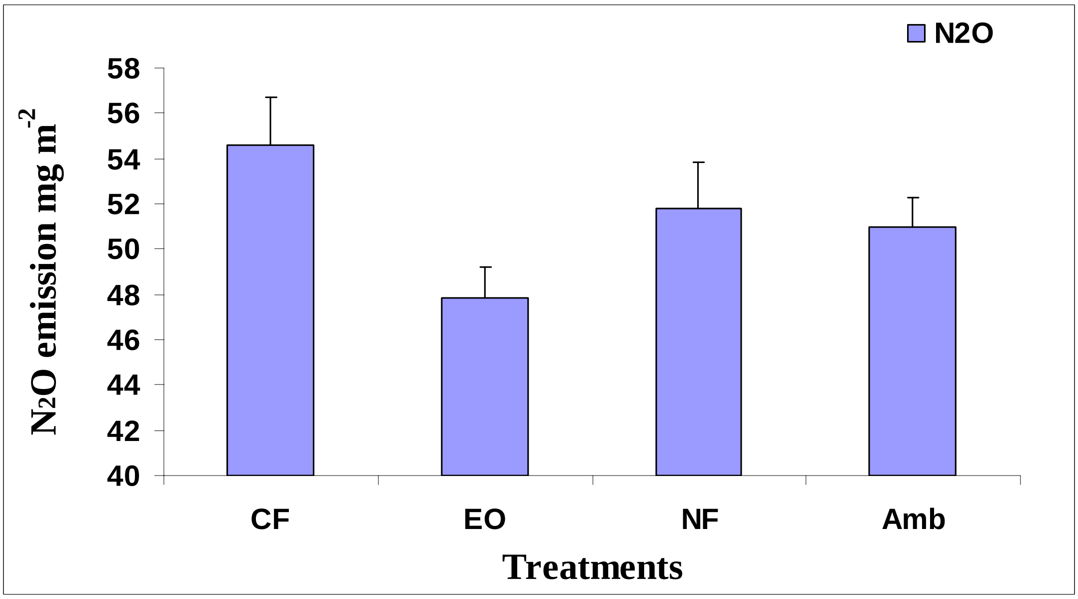

Fig. 5. Cumulative seasonal N_2O-N emission from rice soil under different ozone treatments.

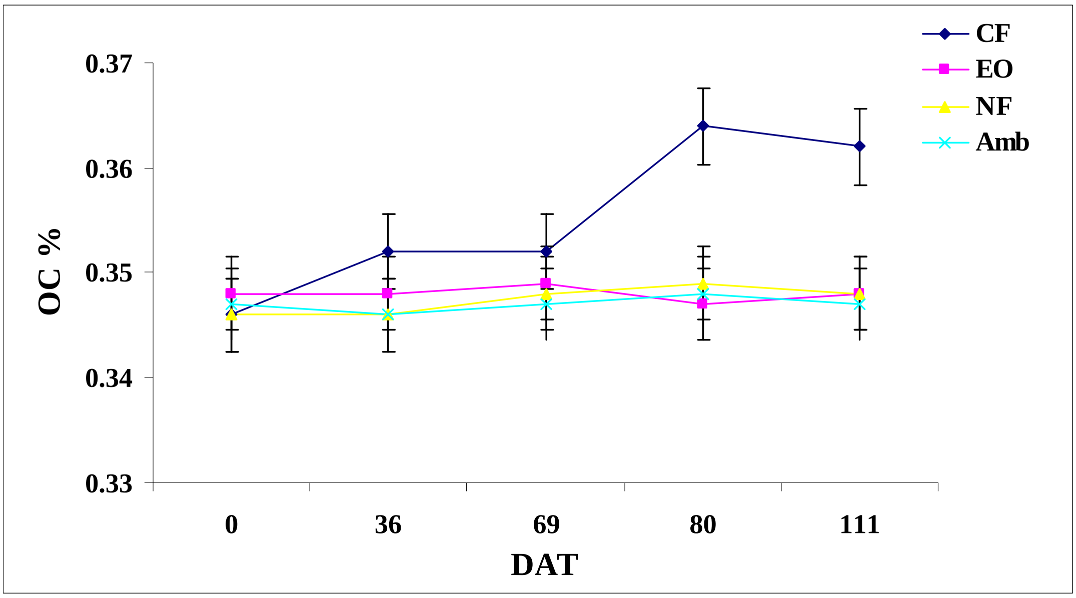

Fig.7. – Effect of different ozone treatments on soil organic carbon.

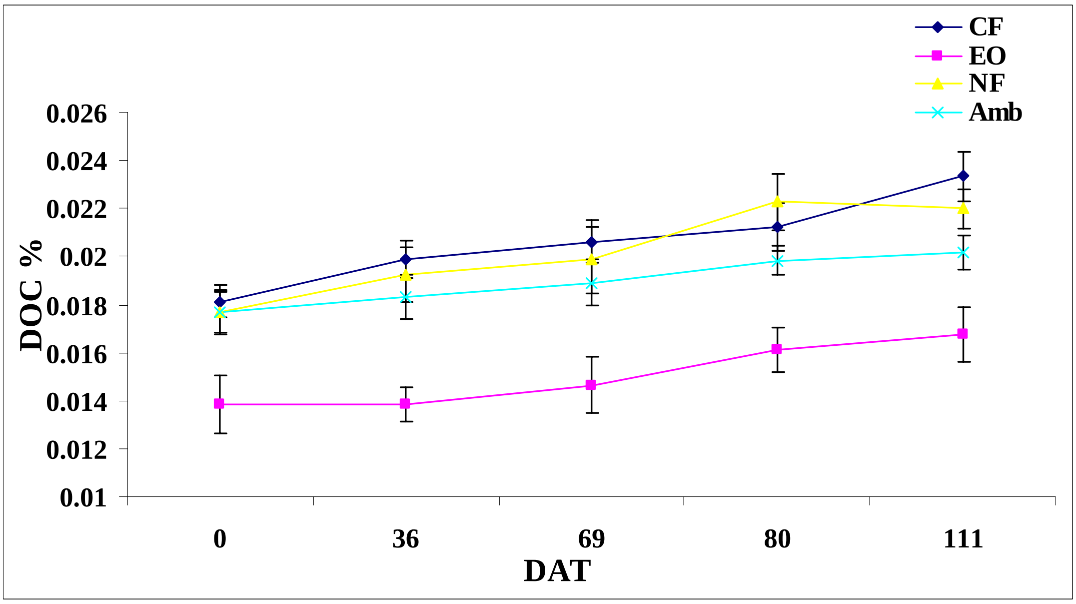

Fig.8. – Effect of different ozone treatments on dissolved organic carbon.

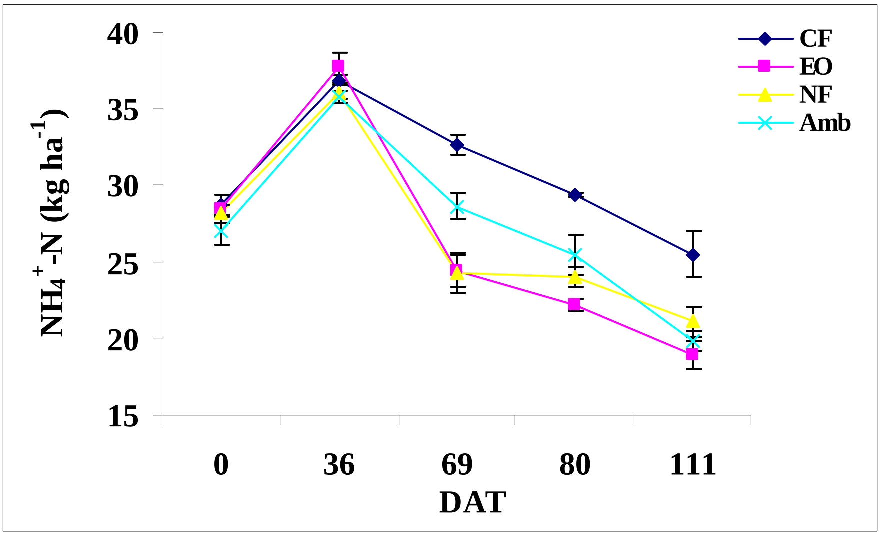

Fig.9. – Effect of different ozone treatments on soil NH_4^+- N.

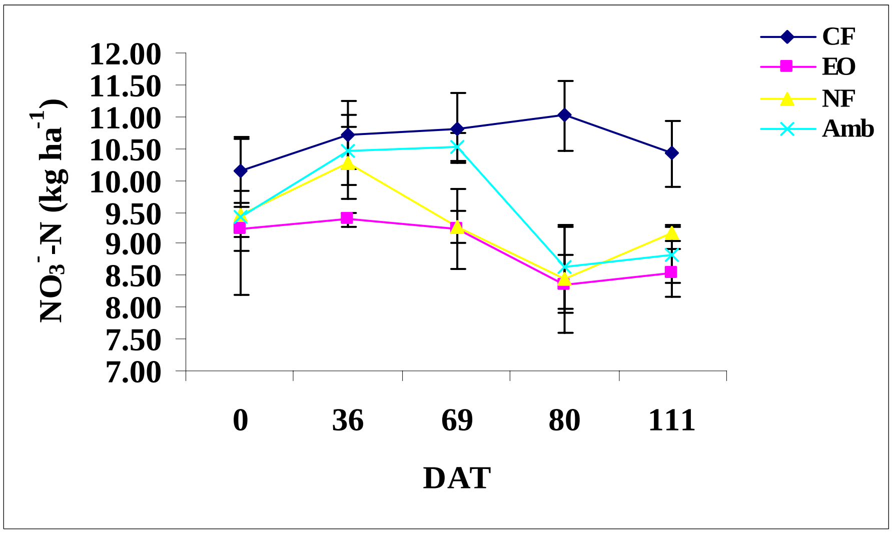

Fig.10. – Effect of different ozone treatments on soil NO_3^--N.

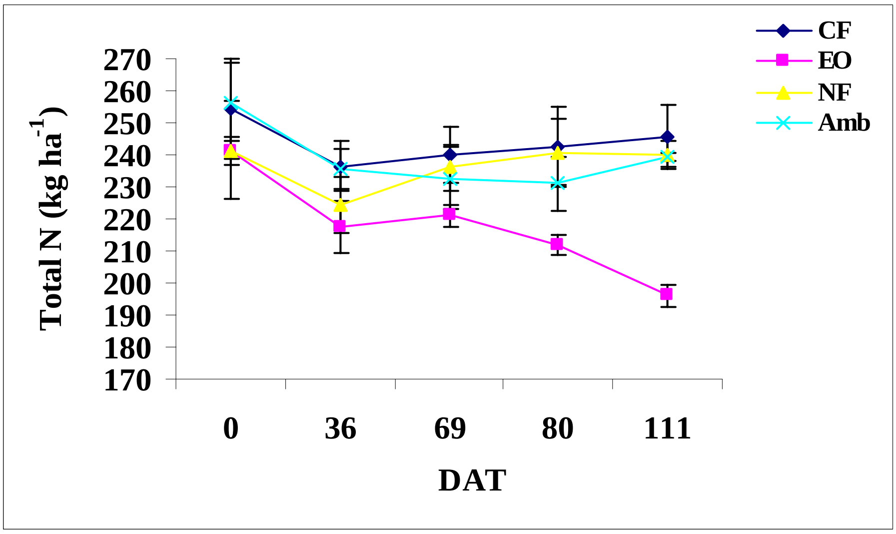

Fig.11. – Effect of different ozone treatments on soil total N.

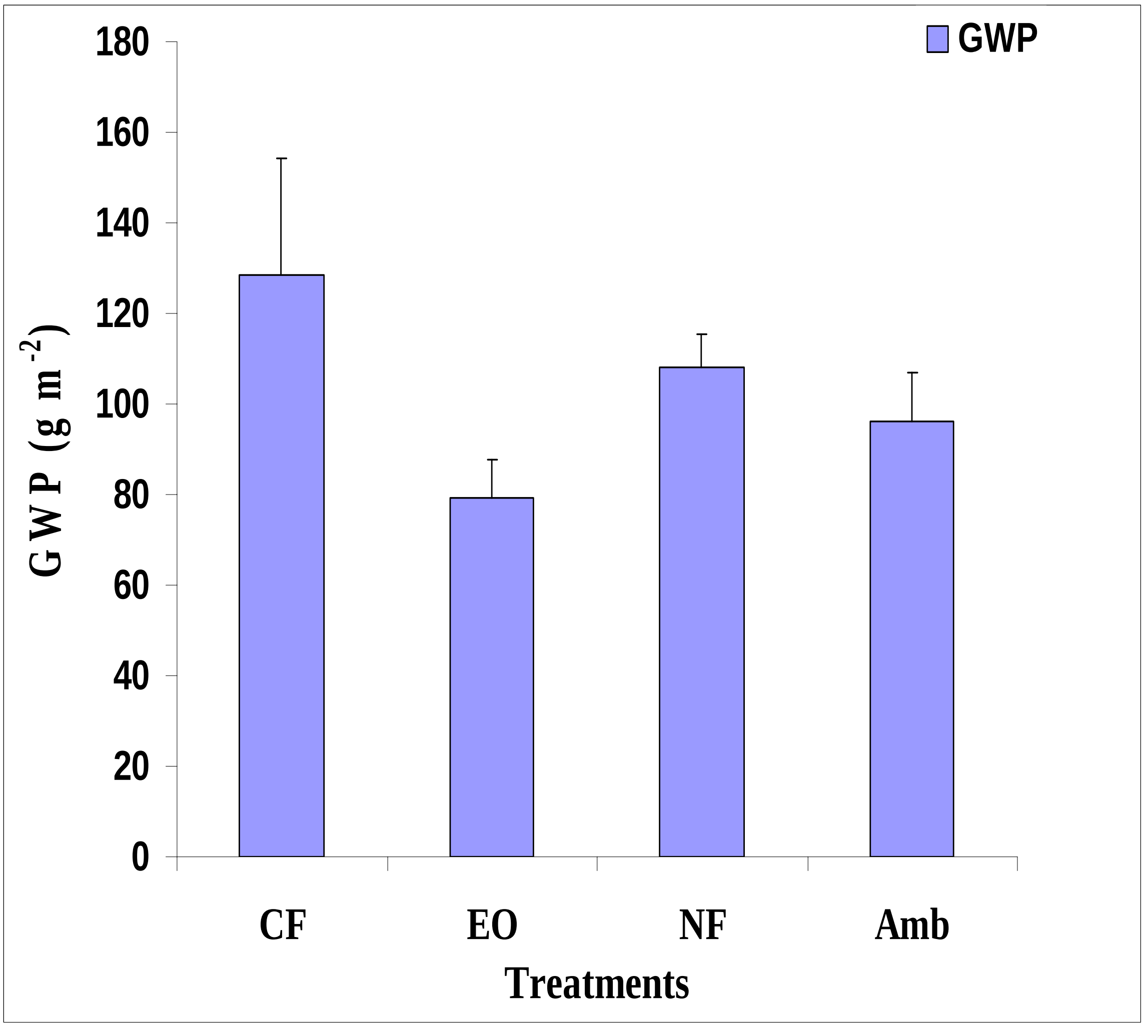

Fig. 12. - GWP of different ozone treatments.

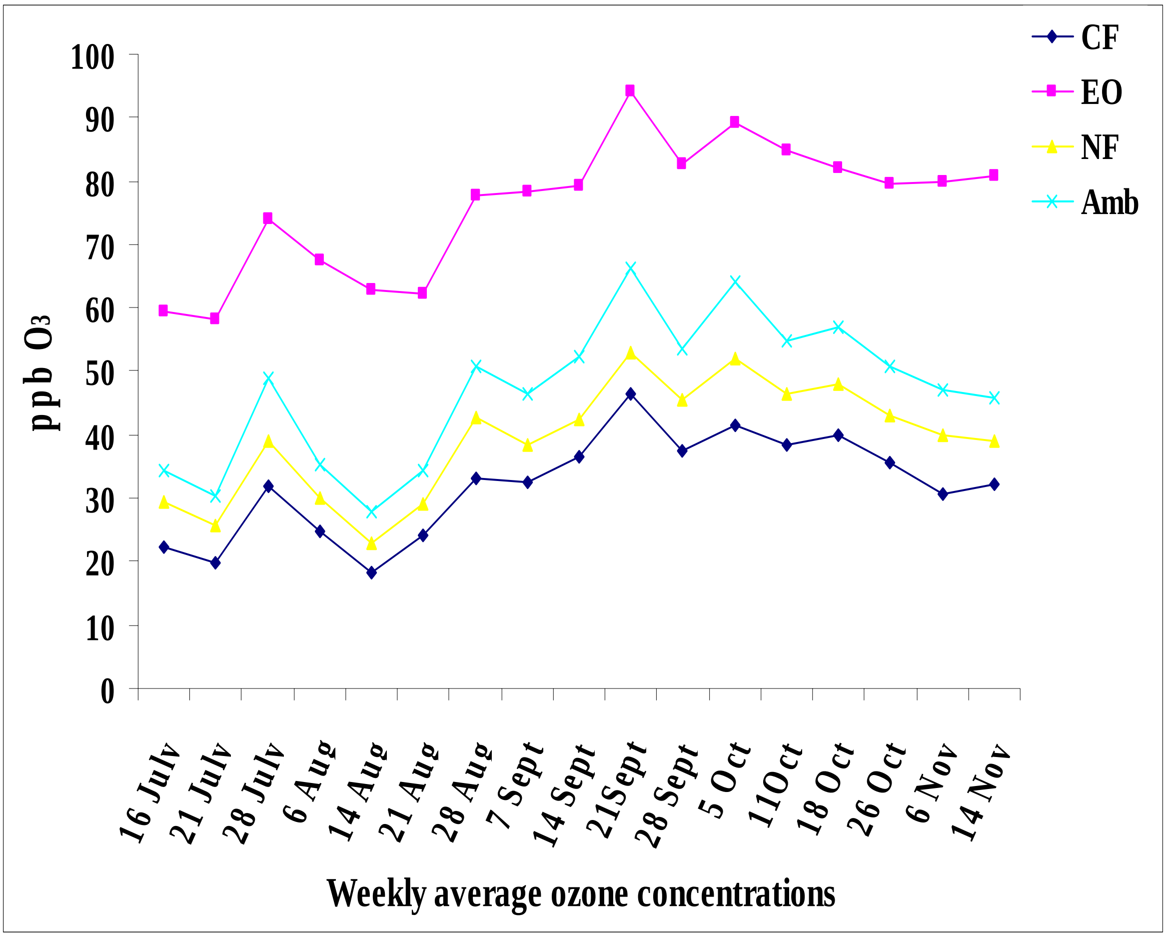

Fig. 2. – Weekly average ozone concentrations (ppb) in different treatments during experimental period.

Plate 1. Gas sampling from rice soil for methane and nitrous oxide analysis.

Plate 2. **Analysis of gas samples for CH_4 and N_2O-N.**

Table 5. Effect of different ozone treatments on average no. of panicles/hill and average no. of filled grains/panicle.

Yield Parameters	Treatments			
	Ambient	**Non filtered**	**Charcoal filtered**	**Elevated Ozone**
No. of panicles/hill	17a	17.60a	19.30a	14.33b
No. of filled grains /panicle	138b	144a	152a	124c

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range test.

Table 6. Effect of different ozone treatments on grain yield, straw yield and harvest index.

Yield Parameters	Treatments			
	Ambient	**Non filtered**	**Charcoal filtered**	**Elevated Ozone**
Grain yield (g/m^2)	126.8b	130.8b	152.8a	116.0c
Straw yield (g/m^2)	189.5a	195.3a	199.3a	183.0b
Harvest Index	0.40b	0.40b	0.43a	0.39c

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range test.

Table 7. Effect of different ozone treatments on no. of tillers and 1000 grain weight.

Yield Parameters	Treatments			
	Ambient	**Non filtered**	**Charcoal filtered**	**Elevated Ozone**
No of Tillers/hill	13.86c	15.28b	18.72a	13.46c
1000 grain weight	20.68 a	21.42 a	22.70a	19.18 b

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range test.

Table 8. Effect of different ozone treatments on root length and shoot length.

Growth Parameters	**Treatments**			
	Ambient	**Non filtered**	**Charcoal filtered**	**Elevated Ozone**
Root length (cm)	29.96b	31.20a	34.48a	25.42c
Shoot length (cm)	54.98b	55.48b	70.32a	51.02bc

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range test.

Table 9. Effect of different ozone treatments on root dry weight and shoot dry weight.

Growth Parameters	**Treatments**			
	Ambient	**Non filtered**	**Charcoal filtered**	**Elevated Ozone**
Root dry wt. (g)/plant	0.65b	0.72a	0.76a	0.56c
Shoot dry wt. (g)/plant	3.63a	3.67a	4.14a	3.08b

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range test.

Table 10. Carbon Efficiency Ratio (CER) of different ozone treatments.

Treatments	Total CH4 flux per season ($g\ m^{-2}$)	Total N_2O-N flux per season ($mg\ m^{-2}$)	CEE C equivalent emissions (gm^{-2})	C fixed (gm^{-2})*	CER
Charcoal filtered	5.31a	54.59a	35.03a	73.32a	2.09
Elevated Ozone	3.07c	47.82c	21.62c	55.68c	2.57
Non filtered	4.37a	51.82b	29.45b	62.76b	2.13
Ambient	3.82ab	50.98b	26.19b	60.84b	2.32

In a row values followed by the same letter are not significantly different at $P<0.05$ by Duncan's multiple range test.

*****Carbon content in rice was 48% of total biomass.

Treatments	**Total CH_4 flux per season (gm^{-2})**	**Total N_2O flux per season ($mg\ m^{-2}$)**

Charcoal filtered		
Elevated ozone		
Non filtered control		
Ambient control		

Table 5. Effect of different ozone treatments on Cummulative seasonal CH_4 and N_2O emissions from rice soil.

In a row values followed by the same letter are not significantly different at *P*<0.05 by Duncan's multiple range tests.